



Dissertation submitted in fulfilment of the requirements for the degree of Doctor of Sciences

PETROGRAPHIC AND GEOCHEMICAL CHARACTERIZATION OF THE MICROMETEORITE COLLECTION FROM THE SØR RONDANE MOUNTAINS

NATURE AND ORIGIN OF THE EXTRATERRESTRIAL FLUX TO EARTH



BASTIEN SOENS

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Abstract

The Antarctic continent has traditionally been a successful searching ground for meteoritic material due to its cold and dry climate. Meteorites, and their microscopic analogues micrometeorites, were originally sampled from Antarctic ice and snow. Recently, however, a large collection of micrometeorites was discovered in sedimentary traps and moraine deposits from the Transantarctic Mountains, where extraterrestrial dust particles have accumulated for a prolonged time span (ca. 3–4 Ma). Micrometeorites (or 'cosmic dust') show unique chemical and isotopic signatures, which originate from a large and diverse amount of asteroidal and cometary bodies within the Solar System. In addition, they document major events such as the origin and evolution of the Solar System, and provide insight into the source region of their precursor bodies. These sedimentary deposits consequently represent a valuable archive that documents the flux of extraterrestrial material to Earth and ancient meteoritic events over Antarctica.

Yet, much of this information is lost during the atmospheric entry stage, where cosmic dust is subjected to frictional heating and is partially or completely molten down. This may significantly alter the original physicochemical and isotopic properties of extraterrestrial dust particles. A thorough understanding of these physicochemical processes is thus required to reconstruct the atmospheric entry of cosmic dust (but also larger objects) and interpret their chemical and isotopic data. During the course of this PhD research, multiple sedimentary deposits from the Sør Rondane Mountains (Dronning Maud Land, East Antarctica) were petrographically examined and chemically-isotopically characterized using state-of-the-art instruments. Furthermore, various experiments and numerical models were constructed to replicate the atmospheric entry stage of both small- and large-sized meteoritic material.

This study has demonstrated that the Sør Rondane Mountains sedimentary deposits contain a rich and pristine variety of extraterrestrial- and impact-related materials, including micrometeorites, microtektites and meteoritic condensation spherules. Statistical analysis suggests that the Sør Rondane Mountains micrometeorite collection is representative of the contemporary flux of cosmic dust to Earth. Extraterrestrial material is subjected to a complex interplay of redox and volatilization processes during atmospheric entry heating, which allow to explain the chemical trends observed in cosmic dust. Isotopic studies also suggest that at least a minor fraction of the micrometeorite population has sampled new, unknown types of asteroidal and/or cometary bodies. Microtektites and meteoritic condensation spherules have been linked to major meteoritic events on Earth ca. 790 ka and ca. 430 ka ago, respectively, and underline the importance of the Earth's atmosphere during their formation. The results of this PhD research emphasize the scientific value of Antarctic sedimentary deposits and provide more insight into the processes taking place during the atmospheric entry of extraterrestrial material.

Samenvatting

Het Antarctische continent is traditioneel een succesvolle zoekplaats geweest voor buitenaards materiaal vanwege zijn koude en droge klimaat. Meteorieten, en hun microscopische varianten micrometeorieten, werden oorspronkelijk bemonsterd uit het Antarctische ijs en sneeuw. Recent werd echter een grote micrometeorietverzameling ontdekt in sedimentvallen en morene afzettingen uit het Transantarctische Gebergte, waar buitenaardse stofdeeltjes gedurende een lange tijd (ca. 3-4 miljoen jaar) konden accumuleren. Micrometeorieten (of 'kosmisch stof') vertonen unieke chemische en isotopische signaturen die afkomstig zijn van een groot en divers aantal asteroïde- en komeetlichamen uit het Zonnestelsel. Daarnaast documenteren ze ook belangrijke gebeurtenissen zoals de oorsprong en evolutie van het Zonnestelsel, en verlenen ze meer inzicht in de bronregio van kosmisch stof. Deze afzettingen zijn bijgevolg waardevolle archieven die de toestroom van buitenaards materiaal naar de Aarde documenteren en getuige zijn van prehistorische, buitenaardse gebeurtenissen boven Antarctica.

Een grote hoeveelheid van deze informatie gaat echter verloren gedurende de atmosferische intredingsfase, waar kosmisch stof onderworpen wordt aan wrijvingswarmte en gedeeltelijk of volledig opsmelt. Dit kan de originele fysicochemische en isotopische eigenschappen van buitenaardse stofdeeltjes sterk beïnvloeden. Een grondig begrip van deze fysicochemische processen is dus noodzakelijk om de atmosferische intrede van kosmisch stof (maar ook grotere objecten) te reconstrueren en hun chemische en isotopische data te interpreteren. Gedurende dit doctoraatsonderzoek werden diverse sedimentaire afzettingen uit het Sør Rondane Gebergte (Koningin Maudland, Oost-Antarctica) petrografisch onderzocht en chemisch-isotopisch gekarakteriseerd m.b.v. *state-of-the-art* instrumenten. Daarnaast werden diverse experimenten uitgevoerd en numerieke modellen opgesteld om de atmosferische intrede van zowel kleinere als grotere buitenaardse objecten na te bootsen.

Dit onderzoek heeft aangetoond dat de sedimentaire afzettingen uit het Sør Rondane Gebergte een rijke en authentieke variëteit aan buitenaardse- en impact-gerelateerde materialen bevatten, inclusief micrometeorieten, microtektieten en condensatiedeeltjes afkomstig van meteorieten. Statistisch onderzoek wijst aan dat de micrometeorietcollectie uit het Sør Rondane Gebergte representatief is voor de hedendaagse toestroom van buitenaards materiaal naar de Aarde. Dit materiaal wordt gedurende de atmosferische intredingsfase blootgesteld aan een complexe wisselwerking van redox- en evaporatieprocessen die de chemische tendensen in kosmische stofdeeltjes kunnen verklaren. Isotopische studies wijzen aan dat minstens een kleine fractie van de micrometeorietpopulatie nieuwe, onbekende asteroïde- en/of komeetlichamen heeft bemonsterd. Microtektieten en condensatiedeeltjes konden gelinkt worden aan grote impactgebeurtenissen op Aarde rond ca. 790 en ca. 430 duizend jaar geleden, respectievelijk, en beklemtonen de belangrijke rol van de atmosfeer gedurende hun vorming. De resultaten uit dit doctoraatsonderzoek benadrukken bijgevolg de wetenschappelijke waarde van Antarctische sedimentaire afzettingen en verlenen een beter inzicht in de processen die plaatsvinden gedurende de atmosferische intrede van buitenaards materiaal.

Introduction

The scientific contribution of micrometeorite investigations

Micrometeorites (or cosmic dust) is a collective term for extraterrestrial dust particles 10–2000 µm in size (Rubin and Grossman, 2010). They predominantly originate from the Jupiter Family Comets and, to a lesser extent, the Main Asteroid Belt prior to their transportation to Earth through Poynting–Robertson drag (Whyatt and Whipple, 1950; Nesvorný et al., 2010; Carrillo-Sánchez et al., 2015; 2020; Kral et al., 2017; Shyam Prasad et al., 2018; Genge et al., 2020; Rojas et al., 2021). Micrometeorites represent the majority of the ca. 40,000 tonnes of extraterrestrial material entering Earth's atmosphere annually (Love and Brownlee, 1993; Zolensky et al., 2006). However, recent estimates have suggested that only a minor fraction of the extraterrestrial dust particles accumulate on the Earth's surface, contributing a total mass of ca. 239–5200 tonnes/year (Shyam Prasad et al., 2018; Suttle and Folco, 2020; Rojas et al., 2021).

The vast majority of cosmic dust evaporates due to frictional heating in the upper atmosphere (Love and Brownlee, 1991). Particles which survive this atmospheric descent display significant physical, textural, chemical and isotopic modifications, similar to meteorite fusion crusts, which obscure the primary properties of micrometeorite precursor bodies (e.g., Genge and Grady, 1998; Alexander et al., 2002; Engrand et al., 2005; Taylor et al., 2005; Genge, 2006; Suavet et al., 2010; Cordier et al., 2011a; van Ginneken et al., 2017; Riebe et al., 2020). For instance, oxygen isotopes are subjected to mass-dependent fractionation processes, but they can also exchange oxygen isotopes with the surrounding atmosphere during flash melting. A thorough understanding of both processes is required to constrain the primary oxygen isotopic signature of micrometeorite precursor bodies. Yet, oxygen isotope fractionation can also serve to characterize the structure and composition of Earth's atmosphere throughout geological time, specifically during the Archean (Tomkins et al., 2016; Rimmer et al., 2019; Lehmer et al., 2020). This information is obtained from I(ron)-type cosmic spherules (Genge et al., 2008), which were possibly inherited from (a)chondritic metal fragments that oxidized and incorporated atmospheric oxygen during entry heating (Genge et al., 2017a; Shyam Prasad et al., 2017; Genge and van Ginneken, 2018).

Oxygen isotopes have previously revealed the presence of a unique and abundant group of micrometeorites ('Group 4') exhibiting anomalous isotopic signatures, incompatible with the contemporary meteorite record (e.g., Yada et al., 2005; Suavet et al., 2010; van Ginneken et al., 2017). According to Suttle et al. (2020), these 'Group 4' micrometeorites have possibly been inherited from intensely altered ¹⁶O-poor water-rich asteroids, similar to the newly identified CY chondrite meteorite group (Ikeda, 1992; King et al., 2019). Statistical analysis demonstrates that cosmic dust is primarily affiliated to carbonaceous chondrites, especially for small particle sizes (<300 μ m), and suggests that the micrometeorite population essentially samples different types of precursor bodies than macroscopic meteorites (e.g., Gounelle et al., 2009; Cordier and Folco, 2014).

In recent years, micrometeorite investigations have increasingly focused on the analysis and characterization of extraterrestrial chromite and Cr-rich spinel phases in Phanerozoic sedimentary records (e.g., Schmitz et al., 2017; 2019; Martin et al., 2018; 2019; Boschi et al., 2020). Cosmic-ray exposure ages have demonstrated that the aforementioned mineral phases were presumably liberated from their precursor bodies during collisional events, implying their contribution to the micrometeorite population (e.g., Heck et al., 2004; 2008; Alwmark et al., 2012; Meier et al., 2014). The precursor bodies of extraterrestrial chromite and Cr-rich spinel phases can be determined using its chemical composition and oxygen isotope systematics. As such, it is possible to reconstruct the contribution of different meteorite or asteroid groups to the flux of extraterrestrial matter to Earth throughout the geological record (e.g., Schmitz et al., 2017; 2019; Martin et al., 2018; 2019; Boschi et al., 2020). For instance, the breakup of the L-chondrite parent body during the mid-Ordovician is marked by a significant change in the chromite content of the Swedish Hällekis-Thorsberg section (Heck et al., 2016). Similar reconstructions have been made for Silurian, Cretaceous and Paleogene sedimentary sections (Martin et al., 2018; 2019; Boschi et al., 2016).

Micrometeorites thus form a robust and versatile tool to investigate: (i) the development and evolution of the Solar System, (ii) physicochemical processes taking place during atmospheric entry heating, (iii) the source region, type and abundance of micrometeorite precursor bodies and their contribution to the flux of extraterrestrial material to Earth, and (iv) the reconstruction of ancient atmospheric and climatic regimes. These examples demonstrate the scientific value of micrometeorites and underline the importance of their recovery from continental and oceanographic deposits.

A historical overview of Antarctic micrometeorite collections

Cosmic dust was originally discovered in deep-sea sediments (e.g., Murray and Reynard, 1891; Blanchard et al., 1980; Brownlee, 1981; Parashar et al., 2010) and has subsequently been recovered from large volumes of natural and artificially molten ice from Greenland (e.g., Maurette et al., 1987) and the Novaya Zemlya glacier in Russia (e.g., Badjukov and Raitala, 2003). Over the course of the last three decades, however, the micrometeorite search has shifted its focus on the Antarctic continent (Fig. 1). This can primarily be attributed to the cold and dry Antarctic climate, which preserves meteoritic material relatively better than other terrestrial collection sites. In addition, cosmic dust is more easily identified due to the absence of anthropogenic contamination. As such, Maurette et al. (1991) reported the first Antarctic micrometeorite collection from Cap-Prud'homme (Adélie Land) by melting and filtering ca. 100 tonnes of blue ice. This yielded a large and abundant variety of unmelted and molten micrometeorites (see Genge et al., 2008 for classification), providing a wealth of information with regards to the composition and source region of extraterrestrial dust particles arriving on Earth. Similar attempts were made at the Meteorite Ice Field around the Yamato Mountains where ca. 36 tonnes of blue ice was molten and filtered (Yada and Kojima, 2000; Terada et al., 2001; Yada et al., 2004). The Antarctic micrometeorite collection was significantly expanded by Taylor and Harvey (1998) and Taylor et al. (2000), who retrieved a large number (>1000s) of pristine, molten micrometeorites from the ice layers beneath the South Pole Water Well (SPWW). The cosmic spherules recovered from the SPWW are essentially unbiased with respect to the contemporary flux of extraterrestrial matter to Earth and cover a time span of several 100s of years. Novel types of fine-grained, friable micrometeorites (i.e., the ultracarbonaceous micrometeorites – Genge et al., 2008) were recovered from freshly accumulated snow near the CONCORDIA station, which offers a better preservation potential compared to blue ice (Duprat et al., 2007).

Yet, the largest and most diverse collection was discovered at nunataks in the Transantarctic Mountains (TAM), where cosmic dust accumulated within sedimentary traps (e.g., weathering pits and joints) and surrounding moraine deposits as a result of wind activity and migration of the Antarctic ice sheet (Rochette et al., 2008; Genge et al., 2018). Based on bedrock exposure ages of the surrounding host rocks using cosmogenic nuclides (i.e., ¹⁰Be, ²¹Ne, ²⁶Al – Welten et al., 2008) and paleomagnetic dating, it was revealed that the TAM sedimentary traps were exposed to atmospheric fallout considerably longer (>1 Ma) compared to other Antarctic micrometeorite collections. Statistical analysis furthermore suggests that the size–frequency distribution and abundance of chemical and textural



Figure 1: Simplified map of the Antarctic continent illustrating major micrometeorite collection sites.

subtypes in the TAM sedimentary traps is very similar to the SPWW collection (Suavet et al., 2009). The TAM micrometeorite collection thus presents an excellent opportunity to study the flux of extraterrestrial matter over a prolonged time span.

The atmospheric interaction of extraterrestrial- and impact-related materials

The Earth's atmosphere operates as a protective barrier against small-sized (i.e., mm- and cm-size) extraterrestrial objects, including micrometeoroids, which are largely vaporized as a result of frictional heating during the atmospheric entry stage (Love and Brownlee, 1991). This process is commonly associated with major physicochemical changes in the original dust particle (see examples above). In contrast, larger meteoritic objects (>20 m) appear to transfer a considerable amount of kinetic energy to the Earth's atmosphere, which may result in (catastrophic) airburst and impact events that directly influence the Earth's system as a whole (e.g., Schulz, 1992; Melosh and Collins, 2005; Boslough and Crawford, 2008; Artemieva and Shuvalov, 2016). Following the discovery of micrometeorites in sedimentary traps from the TAM, different types of extraterrestrial- and impact-related materials, including meteoritic ablation debris and microtektites, were recovered (e.g., Folco et al., 2008; 2009; 2016; van Ginneken et al., 2010). These materials consequently provide a unique opportunity to study the atmospheric interaction of small- and large-sized meteoritic objects.

For instance, meteoritic ablation spherules recovered from the Miller Butte sedimentary trap presumably record a Tunguska-like airburst event where a medium-sized object (ca. 10–150 m) was fragmented and subsequently exploded in the lower atmosphere (van Ginneken et al., 2010). Based on the presence of high NiO olivine and magnesioferrite – a feature previously observed within meteoroid ablation spheres and meteorite fusion crusts (Harvey et al., 1998; Genge and Grady, 1999), it was concluded that the spherules were formed as a direct consequence of the interaction between the meteoritic object and the lower atmosphere. Yet, their extremely light oxygen isotope compositions ($\delta^{17}O = -17\%$) remain puzzling and suggest a potential interaction with the Antarctic ice sheet (Engrand et al., 2008; Misawa et al., 2010). As such, their formation mechanism is not well constrained, which is required to evaluate the scale and hazard of (future) airburst events, and identify their residual products within the geological record.

In parallel, microtektites are SiO₂-rich glasses that formed during oblique hypervelocity impact events with the Earth's surface, which were subsequently ejected into the Earth's atmosphere and transported over distances of 100s to 1000s of kilometers (e.g., Koeberl, 1994; Artemieva et al., 2002; Glass et al., 2004). A large number (>100) of SiO₂-rich, vitreous spherules were previously recovered from the TAM sedimentary traps and have been linked to the Australasian (micro)tektite strewn field (788 \pm 3.0 ka – Schwarz et al., 2016; Jourdan et al., 2019; Di Vincenzo et al., 2021) based on major, trace element and Sr-Nd isotope geochemistry, as well as fission track and ⁴⁰Ar/³⁹Ar dating (Folco et al., 2008; 2009; 2011; 2016; Di Vicenzo et al., 2021). Furthermore, recent studies have demonstrated that the abundance of volatile compounds (i.e., average Na₂O, K₂O, H₂O contents) in Australasian (micro)tektites progressively decreases as the distance between the source crater and recovery sites increases (Beran and Koeberl, 1997; Folco et al., 2010; van Ginneken et al., 2018). Multiple mechanisms have previously been proposed, including the 'bubble-stripping' (Melosh and Artemieva, 2004) and 'diffusive loss' theories (Moynier et al., 2009a,b; Folco et al., 2010), which suggest that the volatile depletion may potentially originate during the atmospheric transit of Australasian (micro)tektites. However, none of the aforementioned processes have fully been able to reproduce the chemical and isotopic trends observed in Australasian (micro)tektites.

Consequently, the Earth's atmosphere largely appears to control the physicochemical and isotopic properties of extraterrestrial- and impact-related materials recovered from Antarctic sedimentary traps. The key to accurately interpret their chemical and isotopic data therefore lies within a thorough investigation and understanding of atmospheric entry processes occurring within both small- and large-sized meteoritic objects. This will represent an overarching topic within this PhD dissertation.

Dissertation overview

This PhD dissertation is subdivided into five sections. The first section 'Introduction' demonstrates the significance of micrometeorite investigations and provides a historical overview of Antarctic micrometeorite collections. In addition, this section illustrates how extraterrestrial- and impact-related materials contained within these collections are affected by the Earth's atmosphere and complicate their overall interpretation. The 'Objectives' section briefly summarizes the main research questions addressed during this work and elaborates the methodological approach undertaken. Next, the 'Peerreviewed articles & submitted manuscripts' section provides an overview of the research articles that are related and were published or submitted during the course of this PhD research. A small preface is included to put each article in perspective of the main research questions. Furthermore, the contribution of BS to each of the respective articles is specified. The fourth section 'Summary' summarizes the general and major conclusions obtained from the respective research articles. Finally, the 'Future outlook' section briefly discusses the aspects of this PhD dissertation that can be improved upon or which require further investigation.

Objectives

This PhD dissertation will mainly focus on micrometeorites and other types of extraterrestrial- and impact-related materials that were recovered from sedimentary deposits (e.g., within cracks and fissured surfaces) at high-altitude (>2000 m.a.s.l.) and wind-exposed granitoid and metatonalite summits in the Sør Rondane Mountains (SRM - Dronning Maud Land, East Antarctica) during the 2012-2013 MICROMETA (MicroMeteorites from Antarctica) and the 2018-2019 BAMM! (Belgian Antarctic MicroMeteorite) expeditions. The data presented during this PhD dissertation has predominantly been acquired from the Widerøefjellet, and to a lesser extent, the Walnumfjellet sedimentary deposits due to the high abundance and overall pristine nature of extraterrestrial dust particles recovered (see below). The reader is referred to the article below 'Cosmic spherules from Widerøefjellet, Sør Rondane Mountains (East Antarctica)' by Goderis et al. (2020) for a detailed description and geological background of the sampling area. We define two main objectives, which are elaborated below.

- Firstly, a detailed inventory and statistical analysis of the Widerøefjellet sedimentary trap will be performed to identify the various types of particles that have accumulated within the SRM sedimentary deposits. Petrographic, chemical and oxygen isotopic analyses will be conducted on a representative number of chondritic cosmic spherules for characterization. These results are compared to other Antarctic micrometeorite collections, including the SPWW and TAM collections, to test whether the Widerøefjellet micrometeorite collection (WMC) is representative of the contemporary flux of extraterrestrial matter to Earth and thus largely remained pristine and unaffected by sorting processes (e.g., weathering and alteration through the interaction with Antarctic precipitation, wind sorting, etc.). This step is pivotal to accurately interpret and compare the research data obtained throughout this PhD research. However, this information is also relevant for other types of particles that have been recovered from the Widerøefjellet and Walnumfjellet sedimentary traps, such as microtektites and meteoritic condensation spherules. For instance, the size-frequency distribution of microtektites and the presence of microtektite subtypes may provide more information regarding the distribution pattern and mechanisms of distal impact ejecta following major impact events. These statistics are, however, directly controlled by the extent of potential sorting processes, which may or may not target specific types of particles.
- Secondly, this work aims to constrain and quantify the physicochemical processes occurring during the atmospheric transit of small- and large-sized meteoritic objects. To analyze the atmospheric entry of smaller objects, including meteoroids and micrometeoroids, a melting experiment using alkali basalt and ordinary chondrite samples was conducted in a high enthalpy facility to replicate the atmospheric entry of extraterrestrial material. The residue materials were subsequently petrographically and chemically analyzed and compared with numerical models. Oxygen isotope fractionation in micrometeorites is quantified through the analysis of iron isotope compositions in

a representative number of chondritic (and achondritic) cosmic spherules spanning the complete textural range. In addition, we attempt to identify the parameters (e.g., mineralogy, chemistry, etc.) responsible for the chemical and isotopic fractionation processes occurring during atmospheric entry heating. By doing so, we attempt to reconstruct the original chemical and isotopic compositions of micrometeorite precursor bodies. This information can subsequently be used to reconstruct the atmospheric entry parameters of micrometeoroids and provides insight into the source region and delivery mechanisms of cosmic dust. To constrain the physicochemical processes occurring during the atmospheric transit of larger meteoritic objects and their derivative products, we analyze the petrographic, chemical and isotopic properties of microtektites and meteoritic condensation spherules recovered from the Widerøefjellet and Walnumfjellet sedimentary deposits, respectively. Microtektites are initially characterized and compared to TAM microtektites (e.g., Folco et al., 2008; 2009; 2016; Brase et al., 2021) to test their potential affiliation to the Australasian (micro)tektite strewn field. Next, we have analyzed the iron isotope compositions of a representative number of Australasian tektites and microtektites and provide numerical models in an attempt to replicate their chemical and isotopic trends. A similar approach is conducted for the meteoritic condensation spherules.

Peer-reviewed articles & submitted manuscripts

Cosmic spherules from Widerøefjellet, Sør Rondane Mountains (East Antarctica)

by Goderis et al. (2020). Geochim. Cosmochim. Acta 270, 112-143.

The following article discusses the petrographic properties, chemical and oxygen isotopic compositions of a representative number (n = 28) of chondritic cosmic spherules recovered from the Widerøefjellet sediment trap. We present a statistical analysis based on a comparison with other Antarctic micrometeorite collection sites, including the SPWW (Taylor and Harvey, 1998; Taylor et al. 2000) and TAM (Rochette et al., 2008; Suavet et al., 2009), to test whether the WMC is representative of the cosmic dust flux to Earth. This would imply that the extraterrestrial- and impact-related dust particles recovered from the WMC have not been subjected to major sorting processes, including wind sorting or aqueous alteration processes. As such, we can guarantee that the physicochemical and isotopic properties of the WMC are restricted by the composition of micrometeorite precursor bodies and the subsequent effects of atmospheric heating processes. In addition, this would allow a meaningful comparison between the WMC and other pristine Antarctic micrometeorite collections. This study therefore sets an important baseline for future investigations.

BS has assisted Steven Goderis with the textural and chemical classification of cosmic spherules and interpretation of the chemical and oxygen isotopic dataset.

The supplementary materials related to this manuscript are available on the following website: https://doi.org/10.1016/j.gca.2019.11.016.





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Cosmic spherules from Widerøefjellet, Sør Rondane Mountains (East Antarctica)

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Abstract

A newly discovered sedimentary accumulation of micrometeorites in the Sør Rondane Mountains of East Antarctica, close to the Widerøefjellet summit at \sim 2750 m above sea level, is characterized in this work. The focus here lies on 2099 melted cosmic spherules larger than 200 µm, extracted from 3.2 kg of sampled sediment. Although the Widerøefjellet deposit shares similarities to the micrometeorite traps encountered in the Transantarctic Mountains, both subtle and more distinct differences in the physicochemical properties of the retrieved extraterrestrial particles and sedimentary host deposits are discernable (e.g., types of bedrock, degree of wind exposure, abundance of metal-rich particles). Unlike the Frontier Mountain and Miller Butte sedimentary traps, the size fraction below 240 µm indicates some degree of sorting at Widerøefjellet, potentially through the redistribution by wind, preferential alteration of smaller particles, or processing biases. However, the cosmic spherules larger than 300 µm appear largely unbiased following their size distribution, frequency by textural type, and bulk chemical compositions. Based on the available bedrock exposure ages for the Sør Rondane Mountains, extraterrestrial dust is estimated to have accumulated over a time span of $\sim 1-3$ Ma at Widerøefjellet. Consequently, the Widerøefjellet collection reflects a substantial reservoir to sample the micrometeorite influx over this time interval. Petrographic observations and 3D microscopic CT imaging are combined with chemical and triple-oxygen isotopic analyses of silicate-rich cosmic spherules larger than 325 µm. The major element composition of 49 cosmic spherules confirms their principally chondritic parentage. For 18 glassy, 15 barred olivine, and 11 cryptocrystalline cosmic spherules, trace element concentrations are also reported on.

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https://doi.org/10.1016/j.gca.2019.11.016 0016-7037/© 2019 Elsevier Ltd. All rights reserved. Based on comparison with evaporation experiments reported in literature and accounting for siderophile and chalcophile element losses during high-density phase segregation and ejection, the observed compositional sequence largely reflects progressive heating and evaporation during atmospheric passage accompanied by significant redox shifts, although the influence of (refractory) chondrite mineral constituents and terrestrial alteration cannot be excluded in all cases. Twenty-eight cosmic spherules larger than 325 μ m analyzed for triple-oxygen isotope ratios confirm inheritance from mostly carbonaceous chondritic precursor materials (~55% of the particles). Yet, ~30% of the measured cosmic spherules and ~50% of all glassy cosmic spherules are characterized by oxygen isotope ratios above the terrestrial fractionation line, implying genetic links to ordinary chondrites and parent bodies currently unsampled by meteorites. The structural, textural, chemical, and isotopic characteristics of the cosmic spherules from the Sør Rondane Mountains, and particularly the high proportion of Mg-rich glass particles contained therein, imply a well-preserved and representative new sedimentary micrometeorite collection from a previously unstudied region in East Antarctica characterized by distinct geological and exposure histories. © 2019 Elsevier Ltd. All rights reserved.

Keywords: Cosmic spherules; Extraterrestrial dust; Parent bodies; Atmospheric heating; Oxygen isotope ratios

1. INTRODUCTION

Micrometeorites (MMs), dust particles within the size range of 10 µm-2 mm (Rubin and Grossman, 2010), dominate the 40,000 \pm 20,000 metric tons of extraterrestrial matter accreting to Earth every year (Love and Brownlee, 1993). Due to different production mechanisms in and transportation pathways from their source regions, these microscopic particles sample parent bodies different from those of meteorites (e.g., Fredriksson and Martin, 1963; Ganapathy et al., 1978; Engrand and Maurette, 1998; Flynn et al., 2009; Gounelle et al., 2009; Dartois et al., 2013; Cordier and Folco, 2014; Rubin, 2018). Generally recovered from deep-sea sediments, seasonal lakes in Greenland, ice and snow in Greenland and Antarctica, Antarctic moraines, continental sands and soils, and more recently also urban environments (e.g., Brownlee et al., 1979; Blanchard et al., 1980; Koeberl and Hagen, 1989; Hagen et al., 1989; Engrand and Maurette, 1998; Taylor and Lever, 2001; Genge et al., 2016, 2017; Rudraswami et al., 2016; van Ginneken et al., 2017), MMs have also been found concentrated in high-altitude sedimentary traps, i.e., a pits, fissures and cracks of glacially eroded surfaces, in the Transantarctic Mountains (TAM) (e.g., Rochette et al., 2008; Suavet et al., 2009). To concentrate MMs in numbers sufficient to be able to efficiently distinguish them from terrestrial particles in sedimentary deposits, the accumulation time of such traps is ideally of the order of millions of years, while at the same time alteration must have remained limited, with minimal background or anthropogenic contributions (Suavet et al., 2009). In the case of the Antarctic collections from the Cap Prud'homme blue ice field, the Yamato Mountain blue ice field, and the South Pole Water Well at the Scott-Amundsen Station (USA), the sampled time intervals cover the last few kyr (Maurette et al., 1994), 27-33 kyr (Yada et al., 2004), and 1100-1500 AD (Taylor et al., 1998, 2000), respectively. For the most recent flux of extraterrestrial material to Earth, the MMs in central East Antarctica near the French-Italian Concordia Station - Dome C recovered from the melting and filtering of snow are considered among the most representative (Duprat et al., 2001, 2007; Gounelle et al., 2005; Dobrică et al., 2010). However, significantly older Antarctic surface sediments have also been found enriched in MMs, particularly the melted types (Hagen et al., 1989; Koeberl and Hagen, 1989; Harvey and Maurette, 1991). In the case of the TAM, sedimentary traps yield exposure ages on the order of several Ma (up to 4 Ma), linked to the high resistance of the bedrock to weathering and erosion. This is based on cosmic spherule fluences in combination with unbiased flux rate estimates, cosmogenic nuclide measurements of the exposed surface surrounding the trap, the occurrence of ~ 0.8 Myr old microtektites, the presence of \sim 480 kyr old ablation debris related to a large meteoritic airburst, and the paleomagnetic record of melted MMs (e.g., Folco et al., 2008, 2009; Rochette et al., 2008; Welten et al., 2008; van Ginneken et al., 2010; Suavet et al., 2011b). The TAM sedimentary traps have proven an exceptionally productive source, yielding several 1000s MMs larger than 400 µm and 100s larger than 800 µm (e.g., Rochette et al., 2008; Suavet et al., 2009).

Based on the degree of melting experienced during atmospheric passage, the distinction is generally made between melted MMs (hereafter cosmic spherules, CSs), partially melted MMs (or scoriaceous MMs), and unmelted or angular MMs (e.g., Maurette et al., 1994; Taylor et al., 1998; Genge et al., 2008). Cosmic spherules form after significant melting of micrometeoroids during atmospheric passage and subsequent cooling (Folco and Cordier, 2015). Cosmic spherules are distinct from meteorite ablation spheres, which are quenched melt droplets separated from the fusion crust of macroscopic meteorites. The latter can often be differentiated from CSs based on their lower cosmic-ray induced ²⁶Al and ¹⁰Be contents and higher volatile element (mainly alkali metal) content (Raisbeck et al., 1986; Genge and Grady, 1999; van Ginneken et al., 2010).

In this work, a new sedimentary MM collection from mount Widerøefjellet in the Sør Rondane Mountains (SRM) of Dronning Maud Land in eastern Antarctica is documented, and the physicochemical characteristics of the deposits and most obvious CSs larger than 200 μ m are compared to those of the TAM and other MM collections. As CSs dominate the MM influx in the size fraction larger than 50 μ m, constituting a representative subpopulation for the entire MM flux (e.g., Brownlee et al., 1997; Taylor et al., 2012; Cordier and Folco, 2014), a fraction of the largest CSs recovered from Widerøefjellet has been characterized for major (n = 49) and trace (n = 44) element concentrations, as well as for high-precision oxygen isotopic compositions (n = 28), after structural characterization by μ CT. While the textures and chemical compositions of extraterrestrial particles are reprocessed by alteration during their terrestrial residence, this work focuses on confirming the primary nature of the MM precursor materials and refining the processes that affected these particles during atmospheric passage. While there is convincing evidence, based on elemental compositions and oxygen isotope ratio studies (e.g., Genge et al., 1997; Noguchi et al., 2002), that a large fraction of the MMs is related to carbonaceous chondrites of various clans and groups, the ratio of MMs related to ordinary as compared to carbonaceous chondrites and their distribution per size fraction, is currently based on only a limited number of analyses, especially for the larger size fractions (e.g., Steele, 1992; Kurat et al., 1994; Brownlee et al., 1997; Engrand and Maurette, 1998; Engrand et al., 2005; Gounelle et al., 2005; Genge et al., 2008; Suavet et al., 2010; Cordier et al., 2011a, 2011b; Taylor et al., 2012; Rudraswami et al., 2012, 2015a, 2015b, 2016; van Ginneken et al., 2012, 2017; Imae et al., 2013; Cordier and Folco, 2014). The ratio of carbonaceous chondrite relative to ordinary chondrite material decreases as CS diameters increase, from a factor of 10 for small particles $(<500 \ \mu m \text{ in diameter})$ to a factor of 0.3 for larger particles, indicating that the contribution of ordinary chondrite material to the composition of the micrometeoroid complex increases with MM size, with a possible continuum between meteorites and MMs (Cordier and Folco, 2014). The present study provides an independent assessment of the flux of large (>200 μ m) micrometeoroids over the last ~3 Ma and a means to evaluate the relative contributions of primitive asteroids (and comets) compared to more evolved asteroids within the interplanetary dust cloud.

2. MATERIALS AND METHODS

2.1. Sedimentary micrometeorite traps in the Sør Rondane Mountains

The Sør Rondane Mountains (SRM) within Dronning Maud Land of East Antarctica cover a surface area of approximately 2000 km², mainly composed of low- to high-grade metamorphic lithologies that were intruded by various plutonic rocks (e.g., Shiraishi et al., 1997). Sensitive high-resolution ion microprobe U-Pb zircon ages indicate that the last tectonothermal event in the SRM range took place 650-500 Myr ago, after which the SRM have remained geologically stable (Shiraishi et al., 2008). Ice sheet surfaces reach an elevation of about 1000 meter above sea level (masl) north of the SRM and rise to 2500 masl to the South (Suganuma et al., 2014). The region surrounding the Belgian Princess Elisabeth Antarctica (PEA) station was studied using satellite images and geological maps before the start of the 2012-2013 field campaign (Imae et al., 2015). Based on descriptions of the TAM traps

(e.g., Rochette et al., 2008; Suavet et al., 2009), erosional and eolian sediment, expected to contain significant extraterrestrial contributions, was subsequently sampled from exposed cracked and fissured surfaces at windexposed, high altitude (>2000 masl) granitoid summits in the western part of the SRM (Figs. 1 and 2). The current work focuses on CSs separated from a single batch of ~6.6 kg detritus collected at Widerøefjellet (~2755 masl; S72°8′41″, E23°16′41″). The main lithotype found at Widerøefjellet is a gneissose biotite-hornblende metatonalite, geochemically categorized as a low-K tholeiitic intrusion in volcanic arc granitoids (Kamei et al., 2013; Kojima and Shiraishi, 1986).

Limited information exists on the deglaciation history of the Widerøefjellet peak, as fully exposed or glacially abraded bedrock surfaces suitable for cosmogenic dating methods are lacking near the sampled sediment trap. However, an abraded coherent surface showing glacial striations on the granitoid Walnumfjellet in the western central part of the SRM (Fig. 1), 30 km East of Widerøefjellet at 2489 masl (S72°04'57", E24°17'16"), indicates a ¹⁰Be exposure age of 1.9 ± 0.2 Ma after correction for glacial isostatic adjustment (Suganuma et al., 2014). This exposure age is in agreement with the general glacial history for the western part of the Sør Rondane Mountains, as interpreted based on the height and degree of weathering of tills (Moriwaki et al., 1991) that were correlated to absolute ¹⁰Be and ²⁶Al exposure ages (Nishiizumi et al., 1991). Prior to 4 Ma, a large part of the SRM was covered with an ice sheet that retreated progressively with some pauses prior to 1 Ma, was stagnant or re-advanced after 1 Ma, and subsequently retreated to nearly the same level as at present until ten thousand years ago (Moriwaki et al., 1991). The summit height and degree of weathering in the western part of the Sør Rondane Mountains correspond to an exposure age of $\sim 1-3$ Ma. The Walnumfjellet exposure age is taken here as a workable approximation for the deglaciation history of Widerøefjellet, until more precisely constrained. Given the annual mean air temperature of approximately -19 °C at the PEA research station (1390 masl; Pattyn et al., 2010; Gorodetskaya et al., 2013), the Widerøefjellet sediment, which lies at altitudes more than 1350 m higher than PEA, is assumed to mostly have remained below freezing point since the time of exposure. In the TAM deposits, which lie at 2600 masl (Folco et al., 2008), extraterrestrial particles have clearly been exposed to liquid water (e.g., van Ginneken et al., 2016), suggesting that melting may occur at high altitudes and ambient temperatures well below 0°C. However, contact with liquid water appears to have been less pervasive at Widerøefjellet based on the observed degree of weathering and the type of weathering minerals found on the CSs (cf. below).

2.2. Collection, sampling, and first classification

After removal of the largest rock fragments and boulders, 6.6 kg of Widerøefjellet sediment was sampled using dedicated polypropylene and wooden sampling tools, to avoid contamination by metal (Figs. 1 and 2). The sediment was gradually defrosted at temperatures only slightly



Fig. 1. Location of the Sør Rondane Mountains within Antarctica, the sites of the Princess Elisabeth (Belgium) and former Asuka (Japan) Antarctic research stations (circles), and the position of the Widerøefjellet CS accumulation site (star) relative to the Sør Rondane Mountains. Map adapted after Suganuma et al. (2014).

exceeding the freezing point at the PEA station. After sample splitting, about half of the sediment (3.2 kg) was processed by washing in milli-Q H₂O and sieving at the Vrije Universiteit Brussel (VUB, Belgium) to separate size fractions of less than 125 µm, 125-200 µm, 200-400 µm, 400- $800 \,\mu\text{m}$, $800-3000 \,\mu\text{m}$, and more than $3000 \,\mu\text{m}$, while the remaining half is kept for reference. Using optical microscopy, 2099 CSs were handpicked from the >200 µm size fractions of the Widerøefjellet deposit, with 1707 CSs extracted from the 200-400 µm, 375 CSs from the 400-800 µm, and 17 CSs from the 800-3000 µm size fractions. No extraterrestrial particles were found in the $>3000 \,\mu m$ size fraction, while the smaller fractions and unmelted particles remain the subject of further study. For 985 randomly picked CSs, the surface textural and compositional characteristics were determined using a JEOL JSM-IT300 or field emission JEOL JSM-7000F scanning electron microscope (SEM), both equipped with energy-dispersive X-ray spectrometers (EDS), at the VUB. Cosmic spherules are traditionally divided into three compositional types following their main mineralogy: the silicate-rich (S-type) spherules, the iron-rich (I-type) spherules, and the G-type spherules, which represent an intermediate class (e.g., Blanchard et al., 1980; Taylor et al., 2000; Genge et al., 2008). Stony or silicate CSs are commonly further subdivided into four types based on quench textures, i.e., porphyritic (Potype), cryptocrystalline (CC-type), barred olivine (BOtype) and glass or vitreous (V-type) spherules (Taylor and Brownlee, 1991; Taylor et al., 2000, 2007a; Genge et al., 2008, 2018). Recently, this classification has been expanded to include a microporphyritic type (μ Po-type), as the μ Po CSs appear to derive from a parent body distinct to the Po-type spherules (van Ginneken et al., 2017). Backscattered electron images for examples of the various textural groups of silicate CSs are shown in Fig. 3. Using optical microscopy, SEM and/or μ CT (cf. below), the diameters for a fraction of the extracted CSs were determined. Fig. 4 illustrates the size distribution of the Widerøefjellet CS collection and compares the size distributions of the subgroups of CSs characterized using different analytical techniques.

2.3. Micro computer-assisted X-ray tomography (µCT)

Of these 985 CSs, 45 particles in the 200–400 μ m size fraction and 101 particles in the 400–800 μ m size fraction were analyzed using the HECTOR (High-Energy μ CT system Optimized for Research) X-ray scanner at the Centre for X-ray Tomography of Ghent University (Supplementary Fig. S1). This instrument is equipped with a 240 kV X-ray tube from X-RAY WorX and a PerkinElmer 1620 flat-panel detector of 2048 × 2048 pixels (Masschaele et al., 2013). The beam was operated at 15 kV with 90 min-



Fig. 2. Widerøefjellet CS accumulation site in the Sør Rondane Mountains. (A) Map detail of the Widerøefjellet site within the Sør Rondane Mountains region, where the CSs described in this work have been recovered. The orange line highlights the track used to reach this site, the black dashed lines represent contour lines that connect points of equal elevation (height) in meter above sea level (masl). (B) View on the Widerøefjellet summit ridge (72°09′S, 23°17′E, 2755 masl), with the box highlighting the approximate location of the MM accumulation site. Orientation and dominant wind direction are also indicated. (C-D) After removal of the largest rock fragments and boulders, the surface delineated by the orange dashed line in (D) yielded the described collection of CSs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

utes of exposure time per scan. Because of the size and number of MMs, packets of up to 50 particles were scanned simultaneously. Because of the variable total scanned volume, this set-up generated transmission images with a pixel size of $2\times2\,\mu\text{m}^2$ and $4\times4\,\mu\text{m}^2$ for the 400–800 μm and 200-400 µm particles, respectively. The Octopus Reconstruction software (Masschaele et al., 2007; Vlassenbroeck et al., 2007) was used to transform the acquired µCT data into a stack of 2D image slices that were consequently processed into 3D models using the open source program 3dmod Version 4.5.8. For the latter, the voxel size of the reconstructions was preferred to approximate the pixel size and ranged from $2 \,\mu m \times 2 \,\mu m \times 2 \,\mu m$ to $4 \,\mu\text{m} \times 4 \,\mu\text{m} \times 4 \,\mu\text{m}$. A selection of 3D μCT models is presented in Fig. 5, while examples of 2D μ CT slices are shown in Supplementary Fig. S2.

2.4. Major and trace element analysis

Following the acquisition of the μ CT images, 49 CSs, ranging between 439 and 916 μ m, were arbitrarily selected

from the larger size fractions and mounted in epoxy resin (Polyfast[™]) under vacuum conditions and polished using silicon carbide paper with 1200-4000 grit (mesh) size. The exposed interiors of the spherules were subsequently polished with diamond paste in an alcohol-based suspension (particle sizes 6, 3 and 1 µm) on a synthetic cloth, and carbon-coated prior to further textural and chemical characterization using the SEM-EDS systems at VUB and electron microprobe (EMP) at the Natural History Museum (NHM) in Vienna, Austria. Quantitative wavelengthdispersive X-ray spectrometric (WDS) analyses were performed with a field emission gun electron microprobe analyser (EMPA) JEOL Hyperprobe JXA 8530F in the Central Laboratory at the NHM. Between 2 and 19 EMPA data points were gathered for relatively homogeneous particles (V- and CC-type), while more analyses were carried out for CSs with significant heterogeneity, with up to 50 points for BO- and Po-type CSs. In each CS, olivine, glass, metal and magnetite phases were examined and averaged proportional to their abundances estimated from SEM images using image processing software to obtain bulk composi-



Fig. 3. Back-scattered electron images of silicate cosmic spherules characterized in this work. (A) V-type CS WF1202B-0001, displaying limited alteration. (B) Section through the same spherule. (C) V-type cosmic spherule WF1202B-0057, exhibiting a more altered, crackled surface relative to (A). (D) BO-type CS WF1202B-0013. (E) Section through the same spherule indicating local dissolution of the interstitial glass. (F) Textural detail of the same spherule showing Mg-rich olivine bars (dark grey) and magnetite crystallites (white) in Fe-rich glass (grey). (G) CC-type CS WF1202B-0030 with characteristic turtle-back (polyhedral-like) morphology. (H) A section through the same particle. (I) Textural detail of the same sectioned spherule showing olivine (grey) and magnetite crystallites (white). (J) Po-type CS WF1202B-0025, consisting mainly of olivine microphenocrysts (dark grey) in glass (grey) and magnetite (white). (K) A section through the same spherule. Note the presence of two larger, relict mineral phases, which have partially been resorbed due to atmospheric heating (indicated by arrows). (L) Textural detail of the same sectioned spherule showing microphenocryst with variable Fe-Mg contents. (M) Cosmic spherule WF1202B-0071, exhibiting a mixed BO/CC-type texture. (N) μPo-type CS WF1202B-0073. (O) Po-type "*Group 4*" CS WF1202B-0070. (P) Irregular CS WF1202B-0079. Particles WF1202B-0001, 0013, 0025 and 0030 were sectioned and characterized using EMPA and LA-ICP-MS, while CSs WF1202B-0057, 0070, 0071, 0073 and 0079 were analyzed as a whole for oxygen isotope ratios using LF-IRMS.



Fig. 4. (A) Cumulative size distribution for CSs from the Widerøefjellet (>200 μ m size fraction, filled diamonds) and Transantarctic Mountains (>400 μ m size fraction, filled circles) collections. The slopes are calculated for all samples with diameters larger than 240 μ m and 440 μ m, respectively, following the method described in Suavet et al. (2009). (B) Comparison of size distributions for CSs characterized for oxygen isotope ratios to those characterized for major and trace element concentrations.



Fig. 5. Micro computer-assisted X-ray tomographic renderings for four CSs, BO-type CSs WF1202B-0002 (A), WF1202B-0042 (C) and WF1202B-0052 (D), and V-type CS WF1202B-0021 (B), highlighting the presence of metal beads (red), vesicle inclusions, or both. Additional cross-sections are provided in Supplementary Fig. S2.

tions. Note that this methodology depends on the CS section obtained and the phase contrasts within individual particles but can in part be validated through the subsequent laser ablation - inductively coupled plasma - mass spectrometry (LA-ICP-MS) analysis (cf. below). Operating conditions included an accelerating voltage of 15 kV, a beam current of 20 nA with WDS and EDS (Bruker), and a counting time of 10 s for the peak and 5 s for the background for all element K_{α} lines. The spot size was varied from 0.07 µm (fully focused, in the case of spatially limited phases) to 2 µm. Synthetic compounds Al₂O₃, Cr₂O₃, TiO₂, NiO, NaCl, KCl and natural minerals vanadinite Pb₅(VO₄)₃Cl, tephroite Mn₂SiO₄, wollastonite CaSiO₃, Durango apatite Ca₅(PO₄)₅F and Marjalahti olivine (Mg, Fe)₂SiO₄ were used for calibration of Al, Cr, Ti, Ni, Na, K, V, Mn, Ca, P, Mg, Si, and Fe, respectively. The data reduction was carried out using the on-line ZAFcorrections provided by JEOL. The mean detection limits (LOD, in wt% and ppm) for the measured oxides (with standard deviation for the LOD in ppm), calculated from 50 analysis points on glass and olivine, are presented in Supplementary Table S1. The analytical precision for major elements (Si, Mg and Fe) is typically better than 1% relative

standard deviation (RSD) based on repeated measurements of calibration standards and V-type CSs, but the total uncertainty associated with the EMPA analysis, due to sample heterogeneity, is estimated to be 2–5% RSD for BO-, CC-, and Po-type CSs. For the analyzed minor and trace elements (Ti, Cr, Mn, Na, K, P, V and Ni), the total uncertainty associated with the EMP analysis is calculated to be on the order of 5–15% RSD, taking the presence of olivine and magnetite phenocrysts and changes in the composition of the interstitial glass into account. The major element data obtained using EMPA are summarized in Table 1 and Supplementary Table S1.

Selected major and trace element concentrations were determined by means of LA-ICP-MS analysis using a Teledyne Photon Machines (Bozeman, MT, USA) Analyte G2 ArF* excimer-based LA system coupled to a Thermo Scientific Element XR double-focusing sector field ICP-mass spectrometer at the Department of Chemistry of Ghent University, following the procedures outlined in Martin et al. (2013) and Van Roosbroek et al. (2015). Using a repetition rate of 30 Hz and energy density of \sim 8.27 J/cm², each CS was ablated multiple times for 15 s using a laser spot size of 50 µm. The 18 V-type CSs were each ablated

Table 1

Average major (oxide wt%) and trace (ppm) element composition with standard deviations (1 SD; italic) of textural and chemical groups of cosmic spherules determined by electron microprobe analysis (EMPA) and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), compared to the literature values compiled by Folco and Cordier (2015) for particles from other micrometeorite collections.

Intimigrare (mignar/mar) Intimigrare (mignar/mar) Intimigrare Intinitity Intimigrare <	Туре	V norm	nal	V not	rmal	BO	9	WF1202B-	BO		CC		CC n	ormal	CAT-li	ke	V + BC)	High		WF1202B-	V hig	h
Avg. I SD Avg. I SD <th< th=""><th>n (major/trace)</th><th>13/13</th><th></th><th>lit. 422/1</th><th>26</th><th>normal 11/11</th><th>a</th><th>0013 1/1</th><th>normal 294/7</th><th>lit.</th><th>normal 9/9</th><th></th><th>lit. 98/7</th><th></th><th>6/6</th><th></th><th>CAT-lil 45/17</th><th>ke lit.</th><th>Ca-Al⁶ 3/3</th><th></th><th>0001 1/1</th><th>Ca-Al 33/19</th><th>l lit.</th></th<>	n (major/trace)	13/13		lit. 422/1	26	normal 11/11	a	0013 1/1	normal 294/7	lit.	normal 9/9		lit. 98/7		6/6		CAT-lil 45/17	ke lit.	Ca-Al ⁶ 3/3		0001 1/1	Ca-Al 33/19	l lit.
SiO ₂ (we/s) 4.7 1.6 3.7 3.0 0.6 3.9 3.0 0.5 1.5 1.6 0.5 1.6 0.5 0.16 0.5 0.16 0.5 0.16 0.5 0.16 0.5 0.16 0.5 0.16 0.5 0.16 0.5 0.16 0.5 0.16 0.5 0.16 0.5 0.16 0.5 0.16 0.5 0.16 0.5 0.16 0.5 0.16		Avg.	1 SD	Avg.	1 SD	Avg.	1 SD		Avg.	1 SD	Avg.	1 SD	Avg.	1 SD	Avg.	1 SD	Avg.	1 SD	Avg.	1 SD		Avg.	1 SD
TrO ₂ 0.14 0.07 0.14 0.07 0.13 0.07 0.30 0.17 0.26 0.13 0.10 0.30 0.17 0.14 0.05 0.03 0.17 0.14 0.03 0.17 0.14 0.03 0.17 0.14 0.23 0.16 0.03 0.17 0.14 0.28 0.15 0.17 0.13 0.26 0.16 0.07 0.30 0.17 0.28 0.27 0.88 0.06 0.16 0.10 0.10 0.10 0.10 0.11 0.28 0.17 0.28 0.17 0.28 0.17 0.28 0.16 0.10 0.10 0.10 0.10 0.10 0.10 0.10 0.10 0.10 0.10 0.10 0.11 0.10 0.11 0.28 0.11 0.10	SiO ₂ (wt%)	45.7	2.4	48.8	3.8	33.2	3.9	30.6	39.5	4.4	41.6	3.1	43.4	4.0	42.4	6.2	46.3	5.7	43.0	0.64	39.7	48.4	4.7
CreOs 0.06 0.33 0.17 0.14 0.49 0.16 0.10 0.07 0.80 0.06 0.10 - 0.07 0.31 0.28 0.35 3.1 1.4 2.84 0.42 0.15 1.4 0.84 0.40 0.35 0.16 0.10 0.16 0.10 0.17 0.33 0.04 0.49 0.41 3.3 FeO 0.33 0.10 0.30 0.31 0.41 0.33 0.40 0.43 0.10 0.10 0.10 0.10 0.10 0.10 0.10 0.10 0.10 0.10 0.10 0.17 0.43 0.04 0.49 0.10 0.04 0.10 0.04 0.10 0.04 0.10 0.04 0.04 0.06 0.03 0.04 0.04 0.05 0.04 0.06 0.05 0.06 0.01 0.01 0.00 0.10 0.00 0.10 0.01 0.00 0.10 0.01 0.01 0.01 0.01 0.01	TiO ₂	0.14	0.07	0.14	0.25	0.16	0.05	0.18	0.15	0.11	0.13	0.05	0.15	0.07	0.30	0.11	0.26	0.12	0.33	0.10	0.32	0.30	0.12
Al-O 3.06 0.98 2.80 0.98 2.80 1.1 3.1 1.4 2.84 0.62 3.1 1.4 0.63 3.3 FeO 13.2 5.4 12.7 5.3 3.2 8.1 2.2 3.3 0.00 0.33 0.00 0.25 0.28 0.14 0.04 0.16 0.10 0.16 0.10 0.16 0.10 0.16 0.01 0.01 0.00 0.00 0.00 0.00 0.01 0.04 0.02 0.04 0.02 0.04 0.02 0.04 0.02 0.04 0.00	Cr_2O_3	0.06	0.03	0.17	0.14	0.49	0.54	1.15	0.39	0.26	0.16	0.10	0.30	0.24	<lod< td=""><td>_</td><td>0.08</td><td>0.06</td><td>0.10</td><td>_</td><td>0.07</td><td>0.31</td><td>0.28</td></lod<>	_	0.08	0.06	0.10	_	0.07	0.31	0.28
FeO 13.2 5.4 12.7 5.3 34.2 8.1 9.7 24.8 9.5 19.8 4.6 9.0 40.9 40.2 14.1 10.0 81.1 1.2 2.9 9.1 3.3 MgO 34.0 6.9 10.0 10.2 0.21 0.22 0.14 0.33 0.01 0.10 0.10 0.10 0.10 0.01 0.00 1.02 0.21 0.24 0.14 1.5 5.9 3.0 4.5 2.1 3.4 0.64 0.20 0.10 0.01 0.00 1.02 0.21 0.21 0.22 0.10 0.05 0.04 0.10 0.01 0.05 0.04 0.10 0.01 0.01 0.00 0.01 0.00 0.05 0.04 0.10 0.01 0.01 0.03 0.01 0.01 0.05 0.04 0.10 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.02 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0	Al_2O_3	3.06	0.98	2.80	0.98	2.8	1.1	3.5	3.1	1.4	2.84	0.62	3.15	1.47	6.8	3.0	5.9	2.8	5.72	0.68	31.28	6.9	3.5
MnO 0.33 0.10 0.38 0.17 0.23 0.14 0.32 0.04 0.35 0.20 0.10 0.01 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.00 0.01 0.00 0.01 0.00 0.01 0.00 0.01 0.00 0.01 0.00 0.01 0.00 0.01 0.00 0.01 0.00 0.01 0.00 <	FeO ^c	13.2	5.4	12.7	5.3	34.2	8.1	39.7	24.8	9.5	19.8	4.6	19.6	6.4	0.94	0.82	1.4	1.0	8.1	1.2	3.9	9.1	3.3
MgO 34.0 6.9 31.7 4.7 23.7 6.9 19.0 29.0 6.8 30.4 4.20 3.6 4.18 5.2 35.4 1.7 3.7 28.1 6.4 CaO 2.09 1.0 2.32 1.4 1.90 0.02 0.01 0.01 0.01 0.00	MnO	0.33	0.10	0.38	0.17	0.23	0.05	0.25	0.28	0.14	0.32	0.08	0.33	0.20	0.10	0.10	0.16	0.10	0.17	0.03	0.04	0.29	0.14
Ca0 1.0 1.2 2.1 1.5 2.8 0.2 2.1 1.35 2.9 3.0 4.5 2.1 4.36 0.00 1.86 7.0 3.0 Na_Q 0.00 0.00 0.01 0.00 0.01 0.00 0.01 0.00 <	MgO	34.0	6.9	31.7	4.7	23.7	6.9	19.0	29.0	6.8	30.4	4.5	30.3	5.0	42.0	3.6	41.8	5.2	35.4	1.7	3.7	28.1	6.4
Na ₂ O 0.02 0.06 0.01 0.02 0.01 0.01 0.02 0.02 0.03 0.01 0.02 0.03 0.01 0.00 0.03 0.01 0.00 0.03 0.01 0.00 0.03 0.01 0.00 0.03 0.01 0.00 0.03 0.01 0.00 0.03 0.01 0.00 0.03 0.01 0.00 <	CaO	2.09	1.0	2.32	1.14	1.90	0.73	1.92	2.4	1.5	2.38	0.82	2.51	1.35	5.9	3.0	4.5	2.1	4.36	0.06	18.66	7.0	3.0
K-O - 0.03 0.01 CLOD - CLOD - 0.03 0.00 CLOD - 0.00 <td>Na₂O</td> <td>0.02</td> <td>0.06</td> <td>0.13</td> <td>0.04</td> <td><lod< td=""><td>_</td><td><lod< td=""><td>0.21</td><td>0.22</td><td><lod< td=""><td>_</td><td>0.60</td><td>0.80</td><td>0.02</td><td>0.09</td><td>0.02</td><td>0.01</td><td>0.01</td><td>0.01</td><td>0.02</td><td>0.30</td><td>0.12</td></lod<></td></lod<></td></lod<></td>	Na ₂ O	0.02	0.06	0.13	0.04	<lod< td=""><td>_</td><td><lod< td=""><td>0.21</td><td>0.22</td><td><lod< td=""><td>_</td><td>0.60</td><td>0.80</td><td>0.02</td><td>0.09</td><td>0.02</td><td>0.01</td><td>0.01</td><td>0.01</td><td>0.02</td><td>0.30</td><td>0.12</td></lod<></td></lod<></td></lod<>	_	<lod< td=""><td>0.21</td><td>0.22</td><td><lod< td=""><td>_</td><td>0.60</td><td>0.80</td><td>0.02</td><td>0.09</td><td>0.02</td><td>0.01</td><td>0.01</td><td>0.01</td><td>0.02</td><td>0.30</td><td>0.12</td></lod<></td></lod<>	0.21	0.22	<lod< td=""><td>_</td><td>0.60</td><td>0.80</td><td>0.02</td><td>0.09</td><td>0.02</td><td>0.01</td><td>0.01</td><td>0.01</td><td>0.02</td><td>0.30</td><td>0.12</td></lod<>	_	0.60	0.80	0.02	0.09	0.02	0.01	0.01	0.01	0.02	0.30	0.12
Pack CLOD - 0.08 0.04 0.06 0.04 0.13 0.10 CLOD - 0.08 0.09 - 0.18 0.09 0.05 - 0.18 0.09 0.05 0.09 0.05 0.07 0.30 0.30 - 0.13 0.09 0.05 0.07 0.30 0.30 - 0.13 0.09 0.07 0.02 0.00 0.04 0.02 CaO A.16 I.2 A.20 I.2 I.2 <thi.2< t<="" td=""><td>K₂O</td><td><lod< td=""><td>_</td><td>0.03</td><td>0.01</td><td><lod< td=""><td>_</td><td><lod< td=""><td>0.10</td><td>0.03</td><td><lod< td=""><td>_</td><td>0.05</td><td>0.04</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td><td>0.01</td><td>0.00</td><td><lod< td=""><td>0.06</td><td>0.01</td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></thi.2<>	K ₂ O	<lod< td=""><td>_</td><td>0.03</td><td>0.01</td><td><lod< td=""><td>_</td><td><lod< td=""><td>0.10</td><td>0.03</td><td><lod< td=""><td>_</td><td>0.05</td><td>0.04</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td><td>0.01</td><td>0.00</td><td><lod< td=""><td>0.06</td><td>0.01</td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	_	0.03	0.01	<lod< td=""><td>_</td><td><lod< td=""><td>0.10</td><td>0.03</td><td><lod< td=""><td>_</td><td>0.05</td><td>0.04</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td><td>0.01</td><td>0.00</td><td><lod< td=""><td>0.06</td><td>0.01</td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	_	<lod< td=""><td>0.10</td><td>0.03</td><td><lod< td=""><td>_</td><td>0.05</td><td>0.04</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td><td>0.01</td><td>0.00</td><td><lod< td=""><td>0.06</td><td>0.01</td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	0.10	0.03	<lod< td=""><td>_</td><td>0.05</td><td>0.04</td><td><lod< td=""><td>_</td><td><lod< td=""><td>_</td><td>0.01</td><td>0.00</td><td><lod< td=""><td>0.06</td><td>0.01</td></lod<></td></lod<></td></lod<></td></lod<>	_	0.05	0.04	<lod< td=""><td>_</td><td><lod< td=""><td>_</td><td>0.01</td><td>0.00</td><td><lod< td=""><td>0.06</td><td>0.01</td></lod<></td></lod<></td></lod<>	_	<lod< td=""><td>_</td><td>0.01</td><td>0.00</td><td><lod< td=""><td>0.06</td><td>0.01</td></lod<></td></lod<>	_	0.01	0.00	<lod< td=""><td>0.06</td><td>0.01</td></lod<>	0.06	0.01
NiO 0.07 0.17 2.46 4.42 0.30 0.49 0.60 0.77 100 98.7 100 90.7 100 98.7 100.7 96.6 100.7 90.7 100 98.7 100.7 97.4 97.7 100.8 98.4 100.7 98.4 100.7 98.4 100.7 98.4 100.7 98.4 100.7 98.4 100.7 98.4 100.7 98.4 100.7 98.4 100.7 98.4 100.7 98.4 100.7 98.4 100.7 98.4 100.7 98.4 100.7 98.4 100.7 98.4 100.7 98.4 100.7 98.4 100.7 100.7 98.4 12.7 0.1 12.1 12.5 50.0 1.7 49.4 4.4 4.4 100.7	P_2O_5	<lod< td=""><td>_</td><td>0.08</td><td>0.04</td><td>0.06</td><td>0.04</td><td>0.14</td><td>0.13</td><td>0.10</td><td><lod< td=""><td>_</td><td>0.08</td><td>0.09</td><td><lod< td=""><td>_</td><td>0.18</td><td>0.09</td><td>0.05</td><td>_</td><td><lod< td=""><td>0.24</td><td>0.09</td></lod<></td></lod<></td></lod<></td></lod<>	_	0.08	0.04	0.06	0.04	0.14	0.13	0.10	<lod< td=""><td>_</td><td>0.08</td><td>0.09</td><td><lod< td=""><td>_</td><td>0.18</td><td>0.09</td><td>0.05</td><td>_</td><td><lod< td=""><td>0.24</td><td>0.09</td></lod<></td></lod<></td></lod<>	_	0.08	0.09	<lod< td=""><td>_</td><td>0.18</td><td>0.09</td><td>0.05</td><td>_</td><td><lod< td=""><td>0.24</td><td>0.09</td></lod<></td></lod<>	_	0.18	0.09	0.05	_	<lod< td=""><td>0.24</td><td>0.09</td></lod<>	0.24	0.09
Sum 98.7 101.7 97.1 96.6 100.7 97.7 100.8 98.4 100.7 97.4 97.7 100.9 CaO + Al_O_3 (wf%) 5.16 1.49 4.93 2.05 5.5 5.6 5.2 1.6 5.6 2.23 1.27 6.0 10.5 5.2 1.00 0.7 49.94 4.23 4.2 4.2 Fe/Mm (atomic) 0.40 0.21 0.20 0.42 1.17 0.51 0.27 0.50 1.5 0.10 0.13 0.02 0.00 0.71 49.94 4.20 0.70 Fe/Mm (atomic) 0.24 0.10 0.22 0.20 0.40 0.72 0.30 0.15 0.01 0.02 0.01 0.10 0.02 0.10 0	NiO	0.07	0.17	2.46	4.42	0.30	0.32	0.13	0.59	0.49	0.06	0.07	0.30	0.30	<lod< td=""><td>_</td><td>0.13</td><td>0.16</td><td>0.09</td><td>0.17</td><td>0.02</td><td>0.04</td><td>0.02</td></lod<>	_	0.13	0.16	0.09	0.17	0.02	0.04	0.02
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Sum	98.7		101.7		97.1		96.6	100.7		97.7		100.8		98.4		100.7		97.4		97.7	100.9	
Fe/Mn (atomic)40.6/2.6/4.0/2.0/1.5/5.8/1.55/9.3/4.9/6.6/2.8/7.7/4.52/1.7/1.51/1.2/2.5/5.0/1.5/5.0/3.9/2.0Fe/Mg0.240.120.240.120.240.100.220.100.130.170.390.170.390.150.100.010.020.010.130.020.000.010.020.000.020.010.020.010.020.010.020.010.020.010.020.010.020.010.020.010.010.020.010.010.020.010.010.020.010.010.020.010.010.020.010.010.020.010.01	$CaO + Al_2O_3 (wt\%)$	5.16	1.49	4.93	2.05	4.7	1.6	5.4	5.5	2.6	5.2	1.4	5.66	2.23	12.7	6.0	10.5	5.2	10.09	0.71	49.94	14.2	4.4
Fe/Mg 0.24 0.12 0.48 4.72 0.92 0.42 1.17 0.51 0.27 0.39 0.17 0.39 0.15 0.01 0.01 0.02 0.01 0.13 0.02 0.08 0.02 0.09 0.22 0.10 0.12 0.39 0.15 0.02 0.01 0.01 0.02	Fe/Mn (atomic)	40.6	12.6	40.0	20.9	156	58	155	93	49	66	28	74.7	45.2	12.7	9.1	21	25	50	15	87.0	39	20
Fe/Si 0.24 0.10 0.22 0.10 0.89 0.29 1.09 0.52 0.26 0.40 0.12 0.39 0.15 0.02 0.01 0.02 0.02 0.02 0.03 0.02 0.01 0.02 0.02 0.02 0.02 0.02 0.01 0.02 0.02 0.02 0.01 0.01 0.01 0.02 0.01 0.01 0.01 0.02 0.01 0.01 0.01	Fe/Mg	0.24	0.12	0.48	4.72	0.92	0.42	1.17	0.51	0.27	0.39	0.17	0.39	0.15	0.01	0.01	0.02	0.01	0.13	0.02	0.58	0.20	0.10
Mg/Si 1.12 0.27 0.95 0.23 1.06 0.26 0.93 1.09 0.22 1.09 0.15 1.04 0.17 1.51 0.28 1.38 0.30 1.23 0.66 0.14 0.89 0.28 Li (ppm) 0.64 0.71 0.8 - 0.37 0.50 1.72 0.66 0.4 0.74 0.56 0.9 0.6 <lod< td=""> - 1.1 0.7 1.11 - 3.15 0.7 0.5 Sc 11.8 6.2 13.8 5.5 11 4.3 10 10.3 3.4 11.5 1.9 1.23 3.7 2.24 1.46 71 1.6 14 18 13 2.1 50 69 10 57 76 Cr 377 338 915 910 1054 3205 2420 1400 1204 841 1650 1320 37 72 218 326 3.66 1132 2075 132 361 328 3675 367 365 161 120 36</lod<>	Fe/Si	0.24	0.10	0.22	0.10	0.89	0.29	1.09	0.52	0.26	0.40	0.12	0.39	0.15	0.02	0.01	0.02	0.02	0.16	0.02	0.08	0.16	0.05
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Mg/Si	1.12	0.27	0.95	0.23	1.06	0.26	0.93	1.09	0.22	1.09	0.15	1.04	0.17	1.51	0.28	1.38	0.30	1.23	0.06	0.14	0.89	0.28
Sc 11.8 6.2 13.8 5.5 11 4.3 10 10.3 3.4 11.5 1.9 12.7 3.7 22.8 9.0 28 25 24 11 9 35 17 V 40 18 49 25 71 14 67 58 21 58 14 71 16 14 18 13 21 50 69 10 57 76 Cr 377 338 915 910 2091 1054 3205 240 1460 1204 841 1650 1320 37 72 291 391 55 954 328 1132 2075 Ni 381 952 568 803 2340 2761 933 3635 3675 367 436 1490 2355 1.21 0.75 422 1382 726 1539 7 134 173 Cu 0.13 0.25 NR NR 0.06 6.03 2.27 1.48 5 11 <t< td=""><td>Li (ppm)</td><td>0.64</td><td>0.71</td><td>0.8</td><td>_</td><td>0.37</td><td>0.50</td><td>1.72</td><td>0.6</td><td>0.4</td><td>0.74</td><td>0.56</td><td>0.9</td><td>0.6</td><td><lod< td=""><td>_</td><td>1.1</td><td>0.7</td><td>1.11</td><td>-</td><td>3.15</td><td>0.7</td><td>0.5</td></lod<></td></t<>	Li (ppm)	0.64	0.71	0.8	_	0.37	0.50	1.72	0.6	0.4	0.74	0.56	0.9	0.6	<lod< td=""><td>_</td><td>1.1</td><td>0.7</td><td>1.11</td><td>-</td><td>3.15</td><td>0.7</td><td>0.5</td></lod<>	_	1.1	0.7	1.11	-	3.15	0.7	0.5
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Sc	11.8	6.2	13.8	5.5	11	4.3	10	10.3	3.4	11.5	1.9	12.7	3.7	22.8	9.0	28	25	24	11	9	35	17
Cr 377 338 915 910 2091 1054 3205 2420 1460 1204 841 1650 1320 37 72 291 391 555 954 328 1132 2075 Co 31 42 32 37 270 156 370 151 113 61 27 88 52 0.21 0.15 2.6 3.6 117 202 5 19 29 Ni 381 952 568 803 2340 2761 933 3655 3675 367 436 1490 2355 1.21 0.75 422 1382 761 0.14 173 Cu 0.13 0.24 0.39 0.13 1.84 0.70 0.35 0.68 0.73 2.27 1.48 5 11 1.3 1.5 0.45 0.13 0.65 1.8 2.9 Rb 0.2 1.1 0.17	V	40	18	49	25	71	14	67	58	21	58	14	71	16	14	18	13	21	50	69	10	57	76
Co 31 42 32 37 270 156 370 151 113 61 27 88 52 0.21 0.15 2.6 3.6 117 202 5 19 29 Ni 381 952 568 803 2340 2761 933 3635 3675 367 436 1490 2355 1.21 0.75 422 1382 726 1539 7 134 173 Cu 0.13 0.25 NR NR 0.06 6.62 NR NR 0.14 0.19 NR NR 0.9 1.6 NR NR 0.07 0.04 0.13 0.65 1.8 2.9 Rb 0.2 1.1 0.12 0.17 0.01 - 2.43 0.05 0.03 <lod< td=""> - 0.62 0.01 - 0.05 0.04 LOD - 0.05 0.04 LOD - 0.02 0.17 0.21 State 1.1 1.3 1.2 2.6 11 1.3 1.2 <</lod<>	Cr	377	338	915	910	2091	1054	3205	2420	1460	1204	841	1650	1320	37	72	291	391	555	954	328	1132	2075
Ni 381 952 568 803 2340 2761 933 3635 3675 367 436 1490 2355 1.21 0.75 422 1382 726 1539 7 134 173 Cu 0.13 0.25 NR NR 0.06 6.62 NR NR NR 0.14 0.19 NR NR 0.9 1.6 NR NR 0.07 0.04 0.11 NR NR NR 0.73 2.27 1.48 5 11 1.3 1.5 0.45 0.13 0.65 1.8 2.9 Rb 0.2 1.1 0.12 0.17 0.01 $ 2.43$ 0.05 0.33 <2.07 1.48 5 11 1.3 1.5 0.45 0.13 0.65 1.8 2.9 Sr 10.7 4.6 11.6 7.6 13 3.2 12 10.2 2.4 15.0 4.3 12.9 6.7 2.9 12 6.6 <	Co	31	42	32	37	270	156	370	151	113	61	27	88	52	0.21	0.15	2.6	3.6	117	202	5	19	29
Cu 0.13 0.25 NR NR 0.06 6.62 NR NR 0.14 0.19 NR NR 0.6 NR NR 0.9 1.6 NR NR 0.07 0.04 0.11 NR NR NR Zn 0.47 0.24 2.3 4.4 0.39 0.13 1.84 0.70 0.35 0.68 0.73 2.27 1.48 5 11 1.3 1.5 0.45 0.13 0.65 1.8 2.9 Rb 0.2 1.1 0.12 0.17 0.01 $ 2.43$ 0.05 0.03 $ 0.05 0.04 0.09 0.17 0.21 Sr 10.7 4.6 11.6 7.6 13 3.2 12 10.2 2.4 15.0 4.3 12.9 6.7 2.9 12 26 11 21 8.8 161 33 17 Y 1.63 0.78<$	Ni	381	952	568	803	2340	2761	933	3635	3675	367	436	1490	2355	1.21	0.75	422	1382	726	1539	7	134	173
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Cu	0.13	0.25	NR	NR	0.08	0.06	6.62	NR	NR	0.14	0.19	NR	NR	0.9	1.6	NR	NR	0.07	0.04	0.11	NR	NR
Rb 0.2 1.1 0.12 0.17 0.01 $ 2.43$ 0.05 0.03 $< LOD$ $ 0.26$ 0.42 0.01 $ 0.05$ 0.04 $< LOD$ $ 0.09$ 0.17 0.21 Sr 10.7 4.6 11.6 7.6 13 3.2 12 10.2 2.4 15.0 4.3 12.9 6.7 29 12 26 11 21 8.8 161 33 17 Y 1.63 0.78 2.2 1.4 2.7 1.0 5.3 2.11 0.81 2.5 0.8 2.2 1.1 5.6 2.4 5.3 2.4 6.6 2.5 26.1 5.4 3.6 Zr 6.8 3.4 6.2 3.4 6.8 2.4 9.0 5.0 1.8 7.1 1.4 6.0 1.9 15.1 6.3 13 5.3 15.3 7.6 119.6 19.2 6.2 Nb 0.58 0.36 0.51 0.22 0.54 0.13 0.70 0.39 0.14 0.55 0.09 0.66 0.24 1.1 0.4 0.90 0.51 1.1 0.53 6.7 1.37 0.63 Cs $ 0.020.010.030.28 0.010.0020.030.020.01 0.010.01 0.010.01 0.020.02Ba4.0$	Zn	0.47	0.24	2.3	4.4	0.39	0.13	1.84	0.70	0.35	0.68	0.73	2.27	1.48	5	11	1.3	1.5	0.45	0.13	0.65	1.8	2.9
Sr 10.7 4.6 11.6 7.6 13 3.2 12 10.2 2.4 15.0 4.3 12.9 6.7 29 12 26 11 21 8.8 161 33 17 Y 1.63 0.78 2.2 1.4 2.7 1.0 5.3 2.11 0.81 2.5 0.8 2.2 1.1 5.6 2.4 5.3 2.4 6.6 2.5 26.1 5.4 3.6 Zr 6.8 3.4 6.2 3.4 6.8 2.4 9.0 5.0 1.8 7.1 1.4 6.0 1.9 15.1 6.3 13 5.3 15.3 7.6 119.6 19.2 6.2 Nb 0.58 0.36 0.51 0.22 0.54 0.13 0.70 0.39 0.14 0.55 0.09 0.66 0.24 1.1 0.4 0.90 0.51 1.1 0.53 6.7 1.37 0.63 Cs $ 0.020.010.030.28 0.010.020.01 0.010.01 0.020.020.01 0.020.020.01 0.020.020.01 0.010.01 0.020.020.01 0.010.01 0.020.020.01 0.020.020.01 0.010.01 0.$	Rb	0.2	1.1	0.12	0.17	0.01	_	2.43	0.05	0.03	<lod< td=""><td>_</td><td>0.26</td><td>0.42</td><td>0.01</td><td>_</td><td>0.05</td><td>0.04</td><td><lod< td=""><td>_</td><td>0.09</td><td>0.17</td><td>0.21</td></lod<></td></lod<>	_	0.26	0.42	0.01	_	0.05	0.04	<lod< td=""><td>_</td><td>0.09</td><td>0.17</td><td>0.21</td></lod<>	_	0.09	0.17	0.21
Y 1.63 0.78 2.2 1.4 2.7 1.0 5.3 2.11 0.81 2.5 0.8 2.2 1.1 5.6 2.4 5.3 2.4 6.6 2.5 26.1 5.4 3.6 Zr 6.8 3.4 6.2 3.4 6.8 2.4 9.0 5.0 1.8 7.1 1.4 6.0 1.9 15.1 6.3 13 5.3 15.3 7.6 119.6 19.2 6.2 Nb 0.58 0.36 0.51 0.22 0.54 0.13 0.70 0.39 0.14 0.55 0.09 0.66 0.24 1.1 0.4 0.90 0.51 1.1 0.53 6.7 1.37 0.63 Cs $ 0.02 0.01 0.03 0.28 0.01 0.01 0.01 0.02 0.01 0.01 0.01 0.02 0.02 0.02 0.02 0.0$	Sr	10.7	4.6	11.6	7.6	13	3.2	12	10.2	2.4	15.0	4.3	12.9	6.7	29	12	26	11	21	8.8	161	33	17
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Y	1.63	0.78	2.2	1.4	2.7	1.0	5.3	2.11	0.81	2.5	0.8	2.2	1.1	5.6	2.4	5.3	2.4	6.6	2.5	26.1	5.4	3.6
Nb 0.58 0.36 0.51 0.22 0.54 0.13 0.70 0.39 0.14 0.55 0.09 0.66 0.24 1.1 0.4 0.90 0.51 1.1 0.53 6.7 1.37 0.63 Cs $< LOD 0.02$ 0.01 0.01 0.03 0.28 $< LOD 0.01$ 0.002 0.03 0.02 0.01 $ 0.01$ 0.01 $ 0.02$ 0.02 0.01 Ba 4.0 1.6 4.0 2.1 4.21 0.80 13.2 3.2 1.7 5.1 1.9 4.4 2.5 9.1 3.0 8.2 3.3 5.8 3.8 80.4 10.0 4.5 La 0.33 0.26 0.35 0.27 0.48 0.14 3.42 0.33 0.15 0.47 0.14 0.40 0.27 1.0 0.48 0.85 0.38 0.95 0.11 9.18 0.99 0.78 Ce 0.80 0.54 0.89 0.66 1.17 0.35 4.97 0.78 0.34 1.07 0.31 1.11 0.85 1.3 0.48 1.61 0.69 2.1 0.80 23.4 2.1 1.7 Pr 0.12 0.08 0.14 0.07 1.25 0.12 0.05 0.17 0.17 0.11 0.36 0.13 0.31 0.13 0.31 0.13 0.31 0.13 0.31 0.13 0.31 0.13 0.31 </td <td>Zr</td> <td>6.8</td> <td>3.4</td> <td>6.2</td> <td>3.4</td> <td>6.8</td> <td>2.4</td> <td>9.0</td> <td>5.0</td> <td>1.8</td> <td>7.1</td> <td>1.4</td> <td>6.0</td> <td>1.9</td> <td>15.1</td> <td>6.3</td> <td>13</td> <td>5.3</td> <td>15.3</td> <td>7.6</td> <td>119.6</td> <td>19.2</td> <td>6.2</td>	Zr	6.8	3.4	6.2	3.4	6.8	2.4	9.0	5.0	1.8	7.1	1.4	6.0	1.9	15.1	6.3	13	5.3	15.3	7.6	119.6	19.2	6.2
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Nb	0.58	0.36	0.51	0.22	0.54	0.13	0.70	0.39	0.14	0.55	0.09	0.66	0.24	1.1	0.4	0.90	0.51	1.1	0.53	6.7	1.37	0.63
Ba 4.0 1.6 4.0 2.1 4.21 0.80 13.2 3.2 1.7 5.1 1.9 4.4 2.5 9.1 3.0 8.2 3.3 5.8 3.8 80.4 10.0 4.5 La 0.33 0.26 0.35 0.27 0.48 0.14 3.42 0.33 0.15 0.47 0.14 0.40 0.27 1.0 0.48 0.85 0.38 0.95 0.11 9.18 0.99 0.78 Ce 0.80 0.54 0.89 0.66 1.17 0.35 4.97 0.78 0.34 1.07 0.31 1.11 0.85 1.3 0.48 1.61 0.69 2.1 0.80 23.4 2.1 1.7 Pr 0.12 0.08 0.14 0.10 0.18 0.07 1.25 0.12 0.05 0.17 0.11 0.36 0.13 0.31 0.13 0.31 0.13 0.31 0.13 0.31 0.13 0.31 0.13 0.31 0.13 0.31 0.13 0.31 0.33 0.14 <td>Cs</td> <td><lod< td=""><td>_</td><td>0.02</td><td>0.01</td><td>0.01</td><td>0.03</td><td>0.28</td><td><lod< td=""><td>_</td><td>0.01</td><td>0.002</td><td>0.03</td><td>0.02</td><td>0.01</td><td>_</td><td>0.01</td><td>0.01</td><td>0.01</td><td>_</td><td>0.02</td><td>0.02</td><td>0.01</td></lod<></td></lod<></td>	Cs	<lod< td=""><td>_</td><td>0.02</td><td>0.01</td><td>0.01</td><td>0.03</td><td>0.28</td><td><lod< td=""><td>_</td><td>0.01</td><td>0.002</td><td>0.03</td><td>0.02</td><td>0.01</td><td>_</td><td>0.01</td><td>0.01</td><td>0.01</td><td>_</td><td>0.02</td><td>0.02</td><td>0.01</td></lod<></td></lod<>	_	0.02	0.01	0.01	0.03	0.28	<lod< td=""><td>_</td><td>0.01</td><td>0.002</td><td>0.03</td><td>0.02</td><td>0.01</td><td>_</td><td>0.01</td><td>0.01</td><td>0.01</td><td>_</td><td>0.02</td><td>0.02</td><td>0.01</td></lod<>	_	0.01	0.002	0.03	0.02	0.01	_	0.01	0.01	0.01	_	0.02	0.02	0.01
La 0.33 0.26 0.35 0.27 0.48 0.14 3.42 0.33 0.15 0.47 0.14 0.40 0.27 1.0 0.48 0.85 0.38 0.95 0.11 9.18 0.99 0.78 Ce 0.80 0.54 0.89 0.66 1.17 0.35 4.97 0.78 0.34 1.07 0.31 1.11 0.85 1.3 0.48 1.61 0.69 2.1 0.80 23.4 2.1 1.7 Pr 0.12 0.08 0.14 0.10 0.18 0.07 1.25 0.12 0.05 0.17 0.11 0.36 0.13 0.31 0.13 0.31 0.13 0.38 0.10 3.15 0.37 0.28 Nd 0.58 0.38 0.71 0.52 0.86 0.31 5.06 0.64 0.28 0.24 0.82 0.51 1.9 0.88 1.63 0.71 1.94 0.60 14.00 1.9 1.4	Ba	4.0	1.6	4.0	2.1	4.21	0.80	13.2	3.2	1.7	5.1	1.9	4.4	2.5	9.1	3.0	8.2	3.3	5.8	3.8	80.4	10.0	4.5
Ce 0.80 0.54 0.89 0.66 1.17 0.35 4.97 0.78 0.34 1.07 0.31 1.11 0.85 1.3 0.48 1.61 0.69 2.1 0.80 23.4 2.1 1.7 Pr 0.12 0.08 0.14 0.10 0.18 0.07 1.25 0.12 0.05 0.17 0.11 0.36 0.13 0.31 0.13 0.38 0.10 3.15 0.37 0.28 Nd 0.58 0.38 0.71 0.52 0.86 0.31 5.06 0.64 0.28 0.24 0.82 0.51 1.9 0.88 1.63 0.71 1.94 0.60 14.00 1.9 1.4	La	0.33	0.26	0.35	0.27	0.48	0.14	3.42	0.33	0.15	0.47	0.14	0.40	0.27	1.0	0.48	0.85	0.38	0.95	0.11	9.18	0.99	0.78
Pr 0.12 0.08 0.14 0.10 0.18 0.07 1.25 0.12 0.05 0.17 0.05 0.17 0.11 0.36 0.13 0.13 0.38 0.10 3.15 0.37 0.28 Nd 0.58 0.38 0.71 0.52 0.86 0.31 5.06 0.64 0.28 0.82 0.24 0.82 0.51 1.9 0.88 1.63 0.71 1.94 0.60 14.00 1.9 1.4	Ce	0.80	0.54	0.89	0.66	1.17	0.35	4.97	0.78	0.34	1.07	0.31	1.11	0.85	1.3	0.48	1.61	0.69	2.1	0.80	23.4	2.1	1.7
Nd 0.58 0.38 0.71 0.52 0.86 0.31 5.06 0.64 0.28 0.82 0.24 0.82 0.51 1.9 0.88 1.63 0.71 1.94 0.60 14.00 1.9 1.4	Pr	0.12	0.08	0.14	0.10	0.18	0.07	1.25	0.12	0.05	0.17	0.05	0.17	0.11	0.36	0.13	0.31	0.13	0.38	0.10	3.15	0.37	0.28
	Nd	0.58	0.38	0.71	0.52	0.86	0.31	5.06	0.64	0.28	0.82	0.24	0.82	0.51	1.9	0.88	1.63	0.71	1.94	0.60	14.00	1.9	1.4

(continued on next page) ¹₁⁵

Table 1 (continued)																						
Type	V norn	nal	V no lit. 422/1	rmal 26	BO norma	l ^a	WF1202B- 0013	BO normal	l lit.	CC normal	l	CC n lit.	ormal	CAT-li	ke	V + BC CAT-li) ke lit.	High Ca-Al ^b	1	WF1202B- 0001	V hig Ca-A	h 1 lit.
n (major/trace)	Avg.	1 SD	Avg.	1 SD	Avg.	1 SD	1/1	$\frac{29477}{\text{Avg.}}$	1 SD	Avg.	1 SD	Avg.	1 SD	Avg.	1 SD	$\frac{43/17}{\text{Avg.}}$	1 SD	Avg.	1 SD	1/1	Avg.	1 SD
Sm	0.19	0.13	0.24	0.18	0.32	0.13	1.18	0.19	0.10	0.28	0.08	0.31	0.17	0.57	0.26	0.55	0.23	0.66	0.26	4.16	0.61	0.45
Eu	0.10	0.05	0.09	0.05	0.12	0.03	0.23	0.07	0.03	0.10	0.02	0.11	0.03	0.24	0.08	0.21	0.08	0.23	0.05	1.00	0.25	0.12
Gd	0.25	0.15	0.31	0.22	0.41	0.16	1.06	0.31	0.13	0.37	0.10	0.29	0.19	0.86	0.37	0.71	0.29	0.93	0.32	4.36	0.79	0.57
Tb	0.05	0.03	0.05	0.04	0.07	0.03	0.20	0.05	0.02	0.06	0.02	0.06	0.02	0.15	0.06	0.13	0.05	0.19	0.09	0.74	0.14	0.10
Dy	0.30	0.16	0.40	0.25	0.51	0.19	1.11	0.36	0.14	0.44	0.15	0.39	0.12	1.00	0.41	0.91	0.37	1.13	0.42	4.57	1.01	0.67
Но	0.07	0.03	0.09	0.05	0.11	0.04	0.24	0.08	0.03	0.11	0.03	0.09	0.05	0.23	0.11	0.20	0.09	0.26	0.12	0.94	0.21	0.13
Er	0.21	0.11	0.25	0.15	0.34	0.12	0.71	0.25	0.11	0.32	0.08	0.27	0.14	0.73	0.33	0.60	0.26	0.77	0.30	2.91	0.64	0.4
Tm	0.03	0.02	0.04	0.02	0.05	0.02	0.11	0.03	0.01	0.05	0.01	0.05	0.02	0.11	0.04	0.09	0.05	0.11	0.04	0.38	0.10	0.05
Yb	0.23	0.14	0.29	0.15	0.34	0.12	0.61	0.24	0.10	0.32	0.08	0.29	0.14	0.70	0.29	0.62	0.23	0.79	0.38	2.40	0.64	0.32
Lu	0.04	0.02	0.04	0.02	0.06	0.02	0.11	0.04	0.02	0.05	0.01	0.05	0.02	0.10	0.05	0.10	0.05	0.12	0.05	0.34	0.10	0.05
Hf	0.21	0.13	0.19	0.10	0.22	0.08	0.30	0.15	0.05	0.23	0.04	0.19	0.06	0.46	0.21	0.39	0.14	0.50	0.29	2.76	0.51	0.20
Та	0.03	0.03	0.03	0.01	0.03	0.01	0.03	0.02	0.01	0.024	0.005	0.04	0.01	0.06	0.03	0.06	0.03	0.06	0.03	0.26	0.08	0.04
W	0.03	0.04	NR	NR	0.21	0.14	0.18	NR	NR	0.09	0.05	NR	NR	0.01	0.01	NR	NR	0.18	0.22	0.06	NR	NR
Re ^d	0.001	0.001	NR	NR	0.01	0.02	<lod< td=""><td>NR</td><td>NR</td><td><lod< td=""><td>_</td><td>NR</td><td>NR</td><td><lod< td=""><td>_</td><td>NR</td><td>NR</td><td>0.0044</td><td>0.0003</td><td><lod< td=""><td>NR</td><td>NR</td></lod<></td></lod<></td></lod<></td></lod<>	NR	NR	<lod< td=""><td>_</td><td>NR</td><td>NR</td><td><lod< td=""><td>_</td><td>NR</td><td>NR</td><td>0.0044</td><td>0.0003</td><td><lod< td=""><td>NR</td><td>NR</td></lod<></td></lod<></td></lod<>	_	NR	NR	<lod< td=""><td>_</td><td>NR</td><td>NR</td><td>0.0044</td><td>0.0003</td><td><lod< td=""><td>NR</td><td>NR</td></lod<></td></lod<>	_	NR	NR	0.0044	0.0003	<lod< td=""><td>NR</td><td>NR</td></lod<>	NR	NR
Ir ^d	0.01	0.02	NR	NR	0.01	0.03	0.00	NR	NR	0.003	0.003	NR	NR	0.00	0.01	NR	NR	0.66	1.4	<lod< td=""><td>NR</td><td>NR</td></lod<>	NR	NR
Pt ^d	0.002	0.005	NR	NR	0.02	0.05	0.00	NR	NR	0.005	0.005	NR	NR	0.01	0.02	NR	NR	0.19	0.40	<lod< td=""><td>NR</td><td>NR</td></lod<>	NR	NR
Au ^d	<lod< td=""><td>-</td><td>NR</td><td>NR</td><td>0.004</td><td>0.003</td><td><lod< td=""><td>NR</td><td>NR</td><td>0.002</td><td>0.003</td><td>NR</td><td>NR</td><td>0.001</td><td>-</td><td>NR</td><td>NR</td><td>0.002</td><td>-</td><td><lod< td=""><td>NR</td><td>NR</td></lod<></td></lod<></td></lod<>	-	NR	NR	0.004	0.003	<lod< td=""><td>NR</td><td>NR</td><td>0.002</td><td>0.003</td><td>NR</td><td>NR</td><td>0.001</td><td>-</td><td>NR</td><td>NR</td><td>0.002</td><td>-</td><td><lod< td=""><td>NR</td><td>NR</td></lod<></td></lod<>	NR	NR	0.002	0.003	NR	NR	0.001	-	NR	NR	0.002	-	<lod< td=""><td>NR</td><td>NR</td></lod<>	NR	NR
Pb	0.01	0.03	0.63	1.61	0.008	0.005	0.750	0.21	0.33	0.04	0.10	0.08	0.06	0.02	0.03	0.22	0.27	<lod< td=""><td>_</td><td><lod< td=""><td>1.39</td><td>3.24</td></lod<></td></lod<>	_	<lod< td=""><td>1.39</td><td>3.24</td></lod<>	1.39	3.24
Th	0.06	0.04	0.05	0.03	0.08	0.04	0.58	0.04	0.02	0.06	0.03	0.06	0.03	0.13	0.06	0.11	0.05	0.13	0.05	1.28	0.14	0.06
U	0.00	0.01	0.01	0.00	0.01	0.02	1.00	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.05	0.01	0.01	0.00	0.10	0.14	0.01	0.00
Sc + Y + Zr + Hf	20.5	9.6	22.4		20.9	7.2	24.9	17.6		21.3	3.7	21.1		44	18	46.4		46	58	157	60	
(ppm)																						
(La/Yb) _N	0.91	0.28	0.82		1.01	0.88	3.83	0.93		0.99	0.22	0.94		0.99	0.15	0.93		0.92	0.34	2.60	1.05	
Eu*	1.7	1.0	1.0		1.20	0.64	0.63	0.88		1.04	0.21	1.12		1.06	0.16	1.02		0.94	0.16	0.71	1.10	
Avg. REE _N	1.33	0.76	1.57		2.0	1.6	7.0	1.4		1.88	0.49	1.77		4.1	1.5	3.6		4.5	1.6	24.1	4.0	

 Notes: <LOD - below limit of detection; NR - not reported or measured.</td>

 ^a Excepting WF1202B-0013.

 ^b Excepting WF1202B-0001.

 ^c All Fe as FeO*.

 ^d Information values only.

on 2 to 4 locations, while 15 BO-type and 11 CC-type CSs were all ablated on 2–3 locations, making sure no visibly recognizable vesicles or high-density phases were targeted. The Po-type CSs were not analyzed for trace elements because of potential biases linked to individual mineral crystals.

Replicates were compared to ensure similar phases were sampled by monitoring signal intensities for the major elements Mg, Si, Ca, and Fe. Quantification was achieved through external calibration against multiple certified reference materials produced by the United States Geological Survey (USGS) and the National Institute of Standards and Technology (NIST), i.e., natural basaltic glasses USGS BCR-2G, USGS BHVO-2G, USGS BIR-1G, natural nephelinite glass NKT-1G, and synthetic glasses USGS GSC-1G, USGS GSD-1G, USGS GSE-1G, NIST SRM 610, and NIST SRM 612, using ²⁹Si as an internal standard. Based on the reference materials, the reproducibility for the reported elements is typically of the order of 5-10% RSD. The trace element data obtained for the different textural and chemical CS groups are summarized in Table 1, while the data for individual CSs are also presented in Supplementary Table S1.

2.5. High-precision oxygen isotope ratio measurements

Measurements of δ^{18} O and δ^{17} O were carried out on 28 CSs, randomly selected from the same fraction from which the CSs were prepared for major and trace element concentrations (Supplementary Fig. S1), using infrared laserassisted (IR) fluorination isotope ratio mass spectrometry (IRMS) at the Open University in Milton Keynes, UK (Miller et al., 1999; Greenwood et al., 2017). The particles had diameters between 325 and 715 µm and were studied using SEM-EDS and µCT beforehand (Supplementary Fig. S1). Fig. 3 includes back-scattered electron images for a selection of the silicate CSs characterized for oxygen isotope ratios. Supplementary Fig. S3 indicates that the atomic Mg-Si-Fe data based on SEM-EDS for these particles fall within or close to the compositional range determined for CSs from other Antarctic, Greenland, and deep-sea collections (Taylor et al., 2000). As most of the selected CSs showed limited degrees of chemical alteration, no fracturing, and no encrustation by secondary phases based on binocular microscopy and BSE imaging (cf. below; Fig. 3; Table 2), the particles of interest were washed in acetone to remove adhesive material, but not acid-leached. Following weighing and loading, oxygen was released from the samples by reaction with BrF₅. After fluorination, the released oxygen was purified by passing the gas through two cryogenic nitrogen traps and over a bed of heated KBr. The oxygen three-isotopic composition was determined using a MAT 253 dual-inlet IRMS unit. Oxygen isotope ratios are reported in standard δ notation, where $\delta^{18}O$ is calculated as $\delta^{18}O = [({}^{18}O/{}^{16}O)_{\text{sample}}/({}^{18}O/{}^{16}O)_{\text{ref}} - 1] \times 1000 \ (\%)$ and $\delta^{17}O$ using the ${}^{17}O/{}^{16}O$ ratio, relative to Vienna Standard Mean Ocean Water (V-SMOW; Table 2). To allow comparison to previously published data, Δ^{17} O, which represents the deviation from the terrestrial fractionation line (TFL), is calculated as $\delta^{17}O - 0.52 \times \delta^{18}O$

(Clayton, 1993). Accuracy and analytical precision of the method were validated by replicate analysis of international reference materials (NBS-28 guartz and UWG-2 garnet; Miller et al., 1999). Based on repeated measurement of an in-house obsidian standard, the results for subsamples with masses between 0.062 and 0.193 mg (n = 21; 3.69 \pm 0.21‰ for δ^{17} O; 7.09 ± 0.42% for δ^{18} O; 0.006 ± 0.035% for Δ^{17} O; 2 σ) show a slight systematic offset and decreased precision compared to the values obtained for larger subsamples of ~2 mg (n = 39, $3.81 \pm 0.05\%$ for δ^{17} O; 7.27 + 0.09% for δ^{18} O: 0.029 + 0.017% for Λ^{17} O: 2σ). This offset has been observed during previous analytical campaigns as well and may result from isotopic fractionation associated with the transfer of gas in the inlet system (e.g., Greenwood et al., 2007: Suavet et al., 2010: Cordier et al., 2011b). As the precision obtained for the small obsidian subsamples reflects the typical analytical uncertainties associated with MM analysis and the determined values for the small obsidian subsamples overlap within uncertainty with those of larger subsamples, no additional (bias) corrections were carried out. The results of the oxygen isotope measurements are summarized in Table 2, together with information on textural group, apparent diameter, mass, degree of alteration, presence of vesicles and high-density phases in the selected particles.

3. RESULTS

3.1. Textural classification and cumulative size distribution

Following SEM-EDS and µCT analysis, a selection of particles, including whole CSs and sectioned particles, were classified according to their mean bulk compositions and textural characteristics (Tables 1-3; Supplementary Fig. S1; Supplementary Table S1). The majority of CSs larger than 200 µm in the Widerøefjellet collection belong to the stony, S-type CSs (95% by number). The iron (I-type, 3%) and mixed stony-iron (G-type, 2%) types represent only small contributions to the fractions analyzed. These contributions are similar to what is observed for the TAM collections (3% I-type and 1% G-type particles; Suavet et al., 2009; Table 3). Unmelted and scoriaceous MMs have been observed but are relatively uncommon (<5%) and difficult to distinguish from mafic background mineral contributions. Of 109 randomly sampled CSs larger than 400 µm, 95% are classified as S-type (33% as Vsubtype), while the G- and I-type spherules contribute 1% and 4%, respectively. A comparable distribution is observed for 228 different particles larger than 200 µm, of which 95% are classified as S-type (27% as V-subtype), with 2% and 3% contributions to the G- and I-type CSs, respectively (Table 3). The CSs studied for elemental and oxygen isotopic composition exhibit similar distributions between the textural CS groups. Of the 49 particles studied for major and trace elements, 18 (37%) are classified as V-type, 15 (31%) as BO-type, 11 (22%) as CC-type, while 5 (10%) are Po-type (Fig. 3; Table 1; Supplementary Table S1). In the case of the latter, an additional CS subtype is distinguished, the µPO-type CSs, which are mainly composed of euhedral submicron olivine crystals and are highly

Table 2

Three-oxygen isotope data for a selection of cosmic spherules from the Widerøefjellet collection, in addition to the textural group, apparent diameter and mass, degree of alteration as determined using SEM-EDS, and the presence of vesicles and high-density phases based on μ CT images. A rudimentary classification summarizing to which oxygen isotopic group, as identified by Suavet et al. (2010), each particle belongs, is also included (see text for additional explanation).

Sample name	Textural group	Diameter (µm)	Mass (µg)	Weathering stage ^a	Vesicles or high-density phases (HDP)	Isotopic group	δ ¹⁷ O ‰ VSMOW	δ^{18} O‰ VSMOW	Δ^{17} O‰ VSMOW	
WF1202B-0053	V	465	128	Fresh (0a)	Not present	CC - Group 1	13.30	32.86	-3.79	
WF1202B-0054	V	459	124	Fresh (0a)	HDP	OC - Group 3	8.19	14.68	0.56	
WF1202B-0055	V	689	350	Fresh (0a)	HDP	CC - Group 1	7.15	17.91	-2.16	
WF1202B-0056	BO	536	191	Fresh (0a)	Not present	OC - Group 3	8.18	14.89	0.44	
WF1202B-0057	V	685	362	Moderate alteration (2a)	Vesicles	CC - Group 2	8.16	18.51	-1.46	
WF1202B-0058	BO	505	166	Fresh (0a)	Not present	CC - Group 1	6.34	19.99	-4.05	
WF1202B-0059	V	625	274	Fresh (0a)	Not present	¹⁶ O-poor - Group 4	23.96	43.54	1.32	
WF1202B-0060	V	601	276	Fresh (0a)	Not present	OC - Group 3	9.04	15.83	0.81	
WF1202B-0061	CC	606	253	Fresh (0a)	HDP	CC - Group 1	3.94	11.31	-1.95	
WF1202B-0062	CC	522	192	Fresh (0a)	Vesicles	¹⁶ O-poor - Group 4	22.90	40.34	1.92	
WF1202B-0063	V	622	413	Fresh (0a)	Vesicles	OC - Group 3	10.09	18.69	0.37	
WF1202B-0064	BO	592	310	Fresh (0a)	Not present	CC - Group 1	2.76	12.76	-3.87	
WF1202B-0065	BO	516	187	Fresh (0a)	Vesicles	¹⁶ O-poor - Group 4	22.59	40.03	1.77	
WF1202B-0067	V	715	450	Fresh (0a)	Vesicles	OC - Group 3	9.40	17.25	0.43	
WF1202B-0068	CC	492	150	Fresh (0a)	Not present	CC - Group 1	16.62	36.35	-2.28	
WF1202B-0069	CC	524	143	Fresh (0a)	Not present	CC - Group 1	4.12	11.03	-1.61	
WF1202B-0070	Ро	439	127	Fresh (0a)	Not present	¹⁶ O-poor - Group 4	23.20	41.62	1.56	
WF1202B-0071	BO/CC	482	187	Fresh (0a)	HDP	Ambiguous	19.08	37.18	-0.25	
WF1202B-0072	CC	490	143	Fresh (0a)	Vesicles	OC - Group 3	6.42	10.51	0.96	
WF1202B-0073	μΡο	491	162	Fresh (0a)	Vesicles	CC - Group 1	9.42	22.77	-2.42	
WF1202B-0075	V	483	144	Fresh (0a)	Not present	OC - Group 3	9.91	17.68	0.72	
WF1202B-0076	BO	497	161	Fresh (0a)	Not present	CC - Group 1	14.55	32.41	-2.31	
WF1202B-0077	BO	472	163	Fresh (0a)	Not present	CC - Group 1	13.05	30.65	-2.88	
WF1202B-0078	CC	471	133	Fresh (0a)	Vesicles	CC - Group 1	6.18	22.04	-5.28	
WF1202B-0079	Irregular	479	134	Fresh (0a)	Not present	OC - Group 3	6.43	10.95	0.73	
WF1202B-0080	BO/CC	542	161	Fresh (0a)	Vesicles	CC - Group 1	11.65	28.01	-2.91	
WF1202B-0101	BO	418	117	Minor alteration (1a)	Vesicles	CC - Group 1	6.25	16.25	-2.20	
WF1202B-0105	V	325	45	Fresh (0a)	Not present	CC - Group 1	4.59	12.07	-1.69	

Notes: Textural group: V = glassy; BO = barred olivine; CC = cryptocrystalline; PO = porphyritic; $\mu PO =$ microporphyritic.

Isotopic group: CC = carbonaceous chondrite; OC = ordinary chondrite.

^a Following classification by van Ginneken et al. (2016).

Table 3

Distribution by textural type for Widerøefjellet (WF), Frontier Mountain (FRO), Miller Butte (MIL), Larkman nunatak (LAR), Walcott Névé (WAL), South Pole Water Well (SPWW), and Indian Ocean (IO) cosmic spherules. The FRO and MIL data represent mostly magnetically separated fractions, while for the WAL data, a separation was made with heavy liquids and the light fraction was further sorted magnetically. The IO particles were separated magnetically, while the non-magnetic fractions did not yield any cosmic spherules after heavy liquid separation. Magnetic separation techniques were employed for some of the LAR samples to concentrate MMs. For the SPWW and WF collections, no bias was introduced. Data for all collections but Widerøefjellet compiled in Suavet et al. (2009), Shyam et al. (2013), and Genge et al. (2018).

Sample	Size	S-type	V-subtype	G-type	I-type	Number
WF	>400 µm	95%	33%	1%	4%	109
	>200 µm	95%	27%	2%	3%	228
FRO	>400 µm	na	na	2%	3%	331
	>200 µm	95%	15%	1%	4%	254
MIL	>400 µm	na	na	1%	3%	729
	>200 µm	na	na	na	3%	920
LAR	>60 µm	92%	19%	2%	6%	634
WAL	>100 µm	92%	10%	2%	6%	126
SPWW	>100 µm	98%	15%	1%	1%	1130
IO	>60 µm	91%	8%	3%	6%	453

Notes: na - identification of this type was not attempted or reported.

vesicular relative to normal Po-type CSs (Fig. 3; van Ginneken et al., 2017). Of the CSs characterized for oxygen isotope ratios, 10 (36%) represent V-type spherules, 7 (25%) are BO-type, 6 (21%) are CC-type, 1 (4%) belongs to the Po-type, 1 (4%) belongs to the μ Po-type, while a single sub-angular, vesicular particle with dendritic and skeletal spinel crystals is classified as irregular (4%) and 2 are designated as BO/CC-type mixtures (7%; Table 2).

The diameters of the individual CSs studied here have been determined combining optical microscopy, SEM and µCT (Table 2; Supplementary Table S1). Similar to the work of Suavet et al. (2009), the particles are assumed to represent ellipsoids with equal minor and intermediate axes (a > b = c). As such, the diameters used in the size distribution are defined as $d_{\text{ellipsoid}} = (a \times b^2)^{1/3}$, where $d_{\text{ellipsoid}}$ represents the reported diameter of the CSs (Table 2; Supplementary Table S1). Due to the sieving process, particles may fall outside of their size fraction. As a result, a larger size fraction may contain CSs with diameters slightly below the mesh size, while conversely particles larger than the mesh size may pass into smaller mesh size sieves due to elongated shapes or mesh imperfections (e.g., Rochette et al., 2008). In Fig. 4A, the cumulative size distribution for Widerøefjellet CSs larger than 200 µm is plotted, displaying the number N of CSs larger than a certain diameter. A similar curve for a subpopulation of TAM particles larger than 400 µm, for which the unprocessed diameters were provided, is shown for comparison (Suavet et al., 2009). The size distributions for the CSs separated for chemical and oxygen isotopic analyses are plotted in Fig. 4B. Both subgroups of analyzed CSs display similar size distributions.

3.2. Metal and vesicle content

Based on the μ CT scans (2D slices and 3D volumes) and sectioned SEM images (2D slices), vesicles, Fe–Ni metal beads, sulfides, and/or other inclusions with contrasting densities (including spinel group minerals) can be detected (Table 2; Fig. 5; Supplementary Table S1; Supplementary Fig. S2). Using the applied μ CT system, the distinction between silicate glass and olivine cannot be made in most cases, due to the similar X-ray attenuation by these phases and the often small sizes (mostly $\leq 10 \mu m$) of olivine crystals in BO-, CC, and Po-type CSs. Rarely, Po-type CSs are characterized by large enough olivine crystals (larger than 10 µm and up to 150 µm in size; Supplementary Fig. S2B) to be distinguished on μCT scans (e.g., WF1202B-0006, 0036, 0137, 0202). In various CSs (WF1202B-0013, 0028, 0042, 0050, 0120, 0114), µCT scans reveal internal structures in BO-type CSs that may be related to crystal orientation, although indicative lines can also be generated through interference patterns. The lower size range of vesicles and high-density phases is limited by the spatial resolution obtained for the µCT system applied. Vesicles range in diameter from $<10 \,\mu\text{m}$ to $\sim 200 \,\mu\text{m}$, while high-density phases vary between $\leq 15-20 \mu m$ and $\sim 100 \mu m$ (Fig. 5; Supplementary Fig. S2).

Based on the data for 146 CSs, only in part validated through 2D sections for a subset of these particles studied using SEM-EDS (Supplementary Table S1), the distinction can be made between groundmass silicate phases, high-density phases, which may include rounded Fe–Ni metal (often as metal beads), irregular sulfides, rounded to angular spinel group mineral phases, or micrometeorite-sized platinum group element nuggets (e.g., Brownlee et al., 1984; Taylor et al., 2000; Rudraswami et al., 2011; Cordier et al., 2011b), and vesicles. While most CSs with high-density phases, presumably FeNi metal beads, can be encountered, with up to five metal-rich inclusions within a single particle (e.g., WF1201B-0129; Supplementary Fig. S2).

Approximately 46% of the CSs between 200 and 800 μ m contain no vesicles or high-density inclusions (Fig. 5; Supplementary Fig. S4A). Second most abundant (~23%) are

CSs with high-density phases but no vesicles, while CSs with vesicles, but no high-density inclusions, contribute \sim 22% to the studied Widerøefjellet CSs. Least abundant (\sim 9%) are the CSs with both vesicles and high-density phases. No significant differences are observed between the studied CSs in the 200–400 µm and 400–800 µm size fractions, with the exception of a higher relative abundance

of CSs with no vesicles and high-density phases in the 400–800 μ m fraction relative to the 200–400 μ m fraction (Supplementary Fig. S4A). When combining μ CT data with textural information (Supplementary Fig. S4B), V-, BO- and Po-type CSs are dominated by particles with no vesicles or high-density phases (>57%), while only 14% of Po-type CSs fall in this category. In the case of Po-type



Fig. 6. Molar Fe/(Si + Mg) histograms for Widerøefjellet Mountain (WF; this work), Frontier Mountain (FRO, magnetic extract; Suavet et al., 2009), Miller Butte (MIL; Suavet et al., 2009), Walcott Névé (WAL, heavy fraction [methylene iodide, $\rho = 3300 \text{ kg/m}^3$] and magnetic extract of the light fraction; Suavet et al., 2009) and South Pole Water Well (SPWW; Taylor et al., 2000) micrometeorites. All data except for Widerøefjellet extracted from Suavet et al. (2009).

CSs, particles with vesicles prevail, either with (43%) or without (43%) high-density phases. Based on these abundances, relict grain survival, vesicle formation and high-density phase segregation are linked to different degrees of atmospheric heating.

3.3. Major element composition

V-type CSs (n = 18) show the largest compositional variations in terms of Al, Mg, and Ca (i.e., 0.86-31.3 wt% Al₂O₃, 3.73–48.5 wt% MgO, and 0.78–18.7 wt% CaO; Table 1; Supplementary Table S1). These ranges are comparable to or larger than those reported for 187 V-type CSs from the TAM collection, with 0.06–14.1 wt% Al₂O₃, 0.85-43.0 wt% MgO, and 0.04-11.9 wt% CaO (Cordier et al., 2011b). For the CSs studied here, the largest range in SiO₂, Cr₂O₃, and FeO* (all Fe reported as FeO) concentrations is observed for BO-type spherules (Supplementary Table S1). The SiO₂ concentrations of V-type CSs display a range of 39.7-50.5 wt%, while SiO₂ contents vary between 27.4 and 42.4 wt%, 36.9 and 47.0 wt%, and 40.5-46.2 wt% for BO-type (n = 15), CC-type (n = 15), and Po-type (n = 5) CSs, respectively, partly overlapping (average values with 1 SD can be found in Table 1). On average, BO-type CSs contain higher bulk Fe contents than their CC-type and Po-type textured counterparts, with 28.2 wt % FeO* for BO-type versus 17.0 and 18.0 wt% FeO* for CC-type and Po-type CSs, respectively (Table 1; Supplementary Table S1). CC-type and Po-type CSs generally display comparable major element compositions, although Po-type CSs often show higher Ni contents

(1.3 wt% NiO on average) relative to other textural types (less than 0.3 wt% NiO on average for V-type, BO-type, and CC-type CSs based on EMPA data; Table 1; Supplementary Table S1). To highlight possible extraction biases, the molar Fe/(Si + Mg) ratios of the Widerøefjellet particles are compared to those of particles from various other collections (Fig. 6). On Mg-Si-Fe and K + Na-Ca-Al ternary diagrams, the SRM particles plot within the compositional ranges of CSs defined in the literature (e.g., Brownlee et al., 1997; Taylor et al., 2000; Rochette et al., 2008; Fig. 7). The extraterrestrial field is clearly distinct from literature data for Antarctic volcanic rocks and tephra. All particles studied for major and minor elements contain less than 0.35 wt% Na₂O, 0.06 wt% K₂O, and 51 wt% SiO₂, making these CSs distinct from volcanic glass shards, microtektites or meteorite ablation debris (e.g., Cordier et al., 2011b; Folco and Cordier, 2015).

All CSs characterized here exhibit relatively chondritic Mn/Mg ratios with positively correlated Fe/Mg and Fe/Mn ratios (Fig. 8A). This suggests that no particles from differentiated or basaltic precursors were sampled, as particles from differentiated parent bodies are often marked by higher Fe/Mg but similar Fe/Mn ratios relative to chondrites plotting along the horizontal lines marked "*Moon*" and "*4Vesta/Mars*" in Fig. 8A (e.g., Goodrich and Delaney, 2000; Taylor et al., 2007a; Gounelle et al., 2009; Cordier et al., 2011a,b, 2012; Cordier and Folco, 2014). Based on the atomic Fe/Si ratio and CaO and Al₂O₃ contents, chondritic CSs have previously been assigned to three distinct chemical groups (Cordier et al., 2011b): (i) the normal group containing most chondritic CSs, (ii) the



Fig. 7. Ternary atomic Mg-Si-Fe (A) and K + Na-Ca-Al (B) diagrams presenting EMPA data for a selection of CSs (V-type, BO-type, CC-type, and Po-type) recovered from the Widerøefjellet sedimentary accumulation. The elemental ranges for Antarctic volcanic rocks and tephra are based on those compiled in Rochette et al. (2008) and Suavet et al. (2009), while individual compositions of V-type CSs by Cordier et al. (2011b) are also shown. The ranges for CSs are based on other Antarctic, Greenland, and deep-sea collections (Taylor et al., 2000). Also indicated are a range of compositions of Australasian microtektites from the Transantarctic Mountains (Folco et al., 2009).



Fig. 8. Classification diagrams for silicate CSs (see details in Folco and Cordier, 2015 for A, B, and D). (A) Relationships between Fe/Mn and Fe/Mg atomic ratios. Field for chondrites and trends for achondrites are based on Goodrich and Delaney (2000). (B) CaO + Al₂O₃ content in wt.% versus Fe/Si atomic ratio. The definition for the three groups of chondritic V-type CSs are based on estimates by Taylor et al. (2000) and Cordier et al. (2011b). (C) Refractory lithophile major element content as the sum of CaO and Al₂O₃ in wt.% versus refractory lithophile trace element content, taken here as the sum of Sc, Y, Zr, and Hf in ppm. (D) Mg/Al versus Si/Al atomic ratios. An evaporation trajectory is drawn from the Ivuna-type (CI) carbonaceous chondrite precursor (fields from Jarosewich, 1990). Regardless of the starting composition, evaporation trajectories for carbonaceous and ordinary chondritic compositions converge after ~30% of the material has evaporated (Alexander et al., 2002). The arrows labeled "enstatite" and "forsterite" show the mineralogical control of precursor material on the bulk CS composition (CC = carbonaceous chondrite field; OC = ordinary chondrite field). V-type (Lit.) from Cordier et al. (2011b).

Ca-Al-Ti-rich (CAT-like) group with Fe/Si < 0.06, Mg/ Si > 0.9 (at%) and $CaO + Al_2O_3 > 5$ wt%, and (iii) the high Ca-Al group with Fe/Si > 0.06 (at%) and $CaO + Al_2$ - $O_3 > 9$ wt% (Fig. 8B). This classification extends and refines the chemical characteristics (low Fe/Si and high Mg/Si ratios) of the previously identified "CAT" group, defined by Taylor et al. (2000) and Alexander et al. (2002). Applying the criteria defined above, 6 (12%) of the CSs studied here belong to the CAT-like group (V-type WF1202B-0010, 0029 and 0048, BO-type WF1202B-0002 and 0016, CC-type WF1202B-0037; Supplementary Table S1), while 4 of these 49 CSs (8%) can be classified as high Ca-Al spherules (V-type WF1202B-0001 and 0020, CC-type WF1202B-0011, BO-type WF1202B-0038). It should be noted that high Ca-Al particle WF1202B-0038 is also characterized by a high TiO₂ content of 0.36 wt%, perhaps rendering this classification scheme incomplete. Both CAT-like and high Ca-Al particles are thus represented among all textural CS groups, excepting Po-type CSs. While the abundance of high Ca-Al particles is comparable to that observed in the V-type CS population of the TAM collection (10%), CAT-like particles are significantly less abundant in the V-type subpopulation of the TAM collection ($\sim 2\%$; Cordier et al., 2011b). As the V-type CSs in the latter work are comparable in size (220–850 µm) to the Widerøefjellet particles studied here, the higher abundance of CAT-like particles here indicates a higher proportion of such CSs among the non-glassy textural groups.

3.4. Trace element composition

The CSs studied exhibit a large diversity in REE contents and patterns (Figs. 8C, 9, 10, 11), which are difficult to relate to any particular chemical or textural group. On average, the V-type, BO-type, and CC-type textural groups show fully chondritic REE ratios and superchondritic con-



Fig. 9. The categories of REE patterns observed among CSs of Widerøefjellet. Normalization to CI chondrite composition (McDonough and Sun, 1995). While five of the patterns correspond to those identified by Cordier et al. (2011b), the LREE-enriched patterns in (F) differ slightly from the previously identified "U-shaped" pattern.

centrations (La/Yb_N of 1.0, 1.2, and 0.95, Eu* of 1.6, 1.1, and 1.0, average REE_N of 3.0, 3.0, and 2.3 for V-, BO-, and CC-type, respectively; Table 1). CC-type CSs exhibit the least variable REE patterns, while BO-type CSs display the most pronounced Ce depletions, with a mean Ce* of 0.84 (with Ce* = Ce_N/ $\sqrt{$ [La_N * Nd_N]), compared to mean Ce* of 1.0 and 0.92 for V- and CC-type CSs, respectively. These Ce anomalies in BO-type spherules are mostly inher-

ited from CAT-like and high Ca-Al group CSs (mean Ce^{*} of ~0.36 for CAT-like WF1202B-0002 and 0016, and high Ca-Al WF1202B-0038; Fig. 11). Based on the fractionation observed between light, medium, and heavy REEs, in combination with the presence or absence of Ce and Eu anomalies (defined based on $Eu^* = Eu_N/\sqrt{[Sm_N * Gd_N]}$), seven different REE patterns can be recognized among the CSs characterized in this work (n = 44; Fig. 9A–F; Supplemen-



Fig. 10. Comparison of major and trace element compositions for the normal V-type, BO-type, and CC-type, CAT-like, and high Ca-Al CS groups recognized among the Widerøefjellet particles and in literature (Folco and Cordier, 2015; Table 1). Concentrations are normalized to CI chondrites (McDonough and Sun, 1995). Elements are ordered according to increasing volatility (i.e., 50% decreasing condensation T_C at 10⁻⁴ bar; Lodders, 2003) from left to right.

tary Table S1): (A) CSs with flat patterns (La/Yb_N = 0.7– 1.4; Eu^{*} = 0.8–1.3; n = 29). These CSs make up 82% of the CC-type, 75% of the BO-type, and 50% of the V-type spherules. Most of these CSs exhibit fully chondritic REE patterns (Ce^{*} ~0.7–1.2), while two CAT-like BO-type spherules show strong Ce depletions with Ce^{*} of less than 0.3 (WF1202B-0002 and 0016). (B) One BO-type CS

(WF1202B-0040) shows a flat REE pattern with a negative Eu anomaly (La/Yb_N = 0.9; Eu* = 0.6). (C) Eight CSs, mostly V-type (75%), are characterized by a flat REE pattern with positive Eu anomaly (La/Yb_N = 0.6–1.2; Eu* = 1.4–4.6). One of the V-type CSs of this group (WF1202B-0017) exhibits a positive Ce anomaly (Ce* of 2.0 compared to 0.8–1.1 for the other CSs with this type of pattern). (D) One CC-type CS (WF1202B-0011) exhibits a LREE-depleted pattern (La/Yb_N = 0.5; Eu* = 0.8). (E) Two V-type spherules (WF1202B-0019 and 0039) show LREE-depleted patterns with positive Eu anomalies (La/ Yb_N = 0.5; Eu* = 1.6–2.7). (F) One V-type (WF1202B-0001) and one BO-type (WF1202B-0013) CS are characterized by LREE-enriched patterns with negative Eu anomalies $(La/Yb_N = 2.6-3.8; Eu^* = 0.6-0.7)$. The BO-type CS also shows a slight negative Ce anomaly (Ce* of 0.6). (G) BO-type CS WF1202B-0042 exhibits a LREE-enriched pattern with a positive Eu anomaly $(La/Yb_N = 2.1; Eu^* = 2.5)$.

The chemical groups of CSs also vary in their trace element compositions (Table 1; Figs. 8-11). The mean



Fig. 11. (A–C) Binary plots of (partially) siderophile elements V, Cr, and Ni versus FeO*, as determined by LA-ICP-MS in this work. Fields for ordinary chondrites and carbonaceous chondrites (2 SD of the mean) based on Cr, Ni, and FeO* data from Jarosewich (1990) and V data from Friedrich et al. (2002). (D–F) Comparison of average major and trace refractory element concentrations in residues of heating experiments with varying total weight loss in % (Wang et al., 2001) with the CAT-like and high Ca-Al CS patterns determined in this work. The compositions of the CSs are normalized to CI chondrite (McDonough and Sun, 1995), while those of the residues are normalized to the starting solar composition (Wang et al., 2001).

values for the chemical CS groups determined in this work indicate excellent correspondence to the group averages compiled in literature based on particles from different MM collections (Table 1; Fig. 10; Folco and Cordier, 2015). Relative to CI chondrites, the normal group exhibits an enrichment in refractory elements (50% condensation temperatures above 1360 K), excluding siderophile W and chalcophile V as well as redox-sensitive Th and U, to values of ~1.5–2.3, with a mean REE_N equal to 1.9 ± 1.2 times CI (1 SD; n = 34; Fig. 10). On average, the siderophile elements W, Ni, and Co and chalcophile elements V and Cr are depleted by approximately one order of magnitude relative to refractory elements, although particular CSs show element depletions by four orders of magnitude. The flat refractory element patterns of these CSs are occasionally also interrupted by both positive and negative anomalies in Sc, Y, Th, U, Ta, Nb, and Ce, but on average most of these elements, except for Th, U, and Ce, are not depleted relative to chondrites and exhibit chondritic ratios (Fig. 10). Mean positive Th and U anomalies were previously not observed for Vtype spherules (Cordier et al., 2011b), but can be present in CSs as exemplified by BO-type CS WF1202B-0013, for this reason this particle is not included in the BO-type average in Fig. 10A. The depletion in volatile Rb. Na. Cu, Zn, and Pb may not be linked directly to element condensation temperatures, as Pb is present at higher concentrations than all other volatile elements. Alternatively, the relative Pb enrichment may be due to contamination during LA-ICP-MS analysis.

The CAT-like CSs are distinct from the normal group by a higher enrichment in refractory elements ($\sim 2.1-4.9 \times CI$), with a mean REE_N equal to 4.1 ± 1.5 times CI (1 SD; n = 6; Fig. 10), and a stronger mean depletion in siderophile elements W, Co and Ni (by $\sim 1-4$ orders of magnitude). Chalcophile Cr, V, and Mn are depleted to 0.2–0.02 times CI on average (Fig. 10). On average, CAT-like CSs exhibit a negative U anomaly comparable to that of the normal chondritic CS group, although individual spherules can be U-enriched, as seen for BO-type CS WF1202B-0016 (Supplementary Table S1). The depletion in volatile Rb, Na, Cu, Zn, and Pb is not as pronounced as for the normal chondritic CSs, mostly as the result of V-type CS WF1202B-0029 that shows a less volatile element-depleted signature.

The high Ca-Al spherules show the highest enrichment in refractory elements of all groups ($\sim 2.4-5.2 \times CI$), with a mean REE_N equal to 4.5 ± 1.6 times CI (1 SD; n = 3; Fig. 10). This mean value excludes V-type CS WF1202B-0001 characterized by an even higher REE enrichment factor of ~ 24 relative to CI chondrites (Supplementary Table S1). All high Ca-Al spherules exhibit a negative U anomaly, although limited in WF1202B-0001. The relative depletions in siderophile W, Co, and Ni and chalcophile Cr, V, and Mn for the average high Ca-Al group are intermediate between those of the normal and CAT-like groups (Table 1; Fig. 10). The depletion in volatile Rb, Na, Cu, Zn, and Pb is similar to or larger than that observed for the normal CSs.

3.5. Oxygen isotope ratios

The δ^{18} O, δ^{17} O and Δ^{17} O values for 28 CSs are reported in Table 2. These CSs, with diameters ranging from 325 to 715 µm and masses between 45 and 450 µg (see Section 2.5; Supplementary Fig. S5), were randomly selected from the Widerøefjellet collection and analyzed for their threeoxygen isotopic compositions. Based on BSE images of whole particles, these CSs have been assigned to the BOtype $(n = 7, \sim 25\%)$, Po-type $(n = 2, \sim 7\%)$, V-type $(n = 10, \sim 7\%)$ \sim 36%), and CC-type (n = 6, \sim 21%) textural groups (Genge et al., 2008: Table 2). One CS has an irregular appearance, while 2 other particles represent BO/CC-type mixtures (Fig. 3; Table 2). This distribution by types is similar to that of unbiased collections (e.g., Taylor et al., 2000; Cordier and Folco, 2014), and consistent with the 49 Widerøefjellet CSs characterized for major and trace element concentrations (Supplementary Table S1). In Fig. 12, the Δ^{17} O data versus δ^{18} O of the CSs are shown relative to the TFL and the oxygen isotopic compositions of various chondrite groups (Clayton et al., 1991; Clayton and Mayeda, 1999; Newton et al., 2000). Fig. 12A compares the data from this work to high-precision oxygen isotopic data determined for Antarctic CSs by IRMS available from literature (Cordier et al., 2011a, 2012; Suavet et al., 2010, 2011a), while Fig. 12B links the acquired data to the values determined for eighteen $>500 \,\mu\text{m}$ diameter CSs from the Atacama Desert in Chile (van Ginneken et al., 2017) and includes textural information.

The oxygen isotopic compositions of the CSs characterized here can be compared to the four groups previously defined qualitatively by Suavet et al. (2010) (Fig. 12A). A fifth group is often added to these four to accommodate for HED-like materials (e.g., Cordier and Folco, 2014 and references therein). Below the TFL, 3 of 10 V-type, 5 of 7 BO-type, 1 of 2 Po-type, 4 of 6 CC-type CSs, and 1 mixed BO/CC-type CS exhibit isotopic compositions that fall within or close to the Group 1 field, defined to exhibit Δ^{17} O values below -2.2% and δ^{18} O values of 8 to 32% (Suavet et al., 2010). A single V-type CS WF 1202B-0057 has an isotopic composition that can be considered to be part of Group 2, previously constrained to range from -0.2 to -1.5% for Δ^{17} O with δ^{18} O of $\sim 25\%$ (Suavet et al., 2010). One V-type (WF1202B-0105) and 2 CC-type CSs (WF1202B-0061 and 0069) fall in between Group 1 and Group 2 and cluster closer to meteoritic values, with Δ^{17} O between -2.0 and -1.6% and δ^{18} O around 12%. Mixed BO/CC-type CS WF1202B-0071 with a Δ^{17} O of -0.25 and δ^{18} O of 37.2% remains ambiguous and cannot be assigned to either Group 1 or Group 2, or any particular chondrite group. Above the TFL, five V-type, 1 BO-type, 1 CC-type CS, as well as 1 CS with an irregular texture have isotopic compositions that fall within or close to the Group 3 field, defined to display Δ^{17} O values between 0.1 and 1.0% and δ^{18} O values of ~15%; Suavet et al., 2010). One CS of each main textural group (V-, BO-, CC-, and Potype) is characterized by an isotopic composition close to that of the ¹⁶O-poor Group 4, with $\Delta^{17}O$ of ~2‰ and δ^{18} O equal or larger than 40% (Suavet et al., 2010).



Fig. 12. $\delta^{18}O$ (horizontal) versus $\Delta^{17}O$ (vertical) in % for the individual CSs from Widerøefjellet measured in this work compared to literature IRMS data for (A) Antarctic CSs (Suavet et al. 2010, 2011a; Cordier et al., 2011a, 2012) and (B) CSs from the Atacama Desert in Chile (open symbols; van Ginneken et al., 2017). The data from this work are shown by orange squares in (A) and filled dark grey symbols in (B). The solid line labeled TFL represents the terrestrial fractionation line ($\approx \delta^{17}O = 0.52 \times \delta^{18}O$), while the average isotopic composition of oxygen around the transition from the stratosphere to the mesosphere ($\delta^{18}O \approx 23.5\%$ and $\delta^{17}O \approx 11.8\%$; Thiemens et al., 1995) is represented by a star. Plot (A) is adapted after Suavet et al. (2010) and Cordier and Folco (2014), with colored domains representing potential parent bodies (Clayton et al., 1991; Schulze et al., 1994; Clayton and Mayeda, 1999; Newton et al., 2000) and shaded areas indicating the range of possible values for a micrometeorite derived from a particular parent body. Mass fractionation lines for asteroid 4 Vesta (EFL, $\Delta^{17}O = -0.242 \pm 0.016\%$; Scott et al., 2009) and Mars (MFL, $\Delta^{17}O = 0.301 \pm 0.013\%$; Franchi et al., 1999) are also shown. The outlines of the 4 groups originally identified by Suavet et al. (2010) are represented using dotted lines, while the dashed arrows reflect the direction of possible shifts due to the formation of alteration products in equilibrium with Antarctic precipitation. Individual CSs are highlighted using their number designation only, as these all share the common prefix "WF1202B-". Plot (B) includes textural information on the individual particles and illustrates the three possible effects by which the bulk O isotopic composition of a CS can be changed starting from chondritic parent body values. Analytical uncertainties ($\pm 1\%$ of $\delta^{18}O$ and ± 0.7 for $\Delta^{17}O$ (2σ). As ion microprobe data are generally associated with larger uncertainties ($\pm 1\%$ of $\delta^{18}O$ and ± 0

4. DISCUSSION

4.1. Accumulation mechanism for Widerøefjellet

Natural concentration and alteration processes (e.g., wind sorting, interaction with fluids) and sampling methods (e.g., sieving, magnetic separation, hand-picking) may introduce biases in the physicochemical properties of a MM collection. The Concordia collection, recovered by melting large volumes of Antarctic snow, is considered one of the least biased collections based on the high abundance of fragile fine-grained fluffy and ultracarbonaceous particles as well as the occurrence of sulfides prone to weathering (e.g., Nakamura et al., 1999; Duprat et al., 2007, 2010; Dobrică et al., 2012; Genge et al., 2018). However, CSs are not described for this collection (Dobrica et al., 2010), preventing a direct comparison with collections recovered from deposits with longer accumulation ranges, such as blue ice-derived collections and sedimentary accumulations. As an example, fine- and coarse-grained unmelted particles are significantly less abundant in the SPWW (Taylor et al., 1998, 2000, 2007b), Cap Prud'homme (Kurat et al., 1994; Genge et al., 1997), Larkman Nunatak (Genge et al., 2018), or TAM (Rochette et al., 2008) collections relative to the Concordia collection (Dobrică et al., 2010), indicating terrestrial reprocessing or collection and operator biases.

Despite different particle size distributions for various collections, the abundance of CS types may also provide some insight regarding potential collection biases. For example, magnetite and wüstite-dominated I-type CSs, relatively resistant to weathering, represent 1% of all CSs larger than 100 µm in the SPWW collection, generally considered a relatively unbiased MM collection (Table 3; Taylor et al., 2000, 2007a; Rochette et al., 2008; Genge et al., 2018). Slightly higher abundances of I-type particles (3-4% of all CSs $> 200 \,\mu\text{m}$) have been observed in the TAM collection, while even higher values in the Larkman (6% of all $CSs > 60 \mu m$), Walcott Névé (6% of all $CSs > 100 \ \mu m$), and Indian Ocean (6% of all $CSs > 60 \ \mu m$) collections likely indicate higher weathering degrees, taking into account the respective collection size ranges (Table 3). Mid-Pacific abyssal clays up to 500 kyr old form an extreme example, with I-type particles constituting 25 to 50% of the extracted CSs, based on 700 particles of 0.1-1 mm where the variation depends on the core samples and magnetic extraction procedures employed (Blanchard et al., 1980). If no metal-bearing I-type spherules were lost, the comparable degree of I-type enrichment in the Widerøefjellet and TAM collections relative to the SPWW collection may indicate a significant loss of S-type particles due to weathering or wind transport, although potential biases linked to particle size distributions remain difficult to evaluate.

Particle losses may be detected by studying the cumulative size distribution of the Widerøefjellet collection relative to those of other collections (Fig. 4A). To account for the diversity of procedures that exist to construct cumulative size distributions (e.g., Taylor et al., 2000, 2007b; Suavet et al., 2009; Genge et al., 2018), the cumulative size distribution for CSs from Widerøefjellet (>200 µm size fraction) was compared to the data provided for a set of CSs from the TAM (>400 µm size fraction; Suavet et al., 2009). The diameters were first collected in 20 µm bins, after which power law functions were fitted to the diameters larger than 240 µm and 440 µm, respectively, to account for potential sieving biases, using the OriginPro software. As the studied size fractions were picked in their entirety, no mathematical corrections were applied. The calculated slope exponent of the TAM cumulative size distribution equals to -4.8 ± 0.2 for the particles larger than 440 µm, in good agreement with values of -4.8 and -5 determined for the nonmagnetic and magnetic fractions of the TAM collection (Suavet et al., 2009). The slope exponent of the Widerøefjellet cumulative size distribution equals to -4.4 ± 0.2 (for particles $>240 \mu m$), which overlaps within uncertainty with the exponent obtained for the TAM collection (Fig. 4A). These values are close to the -5.0 and -5.4 slopes determined for the SPWW collection (Taylor et al., 2000, 2007b), but may still indicate minor weathering or transport losses for the Widerøefjellet collection. The Walcott Névé collection represents a more extreme case, where a strong deficit in smaller particles not accounted for by a sieving bias (~6% of all CSs > 100 μ m is I-type; Table 3) with a large fraction of the MMs exhibiting moderate to severe alteration led to a slope exponent of -2.9 determined for the 200-400 µm size fraction (Suavet et al., 2009). Similarly, the Larkman nunatak collection (~6% of all $CSs > 60 \ \mu m$ is I-type) exhibits a power law distribution with an exponent of -5.3 only for diameters from 210 to 330 µm, with abundances decreasing below the power law at both higher and lower diameters (Genge et al., 2018).

Taking into account subtle differences in the classification scheme used for S-type CSs, the relative abundances of Po-, BO-, CC-, and V-type CSs are fairly comparable for the older Larkman nunatak, Cap Prud'homme, and TAM collections on one hand and for the younger Indian Ocean and SPWW collection on the other (Genge et al., 2018). The diversity in quench textures among melted silicate particles has previously been attributed to (i) different peak temperatures and cooling rates experienced during atmospheric entry, with peak temperatures increasing from Po-, over BO- and CC-, to V-type CSs (e.g., Taylor et al., 2000), as supported by the μ CT data in this work (Section 3.2), and (ii) the grain size of the precursor material, as coarser-grained micrometeoroids have higher probabilities to evolve into relict-bearing spherules (e.g., Taylor et al., 2012; van Ginneken et al., 2017). Here, it should be noted that the distinction between BO- and CC-type CSs may be biased by the operator, with the existence of a continuum in particle textures and the occurrence of CSs exhibiting dual textures, including mixed BO/CC-type CSs. Based on the comparable abundance of V-type CSs for all collections (except Widerøefjellet), which requires limited subjectivity in classification, such differences have been interpreted to reflect systematic changes in the velocities of the dust particles arriving to Earth (Genge et al., 2018). When comparing the frequency of the different CS types (Table 3), the Widerøefjellet collection is characterized by a significantly higher contribution of V-type CSs for different size fractions above 200 µm. Glass spherules
are generally more prone to fracturing and chemical alteration, mostly due to secondary wind transport and/or strong interaction with ice or fluids over time. This is demonstrated by the heavily altered Walcott Névé and Larkman nunatak collections, where CSs frequently contain surface and penetrative fractures as the result of impact after wind transportation and swelling or cryoclasty (freezethaw weathering), respectively (Suavet et al., 2009; van Ginneken et al., 2016; Genge et al., 2018). Although these sites have been accumulating material for at least one Myr, the main factor controlling weathering may be the temperature variation of the local environment, such as seasonal melting of the thin layer of snow covering the MM accumulation sites. The effects of chemical weathering include the removal of primary mineral phases, such as olivine and glass, and incrustations by weathering products (van Ginneken et al., 2016). Ferrihydrite and jarosite have been shown to precipitate within cavities of TAM MMs, resulting in pseudomorphic textures within heavily altered particles. Glass is known to alter into palagonite gels with sequential replacement indicative of varying water-to-rock ratios. Metal may be replaced by Fe-oxide/hydroxide (e.g., goethite, lepidocrocite, and maghemite), although magnetite formed during atmospheric entry is generally resistant to alteration by interaction with the terrestrial environment (van Ginneken et al., 2016).

Physical weathering is mainly due to frequent freezethaw cycles occurring due to daily change in surface temperature within the MM traps. Such weathering results in the fracturing of a fraction of the MMs (Rochette et al., 2008; Suavet et al., 2009). In the Widerøefjellet collection, the effects of both chemical and physical weathering of CSs appear limited and similar to what is observed for MMs from the TAM (Tables 1 and 2; Supplementary Table S1), although jarosite weathering products are not abundant (van Ginneken et al., 2016). This is consistent with the assumption of limited variation in the environment over the period of accumulation of the CSs and insubstantial interaction with ice melts. Following the weathering scale for MMs of van Ginneken et al. (2016), based on both the degree of terrestrial alteration and the level of encrustation by secondary phases, the Widerøefjellet particles studied can be assigned to the 0a to 2c scales, indicating no visible to moderate loss and/or alteration of primary material with no visible to complete encrustation (Fig. 3). The limited degree of chemical alteration observed for Widerøefjellet particles may be linked to the high altitude, the presence of a permanent snow layer, or the observation that the CS-rich sediment was sampled in a shadow-rich zone during the peak of the austral Summer.

The bulk geochemical composition of different CS collections can to a certain degree also be used to evaluate possible biases through comparison of the molar Fe/(Mg + Si) ratios of the CSs studied (Fig. 6). Magnetic separation will favor the extraction of magnetite-bearing CSs (e.g., G- and I-type spherules), while non-magnetic V-types will be underrepresented. Hence, CSs with molar Fe/(Mg + Si) above 0.1 ratios will be overrepresented when applying magnetic separation, as observed for the Frontier Mountain and Walcott Névé collections (Suavet et al., 2009).

The molar Fe/(Mg + Si) distribution for a Miller Butte subsample that did not undergo magnetic separation is more similar to that of the SPWW collection (Fig. 6). During the sample preparation of the Widerøefjellet collection, no magnetic or density separation was performed, and the molar Fe/(Mg + Si) ratio distribution is comparable to that of the SPWW (Taylor et al., 2000). Compared to the other collections shown, the Widerøefjellet and SPWW collections both have a significant contribution of particles with molar Fe/(Mg + Si) below 0.1.

Combining the various physicochemical properties of the SRM collection (degree of alteration, abundance by type, size-frequency distribution, Fe/(Mg + Si) ratio, etc.), the Widerøefjellet collection may thus be largely unbiased for the size fractions studied (Table 1; Supplementary Table S1). While the Widerøefjellet collection shares properties with both old and young (Antarctic) MM collections in terms of CSs, the most obvious feature is the high abundance of V-subtype CSs, consistent across different size fractions (Table 3). While secondary trapping and transportation effects, for example due to lack of wind or the presence of a stabilizing fine-grained dust below the snow layer (Genge et al., 2018), cannot be excluded, the high V-subtype abundance, and overall distinct relative abundances of V-, BO-, CC-, and Po-type CSs, in the Widerøefjellet collection could perhaps also be explained by systematic changes in the entry velocities of dust caused by quasi-periodic gravitational perturbation during transport to Earth over the different time periods of CS accumulation. This was first suggested by Genge et al. (2017) to explain the textural differences between recent and older CS collections. Such changes may not be expressed in the Larkman, Cap Prud'homme, TAM and Walcott Névé collections due to higher degrees of weathering or the implementation of magnetic separation techniques.

4.2. Parent body precursors of Widerøefjellet cosmic spherules

4.2.1. Constraints from elemental chemistry

Based on the major element compositions, most, if not all, of the Widerøefjellet particles studied derive from chondritic precursors. This interpretation is based on both major (Figs. 7, 8, 10) and trace (Figs. 9, 10) element compositions and trends, which all indicate compositional ranges close to or within the chondritic fields. This chondritic parentage indicates that the majority of the dust delivered to the Earth samples specific source regions (Section 4.4) and arrives through particular transportation mechanisms (Poynting-Robertson drag for µm to cm particles; Rubin, 2018). The achondritic particles described in literature are thus relatively rare (e.g., Folco and Cordier, 2015). While largely chondritic (e.g., Brownlee et al., 1997), the chemical groups of CSs reflect the degree of heating experienced and the degree of evaporation undergone during atmospheric entry. Decreasing Si/Al and Mg/Al ratios are generally thought to reflect higher degrees of evaporation (e.g., Alexander et al., 2002; Wang et al., 2001) and CSs evolve from the normal group (Si/Al = 14.6 and Mg/Al = 14.2), through the CAT-like group (Si/Al = 9.8 and Mg/Al = 9.9), to the high Ca–Al group (Si/Al = 6.6 and Mg/Al = 8.0), with variable Fe/Si, Mg/Si, and CaO and Al₂O₃ contents as a result (Taylor et al., 2005; Cordier et al., 2011b; Fig. 8).

The bulk spherule composition is also controlled by the mineralogy of the precursor material (e.g., Imae et al., 2013). This is clear from major element trends, but also from the trace element plots, where the occurrence of specific REE patterns highlights the influence of mineral precursors, such as enstatite and forsterite (Figs. 8D, 9), but possibly also Cr-rich spinel crystals (e.g., WF1202B-0013 and 0041 with >1 wt% Cr₂O₃). As atmospheric melting and concomitant evaporation experienced by CSs strongly affected primary textures, mineralogy and chemical compositions, precisely constraining the nature of the chondritic sources remains highly challenging (e.g., Alexander et al., 2002; Taylor et al., 2005). Most elemental concentrations and ratios are either not sufficiently discriminative or underwent too large a modification to deduce the type of precursor body (e.g., Rudraswami et al., 2016).

4.2.2. Constraints from oxygen isotope ratios

Triple-oxygen isotope ratios have been shown to be a powerful tracer of the origin of CSs and MMs in general (e.g., Engrand et al., 1999; Yada et al., 2005; Taylor et al., 2005; Suavet et al., 2010; Cordier and Folco, 2014). Based on their distribution in three-O isotopic space, bulk CSs have previously been assigned to five large isotopic groups depending on the identification scheme used (Fig. 12; Section 3.5). These assignments take into account mixing with atmospheric oxygen (constant at δ^{18} O $\approx 23.5\%$ and δ^{17} O $\approx 11.8\%$ up to 60.9 km altitude; Thiemens et al., 1995) and mass-dependent fractionation during atmospheric entry. Loss of material by evaporation (Engrand et al., 2005) and separation of iron-nickel droplets (Brownlee et al., 1984; Genge and Grady, 1998) may lead to mass-dependent oxygen isotope fractionation with higher δ^{17} O and δ^{18} O values (Suavet et al., 2010; Fig. 12). Here, the data collected indicate the existence of a third process affecting the bulk oxygen isotopic compositions of Antarctic CSs, involving the interaction with Antarctic precipitation (Fig. 12). While surface snow samples in Antarctica have revealed highly variable O isotopic compositions, the nearby Nansen blue icefield indicates δ^{18} O values of $-43 \pm 3\%$ (1 SD; n = 185; Zekollari et al., 2019). Although alteration products of Antarctic CSs vary widely depending on the sample location, exposure age, and textural type of the particles. these will be dominated by Feoxyhydroxides, clay minerals, or palagonite (van Ginneken et al., 2016). Alteration products in equilibrium with meteoric waters at 0°C will be offset from the surrounding ice by δ^{18} O values varying between 0 and 20% depending on the minerals concerned (Beaudoin and Therrien, 2009; Alexander et al., 2018), with a secondary mineral assemblage to the right of the surrounding meteoric water along the TFL, with an average δ^{18} O of roughly -30%. As a result, the bulk composition of the affected CSs will have moved in this general direction (see dashed arrows for Group 1 extremes on Fig. 12A). This effect is likely important in other collections and previously reported O isotope data as well but remains difficult to evaluate due to varying preparation and measurement protocols (e.g., washing with aceton versus acid leaching).

Chondritic spherules that plot well below the TFL are commonly assigned to bulk carbonaceous chondrites CV. CO, CM, CR, or their constituent chondrules and refractory inclusions (e.g., Ca-Al-rich inclusions, CAIs). As the isotopic compositions for Wild 2 anhydrous mineral grains partially overlap with the fields defined for both carbonaceous and ordinary chondrites (with Δ^{17} O between -21.4and +3.4‰ and δ^{18} O between -47.2 and +3.5‰, with 2σ analytical uncertainties ranging from 1 to 4% for δ^{18} O; Nakamura et al., 2008), cometary particles cannot be discriminated from asteroidal material. Suavet et al. (2010) discriminated Group 1 from Group 2 carbonaceous CSs based on their isotopic signatures (Fig. 12). In this classification scheme, Group 1 CSs have $\Delta^{17}O \approx -3$ to -5%, and δ^{18} O in the range of 10-30%, while Group 2 CSs have $\Delta^{17}O \approx -1\%$, and $\delta^{18}O$ between 15-35‰. For the Widerøefjellet dataset, only a single CS falls close to the Group 2 (V-type WF1202B-0057; Table 2; Fig. 12). Fourteen of 16 Widerøefjellet spherules below the TFL plot significantly lower than Group 2, extending the ranges of the previously identified Group 1, and likely indicate the existence of a continuum between particles deriving from CV, CO. CM and possibly CR carbonaceous chondrites (Fig. 12). Based on mixing lines starting from the chondrite fields, CC-type CS WF1202B-0078 is likely connected to CV carbonaceous chondrites or derives from chondritic refractory inclusions, while V-type WF1202B-0053, BOtype WF1202B-0058, 0064, 0077, and mixed BO/CC-type WF1202B-0080 can conclusively not have a CR chondritic parentage, and share a CV, CO, or CM-related origin (Fig. 12; Table 2).

Group 2 particles, in part linked to CR carbonaceous chondrites, thus constitute only 4% of the Widerøefjellet collection relative to 21% and 17% of similar particles in the TAM and Atacama Desert collections (Suavet et al., 2010; van Ginneken et al., 2017). The cosmic-ray exposure ages for Atacama Desert and TAM surfaces indicate collection windows between the present and 4-5 Myr ago (Suavet et al., 2010; van Ginneken et al., 2017). The measured terrestrial ages of individual TAM particles, based on their thermal remanent magnetization, indicate that most particles (\sim 66%) fell to Earth 1–2 Myr ago, while the remainder $(\sim 33\%)$ fell more recently (Suavet et al., 2011b). Thus, in practice, the TAM collection has an accumulation window of up to 2 Ma and is possibly biased toward the latter half of this window. This seems comparable to the collection age for Widerøefjellet, where the deglaciation history of the SRM indicates possible accumulation during the last \sim 1– 3 Ma. This implies that the relative contributions of the O isotopic groups to these collections are not linked to accumulation windows alone, and the observed underrepresentation of Group 2 particles at Widerøefjellet (Table 2; Fig. 12) may rather reflect the preservation state of the Widerøefjellet collection or the preparation procedures applied before analysis. However, if Group 2 particles formed from CR chondritic precursors and Group 1 spherules are dominated by CM-CO-CV carbonaceous chondrites, with the latter much more common than the CRs in the relatively recent meteorite record (<3 Ma) (Meteoritical Bulletin Database: http://www.lpi.usra.edu/ meteor/metbull.php, accessed 17 October 2019), detailed comparison between collections with distinct accumulation windows (e.g., CSs from rooftops; Genge et al., 2017) and analysis of more representative numbers of CSs may reveal changes in the MM source regions.

Particle WF1202B-0071 with a mixed BO-/CC-type texture (Fig. 3) plots slightly below the TFL and to the right of the *Group 2* field (Δ^{17} O $\approx -0.25\%$, δ^{18} O of 37.18\%). Based on its triple-oxygen isotopic composition, WF1202B-0071 may have derived from HED asteroids, or the CI-type or enstatite chondrite parent bodies (Fig. 12). When considering the major element ratios (including Mg/Al, Si/Al, and Fe/Mg) determined using semi-quantitative SEM-EDS before IRMS (Supplementary Fig. S3), this particle likely does not originate from a differentiated parent body and its origin remains ambiguous, as the field for enstatite chondrites overlaps with that of CI chondrites. However, a large degree of mass-dependent isotope fractionation (>30%) would be required to explain the observed δ^{18} O from an chondritic starting composition. enstatite Particle WF1202B-0071 could thus potentially originate from a CI chondrite precursor. Based on textural and geochemical observations on unmelted particles, MMs deriving from CI chondrites are known to exist (Kurat et al., 1992; van Ginneken et al., 2012), yet no particles have previously been assigned to CI precursors based on O-isotope data. Such particles are likely more abundant in the smallest size fractions.

Above the TFL, two fairly well-defined groups have been identified that are confirmed by the particles characterized in this work. Group 3 CSs are mostly related to ordinary chondrites, although contributions from enstatite, R and CI chondrites cannot be excluded (Fig. 12). Group 4 spherules are characterized by significantly elevated $\delta^{17}O$ and δ^{18} O (above stratospheric oxygen) and Δ^{17} O above 1.0% (Fig. 12), which have been described as ¹⁶O-poor spherules in literature (Yada et al., 2005; Suavet et al., 2010, 2011a,b). To date, the nature of these spherules remains unclear but a derivation from a known ordinary chondritic progenitor appears improbable, as the amount of evaporation required to shift ordinary chondritic compositions towards such high δ^{17} O and δ^{18} O does not agree with their measured bulk major element compositions (e.g., Yada et al., 2005; Cordier and Folco, 2014; Supplementary Fig. S3). Instead, fragments of unequilibrated ordinary chondrites, dominated by secondary magnetite grains ($\Delta^{17}O = +5$ to +7%; Choi et al., 1998) or chondrules with glass or feldspathic mesostasis ($\Delta^{17}O = +3\%$; Franchi et al., 2001) have been suggested. As all textural subtypes of S-type CSs are represented among the Group 4 particles studied in this work (V-, CC-, BO-, and Po-type), the latter ideas are no longer considered reasonable, as this would require a magnetite or feldspathic component to be the main contributor to the oxygen isotopic compositions of Group 4 CSs, which is not tenable considering the modal mineralogy of the particles studied here. Alternatively, these MMs may represent ¹⁶O-poor nebular material from a reservoir that currently remains unsampled by normalsized meteorites (Yada et al., 2005; Suavet et al., 2010). Based on the observed mass-dependent isotope fractionation effects and exchange with atmospheric oxygen for *Group 1* and *Group 3* particles, the probable starting composition of *Group 4* spherules was around $\delta^{18}O \approx +20\%$ and $\Delta^{17}O \approx +3\%$, which, albeit large analytical uncertainties, is within range of the bulk O-isotopic measurements reported for particular interplanetary dust particles (IDPs; Starkey et al., 2014).

While metal bead segregation is assumed to induce mass-dependent oxygen isotope fractionation (Genge and Grady, 1998; Suavet et al., 2010), no direct relationship between the presence of high-density phases or high δ^{18} O is observed for the Widerøefjellet particles, although the nature of the high-density phases (metal bead, sulfide, spinel group mineral, etc.) mostly remains ambiguous (Table 2). This indicates that mass-dependent isotope fractionation may be caused by a variety of processes, including evaporation, high-density phase segregation or kinetic isotope effects during interaction with atmospheric oxygen (Taylor et al., 2005). Similarly, the presence of vesicles does not seem to influence the degree of mass-dependent fractionation experienced (Table 2). While also no correlation is observed between the meteorite type from which the CSs are derived based on oxygen isotope ratios and their chemical group (Cordier et al., 2011b), general trends between the oxygen isotopic composition and textural groups of CSs have previously been observed (van Ginneken et al., 2017) and are discussed in Section 4.4.

4.3. Chemical modification during atmospheric heating

In the following paragraphs, we argue that the observed deviations from chondritic values in bulk chemistry (Figs. 8–11) largely stem from effects linked to evaporation, high-density phase segregation, and redox shifts taking place during atmospheric passage on mostly originally chondritic particles or (refractory) mineral components, rather than from chemical alteration taking place during the terrestrial residence of the studied particles, supporting the pristine nature and representativeness of the Widerøefjellet CS collection. Here, the fragmentation dynamics in specific Solar System source regions, resulting in unrepresentative subsampling of the parent bodies involved, most likely play an important role in determining the bulk composition of CSs.

To study the individual effects of the processes mentioned above, the data for all CS analyzed here are compiled for textural (V-, BO-, and CC-type) and chemical (normal, CAT-like, high Ca-Al) groups, to minimize the effects related to heterogeneity in precursor mineralogy and individual CS chemistry (Table 1; Fig. 10). To obtain an average chemical composition for the normal BO-type CSs, the composition of WF1202B-0013 was excluded, as this normal CS (Fe/Si of 1.09 and Mg/Si of 0.93) is characterized by a high enrichment in REE (average REE_N of 7.03) with a fractionated LREE-enriched pattern ((La/Yb)_N of 3.83), exhibiting negative Ce and Eu anomalies (Supplementary Table S1). Similarly, the composition of WF1202B-0001 was excluded from the high Ca-Al CSs because of its extreme enrichment in REE (more than 10 times CI) and fractionated REE pattern ((La/Yb)_N of 2.60; Figs. 8, 9; Table 1). Overall, the average REE patterns for the 3 characterized textural (V-, BO-, and CC-type) and chemical (normal, CAT-like, and high Ca-Al) CS groups are consistent with bulk chondrite compositions and exhibit relatively flat REE patterns (La/Yb_N = 0.91-1.01; Table 1; Figs. 8, 9, 10; Supplementary Table S1): 33 out of 34 normal, 6 out of 6 CAT-like, and 3 out of 4 high Ca-Al CSs have relatively chondritic REE patterns (Fig. 9), consistent with literature data (e.g., Folco and Cordier, 2015). With the exception of the LREE-enriched REE patterns recognized in the current work (Fig. 9F), all REE patterns have previously been observed among the 76 V-type spherules of Cordier et al. (2011b). Conversely, U-shaped REE patterns $(La/Yb_N = 0.8-2.2; Eu^* = 3.8-10.6)$, the least abundant signature among the V-type spherules of Cordier et al. (2011b), are not observed among the CSs studied here, although perhaps the case could be made that the LREEenriched patterns observed for WF1202B-0001, 0013, and 0042 (Fig. 9F) partly resemble the U-shaped REE patterns described. A positive Ce anomaly, a feature typical of Ushaped REE patterns (Cordier et al., 2011b), has only been observed in a single V-type spherule (WF1202B-0017) that could also be interpreted to represent a member of the Ushaped group. Likely, a continuum exists between these subtypes, reflecting competing processes linked to the thermal and redox processes taking place during atmospheric passage.

4.3.1. Evaporation

The observed diversity in quench textures and chemical compositions in CSs has previously been interpreted to result from variable peak temperatures and evaporative loss during atmospheric entry and heating (e.g., Taylor et al., 2000; Genge et al., 2008). From Po-type to BO- and CCtype, V-type spherules and then the more strongly evaporated CAT and high Ca-Al spherules, peak temperatures are thought to increase, leading to increases in CaO, Al₂O₃, TiO₂, and MgO contents, as well as decreases in FeO contents relative to chondritic values (Taylor et al., 2000; Cordier et al., 2011b; Section 3.3). These chemical trends are consistent with both geochemical models (Alexander et al. 2002) and experimental simulations (Floss et al., 1996; Wang et al., 2001) of heating and evaporation starting from chondritic and solar compositions (Fig. 11).

By comparing the refractory major element and REE compositions of the CSs with those of the residues obtained after heating of experimental charges with solar composition (Wang et al., 2001), Cordier et al. (2011b) estimated that CSs of the normal group experienced between 40% and 50% mass loss, CAT-like CSs between 50% and 60% mass loss, and high Ca–Al spherules between 80% and 90% mass loss. These calculated values based on the elemental compositions are similar to those estimated for CAT-like spherules based on isotopic values (~50% mass loss; Alexander et al., 2002) and fit with the mass losses of 70–90% proposed by Love and Brownlee (1991), at least for the high Ca-Al CSs. However, these values need to be

considered upper estimates for the mean values, as individual particles can show even larger variations in the degree of evaporation (Fig. 11). According to Taylor et al. (2005), evaporative losses can also be approximated through trends on a plot of the atomic Si/Al versus atomic Mg/Al ratio (Fig. 8D), provided that the bulk composition of the MM precursor can be estimated adequately. Aluminum, with a 50% condensation temperature T_C of 1653 K, is progressively enriched relative to Mg and Si (50% T_C of 1336 K and 1310 K, respectively; Lodders, 2003). Extraterrestrial particles that are progressively evaporated will therefore, follow an evaporation trajectory starting from the carbonaceous and ordinary chondrite source fields. In Fig. 8D, the majority of normal CSs lie within or near the chondrite fields, attesting to minor to moderate degrees of evaporation. The CAT-like and high Ca-Al spherules are positioned further down the evaporation trajectory, which reflects more extreme atmospheric heating conditions. Particle WF1202B-0001 lies at the extreme end of the evaporation curve, with evaporative loss estimates exceeding 90%.

The degree of evaporative loss in CSs during atmospheric entry can also be estimated from refractory trace elements other than the REE (e.g., Sc, Y, Zr, and Hf; Fig. 8C). Refractory trace element contents display a positive correlation with the degree of evaporation and consequently the CaO and Al₂O₃ contents. While the majority of CSs from the 3 chemical groups fall within a limited range (CaO $+ Al_2O_3 < 9$ wt%, Sc $+ Y + Zr + Hf < 33 \mu g/g$) and fairly close to the observed correlation curve with a slope of ~ 0.27 (Fig. 8C), a number of CSs fall significantly outside this range with strong deviations from the slope (e.g., WF1202B-0001, 0002, 0016, and 0011). The majority of CSs belonging to the normal group are positioned at the lower end of the correlation curve, reflecting minor evaporative losses. In contrast, the CAT-like and high Ca-Al CSs lie at the middle and higher end of the correlation line, suggesting $\sim 50\%$ and >75% mass losses, respectively. Particle WF1202B-0001 is an extreme case positioned at the far end of the correlation line, again indicating strong evaporative loss (\sim 90%). While this particle may have been affected by some terrestrial alteration, the elements used in Fig. 8C are relatively immobile and should only undergo limited effects from such process. As the slope of the correlation curve is defined by the volatility of the combination of elements considered, CSs that deviate from this trend may reflect highly variable precursor mineralogy and geochemistry (e.g., Imae et al., 2013).

4.3.2. Depletion in siderophile and chalcophile elements

Both siderophile (including W, Co, Ni) and chalcophile (including V, Cr, Mn) trace elements show systematic negative anomalies relative to their neighboring lithophile elements when ordered according to increasing volatility (Fig. 10). In the CSs studied in this work, the depletion in siderophile elements is most pronounced for CAT-like CSs, while the high Ca-Al spherules exhibit siderophile element depletions of similar magnitude as those observed for normal CSs. Among normal CSs, the depletions are comparable for CC- and V-type spherules, while the effects are less Relative to experimentally defined evaporation trends, CAT-like spherules, presumably affected by intermediate degrees of evaporative loss, display FeO concentrations significantly lower than those measured for the high Ca–Al and normal groups (Figs. 10, 11D–F; Cordier et al., 2011b). This confirms that Fe concentrations in CSs are not only governed by the evaporation process. This is consistent with the Fe isotope fractionation observed in CSs, indicating that Fe is mainly lost by physical separation of metal-rich phases, with minor free evaporation, except perhaps in the case of CAT-like and high Ca-Al spherules (Alexander et al., 2002; Engrand et al., 2005; Taylor et al., 2005).

The data reported here confirm the observations of Cordier et al. (2011b) who propose that mechanical separation of siderophile- and chalcophile-rich phases occurs during atmospheric entry, rather than partitioning of chalcophile elements into metal phases or loss by evaporation alone (Brownlee et al., 1997; Genge and Grady, 1998). While removal of Fe-Ni metal or sulfide beads from silicate melts has long been considered to cause depletions in siderophile and possibly chalcophile elements (e.g., Brownlee et al., 1997; Genge and Grady, 1998), the separation of chalcophile-rich solids, such as chromites, is a more recent idea (Cordier et al., 2011b). The latter authors suggest that the migration of chromite grains toward the particle periphery may result from differential acceleration between contained chromite grains and silicate melt, or as proposed for metal beads in spinning CSs from centrifugal forces or floating of chromite grains on rising vesicles, as surface tension allows for their fixation on the vesicle surface. However, the density range for chromite between 4.5 and 5 g/cm³ perhaps renders the latter unlikely.

As chromite is a potential refractory phase in basaltic melts (e.g., Longhi and Pan, 1988; Roeder and Reynolds, 1991), incomplete melting during atmospheric heating could lead to a depletion of chalcophile elements in silicate melts. When chromite grains are small, their melting may take place relatively fast, while the contrast in density relative to silicate melt may be less effective and inhibit settling (Genge et al., 2016). However, if chalcophile and siderophile element depletions result from (refractory) metal, sulfide or spinel group mineral losses, then the enrichment in siderophile and to lesser extent chalcophile elements observed in high Ca-Al CSs would require that these particles underwent less efficient separation of such high-density phases during atmospheric passage, relative to the other chemical CS groups. As high Ca-Al spherules are interpreted to have experienced the highest evaporative losses and peak temperatures, their enrichment in siderophile and chalcophile elements relative to spherules that formed at lower temperatures may simply result from the oversampling of more refractory phases within the MM, i.e., a slight excess of spinel group minerals or refractory metal nuggets (e.g., as in the refractory Ir and Pt-enriched high Ca-Al WF1202B-0011) rather than high-density phase ejection.

4.3.3. Effects from redox conditions

Following the work of Cordier et al. (2011b) on V-type spherules and extending these observations to BO-type and CC-type CSs, the CS compositions determined here can be compared to those of residues obtained after heating of experimental charges with solar composition in terms of refractory major element and REE compositions (Fig. 11; Wang et al., 2001; Cordier et al., 2011b). The progressive enrichment observed for refractory REEs from the normal group (avg. $REE_N = 1.8 \times CI$) over the CAT-like group (avg. $REE_N = 4.1 \times CI$) to the high Ca–Al group (avg. $REE_N = 4.5 \times CI$; Table 2) is consistent with increasing levels of evaporation. Evaporation mostly does not fractionate the REEs, yet Ce does not always occur in chondritic proportions in CSs (Figs. 9, 11). While some of the observed Ce anomalies may be linked to terrestrial alteration (e.g., WF1202B-0013 and 0017), this is unlikely to be the case for all particles studied here, as most are relatively fresh, devoid of fracturing and surficial alteration. In addition, the CSs showing Ce depletions are not equally distributed among the different chemical groups studied, with 83% (by number) of the CAT-like, 67% of the high Ca-Al, and only 15% of the normal chondritic CSs exhibiting REE patterns characterized by a negative Ce anomaly (with $Ce^* < 0.88$; Figs. 9, 11). While experimental residues systematically show large negative anomalies in Ce for mass losses larger than 50% (Floss et al., 1996; Wang et al., 2001), Ce anomalies observed in CSs are generally smaller in magnitude (1-2 versus 3 orders of magnitude in experiments; Fig. 11). As these Ce anomalies are thought to result from the volatile behavior of Ce⁴⁺ under highly oxidizing conditions prevalent during non-equilibrium kinetic evaporation in Earth's atmosphere (Hashimoto, 1990; Floss et al., 1996; Wang et al., 2001), Ce depletions in CSs hint at moderately oxidizing conditions during atmospheric passage or incomplete vacuum during the experiments. As the Ce anomalies are mainly observed in CAT-like and high Ca-Al spherules that are interpreted to have experienced mass losses of 50% or higher, Ce anomalies in CSs may relate to high degrees of evaporation experienced during atmospheric entry, which could allow for local increases in the partial pressure of oxygen (Cordier et al., 2011b).

4.4. Comparison to other Antarctic micrometeorite collections and implications for the interplanetary dust complex

While major and trace element concentrations indicate a largely chondritic parentage for the CSs studied in this work, oxygen isotope ratios can refine the relative contributions of each chondrite class. Cordier and Folco (2014) compiled previously reported three-oxygen isotope data for 136 CSs. Of these 136 spherules, ranging from 50 µm to 2280 µm in diameter and studied using both IRMS and ion microprobe, ~60% relate to carbonaceous chondrite asteroids (or comets), ~17% to ordinary chondrites, ~8% to a ¹⁶O-poor reservoir, and ~4% to HED asteroids, while ~11% remain ambiguous. Importantly, the ratio of carbonaceous chondrite relative to ordinary chondrite material decreases as the CS diameter increases, from ~10 for small

Table 4

Groups ^a	OC-related	CC-related	¹⁶ O-poor	Ambiguous	HED-related	Total ^b
# of spherules in this work	8	15	4	1	0	28
% all sizes	29	54	14	4	0	
% 250–500 μm	29	57	7	7	0	14
% 500–1000 μm	29	50	21	0	0	14
% V-type	50	40	10	0	0	10
% BO-type	14	71	14	0	0	7
% Po-type	0	50	50	0	0	2
% CC-type	17	67	17	0	0	6
# of spherules in literature	23	81	11	15	6	136
% all sizes	17	60	8	11	4	
% <100 μm	7	66	17	10	0	29
% 100–250 μm	6	68	10	16	0	31
% 250–500 μm	9	80	6	6	0	35
% 500–1000 μm	38	38	0	6	19	32
$\% > 1000 \mu m$	44	11	11	33	0	9

Parentage statistics for 28 silicate cosmic spherules determined in this work, compared to previously compiled literature data (Cordier and Folco, 2014).

^a The proportion of CSs assigned to the ambiguous group provides some indication on the degree of certainty in the assignment of particles to these isotopic groups.

^b Totals are expressed as the number of spherules.

particles ($\leq 500 \,\mu\text{m}$) to ~ 0.3 for particles larger than 500 µm. For CSs in the range of 500-1000 µm (32 in the compiled dataset), $\sim 38\%$ can be linked to ordinary chondrites, while $\sim 38\%$ relate to carbonaceous chondrites, $\sim 6\%$ remain ambiguous and $\sim 19\%$ are related to HED asteroids (Table 4). Note that the latter were the focus of the work by Cordier et al. (2011a) and the particles analyzed were selected based on their chemical composition, leading to a population bias. In the 250-500 µm size fraction, the number of CSs in the literature linked to ordinary chondrites decreases to $\sim 9\%$, while those related to carbonaceous chondrites increase to $\sim 80\%$, with ¹⁶O-poor and ambiguous CSs both contributing $\sim 6\%$ of the population. Cosmic spherules below 500 µm are composed of \sim 70% carbonaceous chondrite-derived material (Cordier and Folco, 2014), consistent with the Mg-Si-Al compositions of various MM collections (Taylor et al., 2012; Genge, 2008). This distribution indicates that a significant proportion of large (>200 µm) MMs are related to ordinary chondrites or to CO, CV, CK carbonaceous chondrites, whereas smaller MMs (from 20 to $100 \,\mu\text{m}$) are mainly linked to CM2 or CR2 chondrites (Kurat et al., 1994; Brownlee et al., 1997; Engrand and Maurette, 1998; Engrand et al., 2005). This relationship may reflect the lower mechanical resistance of phyllosilicate-bearing chondrites, leading to enhanced fragmentation into smaller particles during dust production in space as a result of the collisions between their parent asteroids (Flynn et al., 2009). Examples of large anhydrous chondritic MMs include a >1000 µm CV-like and a >700 µm CK-like MM (van Ginneken et al., 2012; Cordier et al., 2018). However, exceptions exist, as illustrated by unambiguously hydrated fine-grained chondritic CM/CR MMs recovered from the $>400 \,\mu\text{m}$ size fraction (Suttle et al., 2019).

For Widerøefjellet, a fairly similar particle parentage is observed for the 500–1000 μ m size fraction, with ~50% of the spherules relating to carbonaceous chondrites, ~29%

to ordinary chondrites, and ~21% to ¹⁶O-poor material. Although the set of analyzed CSs remains limited, no clear population shift is observed for the 250–500 μ m size fraction (~29% OC, ~57% CC, ~7% ¹⁶O-poor, 7% ambiguous; Table 4). However, it should be noted that most of the CSs characterized in this size fraction fall between ~400 and 500 μ m, so the expected transition in terms of relative abundance between the two CS size populations at around 500 μ m (Cordier and Folco, 2014) might in fact lie between 250 and 400 μ m. This agrees with impact destruction experiments on hydrous (e.g., CM chondrite) and anhydrous (e.g., ordinary chondrite) targets that show that small dust particles less than 300 μ m are favored in hydrous (carbonaceous) targets (Flynn et al., 2009).

In the compilation of Cordier and Folco (2014), no correlation was observed between CS texture and their assigned precursor material, except that most spherules related to HED asteroids primarily belong to the V-type subtype. Van Ginneken et al. (2017) recently studied a number of CSs recovered from the Atacama Desert and compared these to TAM CSs to determine possible relationships between the different textural CS types and their respective parent bodies. These authors concluded that coarse-grained dust particles, with affinities toward the ordinary chondrite parent bodies, are more prone to produce Po textures. At higher peak temperatures, these dust particles will preferably develop a CC-type texture, rather than a BO texture, due to the lack of nuclei available to develop new crystal faces. In contrast, BO spherules are predominantly thought to originate from the matrices of fine-grained carbonaceous chondrite particles (van Ginneken et al., 2017). This is mainly attributed to the mineralogical variety present in the matrices of carbonaceous chondrites, favoring supercooling, as well as the presence of accessory mineral phases, which may act as nuclei for the development of BO textures. No correlations have been found for V-type spherules as the highest peak

temperatures ensure complete melting of the MM precursor, regardless of composition. Based on the triple-oxygen isotopic data of the Widerøefjellet collection (Table 2), the predominance of BO-type CSs toward a carbonaceous chondrite precursor (71% of BO-type), and the lack of correlation between V-type spherules and a specific precursor is confirmed. Yet, Po- and CC-type spherules do not follow the trends mentioned above. More specifically, one Po-type CS appears to be related to the Group 4 CSs, while another is linked to carbonaceous chondrites (Tables 2 and 4). CCtype spherules at Widerøefjellet have a predominant affinity with carbonaceous chondrites (67%), as opposed to ordinary chondrites (17%). Group 4 CSs are represented by all four major textural types. Hence, accurate predictions of the parent body composition of CSs solely based on textural properties remains challenging.

The oxygen isotope composition of the SRM CS collection confirms that the composition of the micrometeoroid complex is different from that of macroscopic meteoroids. Materials with compositions similar to CI, CR, CM, CV, and CO chondrites dominate the former, whereas ordinary chondrites (~86%) and evolved meteorites (e.g., HED, making up $\sim 4\%$) dominate the latter (Meteoritical Bulletin Database: http://www.lpi.usra.edu/meteor/metbull.php. accessed 17 October 2019). Cosmic spherule statistics thus indicate that asteroids commonly observed in the inner asteroid belt (e.g., S-type ordinary chondrite and V-type HED parent asteroids) feed 20-30% or more of the micrometeoroid complex (Table 4). The other 55-60% are related to primitive solar system objects with carbonaceous chondritic compositions (Cordier and Folco, 2014). These materials could be associated to silicate dust released by short-period comets (e.g., Nesvorný et al., 2010) or with primitive asteroids belonging to the C-, D- or P-type spectral classes in the middle and outer asteroid belt (from 2.8 AU to Jupiter's orbit). In the case of the latter, recently disrupted asteroid families represent the primary source of MMs. Based on dynamic modeling and observations using the Infrared Astronomical Telescope (IRAS), three major dust bands produced by the C-type Veritas, older C-type Themis, and S(IV)-type Koronis asteroid families supply the majority of asteroidal dust delivered to the Earth (Kortenkamp, 1998; Nesvorný et al., 2002; Genge, 2008). Continued oxygen isotope ratio work on CSs, and MMs in general, extending the numbers of characterized particles as well as the currently sampled size fractions, will lead to a more refined understanding of the contributions of the various parent bodies in the solar system to the different fractions of the extraterrestrial flux to Earth and more accurately point out possible fluctuations with time.

5. CONCLUSIONS

To demonstrate the representativeness of the Widerøefjellet CS collection, the physicochemical properties of the CSs in this deposit, including cumulative size distribution, frequency by type and chemical composition, presence of vesicles and high-density phases, major and trace element chemical compositions, and oxygen isotope ratios, have been compared to those of other Antarctic MM deposits, including the TAM and SPWW collections. Although the Widerøefjellet deposit contains unmelted and scoriaceous MMs (<5% of all MMs) as well as both silicate- and metal-rich CSs (\sim 95% and \sim 5% of all CSs, respectively), this work focused on characterizing the silicate-rich CSs larger than 200 µm. All major textural (V-, BO-, CC-, and Potype) and chemical (normal, CAT-like, high Ca-Al) CS groups are present. Most particles appear relatively unaltered, while the proportions for each CS type are comparable to those of the least biased Antarctic collections. While the molar Fe/(Mg + Si) ratios of the studied CSs are similar to that of the SPWW, a higher proportion of V-type CSs relative to other deposits was found. A relatively unbiased cumulative size distribution plot supports the claim of an essentially representative MM deposit. The -4.4 exponent slope of the size distribution is similar to that of the TAM collection, suggesting direct infall to be the dominant process controlling the MM accumulation. The widely varying degree of alteration for Widerøefjellet and TAM particles, from fresh to heavily altered, confirms the long accumulation ranges from respectively ~ 3 and ~ 4 Myr ago to present.

A subset of Widerøefjellet CSs larger than 325 µm was characterized for major and trace element concentrations and oxygen isotope ratios. The collected data confirm the major trends observed in literature, linking the Widerøefjellet CSs to chondritic precursors and their mineralogical constituents, which underwent chemical changes during atmospheric passage. Various factors control the CS composition, including the primary characteristics of the parent body precursors, the presence and expulsion of high-density phases (including metal bead, sulfides, and spinel crystals) as well as evaporation linked to differential redox and thermal conditions following atmospheric entry, and subsequent terrestrial alteration. The parent bodies of MMs are thought to differ from those sampled by normal-sized meteorites due to different production and transport mechanisms. At least 50% by number of CSs from all size fractions relate to primitive solar system objects with carbonaceous chondrite compositions, either to the C-, D-, or P-type spectral class asteroids in the outer asteroid belt or, alternatively, to comets. The contribution of ordinary chondrite particles shows larger variations, and strongly depends on the size fraction of the particles studied. A relatively constant proportion of CSs ($\sim 10\%$) is related to a chondritic reservoir depleted in ¹⁶O. Overall, the physicochemical properties of the Widerøefjellet particles denote a distinctive and representative collection of CSs from East Antarctica, including a statistically significant number of particles with diameters larger than 800 µm. The Widerøefjellet collection complements currently existing collections and offers an important addition to study the composition of the MM flux over the last few million years.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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APPENDIX A. SUPPLEMENTARY MATERIAL

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Meteoroid atmospheric entry investigated with plasma flow experiments: Petrography and geochemistry of the recovered material

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The atmospheric entry of (micro)meteoroids is a complex process involving evaporation, redox reactions, metal bead extraction, and potentially other types of processes (e.g., Genge and Grady, 1998; Alexander et al., 2002; Engrand et al., 2005; Taylor et al., 2005; Genge, 2006; Suavet et al., 2010; Cordier et al., 2011a; van Ginneken et al., 2017; Riebe et al., 2020). The extent of the aforementioned processes largely depends on the physicochemical properties of the meteoritic material and its entry parameters (Love and Brownlee, 1991). However, the nature of these processes is currently not well understood despite its pervasive influence on the physicochemical and isotopic properties of micrometeorites. This may severely complicate the identification of micrometeorite precursor bodies and thus instigates a thorough investigation of the physicochemical processes occurring during atmospheric entry heating. This article is a companion paper of 'Analysis of meteoroid ablation based on plasma wind-tunnel experiments, surface characterization, and numerical simulations' by Helber et al. (2019), which both discuss the results of an experimental setup where the atmospheric entry of meteoroids was replicated in a high enthalpy facility. Here, an alkali basalt and ordinary chondrite sample were heated to extremely high temperatures and the resulting materials were collected and characterized (i.e., petrography, chemistry) in an attempt to constrain the nature of atmospheric heating processes.

BS has assisted Lidia Pittarello with sample acquisition; sample preparation; and acquisition of Scanning Electron Microscopy (SEM) images of the alkali basalt and ordinary chondrite samples and their respective melt products. In addition, BS has acquired and processed the major and trace elemental dataset following Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS).

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Meteoroid atmospheric entry investigated with plasma flow experiments: Petrography and geochemistry of the recovered material

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ABSTRACT

Melting experiments attempting to reproduce some of the processes affecting asteroidal and cometary material during atmospheric entry have been performed in a high enthalpy facility. For the first time with the specific experimental setup, the resulting material has been recovered, studied, and compared with natural analogues, focusing on the thermal and redox reactions triggered by interaction between the melt and the atmospheric gases under high temperature and low pressure conditions. Experimental conditions were tested across a range of parameters, such as heat flux, experiment duration, and pressure, using two types of sample holders materials, namely cork and graphite. A basalt served as asteroidal analog and to calibrate the experiments, before melting a H5 ordinary chondrite meteorite. The quenched melt recovered after the experiments has been analyzed by µ-XRF, EDS-SEM, EMPA, LA-ICP-MS, and XANES spectroscopy.

The glass formed from the basalt is fairly homogeneous, depleted in highly volatile elements (e.g., Na, K), relatively enriched in moderately siderophile elements (e.g., Co, Ni), and has reached an equilibrium redox state with a lower Fe^{3+}/Fe_{tot} ratio than that in the starting material. Spherical objects, enriched in SiO₂, Na₂O and K₂O, were observed, inferring condensation from the vaporized material. Despite instantaneous quenching, the melt formed from the ordinary chondrite shows extensive crystallization of mostly olivine and magnetite, the latter indicative of oxygen fugacity compatible with presence of both Fe^{2+} and Fe^{3+} . Similar features have been observed in natural meteorite fusion crusts and in micrometeorites, implying that, at least in terms of maximum temperature reached and chemical reactions, the experiments have successfully reproduced the conditions likely encountered by extraterrestrial material following atmospheric entry.

1. Introduction

Atmospheric entry of asteroidal and cometary material likely implies melting, evaporation, loss of mass, physical separation of metalrich phases, and redox variations. All these processes may affect microstructures of, and induce chemical changes, in the recovered meteorites and micrometeorites. Ablation is an important factor, but if the meteoroid is large enough a portion survives and falls on the Earth surface, covered by a quenched melt film called fusion crust (e.g., Genge and Grady, 1999a). Similar processes might also affect microscopic dust particles (10–2000 μ m) that enter the Earth's upper atmosphere and are recovered on Earth as micrometeorites (e.g., Genge et al., 2008; Rubin and Grossman, 2010), as locally similar features are observed, for example in the form of a melt film coating the surface

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(e.g., Toppani and Libourel, 2003; Genge, 2006). The degree of melting and therefore the preservation potential of internal features mainly depend on the physico-chemical parameters of the extraterrestrial material (i.e., size, density, composition) and on the entry conditions (i.e., velocity, angle; e.g., Love and Brownlee, 1991). Based on the degree of melting experienced during atmospheric passage by micrometeoroids, the distinction is generally made between fully melted micrometeorites (or cosmic spherules), partially melted micrometeorites (or scoriaceous MMs), and unmelted or angular micrometeorites (e.g., Maurette et al., 1994; Taylor et al., 1998; Genge et al., 2008). Thus, to some degree, analogies may exist between the processes that lead to the formation of cosmic spherules and those that generate meteorite fusion crusts.

Physical effects of atmospheric entry have been investigated both by numerical modeling (e.g., Love and Brownlee, 1991; Dias et al., 2016) and experimentally, in the form of static heating (e.g., Greshake et al., 1998; Toppani et al., 2001), impact ballistics (Thomas and White, 1953; Zotikov, 1959), plasma flow (Shepard et al., 1966; Loehle et al., 2017; Agrawal et al., 2018; Pratesi et al., 2018), and laser (Milley et al., 2007; Stern 2015, personal communication) set-ups. A review of the historical experiments is presented in Helber et al. (2019). In the past, experimental conditions were generally quite different from those experienced by planetary material during atmospheric entry in terms of temperature, duration, and employed materials, and so far, only rarely glass could be recovered after the experiments.

In this work, petrographic and geochemical characterization of the quenched melt formed during experiments in the high-enthalpy Plasmatron facility at the von Karman Institute for Fluid Dynamics (VKI) in Sint-Genesius-Rode, Belgium, is presented. As starting material, a terrestrial basalt and an ordinary chondrite (H5) meteorite were used. The resulting glass was then compared with natural meteorite fusion crusts and micrometeorites, in an attempt to advance our understanding of the thermal and chemical processes occurring during and following atmospheric entry.

2. Experimental setup, sample description, and analytical methods

The VKI Plasmatron, an induction heated plasma wind-tunnel commonly used to test spacecraft heat shields, can produce a steadystate air plasma flow of over 10,000 K temperature, and a maximum heat flux of 16 MW/m². The high velocity typical for atmospheric entry is transformed into high thermal energy by a strong shock wave compressesing the air in the front of the entering object, rising the temperature in the boundary layer to above 10,000 K. For this reason, the high velocity typical during atmospheric entry transforms into high total enthalpy. A subsonic ground-test facility, such as the VKI Plasmatron, is thus able to replicate the atmospheric entry flight conditions in a subsonic environment through the so-called Local Heat Transfer Simulation methodology, developed by Kolesnikov (1993). Experiments were performed in the spring of 2016 under the conditions listed in Table 1, using air as source for the plasma flow. Cylindrical samples of diameter 16 mm were cored from raw experimental materials. Before injection into the hot plasma flow, the sample was held in a protective, water-cooled metallic housing, maintaining a temperature

range between room temperature and 70 °C. During the experiments, the material has been exposed to a cold wall heat flux of 3 MW/m^2 at 15 hPa as well as 1 MW/m^2 at 200 hPa (Table 1), corresponding to enthalpies of approximately 54 and 24 MJ/kg and flow velocities of approximately 687 and 26 m/s, respectively. These conditions reproduce the flight of an object ca. 4 m in diameter, entering with a velocity of ca. 6.5 km/s at an altitude of ca. 55 km. During the experiments, the surface temperature, the temperature of the sample in contact with the holder, and vapor ablation products at the very contact between plasma and sample were directly measured and subsequentely modeled. Further detailed information on the analytical setup is provided in Helber et al. (2019).

The specimen was placed in a hemispheric holder made of cork or graphite for different sets of experiments (Table 1). The test sample, initially at room temperature and positioned on a water-cooled holding arm, was hydraulically inserted into the plasma flow when the experimental conditions, continuously monitored, had reached the desired state. For the first set of experiments, an alkali-rich basalt was used, in order (i) to enable the possibility of investigating evaporation phenomena of the volatile alkali metals, (ii) to act as a general analog for some basaltic achondrite meteorites and micrometeorites, and (iii), to serve as a reproducible testing material before subjecting a chondrite meteorite to full test conditions. The selected sample consists of alkalirich basalt collected in the locality of Château de Pourcheyrolles (France), where columnar basalt occurs from the strombolian volcanic sequence of the Montpezat-sous-Bauzon, Ardèche, active between 65 Ma and 7 ka. This basalt is particularly homogeneous on the scale of a hand sample and consists of clinopyroxene phenocrysts embedded in a feldspathic groundmass, with flow fabric marked by clinopyroxene and ilmenite crystal alignment (Fig. 1a). No sulfides or sulfates were observed. According to our analyses, this alkali-rich basalt can technically be referred to as a tephry-phonolite, according to the classification by Le Bas et al. (1992). Bulk compositional data are provided in the supplemental material. Different experimental conditions were tested on the basalt, to constrain the behavior of the sample, before testing a drilled fragment of ordinary chondrite El Hammami (H5), purchased for this purpose. Ordinary chondrites represent the vast majority of all meteorites recovered on Earth (e.g., Hutchison, 2004; Grady et al., 2014). Among ordinary chondrites, type H represents a relatively reduced chemical composition and, therefore, is suitable to highlight possible redox processes induced by interaction between the melt and the atmospheric oxygen. The selected fragment contains a few relic chondrules, largely recrystallized, coarse-grained olivine (Fa_{18.8}), pyroxene (Fs_{16.7}Wo_{1.4}), and rare small plagioclase crystals and metal (Grossman, 1998).

The material recovered from experiments B1.1 (basalt in cork sample holder) and B1.2 (basalt in graphite sample holder; Table 1) was analyzed using a M4 Bruker Tornado μ -XRF at the Vrije Universiteit Brussel (VUB), Brussels, Belgium, for element mapping and semiquantitative chemical analysis, with a Rh X-ray tube and spot size of 25 μ m. Preliminary observations and rough chemical characterization were also performed with a JEOL JSM IT-300 scanning electron microscope (SEM), equipped with an EDS detector, at the VUB. Electron microprobe analysis (EMPA) was performed with a JEOL JXA 8530-F instrument at the Natural History Museum of Vienna, Austria, equipped

Table 1	
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Experimental conditions for the runs considered in this work.

Experiment name	Material	Sample holder	Heat flux (MW/m ²)	Heat flux probe	Pressure (hPa)	Duration (s)
B1.1	Basalt	Cork	3.04	Hemispherical	15	41
B1.2	Basalt	Graphite	3.12	Hemispherical	15	21
B2.1	Basalt	Cork	1.01 (1.2) ^a	Flat (hemispherical)	200	12
OC2.1	Ordinary chondrite	Cork	1.01 (1.2) ^a	Flat (hemispherical)	200	21

^a Calculated by applying a similarity rule for the heat flux.



Fig. 1. Basalt before and after the melting experiments. a) BSE-SEM image of the pristine basalt, showing flow fabric marked by aligned clinopyroxene and ilmenite crystals (mineral abbreviations according to Whitney and Evans, 2010). b) Microphotographs of an ejected fragment of basalt coated with vesiculated melt. Reflected light, optical image. Experiment B2.1. c) SE-SEM image of the melt coating the edge of a basalt fragment. Experiment B2.1. d) Detail of (c), showing splattered melt on the surface of the basalt. SE-SEM image of the transition between the preserved portion of the basalt and the melt. Experiment B2.1. f) SE-SEM image of the spherical objects. Experiment B2.1. g) Detail of a spherical object. SE-SEM image. h) Trails of metallic Fe-Si alloys crystallizing at the contact with the sample holder in graphite and globular magnetite. BSE-SEM image. Experiment B1.2. i) Microlites, likely of plagioclase, growing over a clast of ilmenite in the melt. BSE-SEM image. Experiment B1.2.

with five wavelength-dispersive spectrometers (WDS) and one EDS, on polished chips prepared from the material recovered from experiments B1.2, B2.1, and OC2.1 (Table 1). Operative conditions were 15 kV acceleration voltage, 12 nA beam current, and with a fully focused beam. For glassy material, a defocused beam with a spot size of 10 µm was used. For quantification, a ZAF correction was applied and the content was calculated in oxides, except for the metal in the ordinary chondrite. Detection limits for major elements are listed in Table S1 in the Supplemental Material. The composition of olivine ([Mg,Fe]₂SiO₄) is expressed as fayalite Fe₂SiO₄ (Fa) mol% (Mg/(Mg + Fe)*100). The mineral abbreviations Ol for olivine and Fa for favalite, as well as Mag for magnetite and other abbreviations, are used according to Whitney and Evans (2010). Major and trace element concentrations were additionally determined using a Teledyne Cetac Technologies Analyte G2 ArF* excimer-based laser ablation system coupled to a Thermo Scientific Element XR double-focusing sector field ICP-mass spectrometer (LA-ICP-MS) at the Department of Chemistry of Ghent University, Belgium, following the procedures described in Das Gupta et al. (2017).

The oxidation state of Fe in the basalt before and after the experiments B1.1 and B1.2, as indication of the redox conditions, was determined using Fe K-edge X-ray Absorption Near Edge Structure (XANES) spectroscopy. X-ray absorption spectroscopy (XAS) spectra were collected at the LISA beamline BM08 (d'Acapito et al., 2019) at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). All samples were measured in fluorescence mode by means of a 12element solid state (high-purity Germanium) detector. The monochromator was equipped with a pair of Si [111] flat crystals; higher order harmonics were rejected by using Si-coated focusing mirrors ($E_{cutoff} \approx 15 \text{ keV}$); beam size on the sample was approximately $200 \times 200 \,\mu\text{m}^2$. The basalt was analyzed as a powder mixed with cellulose and pressed into a pellet, with an amount of material such as to keep the maximum total absorption (µ) below 1.5. From the material after experiment B1.2, XAS data were collected on molten droplets embedded in a resin pellet and then polished. Material recovered after experiment B2.1, due to the low amount of quenched melt available, required manual glass separation, and only after ascertaining the absence of crystalline phases was prepared as powder sputtered onto a kapton tape. XAS spectra were collected along the Fe K-edge from 200 eV below the edge up to 650 eV after the edge, with variable energy step (0.10 eV across the pre-edge and 0.3 eV on the edge regions). The

software ATHENA (Ravel and Newville, 2005) was used to average multiple spectra. Standard procedures (Lee et al., 1981) were followed for pre-edge background removal, spline modeling of bare atomic background, edge step normalization using a far above the edge region, and energy calibration. Pre-edge peak data analysis was done according to the method described in Wilke et al. (2001) and Giuli et al. (2002 and 2011).

3. Results

In all experiments, the plasma flow temperature was estimated to be roughly between 5000 and 9000 K (Helber et al., 2019). The temperature on the surface of the sample, measured and modeled, reached an asymptotic value in the range of 2280-2360 K, regardless of the nature of the material and of the sample holder (Helber et al., 2019). All samples started at room temperature and cooled slightly during pumping down of the test chamber to reach the required vacuum. The temperature gradient throughout the sample material strongly depended on the sample holder material (graphite or cork). In the case of graphite, which is a good thermal conductor, the temperature at the back of the sample rapidly increased by 640 K compared to the initial temperature. In the case of cork, which in contrast to graphite is a good thermal insulator, the temperature at the back of the sample almost did not vary during the experiments, with limited temperature rise differences between only 3 K and 100 K. Nevertheless, all samples exhibited melting, boiling and evaporation during the experiments. Detailed information is provided for the individual experiments.

3.1. Petrographic and geochemical observations in experiments with basalt

The response of the basalt strongly depended on the nature of the sample holder. In the case of cork, the basalt experienced intense fracturing and ejection of material, due to the insulation properties of cork, causing a strong thermal gradient within the sample between the exposed surface and the cold interior. Here, it should be noted that fracturing has been also observed after drying the sample by exposure to 100 °C overnight. In the case of graphite, low-viscosity melt dropped away on the surface of the sample holder and melting also occurred along the sides of the sample, triggered by the high thermal conductivity of graphite. A few mm of sample were lost at the front of the plasma flow by vaporization and removal of melt during the experiments. Upon quenching, the melt appears as a thin ($< 500 \,\mu$ m) film of glass coating the preserved basalt, also in ejected fragments from experiment B1.1 (Fig. 1b, c), locally splattered on the surface of the basalt (Fig. 1c, d), as droplets of blackish glass after experiment B1.2. The transition between the preserved portion of basalt and the glass is marked by abundant vesiculation, with vesicles of various size (50 µm-1 mm) (Fig. 1e). Spherical objects, 200-500 µm in size, have formed at the front of the glass film (Fig. 1f, g). In the experiment B1.2, Fe-Si metal alloys crystallized at the contact between the melt and the graphite (Fig. 1h). These alloys have a calculated mineral formula of Fe_{2.5}Si, which is in between that of hapkeite (Fe₂Si) and gupeiite (Fe₃Si), both of extraterrestrial origin and observed in lunar soils and likely in metallic cosmic spherules, respectively. Hapkeite has been suggested to form by condensation of impact vaporized phases (Anand et al., 2003). In BSE-SEM images, local schlieren and domains with different BSE contrast in BSE-SEM images can be observed (Fig. 1h). Locally, evidence of devitrification and incipient crystallization, with skeletal growth of unidentified phases over relic nuclei, is present (Fig. 1i).

Chemically, the glass formed from the basalt shows overall depletion in volatile alkali metals (40–60% of the original content for Na, 50% for K) and highly volatile elements, with apparent enrichment in more refractory elements (Mg and Ca contents are doubled; Fig. 2a, Tables S2–3). In detail, the difference between the bright and dark glass *schlieren* in BSE images is limited to a more marked enrichment in Ti,



Fig. 2. Chemical differences of the melt with respect to the original basalt. a) Major element content, plotting the elements according to the 50% condensation temperature (after Lodders, 2003). b) REE and Y contents in the basalt before the experiment and in the melt, averaged between experiment B1.2 and B2.1, normalized to CI chondritic abundances (McDonough and Sun, 1995).

Fe, and Mn in the bright domains than in those with darker appearance. The enrichment in Ti, Ca, Mg, Fe, and Mn with a factor 2 or more in the glass is common, regardless of the sample holder. Additionally, in experiment B1.2, a considerable enrichment in Ni (20 times higher than the preserved basalt) and Cr in the glass is observed. Spectroscopic analysis during the experiments indicates that Na, K, Mg, Ca, Fe, and Ti are volatilized, but the relative abundance could not be unambiguously determined, because both the cork and the graphite produced a strong K and Na emission in addition to those from the samples (Helber et al., 2019). Relative to the pristine basalt before the experiments, the glass is enriched in rare earth elements (REE) and Y (Fig. 2b) and in moderately siderophile elements, such as Co, Ni, and Cu (Table S5). Among the spherical objects, two populations can be distinguished based on their size. While the observed larger objects (Fig. 1f, g) have a clear, relatively "feldspathic" composition (Table S2), the composition of smaller objects was difficult to be determined, due to contamination from the surrounding unmelted basalt. According to the pre-edge peak analysis of XAS data (reported in Fig. 3), the glass in both experiments B1.2 and B2.1 (0.17 \pm 0.05 and 0.11 \pm 0.05, respectively) exhibits a lower Fe^{3+}/Fe_{tot} ratio than that in the original basalt (0.75 \pm 0.15).

3.2. Petrographic and geochemical observations in the experiment with the ordinary chondrite

The meteorite sample experienced only melting and limited evaporation during the experiment. No material was ejected or escaped from the sample holder. The resulting glass displays large vesicles and coats the exposed surface of the sample (Fig. 4a). There is no sharp transition between the unaffected interior of the meteorite sample and the molten and quenched portion and the glass is largely crystallized.

Olivine crystals in contact with the glass exhibit cracks filled by



Fig. 3. Fe K-edge XANES spectra of the starting basalt (black line) and the glass produced by melting with a cork sample holder (continuous grey line) and with a graphite sample holder (dotted grey line). The edge energy of the glass samples has lower values than that of the basalt, due to a lower Fe oxidation state.

glassy melt, trails of metal-rich inclusions, and an overgrown rim with a higher Mg/Fe ratio than that of the host olivine (relative average Mg# from 81 to 85; Fig. 4b, Table S4). The glass resulting from the experiment is dominated by olivine showing a variety of morphologies, including tabular, skeletal, and hopper crystal shapes (Fig. 4c-e), consistent with the olivine morphology description from quenched melt in Faure et al. (2003). Relic olivine clasts exhibit evidence of incipient melting and overgrowth of sub-euhedral rims (Fig. 4c). Such rims represent inverse zoning with respect to the host olivine, as their composition at the contact with the host olivine is more enriched in Mg than that in the preserved nucleus. The rim composition eventually evolves into normal zoning, showing a progressive change of the Mg/Fe ratio towards more Fe-rich compositions at the contact with the glassy groundmass (Mg# from 85 to 75 on average; Fig. 4b-d; Table S4). In the groundmass, skeletal magnetite has crystallized (Fig. 4e). In the interior of the meteorite, kamacite and taenite appear in coarse-grained exsolution bands. In the quenched melt, only botryoidal kamacite, with higher Ni content than in the interior of the meteorite (from ca. 6 wt% to 12 wt% on average), occurs, set within a troilite groundmass (Fig. 4f). Locally, fine-grained, skeletal crystals of chromite occur (Fig. 4g). Fig. 4h and 4i show the corresponding features in natural fusion crusts of H-chondrites.

The quenched melt from the experiment with ordinary chondrite, considered as bulk, (including the crystals) is overall slightly enriched in Ti, Fe, and Cr, with moderate siderophile element variations, and slight depletion in volatile elements, such as K and Na, which were present in low amounts in the pristine material, as semi-quantitatively evaluated, considering the high analytical uncertainties due to the coarse grained nature of the crystalline phases (Tables S4–6). The REE and Y contents in the glass are depleted with respect to the original

chondrite, contrasting the observations made for the experiments involving basalt (Fig. 5a). The concentrations of the moderately siderophile elements (Co, Ni, Cu) are highly variable and difficult to interpret, likely due to the large internal variability in the ordinary chondrite data (Table S5) and to the limited laser beam diameter during LA analysis (50 μ m) in comparison to the coarse grain crystal size in the ordinary chondrite (e.g., Fig. 4).

Olivine that crystallizes from the melt can be subdivided into two populations on the basis of the MgO content with respect to the olivine in the interior of the meteorite (Fig. 5b). However, both populations exhibit similar enrichment in refractory elements, such as (Al, Cr, Ni, Ca, but not Ti) with apparent depletion in the moderately volatile elements and Mn. In particular, newly crystallized olivine seems to contain "impurities", such as Cr, Ni, and Ca, even though this might be apparent and due to analytical limitations. In fact, the apparent enrichment in Na and Al is likely related to local contamination from the groundmass, due to the size of the analyzed material (olivine rims have a thickness of a few μ m; Fig. 4) with respect to the interaction volume of the electron microprobe beam (also on the order of some μ m; Table S4).

4. Discussion

4.1. Melting, evaporation, and condensation

In all experiments, regardless of the nature of the material and of the sample holder, the resulting glass composition clearly shows minor enrichment in some moderately refractory elements (e.g., Ti and Ca) and relative depletion in highly volatile elements (such as K and Na). The evaporation of highly volatile alkali metals is particularly obvious in the case of the basalt, as the selected basalt has significantly higher concentrations of Na₂O (6.7 wt%) and K₂O (5.8 wt%; Table S2) relative to the H chondrite (Na₂O of 1.6 wt% and K₂O of 0.15 wt%; Table S6). The formation of vesicles in both the basaltic and chondritic glasses is obviously related to the vaporization of such highly volatile elements (50% condensation temperature T_c of 958 K and 1006 K for Na and K, respectively; Lodders, 2003) with a possible contribution from elements such as Fe (50% T_c of 1334 K; Lodders, 2003). The latter element was detected by spectroscopic analyses and is observed as Fe-oxide condensates along the rim of the vesicles. Vesiculation is commonly observed in natural meteorite fusion crusts (e.g., Genge and Grady, 1999a; Pittarello et al., 2019), but also in micrometeorites (e.g., Genge, 2016b; Suttle et al., 2019), where a high content of volatiles in the original precursor material has been invoked to explain vesicle formation. In the case of the basalt, a high abundance of volatiles, such as water and halogens, is likely present. However, this is not the case for the ordinary chondrite, which in contrast to carbonaceous chondrites is relatively dry (e.g., Brearley, 2006). The quenched melt in the experiments does not display any lateral variation reflecting melting of local phases but is rather homogeneous. This observation is consistent with what observed in natural fusion crusts of H5 chondrites (Pittarello et al., 2019) and in contrast with previous works (e.g., Genge and Grady, 1999a; Thaisen and Taylor, 2009). However, in the case of the experiments, the small sample size and the geometry of the experiments favor mixing and homogenization. In natural fusion crusts, homogenization may be additionally aided by the spinning of the meteorite during flight.

The origin of the spherical objects found at the interface of the glass formed from the basalt remains unclear. In some cases, chemical compositions rich in alkali metals and silica might suggest possible condensation of vaporized phases. No spherical objects were observed in the glass obtained from the ordinary chondrite. In natural fusion crust, a possible ablation spherule, with a composition close to that of the bulk chondrite, was observed (Pittarello et al., 2019). This suggests that the observed spherical objects on the surface of the basaltic glass formed by a different mechanism than meteorite ablation spherules.

Moderately siderophile elements, such as Co, Ni, and Cu are enriched in the glass formed in all the experiments. Partitioning of such



Fig. 4. Melt formed in the experiment OC2.1, from a fragment of the H5 ordinary chondrite El Hammani, and comparison with natural meteorite fusion crust. a) Microphotograph of the thin chip used for analysis, showing the interior of the meteorite and the vesiculated melt. Reflected light, optical image. b) BSE-SEM image of the transition zone between the unaffected interior of the meteorite and the melt, showing olivine crosscut by cracks and by trails of opaque phases and with a darker rim towards an apparently homogeneous melt. c) BSE-SEM image of olivine relic clast exhibiting overgrowth from the melt with initial crystallization of Mgrich olivine, followed by crystallization of progressively more Fe-rich olivine. Note the fine grained skeletal phases crystallized in the melt. d) BSE-SEM image of hopper and skeletal olivine crystallizing from the melt. e) BSE-SEM image of but groundmass between new crystals of olivine, with skeletal magnetite and likely olivine. f) BSE-SEM image of a metal bleb in the melt consisting of botryoidal kamacite in a troilite matrix. g) BSE-SEM image of a chromite crystal in a groundmass consisting of likely skeletal olivine, troilite blebs, and glass. h) BSE-SEM image of zoning in olivine class and crystals in the Antarctic meteorite Asuka 09502, classified as H5 (Pittarello et al., 2019). Note the similarity with (c).

elements between melt and silicates may be controlled by the oxygen fugacity (Gaetani and Grove, 1997). In this case, the partitioning would be between vapor and melt. The enrichment in moderately siderophile elements shown in the glass is likely the result of the evaporation of the more volatile elements. However, despite the relatively large uncertainties associated with these analyses, simple mass balance calculations suggest passive enrichment not to be the sole cause for the observed concentration ranges.

4.2. Redox processes

For the selected basalt, Log $f(O_2)$ was estimated with the software MAGMA (Schaefer and Fegley, 2004), yielding -4 at 2200 K, which is close to the temperature reached during the experiments. Oxygen partial pressure in the gas during the experiment can be calculated. Such estimates suggest high f(O), such as Log f(O) - 1.25 and Log $f(O_2) - 4.86$ on the assumption of finite rate chemistry at boundary, and Log $f(O_2) - 1.41$ assuming chemical equilibrium, which represents a

relatively oxidizing environment during the experiments. This is valid if we ignore the potential reducing effect induced by the presence of graphite and the organic matter in the sample holder, although the geometry of the experiment ensures that any interaction between the melt and the sample holder is generally avoided, except at the very contact between the two. This local effect is negligible in the scope of the overall redox reactions. The $\mathrm{Fe}^{3\,+}/\mathrm{Fe}_{\mathrm{tot}}$ ratios observed in the exwith $(Fe^{3+}/$ periment B1.2 graphite sample holder $Fe_{tot} = 0.17 \pm 0.05$) and in experiment B2.1 with cork sample holder $(Fe^{3\,+}/Fe_{tot}=0.11\,\pm\,0.05)$ are very close to those calculated according to the Kress and Carmichael (1991) model using the glass composition, the estimated T and oxygen fugacity conditions of the experiment. This correspondence suggests that the melt was in equilibrium (or close to equilibrium) with the surrounding atmosphere. Despite the short duration of the experiments, it is not surprising that equilibrium can be achieved for the Fe redox reaction, because at extremely high temperature, as recorded during the experiments, Fe redox kinetics are extremely fast. In an experiment, where basalt was molten



Fig. 5. Chemical properties of the melt formed in the experiment OC2.1. a) REE and Y contents in the interior of the meteorite (OC) and in the melt, normalized to CI chondritic abundances (McDonough and Sun, 1995). b) Olivine composition in the melt compared to that in the interior of the meteorite. Oxides ordered according to the 50% condensation temperature (Lodders, 2003).

at ca. 1770 K, equilibrium was reached after 66 s (Cicconi et al., 2015). The experimental data indicate that at such high temperature the produced melt can quickly equilibrate with the surrounding medium and, for the conditions used here, produce a melt where Fe^{2+} and Fe^{3+} coexist (in our case with the Fe^{3+}/Fe_{tot} ratio ranging between 0.11 and 0.17). These data are compatible with the formation of magnetite in the produced chondrite melt, where the oxygen fugacity in H chondrites has been calculated to be ca. Log $f(O_2) - 20$ at 800 °C (Rubin et al., 1988). It must be noted that, as soon as the melt achieves equilibrium, the resulting Fe^{3+}/Fe_{tot} ratio would be the same, regardless of the oxidation of the starting material.

Experiments with sample holders of different materials, namely graphite and cork, were performed to control the possible influence of sample holders on the resulting glass. While graphite is a good heat conductor, cork is a good insulator. Chemically, both contain carbon, a potentially reducing agent, but because of their individual thermal response, carbon is released under different conditions. The thermal properties of the two materials affected the temperature rise of the samples at the exposed surfaces (Table 1), as the basalt embedded in graphite reached boiling temperatures much earlier than that inserted in cork. At a local scale, at the direct contact between the quenched melt and the graphite, metal droplets (Fe-Si alloys) crystallized (Fig. 1h), suggesting that the interaction between the still hot melt and graphite induced chemical reduction of the melt. However, considering the geometry of the experimental set up, the glass not in direct contact with the graphite holder should not have been chemically affected by the sample holder.

The redox process is more complex in the case of the ordinary chondrite, which was originally relatively reduced (e.g., Rubin et al., 1988), and contains metallic Fe and Ni. Nevertheless, considering olivine crystallization as a proxy for the redox process occurring in the melt, an initial reduction is indicated by the occurrence of olivine compositions at the direct contact with relict olivine crystals with higher Mg/Fe ratios than those of olivine crystals in the interior of the meteorite. However, this observation might reflect the melt

temperature, as Mg-rich terms have higher crystallization temperature than the Fe-rich terms. Nevertheless, in experiment OC2.1, oxidation is the dominant process, as suggested by the crystallization of magnetite in the groundmass, the absence of taenite in the melt, and the growth of Fe-rich olivine at the outer rim of relict olivine fragments in the melt or as dendrites (Fig. 4). Even though no significant variations in the amount of magnetite have been observed in this experiment, previous works have related the abundance of magnetite in the groundmass to the extension of oxidation, suggesting that oxidation shows a gradient from the interior of the meteorite to the fusion crust (e.g., Genge and Grady, 1999a, 1999b). Additionally, we have identified $< 5 \, \text{um}$ skeletal chromite grains in the quenched melt of our ordinary chondrite sample. Chromite is essentially absent in low grade type-3 ordinary chondrites. but grew during metamorphism in the ordinary chondrite parent body/ ies and is present as relatively large (\sim 50–100 µm) anhedral grains in higher grade specimens such as our test sample (Ramdohr, 1967; Huss et al., 1981; Rubin, 2003; Wlotzka, 2005). Although it is possible that the grains we have found may represent surviving relics, their small size and skeletal structure seem to imply fast crystallization from the experimentally produced melt (albeit possibly over relict chromite nuclei). Such chromite grains may indicate further oxidation of Cr²⁺ originally hosted in silicate minerals to Cr³⁺ and the stabilization of chromite in the newly formed melt.

In conclusion, our observations that (i) the basaltic glass is relatively "reduced" with respect to the highly oxidized pristine basalt and that (ii) magnetite and Fe-rich olivine rims occur in the chondritic glass, indicating oxidation of the originally relatively reduced ordinary chondrite. This all points to an equilibrium redox condition proper of the experimental setup. This equilibrium condition is rapidly reached at high temperature, within the duration of the experiment. The characteristic oxidation state of the experimental setup is intermediate between that of the basalt and that of the chondrite. Disregarding the original oxidation state of the material, the equilibrium depends on temperature, composition and oxygen fugacity, and it is reached by varying of the relative amounts of Fe⁰ (in the chondrite), Fe²⁺, and Fe³⁺.

4.3. Comparison with meteorite fusion crust, ablation spherules, and melted micrometeorites

The experiment OC2.1 aimed to reproduce meteorite fusion crust by simulating atmospheric entry of a fragment of ordinary chondrite. The quenched melt produced in the experiment presents the same features observed in natural meteorite fusion crusts from chondrites (for a detailed description, see Genge and Grady, 1999a; and Pittarello et al., 2019), such as extensive crystallization of olivine, the presence of magnetite in the groundmass, and the peculiar zoning in the overgrown olivine (Fig. 3). The extensive crystallization of the melt after experiment OC2.1 was not expected, considering the contrasting conditions with respect to the natural atmospheric entry, such as the duration of the experiment (seconds vs. minutes) and the size of the sample (14 mm in diameter of exposed surface). However, the cooling rate seems to have been similar to that experienced by meteoroids, allowing crystallization of olivine. Thus, based on a comparison of the resulting material with the natural samples, the experiment successfully reproduced the (chemical) conditions encountered by asteroidal material when entering Earth's atmosphere.

Micrometeoroids experience partial (similarly to regular meteoroids) to complete melting (i.e., cosmic spherules), involving evaporation of (moderately) volatile components, oxidation of Fe-Ni alloys to Fe oxides (such as magnetite or wüstite, whose presence has been used to determine the oxygen fugacity), reduction of Fe and formation of immiscible metal beads when the precursor material is particularly enriched in carbon, and loss of siderophile and potentially chalcophile elements as a result of Fe-Ni metal and sulfide beads mechanical ejection or spinel group mineral expulsion (e.g., Taylor et al., 2005; Cordier et al., 2011; Genge, 2016a). Evaporation in cosmic spherules can reach up to 60%–90% in the Ca-Al-Ti-rich (therefore, more refractory) terms, depending on the original composition (Herzog et al., 1999; Alexander et al., 2002; Engrand et al., 2005; Taylor et al., 2005; Cordier et al., 2011); however, condensation products have never been identified in micrometeorites. More recent studies have highlighted that the presence of volatile elements in micrometeorites might be responsible for the fracturing and heating of particles during atmospheric entry, favoring interaction with atmospheric gases (e.g., Suttle et al., 2019).

The most important process controlling the melt evolution during the atmospheric entry is the oxidation of Fe. This mostly implies the formation of magnetite crystals and, locally, the formation of new, relatively FeO-rich olivine, generally overgrowing pre-existing olivine crystal nuclei (Genge et al., 1997; Genge and Grady, 1999a, 1999b; van Ginneken et al., 2017), similarly to what is observed in meteorite fusion crust and in the experiment OC2.1. However, reduction processes may play an important role during the atmospheric entry of micrometeoroids when the precursor material is particularly rich in carbon (e.g., Genge and Grady, 1999a). This leads to the formation of carbon and metal-rich liquids that are immiscible with the surrounding silicate melt and tend to be ejected from the host material (i.e., pyrolysis; Genge and Grady, 1998).

The maximum temperature achieved during atmospheric entry of micrometeoroids might have been different from that reached in the experiments (ca. 2200 K in the experiments vs. likely 900–2000 K for micrometeoroids; e.g., Love and Brownlee, 1991; Taylor et al., 2000), as well as the oxygen fugacity related to the altitude, where melting generally occurs for the specific material. Micrometeorites experience peak heating at much higher altitudes in the atmosphere, where the partial pressure of oxygen is significantly lower, than regular meteoroids (e.g., Genge, 2016a; Genge et al., 2017). This implies that a direct comparison between the results of the experiments presented here and the features contained in micrometeorites might not be completely appropriate. Further experiments, using several precursor materials (including carbonaceous and iron meteorites), are planned in the attempt to reproduce the variety of textural, chemical and isotopic features observed in micrometeorites.

5. Conclusions

The quenched melt recovered from a series of melting experiments in a plasma facility, involving both basaltic and ordinary chondritic starting materials, provides constraints on the thermal and chemical processes that affect extraterrestrial material during atmospheric entry. Chemically, the composition of the resulting glass is depleted in highly volatile alkali metals and slightly enriched in moderately siderophile elements. In the experiments involving the alkali basalt, spherules derived from the condensation of the volatilized elements were observed. In terms of redox reaction, the selected experimental conditions affect the redox state of the samples. Regardless of the initial conditions of the starting material, equilibrium between the sample and the surrounding medium is rapidly reached. For this reason, the terrestrial basalt (with a starting Fe³⁺/Fe_{tot} ratio of 0.75) has been reduced to a Fe³⁺/Fe_{tot} ratio of 0.11–0.17 \pm 0.05, within the stability field of olivine + magnetite. In contrast, the chondrite is oxidized, as suggested by the crystallization of magnetite, which indicates the presence of Fe³⁺. However, the path to reach this equilibrium might have not been linear, with possible reduction during the initial stages of melting in the ordinary chondrite. In general, the microstructures observed in the material recovered after experiment OC2.1, with an H5 ordinary chondrite, compare well to whose present in melted micrometeorites and in natural meteorite fusion crusts from the same type of chondrite. As the experiments have demonstrated to have successfully reproduced the features observed in natural samples, we can consider that these experiments have closely approximated the thermal and redox conditions likely encountered by meteoroids during atmospheric entry.

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Appendix A. Supplementary data

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Analysis of meteoroid ablation based on plasma wind-tunnel experiments, surface characterization, and numerical simulations

by Helber et al. (2019). Astrophys. J. 876, 14 pp.

This article is a companion paper of 'Meteoroid atmospheric entry investigated with plasma flow experiments: Petrography and geochemistry of the recovered material' by Pittarello et al. (2019), and discusses the same experimental setup from a physical and mathematical (i.e., modelling) perspective.

BS has assisted Bernd Helber with the sample acquisition and preparation.

CrossMark

Analysis of Meteoroid Ablation Based on Plasma Wind-tunnel Experiments, Surface Characterization, and Numerical Simulations

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Abstract

Meteoroids largely disintegrate during their entry into the atmosphere, contributing significantly to the input of cosmic material to Earth. Yet, their atmospheric entry is not well understood. Experimental studies on meteoroid material degradation in high-enthalpy facilities are scarce and when the material is recovered after testing, it rarely provides sufficient quantitative data for the validation of simulation tools. In this work, we investigate the thermo-chemical degradation mechanism of a meteorite in a high-enthalpy ground facility able to reproduce atmospheric entry conditions. A testing methodology involving measurement techniques previously used for the characterization of thermal protection systems for spacecraft is adapted for the investigation of ablation of alkali basalt (employed here as meteorite analog) and ordinary chondrite samples. Both materials are exposed to a cold-wall stagnation point heat flux of 1.2 MW m⁻². Numerous local pockets that formed on the surface of the samples by the emergence of gas bubbles reveal the frothing phenomenon characteristic of material degradation. Time-resolved optical emission spectroscopy data of ablated species allow us to identify the main radiating atoms and ions of potassium, calcium, magnesium, and iron. Surface temperature measurements provide maximum values of 2280 K for the basalt and 2360 K for the chondrite samples. We also develop a material response model by solving the heat conduction equation and accounting for evaporation and oxidation reaction processes in a 1D Cartesian domain. The simulation results are in good agreement with the data collected during the experiments, highlighting the importance of iron oxidation to the material degradation.

Key words: meteorites, meteoroids - plasmas - techniques: spectroscopic

1. Introduction

Meteoroids provide our primary source of extraterrestrial materials from the various nebular and planetary environments of the solar system and beyond. These naturally delivered samples, bringing in 50–100 tons of material every day (Flynn 2002), undergo melting and evaporation during their entry into the Earth's atmosphere. This results in variable levels of modification that need to be distinguished from pre-entry features in order to understand processes occurring during transport in open space, residence in or on their parent body, and ultimately their original formation during the earliest history of the solar system.

Among the daily material delivered to our planet, the Chelyabinsk event in 2013 (Brown et al. 2013) renewed awareness of potential hazards, motivating the planning of deflection and mitigation strategies of incoming asteroids (Prabhu et al. 2015). These strategies rely on knowledge of the physical properties of the material and structure of the incoming object. Space agencies launched sample–return missions to asteroids such as Hayabusa II (Vilas 2008), and to comets such as 67P/Churyumov–Gerasimenko (Taylor et al. 2017) to collect data relevant to their formation and

composition. The complexity and operational costs of these missions motivated scientists to study the meteor phenomenon as a bridge between meteorites and their parent bodies.

Our knowledge of this phenomenon mainly relies on geochemical characterization of the samples that survived entry and were collected on the ground, or on visual observations, such as radar and radio detection (Martínez Picar et al. 2016). The interpretation of these data derives from models that correlate the plasma signature to a signal from which the size, velocity, and composition of the body are inferred. On the other hand, chemical inspection of meteorites provides information only about the final outcome of the trajectory without the possibility to understand which conditions these features are related to. Ground experiments provide an opportunity to look at the meteor phenomenon in detail, with the possibility of focusing on the gas-surface interaction for well-defined flight conditions and material properties, which remain poorly understood. The goal of this work is to contribute to a better understanding of the gas-surface interaction processes during a meteoroid entry with new plasma wind-tunnel experimental data, surface characterization, and numerical simulations, leading to the development of thermo-chemical ablation models.

Validation of models through ground experiments is part of the margin analysis for thermal protection systems (TPSs), which protect the astronauts and payload from severe heat loads to the spacecraft during its re-entry. Although different in nature (e.g., the silicate melt can be removed from the body due to

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aerodynamic forces), meteoroids present many similarities with TPSs and they can be studied taking advantage of the well established techniques in the field of heat shield characterization.

The first wave of ground experiments for meteor studies dates back to the middle of the 20th century. Thomas & White (1953) compared the atomic spectra of observed meteors with those obtained by ultra-speed pallets in a ballistic facility. Almost 10 years later, the interaction between a hypersonic flow and an axial symmetric ablator was investigated by Zotikov (1962) by ensuring that the stagnation temperature of the flow exceeded the melting temperature of the body. The process of ablation was observed visually and photographed with a motion picture camera. Attention was paid to the shape and form of the samples after ablation. As a result, general laws of the process of body ablation were obtained, as well as quantitative data on heat transfer in the range of parameters of the experiment.

The first experiments in an Arcjet facility at NASA Ames Research Center were performed by Shepard et al. (1967) who compared the luminous intensity of meteorite analogues such as gabbro and basalt with stony meteorites. The authors observed similar intensities from artificial and natural meteorites, proposing the use of artificial samples to gain better knowledge on the ablation of asteroidal meteors. Using the same facility, Allen & Baldwin (1967) studied the effective density variation of potential cometary-type meteors due to the frothing phenomenon. These types of meteors are expected to include a high water content, which evaporates when certain conditions are reached, resulting in a density anomaly. Bronshten (1983) conducted experiments on samples of stony and iron meteorites in an inductively coupled plasma (ICP) facility. After an initial stage during which the sample warmed up, softened, and liquefied, the sample started to ablate. From the observations, it was possible to infer that melting and mechanical disintegration were probably dominant at altitudes lower than 100 km, with the direct vaporization of material dominating only above 120 km. As the author admitted, however, it is questionable that the mentioned experiments had been able to replicate the extreme environment taking place during hypervelocity atmospheric entry, with realistic surface temperatures and heat fluxes. A series of experimental studies on ablation were also conducted by Blanchard & Cunningham (1974). Experiments on a meteorite analog, olivine, showed a similar fusion crust and oxidation level as the recovered carbonaceous chondrite meteorites. The authors pointed out that the elemental and mineralogical composition as well as the morphological and textural features must be taken into account.

More recently, two series of experiments were performed making use of improved measurement and inspection techniques. Loehle et al. (2017) tested an H4 chondrite and analog samples at the Institut für Raumfahrtsysteme (IRS) with the objective of gaining a better understanding of the ablation process and associated spectral features. Cylindrical-shaped samples were exposed to high heat flux until complete disintegration. The spectra measured by Echelle spectroscopy gave a good comparison with flight data. The surface quickly reached a constant temperature at around 2400 K. In the work by Agrawal et al. (2018), the extreme entry conditions experienced by the Chelyabinsk meteorite during its entry were reproduced. Two samples of the H5 Tamdakht chondrite and one iron meteorite, all carved into a spherical cone shape, were exposed for few seconds to a plasma flow in the Arcjet Interaction Heating Facility of NASA Ames. The chondrite resisted for 2 s while the iron meteorite was completely destroyed after 2.5 s. For all samples, substantial removal of the melt by shearing effects was observed and values for the effective heat of ablation were derived, leading to an improvement of the current models.

In parallel to the experiments in high-enthalpy facilities, intensive evaporation has been studied by directing a highpower laser beam toward the surface of meteorite test samples. This type of experiment is designed to reproduce the strong heating rate on the surface upon the entry of a bolide at high velocities. Milley et al. (2007) investigated the production of light during meteor ablation to better estimate the luminosity efficiency. The expanding vapor was observed by chargecoupled device (CCD) detectors used for meteor observations. The spectral features contained mainly neutral atoms and light production from the vapor was observed even in the absence of high-speed collisions with air constituents. The same technique was used to study the thermo-chemical behavior of the material when subjected to high heat fluxes (White & Stern 2017). Ferus et al. (2018) developed a methodology to analyze and interpret real-time plasma spectra from meteor detections using a calibration-free method. The method was validated by comparison with laboratory experiments in which measurements, performed using laser-induced breakdown spectroscopy, allowed quantitative determination of elemental compositions and temperatures in Perseid and Leonid events.

In the work of Bones et al. (2016), a novel facility (the Meteoric Ablation Simulator) was presented to study differential evaporation in interplanetary dust particles ($<50 \mu$ m) in free-molecular flow. The authors were able to produce a controlled heating rate to represent entry conditions and to measure impact ionization coefficients for the interpretation of radio and radar observations. Gómez Martín et al. (2017) observed differential ablation effects, showing that sodium is the major contributor for radio observation due to its high volatility and low ionization energy.

Experimental replication of meteor entry in a clean plasma flow is a challenging procedure. For instance, the main disadvantage of Arcjet facilities is the presence of copper in the flow due to cathode erosion and degradation, possibly catalyzing surface reactions (Hardy & Nakanishi 1984). Furthermore, although laser ablation guarantees high heat fluxes and is suitable for detailed analysis of gas–surface interactions thanks to the controlled environment, it essentially fails in reproducing the highly reactive plasma around the material, which is generated by the entry shock wave. Moreover, understanding of the ablation process requires surface temperature measurements, spectral features of the evaporating gases, visual observation of the surface, and sample recovery for a posteriori material analysis.

In this paper, we present the results from an experimental campaign using an ICP wind-tunnel (Plasmatron), which took place at the von Karman Institute for Fluid Dynamics (VKI) (Table 1). The subsonic 1.2 MW Plasmatron facility is able to reproduce the aerothermodynamic environment of atmospheric entry in the boundary layer of a test object for a wide range of pressures and heat fluxes (Bottin 1999; Bottin et al. 1999). The focus of our study is the characterization of the gas–surface interaction processes occurring during meteoroid entry. We propose to employ experimental diagnostic techniques previously developed for the in situ material response

 Table 1

 Comparison of Recent Meteoroid Ablation Test Campaigns in Different High-enthalpy Facilities

Facility	p _s (hPa)	$(MW m^{-2})$	$h_{\rm e}$ (MJ kg ⁻¹)	Configuration	Reference
VKI Plasmatron	15-200	1–3	24–54	Stagnation point	Present study
IRS Arcjet	24	16	70	Cylindrical sample	Loehle et al. (2017)
Ames Arcjet	14	40	20	Full axisymmetric body	Agrawal et al. (2018)

characterization of heat shield materials (Helber et al. 2016a), with the objectives to record the surface temperature evolution, visually observe the ablation process, and recover tested samples for their comparison with fusion crusts on natural meteorites (Pittarello et al. 2019). In addition, three emission spectrometers are focused on the boundary layer forming in front of the ablating material, providing temporally resolved emission profiles of the main radiators ejected by the test sample during the entire test time. The retrieved data are then used to build a thermal response model of the material by solving the heat conduction equation in a 1D Cartesian domain, which provides a more detailed insight into the surface energy balance and chemical reaction of iron oxidation. Two types of materials are studied, alkali basalt (AB), as a meteorite analog to optimize the experimental conditions, and ordinary chondrite (OC), with the main focus on the temperature response, surface characterization, and gas-phase radiation.

We describe the methodology and experimental facility in Section 2. Section 3 deals with the testing conditions. After sketching the theory, the similarity rules are applied to rebuild flight conditions from the experiment. Section 4 presents the experimental results obtained in this work: after a qualitative analysis, surface measurements and emission spectra are shown and discussed. Finally, in Section 5, the surface measurements are compared with simulations results obtained by means of the material response code.

2. Experimental Facility, Measurement Techniques, and Methods

The experimental setup installed at the Plasmatron facility offers intrusive and non-intrusive (optical) measurement techniques. Instrumentation for the material analysis of this work consisted of a digital camera, a two-color pyrometer, a broadband radiometer, and three spectrometers as detailed below. During this investigation, the main data of interest comprised the surface response to the incoming air plasma in terms of temperature, mass loss, and species ejected into the boundary layer.

2.1. Plasmatron Facility Description

The VKI Plasmatron facility has been used for the reproduction of the aerothermodynamic environment of atmospheric entry plasma flows, creating a high-enthalpy, highly dissociated subsonic gas flow (Bottin et al. 1999). It is equipped with a 160 mm diameter ICP torch powered by a high-frequency, high-power, high-voltage (400 kHz, 1.2 MW, 2 kV) generator (MOS technology). The gas is heated by induction through a coil, creating a high-purity plasma flow. Three probe holders are installed in the Plasmatron facility next to each other, which can be exchanged independently by a pneumatic mechanism. One holds the test sample, while the other two are used for heat flux and Pitot pressure



Figure 1. Schematic of experimental setup (not to scale) with diagnostics for meteor ablation analysis.

measurements in the same experimental run as the ablation test. The cold-wall (~350 K) stagnation point heat flux \dot{q}_{cw} is measured with a water-cooled calorimeter having a sensing surface 14 mm in diameter and made of copper. A water-cooled Pitot probe, connected to a Validyne variable reluctance pressure transducer, is used to determine the dynamic pressure of the plasma flow. Atmospheric air at a mass flow of $\dot{m} = 16 \text{ g s}^{-1}$ is used to create the plasma flow. For the results presented throughout this paper, the time indication t = 0 s corresponds to the injection of the test sample into the plasma flow. The sample is attached to a sample holder located 445 mm downstream of the plasma jet exit. After reaching the target testing condition (testing chamber static pressure and heat flux), the sample is inserted using the pneumatic mechanism.

2.2. Experimental Diagnostics and Methods

A schematic of the experimental setup for in situ ablation measurements can be found in Figure 1 (Helber et al. 2014, 2016a), and is reviewed below. We used a two-color Raytek Marathon MR1S-C pyrometer, employing a wide (0.75–1.1 μ m) and narrow (0.95–1.1 μ m) spectral band for the temperature determination at a 1 Hz acquisition rate (1300–3300 K). Using two narrow wavelength bands and assuming a constant emissivity over this wavelength range allows an emissivity-independent surface temperature determination. The pyrometer was pointed and focused at the stagnation area of the sample through a 1 cm thick glass window, at an angle of ~35° with respect to the stagnation line. The instrument was calibrated up to 3300 K at the National Physical Laboratory (London, UK) using a high-temperature

graphite blackbody, including a spot-size and uncertainty analysis, which resulted in $\delta T_{\rm w} = \pm 15$ K in the observed temperature range. The highest uncertainty was attributed to the positioning of the pyrometer with respect to the quartz window, introducing measurement inaccuracies.

A broadband infrared radiometer (KT19 HEITRONICS Infrarot Messtechnik GmbH, Wiesbaden, Germany) recorded the surface radiance in a broad spectral range (0.6–39 μ m). Assuming a test object following graybody behavior, this instrument allows estimation of the hot wall emissivity using the two-color pyrometer surface temperature as a blackbody radiance reference and the in-band (0.6–39 μ m) radiance provided by the radiometer.

For this work, the broadband radiometer was calibrated using a blackbody source up to 1770 K, assuming that emissivity is constant up to 10 μ m. The integrated spectral radiance beyond 10 μ m ($L_{10-39\mu m}$) at this temperature only constitutes 2% of the total radiation and it is thus assumed that emission above 10 μ m can be neglected. A KRS-5 window was used for the radiometer measurements as it offers transmissivity over the radiometer operating range.

The front surface was monitored by a 14 bit CCD camera (pco.pixelfly developed by PCO AG) providing snapshots throughout the experiment. Camera acquisitions were triggered using a digital delay generator before injection of the test sample. This allowed for a precise determination of the total injection time. Synchronized with the camera were optical emission spectroscopy (OES) measurements, which consisted of three low-resolution, wide-range Ocean Optics HR4000 spectrometers, providing information on the emission spectrum upstream of the test specimen. The HR4000 spectrometers covered a wide spectral range (200-1000 nm) within a single acquisition and a minimum integration time of 5 ms. The light emitted by the plasma was collected through a variable aperture and focused by a plano-convex, uncoated fused silica lens (LA4745, 750 mm focal length) via two mirrors onto the three optical fiber entries (Ocean Optics QP600-2-SR/BX, $600 \pm 10 \,\mu\text{m}$ core diameter). The optical path was aligned perpendicular to the flow and tangential to the test sample surface. The magnification of the optical system was set to m = 3, resulting in a distance between each probing volume of $\Delta d = 2$ mm. The fixed entrance slit width of 5 μ m and a 300 grooves/mm grating led to a typical resolution of approximately 0.7 nm full width at half maximum, as was determined using a low-pressure mercury lamp (Oriel 6060), which provides a lower line broadening than covered by a single pixel of the CCD array ($\Delta \lambda_{range}/3648 \approx 0.22 \text{ nm}$). For conversion of the data into spectral intensities $(W m^{-2} sr^{-1} nm^{-1})$, we performed a calibration of the whole system, consisting of the light collection mechanism and the spectrometer efficiency, by placing a tungsten ribbon lamp (OSRAM WI 17G) in the focus of the collection optics inside the test chamber. The lamp was operated at a single power input, producing a stable radiance I_{λ}^{ref} , known from prior calibration.

2.3. Test Samples

Two different samples were cut into a cylindrical shape with diameter d = 16 mm and length l = 6 mm, using a commercial diamond-embedded drill bit. Each sample was embedded in a hemispherical holder of 50 mm diameter and 45 mm length made out of cork-composite ablative material (Figure 2). This

sample holder had two main objectives: first, insulating the test sample from side-wall heating, allowing a 1D heat conduction approach and, second, to provide a test shape of known geometry in order to be able to perform an extensive plasma flow characterization by intrusive probes and numerical rebuilding. The employed cork composite material is highly insulating and the only source of heat delivered to the test sample can be assumed to be coming from the stagnation region. A graphite holder of the same geometry was also designed and employed in a second test campaign for which the results are presented in Pittarello et al. (2019). The main disadvantage of the graphite configuration was a strong 3D heating of the test sample due to the high thermal conductivity of graphite, making a numerical analysis of the experimental results difficult. By contrast, the main drawback of using a cork housing was the pollution of the boundary layer with cork ablation products as detected by the spectrometers, as will be seen in Section 4.2. Another possibility for future experiments could be to invest in a water-cooled metallic housing of the meteor sample. This would provide the desired test shape (for example, hemisphere) without polluting the boundary layer, and at the same time would provide 1D thermal conduction inside the sample if well insulated from the cooled holder walls. Unfortunately, such thermal insulation from the sidewalls would not be trivial as ablation of the sample was one main objective, which would lead to destruction of the insulation material as well, again polluting the test material and boundary layer. We suggest using a pure test sample, as done by Loehle et al. (2017), without any additional interfaces that could contaminate the recorded data, such as a single sample in the desired test shape (e.g., hemisphere). However, meteorite samples for such destructive tests are difficult to obtain, especially at a reasonable size to be machined into the desired shape, and the strong side-wall heating in such case would make the thermal analysis more difficult compared to the 1D approach we applied in this work. In addition, such a sample might be completely destroyed during the experiment because of the rapid heating, hampering recovery and further analyses of the resulting material (no material remainders were analyzed in Loehle et al. 2017).

Two different materials were chosen as test samples: a fragment of AB serving as an analog meteoritic material, and a piece of El Hammami H5 OC. Their main characteristics are reported in Table 2. The densities were obtained by weighing the samples and assuming a perfectly cylindrical shape. Physico-chemical properties determined by X-ray fluorescence (XRF) and scanning electron microscopy (SEM) are briefly presented below.

Alkali basalt. Being a mineralogically simple material, basalt is one of the most common igneous rocks on Earth and its bulk composition roughly resembles that of chondrites and more closely matches stony achondrites. This specific sample is an AB with approximately 50 wt% of SiO₂. The chemical composition of the basalt was determined by means of μ -XRF and SEM-EDS and the results are presented in Table 3. For details on the analytical conditions, we refer to Pittarello et al. (2019). The semi-quantitative analysis shows a material particularly enriched in volatiles with SiO₂ and Al₂O₃ as major components, indicating a high feldspar content typical of mafic, basaltic rocks. Basalt densities commonly vary between 2700 and 3300 kg m⁻³, making our sample slightly lighter (2400 kg m⁻³) than average basalt. The equilibrium melting



Figure 2. Schematic of the sample and its cork holder. The material sample (ordinary chondrite or alkali basalt), 16 mm in diameter, is embedded in the sample holder in a stagnation point configuration.

 Table 2

 Characteristics of the Two Samples

Material ID	l (mm)	d (mm)	<i>m</i> (g)	(kg m^{-3})
AB	6	16	2.74	2400
OC	6	16	3.65	3026

 Table 3

 Major Species Chemical Composition before the Experiments

Species	AB	OC	OC-Ref.
	(wt%)	(wt%)	(wt%)
SiO ₂	52.28	50.71	36.6
TiO ₂	1.23	0.07	0.1
Al_2O_3	22.33	1.74	2.1
Na ₂ O	6.66	1.55	0.8
K ₂ O	6.09	0.10	
CaO	5.16	2.33	1.7
FeO	4.95	15.93	11.9
MgO	0.61	26.03	23.1

Note. Chemical composition was determined by means of μ -XRF for the alkali basalt (AB) and laser ablation–ICP–mass spectrometry for the ordinary chondrite (OC-silicate portion). For the latter, a reference value from literature is also provided (Jarosewich 1990).

temperature of most basalts is generally in the range between 1273 and 1473 K, whereas average thermal conductivities vary between 1.69 and 2.11 W m⁻¹ K⁻¹ (Eppelbaum et al. 2014). The specific heat of basalts is generally between 840 and 1230 J kg⁻¹ K⁻¹ with a heat of fusion of \sim 500 kJ kg⁻¹ (Kojitani & Akaogi 1995).

Ordinary chondrite. OCs represent the vast majority of all meteorites recovered on Earth. These meteorites are thought to come from a relatively small number of asteroids located in near-Earth orbits (e.g., Vernazza et al. 2015). They comprise a range of particle types, from fine dust-like matrix to millimeter-scale chondrules, which are solidified molten droplets after which chondrites are named. They are often considered the primary building blocks of most large solar system objects. Among these, class H OCs have a relatively reduced chemical composition and therefore are suitable to highlight possible redox processes induced by interaction with atmospheric oxygen. The class H OC El Hammami (petrologic type 5) was selected. The petrologic type defines the thermal metamorphism experienced in the parent body, from 3 to 6 (or 7) for OCs, for increasing chemical equilibration. A

meteorite with a high petrologic type (5–6) will therefore exhibit homogeneous compositions for each mineral phase. The chemical characterization of a silicate portion of the sample obtained via laser ablation–ICP–mass spectrometry (Pittarello et al. 2019) is reported in Table 3, where the average composition of H chondrites reported by Jarosewich (1990) is also presented as a reference. In Yomogida & Matsui (1983), the authors computed bulk densities in a range between 3350 and 3690 kg m⁻³ for H chondrites. In the same study, thermal conductivities were measured between 0.415 and 3.85 W m⁻¹ K⁻¹. In the case of H chondrites, the specific heat range is 500–900 J kg⁻¹ K⁻¹ between 200 and 600 K (Yomogida & Matsui 1983), while several studies show average values around 700 J kg⁻¹ K⁻¹ for temperatures close to 300 K (Consolmagno et al. 2013).

3. Test Parameters and Rebuilding of Flight Free-stream Conditions

The local heat transfer simulation methodology was originally developed by Kolesnikov (1993), allowing us to duplicate flight conditions at the stagnation point by matching the boundary layer edge total enthalpy $h_{\rm e}$, pressure $p_{\rm e}$, and the radial velocity gradient in the radial direction at the wall $(\beta_{\rm e} = (\partial u/\partial x)_{\rm e})$ between ground experimental and flight conditions.

The subsonic Plasmatron flowfield was numerically simulated by solving the Navier-Stokes equations coupled with the Maxwell equations for the electromagnetic field created by the coil (VKI ICP code; Vanden Abeele & Degrez 2000; Degrez et al. 2004; Magin & Degrez 2004). This provides the boundary layer velocity gradient β and boundary layer thickness δ , as well as an initial streamwise velocity v for the characterization of the boundary layer around the test sample under local thermodynamic equilibrium and axisymmetric flow assumptions (Barbante & Chazot 2006). The hydrodynamic boundary layer edge parameters (temperature $T_{\rm e}$, density $\rho_{\rm e}$, and velocity v_e) are determined through an iterative procedure using the VKI boundary layer code (Barbante et al. 2002), which takes as input conditions the flow quantities determined from the VKI ICP code, as well as the experimental heat flux and Pitot pressure measurements. The VKI boundary layer code consists of solving the chemically reacting stagnation line boundary layer over a catalytic surface under chemical nonequilibrium conditions, assuming fixed wall catalytic properties for copper and a cold-wall temperature for the heat flux probe. A more detailed description of this procedure applied to ablation tests can be found in Helber et al. (2015).

We chose three test conditions, often used for TPS testing, which are characterized by a high level of confidence in terms of repeatability and flow behavior. In addition, these experimental conditions were chosen to allow the recovery of the sample for surface characterization analysis after the tests. The experimental conditions are listed in Table 4. In this work, we present results for condition (1), while conditions (2) and (3) are relevant for the surface characterization presented in Pittarello et al. (2019). Notice that the cold-wall heat flux \dot{q}_{cw} was measured by means of a cylindrical calorimeter probe for conditions (2) and (3). The values presented in Table 4 are given for a hemispherical calorimeter, or its equivalent for condition (1).

		Experimental			Numerical			
Condition ID	p _s (hPa)	P _{el} (kW)	$\dot{q}_{\rm cw}$ (MW m ⁻²)	$\frac{h_{\rm e}}{({ m MJ~kg}^{-1})}$	$(g m^{-3})$	Т _е (К)	$(m s^{\nu_e})$	(1 s^{-1})
(1)	200	206	1.2	24	7.0	6293	26	1230
(2)	220	310	3.0	42	4.3	8079	55	4480
(3)	15	373	3.1	54	0.3	9229	687	29790

 Table 4

 Plasmatron Test Conditions

Note. Data include experimentally measured static pressure p_s , generator electric power P_{el} , and mean cold-wall heat flux \dot{q}_{cw} , as well as numerically rebuilt boundary layer edge values of enthalpy h_e , gas density ρ_e , gas temperature T_e , velocity v_e , and boundary layer gradient β_e .

A numerical procedure was used to infer flight conditions from the experimental ones. By solving the Rankine–Hugoniot jump relations, assuming a thermally perfect gas, a contour map of post-shock enthalpy h_e and pressure p_e was defined for a range of free-stream velocities and altitudes. An equivalent flight radius can also be computed by means of modified Newtonian theory (Anderson 1989):

$$R_{\text{equ},f} = \frac{1}{\beta} \sqrt{\frac{2(p_e - p_\infty)}{\rho_{e,f}}} \tag{1}$$

where p_{∞} represents the atmospheric pressure at the flight altitude and $\rho_{e,f}$ the flight boundary layer edge density obtained from the Rankine-Hugoniot jump relations. The three experimental conditions are shown in Figure 3. For the experimental results reported here, condition (1) corresponds to a 3.8 m diameter object $(2 \times R_{equ,f})$, flying at a velocity of 6.9 km s⁻¹, at an altitude of 54.7 km. Fireball trajectories for two wellknown events are also reported in Figure 3: one can observe that the range of velocities of the two bolides, Benešov and Chelyabinsk, are higher than our experimental conditions. We chose a lower heat flux condition than what can be assumed from existing meteor observations to avoid complete destruction of the samples and ensure successful recovery of the modified basaltic and chondritic materials. Recovery of modified experimental samples enabled us to set a further objective in this experimental campaign, which was a complete petrographic and geochemical characterization and comparison with natural meteorite fusion crust. Future work may include testing at higher heat fluxes, reproducing smaller meteoroids at higher entry velocities.

It should be noted here that most of the mass of extraterrestrial material falling on Earth consists of micrometeorites (between 50 and 2000 μ m, producing 40,000 ± 20,000 metric tons of extraterrestrial matter to Earth every year; Love & Brownlee 1993). But most significant discoveries about meteorite parent bodies and the early stages of the solar system formation have so far been made by focusing on actual meteorites. It is therefore important to constrain the modifications induced on this material during atmospheric entry. Micrometeorites, including their innermost parts, undergo degassing, melting, and evaporation, with limited material remaining as required for high-precision analytical studies. To amplify the detectable effects of atmospheric passage on geological materials and at the same time recover material required to make our observations, we opted for the experimental design described above.

 Table 5

 Overview of Plasmatron Results for Condition (1)

Material	au (s)	T _w (K)	Δm (mg)	ϵ (\cdots)
AB	8	2280	n/a	0.74
OC	21	2360	3	0.69

Note. Data for alkali basalt (AB) and ordinary chondrite (OC) include test sample exposure time τ , mean surface temperature T_w , total mass loss Δm , and surface emissivity ϵ . Due to the fracturing of the material, the total mass lost by the basalt sample could not be determined.



Figure 3. Duplication of the Plasmatron test conditions to flight conditions. The Benešov fireball reported by Borovička & Spurný (1996) has an estimated value at entry conditions of 2.3 m diameter body with 21.3 km s⁻¹ velocity. The Chelyabinsk event (Borovička et al. 2013) is estimated to be 18 m in size, with an entry velocity of 19 km s⁻¹. The trajectory #6882 is one of the 413 photographic meteors reported by Shepard et al. (1967) and Jacchia & Whipple (1961). The sizes of these bodies are not reported.

4. Experimental Results

In Table 5, we present an overview of the main results for both materials in terms of maximum surface temperature, test time, and total mass loss. In our tests, the basalt sample broke soon after injection into the plasma (after ~ 8 s) and the test run was aborted. In a similar experiment, not further detailed in this paper, the sample was first dried at 120 °C for two hours to remove any possible water contamination and was also held in a cork holder with a gap between the lateral side of the sample to release any mechanical stress on the basalt sample from an expansion of the cork. However, also in this experiment the



Figure 4. Snapshots (upper left to lower right) during the AB test at 1.2 MW m^{-2} and 200 hPa highlighting boiling of the surface after 2 s (time from injection indicated in each image); the sample broke out of the sample holder after 8 s and the test was aborted.



Figure 5. Snapshots (upper left to lower right) during the OC test at 1.2 MW m^{-2} and 200 hPa highlighting boiling of the surface after 5 s (time from injection indicated in each image); a melted surface state remained present throughout the remaining 15 s of the test.

basalt underwent fracturing, which can be ascribed to thermal fracturing, probably resulting from the mineral flow fabric (crystal alignment reflecting flow of the original lava before solidification) and strong, igneous crystalline texture. Anisotropies in the basalt result in internal stress during temperature increase, due to different thermal expansion coefficients among







Figure 7. AB (a) and OC (b) samples after plasma exposure. In (a), glassy features formed after the resolidification. In (b), a change of color, probably a sign of the change in the oxidation state of iron, is visible.

minerals or even preferred orientation of minerals. In contrast, the OC withstood the plasma flow during the entire test time of 21 s without fracturing, probably because of a predominantly granular metamorphic texture (rather than igneous). In fact, the OC sample only lost 3 mg during those 21 s, starting from an original weight of 3.65 g. This illustrates that, although the surface appeared to be boiling and frothing, only a little material volatilization took place and not much mass was injected into the boundary layer, allowing recovery of the ablated material.

Snapshots taken throughout the experiment indicate the formation of gas bubbles on the surface, shown in Figures 4 and 5. The frothing appeared earlier for the AB sample (after 2 s of plasma exposure) than for the OC (5 s after plasma exposure). A possible explanation for this observation may lie in the fast evaporation of the volatile elements for which the concentration is considerably higher in the basalt sample (see Table 3). In gases of solar composition, Na and K have 50% condensation temperatures of 958 K and 1006 K respectively; for Fe this is 1334 K (Lodders 2003). One should note that during hypersonic flight this frothing layer can be removed by the aerodynamic forces as suggested by Allen & Baldwin (1967).

Photographs taken before and after each experiment are shown in Figures 6 and 7. The AB had glassy features on its surface after resolidification upon cooling. These glasses have roughly the same composition as the basalt, with apparent depletion in highly volatile elements (Na and K). The OC, however, displayed a reddish color change, which probably indicates a change of the oxidation state of the high iron content with formation of hematite (Fe_2O_3) at the surface. Global oxidation of the sample is also suggested based on petrographic observations of the resulting material, which contains magnetite (Pittarello et al. 2019).

4.1. Surface Temperature Measurements

The plateau temperatures reached during these test conditions were 2280 K for the AB (Figure 8(a)) and 2360 K for the OC (Figure 8(b)). Although the pyrometers measuring surface areas of 11 mm diameter mostly covered the basalt and chondrite sample surfaces, some additional radiation, coming from the cork housing, may have been recorded by the pyrometer. This cork housing is likely to have resulted in a different surface temperature from the held samples, as well as in different apparent emissivities, affecting the measured temperatures to a small degree.

The delayed temperature rise of the pyrometer with respect to the radiometer in Figure 8 originated from a higher lowtemperature limit for the pyrometer. In particular, for the intact OC sample, the cooling curve due to surface radiation and internal conduction after the plasma was turned off can be clearly



Figure 8. Surface temperature evolution (T_w , full lines) of AB (a) and OC (b); radiometer measurements (dashed lines) were recorded in a wider temperature range but for $\varepsilon = 1$ (see the text); Once the plasma is switched off (AB: 13 s, OC: 21 s), the surface temperature drops immediately due to the high thermal radiation.

observed. In addition, the broadband radiometer measurement served to provide an average apparent directional emissivity at those temperatures for both materials $(T_{\varepsilon=1,0.6-39 \ \mu m}^4/T_w^4)$. This resulted in an emissivity of $\varepsilon_{0.6-39 \ \mu m} = 0.69$ for the AB sample and in $\varepsilon_{0.6-39 \ \mu m} = 0.74$ for the OC. Those data will be used below in Section 5 for comparison with a 1D numerical model.

4.2. Optical Emission Spectroscopy

We present emission spectra recorded in front of the test sample during plasma exposure in Figure 9. The three plots present the radiative signature of the air plasma free-stream (red) together with radiation mostly coming from the ablating cork holder just at injection (a), an emission spectrum recorded in front of the AB sample shortly after injection (b), as well as one recorded in front of the OC sample several seconds into the test (c), when radiative emission was highest. The free-stream emission spectrum presents expected CN violet and N_2^+ radiation, both strong radiators and generally present in atmospheric air plasmas at such gas temperatures (5000-10,000 K). The ablating cork sample, in addition, led to much stronger CN violet emission due to ablation, as well as sodium and potassium. Traces of the volatile elements sodium and potassium in this spectrum may also result from the ablation of the test sample. However, sodium has also been found in the cork material as a result of either the supplier's manufacturing process, or in-house machining of the sample holder.

Table 3 indicates that both materials contain sodium and potassium, and the latter is especially true for basalt. A small contribution of the C_2 Swan system can also be identified between 440 and 550 nm, also due to the ablating cork cover, which is well known to result from the pyrolyzation of typical charring thermal protection materials (Helber et al. 2014, 2016b).

The spectral intensity signal observed by the spectrometers strongly changed during the ablation of the AB or OC. Both spectra are mainly dominated by iron emission, with several strong lines in the UV and visible range of the spectrum, as indicated by the fine markers. As seen in Table 3, high concentrations of iron are present in both samples. Again, the volatile elements sodium and potassium are strongly present; their temporal and spatial emission profiles will be discussed below. The recorded emission signals of sodium (589 nm) actually saturated during the measurement, and therefore did not allow further analysis of their temporal emission profiles. The saturation is not apparent from the plots of Figure 9 as emission lines at lower and higher wavelengths are well captured (at higher calibrated intensity); this comes from the lower quantum efficiency of the HR4000 sensor toward its wavelength wings below 400 nm and above 750 nm.

In addition, especially in the case of AB, strong silicon emission was also visible at 252 and 288 nm. Interestingly, although both sample materials are predominantly composed of SiO₂, the OC did not show any silicon emission during the whole experiment. In general, moderately refractory elements like silicon, magnesium, and truly refractory elements such as aluminum, which are part of the OC elemental composition, are not strongly present in the spectrum. (In solar gases and with a 50% condensation temperature of 1653 K, aluminum is considered truly refractory (1500-1700 K); silicon (1310 K), magnesium (1336 K), and iron (1334 K) are considered moderately refractory (1300-1500 K; Lodders 2003.) The emission of iron lines produced by an ablating OC sample in plasma flows was also reported by Loehle et al. (2017), together with traces of silicon, sodium, potassium, and manganese.

In addition to the radiative species emission, continuum radiation, emitted by the hot surface, was recorded by the spectrometer closest to the surface (Figure 9). This might have been caused by the cork material which tends to swell upon heating, with emission of the hot surface reaching the optics of the closest spectrometer.

Potassium and sodium emission during ablation of meteoritic samples are of particular importance and high interest to the community. However, several constraints limited the possibility of obtaining unpolluted emission spectra from the observed material alone. One limiting factor was the available test sample dimension, which was a cylinder of 16 mm diameter, so an adequate sample holder needed to be used. We decided to embed the test sample in a holder of known shape (i.e., a hemisphere) in order to be able to perform an extensive plasma flow characterization by intrusive probes and numerical rebuilding.







(b) Alkali basalt at injection (gray) and air plasma free-stream (red)



(c) Ordinary chondrite after 16s (gray) and air plasma free-stream (red)

Figure 9. Emission spectra overview of air plasma and cork holder (a), AB (b), and OC (c) tests; the air free-stream spectrum for each test run is given in red, while the spectrum recorded in front of the ablating material sample is given in gray, highlighting the presence of additional radiative contributors ejected by the material (all spectra recorded by the spectrometer closest to the surface).



Figure 10. (a) Temporal emission profiles of Si (full), K (dotted), and Li (dashed) as well as (b) of Ca^+ (dashed–dotted), Mg^+ (dotted), Fe (dashed), and Fe⁺ (full) during AB ablation showing a strong emission peak at injection of the test sample; a sudden emission decrease of K and an increased emission for Fe, Mg^+ , and Ca^+ were then visible when the sample broke after 8 s (all data recorded by the spectrometer closest to the surface).



Figure 11. Temporal emission profiles during OC ablation showing a fast rise of the alkali metal K (dotted), followed by a rise of the alkaline earth metals Ca^+ (dashed–dotted), Mg^+ (full), and finally Fe (dashed) (all data recorded by the spectrometer closest to the surface).

4.2.1. Temporal Emission Profiles

From the temporally resolved emission spectrum data, we obtained the normalized temporal emission profiles of the main radiating species, presented for AB in Figure 10 and for OC in Figure 11. The main behavior of each emission profile is different for each material: the temporal emission of all species resulting from AB presented a strong peak at injection into the plasma flow, followed by a strong emission drop. This was not the case for the OC sample, where an emission rose immediately for the alkali metal potassium, followed by a rise of the alkaline earth metals Ca^+ and Mg^+ , with finally a slow rise of iron.

In both cases, potassium emission is persistent from the beginning of the test. The potassium doublet at 766 nm was observed by Loehle et al. (2017) and Agrawal et al. (2018) in their ground experiments of the OC. Moreover, Borovička et al. (2008) successfully detected the same potassium doublet in meteor spectra observations, suggesting that emission at this wavelength might be usually absorbed by atmospheric oxygen, a possible reason why it is typically not detected. From the snapshots we observed an almost immediately boiling AB

surface (Figure 4), whereas the OC heated up more slowly, reaching a steady boiling phase (Figure 5). The same behavior can be observed in the temporal emission profiles. This is especially visible in Figure 11 for the iron emission.

Figure 10 further shows the effect of the mechanical fracturing of the basaltic sample at 8 s into the test as was already observed from Figure 4. First, the fracturing of the sample causes an abrupt drop in the emission profile of potassium, Figure 10(a). This strengthens the likelihood that a large part of potassium emission comes directly from the sample. Since sodium emission was saturated for all three spectrometers over time for both test cases, no temporal emission profiles are presented. Second, the emission spectrum of several species originating from basalt such as Fe⁺, Mg⁺, and Fe responded with a short rise in intensity at around 8 s, as seen in Figure 10(b). The same fluctuation trends were observed for silicon at around 8 s in Figure 10(a).

4.2.2. Temporal Emission at Three Locations in the Boundary Layer

Three spectrometers were focused in the boundary layer in front of the test sample (Figure 1), with a distance of 2 mm between each other. The temporal emission profiles of silicon and potassium recorded at the three locations in the boundary layer (close to the surface, then increasing by 2 mm increments away from the surface) are displayed in Figure 12. Those profiles are presented in absolute units and have been obtained by integrating the calibrated line-of-sight spectral signal over a wavelength range (enclosing the line wings) for each transition of each individual spectrum. Background emission originating from the sample surface or other radiating contributors was removed by fitting a baseline on the line shape edges and subtracting all underlying radiation.

While silicon showed an emission peak at injection, probably caused by strong pyrolysis outgassing (blowing) within the first second as the cork material heats up, potassium slowly rose during the experiment until the sample broke after 8 s. Interestingly, the potassium emission does not follow the same trend at the three locations in the boundary layer. This might be due to changing chemistry at the basalt surface or inside the boundary layer, as well as due to the higher gas temperatures at greater distances from the surface.



Figure 12. Emission profiles of potassium (dotted) and silicon (full) recorded by the three spectrometers during AB ablation (left: close to surface; middle: away from surface; right: far from surface, in 2 mm increments). An emission peak of silicon at test start was observed for silicon; potassium, however, rose during sample injection at all three locations until dropping after 8 s when the sample broke.

4.3. Chemical and Petrographic Characterization of the Resulting Material

Regarding the AB, the resulting material after the experiment mostly consisted of homogeneous glass. The chemical composition of the glass, in comparison with that of the basalt before the experiment, showed apparent enrichment of the melt in titanium, iron, and manganese and depletion in sodium and potassium. The depletion of highly volatile alkali metals (sodium and potassium) supports the OES measurements during the experiment. On the surface of the glass, spherical objects were observed, with an average composition rich in SiO₂, Na₂O, and K₂O, suggesting condensation from the vaporized material.

The melting of the OC, despite quite rapid quenching, resulted in extensive crystallization after the experiment. A rough comparison between the bulk composition of the resulting material and the interior of the sample, unaffected by melting, showed that the melt was overall enriched in TiO, FeO, and Cr_2O_3 . This apparent enrichment might result from the depletion in most volatile or moderately volatile elements. The crystallized phases were olivine and magnetite, suggesting oxidation of the iron originally in the metal state. Detailed characterization of the resulting material from both experiments is provided in Pittarello et al. (2019).

5. Modeling of the Material Response of the H5 Chondrite

The thermal response of the material was studied and compared with the experimental data by solving numerically the heat conduction equation $\partial T/\partial t = k/(\rho c_p) \ \partial^2 T/\partial x^2$ in a 1D Cartesian domain. The choice of the 1D approximation is supported by the good insulation properties of the cork holder. At the stagnation point, we applied a boundary condition built as a surface energy balance between the gas and the liquid phase:

$$\dot{q}_{\rm w}^{\rm conv} + \dot{q}_{\rm w}^{\rm chem} = k \frac{\partial T}{\partial x} |_{\rm w} + \epsilon \sigma (T_{\rm w}^4 - T_{\infty}^4) + \dot{m}_{\nu} L_{\nu}.$$
 (2)

The left-hand side represents the heat due to the impinging plasma flow $\dot{q}_{w}^{\rm conv}$ and heterogeneous chemical reactions $\dot{q}_{w}^{\rm chem}$, while the right-hand side comprises the energy loss due to the thermal conduction inside the material, re-radiation, and net evaporation of the surface. Concerning the physical properties, density ρ and emissivity ϵ were measured. The specific heat c_p

 Table 6

 Physical Properties Assumed for Numerical Modeling of the Thermal Response in the Samples

Material ID	$(\mathrm{kg}\mathrm{m}^{-3})$	$(W m^{-1} K^{-1})$	ϵ (···)	$(J kg^{-1} K^{-1})$	L_{ν} (J kg ⁻¹)
AB	2400	0.7	0.69	800	6×10^{6}
OC	3026	3	0.74	1000	6×10^{6}

Note. Densities were measured by weighing the cylinders and emissivity calculated as described in Section 4.

and latent heat of vaporization L_{ν} were constrained to the values chosen by Vondrak et al. (2008) and Campbell-Brown et al. (2013) and are summarized in Table 6.

The convective contribution can be estimated by the Fay & Riddell (1958) formula:

$$\dot{q}_{\rm w}^{\rm conv} = \frac{\rm Nu}{\sqrt{\rm Re}} \sqrt{\rho_{\rm w} \mu_{\rm w} \beta} \left(\frac{h_{\rm e} - h_{\rm w}}{\rm Pr}\right),\tag{3}$$

where the non-dimensional parameters are the Nusselt (Nu), Reynolds (Re), and Prandtl (Pr) numbers. The Reynolds number is computed based on the equivalent radius. The subscript "w" is used to refer to the stagnation point condition at the wall, while "e" represents the edge of the boundary layer. More information about this approach can be found in Turchi et al. (2015). Condition (1) reported in Table 4 corresponds to a cold-wall convective heat flux of 1.2 MW m⁻².

In Section 4.3, the change in composition of the OC was interpreted as a possible change in the oxidation state of iron species, resulting in crystallization from the melt of magnetite (Fe₃O₄) and of olivine richer in FeO than the original olivine. The formation of magnetite can be described using a hematite-like component (Fe₂O₃), which is diluted by FeO in the sample. Since oxidation is a strongly exothermic process, one cannot exclude the possibility of such reactions contributing to the energy balance by releasing their formation enthalpy at the wall. Genge (2016) showed, that oxidation is important for iron micrometeoroids because it proceeds faster than vaporization. The author reports that for wüstite (FeO)-dominated particles an increase in mass of up to 23% by reaction with atmospheric oxygen can occur. In this work, we consider reactions of the following type, $2\text{FeO}_{(l)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{FeO}_{(l)}$ and $\text{Fe}_{(l)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{FeO}_{(l)}$.



Figure 13. Comparison of the surface temperature measurements (blue bullets: pyrometer, red triangles: radiometer with estimated emissivity) with the numerical simulation of the thermal response of the AB (a) and OC (b). Exothermic heterogeneous reactions play an important role as discussed in Section 4.3 and have a significant impact on the simulations (full lines: model including oxidation reaction, dashed lines: oxidation disabled). We used the same parameter γ_r for modeling the basalt response as chosen for the ordinary chondrite.

The chemical heat flux related to the former reaction can be written as:

$$\dot{q}_{\rm w}^{\rm chem} = 2\gamma_r \ p_{\rm O_2} \sqrt{\frac{m_{\rm O_2}}{2\pi k_B T_{\rm w}}} \Delta H_{\rm Fe_2O_3}^0 x_{\rm FeO},$$
 (4)

which is obtained by multiplying the impinging oxygen flux for the enthalpy of reaction, $\Delta H_{\text{Fe}_2\text{O}_3}^0$, rescaled by the molar concentration x_{FeO} of FeO in the material. This was computed under the assumption of local thermodynamic equilibrium using the Plasmatron chamber pressure (which for this condition practically equals total pressure inside the flowfield) and test sample wall temperature T_w . In this formula, γ_r plays the role of a recombination probability for the impinging molecular oxygen at the surface and the factor 2 provides the correct stoichiometric constraint.

Now, we estimate the relative importance of the oxidation term with respect to the evaporation one in Equation (2). Since $\Delta H_{\text{Fe}_2\text{O}_3}^0 \approx L_{\nu}$, then $\dot{q}_{w}^{\text{chem}} = 2\dot{m}_{\text{ox}}L_{\nu}$ and their net contribution to the global surface energy balance, $\dot{q}_{w}^{\text{chem}} - \dot{m}_{\nu}L_{\nu}$, can be written as follows:

$$2\dot{m}_{\rm ox}L_{\nu} - \dot{m}_{\nu}L_{\nu} = \frac{1}{2}\dot{q}_{\rm w}^{\rm chem} + (\dot{m}_{\rm ox} - \dot{m}_{\nu})L_{\nu} \approx \frac{1}{2}\dot{q}_{\rm w}^{\rm chem}, \quad (5)$$

where \dot{m}_{ox} is the input of the oxidation reactions to the overall mass balance. The term containing L_{ν} is negligible when compared to the first one, as it is proportional to the small mass loss, $\frac{1}{\pi d^2} \frac{\Delta m}{\tau} L_{\nu}$. This result is used as input in Equation (2). In Figure 13, a comparison between the simulated and

In Figure 13, a comparison between the simulated and experimental values of the wall temperature is shown. Both measurements are presented, the emissivity-independent pyrometer measurement (blue bullets), as well as the emissivity-dependent radiometer measurement (red triangles), accounting for the estimated emissivity (Section 4.1). This was done because the radiometer presents a wider temperature range and was able to capture heating up of the material from room temperature as well as full cooling down.

The heterogeneous exothermic reactions play an essential role in the energy balance and have a significant impact on the temperature profiles, as demonstrated by Figure 13, where the two simulations, with and without oxidation, are compared. Both the plateaux after heating up and cooling down are well captured with the values of recombination coefficient $\gamma_r = 0.6$ ($\gamma_r = 1$ being full recombination). An oxidation probability close to unity is in line with the works of Genge (2016) and Capek & Borovička (2017).

6. Conclusions

We present two experiments carried out in the VKI ICP wind tunnel on AB and OC samples using a methodology to reproduce flight conditions, originally developed for spacecraft applications. At surface temperatures between 2280 and 2360 K we did not observe substantial mass loss of the OC due to evaporation or mechanical removal, although melting and boiling were present. Frothing of the surface appeared to be more heterogeneous for the AB than for the OC.

Exothermic oxidation reactions of iron may play an important role in the surface chemistry. This was first inferred from the change of color of the sample after the experiment but is additionally supported by analysis of the recovered material. Finally, our synthetic model, based on a 1D heat balance in order to match the experimental surface temperature, required a contribution to the chemical heat flux by iron oxidation reactions.

Ionized atoms (Ca II, Mg II, and Fe II) were identified by emission spectroscopy in both cases of AB and OC samples, with the lines of Ca II being the strongest in the range from 350 to 450 nm.

In addition, recorded sodium and potassium emission signals could not be fully assigned to ablation of the test samples because of the use of a cork sample holder, which contaminated the boundary layer with those elements. Ideally, a pure basalt/ chondrite sample in the test shape (hemisphere) is suggested.

For future modeling of such experiments we suggest a comparison with a material code coupled to a flow solver. This

would allow a better comparison of the experimental data, for example, the species evolution in the boundary layer, or the internal thermal response of the test sample if thermocouples are being used inside the sample.

Our experiments, together with petrography and geochemistry of the recovered material presented in an accompanying paper, demonstrate the successful use of a ground-test facility to reproduce the atmospheric entry conditions likely to be encountered by meteoroids. This paves the way for intensified analysis of meteor data by comparing ground-tested materials with collected meteorites and, therefore, may help to better characterize the composition and origin of meteors.

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ORCID iDs

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Decoupling of chemical and isotopic fractionation processes during atmospheric heating of Antarctic micrometeorites

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Oxygen isotope signatures provide important constraints on the precursor body of meteorites and micrometeorites (e.g., Clayton, 1993; Clayton and Mayeda, 1996; Wiechert et al., 2004; Greenwood et al., 2005). Due to their limited size, most micrometeoroids are completely molten as a result of flash melting during their atmospheric entry stage (Love and Brownlee, 1991). Consequently, the primary physical, textural, chemical and isotopic properties of the micrometeorite precursor body are (significantly) altered (e.g., Genge and Grady, 1998; Alexander et al., 2002; Engrand et al., 2005; Taylor et al., 2005; Genge, 2006; Suavet et al., 2010; Cordier et al., 2011a; van Ginneken et al., 2017; Riebe et al., 2020). Oxygen isotopes predominantly experience mass-dependent fractionation processes and frequently incorporate atmospheric oxygen. As such, we require a thorough understanding of the physicochemical parameters controlling oxygen isotope fractionation processes in micrometeoroids in order to identify their precursor bodies. This article presents a new approach to correct for the effects of mass-dependent fractionation processes in micrometeoroids in oisotope compositions. We also investigate whether chemical and isotopic fractionation processes in micrometeorites are correlated.

BS has assisted Seppe Lampe during his Master thesis research, which included processing of the sedimentary deposits; sample acquisition; sample preparation; acquisition of SEM images, major and trace elemental data (LA-ICP-MS), and oxygen isotope data (NanoSIMS, SIMS); and interpretation of the chemical and oxygen isotope dataset.

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1	Decoupling of chemical and isotopic fractionation processes during					
2	atmospheric heating of Antarctic micrometeorites					
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26 Abstract

27 Micrometeorites experience varying degrees of evaporation and mixing with atmospheric oxygen during 28 atmospheric entry. Evaporation due to gas drag heating alters the physicochemical properties of fully 29 melted cosmic spherules (CSs), including the size, chemical and isotopic compositions and is thus 30 expressed in its chemical and isotopic signatures. However, the extent of evaporation and atmospheric 31 mixing in CSs often remains unclear, leading to uncertainties in precursor body identification and 32 statistics. Prior studies have estimated the extent of evaporation based on the contents of major 33 refractory elements Ca and Al in combination with the determined Fe/Si atomic ratios. This chemical 34 classification scheme is now widely adopted but has not yet been integrated to with O and Fe isotopic 35 variability. As evaporation can lead to both chemical and isotopic fractionation, it is important to verify 36 whether the estimated degrees of evaporation based on chemical and isotopic proxies converge. Here, 37 we have analysed the major and trace element compositions of 58 chondritic CSs, along with their Fe 38 isotope ratios. The chemical and isotopic fractionation observed for these particles show no correlation. 39 The interpretation of these results is twofold (i) isotopic and chemical fractionation are governed by 40 distinct processes or (ii) the proxies selected for chemical and isotopic fractionation are inadequate. 41 While the initial Fe isotopic ratios of chondrites are constrained within a relatively narrow range (0.005 42 \pm 0.008‰ δ^{56} Fe), the element concentrations of CSs display larger variability. Cosmic spherules are 43 thus often not chemically representative of their precursor bodies, due to their small size. As oxygen 44 isotopes are commonly used to refine the precursor bodies of meteorites, triple oxygen isotope ratios were measured in thirty-seven of the characterized CSs. Based on the relationship between δ^{18} O and 45 46 δ^{57} Fe, the evaporation effect on the O isotope system can be calculated, which allows for a more precise 47 parent body determination. Via this newly introduced correction method a distinct pattern was 48 recognised in OC CSs, two ECs could be distinguished along with one relatively unfractionated 'Group 4' spherule and one heavily fractionated 'Group 4' CS. This powerful correction advocates for including 49 50 Fe isotope measurements to the regular procedures of CS studies.

51

52 *Keywords:* cosmic spherules, atmospheric entry heating, iron isotope ratios, isotope fractionation, 53 precursor bodies

2

54 **1. Introduction**

55 Annually ~40.000 tonnes of extraterrestrial material accumulates on the Earth, predominantly in the form of micrometeorites (Love and Brownlee, 1993; Zolensky et al., 2006). Micrometeorites are 56 57 extraterrestrial particles in the size range of 10 to 2000 µm that (partially) survived their transit through 58 the atmosphere (Rubin and Grossman, 2010). Their precursors stem from the proximate interplanetary 59 dust cloud, which is mostly composed of asteroidal particles from the Main Asteroid Belt and material 60 from the Jupiter Family Comets (Dermott et al., 1991; Flynn, 1992; Nesvorný et al., 2010). These 61 particles are transported to Earth through Poynting-Robertson drag and in part originate from source 62 reservoirs different from those of macroscopic meteorites (Wyatt and Whipple, 1950; Dermott et al., 63 1991; Flynn, 1992; Kral et al., 2017). Classifications based on oxygen isotope ratios show that at least 64 60% of all micrometeorites in all size fractions are related to more primitive objects, displaying 65 carbonaceous chondritic compositions. Another ~20% of the micrometeoroid complex is fed by evolved 66 asteroids common in the inner asteroid belt, i.e., the ordinary chondrite parent bodies and, subordinately, 67 the howardite-eucrite-diogenite (HED) parent asteroid(s) (Cordier and Folco, 2014). However, these 68 parent body contributions are highly size-dependent, with the relative proportion of ordinary chondrite 69 material in the micrometeorite complex increasing with micrometeorite size and at 250-500 µm the 70 OC/CC relationship approximating 1 (Cordier and Folco, 2014; Goderis et al., 2020). Likely, a continuous 71 relationship exists between the contributions of precursor materials of micrometeorites and macroscopic 72 meteorites, where smaller particles are more often derived from (brittle) carbonaceous chondrites (Flynn 73 et al., 2009; Goderis et al., 2020).

74 Upon entering the Earth's atmosphere, micrometeorites decelerate in a few seconds from velocities of 75 kilometres per second to centimetres per second (Toppani et al., 2001; Genge et al., 2008). Deceleration 76 causes melting and evaporation by pulse heating of the incoming particle, which effectively modify the 77 original texture, chemical composition and isotopic ratios of the micrometeoroids. Particle size, velocity, 78 precursor chemistry, density and entry angle determine the extent of thermal alteration of the 79 micrometeorite during its atmospheric entry (Love and Brownlee, 1991). At low entry angle (~horizontal), 80 low velocity, and limited particle size and density, primary characteristics of the incoming particle are more likely to be preserved (Flynn, 1992; Love and Brownlee, 1993). Consequently, the most pristine 81 82 micrometeorites are often recovered from the smallest size fractions. Cosmic spherules represent those 83 micrometeorites that have completely melted and principally display round morphologies (Genge et al., 84 2008). These particles have often lost their initial textures and a substantial amount of their volatile element contents due to evaporation, while the isotopic ratios of more refractory elements such as Fe, 85 86 Si, and Mg display larger degrees of isotope fractionation (Alexander et al., 2002; Taylor et al., 2005; 87 Engrand et al., 2005). Among CSs, silicate-rich (S-type) CSs are the most abundant form, constituting 88 97% of CSs in collections representative of the flux of micrometeorites to Earth (Taylor et al., 2000; Genge et al., 2008; Rochette et al., 2008; Goderis et al., 2020). According to their guench textures, S-89 90 type cosmic spherules are further subdivided into the porphyritic olivine (PO-type), micro-porphyritic 91 olivine, barred olivine (BO-type), cryptocrystalline (CC-type), vitreous (V-type) and Ca-Al-Ti (CAT) 92 subtypes, reflecting increasingly higher peak temperatures (Taylor and Brownlee, 1991; Taylor et al., 93 2000; Genge et al., 2008; van Ginneken et al., 2017).

Generally considered homogeneous (Genge, 2008), V-type CSs have additionally been divided into 94 95 three chemical subgroups (Cordier et al., 2011a). The 'normal chondritic' spherules, 'CAT-like' spherules and 'high Ca-Al' spherules display a progressive enrichment in the concentrations of the refractory major 96 97 element oxides (including CaO, Al_2O_3 and TiO_2) and refractory trace elements (e.g., Zr and REE; 98 Alexander et al., 2002; Cordier et al., 2011a; Goderis et al., 2020). The gradual enrichment in refractory 99 components relative to volatile and moderately refractory elements in these subgroups has been 100 interpreted to reflect discrete degrees of evaporation and/or separation of high-density phases (e.g., 101 metallic Fe-Ni and sulphide beads, spinel group minerals) during atmospheric entry (Cordier et al., 102 2011a; Goderis et al., 2020). Due to these processes, CSs lose approximately 40-90% of their initial 103 mass during atmospheric entry (Love and Brownlee, 1991; Cordier et al., 2011a). Rounded Fe-Ni beads 104 are formed from immiscible Fe-rich liquids during the melting of CSs. Due to the centrifugal forces in the 105 spinning spherules, these liquids are transported to the outer sides where they can be ejected (Genge 106 and Grady, 1998). Volatile elements such as K, Na and S are lost significantly, while moderately 107 refractory elements such as Fe, Si, Mg, Ni and Cr display distinct evaporation rates (Alexander et al., 108 2002; Engrand et al., 2005). In addition to changes in element concentrations, evaporation can also be 109 traced by a mass-dependent shift of isotope ratios towards heavier values, as previously demonstrated for example for O, Fe, Si, Mg, Ni and Cr (Alexander et al., 2002; Taylor et al., 2005; Engrand et al., 110 111 2005; González De Vega et al., 2020).

112 Extraterrestrial materials are often classified based on their oxygen isotope ratios, as various Solar System and planetary reservoirs display distinct non-mass dependent values of δ^{17} O, inherited from the 113 114 nebular stage. In the case of CSs, the oxygen isotope ratios (17O/16O and 18O/16O) are commonly modified during atmospheric entry through mass-dependent fractionation and mixing with atmospheric 115 oxygen (Clayton et al., 1976; Suavet et al., 2010; Cordier et al., 2011b; Rudraswami et al., 2012; van 116 117 Ginneken et al., 2017). After a particle is guenched and deposited in a sedimentary trap, its oxygen 118 isotope ratios can additionally be modified by alteration processes under Antarctic weathering conditions 119 (Goderis et al., 2020). Despite the isotopic shifts linked to these processes, the oxygen isotope ratios of CSs often enable assignment to a particular parent body or meteorite group (e.g., Suavet et al., 2010; 120 121 Rudraswami et al., 2012; van Ginneken et al., 2017; Goderis et al., 2020).

122 Chondritic meteorites, considered the precursor materials for the majority of micrometeorites, display a 123 narrow δ^{56} Fe isotope range of 0.005 ± 0.008‰ (n=42; Craddock et al., 2013; Barrat et al., 2015; 124 Chernonozhkin et al., 2016). While the ejection of Fe-Ni beads lowers the Fe content of a CS, this 125 process does not significantly influence the isotopic composition of Fe, as metal-silicate isotope fractionation at high temperature is assumed to be generally limited (Taylor et al., 2005). In contrast, 126 127 evaporation during atmospheric passage not only lowers the Fe-content of the precursor but also shifts the Fe isotope ratios to heavier values following a mass-dependent relation (Fig. 1). Advances in mass 128 129 spectrometry over the last few decades allow limited sample sizes to be analyzed at relatively high-130 precision (~0.05‰; 2 SD).

131 This work aims to better constrain the chemical and isotopic fractionation processes that take place 132 during the formation of fully melted micrometeorites and to better constrain the parent bodies from which

- 133 these particles derive. Although complemented by bulk data for CSs of most textural groups, the focus
- here is placed on vitreous CSs because of the absence of potential mineral-dependent analytical
- 135 artefacts CSs because V-type CSs experienced high peak temperatures, which amplifies possible mass-
- 136 dependent isotope fractionation effects.

137 2. Materials and methods

138 All but one (particle number 188-5) of the samples analysed during this study were extracted from the 139 Widerøefjellet 2B deposit collected during the 2012-2013 MICROMETA expedition. The extraction 140 procedure for micrometeorites are described in Goderis et al. (2020). A series of relatively fresh 141 chondritic CSs was selected based on Secondary Electron Microscope Energy-Dispersive X-ray 142 Spectroscopy (SEM-EDS) images and data, acquired using the JEOL JSM IT-300 instrument of the 143 SURF research group at the Vrije Universiteit Brussel (VUB; Fig. 2). Each CS was categorised according 144 to the weathering scale described in van Ginneken et al. (2016) (Supplementary Table EA1). Cosmic 145 spherule 188-5, roughly 200 µm in diameter, was collected within marine sediments during an 146 oceanographic expedition in the Indian Ocean south-west of Australia, at location RC8-52 (41.10S 147 101.42E). The selected micrometeorites were embedded in three epoxy mounts, one ("Mount 1") 148 containing thirteen V-type CSs (WF1202B-0001 up to WF1202B-0048) in the size range of 478-828 149 µm, a second ("Mount 2") holding another twenty-four vitreous CSs (WF1202B-0201 to WF1202B-0224) 150 with a diameter between 208 and 348 µm, and a third ("Mount 3") with nineteen spherules of various 151 textural groups with a diameter of 129-637 µm. Mount 3 contains three PO-type spherules (WF1202B-0226, WF1202B-0227 and WF1202B-0228), four BO-type (WF1202B-0229 - WF1202B-0232) and CC-152 153 type spherules (WF1202B-0233 - WF1202B-0236), six V-type CSs, a single white BO-type (WF1202B-154 0243) and one scoriaceous micrometeorite (WF1202B-0244). The white BO-type CS has a milky-white 155 appearance and barred olivine texture but lacks the high Mg/Si ratio and high Ca, Al and Ti values 156 associated with white barred olivine CAT CSs. Supplementary Table EA1 contains an overview of the 157 measuring techniques that are applied on each CS. The major element concentrations for the particles 158 in Mount 1 have previously been measured relying on a combination of electron microprobe analysis 159 (EMPA) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), while the trace 160 elements have been measured solely with LA-ICP-MS, both are reported in Goderis et al. (2020). The 161 major and trace element concentrations for particles in Mount 2 and 3 were determined using a Teledyne Cetac Analyte G2 laser ablation system in combination with a Thermo Scientific Element XR inductively 162 163 coupled plasma mass-spectrometer at Ghent University, following the procedure outlined in 164 (Chernonozhkin et al., 2021). Following this procedure, precise and accurate major, minor and trace 165 element concentrations were obtained for USGS glass reference materials BCR-2G and BIR-1G. The 166 average bias between reference value and experimentally obtained value is typically <10%. Based on 167 the analyses of the reference materials, the reproducibility for the elements measured is 5-10% relative 168 standard deviation (RSD), depending on the concentration.

169 The oxygen isotope ratios of the particles in Mount 1 were analysed with a NanoSIMS 50L instrument 170 at the Open University (Milton Keynes, UK) according to the procedure outlined in Starkey and Franchi (2013). The 2SD uncertainties are \approx 0.74‰ for δ^{18} O, \approx 1.08‰ for δ^{17} O, and \approx 1.14‰ for Δ^{17} O (Δ^{17} O = 171 172 δ^{17} O - 0.52 * δ^{18} O, which represents the deviation from the TFL; Clayton, 1993). The oxygen isotope 173 ratios of the CSs in Mount 2 were measured using a CAMECA IMS 1270 E7 SIMS at the Centre de 174 Recherches Pétrographiques et Géochimiques (CRPG-CNRS; Nancy, France). For the SIMS measurements, the ${}^{16}O^{-}$, ${}^{17}O^{-}$, and ${}^{18}O^{-}$ ions produced by a Cs⁺ primary ion beam (~15 µm, ~2.5 nA) 175 176 were detected in multi-collection mode using two off-axis Faraday cups (FC) for ¹⁶O⁻ and ¹⁸O⁻ and the

axial FC for ¹⁷O⁻. In order to resolve the ¹⁶OH⁻ interference on the ¹⁷O⁻ peak and to obtain maximum 177 178 flatness on the top of the ¹⁶O⁻ and ¹⁸O⁻ peaks, entrance and exit slits were adjusted to acquire a spectral resolution of \approx 7000 for ¹⁷O⁻ on the central FC. The multicollection FCs were set on slit 1 (MRP = 2500). 179 180 Each micrometeorite was measured three times and each measurement consisted of 275 seconds, 181 including 90 s pre-sputtering. We used three in-house terrestrial standard materials (San Carlos olivine, 182 CLDR01 MORB glass and JV1 diopside) to: (i) define the instrumental mass fractionation line for the 3 183 oxygen isotopes (ii) to correct the instrumental mass fractionation (IMF) due to the matrix effect in samples. The 2SD uncertainties were determined to be \approx 2.25% for δ^{18} O, \approx 1.33% for δ^{17} O, and \approx 184 0.55‰ for Δ^{17} O. 185

186 In-situ Fe isotope ratio measurements of the micrometeorites was performed using a ns-LA-MC-ICP-MS set-up using an Analyte G2 193 nm ArF*excimer-based LA-system (Teledyne Photon Machines 187 188 Inc., Bozeman, MT, USA), equipped with a COBALT ablation cell and ARIS aerosol rapid introduction system (PEEK tubing with 1 mm ø) (Van Malderen et al., 2020), connected to a Thermo Scientific 189 190 Neptune MC-ICP-MS instrument equipped with high-transmission interface and a Pfeiffer (Germany) OnTool[™] Booster 150 dry interface pump (130 m³ h⁻¹ pumping speed) at Ghent University (Ghent, 191 Belgium). Instrumental mass discrimination correction relied on internal doping with a standard solution 192 193 of Ni (500 ng mL⁻¹), continuously aspirated via pneumatic nebulizer and a double pass spray chamber, using a T-piece (5 mm ø) for mixing. The Fe isotope ratios were additionally corrected for potential drift 194 195 by sample-standard bracketing using the United States Geological Survey (USGS) basaltic glass reference material BCR-2G. The BCR-2G reference glass was ablated using a circular spot size of 15 196 197 µm diameter, laser energy density of 1.74 J cm⁻² and a laser repetition rate of 20 Hz. To assure for an adequate correction relative to the reference material, the Fe intensities for the cosmic spherules were 198 199 matched within 5% to those obtained for BCR-2G by adjusting the spot size (10-30 µm) and laser repetition rates (25-45 Hz). Nuclides ⁵³Cr, ⁵⁴Fe, ⁵⁶Fe, ⁵⁷Fe, ⁵⁸Ni and ⁶⁰Ni were measured simultaneously 200 201 in an array of six Faraday cups at medium mass resolution (m/ Δ m ~ 6000). ⁵³Cr was monitored to correct 202 for the potential isobaric interference of ⁵⁴Cr on ⁵⁴Fe, applying the natural abundances of Cr. Further details of the method can be found in González De Vega et al. (2020a). In addition, a set of nineteen 203 204 CSs of different textural and chemical groups were digested in their entirety after LA-ICP-MS for major and trace element characterization. The pure Fe fractions were separated from matrix using anion 205 exchange chromatography and the Fe isotopic compositions were measured using pneumatic 206 207 nebulization (PN-)MC-ICP-MS. The Fe isotope ratios of the CSs are expressed as δ -values relative to IRMM-014 international reference material, with $\delta^{ii}Fe = [(^{i}Fe/^{54}Fe)_{sample}/(^{i}Fe/^{54}Fe)_{reference material} -1] \cdot 1000$ 208 209 (‰) (González de Vega et al., 2020b). Here ⁱFe represents the isotopes of interest i = 56, 57. Based on 210 fifteen measurements in several separate analytical sessions of BCR-2G reference material, the 211 intermediate precision (2SD) is 0.10‰ and 0.14‰ for δ^{56} Fe and δ^{57} Fe, respectively.

212 **3. Results**

213 For the purpose of this study, only chondritic particles were selected based on their distribution in Fe/Mn 214 versus Fe/Mg space (Fig. 3a). This classification is supported by trends observed for CaO + Al₂O₃ versus 215 Fe/Si, and Si/Al versus Mg/Al (Fig. 4), as well as the measured REE patterns (Supplementary Figure 216 EA1; Goodrich and Delaney, 2000; Taylor et al., 2005; Taylor et al., 2007; Cordier et al., 2011a). The 217 CaO + Al₂O₃ vs. Fe/Si plot can be used to subdivide V-type CSs in chemical groups, as the 218 concentrations of refractory major element oxides CaO and Al₂O₃ are appropriate parameters to study 219 the degree of evaporation due to their relatively high condensation temperatures of ca. 50% T_c = 1517220 K (Ca) and 1653 K (Al) (Lodders, 2003). Thirty-nine of the forty-four V-type CSs, along with the three 221 POs, four BOs and CCs and the one scoriaceous spherule, are classified here as part of the normal 222 chondritic subgroup, according to the classification of Cordier et al. (2011a). Spherules WF1202B-0010 223 and 0048 are the only V-types with Fe/Si < 0.06 and CaO + $Al_2O_3 > 5$ wt%, and can thus be designated 224 as 'CAT-like' spherules, although both lack a typical milky-white appearance, as described by Cordier 225 et al. (2011a). In contrast, the white BO-type particle (WF1202B-0243), also classified as 'CAT-like', 226 does display such characteristics. Spherules WF1202B-0001, 0020 and 0217 are classified as 'high Ca-227 Al' spherules (Fe/Si > 0.06 and CaO + Al₂O₃ > 9 wt%). However, two of these, WF1202B-0020 and 228 0217, plot near the boundary between the 'high Ca-Al' and 'normal chondritic' fields (9 wt% CaO + 229 Al₂O₃). Spherule WF1202B-0001 and 0217 both display a pale green colour typical of the 'high Ca-Al' 230 subgroup, while WF1202B-0020 is black. Colourless and completely transparent spherule WF1202B-231 0218 lies close to the triple-junction of the three respective fields but is consistent with a 'normal 232 chondritic' classification. Particle WF1202B-0223, which is part of the 'normal chondritic' group, plots 233 close to the 'normal chondritic'/'high Ca-Al' margin and exhibits intermediate characteristics, such as a 234 pale green colour (Supplementary Table EA3).

235 The δ^{17} O results for all analysed particles range from 0.01‰ to 34.81‰, while the δ^{18} O values vary between 5.90‰ and 64.24‰ and Δ^{17} O values between -5.02‰ and +1.8‰. In Figure 5a, Δ^{17} O values 236 237 are plotted against their corresponding δ^{18} O values for all measured spherules, while the oxygen isotopic 238 dataset is summarized in Table 1. Thirteen CSs plot above the TFL, twenty-one fall below, while two 239 are ambiguous. Ambiguous CSs are those that cannot be assigned to a specific precursor body type 240 within 95% confidence interval. The results of Fe isotope ratio measurements in 56 cosmic spherules 241 using both the ns-LA-MC-ICP-MS and the PN-MC-ICP-MS set-ups (-0.05 \pm 0.04‰ up to 37.01 \pm 0.36‰ δ^{56} Fe, 2SD) greatly exceed the natural Fe isotope fractionations in chondrites (0.005 ± 0.008‰ δ^{56} Fe), 242 and are presented in Table 1 and displayed in Figure 6 (Craddock et al., 2013). The δ^{56} Fe and δ^{57} Fe 243 244 values fall near the terrestrial fractionation line within uncertainty, and no non-mass dependent or 245 nucleosynthetic isotopic effects can be resolved. The δ^{56} Fe values range from -0.05‰ to 37.01‰ and δ^{57} Fe values vary between 0.31‰ and 55.68‰ for vitreous CSs measured by LA-MC-ICP-MS. The data 246 247 for the single scoriaceous micrometeorite overlap with the values compiled for chondrites, with 0.04 \pm 0.06‰ for δ^{56} Fe and 0.06 ± 0.04‰ for δ^{57} Fe (2SD; Table 1). From PO-type (-0.05 ± 0.04‰ to 0.82 ± 248 249 0.04‰, 2SD), BO-type (0.47 \pm 0.04‰ to 1.14 \pm 0.01‰, 2SD), CC-type (-0.04 \pm 0.04‰ to 3.52 \pm 0.04‰, 250 2SD), to V-type CSs (0.17 ± 0.22% to 37.01 ± 0.36%, 2SD), the δ^{56} Fe values increase in line with the 251 increasing peak temperatures suggested for these textural groups (e.g., Taylor et al., 2000). The single

- white barred olivine CS included in this work has a δ^{56} Fe of 11.14 ± 0.05‰ and δ^{57} Fe of 16.88 ± 0.02‰
- 253 (2SD).

254 4. Discussion

255 4.1. Chemical signatures and classification

To confirm the chondritic nature of the CSs studied, first the atomic ratios of Fe/Mn and Fe/Mg are 256 257 compared (Goodrich and Delaney, 2000). Originally used to characterize macroscopic meteorites, this 258 approach can be extended to micrometeorites as well, following a few minor considerations (Taylor et 259 al., 2007). Due to their small appearance, the initial Fe/Mn and Fe/Mg ratios of cosmic spherules can 260 be (slightly) altered by mineralogical biases, evaporation and the ejection of Fe-Ni metal beads. Based 261 on isotopic measurements, Alexander et al. (2002) demonstrated that the evaporation of moderately 262 refractory Mg remains fairly limited. In addition, Taylor et al. (2005) showed that Mn generally behaves 263 as a refractory element, except when evaporation is persistent. In contrast, Fe may be lost through the 264 ejection of Fe-Ni metal beads and/or evaporation and should thus be accounted for. Figure 3a depicts 265 the Fe/Mn and Fe/Mg ratios for the cosmic spherules characterized in this work. On this diagram, the 266 loss of Fe shifts spherules towards the origin. On the other hand, extensive evaporation will shift a 267 particle to the left since Mg is more refractory than Mn. The majority of the spherules plot within or close 268 to the chondritic field, in contrast to stony meteorite types which typically display lower Fe/Mn ratios relative to chondrites (Goodrich and Delaney, 2000; Lodders, 2003). Eight CSs studied here are 269 270 characterized by higher Fe/Mn or lower Fe/Mg ratios compared to those typically observed for 271 chondrites. However, these values can result from (extensive) evaporation of chondritic material. On 272 this plot the white BO-type (WF1202B-0243), along with several V-types, plots close to the origin of the 273 diagram, indicating that considerable Fe was lost through the ejection of (a) metal bead(s). The four BO-274 type CSs and the scoriaceous micrometeorite are positioned away from the origin, indicating that they 275 only experienced relatively small degrees of ejection/evaporation. However, a distinct trend from scoriaceous over PO-type, BO-type and CC-type to vitreous CSs cannot clearly be defined based on 276 277 this diagram.

278 Cordier et al. (2011a) introduced a new classification for V-type CSs, based on their relative degree of 279 evaporation. 'Normal chondritic' spherules are characterized by a variety of different colours based on 280 their Fe content, with lower Fe-contents resulting in higher transparencies (Alexander et al., 2002). These particles have typically lost 40-50% of their mass due to evaporation during atmospheric entry 281 282 heating based on chemical proxies (Cordier et al., 2011a). The 'CAT-like' spherules, not to be confused 283 with CAT spherules, are oblate, colourless to pale green, with low Fe content (Fe/Si < 0.06), high MgO 284 content (Mg/Si > 0.9) and relatively high Ti (Ti/Si ~0.004) and CaO + Al₂O₃ abundances (> 5 wt%). Such particles have lost approximately 50-70% of their mass by evaporation based on the measured chemical 285 286 ratios. 'High Ca-Al' spherules have been defined in Cordier et al. (2011a) as spherules with CaO + Al₂O₃ concentrations > 9 wt%, similar Ti contents as 'CAT-like' spherules, but higher Fe contents (Fe/Si > 287 288 0.06) and lower Mg abundances (Mg/Si < 0.9). These spherules have lost 80-90% of their original mass. 289 Of the 44 vitreous CSs, two belong to the 'CAT-like' group, three are 'high Ca-Al' and the remaining 290 thirty-nine are identified as normal chondritic. Of the particles from the other textural groups, only the 291 white BO-type (WF1202B-0243) micrometeorite is classified as 'high Ca-Al', while all other CSs in this 292 study are identified to be 'normal chondritic'.

293 4.2. Nature of the Fe isotope fractionation process

294 The magnitude of isotope fractionation is positively correlated with the peak temperature experienced 295 by the CS (Alexander et al., 2002). Mass-dependent fractionation can occur in two manners, either as 296 kinetic fractionation or through equilibrium processes (Goderis et al., 2016). Equilibrium fractionation is 297 a quantum mechanical effect caused by the lower zero-point energies and vibrational frequencies of 298 heavier isotopes in a molecule. Equilibrium fractionation takes place when there is chemical equilibrium 299 between two different phases e.g., a fluid melt of a particle and the gaseous atmosphere, or a solid 300 phase and the surrounding melt. It always strives towards a minimal total energy of the system (Young 301 et al., 2002; Schauble, 2007). In contrast, kinetic fractionation occurs due to different reaction rates of 302 isotopes with a different mass (Gussone et al., 2003). Heavier isotopes are generally mobilized by 303 evaporation slower than lighter isotopes, and therefore, a residual particle has heavier isotopic 304 compositions than an initial phase. The latter process is most commonly referred to as the cause of 305 mass-dependent fractionation in CSs (Young et al., 2002; Taylor et al., 2005; Pack et al., 2017). Both 306 equilibrium and kinetic fractionation processes result in a change of isotope ratios based on the masses 307 of the isotopes, but the functional forms of the fractionation laws are slightly but distinctly different (Young 308 et al., 2002). The extreme magnitude of isotope fractionation of Fe in the CS, together with high 309 precisions of the isotope ratios, allows to investigate the nature of the fractionation processes taking 310 place. According to Young et al. (2002), the fractionation exponent β , characterizing the nature of the 311 actual mass-dependent fractionation process (equilibrium or kinetic fractionation), can be calculated as 312 the slope of the linearized three isotope plot in logarithmic scale using $\delta' F$ notations (Equation 1).

313

314 Where ⁱFe represents the abundances of the ⁵⁶Fe or ⁵⁷Fe isotopes. IsoplotR 3.7 offers several options 315 to regress the measured isotopic ratios in the 3-isotope plot taking into account the analytical 316 uncertainties e.g., York algorithm, model-2, and robust regression. The regression algorithm of York assumes that analytical uncertainties are naturally distributed and calculates the weighing factors for 317 318 each point in the 3-isotope plot reversely proportional to its ascribed uncertainty. The algorithm assumes 319 that analytical uncertainty is the only contributor to scatter between the data points. If this assumption is 320 correct, the mean squared weighted deviation (MSWD) will be below 1 (York et al., 2004; Vermeesch, 2018). Due to several data pairs having unrealistically low random uncertainties, the maximum likelihood 321 322 algorithm of line fitting results in a slightly elevated MSWD of 1.7, suggesting that York's algorithm is not 323 an appropriate choice for line fitting in this case. As such, the model-2 and the robust regression fitting algorithms of IsoplotR 3.7 were used instead (Fig. 6), The robust regression algorithm avoids any 324 325 assumption of an uncertainty and calculates the slope as the median of all pairwise slopes (Theil, 1992). 326 with errors calculated according to Rock and Duffy (1986) after Vugrinovich (1981). To avoid weighting 327 the points according to analytical errors, the model-2 algorithm assigns equal weights and zero error-328 correlations to each point, and instead of the analytical uncertainties the 95% confidence-limit uncertainties are calculated from errors including scatter multiplied by student's coverage factor (Ludwig, 329 330 2008). The two latter regression algorithms provide nearly equal regression slopes (1.4850 \pm 0.0053 331 and 1.4913 + 0.011/-0.0052, 95% CI) and MSWD <1. The theoretical fractionation exponents of the 332 kinetic and equilibrium isotope fractionation processes are given in Equations 2a and 2b (Wombacher 333 and Rehkämper, 2003; Audi et al., 2003). As the experimental fractionation exponent is equivalent to

the kinetic constant within the confidence interval, kinetic processes, such as evaporation or diffusion, are the main contributors to extreme isotope fractionation of Fe found in a fraction of the CSs studied here, rather than equilibrium processes, such as metal bead extraction. Despite the large variation in Fe isotope fractionation, the precision of the determined fractionation exponent β does not allow to differentiate between evaporation of atomic Fe or Fe isotopologues, such as FeO (Equation 2c), which is in agreement with the recent findings of Fischer et al. (2021).

340 In nature, kinetic isotope fractionation is known to occur during the processes of 341 evaporation/condensation and diffusion. Although evaporation due to extreme heating during 342 atmospheric entry is the most obvious cause for the isotope fractionation observed, here we evaluate 343 the possibility that a part of the isotope fractionation results from diffusion. While there is no 344 concentration gradient in a (relatively) homogeneous sphere during atmospheric passage to drive 345 chemical diffusion, diffusion can also occur as the result of thermal gradients. The Soret effect is a process in which different ions and isotopes are transported in liquid at different speeds under the force 346 347 of a thermal gradient (Richter et al., 2009a). During atmospheric entry, the outer part of the melted CS 348 experiences frictional heating due to gas drag and is hotter compared to the inner volume. As observed during experimental work, Ti, Mg, Fe and Al will concentrate towards the colder centre, while Si, Na and 349 350 K migrate towards the hotter surface of an initially homogeneous melted spherule (Lesher and Walker, 351 1986). Despite the limited number of experiments in literature, relatively large isotope fractionation 352 effects have been observed as the result of thermal diffusion. The Fe isotopic composition of the hotter end of the basalt sample that was run in a piston cylinder with the temperature gradient of 1410-1520°C 353 354 was found to be significantly isotopically lighter than that of the colder end (Richter et al., 2008; Richter 355 et al., 2009a; Richter et al., 2009b). The thermal fractionation of the Fe isotopes was calculated to be 356 1.1‰ per atomic mass unit per 100 °C of the gradient, and the magnitude of the isotope fractionation is, 357 to a first order, distributed as a linear function of ΔT , nearly independently of the composition of the melt 358 (Huang et al., 2010; Richter, 2011). The thermal gradient of a few hundred K between the inner and 359 outer parts of the spherule can thus correspond to Fe isotope fractionation by several per mille, which 360 is still considerably smaller than the magnitudes of the effects observed in this work. However, if the 361 diffusion in a sub-mm particle can be considered instantaneous, continuous removal of the hotter outer 362 side, where Fe is a few per mille lighter, can hypothetically result in a progressive Rayleigh-like isotope 363 fractionation process that can lead to a significantly heavier Fe isotopic composition of the remaining melt. This process takes place in the same direction as the isotope fractionation by evaporation. At the 364 365 same time, such process would lead to a depletion of the CSs in Na, K, and Si, which is in agreement 366 with the observations. However, the contribution of Soret diffusion to the depletion of volatile elements 367 and the isotope fractionation of Fe relative to thermal evaporation remains unclear, as the thermal 368 parameters of the micrometeorites during the entry are difficult to constrain and require the 369 determination of the isotope ratios of multiple elements at high precision in individual particles, which 370 may require considerable instrumental advances still.

However, it is possible to compare the distinct textural and chemical subgroups based on their δ^{56} Fe values (Table 1, Fig. 7). The average δ^{56} Fe ± 2SD for the scoriaceous (0.04 ± 0.06‰), PO (0.29 ± 0.93‰), BO-type (0.80 ± 0.55‰), CC-type (0.96 ± 3.42‰) and V-type (6.59 ± 16.52‰) textural 374 subgroups indicate an increasing trend from scoriaceous to V-type. The V-type spherules are 375 characterised by a large spread $(0.31 \pm 0.09\%$ to $55.68 \pm 0.22\%)$ in Fe signatures, which is indicated 376 by a large standard deviation, while the median of this subgroup lies at 5.24‰. The 'normal chondritic' subgroup is characterised here by an average δ^{57} Fe ± 2SD of 9.93 ± 13.18‰, the 'high Ca-Al' 16.34 ± 377 378 8.42‰ and the 'CAT-like' 8.21 ± 11.21‰. Based on the measured data set, the expected trend in 379 increasing isotopic fractionation from 'normal chondritic' spherules, over 'CAT-like' spherules to the 380 'high-Ca-Al' subgroup is not observed in our results. If thermal evaporation is the dominant process 381 affecting the Fe isotope signatures of CSs, then these results indicate that the textural subgroups have 382 experienced varying degrees of thermal evaporation, while this not the case for the chemical subgroups. 383 This means that it is not possible to correlate the degrees of chemical and isotopic fractionation as both 384 appear to be unrelated to one another (Fig. 8). As chemical fractionation might be influenced significantly 385 by precursor composition, mineralogical biases, fragmentation, high-density phase expulsion, and secondary alteration, isotopic fractionation may reflect a more representative proxy to estimate the total 386 387 extent of evaporation experienced by the particle than chemical fractionation. At the same time, isotope 388 fractionation depends on factors, such as the initial mineralogy of the micrometeorite, melt composition, redox conditions, etc. to a lesser degree, as evidenced by the extreme magnitudes of isotopic 389 390 signatures.

391 **4.3. Fe loss by evaporation and metal bead ejection**

If the loss of Fe in CSs is dominated by evaporation and metal bead ejection, the respective fractions lost by these processes experienced by a CS upon atmospheric entry can theoretically be calculated (Alexander et al., 2002; Taylor et al., 2005), allowing to reconstruct the original chemical compositions of the particles, which may provide valuable information on the precursor materials. This quantification of Fe loss for a larger set of samples improves our understanding of the relative importance of these distinct processes taking place during atmospheric entry.

Figure 1 depicts two extreme pathways through which a particle with an initial Fe-content and δ^{56} Fe can 398 399 arrive at a final (i.e., the observed) Fe content and δ^{56} Fe. Following metal bead ejection, only the Fe content of a micrometeoroid decreases, while the δ^{56} Fe values of a particle are not altered significantly 400 401 during this process. On the other hand, evaporation lowers the Fe content and increases the δ^{56} Fe 402 values of an incoming micrometeoroid. Because of these effects, the amounts of evaporation and 403 ejection can be calculated according to distinct pathways. Based on the set of equations published in 404 Alexander et al. (2002) and Taylor et al. (2005), it is possible to calculate the amount of Fe that was lost, 405 as well as the hypothetical minimum and maximum amounts of evaporation and ejection that a particle 406 experienced during atmospheric passage. In the case of a fraction of the particles studied here, the 407 results for such calculations remain inconclusive, which can potentially be attributed to the assumption 408 of a CM-like heritage for all spherules in these models. However, the calculations that have proven to 409 be meaningful are summarized in Table 2 and have been used to calculate the initial Fe/Mg vs. Fe/Mn 410 atomic ratios of the CSs (Fig. 4b). Based on these results, CSs appear to have lost between virtually 0 411 and 59% of their initial Fe through evaporation, while between 4 and 99% of their initial iron mass 412 escaped through the ejection of Fe-Ni beads. The fractions of Fe lost by evaporation/ejection calculated using the two extreme pathways are in good agreement when evaporation is limited and the Fe isotope fractionation is small (δ^{56} Fe < ~3‰). When fractionation is high, the modelled pathways can deviate significantly. An independent evaluation of these models is provided by the analysis of O isotope measurements in Chapter 4.4.

417 **4.4. Constraints on CS precursor materials**

- 418 Oxygen isotope ratios are often used to identify precursor bodies of micrometeorites (Taylor et al., 2005; 419 Suavet et al., 2010; Cordier et al., 2011a; Goderis et al., 2020; Rudraswami et al., 2020; Soens et al., 420 2020). In order to determine the corresponding parent body of each micrometeorite, a plot of δ^{17} O versus δ^{18} O, or the more common Δ^{17} O vs. δ^{18} O diagram is used, where Δ^{17} O = δ^{17} O - 0.52 * δ^{18} O represents 421 422 the deviation from the Terrestrial Fractionation Line (TFL; Fig. 5a; Thiemens et al., 1983; Rumble et al., 423 2007). This method is based on the principle that each type of parent body is characterized by a distinct 424 oxygen isotopic signature, inherited from the nebular stage (Clayton et al., 1976; Suavet et al., 2010). 425 Three processes can modify the original oxygen isotopic signature of a micrometeorite, characteristic 426 for the parent body. Firstly, mass-dependent fractionation enriches the particle in the heavier oxygen 427 isotopes, effectively shifting particles to the right on a plot of Δ^{17} O versus δ^{18} O (Suavet et al., 2010). 428 Secondly, mixing with atmospheric oxygen during atmospheric entry shifts the oxygen isotope ratios 429 along the mixing line towards isotopic signatures of the atmosphere ($\delta^{17}O \approx 11.8\%$ and $\delta^{18}O \approx 23.5\%$), 430 which is isotopically homogeneous and is thought not to have changed significantly over the past couple 431 of Myr (Thiemens et al., 1995; Pack et al., 2017; Fischer et al., 2021). Lastly, terrestrial alteration can 432 also influence the original oxygen isotope ratios. Since all spherules selected for this research were 433 extracted from the same sedimentary accumulation trap in the Sør Rondane Mountains (Antarctica), 434 alteration would shift the CS composition to the right of the surrounding meteoric water along the TFL, 435 with an average d18O of roughly -30‰, following the formation of secondary minerals (Goderis et al., 2020). Taking these processes into account, four groups of CSs with distinct oxygen isotopic values 436 437 have been identified (Fig. 5a; Suavet et al., 2010).
- Comparison between the iron (δ^{56} Fe, δ^{57} Fe) and oxygen (δ^{17} O, δ^{18} O) isotope ratios indicates that for 438 439 most spherules a positive correlation exists between the two isotope systems (Fig. 9a). This correlation 440 is mainly influenced by two processes, i.e., mass-dependent fractionation and mixing with atmospheric 441 oxygen. Mass-dependent fractionation will increase both $\delta^{18}O$ and $\delta^{56}Fe$ values, while mixing with 442 atmospheric oxygen only increases the δ^{18} O values. It is important to remark that precursor δ^{18} O values 443 for the different types of chondritic bodies span a broad range from -5% up to +10% (Fig. 9a). However, 444 the majority of chondritic fields has an initial δ^{18} O between 0 and 5‰, which narrows this range down 445 significantly. On Figure 9a, two trends are observed: (i) the first consists of a wide spread of CSs that 446 predominantly experienced mass-dependent fractionation during evaporation, while (ii) the second trend 447 is represented by spherules that are characterized by low δ^{56} Fe values and δ^{18} O of ~12-23‰, indicating that mixing with atmospheric oxygen is the main process modifying the δ^{18} O of these spherules. Of the 448 thirty-six spherules that have both O and Fe isotope ratios measured, only nine exhibit δ^{56} Fe values 449 450 above 9‰. One of those is WF1202B-0207, which presumably has a different initial δ^{18} O value ('Group 4') and was therefore excluded. The remaining eight CSs all define a correlation with δ^{18} O that can be 451

452 used to calculate a correction factor ($R^2 = 0.809$) for mass-dependent isotopic fractionation as the result 453 of evaporation during atmospheric passage, following Equation 3.

454 This correction does not take into account any effects from mixing with atmospheric oxygen or 455 subsequent terrestrial alteration, however, as the CSs are relatively unaltered (Supplementary Table EA1), the latter process can be disregarded. The Δ^{17} O ratio should not be influenced by evaporation 456 and is largely preserved during evaporation. The $\delta^{18}O_{corr}$ is plotted versus $\Delta^{17}O$ in Figure 5b in order to 457 458 improve identification of the parent bodies of the CS. The isotopic ratios of spherule WF1202B-0223 459 (δ^{18} O of ~38‰, Δ^{17} O of ~-0.5‰ and δ^{57} Fe of ~5‰), cannot be explained by the combination of 460 fractionation and mixing, most likely an unknown third process has influenced the isotopic composition 461 of this particle. Of the 36 spherules measure for oxygen isotopes, eleven could not be classified within 462 the 95% certainty interval and were therefore classified as ambiguous, seventeen can be regarded as CC (68% of those classified), four as OC (16%), two as EC (8%) and two as Group 4 (8%) (Table 1; Fig. 463 464 10a), similar distributions have been reported in previous studies (Cordier and Folco, 2014; Goderis et 465 al., 2020). Furthermore, the improved classification allows to classify four of the CC CSs more 466 specifically as fragments from CR chondrites. Prior to this work, one EC unmelted micrometeorite has 467 been identified and the untangling of the CC precursor types has only been done once on unmelted 468 micrometeorites (Suttle et al., 2020). The identification of ECs and the specification of CR-type for CSs 469 is thus novel and demonstrates the effectiveness of the proposed isotopic evaporation correction. The size of the CSs related to CC ranges from 215-764 µm, while the ones related to OCs fall within the 470 471 narrow range of 208-287 µm (Supplementary Table EA2). Figures 5 and 9b visualize the fractionation 472 patterns of ordinary and carbonaceous chondrites. From these diagrams, CCs appear to be more prone 473 to evaporative fractionation during atmospheric entry than OCs. Relative to CCs, OCs plot relatively 474 clustered, close to their original field when compared to CCs.

475 The 'Group 4' cosmic spherules are hypothesised to represent a chondritic parent body not sampled by 476 larger meteorites (Suavet et al., 2010; van Ginneken et al., 2017; Suttle et al., 2020). In our dataset at 477 least one particle (WF1202B-0220) belongs to the 'Group 4' micrometeorites. To further strengthen the 478 hypothesis that this 'Group 4' effectively represents a separate cluster (Fig. 5), the Fe isotopic data of 479 spherules WF1202B-0220 and WF1202B-0207 is discussed here. Spherule WF1202B-0220 has δ^{56} Fe 480 and δ^{57} Fe values of 1.02‰ and 1.61‰, respectively, implying that the chemical and isotopic composition has not been affected significantly by evaporation. Spherule WF1202B-0207 on the other hand shows 481 extremely fractionated Fe isotopes (δ^{56} Fe = 29.14‰ and δ^{57} Fe = 43.23‰), with a δ^{18} O of 64.24‰ relative 482 483 to the average 40-45‰ for 'Group 4'. The corrected δ^{18} O plot (Fig. 5b) shows that this is in fact also a 484 'Group 4' spherule that has undergone extensive evaporation and some mixing with atmospheric 485 oxygen. The presence of both an unfractionated and fractionated particle of this nature confirms that this is a separate group and that it is not e.g., a cluster of fractionated OCs. Figure 3 and Supplementary 486 487 Figure EA1 indicate that these particles are chondritic in nature, which is in correspondence to Suttle et 488 al. (2020).

By studying the fusion crusts of I-type CSs, Clayton et al. (1986) observed that atmospheric mixing induces a ~8‰ shift in δ^{18} O for I-type CSs. Subsequently, this value was applied to correct the effect of 491 atmospheric mixing on δ^{18} O of achondritic CSs (Cordier et al., 2012). Here, we evaluate the use of this 492 correction for chondritic S-type CSs. Based on Figure 10a, it can be observed that all OC CSs have δ^{18} O 493 values of ~13‰, which is ~8‰ more than the fields of their precursor bodies. The CSs from other 494 precursor bodies (CC, EC, and Group 4 particles) do not appear to cluster ~8‰ to the right of their 495 original field, and while more particles plot within or closer to the CC and EC fields following the 496 atmospheric correction, several particles also plot to the left of the CC fields when applying an ~8‰ 497 shift (Fig. 10b). It is worth mentioning that the two EC CSs have similar Δ^{17} O and δ^{18} O values as their 498 precursor bodies before applying an atmospheric correction. Spherules WF1202B-0012, WF1202B-0201 and WF1202B-0214, which are classified as ambiguous and have small positive Δ^{17} O values, have 499 500 a similar δ^{18} O as the OC CSs, and plot within the EC field when corrected for atmospheric mixing. It 501 should be noted however that the larger uncertainties on the Δ^{17} O preclude them from being assigned 502 to either the OC or EC parent bodies. The low number of EC CSs in our dataset along with the lack of 503 literature data prevents any conclusive statements, and further research will need to determine whether 504 EC CSs experience atmospheric mixing or not. Based on our work, at least a fraction of the chondritic 505 materials that enters the Earth's atmosphere (i) did not experience a positive shift in δ^{18} O of ~8‰ due to mixing with atmospheric oxygen, which may be linked to the oxidation state of the precursor body or 506 507 a differential response of the precursor mineralogy to atmospheric heating, (ii) displayed a starting 508 composition to the left of the established meteorite parent bodies, or (iii) experienced a shift to the left 509 due to variable alteration during the terrestrial residence of the CSs (cf. Goderis et al. 2020).

The correction for atmospheric mixing allows to evaluate the theoretical fraction of O which was evaporated (Cordier et al., 2012). This calculated fraction based on O can be compared to that based on Fe (Fig. 11). While the fraction of O that evaporated is systematically larger than that of Fe, which is to be expected as O is more volatile than Fe, these fractions largely co-vary. This co-variation thus largely confirms the validity of the applied equations for calculating the fractions of O and Fe that evaporated, and emphasises the importance of the precursor composition on the degree of evaporation experienced.

517 **Conclusions**

518 The main goal of this work was to gain further insights into the processes affecting micrometeoroids 519 during atmospheric passage. This was achieved through the analysis of the major element composition, 520 combined with iron and oxygen isotopic data. Based on the Fe isotopic data, kinetic fractionation has 521 been identified as the dominant process causing extreme mass-dependent isotopic fractionation in 522 micrometeoroids during atmospheric entry. The origin of this fractionation is likely thermal evaporation, 523 although the Soret effect and continuous ablation of the overheated exterior of the melted spherule might 524 represent an alternative or contributing isotope fractionation mechanism. Mass-dependent isotope 525 fractionation shows an increasing trend from scoriaceous to PO-type over BO-type and CC-type towards 526 V-type, with the latter having δ^{56} Fe between <1‰ to >30‰. The single white BO-type particle analysed here following acid digestion and Fe isolation also displays a relatively high δ^{56} Fe value of ~11‰. 527 528 Furthermore, comparison of chemical fractionation with isotopic fractionation indicates that no substantial correlation between these two processes exists, implying that either both isotopic 529

fractionation and chemical evaporation are largely controlled by different processes, or that chemical fractionation cannot be estimated correctly due to random mineralogical effects on the initial compositions. Based on the particles studied here, evaporation can contribute up to ~60% of the Fe loss, while Fe-Ni-bead ejection during atmospheric entry can vary from no noticeable effect to the entire loss of all Fe from a CS (0-99%).

535 A second goal of this work was to refine the linkage of CSs to their appropriate precursor bodies. Based 536 on Fe/Mn vs. Fe/Mg ratios, all studied micrometeorites studied in this work are chondritic in nature. By studying the oxygen isotope ratios of vitreous CSs on a modified three oxygen isotope plot (Δ^{17} O vs. 537 δ^{18} O), most of the particles could be linked to either an OC (16%) or CC (68%) heritage, in reasonable 538 539 agreement with literature data. Furthermore, four of the CCs could be more precisely identified as CR. 540 However, the classification of several spherules remains ambiguous, due to significant analytical 541 uncertainties. Importantly, the measured Fe isotope ratios combined with oxygen isotope and chemical 542 data confirm that the 'Group 4' CS population, composed of ¹⁶O-depleted spherules represents an actual 543 Solar System reservoir, composing ~8% of the interplanetary dust complex, and cannot result from the 544 alteration of a known precursor group. These spherules are chondritic in nature but their parent body remains unidentified among larger scale meteorites. Also, the combination of Fe and O isotope values 545 546 allows to recognise an EC contribution which makes up ~8% of the particles studied here.

547 By combining the Fe and O isotope ratios with textural information and elemental compositions, the 548 contributions of the various processes leading to chemical and isotopic fractionation can be 549 disentangled. This approach represents a significant step forward in our understanding the effects that 550 take place during atmospheric passage and helps to precisely constrain the nature of micrometeorite 551 parent bodies.

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740 7. Artwork and Tables with Captions

- Figure 1: The effects of evaporation and ejection on the Fe content and δ^{56} Fe of a CS. Note that the two extreme
- pathways result in varying amounts of evaporation and ejection, yet still end up at the same Fe content and δ^{56} Fe.
- 743 This complicates estimating evaporation from δ^{56} Fe, modified after Taylor et al. (2005).



- Figure 2: SEM images (BSE) of four CSs, from left to right and top to bottom, WF1202B-0004, WF1202B-0009,
- 745 WF1202B-0024 and WF1202B-0048. The black holes are remnants from the LA-ICP-MS measurements, while the
- 746 three larger circular structures in the left upper image are vesicles. The spherules do not display evidence for
- 747 *extensive terrestrial weathering.*



Figure 3: (a) The Fe/Mg (atomic) vs. Fe/Mn (atomic) diagram provides an indication of the (non)chondritic nature of extraterrestrial material. Spherules with a high Fe/Mn relative to the chondritic field most likely experienced a high degree of chemical evaporation. Metal bead ejection moves spherules closer to the origin as it only reduces Fe and does not influence Mn or Mg significantly. (b) The Fe/Mg vs. Fe/Mn diagram with corrected Fe values, note that only spherules present in Table 2 have been plotted. Because of their high Fe/Mn ratios WF1202B-0005 (1275), WF1202B-0020 (620), WF1202B-0048 (620) and WF1202B-0215 (756) are not visible on the corrected diagram.



Figure 4: (a) The chemical classification as proposed by Cordier et al. (2011). (b & c) The Si/Al (atomic) versus

755 Mg/AI (atomic) diagram for data from this work and Taylor et al. (2000 & 2005), the pathways are reconstructed

from Alexander et al. (2002).



- Figure 5: Plot of measured Δ^{17} O versus δ^{18} O (a) and same plot after correction for evaporation based on δ^{57} Fe (b).
- These diagrams can be used to (i) determine the relative degree of isotopic fractionation and mixing, and (ii) derive
 the precursor bodies from which the particles derived, modified from Suavet et al. (2010) and Goderis et al. (2020),
 the 'Group' fields are taken from Suavet et al. (2010).





Figure 6: The δ^{56} Fe vs δ^{57} Fe diagram of the CSs mentioned in this work; the slope has been calculated using the

'model-2' method of IsoplotR 3.7. The slope corresponds within uncertainty with the theoretical value for kinetic
isotope fractionation i.e., 1.4881.





Figure 8: Plot of δ^{56} Fe (in ‰) versus CaO + Al₂O₃ (in wt%), with no distinct correlation indicating that these do not

both reflect evaporation. Note that spherule WF1202B-0001 is not visible in this diagram, as it has a CaO + AI_2O_3 of ~50 wt% (and δ^{56} Fe of ~1‰).



- Figure 9: (a) Plot of δ^{56} Fe (in ‰) versus δ^{18} O (in ‰). The spherules in green, with the exception of WF1202B-0207,
- 769 were used to construct the evaporation slope. (b) Diagram of δ^{56} Fe (in ‰) versus Δ^{17} O (in ‰), visualizing the degrees
- of isotopic fractionation experienced by particles of the respective parent bodies. CSs below the TFL generally
- 771 display more fractionated than CSs above the TFL.



- Figure 10: (a) Diagram of Δ^{17} O versus δ^{18} O corrected for evaporation based on δ^{57} Fe, with particles assigned to a
- specific chondrite group (OC, EC, CC, or Group 4), when possible. (b) Diagram of Δ^{17} O versus δ^{18} O corrected for
- evaporation based on δ^{56} Fe and atmospheric mixing. The ~8‰ correction for atmospheric mixing was not applied
- on the Group 4 CSs, as the correction is expected to be in the opposite direction with an unknown magnitude.



Figure 11: (a) The evaporated fraction calculated based on O isotopes versus that based on Fe isotopes. (b) spherule-based comparison of the fractions of Fe and O that evaporated. Only the four OCs and three ambiguous spherules that have a high probability of deriving from OC parent bodies have been considered here as the 'atmospheric correction method' is only largely applicable to OCs.



780 Table 1: The O and Fe isotope ratios of all spherules mentioned in this work, along with their textural and chemical

Sample Name	δ ¹⁸ O ± 2SE (‰)	δ ¹⁸ O _{Corr} (‰)	$\Delta^{17}O \pm 2SE$	δ^{56} Fe ± 2SE	δ ⁵⁷ Fe ± 2SE	Chemical subtype	Parent body	Textural subtype
WF1202B-0001	9.00 ± 0.04	7.89	1.7 ± 0.22	1.23 ± 0.20	1.59 ± 0.18	CAT-like	Amb.	V
WF1202B-0004	10.80 ± 0.76	10.50	-0.1 ± 0.62	0.29 ± 0.06	0.43 ± 0.10	Normal	Amb.	V
WF1202B-0005	32.90 ± 1.14	7.00	-1.9 ± 0.55	24.99 ± 0.32	37.11 ± 0.29	Normal	CC	V
WF1202B-0009	13.20 ± 0.41	8.21	-2.3 ± 0.51	4.76 ± 0.34	7.08 ± 0.14	Normal	CC	V
WF1202B-0010	6.10 ± 0.41	0.71	-3.1 ± 0.64	5.13 ± 0.10	7.67 ± 0.13	High Ca-Al	CC	V
WF1202B-0012	17.30 ± 0.35	13.33	0.1 ± 0.62	3.92 ± 0.10	5.61 ± 0.07	Normal	Amb.	V
WF1202B-0017	17.6 ± 0.61	13.91	-0.8 ± 0.85	3.56 ± 0.22	5.24 ± 0.33	Normal	Amb.	V
WF1202B-0019	23.6 ± 0.68	10.38	-0.9 ± 0.49	12.82 ± 0.06	18.88 ± 0.18	Normal	CC	V
WF1202B-0020	24.0 ± 0.27	9.18	-1.7 ± 0.75	14.16 ± 0.16	21.16 ± 0.23	CAT-like	CC	V
WF1202B-0021	14.7 ± 0.51	14.46	1.8 ± 0.07	0.25 ± 0.16	0.38 ± 0.17	Normal	Amb.	V
WF1202B-0024	n.a.	n.a.	n.a.	3.16 ± 0.18	4.87 ± 0.23	Normal	n.a.	V
WF1202B-0039	13.7 ± 0.42	12.74	-0.6 ± 0.80	0.93 ± 0.08	1.35 ± 0.08	Normal	Amb.	V
WF1202B-0048	15.1 ± 0.33	-2.00	-3.9 ± 0.41	16.38 ± 0.24	24.48 ± 0.22	High Ca-Al	CC	V
WF1202B-0201	16.90 ± 2.72	13.39	0.42 ± 0.55	3.38 ± 0.26	5.02 ± 0.15	Normal	Amb.	V
WF1202B-0202	23.46 ± 7.78	20.46	-0.61 ± 0.69	2.88 ± 0.19	4.28 ± 0.17	Normal	Amb.	V
WF1202B-0203	13.72 ± 1.94	11.73	-1.69 ± 0.24	1.87 ± 0.19	2.85 ± 0.17	Normal	CC	V
WF1202B-0204	20.97 ± 1.82	19.00	0.56 ± 0.24	1.83 ± 0.17	2.83 ± 0.17	Normal	Amb.	V
WF1202B-0205	6.51 ± 0.93	6.30	0.29 ± 0.73	0.17 ± 0.23	0.31 ± 0.13	Normal	EC	V
WF1202B-0206	21.89 ± 3.56	17.31	-1.21 ± 0.54	4.29 ± 0.17	6.56 ± 0.15	Normal	CC	V
WF1202B-0207	64.24 ± 0.47	34.04	1.40 ± 0.48	29.14 ± 0.27	43.23 ± 0.22	Normal	Group 4	V
WF1202B-0208	5.90 ± 0.91	1.68	-3.06 ± 0.25	3.87 ± 0.16	6.04 ± 0.16	Normal	cc	V
WF1202B-0209	21.87 ± 6.08	18.41	-4.10 ± 0.39	3.24 ± 0.23	4.95 ± 0.18	Normal	CC	V
WF1202B-0210	13.49 ± 3.47	12.76	0.62 ± 0.40	0.62 ± 0.15	1.04 ± 0.14	Normal	OC	V
WF1202B-0211	22.64 ± 5.27	5.77	0.26 ± 0.35	16.01 ± 0.26	24.15 ± 0.19	Normal	EC	V
WF1202B-0212	40.95 ± 4.46	2.05	-1.38 ± 0.29	37.01 ± 0.36	55.68 ± 0.31	Normal	CC	V
WF1202B-0213	12.46 ± 1.71	10.80	0.94 ± 0.03	1.62 ± 0.24	2.39 ± 0.11	Normal	OC	V
WF1202B-0214	20.41 ± 2.17	13.55	0.37 ± 0.23	6.49 ± 0.18	9.82 ± 0.21	Normal	Amb.	V
WF1202B-0215	23.13 ± 2.51	7.84	-2.93 ± 0.38	14.51 ± 0.23	21.88 ± 0.24	Normal	CC	V
WF1202B-0216	17.17 ± 0.64	12.90	0.99 ± 0.50	3.96 ± 0.13	6.11 ± 0.20	Normal	OC	V
WF1202B-0217	10.27 ± 2.37	8.95	-2.25 ± 0.21	1.25 ± 0.18	1.89 ± 0.14	CAT-like	CC	V
WF1202B-0218	8.60 ± 1.25	4.83	-1.07 ± 0.32	3.81 ± 0.32	5.40 ± 0.15	Normal	CC	V
WF1202B-0219	14.93 ± 2.13	12.18	-1.35 ± 0.29	2.64 ± 0.19	3.93 ± 0.07	Normal	CC	V
WF1202B-0220	39.50 ± 1.32	38.37	1.32 ± 0.56	1.02 ± 0.2	1.61 ± 0.12	Normal	Group 4	V
WF1202B-0221	17.77 ± 1.72	7.60	-5.02 ± 0.52	9.45 ± 0.15	14.57 ± 0.22	Normal	cc	V
WF1202B-0222	14.08 ± 2.40	10.35	-0.82 ± 0.17	3.52 ± 0.23	5.34 ± 0.19	Normal	CC	V
WF1202B-0223	38.19 ± 0.79	33.62	-0.54 ± 0.51	4.31 ± 0.19	6.54 ± 0.20	Normal	Amb.	V
WF1202B-0224	14.97 ± 3.82	13.31	0.87 ± 0.18	1.56 ± 0.14	2.38 ± 0.14	Normal	OC	V
WF1202B-0226	n.a.	n.a.	n.a.	0.10 ± 0.06	0.17 ± 0.10	Normal	n.a.	PO
WF1202B-0227	n.a.	n.a.	n.a.	-0.05 ± 0.04	-0.08 ± 0.02	Normal	n.a.	PO
WF1202B-0228	n.a.	n.a.	n.a.	0.82 ± 0.04	1.20 ± 0.06	Normal	n.a.	PO
WF1202B-0229	n.a.	n.a.	n.a.	0.85 ± 0.07	1.29 ± 0.17	Normal	n.a.	BO
WF1202B-0230	n.a.	n.a.	n.a.	0.47 ± 0.04	0.68 ± 0.02	Normal	n.a.	BO
WF1202B-0231	n.a.	n.a.	n.a.	0.73 ± 0.06	1.19 ± 0.05	Normal	n.a.	BO
WF1202B-0232	n.a.	n.a.	n.a.	1.14 ± 0.01	1.72 ± 0.04	Normal	n.a.	BO
WF1202B-0233	n.a.	n.a.	n.a.	0.22 ± 0.14	0.30 ± 0.10	Normal	n.a.	CC
WF1202B-0234	n.a.	n.a.	n.a.	-0.04 ± 0.04	-0.07 ± 0.04	Normal	n.a.	CC
WF1202B-0235	n.a.	n.a.	n.a.	0.16 ± 0.07	0.25 ± 0.10	Normal	n.a.	CC
WF1202B-0236	n.a.	n.a.	n.a.	3.52 ± 0.04	5.45 ± 0.05	Normal	n.a.	CC
WF1202B-0237	n.a.	n.a.	n.a.	2.06 ± 0.02	3.06 ± 0.06	Normal	n.a.	V
WF1202B-0238	n.a.	n.a.	n.a.	1.66 ± 0.05	2.46 ± 0.02	Normal	n.a.	V
WF1202B-0239	n.a.	n.a.	n.a.	2.46 ± 0.08	3.88 ± 0.16	Normal	n.a.	V
WF1202B-0240	n.a.	n.a.	n.a.	4.13 ± 0.08	6.17 ± 0.01	Normal	n.a.	V
WF1202B-0241	n.a.	n.a.	n.a.	3.61 ± 0.01	5.65 ± 0.10	Normal	n.a.	V
WF1202B-0242	n.a.	n.a.	n.a.	4.10 ± 0.09	6.10 ± 0.08	Normal	n.a.	V
WF1202B-0243	n.a.	n.a.	n.a.	11.14 ± 0.05	16.88 ± 0.02	High Ca-Al	n.a.	White BO
WF1202B-0244	n.a.	n.a.	n.a.	0.04 ± 0.06	0.06 ± 0.04	Normal	n.a.	Scor.
188-5	n.a.	n.a.	n.a.	21.74 ± 0.16	32.52 ± 0.27	Normal	n.a.	V

Table 2: Evaporation and ablation as calculated with the formulas of Alexander et al. (2002) and Taylor et al. (2005).

^a Fraction of the initial Fe retained in the particle, the Rayleigh evaporation law: $f = (\varphi/1000 * (Y-A) + 1)^{(1/(1/\alpha-1))}$ was

785 implemented to calculate these results. φ equals δ^{57} Fe/(Y-A) with Y the atomic mass of 57 fe and A the atomic mass

786 of 54 Fe. α is 57 Fe/ 54 Fe isotope fractionation factor which equals 1.0274 (Wang et al., 1994).

^b Fraction of the initial Fe retained in the particle, calculated from the measured Fe/AI (mass ratio), assuming the
 initial Fe/AI ratio of CM-chondrite.

789 ^c Fraction of the lost Fe which evaporated (Fe) or was lost via ablation/ejection (Fa) when evaporation precedes

- ablation entirely.
- 791 ^d Fraction of the lost Fe which evaporated or was lost via ablation/ejection when ablation precedes evaporation.

				evaporation precedes ablation		ablation precedes evaporation		
Sample Name	δ ⁵⁷ Fe (‰)	f _{ret} a	f _{ret} b					
				Fe ^c	Fac	Fe ^d	Fa ^d	
WF1202B-0226	0.10	0.99	1.00	0.00	0.38	0.00	0.38	
WF1202B-0233	0.22	0.99	0.99	0.01	0.25	0.01	0.25	
WF1202B-0021	0.25	0.99	0.99	0.01	0.66	0.00	0.67	
WF1202B-0004	0.29	0.98	0.98	0.01	0.77	0.00	0.78	
WF1202B-0205	0.43	0.99	0.99	0.01	0.69	0.00	0.69	
WF1202B-0210	0.69	0.96	0.98	0.02	0.28	0.02	0.29	
WF1202B-0228	0.82	0.96	0.97	0.03	0.32	0.02	0.33	
WF1202B-0039	0.93	0.95	0.95	0.03	0.61	0.01	0.63	
WF1202B-0220	1.06	0.94	0.96	0.04	0.13	0.03	0.14	
WF1202B-0217	1.21	0.93	0.96	0.04	0.81	0.01	0.85	
WF1202B-0001	1.23	0.94	0.94	0.04	0.95	0.00	0.99	
WF1202B-0224	1.56	0.91	0.94	0.06	0.04	0.05	0.04	
WF1202B-0213	1.60	0.91	0.94	0.06	0.36	0.04	0.38	
WF1202B-0238	1.66	0.91	0.94	0.06	0.56	0.02	0.60	
WF1202B-0204	1.77	0.90	0.94	0.06	0.48	0.03	0.51	
WF1202B-0237	2.06	0.89	0.93	0.07	0.59	0.03	0.63	
WF1202B-0239	2.46	0.86	0.91	0.09	0.86	0.00	0.94	
WF1202B-0219	2.66	0.86	0.91	0.09	0.51	0.04	0.56	
WF1202B-0202	2.76	0.85	0.90	0.10	0.12	0.09	0.14	
WF1202B-0024	3.16	0.83	0.84	0.11	0.73	0.02	0.82	
WF1202B-0209	3.26	0.83	0.89	0.11	0.42	0.06	0.48	
WF1202B-0222	3.42	0.82	0.88	0.12	0.40	0.07	0.45	
WF1202B-0236	3.52	0.82	0.88	0.12	0.18	0.10	0.21	
WF1202B-0241	3.61	0.81	0.88	0.12	0.70	0.02	0.80	
WF1202B-0218	3.73	0.82	0.87	0.13	0.78	0.01	0.90	
WF1202B-0012	3.92	0.81	0.82	0.13	0.56	0.05	0.65	
WF1202B-0208	4.02	0.80	0.87	0.13	0.55	0.05	0.63	
WF1202B-0242	4.10	0.80	0.86	0.14	0.60	0.04	0.70	
WF1202B-0240	4.13	0.79	0.86	0.14	0.58	0.04	0.68	
WF1202B-0216	4.26	0.80	0.87	0.13	0.54	0.05	0.62	
WF1202B-0206	4.31	0.78	0.86	0.14	0.48	0.06	0.56	
WF1202B-0223	4.35	0.78	0.85	0.15	0.47	0.07	0.55	
WF1202B-0009	4.76	0.77	0.77	0.16	0.67	0.03	0.80	
WF1202B-0010	5.13	0.75	0.76	0.17	0.81	0.00	0.98	
WF1202B-0214	6.80	0.69	0.79	0.21	0.45	0.09	0.57	
WF1202B-0221	9.43	0.58	0.71	0.29	0.32	0.16	0.45	
WF1202B-0243	11.14	0.53	0.67	0.33	0.65	0.01	0.97	
WF1202B-0019	12.82	0.50	0.51	0.37	0.29	0.20	0.47	
WF1202B-0215	13.90	0.44	0.59	0.41	0.43	0.11	0.73	
WF1202B-0020	14.16	0.46	0.47	0.40	0.50	0.07	0.83	
WF1202B-0211	16.25	0.41	0.56	0.44	0.29	0.21	0.51	
WF1202B-0048	16.38	0.40	0.41	0.45	0.54	0.01	0.98	
188-5	21.74	0.30	0.46	0.54	0.33	0.15	0.73	
WF1202B-0005	24.99	0.26	0.26	0.59	0.36	0.07	0.88	
793 8. Equations

794 Equation 1:
$$\delta'^{i}Fe = 1000 * \ln\left(\frac{{}^{i}Fe}{\sqrt{5^{4}Fe_{sample}}}\right)$$
795 Equation 2a:
$$\beta_{kin} = \frac{\ln({}^{m^{54}}/{}_{m^{56}})}{\ln({}^{m^{54}}/{}_{m^{56}})} = 1.4881$$

796 Equation 2b:
$$\beta_{eq} = \frac{\ln(1/m^{54} - 1/m^{57})}{\ln(1/m^{54} - 1/m^{56})} = 1.4750$$

797 Equation 2c:
$$\beta_{kin,Fe0} = \frac{\ln(m^{54} + m^{16})}{\ln(m^{54} + m^{16})} = 1.4910$$

798 Equation 3:
$$\delta^{18}O_{corr} = \delta^{18}O_{meas} - 1.044 * \delta^{56}Fe_{meas}$$

Evidence for the presence of chondrule- and CAI-derived material in an isotopically anomalous Antarctic micrometeorite

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This article reports on the discovery of a chondrule- and CAI-bearing micrometeorite (particle WF1202A-001) recovered from the WMC. The preservation of complete chondrules within (Antarctic) micrometeorites is exceptionally rare, and thus provides an excellent opportunity to study the effects of atmospheric entry heating on chondrules and micrometeorite precursor particles. Based on the physicochemical and isotopic properties of micrometeorite WF1202A-001, we attempt to reconstruct its atmospheric entry parameters and infer its source region within the Solar System. Furthermore, we attempt to constrain the precursor body of micrometeorite WF1202A-001 using oxygen isotope ratios and discuss the possibility of the micrometeorite population to sample new types of asteroidal or cometary bodies that have currently not been identified in the macroscopic meteorite inventory.

BS is first author of this manuscript and has performed sample acquisition; sample preparation; sample imaging (SEM); acquisition and processing of the major and trace elemental dataset (LA-ICP-MS); acquisition of oxygen isotope data (SIMS); and dataset interpretation.

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Evidence for the presence of chondrule- and CAI-derived material in an isotopically anomalous Antarctic micrometeorite

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Abstract-We report the discovery of a unique, refractory phase-bearing micrometeorite (WF1202A-001) from the Sør Rondane Mountains, East Antarctica. A silicate-rich cosmic spherule (~400 µm) displays a microporphyritic texture containing Ca-Al-rich inclusion (CAI)-derived material (~5-10 area%), including high-Mg forsterite (Fo₉₈₋₉₉) and enstatite (En_{98-99}, Wo_{0-1}) . The micrometeorite also hosts a spherical inclusion (~209 µm), reminiscent of chondrules, displaying a barred olivine texture. Oxygen isotopic compositions of the micrometeorite groundmass ($\delta^{17}O = -3.46_{00}^{\circ}, \delta^{18}O = 10.43_{00}^{\circ}, \Delta^{17}O = -1.96_{00}^{\circ}$) are consistent with a carbonaceous chondrite precursor body. Yet, a relict forsterite grain is characterized by $\delta^{17}O = -45.8\%$, $\delta^{18}O = -43.7\%$, $\Delta^{17}O = -23.1\%$, compatible with CAIs. In contrast, a relict low-Ca pyroxene grain ($\delta^{17}O = -4.96\%$, $\delta^{18}O = -4.32\%$, $\Delta^{17}O = -2.71\%$) presumably represents a first-generation silicate grain that accreted ¹⁸O-rich gas or dust in a transient melting scenario. The spherical inclusion displays anomalous oxygen isotope ratios ($\delta^{17}O$ = $-0.98\%_{00}$, $\delta^{18}O = -2.16\%_{00}$, $\Delta^{17}O = 0.15\%_{00}$, comparable to anhydrous interplanetary dust particles (IDPs) and fragments from Comet 81P/Wild2. Based on its major element geochemistry, the chondrule size, and oxygen isotope systematics, micrometeorite WF1202A-001 likely sampled a carbonaceous chondrite parent body similar to, but distinct from CM, CO, or CV chondrites. This observation may suggest that some carbonaceous chondrite bodies can be linked to comets. The reconstructed atmospheric entry parameters of micrometeorite WF1202A-001 suggest that the precursor particle originated from a lowinclination, low-eccentricity source region, most likely either the main belt asteroids or Jupiter family comets (JFCs).

INTRODUCTION

Chondrules are mm-sized, ferromagnesian objects formed by repeated flash-melting events in the solar nebula (Gooding et al. 1980; Wasson 1993; Hewins 1996; Rubin 2000a). As such, they represent a valuable archive recording the pre-accretionary history of the solar nebula. Various models have previously been proposed to explain chondrule formation, including gamma-ray bursts (McBreen and Hanlon 1999); nebular shock waves (Ciesla and Hood 2002; Desch and Connolly 2002); planetesimal collisions and impacts (Sanders and Scott 2012; Johnson et al. 2015); or, more recently, radiative heating from molten planetesimals or planetary bodies (Herbst and Greenwood 2016), but none are currently able to fully explain chondrule characteristics. A better understanding of chondrule formation is critical to understand the evolution of the solar system, as chondrules may have played a pivotal role in the development of planetary bodies.

Within chondritic meteorites, chondrules represent one of the three main constituents (up to 80 vol%). along with refractory inclusions (up to 13 vol%), such as CAIs and amoeboid olivine aggregates, and a finegrained matrix or groundmass (up to 100 vol%). Chondrules display igneous textures, which are commonly subdivided into porphyritic and nonporphyritic subtypes (Gooding et al. 1978). Chondrule textures are mainly determined by two parameters, that physical (e.g., size) and mineralogical is. the characteristics of the precursor material, and second, their subsequent cooling rate from a molten precursor droplet (Lofgren and Russell 1986). For instance, porphyritic chondrules reflect incomplete melting, allowing residual crystals to act as nucleation points for the development of secondary olivine and/or pyroxene crystals (Lofgren 1996; Connolly and Love 1998). These textures have previously been reproduced and verified by numerous lab experiments (e.g., Hewins and Connolly 1996; Lofgren 1996). In contrast, nonporphyritic chondrules display quench textures. including barred olivine, cryptocrystalline, or radial pyroxene patterns. These textures are developed when the precursor material is superheated above the liquidus, destroying all primary crystal nuclei, and subsequently cooled down at highly variable cooling rates (e.g., Connolly and Hewins 1995; Desch and Connolly 2002). Overall, porphyritic chondrules tend to vastly outnumber nonporphyritic subtypes, especially in carbonaceous chondrites (Scott 1988; Kallemeyn et al. 1994; Rubin 2000b; Weisberg et al. 2001; -see also Table 1).

Chondrule fragments have previously been observed in micrometeorites, extraterrestrial dust particles ranging between 10 and 2000 µm in size (Rubin and Grossman 2010; Folco and Cordier 2015), albeit in lower abundances compared to their larger counterpart (e.g., <0.5% in the South Pole Water Well collection—Taylor et al. 2012). As a result, Engrand and Maurette (1998) proposed that micrometeorites may primarily sample a distinct population of "chondrites without chondrules," for example, derived from CI chondrites or another type of chondrule-poor and otherwise unknown extraterrestrial material. According to Genge et al. (2005), this would imply that either (1) meteorites recovered on Earth represent a minor fraction of the supposedly predominant chondrule-poor main belt asteroids, (2) micrometeorites form a strongly biased Table 1. Average chondrule diameter size (μ m) in chondritic meteorites. Note that chondrules may vary in size considerably within different types of chondritic meteorites and that average chondrule sizes are not necessarily representative for specific meteorites. Values reproduced from Scott et al. (1996), McSween (1977), Weisberg et al. (1996, 2001), Grossman et al. (1988), Kallemeyn et al. (1994), Scott (1988), and Rubin (2000b). The "–" symbol indicates the absence of chondrules in CI chondrites and textural data for chondrules in K chondrites.

		Average	
		diameter	Texture (%por.
Class	Type	(µm)	versus %nonpor.)
Spherical inclusion (WF1202A-001)		209	Barred olivine
Carbonaceous	CI	_	_
	CM	300	95 – 5
	CO	150	95 – 5
	CR	700	96(98) - 4(2)
	CH	20	20 - 80
	CB	100 - 20.000	1 – 99
	CV	1000	94 - 6
	CK	800	99 – 1
Ordinary	Н	300	84 - 16
	L	500	
	LL	600	
Enstatite	EH	200	82 - 18
	EL	600	87 – 13
Other	Κ	600	_
	R	400	92 - 8

representation of main belt asteroids and sample parent bodies different from meteorites, or (3) micrometeorites mainly sample cometary bodies (and assumes that comets contain fewer chondrules than asteroids). To differentiate between these possibilities, Genge et al. (2005) and Genge (2006) examined eight coarse-grained and composite (i.e., containing both coarse- and finegrained components) unmelted micrometeorites, which contained (spherical) igneous objects reminiscent of chondrules based on their textural and geochemical properties. The authors concluded that the fine-grained matrix in composite unmelted micrometeorites was most similar to fine-grained unmelted micrometeorites, previously linked to primitive carbonaceous chondrites such as CI, CR, and CM chondrites (Kurat et al. 1994; Genge et al. 1997; Engrand and Maurette 1998). Hence, at least a fraction of the coarse-grained and composite unmelted micrometeorites contain chondrule fragments and can be directly linked to primitive, chondrulebearing carbonaceous chondrites, demonstrating their presence in the micrometeorite record.

Recent studies have reached similar conclusions (e.g., Taylor et al. 2008; Van Ginneken et al. 2012; Reshma et al. 2013), while others have argued that JFCs may contribute significantly to the chondrulebearing micrometeorite population (e.g., Taylor et al. 2012; Suttle et al. 2019a). Dynamical models studying the source bodies of the Zodiacal cloud support a cometary contribution to the micrometeorite source. with possibly up to 85% of the cosmic dust flux to Earth originating from JFCs (Nesvorný et al. 2010). Consequently, micrometeorites appear to sample various types of chondrule-bearing and -free extraterrestrial material that may be (un)known to the meteorite inventory.

Whole or complete chondrules are rare within the micrometeorite record and have only been described in a few instances (e.g., Genge et al. 2005; Genge 2006; Van Ginneken et al. 2012; Suttle et al. 2020; Dionnet et al. 2020). This scarcity can mainly be attributed to the physicochemical properties of chondrules during collisional events and aqueous alteration processes on the parent bodies of micrometeorites, and to the poor preservation potential of chondrules during atmospheric entry heating (see Discussion).

Oxygen isotope ratios may further assist in the identification of micrometeorite precursor bodies and have previously revealed a large discrepancy in the relative contributions from specific meteorite groups (Engrand et al. 2005; Taylor et al. 2005; Yada et al. 2005; Suavet et al. 2010; Cordier et al. 2011, 2012; Cordier and Folco 2014; Van Ginneken et al. 2017; Suttle et al. 2020). For instance, carbonaceous chondrites represent a major component of the micrometeorite population (~60% versus 3% in meteorites), while the abundance of ordinary chondrites is far more limited (~20% versus 72% in meteorites) for particles in the 50–2300 um size fraction. Shock recovery experiments conducted by Tomeoka et al. (2003) demonstrated that hydrated asteroids are more prone to produce dust particles as a result of explosive decompression in phyllosilicates during shock events. Flynn et al. (2009) confirmed the importance of water in hydrated asteroids during collisional events, but concluded that the preferential breakdown of hydrated asteroids is predominantly determined by their mechanical properties (e.g., friability). Carbonaceous chondrites, including the CM, CI, and CR chondrites, thus appear to produce the highest concentration of small (<300 µm) dust particles. Recently, Genge et al. (2017) demonstrated that the majority of igneous rims in scoriaceous and unmelted micrometeorites contained phyllosilicates prior to atmospheric entry. This would suggest that the explosive decompression of

phyllosilicates in the parent asteroids of micrometeorites is negligible and mostly controlled by mechanical disintegration.

Here, we study the Antarctic micrometeorite WF1202A-001, which hosts a unique, complete spherical inclusion, reminiscent of chondrules, that survived both atmospheric entry and subsequent terrestrial alteration. The potential chondrule and surrounding micrometeorite groundmass have been characterized using petrography, geochemistry, and oxygen isotope ratios to constrain the nature of its precursor body. The degree of atmospheric entry heating in micrometeorite WF1202A-001 was estimated and used to constrain its entry parameters and source region within the solar system. This information is used refine our general understanding to of the micrometeorite population in an attempt to identify the variety of parent bodies present within the solar system.

METHODS

Following the discovery of micrometeorites and -tektites in sedimentary traps from the Transantarctic Mountains (Folco et al. 2008; Rochette et al. 2008), the ioint Belgian-Japanese MICROMETA expedition (2012-2013) sampled similar types of sedimentary deposits from a different region on the Antarctic continent, that is, the Sør Rondane Mountains in Drønning Maud Land of East Antarctica (Goderis et al. 2020; Fig. 1). Material was extracted from a series of weathering pits, exposed cracks, and fissured surfaces within a predominant meta-tonalitic host rock (Kojima and Shiraishi 1986; Kamei et al. 2013). The Antarctic environment has proven to be beneficial toward the preservation of meteoritic material due to the (1) cold and dry climate, (2) prolonged accumulation ages (up to several Ma), and (3) absence of anthropogenic contamination. Although weathering conditions vary significantly among the different types of micrometeorite deposits (Van Ginneken et al. 2016), the Sør Rondane Mountain collection appears to be relatively unbiased when compared to other Antarctic collections, including the well-preserved South Pole Water Well collection, and is thus representative of the contemporary cosmic dust flux to Earth (Taylor et al. 2000, 2007; Suavet et al. 2011; Goderis et al. 2020). Based on cosmogenic nuclide dating of granitoid basement rocks from the Walnumfjellet mountain summit, the Sør Rondane Mountains have been deglaciated and exposed to atmospheric fallout, including volcanic ash, microtektites, and cosmic dust, for a time span of ~1-3 Ma (Suganuma et al. 2014), vielding a large, new collection of impact- or extraterrestrial-related materials.



Fig. 1. Detailed map of the Sør Rondane Mountains, indicating the Widerøefjellet sampling site (star symbol) from which micrometeorite WF1202A-001 was extracted. The top left image shows the location of the Sør Rondane Mountains on the Antarctic continent. The abbreviations "DF" and "DC" stand for the Japanese Dome Fuji and French-Italian EPICA Dome C, respectively. (Color figure can be viewed at wileyonlinelibrary.com.)

About 400 g of sedimentary deposits from Widerøefjellet sample site "2A" that was <3000 µm in size was weighed and sieved into six size fractions ranging from $<125 \mu m$ up to $>2000 \mu m$ using ultra-pure water to remove the excess of silt and clay particles. The deposit was subsequently placed into a drying oven for approximately 12 h at a constant temperature of ~60°C. The magnetic fraction was extracted from the bulk size fractions using a simple hand magnet. This procedure was repeated until most magnetic particles were extracted. Finally, micrometeorites were handpicked from both the magnetic and nonmagnetic size fractions using a binocular microscope. Particles were imaged using a JEOL JSM IT-300 scanning electron microscope (SEM), coupled to an Oxford energy-dispersive spectrometer (EDS) at the SURF research unit of the Vrije Universiteit Brussels, Belgium. Following this session, 35 micrometeorites were selected for embedding in epoxy resin based on preliminary SEM-EDS analyses and polished for further analysis. During this stage, we observed the anomalous, spherical inclusion in micrometeorite WF1202A-001, which is characterized and discussed in the current study.

Major and minor elemental compositions were determined using a JEOL JXA-8200 electron probe micro analyzer (EPMA) at the National Institute of Polar Research (Tokyo, Japan) on the embedded and polished micrometeorite WF1202A-001 (Fig. 2). Coreto-rim profiles were acquired for the spherical inclusion (SI), a relict olivine (Ol1), and low-Ca pyroxene grain (Px1), while individual point analyses were performed on metal (M) and sulfide phases (S), and the glassy



Fig. 2. Sectioned backscatter electron images (BSE) of micrometeorite WF1202A-001, including the spherical inclusion. Large olivine (Ol) and low-Ca pyroxene (Px) grains, and high-density mineral phases including Fe-Ni alloys (M1-3) and sulfides (S1-2) are also present. The left image (A) shows a cluster of chromite/Cr-rich spinel (Cr1-2) grains within the spherical inclusion that surrounds a circular depression. The FeO-rich (Fo₆₃) olivine crystals within the spherical inclusion appear to radiate from this particular depression (B). The right image (C) shows the approximate location of EPMA profiles (dashed line) acquired within the spherical inclusion, and a coarse-grained olivine (Ol1) and low-Ca pyroxene (Px1) grain. Scale bar is 100 μ m. (Color figure can be viewed at wileyonlinelibrary.com.)

micrometeorite groundmass (GM). All analyses were carried out using a 15 kV accelerating voltage and a focused beam with a diameter of less than 1 µm. The spherical inclusion, relict olivine, and low-Ca pyroxene grain were analyzed using a 30 nA beam current while monitoring the elements Na, Mg, Al, Si, P, Ca, Ti, Cr, Mn, Fe, Ni, and Zn. Sulfide and metal phases were also analyzed using a 30 nA beam current while monitoring Mg, Si, P, S, Cr, Fe, Co, Ni, and Cu. The glassy micrometeorite groundmass was analyzed using a 10 nA beam current while monitoring Na, Mg, Al, Si, P, K, Ca, Ti, Cr, Mn, and Fe. Counting times range from 10 to 100 s on peaks for each mineral. Correction procedures are based on the ZAF method. Natural and synthetic silicates, oxides, and metals with well-known chemical compositions were used as standards (see Haba et al. [2017] for an overview).

The major and trace elemental (57 in total) compositions were also determined using a Teledyne Cetac Technologies Analyte G2 excimer-based laser ablation system coupled to a Thermo Scientific Element XR double-focusing sector field inductively coupled plasma mass spectrometer (LA-ICP-MS) at the Atomic and Mass Spectrometry (A&MS) unit of the Department of Chemistry (Ghent University, Belgium). Two replicate analyses using a beam size of 35 μ m were performed on both the spherical inclusion and the groundmass. Additional details regarding the LA-ICP-MS procedures can be found in Das Gupta et al. (2017).

Oxygen isotope ratios were determined using a Cameca IMS 1270 secondary ion mass spectrometer (SIMS) at the Centre de Recherches Pétrografiques et Géochimiques (CRPG - Université de Lorraine, France). The particle was analyzed using a Cs^+ ion beam with a spot size of approximately 15 µm and a beam current of ~2.5 nA. Samples were positioned at a physical angle of 10-15° relative to the incoming ion beam. The ions of the three isotopes of oxygen $({}^{16}O^{-},$ ¹⁷O⁻, and ¹⁸O⁻) were monitored simultaneously in multicollection mode using Faraday cups. Particles were analyzed for 275 s, pre-sputtering included. Three reference materials-basaltic glass CLDR01, diopside JV1, and Cody Shale SCo1-were analyzed five times at the start and end of each session to compensate for instrumental mass fractionation effects. Based on repeated analysis of the selected reference materials, the analytical uncertainties for the sessions are $\pm 0.55\%$ (2SE) for δ^{17} O, ~±0.53% (2SE) for δ^{18} O, and ~±0.62% (2SE) for Δ^{17} O, where SE is the standard error calculated based on a total of 61 sample analyses.

RESULTS

Petrography

Particle WF1202A-001 is a $394x358 \mu m$, silicatedominated (S-type) cosmic spherule with a microporphyritic texture, following the classification system of Genge et al. (2008; Fig. 2). This micrometeorite has an asymmetric shape with a smooth rounded margin along most of the particle exterior. This surface is truncated by a subangular, irregular-shaped edge along one side (Fig. 2A,B). As observed in a deeper section (Fig. 2C), the irregular shape arises from the partial detachment of a portion of the micrometeorite, which is almost completely separated from the main mass as the result of a chain of vesicles up to 150 μ m in diameter.

The internal mineralogy of micrometeorite WF1202A-001 is composed primarily of <10 µm olivine micro-phenocrysts (Fo₈₀₋₈₄) and magnetite crystallites suspended within a glassy, Si-Fe-Al-Ca-enriched groundmass. However, several larger (>30 µm) anhydrous silicates are also present. They have strongly Mg-enriched compositions, angular morphologies, and are cut across by internal fractures (Fig. 3). These Mgrich silicates include both olivine (Fo₉₈₋₉₉) and low-Ca pyroxene (En_{98-99} , Wo_{0-1}) grains—the former display normally zoned profiles, while the latter are overgrown by an FeO-rich (Fo₆₆) olivine mantle. Accessory highdensity mineral phases (up to several tens of micrometer in size) are identified as Fe-Ni sulfides. Within the micrometeorite, a large spherical inclusion with an apparent average diameter of ~209 μ m (220 \times 197 μ m, ellipticity: $\varepsilon = 1.12$ —determined from Fig. 2C), as observed in 2-D section view (the maximum diameter is likely slightly larger), is present. The spherical inclusion has a milky white color when viewed with a binocular microscope. The boundary between the host particle and the spherical inclusion is represented by a sharp, well-defined contact, while the micrometeorite's local groundmass adjacent to the inclusion contains tens of micron-sized olivine and oxide mineral phases (Fig. 4). In contrast to the groundmass, the spherical inclusion is primarily composed of FeO-rich olivine (Fo₆₆) crystals up to 10 µm in diameter arranged in a barred olivine texture and embedded in a mesostasis glass. predominantly composed of Si, Fe, Ca, and Al. The fayalitic olivine is characterized by subtle profiles displaying normal zoning and radiate outward from a circular region within the spherical inclusion. This region contains tens of small (up to 10 µm) Cr-rich spinel grains (Fig. 2B; Table 2). Small, rounded Fe-Ni metal grains are also observed within the spherical inclusion and reach up to 10 µm in size. In addition, a series of circular/elliptical voids and microscopic oxide grains, presumably consisting of magnetite, appear to be present along the inclusion's margin (Fig. 2C).

Geochemistry

The groundmass is characterized by a highly variable major elemental composition, reflecting



Fig. 3. Backscatter electron images of internal fractures (arrows) in relict olivine crystals. The latter can be distinguished from neo-formed crystals due to their higher MgO content (characterized by their low Z-contrast in BSE) and anhedral, subrounded shapes. Abbreviations: Ol—olivine, Ox—oxide. (Color figure can be viewed at wileyonlinelibrary.com.)

different proportions of glassy mesostasis (e.g., Al₂O₃ ~7-10 wt%, FeO ~19-29 wt%, MgO ~2-12 wt%, SiO2 ~47-53 wt%) and olivine micro-phenocrysts (e.g., Al₂O₃ ~0.78 wt%, FeO ~15 wt%, MgO ~41 wt%, SiO₂ ~42 wt %), captured in each broad-beam analysis. The EPMA spot analysis mainly sampled the glassy mesostasis, which is predominantly composed of Si, Al, Fe, and Ca, and depleted in Mg compared to the olivine microphenocrysts (Table 3). In contrast, the larger LA-ICP-MS spot analyses sampled a mixture of both components and indicate an overall chondritic signature for the major elemental components (within a factor of 0.5-1.4 times CI chondrite), except for Na and K (Fig. 5; Table 3 and 4). The REE pattern is broadly flat with respect to CI chondrite values (Fig. 6; McDonough and Sun 1995). In an Fe/Mg versus Fe/ Mn diagram (Fig. 7A), the micrometeorite groundmass plots at the edge of the chondritic field. The Mg/Al versus Si/Al ratios support the chondritic nature of the micrometeorite groundmass, displaying similar compositions as the groundmass observed in CM, CI, and CV chondrites (Fig. 7B).

A series of EPMA line transects were conducted on the larger phases within particle WF1202A-001. These include one of the relict MgO-rich olivines (Ol1—Fig. 8) and pyroxene grains (Px1—Fig. 9), as well as the spherical inclusion (Fig. 10). The bulk EPMA data of the spherical inclusion are summarized in Fig. 11. Magnesium-rich olivine grain Ol1 has a core composition (represented by position O1–O10 in Fig. 8, see Data S1 in supporting information) averaging an Mg# of 98 (Mg#=Mg/[Mg + Fe]*100, in at%). This



Fig. 4. Backscatter electron images of the transition (dashed line) between the spherical inclusion and the groundmass (arrows). The transition is sharp, with neo-formed olivine and magnetite crystals nucleating at the rim of the chondrule. (Color figure can be viewed at wileyonlinelibrary.com.)

Table 2. Major and minor elemental concentrations (wt%) of Cr-rich spinel/chromite phases in the spherical inclusion (see Fig. 2A) determined with SEM-EDS.

Analysis no.	Fe	0	Cr	Mg	Al	Si	Mn	Ca	Ti	Ni	V	Total
Cr1	33.7	31.5	18.8	6.0	5.0	3.8	0.5	0.2	0.2	0.2	0.1	100
Cr2	36.1	31.4	16.0	7.1	3.3	4.9	0.4	0.3	0.2	0.2	n.d.	99.9

Table 3. Major and minor elemental oxide abundances (wt%) in the micrometeorite groundmass according to individual EPMA spot analyses. No average compositions were calculated due to the highly heterogeneous nature of the groundmass, consisting of olivine phenocrysts, magnetite, and glassy mesostasis. The heterogeneity observed can be attributed to the local occurrence of different proportions of the aforementioned components.

Analysis no.	Na ₂ O	Al_2O_3	K ₂ O	FeO ^a	TiO_2	MnO	MgO	SiO_2	Cr ₂ O ₃	CaO	NiO	P_2O_5	Total
Limit of detection (LOD)	0.007	0.01	0.01	0.01	0.04	0.03	0.01	0.02	0.02	0.01	0.04	0.02	
GM1	0.11	8.82	<lod< td=""><td>23.8</td><td>0.41</td><td>0.72</td><td>4.16</td><td>51.3</td><td>0.08</td><td>8.00</td><td><lod< td=""><td>0.36</td><td>97.7</td></lod<></td></lod<>	23.8	0.41	0.72	4.16	51.3	0.08	8.00	<lod< td=""><td>0.36</td><td>97.7</td></lod<>	0.36	97.7
GM2	<lod< td=""><td>0.78</td><td><lod< td=""><td>15.3</td><td>0.04</td><td>0.35</td><td>40.7</td><td>41.6</td><td>0.20</td><td>0.69</td><td>0.15</td><td>0.28</td><td>100.1</td></lod<></td></lod<>	0.78	<lod< td=""><td>15.3</td><td>0.04</td><td>0.35</td><td>40.7</td><td>41.6</td><td>0.20</td><td>0.69</td><td>0.15</td><td>0.28</td><td>100.1</td></lod<>	15.3	0.04	0.35	40.7	41.6	0.20	0.69	0.15	0.28	100.1
GM3	0.12	9.75	0.02	28.6	0.43	0.55	2.35	48.1	0.22	7.91	<lod< td=""><td>0.46</td><td>98.5</td></lod<>	0.46	98.5
GM4	<lod< td=""><td>8.76</td><td><lod< td=""><td>28.2</td><td>0.26</td><td>0.54</td><td>2.72</td><td>47.0</td><td>0.04</td><td>9.67</td><td><lod< td=""><td>0.66</td><td>97.8</td></lod<></td></lod<></td></lod<>	8.76	<lod< td=""><td>28.2</td><td>0.26</td><td>0.54</td><td>2.72</td><td>47.0</td><td>0.04</td><td>9.67</td><td><lod< td=""><td>0.66</td><td>97.8</td></lod<></td></lod<>	28.2	0.26	0.54	2.72	47.0	0.04	9.67	<lod< td=""><td>0.66</td><td>97.8</td></lod<>	0.66	97.8
GM5	0.23	7.56	0.02	18.9	0.34	0.71	11.9	52.3	0.05	6.49	<lod< td=""><td>0.40</td><td>99.0</td></lod<>	0.40	99.0

^aAll iron expressed as FeO.

value progressively decreases through the rim toward a final FeO-rich composition with an Mg# of 58. The core displays low Cr_2O_3 (0.31–0.39 wt%), CaO (0.19–0.33 wt%), ZnO (<0.04 wt%—not shown in Fig. 8) and TiO₂ (<0.02–0.04 wt%—not shown in Fig. 8) contents. In contrast, the rim shows a corresponding increase in MnO (0.05–0.35 wt%), NiO (0.05–0.30 wt%), and P₂O₅ (0.02–0.16 wt%) contents concurrent with the higher FeO concentrations.

A similar profile is observed for the large relict low-Ca pyroxene crystal (Px1; Fig. 2C), for which the core (P1–P10, Fig. 9 and see Data S2 in supporting information) concurs with the Mg endmember, with an Mg# of ~99 and minimal Al_2O_3 (<0.04 wt%), MnO (<0.07 wt%), P_2O_5 (<0.03 wt%—not shown in Fig. 9), CaO (<0.05 wt%), TiO₂ (<0.02 wt%—not shown in Fig. 9), and NiO (<0.05 wt%) contents, but with a markedly higher Cr_2O_3 level (0.56–0.80 wt%). A sharp change in SiO₂ content marks a sudden transition from the core to the rim of the grain (P11–P15) and corresponds to an overgrowth by FeO-rich olivine (Fo₆₆). The Na₂O concentrations (not shown in Fig. 9) progressively decrease from the core to rim following a linear trend that is distinct from what is observed for all other elements.

The spherical inclusion has a heterogeneous major and minor elemental composition, with significant geochemical variations on a micrometer-length scale (Fig. 10). Within the inclusion, the Cr_2O_3 concentration is relatively constant at an average of 0.45 wt% and increases only at the rim to a value of ~16.4 wt%, presumably related to the presence of Cr-rich spinel



Fig. 5. Major and minor lithophile elemental pattern determined by LA-ICP-MS and normalized to CI chondrites (McDonough and Sun 1995) and Mg. The dashed lines represent individual measurements acquired on the micrometeorite groundmass, while the full line represents the mean value of both. While the micrometeorite groundmass is overall chondritic, it does not appear to match a specific chondrite group, positioned within the compositional ranges observed for both carbonaceous and noncarbonaceous chondrites, with the exception of the volatile elements Na and K. Reference values for carbonaceous and non-carbonaceous chondrites used are from Kallemeyn and Wasson (1981, 1982, 1985) and Kallemeyn et al. (1978, 1989, 1991, 1994, 1996). (Color figure can be viewed at wileyonlinelibrary.com.)

phases. Less marked enrichments at the inclusion's rim are also observed for TiO₂ (0.45 wt%-not shown in Fig. 10), Al₂O₃ (6.96 wt%), and NiO (0.17 wt%), although the concentrations of these elements display minor variation within the core of the inclusion only (<0.02-0.16 wt%, 0.05-2.92 wt%, and <0.04-0.06 wt%, respectively). By contrast, SiO₂ exhibits a large compositional range (37.8–50.5 wt%), locally increasing up to ~50 wt%, but decreasing to ~25 wt% at the inclusion rim. Similarly, the FeO, MgO, and CaO smaller to moderately contents display large compositional ranges (~26-30 wt%, ~15-35 wt%, $\sim 0.10-3$ wt%, respectively) and display no clear spatial relationship between the core and rim. In contrast, their variations correspond to differences in the proportion of crystals and matrix, as demonstrated by local correlated enrichments in Na₂O, Al₂O₃, TiO₂, SiO₂, and P₂O₅ (primarily in the glass phase) and corresponding depletions in FeO and MgO (primarily in the olivine phenocrysts).

A representative bulk composition was determined by averaging the line transect data (analyses SI1–SI14 in Data S3—see supporting information). This bulk composition falls close to the range reported for type II porphyritic chondrules within the primitive ordinary chondrite LL3.00 Semarkona (Jones 1990), although deviations are observed for Mn and the moderately volatile elements Na and K (Fig. 11). In a Fe/Mg versus. Fe/Mn diagram (Fig. 7A), the spherical inclusion plots around the 4-Vesta reference line, indicating a non-chondritic composition. This is confirmed by the Mg/Al versus Si/Al diagram (Fig. 7B), where the spherical inclusion plots at considerably higher Mg/Al and Si/Al ratios, demonstrating the Alpoor nature of this component. The bulk spherical inclusion shows a broadly flat subchondritic REE pattern (with respect to CI chondrite data). As mentioned above, the spherical inclusion also contains several high-density Fe-Ni-rich phases. These phases generally lack lithophile elements or sulfur (see Data S4 in supporting information) and hence represent Fe-Ni metal. The Fe/Ni ratio within these grains varies from 6.87 in the largest grain to less than 0.19 in the smaller nodules. These lower Fe/Ni ratios correspond to relatively high concentrations of Si, suggesting that at least some of these analyses are affected by beam overlap with the surrounding silicate phases. Stoichiometric considerations based on EPMA data infer the presence of high-Ni kamacite or taenite, and possibly awaruite (Ni₂Fe to Ni₃Fe). The latter phase was previously identified in chondrules from the CV3 Allende meteorite (Rubin 1991). High-density Fe-rich phases are also found within the micrometeorite groundmass, but these contain both Ni and S. Consequently, they are interpreted as sulfides. Based on EPMA data, the sulfides most likely represent

Table 4. Individual and average major (wt%) and trace ($\mu g/g$) element concentrations resulting from LA-ICP-MS analyses of the spherical inclusion (SI) and micrometeorite groundmass (GM).

Element	SI-1	SI-2	SI-avg.	GM-1	GM-2	GM-avg.	LOD
$\overline{\text{Li} (\mu g \ g^{-1})}$	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>11.9</td><td>11.9</td><td>7</td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td>11.9</td><td>11.9</td><td>7</td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>11.9</td><td>11.9</td><td>7</td></lod<></td></lod<>	<lod< td=""><td>11.9</td><td>11.9</td><td>7</td></lod<>	11.9	11.9	7
Be ($\mu g g^{-1}$)	<lod< td=""><td><lod< td=""><td><lod< td=""><td>0.35</td><td><lod< td=""><td>0.35</td><td>0.1</td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>0.35</td><td><lod< td=""><td>0.35</td><td>0.1</td></lod<></td></lod<></td></lod<>	<lod< td=""><td>0.35</td><td><lod< td=""><td>0.35</td><td>0.1</td></lod<></td></lod<>	0.35	<lod< td=""><td>0.35</td><td>0.1</td></lod<>	0.35	0.1
Na ₂ O (wt%)	0.031	0.027	0.029	0.11	0.032	0.073	0.002
MgO (wt%)	23.7	24.9	24.3	21.0	25.8	23.4	0.0004
Al_2O_3 (wt%)	0.67	0.73	0.70	1.89	2.75	2.32	0.0002
SiO_2 (wt%)	45.4	44.2	44.8	44.2	40.0	42.1	0.009
P_2O_5 (wt%)	0.13	0.16	0.15	0.27	0.36	0.32	0.002
$S(\mu g g^{-1})$	2.38	2.19	2.28	3.39	3.44	3.41	0.02
K_2O (wt%)	<lod< td=""><td><lod< td=""><td><lod< td=""><td>0.0044</td><td>0.0031</td><td>0.0038</td><td>0.0003</td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>0.0044</td><td>0.0031</td><td>0.0038</td><td>0.0003</td></lod<></td></lod<>	<lod< td=""><td>0.0044</td><td>0.0031</td><td>0.0038</td><td>0.0003</td></lod<>	0.0044	0.0031	0.0038	0.0003
CaO (wt%)	0.78	0.83	0.80	1.38	1.85	1.61	0.004
Sc ($\mu g g^{-1}$	3.72	3.56	3.64	9.03	9.39	9.21	0.06
TiO_2 (wt%)	0.035	0.032	0.033	0.065	0.092	0.079	0.004
$V(\mu g g^{-1})$	60	59.3	59.6	52.57	72.0	62.3	0.09
Cr ($\mu g g^{-1}$)	3842	2877	3360	2489	3668	3078	0.4
MnO (wt%)	0.90	0.71	0.81	0.30	0.41	0.36	0.00002
FeO* (wt%)	27.9	27.6	27.7	30.4	28.3	29.3	0.0007
Co ($\mu g g^{-1}$)	74.5	200	137	675	200	438	0.2
Ni ($\mu g g^{-1}$)	1128	5434	3281	1567	980	1273	1
Cu ($\mu g g^{-1}$)	<lod< td=""><td>0.66</td><td>0.66</td><td>2.06</td><td>2.38</td><td>2.22</td><td>0.1</td></lod<>	0.66	0.66	2.06	2.38	2.22	0.1
$Zn (\mu g g^{-1})$	<lod< td=""><td>1.58</td><td>1.58</td><td>2.81</td><td>0.20</td><td>1.50</td><td>0.5</td></lod<>	1.58	1.58	2.81	0.20	1.50	0.5
Ga ($\mu g g^{-1}$)	0.066	0.17	0.12	1.13	1.12	1.13	0.06
Ge ($\mu g g^{-1}$)	<lod< td=""><td>0.20</td><td>0.20</td><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>0.06</td></lod<></td></lod<></td></lod<></td></lod<>	0.20	0.20	<lod< td=""><td><lod< td=""><td><lod< td=""><td>0.06</td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>0.06</td></lod<></td></lod<>	<lod< td=""><td>0.06</td></lod<>	0.06
As $(\mu g g^{-1})$	<lod< td=""><td>0.19</td><td>0.19</td><td><lod< td=""><td>0.23</td><td>0.23</td><td>0.05</td></lod<></td></lod<>	0.19	0.19	<lod< td=""><td>0.23</td><td>0.23</td><td>0.05</td></lod<>	0.23	0.23	0.05
Rb ($\mu g g^{-1}$)	0.071	0.11	0.092	0.042	0.14	0.090	0.03
Sr ($\mu g g^{-1}$)	4.79	4.21	4.50	9.13	11.8	10.5	0.1
Y ($\mu g g^{-1}$)	0.78	0.85	0.82	2.24	2.44	2.34	0.01
$Zr (\mu g g^{-1})$	2.13	1.74	1.93	5.04	5.43	5.24	0.02
Nb ($\mu g g^{-1}$)	0.13	0.23	0.18	0.37	0.46	0.42	0.004
Mo ($\mu g g^{-1}$)	0.17	0.14	0.15	1.17	0.40	0.79	0.1
Sn ($\mu g g^{-1}$)	<lod< td=""><td>0.17</td><td>0.17</td><td>0.10</td><td><lod< td=""><td>0.10</td><td>0.04</td></lod<></td></lod<>	0.17	0.17	0.10	<lod< td=""><td>0.10</td><td>0.04</td></lod<>	0.10	0.04
Sb ($\mu g g^{-1}$)	0.14	<lod< td=""><td>0.14</td><td>0.24</td><td><lod< td=""><td>0.24</td><td>0.01</td></lod<></td></lod<>	0.14	0.24	<lod< td=""><td>0.24</td><td>0.01</td></lod<>	0.24	0.01
Cs ($\mu g g^{-1}$)	0.018	<lod< td=""><td>0.018</td><td>0.014</td><td>0.018</td><td>0.016</td><td>0.008</td></lod<>	0.018	0.014	0.018	0.016	0.008
Ba ($\mu g g^{-1}$)	1.21	1.61	1.41	3.53	4.44	3.99	0.1
La ($\mu g g^{-1}$)	0.13	0.13	0.13	0.42	0.37	0.40	0.008
Ce ($\mu g g^{-1}$)	0.47	0.50	0.48	0.87	1.10	0.99	0.0007
Pr ($\mu g g^{-1}$)	0.086	0.023	0.054	0.15	0.11	0.13	0.0001
Nd ($\mu g g^{-1}$)	0.16	0.67	0.42	0.73	1.04	0.89	0.002
Sm ($\mu g g^{-1}$)	0.053	<lod< td=""><td>0.053</td><td>0.11</td><td>0.23</td><td>0.17</td><td>0.0008</td></lod<>	0.053	0.11	0.23	0.17	0.0008
Eu ($\mu g g^{-1}$)	<lod< td=""><td>0.035</td><td>0.035</td><td>0.040</td><td>0.061</td><td>0.051</td><td>0.02</td></lod<>	0.035	0.035	0.040	0.061	0.051	0.02
Gd ($\mu g g^{-1}$)	0.22	0.19	0.21	0.26	0.29	0.28	0.03
Tb ($\mu g g^{-1}$)	0.037	<lod< td=""><td>0.037</td><td>0.057</td><td>0.059</td><td>0.058</td><td>0.004</td></lod<>	0.037	0.057	0.059	0.058	0.004
Dy ($\mu g g^{-1}$)	0.11	0.18	0.14	0.30	0.42	0.36	0.01
Ho ($\mu g g^{-1}$)	0.038	0.021	0.030	0.098	0.083	0.091	0.004
Er ($\mu g g^{-1}$)	0.13	0.14	0.14	0.25	0.31	0.28	0.01
Tm ($\mu g g^{-1}$)	0.025	0.016	0.021	0.040	0.033	0.037	0.0001
Yb ($\mu g g^{-1}$)	0.097	0.0057	0.051	0.23	0.24	0.24	0.0004
Lu ($\mu g g^{-1}$)	0.016	0.013	0.015	0.033	0.051	0.042	0.0001
Hf ($\mu g g^{-1}$)	<lod< td=""><td>0.031</td><td>0.031</td><td>0.13</td><td>0.22</td><td>0.18</td><td>0.0002</td></lod<>	0.031	0.031	0.13	0.22	0.18	0.0002
Ta ($\mu g g^{-1}$)	0.016	0.017	0.017	0.0042	0.021	0.013	0.0001
W ($\mu g g^{-1}$)	0.079	0.072	0.075	0.038	0.23	0.14	0.0003
Re ($\mu g g^{-1}$)	<lod< td=""><td>0.014</td><td>0.014</td><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>0.0007</td></lod<></td></lod<></td></lod<></td></lod<>	0.014	0.014	<lod< td=""><td><lod< td=""><td><lod< td=""><td>0.0007</td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>0.0007</td></lod<></td></lod<>	<lod< td=""><td>0.0007</td></lod<>	0.0007
Ir ($\mu g g^{-1}$)	<lod< td=""><td>0.15</td><td>0.15</td><td>0.059</td><td>0.081</td><td>0.070</td><td>0.0004</td></lod<>	0.15	0.15	0.059	0.081	0.070	0.0004
$Pt (\mu g g^{-1})$	0.081	0.28	0.18	0.15	0.12	0.13	0.0006

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Element	SI-1	SI-2	SI-avg.	GM-1	GM-2	GM-avg.	LOD
$Hg (\mu g g^{-1})$	<lod< td=""><td>0.45</td><td>0.45</td><td><lod< td=""><td>0.039</td><td>0.039</td><td>0.08</td></lod<></td></lod<>	0.45	0.45	<lod< td=""><td>0.039</td><td>0.039</td><td>0.08</td></lod<>	0.039	0.039	0.08
Pb ($\mu g g^{-1}$)	0.079	<lod< td=""><td>0.079</td><td>0.090</td><td>0.092</td><td>0.091</td><td>0.0002</td></lod<>	0.079	0.090	0.092	0.091	0.0002
Th ($\mu g g^{-1}$)	<lod< td=""><td><lod< td=""><td><lod< td=""><td>0.048</td><td>0.075</td><td>0.061</td><td>0.00003</td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>0.048</td><td>0.075</td><td>0.061</td><td>0.00003</td></lod<></td></lod<>	<lod< td=""><td>0.048</td><td>0.075</td><td>0.061</td><td>0.00003</td></lod<>	0.048	0.075	0.061	0.00003
U ($\mu g g^{-1}$)	0.038	0.010	0.024	0.16	0.033	0.095	0.00004

Table 4. *Continued*. Individual and average major (wt%) and trace ($\mu g/g$) element concentrations resulting from LA-ICP-MS analyses of the spherical inclusion (SI) and micrometeorite groundmass (GM).

Abbreviation: LOD = limit of detection.

^aAll iron expressed as FeO.



Fig. 6. Average rare earth element (REE) concentrations of the spherical inclusion and micrometeorite groundmass normalized to CI chondrites (McDonough and Sun 1995). The spherical inclusion is mostly characterized by subchondritic REE concentrations, except for Gd and Tb. The micrometeorite groundmass is mostly characterized by suprachondritic REE concentrations and displays a relatively flat pattern, very similar to the REE pattern modeled for type II chondrules from ordinary chondrites. Reference data for bulk type II chondrules and their components reproduced from Jacquet et al. (2015). (Color figure can be viewed at wileyonlinelibrary.com.)

pentlandite (Fe_{0.66}Ni_{0.34})₉S₈ and monosulfide solutions (Fe_{0.92}Ni_{0.08})S. The presence of these sulfide phases suggests that the terrestrial residence time of the particle was relatively short, and/or that weathering remained limited (Van Ginneken et al. 2016).

Oxygen Isotope Ratios

Triple-oxygen isotope data were collected for the main components of the particle, that is, the groundmass; a relict olivine grain (Ol1); a large, low-Ca pyroxene grain (Px1); and the spherical inclusion (Figs. 12–14 and see Data S5 in supporting information). The micrometeorite groundmass is characterized by an average δ^{17} O of 3.46%, δ^{18} O of 10.43%, and Δ^{17} O of -1.96% (n = 3). These values plot within the CM carbonaceous chondrite field (Fig. 12), at the higher end of the δ^{18} O values for this meteorite group.

The relict olivine grain measured is characterized by an extremely ¹⁶O-rich composition with a δ^{17} O of -45.8‰, δ^{18} O of -43.7‰, and Δ^{17} O of -23.1‰ (n = 1). This isotopic composition plots between the carbonaceous chondrite anhydrous mineral (CCAM with a slope of 0.94 ± 0.01 (2SE) and intercept of -0.94; Clayton and Mayeda 1999) and Young & Russell (Y&R; Young and Russell 1998) lines (Fig. 13), toward solar compositions (δ^{17} O of -59.1%, δ^{18} O of -58.5%; Clayton et al. 1977; McKeegan et al. 2011). The Y&R line represents a slope ~ 1 line defined by the oxygen isotopic composition of CAIs extracted from the CV3 Allende meteorite.

In contrast, the large, low-Ca pyroxene grain plots along the Y&R line but at significantly more ¹⁸O-rich (heavy) compositions with a δ^{17} O of -4.96‰, δ^{18} O of -4.32‰, and Δ^{17} O of -2.71‰ (n = 1). This is close to the intersection between the Y&R line and the terrestrial fractionation line (TFL = δ^{17} O - 0.52 × δ^{18} O; Clayton 1993). Both the values of the relict olivine and pyroxene are consistent with refractory minerals commonly observed in CAIs and This abbreviation was removed in earlier versions of the text. AOAs can thus be changed to 'amoeboid olivine aggregates'

Finally, the spherical inclusion has an average δ^{17} O of -0.98%, δ^{18} O of -2.16%, and Δ^{17} O of 0.15% (n = 3).



Fig. 7. Major elemental composition of the micrometeorite WF1202A-001 groundmass (GM) and spherical inclusion (SI) plotted in Fe/Mg versus Fe/Mn (A) and Si/Al versus Mg/Al (B) diagrams. The micrometeorite groundmass is positioned along the edge of the chondritic compositional field in (A) and appears to display a similar compositional range as observed in the matrix of CM, CI, and CV chondrites (B). The spherical inclusion plots along the 4-Vesta reference line and does not appear to be chondritic in composition (A). Its composition also appears to be extremely depleted in Al, as demonstrated in (B). Reference values for (A) reproduced from Goodrich and Delaney (2000), and (B) from McSween and Richardson (1977), McSween (1987), and Zolensky et al. (1993). (Color figure can be viewed at wileyonlinelibrary.com.)

The oxygen isotopic data of the spherical inclusion are thus positioned close to the TFL, left of the enstatite chondrite field at significantly lower δ^{18} O values (Figs. 12 and 14). This isotopic composition does not match any previously reported data for chondrules or bulk chondrites and is therefore considered anomalous.

DISCUSSION

The Extraterrestrial Nature of Micrometeorite WF1202A-001: Clues from Petrography and Geochemistry

To distinguish microscopic extraterrestrial particles from their terrestrial counterparts, Genge et al. (2008) have defined a number of criteria that are characteristic



Fig. 8. Major (top) and minor (bottom) elemental oxide concentrations (wt%) determined by EPMA along a core-rim transect in a coarse-grained, relict olivine crystal (Ol1—Fig. 2C). The first and last analyses within the transect are referred to as "Core" and "Rim." The distance of intermediate analyses was measured from the start of the transect and is displayed on the X-axis. (Color figure can be viewed at wile yonlinelibrary.com.)

of micrometeorites (1) the presence of a partial or complete magnetite rim, that developed during atmospheric entry (Toppani et al. 2001; Toppani and Libourel 2003); (2) the presence of Fe-Ni metal; and This should be 3) a bulk chondritic composition, provided crystal sizes are considerably smaller than the overall particle size. These features have been observed in micrometeorite WF1202A-001 and we can thus confirm the extraterrestrial nature of this particle (see Figs. 2 and 5–6).

The texture of micrometeorite WF1202A-001 is consistent with porphyritic S-type cosmic spherules, implying high degrees of melting (>50%; Genge et al. 2008) during atmospheric entry with peak temperatures above the solidus of the chondritic matrix (>1400°C; Toppani et al. 2001). Consequently, the pre-atmospheric textural and geochemical properties of such cosmic spherules may potentially have been (severely) modified. A large fraction of the groundmass of WF1202A-001 has recrystallized, producing neo-formed FeO-rich (Fo₈₀₋₈₄) olivine, olivine overgrowth rims, and magnetite embedded in a glassy mesostasis, consistent with quench-cooling during atmospheric entry. Nevertheless, the geochemistry of the groundmass remains broadly chondritic, except for significant depletions in Na and K (Figs. 5 and 6). These moderately volatile elements with

SiO₂

MqO

Cr₂O₃

NiO

CaC

MnO

Al₂O



50% condensation temperatures of 958 and 1006K (Lodders 2003), respectively, are strongly evaporated as a result of atmospheric entry heating. The chondritic nature of micrometeorite WF1202A-001 is further supported by its Fe/Mg versus Fe/Mn relations (Fig. 7A; Goodrich and Delaney 2000; Taylor et al. 2007) and suggests a possible affiliation with matrix compositions from CI. CM. or CV chondrites based on its distribution in Mg/Al versus Si/Al space (Fig. 7B; McSween and Richardson 1977; McSween 1987; Zolensky et al. 1993; Taylor et al. 2005). Since CI chondrites do not contain chondrules as a result of intense aqueous alteration, a CM or CV chondrite parent body appears more plausible. These results thus imply that the geochemical composition of the original dust particle was largely preserved despite atmospheric entry heating.

Within the micrometeorite groundmass, some of the olivine (micro-)phenocrysts have anhedral, irregularshaped cores with diffuse boundaries that gradually transition into the FeO-rich (Fo₆₅) rims. These are characteristic features of relict olivine phases in micrometeorites (Genge et al. 2016) and represent \sim 5–10% of the micrometeorite's surface area (Fig. 2). Their



Fig. 10. Major (top) and minor (bottom) elemental oxide concentrations (wt%) determined by EPMA along a core-rim transect in the spherical inclusion (SI—Fig. 2C). The first and last analyses within the transect are referred to as "Core" and "Rim." The distance of intermediate analyses was measured from the start of the transect and is displayed on the X-axis. (Color figure can be viewed at wileyonlinelibrary.com.)



Fig. 11. Major elemental concentrations (wt%) of the spherical inclusion (SI) and comparison with type II porphyritic chondrules from the LL3.00 Semarkona chondrite (Jones 1990). Elemental abundances have been normalized to CI chondrites (McDonough and Sun 1995) and Si. The spherical inclusion is largely positioned within the elemental range determined for Semarkona type II chondrules, except in the case of Mn, K, and Na.

composition is also highly refractory with Mg# between 98 and 99 (Fig. 8 and see Data S1), typically observed in carbonaceous chondrites and their CAIs.

60

50

0xide (wt.%) 30 50

10

0

0.80

0.60

0 40

0.20



Fig. 12. Triple oxygen isotope diagram (Δ^{17} O and δ^{18} O) of the spherical inclusion (SI) and micrometeorite groundmass (GM). The spherical inclusion is located left of the enstatite chondrite (EC) field, while the micrometeorite groundmass is positioned near the CM chondrite field, offset to δ^{18} O-enriched compositions. Micrometeoroids experience isotopic fractionation processes during atmospheric entry heating. Oxygen isotope ratios can be modified through (1) mass-dependent fractionation, moving the composition to the right of the diagram; (2) mixing with atmospheric oxygen (star symbol-Thiemens et al. 1995); and (3) interaction with Antarctic precipitation, as represented by standard light antarctic precipitation (SLAP). Bulk isotopic compositions of micrometeorites generally fall in four distinct groups (Group 1-4), associated with anhydrous carbonaceous chondrites, hydrated carbonaceous chondrites, ordinary chondrites, and a newly described population of ¹⁶O-poor material (group 4), the affinities of which are currently not well understood. The oxygen isotopic composition of multiple CAIs and a single Al-rich chondrule from the EET 87746, GRO 95517, and Sahara 97072 unequilibrated enstatite chondrites have been added for comparison (polygons—Guan et al. 2000). Oxygen isotopic data for anhydrous IDPs (squares—Aléon et al. 2009) and fragments from Comet 81P/Wild2 (triangles-McKeegan et al. 2006) have been added as well. The dashed line connecting the oxygen isotopic composition of the micrometeorite groundmass contains several hollow, green circles that represent a potential pre-atmospheric composition taking into account ~10, 15, and 20% of oxygen isotope fractionation processes. Figure modified from Suavet et al. (2010). Error bars represent the uncertainty on the Δ^{17} O (2SE for micrometeorite WF1202A-001, anhydrous IDPs and Comet 81P/Wild2 fragments, 1SE for individual analyses from Guan et al. 2000) and δ^{18} O ratio (1SE for individual analyses from Guan et al. 2000). (Color figure can be viewed at wileyonlinelibrary.com.)

In addition to olivine, WF1202A-001 also retained multiple, relict low-Ca pyroxene grains, as the average cooling rate of cosmic spherules kinetically inhibits the crystallization of neo-formed pyroxene phases (Taylor and Brownlee 1991). The relict nature of pyroxene in micrometeorite WF1202A-001 is also demonstrated by its highly refractory composition (Mg# = 99—see Fig. 9 and see Data S2). More specifically, the composition of this particular pyroxene is similar to those of highly refractory low-Fe, Cr-enriched (LICE) silicates (FeO/Cr₂O₃ < 1), previously reported on by Ebel et al. (2012) and Suttle et al. (2019a), which are typically associated with first-generation condensationcrystallized silicates and/or refractory CAIs. Both the relict olivine and pyroxene phases appear to be linked with CAIs.

We cannot verify whether the Ni-bearing sulfide phases in the micrometeorite groundmass are primary or were formed as a consequence of atmospheric entry heating. The latter process should be considered since high-Ni sulfide phases such as pentlandite can also be formed by cooling of high temperature Fe-Ni-S melts (Schrader et al. 2016). These types of melts may be produced due to the immiscibility of chalcophile and siderophile elements from the surrounding silicate melt when the precursor particle is melted during atmospheric entry (Genge and Grady 1998). Alternatively, if the Ni-bearing sulfide phases are primary, then this would suggest a contribution of oxidized chondrites such as the carbonaceous and R chondrites. The preservation of sulfide phases also implies that micrometeorite WF1202A-001 avoided significant weathering during its residence on Earth.



Fig. 13. Oxygen isotope diagram (δ^{17} O and δ^{18} O) of coarse-grained olivine and low-Ca pyroxene in the micrometeorite groundmass. Both mineral phases are positioned in-between the Allende CAI line (Clayton et al. 1977) and the Y&R line (Young and Russell 1998). Olivine grains have ¹⁶O-rich compositions while the pyroxene has a more ¹⁶O-poor composition. The oxygen isotopic composition of the analyzed olivine is similar to that observed for refractory mineral phases (e.g., hibonite, melilite, etc.) in CAIs. (Color figure can be viewed at wileyonlinelibrary.com.)



Fig. 14. Oxygen isotopic composition (δ^{17} O and δ^{18} O) of the spherical inclusion (SI) in WF1202A-001. The range of oxygen isotopic compositions observed in chondrules from a large variety of chondritic meteorites are shown for comparison (Rubin 2000b). The chondrule does not plot close to any known chondrite field. The oxygen isotopic composition of multiple CAIs and a single Al-rich chondrule from the EET 87746, GRO 95517, and Sahara 97072 unequilibrated enstatite chondrites has been added for comparison (polygons—Guan et al. 2000). Oxygen isotopic data for anhydrous IDPs (squares—Aléon et al. 2009) and fragments from Comet 81P/Wild2 (triangles—McKeegan et al. 2006) have been added as well. Error bars represent the uncertainty on the δ^{17} O (2SE for micrometeorite WF1202A-001, anhydrous IDPs and Comet 81P/Wild2 fragments, 1SE for individual analyses from Guan et al. 2000) and δ^{18} O ratio (2SE for micrometeorite WF1202A-001, anhydrous IDPs and Comet 81P/Wild2 fragments, 1SE for individual analyses from Guan et al. 2000). Abbreviations: TFL = terrestrial fractionation line, CCAM = carbonaceous chondrite anhydrous mineral line (Clayton et al. 1977). (Color figure can be viewed at wileyonlinelibra ry.com.)

A Complete and Well-Preserved Chondrule within an Antarctic Micrometeorite

The physical, petrographic, and geochemical properties of the spherical inclusion bear a strong resemblance to chondrules observed in chondritic meteorites. Here, we discuss five parameters—size, shape, texture, mineralogy, and chemistry—supporting the identification of this inclusion as a chondrule.

Chondrule sizes range from tens of micrometers up to several millimeters depending on the class/group of chondrite, and may vary substantially among specific classes or groups of chondritic meteorites (see Jones 2012; Friedrich et al. [2015] for an overview). This variation has previously been attributed to an array of processes including chondrule formation, parent body alteration, or post-solidification nebular sorting (Shu et al. 1996; Weidenschilling 2000; Cuzzi et al. 2001; Cuzzi and Weidenschilling 2006; Chiang and Youdin 2010; Wurm et al. 2010). Combining the average chondrule size and texture can nevertheless provide important information toward the identification and classification of meteorites (Van Schmus and Wood 1967; Weisberg et al. 2006).

The maximum apparent size of the spherical inclusion is approximately 220 µm, which is consistent with average chondrule sizes in CM, CO, H, and EH chondrites (Table 1). Note, however, that chondrule sizes may vary considerably within specific types of chondritic meteorites and that average sizes may not be representative. While peak atmospheric temperatures likely exceeded 1400°C, which predominantly affects the glassy mesostasis (transitional window of glass ~650-850°C) within the spherical inclusion of micrometeorite WF1202A-001, we argue that the size of the chondrule did not change extensively. This is demonstrated by the sharp, welldefined contact between the spherical inclusion and the surrounding micrometeorite groundmass (Fig. 4). In addition, we observe neo-formed olivine phenocrysts and magnetite dendrites, which crystallized following quenchcooling during the later stages of atmospheric entry (Toppani et al. 2001) using the object's rim as substrate.

Second, the shape of the spherical inclusion is rounded and slightly elliptical ($\varepsilon = 1.12$), displaying a smooth surface across the entire object. Chondrules typically display (highly) irregular surfaces at the scale of ~50 µm (Grossman et al. 1988), but barred olivine radial-pyroxene chondrules and (including their respective fragments in micrometeorites) may often display smooth surfaces (Grossman et al. 1988; Genge et al. 2005). The presence of smooth surfaces among barred olivine and radial-pyroxene chondrules is consistent with their formation as igneous droplets with spherical shapes formed as a result of surface tension (Grossman et al. 1988; Genge et al. 2005).

Third, barred olivine textures among chondritic meteorites are predominantly observed within chondrules. Nonporphyritic chondrules. including barred olivine, cryptocrystalline, and radial pyroxene types, are typically outnumbered (~<10%) compared to chondrules (Table 1). porphyritic Nonporphyritic textures develop when the chondrule precursor is superheated above the liquidus, effectively destroying all crystal nuclei, and is subsequently cooled down at highly variable rates of ~500-3000 °C h^{-1} for barred olivine textures (Desch and Connolly 2002). The nucleation of barred olivine and radial pyroxene chondrules presumably initiated after melt droplets collided with solid, neighboring grains (Connolly and 1995). The spherical depression Hewins with surrounding Cr-rich spinel grains in the spherical inclusion of micrometeorite WF1202A-001 may have hosted a solid (relict) grain that served as nucleation point for the barred olivine texture (Fig. 2).

Fourth, the mineral content of the spherical inclusion comprises common major and accessory mineral phases observed in chondrules, including olivine, Fe-Ni metal alloys, and Cr-rich spinel. Olivine crystals within the spherical inclusion are FeO-rich (Fo₆₃) and display normal zoning, while the interstitial mesostasis is more pyroxene-rich with clear enrichments in Si, Fe, Al, and Ca (Fig. 10).

Finally, the major elemental composition of the spherical inclusion appears to be very similar to, for example, porphyritic chondrules from the LL 3.00 Semarkona meteorite (Jones 1990), with the exception of a minor enrichment in Mn (within uncertainty) and a large depletion in Na and K (Fig. 11). The depletion of moderately volatile elements in the spherical inclusion is likely a result of atmospheric entry heating, similar to the micrometeorite groundmass, as observed from the presence of vesicles near the inclusion's margin (Fig. 2). The REE pattern of the spherical inclusion is consistent with a mixture of olivine (subchondritic) and glassy mesostasis (suprachondritic) in chondrules, where olivine is more significant (~70-80 area%) than the glassy mesostasis (Figs. 2 and 6). This may explain the overall subchondritic REE signature of the spherical inclusion.

Based on the physical, petrographic, mineralogical, and chemical properties of the spherical inclusion described above, we interpret this phase as a wellpreserved chondrule.

Oxygen Isotopic Composition of Micrometeorite WF1202A-001: A Link to IDPs and Cometary Bodies?

Apart from the textural and geochemical modifications that extraterrestrial dust particles experience during atmospheric entry heating, oxygen

isotope ratios also undergo significant changes. Previous isotopic studies on cosmic spherules (Yada et al. 2005; Suavet et al. 2010; Van Ginneken et al. 2017; Goderis et al. 2020; Rudraswami et al. 2020; Suttle et al. 2020) have demonstrated that the atmospheric entry of micrometeorites results in two main isotopic overprints. First, a mass-dependent fractionation effect arises due to flash heating and results in a proportional δ^{18} O Second, once molten, the particle enrichment. experiences a progressive isotopic exchange with stratospheric (terrestrial) oxygen. This causes the particle's bulk composition to approach stratospheric oxygen values with a δ^{17} O of 11.8% and δ^{18} O of 23.5% (Thiemens et al. 1995). Suavet et al. (2010) argued that the extent of both processes positively correlates with the texture (and thus maximum heating temperature) of cosmic spherules. Consequently, the effects of oxygen isotopic fractionation and mixing on the final oxygen composition of micrometeorites isotopic should increase from porphyritic over barred olivine and cryptocrystalline to vitreous textures. Rudraswami et al. that (2020)furthermore argue mass-dependent fractionation processes dominate over atmospheric oxygen mixing.

Micrometeorite WF1202A-001 displays а microporphyritic texture, implying a fairly limited shift in the bulk oxygen isotopic composition of this particle. This appears to be the case since the oxygen isotopic composition of the groundmass of micrometeorite WF1202A-001 is positioned at the edge of the CM chondrite field (Fig. 12). Since we cannot quantify the extent of mass-dependent fractionation processes and mixing with atmospheric oxygen, the primordial bulk or matrix oxygen isotopic compositions of micrometeorite WF1202A-001 are difficult to determine. Clayton et al. (1986) observed average shifts in δ^{18} O values of ~8% for iron fusion crusts arising due to mixing with atmospheric oxygen and kinetic effects. Suavet et al. (2010) observed overall larger amounts of fractionation and mixing ranging from ~10 to 50% in cosmic spherules from the Transantarctic Mountains. Recently, Rudraswami et al. (2020) have determined the average increase in δ^{18} O values for a series of cosmic spherules spanning a large textural range. They observed average increases of +12%, +20%, +22%, +25%, +26%, and +50%for cosmic spherules in the following scoriaceous < porphyritic < barred order: olivine < cryptocrystalline < vitreous < CAT. Hence, the original δ^{18} O value of micrometeorite WF1202A-001 may have shifted up to ~10-20%. By applying an ~15% offset to the oxygen isotopic composition of the micrometeorite groundmass, its original oxygen isotopic composition was presumably positioned left of the carbonaceous chondrite fields. Such composition is similar to values reported by Guan et al. (2000), McKeegan et al. (2006), and Aléon et al. (2009) for CAIs and an Al-rich chondrule from the EET 87746, GRO 95517, and Sahara 97072 unequilibrated enstatite chondrites; fragments from Comet 81P/Wild2; and chondritic anhydrous interplanetary dust particles, respectively (see below and Fig. 12). However, since the original oxygen isotopic composition of the micrometeorite precursor body is unknown, and the contribution of massdependent fractionation and mixing processes cannot be quantified accurately, this estimate should be considered with care.

The relict olivine grain (Ol1) displays extreme ¹⁶Orich compositions, with a δ^{17} O of -45.8‰ and δ^{18} O of -43.7‰, preserving primordial solar-like values identical to those found in CAIs (Clayton and Mayeda 1999; Yurimoto et al. 2008; Fig. 13). These values imply that Ol1 formed as a primitive first-generation condensationcrystallized silicate, which survived accretion, parent body alteration, liberation into interplanetary space, atmospheric entry, and terrestrial residence without any significant isotopic overprinting.

In contrast, the large low-Ca pyroxene grain (Px1) plots closer to the intersection with the terrestrial fractionation line (TFL; Fig. 13). Such compositions are also commonly found in chondritic meteorites and can best be explained by isotopic mixing between firstgeneration silicates and later ¹⁸O-rich materials. Mixing may have occurred in a transient melting scenario with either accreted volatile dust or by exchange with surrounding SiO₂ gas (McKeegan et al. 1998; Krot et al. 2005). Thus, Px1 was most likely inherited from either a fragmented type II chondrule or igneous CAI. Micrometeorite WF1202A-001 therefore appears to contain an appreciable amount (~5-10 area%) of CAIderived material. However, due to the fairly small size of micrometeorites in comparison with their respective parent bodies, we cannot verify whether the importance of CAI-derived material is representative.

The unique and anomalous oxygen isotopic composition (δ^{17} O of -0.98‰, δ^{18} O of -2.16‰, and Δ^{17} O of 0.15%) of the chondrule in micrometeorite WF1202A-001 is puzzling since none of the known chondrite groups (including their individual components) matches its composition (Greenwood et al. 2020). Based on petrographic observations, we argue that atmospheric melting of the chondrule within micrometeorite WF1202A-001 was limited to its glassy mesostasis. This occurs at temperatures exceeding the glass transitional window (650-850°C) and results in oxidative volatilization of reduced, volatile compounds, and diffusive exchange with the surrounding (molten) silicate groundmass. The former process is demonstrated by the presence of rounded vesicles near the chondrule's margin (Fig. 2) and the overall depletion of volatile elements such as Na and K (Fig. 11). The latter process is illustrated by the development of microscopic magnetite grains due to the oxidation of Fe-Ni metal (Fig. 2). Both processes have previously been inferred from meteorite fusion crusts (Genge and Grady 1999) and igneous rims in scoriaceous and unmelted micrometeorites (Genge et al. 2005; Genge 2006). We can therefore argue that at least a limited amount of chemical and isotopic modification has taken place, yet the extent of these processes remains difficult to quantify. Since mass-dependent fractionation and/or mixing processes tend to shift the original oxygen isotopic composition of dust particles toward higher δ^{18} O values, this would imply that the original oxygen isotopic composition of the chondrule was even more ^{18}O -depleted. This underlines the anomalous isotopic signature of the chondrule.

Due to its position close to the terrestrial fractionation line, we should also consider a possible contribution of standard light Antarctic precipitation (SLAP-Fig. 12). This isotopic reservoir can modify the oxygen isotopic composition of micrometeorites as a result of aqueous alteration at the Earth's surface (see e.g., Van Ginneken et al. 2016). According to Zekollari et al. (2019), the oxygen isotopic composition of the surrounding Nansen blue ice field is $\sim 43 \pm 3 \%$ (1SD). To produce the anomalous oxygen isotopic composition observed in the chondrule starting from a hypothetical CM-like composition (mean δ^{18} O of + 9‰, and Δ^{17} O of -2.3%, n = 34; Clayton and Mayeda 1999), we would require a SLAP contribution of ~22%, leading to a distinct Δ^{17} O of -1.9%, which is inconsistent with the isotopic composition of the chondrule. Such large contribution is also unlikely since weathering features dissolution, secondary mineral phases) in (e.g., WF1202A-001 are micrometeorite absent (Van Ginneken et al. 2016). In addition, the presence of sulfide phases and the preservation of the glassy mesostasis within the micrometeorite groundmass, both of which are highly susceptible to terrestrial weathering, support this assumption (e.g., Fig. 2).

A potential solution is provided by Guan et al. (2000) who investigated the oxygen isotopic composition of multiple CAIs and a single Al-rich chondrule from the EET 87746, GRO 95517, and Sahara 97072 unequilibrated enstatite chondrites. They have reported similar values (within uncertainty) for both the CAI (mixtures of melilite, spinel, perovskite, hibonite, etc.) and chondrule (spinel and glass from Al-rich chondrule) components as micrometeorite WF1202A-001. Hence, this might suggest that the chondrule in micrometeorite WF1202A-001 may have been inherited from enstatite chondrites. However, this is rather unlikely since the

chondrule was relatively enriched in FeO, and lithophile elements were essentially absent from the Fe-Ni nodules, inconsistent with the highly reduced nature of enstatite chondrites.

Alternatively, the chondrule may affiliate to anhydrous IDPs and fragments from Comet 81P/Wild 2, which display comparable oxygen isotopic ratios (Figs. 12 and 13). Interestingly, the estimated preatmospheric oxygen isotopic composition of the micrometeorite groundmass is also positioned in proximity of these "cometary fields" when the extent of mass-dependent fractionation processes ranges from ~5 to 15%. Micrometeorite WF1202A-001 may possibly have sampled a carbonaceous chondrite parent body, analogous to, but distinct from CM, CO, or CV chondrites based on the major element composition of the groundmass, chondrule size, and the oxygen isotopic systematics. In addition, these results may suggest a genetic link between carbonaceous chondrites and cometary bodies (such as Comet 81P/Wild2) given their comparable oxygen isotope compositions.

The implications of these results are twofold. First, the diversity among solar system materials is much larger than our contemporary (micro)meteorite inventory suggests (see also, e.g., Yada et al. 2005; Gounelle et al. 2009; Suavet et al. 2010; Cordier and Folco 2014; Van Ginneken et al. 2017; Goderis et al. 2020; Suttle et al. 2020). Second, the classical dichotomy (i.e., carbonaceous versus noncarbonaceous chondrites) observed in oxygen isotope space should be reconsidered as the oxygen isotope compositions of carbonaceous chondrites appear to be much more diverse (see also e.g., Goodrich et al. 2019; Kebukawa et al. 2019; King et al. 2019; Kerraouch et al. 2020; Suttle et al. 2020). Micrometeorite WF1202A-001 may thus possibly serve as an example for the (hidden) diversity present among the carbonaceous chondrite class.

The Atmospheric Entry History and Source Region of Micrometeorite WF1202A-001

The preservation of a complete chondrule within micrometeorite WF1202A-001 is unique as asteroids are subjected to a range of collisional events and alteration processes throughout their residence in the solar system. Based on previous studies regarding the behavior of shock waves in heterogeneous media (e.g., Melosh 1996; Ernstson et al. 2001), Genge et al. (2005) proposed that dust production predominantly affects chondrules due to their higher shock impedance with respect to the chondritic matrix. Since particle and shock wave velocities migrate faster through denser materials, chondrules tend to fragment more easily. In addition, chondrule fragmentation may also be amplified by the buildup of heterogeneous peak pressures originating from the reflection and refraction of shock waves at the border between high (cfr. chondrule) and low (cfr. matrix) shock density materials.

Aqueous alteration on parent asteroids may also play a pivotal role in the removal or alteration of chondrules (e.g., Bunch and Chang 1980; Richardson 1981; Ikeda 1983; Tomeoka and Buseck 1985; Hanowski and Brearley 1997, 2001). This is further supported by Suttle et al. (2019b) who argued that chondrules are predominantly replaced by phyllosilicates in hydrated carbonaceous chondrites (e.g., CI, CM, CR) based on a study of scoriaceous and unmelted micrometeorites.

In addition, chondrule(s) (fragments) are also subjected to temperatures up to 1700°C as a result of atmospheric entry heating (Love and Brownlee 1991). The preservation of relict mineral phases in micrometeorite WF1202A-001 such as olivine (melting point at atmospheric pressure: 1890°C) and low-Ca pyroxene (1557°C) suggests that peak atmospheric temperatures were likely not as high, but sufficient to exceed the solidus of chondritic matrix (~1400°C: Toppani et al. 2001). According to Hewins and Radomsky (1990), chondrule liquidus temperatures range between ~1200 and 1900°C, and display a peak in the distribution at ~1500-1550°C for barred olivine textures (Radomsky and Hewins 1990; Yu and Hewins 1998). The peak atmospheric temperature experienced by micrometeorite WF1202A-001 therefore appears to range between 1400 and 1550°C. Note, however, that the chondrule's glassy mesostasis must have melted as the transitional window of glass is situated between 650 and 850°C.

Atmospheric entry heating also governs the size of micrometeorites (Love and Brownlee 1991; Genge and Grady 1998; Genge 2017). During atmospheric entry, a number of competing processes (e.g., evaporation, vesiculation, ejection of high-density sidero- and chalcophile elements, etc.) induce volumetric changes in the micrometeorite precursor particle. On average, micrometeorite precursors are estimated to have been ~1.5–2 times larger than the resulting, recrystallized micrometeorite recovered on Earth as a consequence of evaporative processes (Love and Brownlee 1991). The volumetric effects of vesiculation are more difficult to determine but are mostly relevant for phyllosilicatebearing precursor particles (Genge 2017). Here, we will only consider the effects of evaporation to calculate the original size of micrometeorite WF1202A-001. This information is relevant to re-create the atmospheric entry history (i.e., entry speed, angle, etc.) of micrometeorite WF1202A-001 and serves to identify its source region within the solar system. We estimate that the original micrometeoroid size ranged from 650 to 850 μ m, and that the chondrule size did not change extensively over the course of its atmospheric entry (see earlier).

The fairly large (original) size of micrometeorite WF1202A-001 suggests that the initial atmospheric entry velocity is likely to be asteroidal (~12–15 km s⁻¹) rather than cometary ($\sim 20 \text{ km s}^{-1}$), since larger dust particles are more prone to melting (Love and Brownlee 1991). In addition, the entry angle of micrometeorite WF1202A-001 was presumably close to the horizontal (90°) as this has a moderating effect on the peak atmospheric temperature experienced, relative to the vertical (0°). Micrometeorite WF1202A-001 therefore likely originated from the main belt asteroids, since particles $>20 \ \mu m$ with average (long-period) cometary velocities (i.e., 20 km s^{-1}) are not expected to survive atmospheric entry (Love and Brownlee 1991). However, the particle may also have originated from the JFCs, such as Comet 81P/Wild2, which are short period comets that orbit the Sun in a timespan of less than 20 years. The JFC population have low eccentricities and inclination angles that produce low-velocity dust particles, analogous to main belt asteroids that promote atmospheric survival. Based on numerical modeling, Nesvorný et al. (2010) concluded that dust from the inner solar system is predominantly sourced from the JFC. We therefore suggest that micrometeorite WF1202A-001 likely originated either from a main belt asteroid or JFC, and entered Earth's atmosphere at asteroidal velocities $(12-15 \text{ km s}^{-1})$ and a near horizontal angle.

CONCLUSION

Particle WF1202A-001 is a microporphyritic cosmic the Sør Rondane spherule from Mountain micrometeorite collection that contains relict MgO-rich olivine and low-Ca pyroxene grains, as well as a spherical inclusion, interpreted as a barred olivine chondrule. While the micrometeorite's groundmass melted almost entirely, its bulk geochemical composition is relatively well preserved and consistent with a chondritic parent body, possibly from CM or CV lineage. This is supported by oxygen isotope ratio data, which are consistent with a carbonaceous chondritic precursor body. Micrometeorite WF1202A-001 appears to contain an appreciable amount (~5-10 area%) of CAI-derived material, including forsterite (Fo₉₈₋₉₉) and enstatite (En₉₉Wo₁) grains. At least one olivine grain exhibits extremely negative solar-like values ($\delta^{17}O \approx$ δ^{18} O $\approx -45\%$), reminiscent of primitive first-generation condensation-crystallized silicates. Low-Ca pyroxene plots much closer to the terrestrial fractionation lineinterpreted to represent mixing between first-generation

silicates and later accreted ¹⁸O-rich volatile dust or exchange with SiO_2 gas. As a result, the low-Ca pyroxene grain was presumably inherited from type II chondrules or igneous CAIs.

The chondrule displays a barred olivine texture that is embedded in a glassy mesostasis. Its bulk composition is consistent with type II chondrules observed in chondritic meteorites. However, its oxygen isotopic composition is anomalous, plotting near the terrestrial fractionation line, offset to a lower δ^{18} O relative to the enstatite chondrite field, and incompatible with known chondritic materials. While the chondrule's glassy mesostasis has melted and recrystallized during atmospheric entry, allowing for chemical and isotopic interaction, the combined effects of mass-dependent fractionation and mixing with atmospheric oxygen cannot account for the chondrule's anomalous oxygen isotopic composition. Due to the lack of weathering features in micrometeorite WF1202A-001, we believe the contribution of SLAP is negligible. The chondrule's oxygen isotopic composition is, however, comparable to those observed for anhydrous IDPs and fragments from Comet 81P/Wild2. Consequently, we propose that micrometeorite WF1202A-001 sampled a new type of carbonaceous chondrite parent body that can potentially be linked to cometary bodies.

The peak atmospheric temperature experienced by micrometeorite WF1202A-001 presumably ranged between 1400 and 1550°C based on the melting point of the respective micrometeorite components. Additionally, the fairly large size of micrometeorite WF1202A-001 suggests low, asteroidal entry velocities $(12-15 \text{ km s}^{-1})$ with an inclination angle close to the horizontal (~80°). Such parameters are consistent with cosmic dust originating from low eccentricity, low inclination source regions, which include both the main belt asteroids and the JFCs.

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SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article.

Data S1. Major and minor elemental oxide concentrations (wt%) according to individual EPMA spot analyses in a single, coarse-grained olivine crystal.

Data S2. Major and minor elemental oxide concentrations (wt%) according to individual EPMA spot analyses in a single, coarse-grained low-Ca pyroxene crystal.

Data S3. Major and minor elemental oxide concentrations (wt%) of individual EPMA spot analyses in the spherical inclusion.

Data S4. Major and minor elemental concentrations (wt%) according to individual EPMA spot analyses in a series of Fe-Ni metallic nodules and sulfides.

Data S5. Oxygen isotope ratios ($\delta^{17}O$, $\delta^{18}O$, $\Delta^{17}O$) of major components within the micrometeorite WF1202A-001, including the spherical inclusion (SI), the groundmass (GM), and refractory silicates (olivine and low-Ca pyroxene).

Data S6. Additional images of mineral constituents in micrometeorite WF1202A-001, including the spherical inclusion (A), a resorbed olivine grain (B), the micrometeorite rim containing newly formed Fe-oxide phases (C), and a close-up of the largest low-Ca pyroxene grain with FeO-rich olivine overgrowth (D).

Characterization of achondritic cosmic spherules from the Widerøefjellet micrometeorite collection (Sør Rondane Mountains, East Antarctica)

by Soens et al. (submitted). Geochim. Cosmochim. Acta.

Achondritic micrometeorites represent a small fraction (ca. 0.5–2%) of the cosmic dust population (e.g., Taylor et al., 2007; Badjukov et al., 2010; Cordier et al., 2011b; 2012; Brase et al., 2021). Their major, trace element and oxygen isotope compositions are mostly consistent with HED or HED-like meteorites. However, Gounelle et al. (2009) have reported a single basaltic, unmelted micrometeorite unaffiliated to a known type of meteoritic or asteroidal body, demonstrating the possibility of the cosmic dust population to sample new and unknown types of precursor bodies. In this article, we present new major, trace element and oxygen isotope data for five achondritic cosmic spherules recovered from the WMC to investigate the nature of their achondritic precursor bodies. We also present iron isotope data to constrain and correct for the various types of oxygen isotope fractionation processes occurring within achondritic micrometeoroids during atmospheric entry heating. As such, we attempt to calculate the original oxygen isotope signature of their achondritic cosmic spherules also apply to achondritic micrometeorites. This information is useful to understand and compare the behavior of chondritic and achondritic dust particles during their atmospheric entry stage, and identify which properties are predominantly responsible for oxygen isotope fractionation processes.

BS is first author of this manuscript and has performed sample acquisition; sample preparation; sample imaging (SEM); acquisition and processing of the major and trace elemental dataset (LA-ICP-MS); acquisition of oxygen isotope data (SIMS); and dataset interpretation.

The supplementary materials related to this manuscript are available below or on the following website: https://www.editorialmanager.com/gca/download.aspx?id=771989&guid=69922951-48af-4382-83bf-ddc91ed8799d&scheme=1.

CHARACTERIZATION OF ACHONDRITIC COSMIC SPHERULES FROM THE WIDERØEFJELLET MICROMETEORITE COLLECTION (SØR RONDANE MOUNTAINS, EAST ANTARCTICA)

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ABSTRACT

Achondritic micrometeorites represent one of the rarest (ca. 0.5–2.1%) particle types among Antarctic micrometeorite collections. Here, we present major, trace elemental and oxygen isotope compositions on 5 vitreous, achondritic cosmic spherules (341-526 µm in size) recovered from the Widerøefjellet sedimentary trap in the Sør Rondane Mountains (SRMs) of East Antarctica. We also present the first iron isotope data (n = 4) for achondritic cosmic spherules to date. The particles were initially identified based on the atomic concentrations of Fe-Mg-Mn and their distribution in Fe/Mg vs. Fe/Mn space, spanning a relatively wide range in Fe/Mg ratios (ca. 0.48–1.72). The Fe/Mn ratios cover a more restricted range (ca. 22–32), comparable to or slightly below the values measured for HED and martian meteorites. One particle (WF1801-AC3) displays an elevated Fe/Mn ratio of ~78, comparable to the values determined for lunar rocks. The negative correlation observed between the $CaO+Al_2O_3$ contents and the Fe/Si ratios of achondritic spherules reflects both the mineralogy of the precursor materials, as well as the extent of volatilization experienced during atmospheric entry heating. This trend furthermore suggests that the primary mineralogy of precursor materials may have been compositionally similar to basaltic achondrites. Based on their distribution in Ca/Si vs. Al/Si space, we argue that the majority of achondritic cosmic spherules predominantly samples pyroxene- and/or plagioclase-rich (i.e., basaltic) precursor bodies. Such precursor mineralogy is also inferred from their rare earth element (REE) patterns, which show resemblances to fine-grained basaltic eucrites or Type 1 achondritic spherules (n = 3 - av. REE_N = 11.2–15.5, (La/Yb)_N = 0.93–1.21), pigeonite-rich equilibrated eucrite precursors or Type 2 achondritic spherules (n = 1 - av. REE_N = 27.9, (La/Yb)_N = 0.10), and possibly Caphosphates from (primitive) achondritic bodies (n = 1 - av. REE_N = 58.8, (La/Yb)_N = 1.59). The preatmospheric oxygen isotope composition was reconstructed through compensation of mass-dependent fractionation and kinetic isotope effects, as well as mixing with atmospheric oxygen, using iron isotope data. Two particles (WF1801AC-2, WF1801-AC4) display corrected oxygen isotope compositions ($\delta^{18}O = 3.59-4.37\%$, $\delta^{17}O = 1.34-1.51\%$) largely consistent with HED meteorites and may thus originate from HED-like parent bodies. The corrected oxygen isotope compositions ($\delta^{18}O = 12.54-12.79$ ‰, $\delta^{17}O = 5.70-6.13\%$) of the remaining particles (WF1801-AC3, WF1801-AC5) do not correspond to known meteorite fields and may represent two distinct types of unknown achondritic parent bodies. Alternatively, additional oxygen isotope fractionation processes may have occurred, which have further obscured the oxygen isotope composition of their precursor bodies. Finally, the abundance (ca. 0.5%) of achondritic cosmic spherules within the Widerøefjellet sedimentary trap is comparable to that observed in the South Pole Water Well (SPWW – ca. 0.5%), Novaya Zemlya glacier (ca. 0.25%) and Transantarctic Mountain (TAM) (ca. 2.1%) collections, confirming their rarity in Antarctic micrometeorite collections.

Keywords: oxygen isotopes, iron isotopes, achondrites, cosmic spherules, atmospheric entry

1. INTRODUCTION

Achondrites (or differentiated meteorites) is a collective term for meteoritic fragments characterized by igneous or brecciated textures, which have sampled differentiated asteroids or planetary bodies (Weisberg et al., 2006). They generally lack mm-sized, igneous droplets or 'chondrules', which are commonly observed within the majority of chondritic meteorites, and display more evolved, non-solarlike compositions. This is attributed to a variety of planetary-scale differentiation processes, such as core-mantle segregation and the development of a crust- and mantle-like structure through fractional melting and crystallization processes (Mittlefehldt et al., 1998), essentially destroying primary textural features and modifying the chemical and isotopic composition of the parent body material.

Stony achondrites sample (partial) melts, melt residues and cumulate rocks within the crust or mantle of a differentiated asteroid or planetary body. Chemically, these materials can be distinguished from their chondritic or primitive achondritic analogues based on their distribution in Fe/Mg versus Fe/Mn space (Goodrich and Delaney, 2000). The latter work has demonstrated that achondrites display a characteristic fractionation trend in their Fe/Mg composition due to different compatibilities of Fe, Mg and Mn in common mineral phases during partial melting and fractional crystallization stages, while the Fe/Mn ratios are less affected by this process. This chemical partitioning is particularly useful to determine whether differentiated meteorites sampled a crustal/evolved- (high Fe/Mg) or mantle/primitive-like (low Fe/Mg) source lithology. Furthermore, the Fe/Mn ratio is well-constrained and unique to each achondritic parent body, which demonstrates its potential as an identification criterion. For instance, the howardite-, eucrite- and diogenite-suite (or HED-suite), presumed to have originated from the 4-Vesta asteroid, is characterized by constant Fe/Mn ratios of 30 ± 2 . Similar to the HED-suite, martian or shergotitie-nakhlite-chassignite (SNC) meteorites display Fe/Mn ratios of 32 ± 6

(Papike et al., 2003). This value is considerably higher in lunar meteorites (62 ± 18) and angrites (111 ± 23).

Micrometeorites are extraterrestrial dust particles 10–2000 µm in size (Rubin and Grossman, 2010), which are commonly classified into unmelted, scoriaceous and molten micrometeorites based on their textural properties (Genge et al., 2008). Molten micrometeorites (commonly referred to as 'cosmic spherules') have suffered near-complete melting during atmospheric entry and have subsequently experienced (severe) textural, chemical and isotopic modifications (Love and Brownlee, 1991). Achondritic particles have previously been recovered and identified from the Antarctic micrometeorite record. Taylor et al. (2007) initially reported a small number (n = 7) of vitreous cosmic spherules from the highly pristine SPWW collection and observed Fe/Mn ratios comparable to HED meteorites. They argued that Mg (50% condensation temperature $T_C = 1336-1343$ K – Lodders, 2003; Wood et al., 2019) and Mn (50%T_C = 1123-1158 K – Lodders, 2003; Wood et al., 2019) largely remained unaffected by atmospheric entry heating based on isotopic fractionation trends in cosmic spherules (Alexander et al., 2002; Engrand et al., 2005; Taylor et al., 2005). However, Fe (50%T_C = 1336-1338 K – Lodders, 2003; Wood et al., 2019) appears to be more susceptible to atmospheric heating processes, including evaporation (Engrand et al., 2005; Taylor et al., 2005) and metal bead extraction (Genge and Grady, 1998). Metal bead extraction may occur when micrometeoroids, enriched in fine-grained carbonaceous matter, are heated during atmospheric entry (Brownlee et al., 1997; Genge and Grady, 1998). A strongly reduced environment is formed through pyrolysis of carbonaceous material, concentrating key transitional elements (e.g., Fe, Co, Ni, V) into an immiscible metallic bead due to their siderophile behaviour. The aforementioned processes tend to shift the Fe/Mg and Fe/Mn ratios to lower values, but their impact is considered to be relatively minor. As such, the Fe/Mg versus Fe/Mn relationships of achondritic micrometeorites are interpreted to reflect the parent body composition.

A small number of unmelted achondritic micrometeorites have also been recovered from the Antarctic blue ice fields at Cap Prud'homme (n = 1 – Gounelle et al., 2009) and the Russian Novaya Zemlya glacier (n = 4 – Badjukov et al., 2010). These basaltic micrometeorites have been linked to HEDs, mesosiderites or even unknown types of achondritic parent bodies, demonstrating the potential and importance of micrometeorite investigations. More recently, Cordier et al. (2011a, 2012) have investigated the major, trace elemental and oxygen isotope composition of vitreous achondritic cosmic spherules from the SPWW (n = 4) and sedimentary traps in the TAMs (n = 11). They argued that most achondritic micrometeorites display vitreous textures due to their lower Mg contents, which lowers their melting temperature. Based on their observations, Cordier et al. (2011a, 2012) have suggested several additional parameters that may assist in the identification of achondritic micrometeorites. For instance, achondritic cosmic spherules tend to be depleted in siderophile elements (e.g., Ni: 0.17–131 µg/g and Co: 1.3–68.1 µg/g) and are enriched in REEs (1.4–13.7x CI), which is consistent with the generation and extraction of basaltic melts from a differentiated or planetary body. Furthermore, Cordier et al. (2012) were able to distinguish 3 different types of precursor material based on the REE pattern of the

achondritic cosmic spherules, including fine-grained eucrites consisting of pigeonite and anorthite (Type 1), pigeonite-rich eucrites (Type 2) and a howardite-like precursor containing metal-bearing diogenite fragments (Type 3). However, the oxygen isotope data measured for these achondritic cosmic spherules did not prove to be consistent with reference values for HED meteorites. This was attributed to atmospheric entry heating, which induces mass-dependent fractionation and mixing with atmospheric oxygen, consequently modifying the original oxygen isotopic composition of the precursor body (Yada et al., 2005; Suavet et al., 2010; van Ginneken et al., 2017; Goderis et al., 2020; Rudraswami et al., 2020; Suttle et al., 2020; Soens et al., 2020). Additionally, Antarctic micrometeorites may experience aqueous alteration processes, which shifts the oxygen isotope composition towards Standard Light Antarctic Precipitation (SLAP – Zekollari et al., 2019). Quantification of oxygen isotope fractionation processes is thus essential to identify the precursor body of melted (achondritic) micrometeorites. Recently, Brase et al. (2021) recovered two achondritic cosmic spherules from sedimentary deposits at Mount Raymond and the Jacobs Nunatak in the Transantarctic Mountains. They concluded that the differentiated particles presumably originated from 4-Vesta based on its major and trace elemental composition.

Here, we present new major, trace elemental and oxygen isotope data for five vitreous achondritic cosmic spherules recovered from the Widerøefjellet sedimentary trap in the Sør Rondane Mountains of Dronning Maud Land, East Antarctica. In addition, we provide the first iron isotope data for achondritic cosmic spherules (n = 4). This information is useful to estimate the extent of mass-dependent fractionation processes and thus allow a reconstruction of the pre-atmospheric oxygen isotope composition of achondritic micrometeorites. Finally, we compare the abundance of achondritic micrometeorites among the respective collection sites to investigate potential preservation or sampling biases.

2. MATERIALS AND METHODS

Extraterrestrial- and impact-related material was recently discovered in sedimentary traps at Widerøefjellet in the Sør Rondane Mountains (Dronning Maud Land, East Antarctica) during the joint Belgian-Japanese MICROMETA (2012–2013) and Belgian Antarctic Meteorites and Micrometeorites (BAMM!–2018) expeditions (Goderis et al., 2020; Soens et al., 2021, van Ginneken et al., 2021). Sediment traps primarily consisted of weathering pits, exposed cracks, fissured surfaces within meta-tonalitic host rocks and moraine deposits (Kamei et al., 2013; Kojima and Shiraishi, 1986). The accumulation of microscopic dust particles in the SRMs presumably initiated ca. 1–3 Ma based on the glacial history and ¹⁰Be bedrock exposure ages acquired in the western parts of the SRM (Suganuma et al., 2014). According to Goderis et al. (2020), accumulation of extraterrestrial material is predominantly controlled by atmospheric infall. This was deduced from the physicochemical and isotopic properties of the Widerøefjellet cosmic spherule collection. Due to the unique environmental conditions, including the cold and dry Antarctic climate, lack of anthropogenic influence and the ability to accumulate material

over a prolonged timespan, extraterrestrial material can easily be identified and is generally omitted from significant alteration processes. The Widerøefjellet cosmic spherule collection is thus representative of the modern cosmic dust flux to Earth (Taylor et al. 2000; 2007; Suavet et al. 2009; Goderis et al., 2020).

The bulk sedimentary deposit (ca. 2.65 kg) collected from the Widerøefjellet 1 (2018) sedimentary trap was initially weighed, washed to remove excess silt and clay particles, and sieved into six size fractions ranging from $<125 \mu m$ to $>2000 \mu m$. The respective size fractions were dried in an oven at a temperature of ca. 60°C for a time span of 12 to 24 hours. A magnetic separation was performed using a hand magnet to extract most magnetite-bearing micrometeorites. Magnetite is commonly formed when both ferrous and ferric iron are oxidized during atmospheric entry heating, while metallic iron is oxidized and incorporated into the silicate melt (Genge and Grady, 1999). Vitreous cosmic spherules, which do not display crystal development due to the lack of crystal nuclei and a high cooling rate, mainly reside within the non-magnetic sediment fraction. Micrometeorites from the magnetic and non-magnetic size fractions were subsequently extracted using a binocular microscope and Ti-coated tweezers to prevent the magnetization of micrometeorites and contamination with siderophile elements (e.g., Ni). During this study, we have focused on vitreous cosmic spherules recovered from the non-magnetic sediment fractions based on previous observations which demonstrated that achondritic micrometeorites are predominantly vitreous (e.g., Taylor et al., 2007; Cordier et al., 2011a; 2012). Semi-quantitative compositions were determined with a JEOL JSM IT-300 scanning electron microscope (SEM) coupled to an Oxford energy-dispersive spectrometer (EDS) at the SURF research unit of the Vrije Universiteit Brussel (VUB), Belgium. Achondritic micrometeorites were searched for using the aforementioned Fe/Mg vs. Fe/Mn systematics (Goodrich and Delaney, 2000; Taylor et al., 2007). A total of five V-type cosmic spherules (among 1000s of chondritic particles) was identified which display non-chondritic Fe/Mg–Fe/Mn ratios, and used for further study. Table 1 provides an overview of the physical properties of these five cosmic spherules selected during this study. The particles were subsequently embedded in epoxy resin and polished for further analysis.

Major and trace elemental compositions were analyzed *in situ* using a Teledyne Cetac Technologies Analyte G2 excimer-based laser ablation system equipped with HelexII double volume cell and ARIS aerosol introduction system and coupled to a Thermo Scientific Element XR sector field inductively coupled plasma–mass spectrometer (LA-ICP-MS) at the Department of Chemistry of Ghent University (Ghent, Belgium) using an external calibration by USGS and MPI-DING glass reference materials and established sum normalization data processing approach (see Chernonozhkin, 2021 – see Table S1). To remove potential adhesives on the surface of micrometeorites, a short pre-ablation was run prior to LA-ICP-MS analysis. Three replicate analyses were performed using a spot size of ca. 35 µm. Values reported in Table S1 represent average values for the respective particles. The accuracy of the LA-ICP-MS analysis was determined by comparing the average bias between the experimentally obtained values and the reference values of the glass reference materials, and was found to be less than 10% for all reported elements. The reproducibility of the LA-ICP-MS analysis was determined by calculating the relative standard deviation (RSD) for the repeated analyses of the MPI-DING ATHO-G glass reference material. The reproducibility for most elements is <5% RSD, 5-10% RSD for Li, Ge, As, Mo, Cs, Tb and Tm, and <15% RSD for Be, Cr, Co, Ni, Sb and U. The reproducibility for the latter elements is likely related to their lower concentration (<12 ppm) in the ATHO-G reference glass, and is supported by their overall good reproducibility (<10% RSD) in other USGS and MPI-DING reference glasses, including BHVO-2G and ML3B-G.

The triple-oxygen isotope composition ($\delta^{17}O$, $\delta^{18}O$, $\Delta^{17}O$) of the achondritic cosmic spherules were determined using a Cameca IMS 1270 secondary ion mass spectrometer (SIMS) at the Centre de Recherches Pétrografiques et Géochimiques (CRPG, France). Oxygen isotopes were released from the sample surface by the incident Cs⁺ ion beam at a 10-15° angle (spot size ca. 15 µm and ca. 2.5 nA beam current). The ions ($^{16}O^{-,17}O^{-,18}O^{-}$) were monitored simultaneously in multi-collection mode using Faraday cups. Samples were pre-sputtered and probed for ca. 275 s. To compensate for instrumental mass fractionation effects, a total of three reference materials including the basaltic glass CLDR01, diopside JV1 and San Carlos olivine were measured five times at the start and end of each analysis session. Analytical uncertainties were determined based on repeated analysis of three reference materials and found to be ±0.55‰ (2SE) for $\delta^{17}O$, ca. ±0.53‰ (2SE) for $\delta^{18}O$ and ca. ±0.62‰ (2SE) for $\Delta^{17}O$, where SE stands for the standard error based on the replicate analysis of reference materials.

In-situ Fe isotope ratio measurements of the micrometeorites was performed using a ns-LA-MC-ICP-MS set-up using an Analyte G2 193 nm ArF*excimer-based LA-system (Teledyne Photon Machines Inc., Bozeman, MT, USA), equipped with a COBALT ablation cell and ARIS aerosol rapid introduction system (PEEK tubing with 1 mm ø) (Van Malderen et al., 2020), connected to a Thermo Scientific Neptune MC-ICP-MS instrument equipped with high-transmission interface and a Pfeiffer (Germany) OnToolTM Booster 150 dry interface pump (130 m³ h⁻¹ pumping speed) at Ghent University (Ghent, Belgium). Instrumental mass discrimination correction relied on internal doping with a standard solution of Ni (500 ng mL⁻¹), continuously aspirated via pneumatic nebulizer and a double pass spray chamber, using a T-piece (5 mm ϕ) for mixing. The Fe isotope ratios were additionally corrected for potential drift by sample-standard bracketing (SSB) using the United States Geological Survey (USGS) basaltic glass reference material BCR-2G. The BCR-2G was ablated using a circular spot size of 15 µm diameter, laser energy density of 1.74 J cm⁻² and a laser repetition rate of 20 Hz. To assure for an adequate correction relative to the reference material, the Fe intensities for the cosmic spherules were matched within 5% to those obtained for BCR-2G by adjusting the spot size (10-30 µm) and laser repetition rates (25-45 Hz). Nuclides ⁵³Cr, ⁵⁴Fe, ⁵⁶Fe, ⁵⁷Fe + ⁵⁸Ni and ⁶⁰Ni were measured simultaneously in an array of six Faraday cups at medium mass resolution (m/ Δ m ~ 6000). ⁵³Cr was monitored to correct for the isobaric interference of ⁵⁴Cr on ⁵⁴Fe, applying the natural abundances of Cr. Further details of the method can be found in González de Vega et al. (2020a) and Lampe et al. (submitted). The Fe isotope ratios of the CSs are expressed as δ -values relative to IRMM-014 international reference material, with $\delta^{i}Fe = [({}^{i}Fe/{}^{54}Fe)_{sample}/({}^{i}Fe/{}^{54}Fe)_{reference material} -1] \cdot 1000$ (‰) (González de Vega et al., 2020b). Here ${}^{i}Fe$ represents the isotopes of interest i = 56, 57. Based on fifteen measurements in several separate analytical sessions of BCR-2G reference material, the intermediate precision (2SD) is 0.10‰ and 0.14‰ for $\delta^{56}Fe$ and $\delta^{57}Fe$, respectively.

3. RESULTS

3.1. Physical and petrographic properties

The achondritic cosmic spherules are relatively large and range in size between 341 and 526 µm (Table 1). These particles are classified as 'vitreous' following the classification of Genge et al. (2008) and display a variety of colors ranging from black, brown and dark green/grey. Particles often display palagonitization features as a result of terrestrial aqueous alteration processes (Fig. S2). Following the weathering scale defined by van Ginneken et al. (2016), particles WF1801-AC1, AC3, AC4 and AC5 classify as '1a-b' implying that a minor portion of the vitreous material was altered and these particles possibly exhibit a surficial encrustation (see also Table 1). Particle WF1801-AC2 does not contain such alteration rim and classifies as '0a', indicating a lack of any significant alteration features.

3.2. Major elemental compositions

The achondritic nature of cosmic spherules was determined based on their distribution in Fe/Mg vs. Fe/Mn space (Fig. 1). Four out of five particles reported here display Fe/Mg-Fe/Mn relations similar to or slightly below HED (Fe/Mn = 30 ± 2) and martian (Fe/Mn = 32 ± 6) meteorites, but at widely varying Fe/Mg ratios (ca. 0.48–1.72). These values are representative of achondritic cosmic spherules from literature, and are inconsistent with the distribution of chondritic cosmic spherules from the SRMs. The Fe/Mg ratios furthermore suggest that particles WF1801AC4 and WF1801-AC5 may derive from a more primitive, mantle-like precursor body (e.g., diogenite, howardites, cumulate eucrites), whereas particles WF1801-AC1 and AC2 may have been inherited from a crustal-like (e.g., basaltic eucrite) precursor body. In contrast, particle WF1801-AC3 plots near the Fe/Mg ratios of WF18-AC4 and AC5, but at considerably higher Fe/Mn ratios (ca. 78), comparable only to lunar rocks (Fe/Mn = 62 ± 18).

Achondritic spherules can also be distinguished from chondritic cosmic spherules (Goderis et al., 2020), microtektites (Soens et al., 2021) and meteoritic condensation debris (van Ginneken et al., 2021) previously recovered from the SRMs using the Si-Fe-Mg ternary diagram (Fig. 2). Achondritic spherules partly overlap in the 'chondritic micrometeorite' compositional field, but predominantly display elevated Si contents in comparison (Table S1). The Si content in achondritic spherules (SiO₂ = 40.9–54.1 wt%) is significantly lower than that observed in Australasian microtektites from the same Antarctic micrometeorite trap (SiO₂ = 66.4–76.1 wt% – Soens et al., 2021). Furthermore, Australasian microtektites tend to be enriched in K₂O (ca. 0.65–1.10 wt%). In contrast, meteoritic condensation

spherules are generally Si-poor (33.6–38.4 wt%) and enriched in Na₂O (ca. 0.26–1.34 wt%) and NiO (1,48–2.31 wt%) (van Ginneken et al., 2021).

Cordier et al. (2011b) have previously classified vitreous cosmic spherules into three distinct chemical classes, which reflect increasing degrees of volatilization experienced during atmospheric entry. This includes the 'normal chondritic', 'Ca-Al-Ti- or CAT-like' and 'high Ca-Al' subtypes. The achondritic cosmic spherules reported here all plot within the 'high Ca-Al' field which is consistent with the majority (ca. 63%) of reference values from literature (Fig. 3). The remaining particles (ca. 37%) plot within the 'normal chondritic' field. Interestingly, no achondritic spherules plot within the 'CAT-like' field, which suggests that 'CAT-like' particles may have sampled a different type of precursor material and/or followed an evaporation regime distinct from most (a)chondritic micrometeorite precursor bodies. Furthermore, a subtle trend can be observed that displays a negative correlation ($R^2 = 0.73$) between the CaO+Al₂O₃ content and Fe/Si ratio of (mostly 'high Ca-Al') achondritic cosmic spherules. On a side note, we briefly mention the Ti-rich nature of particle WF1801-AC5 (ca. 3.28 wt%).

The mineralogical control on achondritic spherules can to some extent be determined based on their distribution in Ca/Si vs. Al/Si space (Cordier et al., 2011a) (Fig. 4). The latter study observed Ca/Si and Al/Si atomic ratios ranging from 0.02–0.34 and 0.02–0.72, respectively. The achondritic spherules reported here display overall higher Ca/Si ratios (0.29–0.31), with particles WF1801-AC4 and WF1801-AC5 displaying values of 0.38 and 0.56, respectively. The Al/Si ratios are more consistent with the reference values for achondritic cosmic spherules and range from 0.02–0.70. Figure 4 also displays the compositional fields of common mineral phases (e.g., pyroxene: low Al/Si ratio) observed in achondritic meteorites. Particles WF1801-AC1 and AC3 are located to the right of a cluster of reference values associated to basaltic eucrites. Particle WF1801-AC2 displays a chemical composition similar to high-Ca pyroxene phases, and compatible with nakhlites (augite-rich martian meteorite - Treiman, 2005). Particle WF1801-AC4 is slightly offset from the 'plagioclase' field and in relative close proximity of particle 3.5-7 (green triangle - Cordier et al., 2011a). Finally, particle WF1801-AC5 is positioned away from the mineralogical fields and achondritic reference values at high Ca/Si and moderately high Al/Si ratios.

3.3. Trace elemental compositions

To further constrain the nature and mineralogy of the achondritic precursor bodies, we examine several key elements including the lithophile (e.g., Sr, Ba), siderophile-chalcophile (e.g., Co, Ni, V), and REEs (Fig. 5-6). Strontium abundances are highly variable $(8.1-163 \ \mu g/g)$ but lie within range $(0.60-177 \ \mu g/g)$ of achondritic cosmic spherules previously analyzed by Cordier et al. (2011a, 2012) and Brase et al. (2021). Particles WF1801-AC1 and WF1801-AC3 are positioned close to a cluster of Type 1 spherules, while particle WF1801-AC2 displays similar Sr abundances as Type 2-3 spherules but at a higher Fe/Mg ratio. The Sr concentration of particles WF1801-AC4 and WF1801-AC5 are

elevated and do not match with reference values from literature. Barium concentrations appear to be more restricted $(25.4-48.1 \,\mu g/g)$, except in the case of particle WF1801-AC2 that displays both depleted Sr and Ba (1.37 µg/g) abundances as observed in Type 2-3 spherules. Particles WF1801-AC1 and WF1801-AC3 are located in close proximity of the Type 1 spherule cluster. Analogous to Sr, particles WF1801-AC4 and WF1801-AC5 display elevated Ba contents that do not match reference values from literature. Scandium concentrations in particles WF1801-AC1, WF1801-AC3 and WF1801-AC4 are fairly constant (34.6–39.0 µg/g) and consistent with Type 1 and Type 2 spherules. In contrast, Sc abundances in particles WF1801-AC2 (162 μ g/g) and WF1801-AC5 (71 μ g/g) are (markedly) higher and incompatible with reference values from literature. According to Cordier et al. (2011a), V is an important indicator for the oxidation state of a differentiated or planetary body. Vanadium concentrations are highly variable $(2.05-75.8 \,\mu g/g)$ for the particles measured here and positioned close to a cluster of achondritic cosmic spherules encompassing the three different types reported by Cordier et al. (2012), except for particle WF1801-AC5. Nickel and cobalt are siderophile elements that are generally depleted in stony achondritic (micro)meteorites due to their accumulation and concentration in planetesimal or planetary cores. Most achondritic cosmic spherules have low Ni abundances (3.12-10.7 μ g/g), which is consistent with Type 1 and Type 2 reference values from literature. Particle WF1801-AC2 displays more elevated Ni concentrations (75.2 μ g/g) and cannot be linked to a particular type. A similar observation is made for Co abundances $(0.85-4.94 \,\mu g/g)$, which are compatible with Type 1-2 spherules. Particle WF1801-AC3 displays elevated Co concentrations (18.7 μ g/g) comparable to a Type 1 particle reported by Cordier et al. (2011a).

The REE pattern of achondritic cosmic spherules is useful since the REEs mainly reside within accessory (rather than silicate) mineral phases such as apatite and whitlockite (Harvey et al., 1993; Hsu and Crozaz, 1996). In addition, the refractory nature of these refractory elements leads to a preservation of the REE pattern of the precursor material despite the volatilization occurring during atmospheric entry heating. The REE patterns for the achondritic cosmic spherules are presented in figure 6. All achondritic spherules are highly enriched in REEs (average $REE_N = 11.29-61.80$, Eu excluded) with respect to chondritic (micro)meteorites. Particles WF1801-AC1 and WF1801-AC3 display relatively flat REE patterns ((La/Yb)_N = 1.18-1.21) with minor, negative Eu anomalies (Eu^{*} = 0.72-0.76) and are consistent with bulk eucrites and Type 1 spherules. While particle WF1801-AC3 displays Fe/Mn ratios comparable to lunar rocks (Fig. 1), its REE pattern is somewhat similar to that of Apollo basalts but less enriched (Meyer, 2016). Particle WF1801-AC2 displays an REE pattern similar to eucritic pigeonite/augite and Type 2 achondritic spherules, which are notably enriched in HREE with respect to the LREE $((La/Yb)_N)$ = 0.10) and exhibit a large, negative Eu anomaly ($Eu^* = 0.07$). However, particle WF1801-AC2 is notably enriched in REE (average $REE_N = 29.93$) with respect to Type 2 achondritic spherules. The REE pattern of particle WF1801-AC4 is broadly flat ((La/Yb)_N = 0.93) but exhibits a large, positive Eu anomaly (Eu* = 2.56) and a small positive Tm anomaly, and cannot be linked to a known type of achondritic spherule or does not match the REE pattern of plagioclase. Yet, the contribution of
plagioclase is clearly evidenced by its positive Eu-anomaly. Finally, particle WF1801-AC5 displays the highest REE abundances (average REE_N = 61.80), is slightly enriched in LREE with respect to the HREE ((La/Yb)_N = 1.59), and displays a moderately large, negative Eu anomaly (Eu^{*} = 0.27). Particle WF1801-AC5 can thus not be linked to a known type of achondritic spherule, but its REE pattern is comparable to that of Ca-phosphates (e.g., apatite, whitlockite) in (primitive) achondrites and the KREEP component of lunar basalts. However, unlike KREEP basalts, particle WF1801-AC5 only displays enriched Zr, Nb, Hf, REE, Ta and Th concentrations (Table S1). We have not observed achondritic cosmic spherules with REE patterns similar to Type 3 spherules during this study.

3.4. Oxygen isotope composition

The oxygen isotope data of the Widerøefjellet achondritic spherules displays a large range in δ^{17} O (5.76–21.93‰) and δ^{18} O (12.09–43.44‰) values, much larger than previously reported values for δ^{17} O (6.96–9.99‰) and δ^{18} O (14.37–20.12‰) by Cordier et al. (2012). However, the majority of SRM particles are positioned in close proximity of the TAM achondritic spherules, except for particle WF1801-AC5 that displays a heavily fractionated oxygen isotope signature (Table 2, Fig. 7). All particles are positioned between the Eucrite (EFL) and Martian (MFL) Fractionation Line (EFL), within error. Note that all analyses were conducted on unaltered, fresh areas of the respective micrometeorite sections. As such, we do not expect nor observe evidence for significant contributions of SLAP.

3.5. Iron isotope composition

The iron isotope data records the effects of mass-dependent fractionation. This is demonstrated by the δ^{56} Fe vs. δ^{57} Fe diagram, which shows an excellent, positive correlation (R² = 0.9977) for S- and I-type cosmic spherules previously reported and presented here (Table 3, Fig. 8). In S-type cosmic spherules, Fe isotope fractionation appears to be negatively correlated with the FeO abundance (Fig. 9). This correlation is not observed for I-type spherules. Furthermore, the extent of Fe evaporation and isotope fractionation in porphyritic and barred olivine spherules is not as pronounced as that observed in cryptocrystalline, vitreous and CAT spherules. The vitreous achondritic cosmic spherules do not appear to follow this trend as particles WF1801-AC2 and WF1801-AC3 display similar values as BO spherules. In contrast, particles WF1801-AC4 and WF1801-AC5 are heavily fractionated, similar to V-type and CAT spherules.

4. DISCUSSION

4.1. Oxygen isotope ratios in cosmic spherules: a source of ambiguity

Oxygen isotope signatures are unique and associated to specific types of asteroidal or cometary bodies (e.g., Clayton, 1993; Clayton and Mayeda, 1996; Wiechert et al., 2004; Greenwood et al., 2005). To characterize the parent body of (achondritic) cosmic spherules, we require a thorough understanding

of oxygen isotope systematics in micrometeorites. The oxygen isotope composition of cosmic spherules is generally not compatible with reference values for chondritic or achondritic meteorite groups (Yada et al., 2005; Suavet et al., 2010; Cordier et al., 2011b; Cordier et al., 2012; van Ginneken et al., 2017; Goderis et al., 2020; Rudraswami et al., 2020; Suttle et al., 2020; Soens et al., 2020). This can presumably be attributed to mass-dependent fractionation of oxygen isotopes and mixing with atmospheric oxygen during atmospheric entry heating. Evaporation results in mass-dependent fractionation and a systematic increase of the abundances of heavier (¹⁸O) isotopes of oxygen compared to the lighter (¹⁷O, ¹⁶O) ones. This shifts the original oxygen isotope composition of a micrometeorite precursor body towards the right on a Δ^{17} O vs. δ^{18} O diagram (Fig. 7). Additionally, atmospheric oxygen may be incorporated from the surrounding atmosphere during flash melting, which moves the original oxygen isotope composition along the mixing line towards the stratospheric oxygen isotope value (δ^{18} O $\approx 23.8\%$, δ^{17} O $\approx 11.8\%$ – Thiemens et al., 1995).

Cordier et al. (2012) previously attempted to compensate for the effects of atmospheric fractionation processes on achondritic cosmic spherules based on two main assumptions. Firstly, the interaction with atmospheric oxygen and/or kinetic isotope effects were estimated to amount ca. 8‰ following the observations of Clayton et al. (1986) for I-type cosmic spherules. For simplicity, achondritic cosmic spherules were assumed to behave in a similar manner as I-type spherules during atmospheric entry heating. Secondly, the extent of mass-dependent fractionation was estimated based on reference values for oxygen isotope compositions in HED meteorites (i.e., $\delta^{18}O \approx 3.59\%$ – Greenwood et al., 2005) and the Rayleigh fractionation law $R/R_0 = (1 - f)^{(1/\alpha - 1)}$, where R is the δ^{18} O composition of the cosmic spherule, R_{θ} is the δ^{18} O composition of the parent body, α is the isotopic fractionation factor (1.0237 – Wang et al., 2001), and f is the amount of oxygen that was lost as a result of evaporation/mass-dependent fractionation. Cordier et al. (2012) concluded that achondritic cosmic spherules have lost ca. 10–30% (f = 0.1 - 0.3) of their oxygen due to evaporation when mixing with atmospheric oxygen is considered (i.e., a correction factor of 8‰ was applied). This fraction increases to ca. 30–50% (f = 0.3-0.5) when the latter process is not accounted for. Note that the oxygen isotope compositions reported by Cordier et al. (2012) possibly record a negative offset due to the analytical procedure followed. This effect has previously been demonstrated to produce slightly lower Δ^{17} O values.

Based on the oxygen isotope data of the Widerøefjellet achondritic spherules, we observe evaporation losses of ca. 2–73% when we consider the effects of mixing with atmospheric oxygen and/or kinetic isotope effects. These numbers increase to ca. 30–81% if we assume that mass-dependent fractionation was the sole process at play. It is important to emphasize that we have assumed a bulk eucrite precursor composition (δ^{18} O $\approx 3.59\%$ – Greenwood et al., 2005). This implies that achondritic parent bodies with similar oxygen isotope compositions cannot be distinguished from HED meteorites using this method. In contrast, achondritic parent bodies displaying oxygen isotope compositions vastly different than those observed in HED meteorites will either underestimate or overestimate the extent of mass-dependent fractionation. To illustrate this, we examine the evaporation values of particle WF1801-

AC5 (ca. 81% and ca. 73% when the 8‰ correction factor is applied). These numbers are considerably higher than those reported for stony chondritic ($f = 0.4 \pm 0.3$ – Engrand et al., 2005) or previously measured achondritic spherules (see above – Cordier et al., 2012), and would imply that particle WF1801-AC5 was subjected to extreme degrees of evaporation where the vast majority (>80-90%) of the original mass was lost. While a large extent of evaporation is supported based on the major and trace elemental composition of particle WF1801-AC5 (e.g., Fig. 3, 4, 6), it is also possible that the oxygen isotope composition of the precursor body of particle WF1801-AC5 was estimated incorrectly. A similar conclusion can be drawn for particle WF1801-AC3.

4.2. Correlation between oxygen and iron isotope compositions in achondritic spherules

To quantify the extent of mass-dependent oxygen isotope fractionation, Lampe et al. (submitted) measured the oxygen (δ^{18} O, δ^{17} O, Δ^{17} O) and iron (δ^{56} Fe, δ^{57} Fe) isotope composition for a set of chondritic cosmic spherules (n = 58). They found that the δ^{18} O and δ^{57} Fe ratios covary according to the following empirical equation: δ^{18} O_{corr} = δ^{18} O_{meas} – 0.6986 x δ^{57} Fe_{meas}, where δ^{18} O_{corr} is the δ^{18} O ratio corrected for mass-dependent fractionation effects, δ^{18} O_{meas} is the δ^{18} O ratio measured in the cosmic spherule, and δ^{57} Fe_{meas} is the δ^{57} Fe ratio measured in the cosmic spherule. Note that this correction does not take into account potential effects of interaction with atmospheric oxygen and/or kinetic isotope effects. The extent of mass-dependent fractionation in δ^{18} O for the SRM achondritic spherules ranges from ca. 0.50–12.12‰. This lies within the range reported by Lampe et al. (submitted) for 31 vitreous cosmic spherules (0.21–38.90‰ with an average of ca. 7.18 ± 9.02‰).

To compensate for mixing processes with atmospheric oxygen and/or kinetic isotope effects, we apply an additional correction factor of ca. 8% following the observations of Clayton et al. (1986) in Itype spherules. We can then define and calculate the $\delta^{18}O_{corr}^*$ ratio as follows: $\delta^{18}O_{corr}^* = \delta^{18}O_{corr} - 8\%$ (see Table 3). Furthermore, assuming the Δ^{17} O ratio did not change extensively during atmospheric entry heating, we can estimate the primary δ^{17} O ratio using the equation of the terrestrial fractionation line: $\Delta^{17}O = \delta^{17}O - 0.52 \text{ x } \delta^{18}O$, where $\Delta^{17}O$ is the $\Delta^{17}O$ ratio measured from the cosmic spherule, and δ^{18} O is the δ^{18} O_{corr}^{*} ratio mentioned above. This assumption is plausible since the Δ^{17} O ratio of most achondritic meteorites ranges from 0.32 to -0.26‰ (Clayton and Mayeda, 1996; Franchi et al., 1999), which does not change the calculated primary $\delta^{17}O$ (or $\delta^{17}O_{corr}$) ratio considerably. Due to the lack of iron isotope data for particle WF1801-AC1, we were not able to calculate the $\delta^{18}O_{corr}^*$ ratio. As such, we observe two groups of particles which display comparable $\delta^{18}O_{corr}^*$ ratios (Table 3 and Fig. 10). Particles WF1801-AC2 and WF1801-AC4 are located within or are in close proximity of the HED field, while particles WF1801-AC3 and WF1801-AC5 display δ¹⁸O_{corr}* ratios of ca. 12.21-12.54‰ and $\delta^{17}O_{corr}$ of ca. 5.70–6.13‰, which is inconsistent with achondritic parent bodies observed to date. This could simply represent two new achondritic precursor bodies (since their Fe/Mn ratios vary considerably), but may also suggest that oxygen isotope fractionation is more complex and that certain processes potentially have not been accounted for. Metal bead extraction, while unlikely for achondritic

precursor particles, demonstrates that the chemistry and mineralogy of dust particles have an important control on atmospheric entry processes, including oxygen isotope fractionation (Genge and Grady, 1998). As such, it is plausible that the interaction of achondritic precursor bodies with the Earth's atmosphere will vary following their respective chemical and mineralogical properties. The combined use of oxygen and iron isotope data to elucidate the precursor bodies of (achondritic) micrometeorites has consequently provided some promising results. Yet, we require more data to further constrain the correlation between oxygen and iron isotopes in both chondritic and achondritic micrometeorites to understand how different types of meteoritic material are affected by atmospheric entry heating. As such, our observations support those of Cordier et al. (2011a, 2012), who emphasized the importance of major and trace elemental chemistry in the identification of (a)chondritic precursor bodies in light of the ambiguity associated to oxygen isotope data.

4.3. Mineralogical control and parent body identification of the Widerøefjellet achondritic spherules

In the following section, we attempt to characterize and identify the precursor body of the respective achondritic cosmic spherules based on their major, trace elemental chemistry (cfr. mineralogical control) and corrected oxygen isotope compositions (i.e., $\delta^{18}O_{corr}^*$ – see Table 3) calculated in the previous sections.

4.3.1. Particle WF1801-AC1

The major element chemistry of particle WF1801-AC1 is consistent with a martian or HED-like parent body based on the Fe/Mn ratio of ~30. Additionally, the relatively high Fe/Mg ratio (~1.47) suggests that particle WF1801-AC1 has sampled an evolved, basaltic-like precursor body such as basaltic/polymict eucrites or basaltic shergottites (Fig. 1). Both sources can be discriminated based on their bulk Al₂O₃ and Na contents as well as their Al₂O₃/CaO ratio. On average, eucrites display elevated Al₂O₃ contents (ca. 12 wt% vs. 6.9 wt%) and Al₂O₃/CaO ratios (ca. 1.2 ± 0.1 wt% vs. 0.8 ± 0.2 wt%), but are depleted in Na (0.5 \pm 0.1 wt versus 0.9 \pm 0.4 wt%) compared to martial basalts (Basaltic Volcanism Study Project 1981; Lodders 1998; Dreibus et al., 2000; Zipfel, 2000; Taylor et al., 2002a; Jambon et al. 2002; Barrat et al. 2002; Mars Meteorite Compendium 2003). Particle WF1801-AC1 has a high Al₂O₃ content of ca. 13.7 wt% and intermediate Al₂O₃/CaO ratios (1.06), which are more compatible with a eucritic precursor body. Due to the volatile nature of Na during atmospheric entry heating, the primary Na content cannot be constrained. Consequently, refractory elements including the REE, Ca and Al may have been passively enriched in the process. In addition, we emphasize that caution is required since the mineralogical abundance sampled by cosmic dust particles may not be representative of its precursor body. In the Ca/Si vs. Al/Si diagram (Fig. 4), particle WF1801-AC1 is located to the upper right of a cluster of achondritic spherules, which have presumably sampled a finegrained eucrite-like precursor body (Cordier et al., 2012). Potential deviations from this cluster could be attributed to the type and abundance of mineralogical precursors, as well as potential effects of volatilization during atmospheric entry heating. The position of particle WF1801-AC1 and the neighbouring cluster of TAM achondritic spherules in the Ca/Si vs. Al/Si diagram thus suggest that they sampled a plagioclase- and pyroxene-rich precursor body. Basaltic eucrites are predominantly composed of pigeonite and anorthite-rich plagioclase (An₇₅₋₉₃), but also contain minor amounts of chromite, ilmenite, silica, phosphate phases, Fe-Ni metal alloys, troilite and zircon (McSween et al., 2011). Basaltic eucrites are thus a likely precursor body candidate for particle WF1801-AC1. The trace element chemistry of particle WF1801-AC1 is also consistent with eucrites, except for V (Fig. 5). The REE pattern of particle WF1801-AC1 (Fig. 6A) is roughly similar but enriched compared to Type 1 spherules reported by Cordier et al. (2012), which also suggests that the particle was subjected to a higher degree of volatilization. Type 1 spherules have previously been interpreted to reflect fine-grained (<1.5 mm in size) eucritic precursors predominantly consisting of pigeonite and plagioclase phases (Mittlefehldt et al., 1998; Cordier et al., 2012). Due to the lack of iron isotope data for particle WF1801-AC1, we were not able to fully compensate for oxygen isotope fractionation processes. However, based on its major and trace elemental chemistry, we propose that particle WF1801-AC1 was likely inherited from a fine-grained, eucritic precursor body.

4.3.2. Particle WF1801-AC2

The major element chemistry of particle WF1801-AC2 can also be linked to a martian or HED-like parent body based on the Fe/Mn ratio of ~32. However, unlike particle WF1801-AC1, this cosmic spherule is characterized by even higher Fe/Mg ratios (~1.72), which is consistent with basaltic eucrites or basaltic shergottites (Fig. 1). In addition, the Al₂O₃ contents (ca. 0.98 wt%) and Al₂O₃/CaO ratios (ca. 0.07) of this particle are considerably low (e.g., Fig. 4) and comparable with nakhlites. This implies that the major element chemistry of particle WF1801-AC2 was predominantly controlled by high-Ca pyroxene phases such as pigeonite or augite. Nakhlites, however, display lower Fe/Mg ratios (ca. 0.92– 1.08; Treiman, 2005) compared to particle WF1801-AC2 and are therefore unlikely to represent its precursor body. In contrast, basaltic shergottites are predominantly composed of pyroxene phases (i.e., pigeonite and augite) and plagioclase (which is often transformed into glass or maskelynite due to shock metamorphosis), but commonly lack olivine (Stolper and McSween, 1979). The Mg numbers (Mg# = Mg/(Mg + Fe)*100) of basaltic shergottites are thus rather low (Mg# = 23-52), which is consistent with that of particle WF1801-AC2 (Mg# = 37). The pyroxene-rich nature of particle WF1801-AC2 is also evident from its trace element chemistry (Table S1, Fig. 5), where it displays relatively high Sc (162 $\mu g/g$, V (50 $\mu g/g$) and Cr (1462 $\mu g/g$) contents. Strontium (8.10 $\mu g/g$) and Ba (1.37 $\mu g/g$) concentrations are very low and indicate that the precursor was depleted in plagioclase. To discriminate the precursor body of particle WF1801-AC2, we can compare the siderophile (and to a lesser extent) chalcophile element (e.g., V, Cr, Co) contents of eucritic and martian basalts since their abundance is at least partly controlled by their oxygen fugacity levels during basalt petrogenesis. Righter and Drake (1996) suggested that the oxygen fugacity levels of martian basalts ($f(O_2) = -1.25 \Delta IW$, where ΔIW represents the oxygen fugacity levels relative to the iron-wüstite buffer) were slightly higher than eucritic basalts $(f(O_2) = -2.2 \Delta IW)$, which implies that siderophile and chalcophile elements were more oxidized during the petrogenesis of basaltic shergottites. Consequently, these elements tend to be more enriched in basaltic shergottites compared to basaltic eucrites. Cordier et al. (2011a, 2012) previously demonstrated that V and Co contents largely remained unaltered during atmospheric entry heating and may thus be representative of their precursor body. A comparison of siderophile and chalcophile element contents reveals that particle WF1801-AC2 is more likely affiliated to basaltic eucrites rather than to shergottites (see Ruzicka et al., 2001). The REE pattern of particle WF1801-AC2 is highly comparable to that of pigeonite and augite precursors from HED meteorites, and Type 2 achondritic spherules (Cordier et al., 2012), but is clearly more enriched possibly due to volatilization (Fig. 6B). This signature is inconsistent with the REE pattern of nakhlite meteorites. The corrected oxygen isotope composition of particle WF1801-AC2 is located within the HED meteorite field (Table 3, Fig. 10). We thus conclude that particle WF1801-AC2 was likely inherited from a pigeonite- and/or augite-rich, basaltic eucrite precursor body.

4.3.3. Particle WF1801-AC3

Based on the distribution of various planetary materials in Fe/Mg vs. Fe/Mn space (Fig. 1), particle WF1801-AC3 can only be linked to lunar rocks. Lunar rocks have traditionally been classified into mare basalts and highland rocks, both of which predominantly consist of regolith breccias. Mare basalts fill up the lower-lying plains, originating from meteorite or asteroidal impacts, on the surface of the Moon. In general, they exhibit elevated FeO contents (>16 wt%), are relatively depleted in MgO and Al_2O_3 , but are mostly characterized by their highly variable TiO₂ contents (Haskin and Warren, 1991). As such, mare basalts are commonly distinguished based on their bulk TiO2 content, which ranges from 'high-Ti' (>6 wt% TiO₂), 'medium-Ti' (1.5 wt% < TiO₂ < 6 wt%) and 'very-low-Ti' or 'VLT' (<1.5 wt%) TiO₂). In addition, several compositional parameters including bulk Al₂O₃ (>11 wt%: 'aluminous' or 'high-Al') and K content (>2000 μ g/g: 'high-K') are used to further classify mare basalts (Neal and Taylor, 1992). In comparison, highland rocks tend to be enriched in CaO (on average 15.6 wt%) and Al_2O_3 (on average 26.9 wt%), display higher Mg numbers (on average 67) and have relatively low TiO₂ contents (on average 0.37 wt%). Based on the abovementioned criteria, particle WF1801-AC3 appears to be more consistent with VLT mare basalts (FeO = 21.4 wt%, Al₂O₃ = 11.6 wt%, Mg# = 39, TiO₂ = 0.71 wt%), but does not match completely since its FeO content is relatively high and the corresponding SiO₂ content is low (ca. 40.9 wt%). On the Ca/Si vs. Al/Si diagram, particle WF1801-AC3 is positioned close to particle WF1801-AC1 (Fig. 4), which implies that the mineralogical precursor of particle WF1801-AC3 presumably consisted of a mixture of plagioclase feldspar and pigeonite, similar to basaltic eucrites and mare basalts. Mare basalts mainly consist of pyroxene, plagioclase, olivine and some minor oxide phases such as ilmenite and spinel (Papike et al., 1976), and could thus represent the precursor material of particle WF1801-AC3. Consequently, the trace elemental chemistry of particle WF1801-AC3 should be examined and compared with that of lunar basalts. While certain trace element contents (e.g., Sc, V) in particle WF1801-AC3 are similar to lunar basalts, some of the lithophile and siderophile elements (e.g., Sr, Ba, Ni, Co) clearly are not (Fig. 6). The REE pattern of particle WF1801-AC3 is comparable to that of Type 1 achondritic spherules and fine-grained eucrites, supporting the pigeonite- and plagioclase-rich nature of the precursor material (Fig. 6A). While the Apollo basalts display a similar type of REE pattern, they tend to exhibit higher REE enrichments and a more pronounced negative Eu anomaly. This Eu anomaly appears to be positively correlated with the level of REE enrichment but is only consistent for mare basalts that are saturated with plagioclase (bulk Al_2O_3 ~ 12 wt%). However, the majority of mare basalts, as well as particle WF1801-AC3 ($Al_2O_3 = 11.6$ wt%), do not appear to be saturated with plagioclase at any P-T combination (Taylor et al., 1991; Longhi, 1992; Papike et al., 1998). As such, particle WF1801-AC3 is not compatible with a lunar basalt origin based on its trace elemental chemistry. In addition, the corrected oxygen isotope composition of particle WF1801-AC3 is not consistent with lunar rocks or meteorites and is not positioned within a known asteroid field. Finally, we would like to note that the abundance of lunar and martian meteorites is ca. 20 times lower than HED meteorites, and that the physicochemical properties (e.g., porosity, mechanical strength) of lunar rocks are not beneficial toward the production of lunar dust fragments within the micrometeorite population (Warren, 2001; Taylor et al., 2007). We therefore propose that particle WF1801-AC3 may have sampled a (fine-grained?) unknown type of precursor body, primarily composed of pyroxene and plagioclase, with similar Fe/Mn ratios as lunar rocks, but different elemental and oxygen isotope compositions.

4.3.4. Particle WF1801-AC4

The Fe/Mg and Fe/Mn ratios of particle WF1801-AC4 are similar, but slightly lower, than HED and martian meteorites (Table S1, Fig. 1). Yet, the Fe isotope ratios of particle WF1801-AC4 suggest that Fe was subjected to a high degree of evaporation (Table 3). This is furthermore supported by the f* value (41% - Table 2) of particle WF1801-AC4, and suggests that the Fe/Mn and Fe/Mg ratios may have decreased as a consequence. The interpretation of the Fe/Mg vs. Fe/Mn systematics should thus be considered with care when the extent of iron isotope fractionation is large. The Fe/Mg ratio suggests that particle WF1801-AC4 may have been inherited from cumulate/polymict eucrites and/or howardites. In the Ca/Si vs. Al/Si diagram (Fig. 4), particle WF1801-AC4 is located slightly below the plagioclase (HED) field, implying a large contribution of this mineral phase to its major element chemistry. The trace element chemistry of particle WF1801-AC4 is not compatible with HED meteorites but may depend on the type and abundance of minerals sampled (Fig. 5). The REE pattern of particle WF1801-AC4 is roughly flat and characterized by a moderately large, positive Eu anomaly, a small, negative Ce anomaly, and a small to moderately positive Tm anomaly (Fig. 6C). The positive Eu anomaly supports our observations regarding the contribution of plagioclase to the major element chemistry of particle WF1801-AC4. Negative Ce anomalies have previously been observed in chondritic cosmic spherules,

which have experienced severe degrees of volatilization (i.e., 'CAT-like' and 'high Ca-Al' groups) (Cordier et al., 2011b; Goderis et al., 2020). This has been attributed to the volatile behaviour of Ce⁴⁺ within an oxidizing environment during non-equilibrium kinetic evaporation (Davis et al., 1982; Hashimoto, 1990; Floss et al., 1996; Wang et al., 2001), and has been reproduced by laboratory experiments (Floss et al., 1996; Wang et al., 2001). The REE pattern of particle WF1801-AC4 is not consistent with that observed for plagioclase, and its Eu anomaly is also less pronounced. This could suggest that an additional (accessory) mineral phase was present to produce the REE trends observed in particle WF1801-AC4. The corrected oxygen isotope composition of particle WF1801-AC4 is positioned within the aubrite meteorite field, within relatively close proximity of the HED meteorite field (Table 3, Fig. 10). Consequently, we propose that particle WF1801-AC4 may have sampled a plagioclase-rich precursor body from HED-like asteroids.

4.3.5. Particle WF1801-AC5

Based on its distribution in Fe/Mg vs. Fe/Mn space (Fig. 1), particle WF1801-AC5 cannot be linked to HED, martian or lunar meteorites since its Fe/Mn ratio is relatively low (ca. 22). Note that, analogous to particle WF1801-AC4, the iron isotope composition of particle WF1801-AC5 is heavily fractionated and rivalled only by the most fractionated chondritic cosmic spherules (Table 2-3; Lampe et al., submitted), which may imply that the primary Fe/Mg and Fe/Mn ratios were (significantly) altered. Alternatively, particle WF1801-AC5 may have sampled an extremely iron-poor precursor body or mineral phase. Particle WF1801-AC5 could also have sampled a primitive, mantle-like precursor body (e.g., diogenite), which could potentially explain the relatively high TiO_2 contents (Table S1). Yet, given the extremely fractionated nature of particle WF1801-AC5, this may rather be a consequence of volatilization during atmospheric entry heating. On the Ca/Si vs. Al/Si diagram (Fig. 4), particle WF1801-AC5 is positioned away from mineralogical reference fields. As such, the mineralogical precursor material of particle WF1801-AC5 is difficult to determine based on these observations. Given the extent of iron isotope fractionation, we argue that the primary Ca/Si and Al/Si ratios may have been lower as the respective equilibrium condensation temperatures are markedly higher for Al (50% T_C = 1652-1653 K) and Ca (50% $T_C = 1517-1535$ K) compared to Si (50% $T_C = 1310-1314$ K) (Lodders, 2003; Wood et al., 2019). These values suggest that the Al/Si ratio would increase more rapidly compared to the Ca/Si ratio as the difference between the 50% condensation temperatures of Al and Si is larger. The primary Ca/Si and Al/Si ratios of particle WF1801-AC5 may thus have been more closely positioned to particles WF1801-AC1 and WF1801-AC3 or the high-Ca pyroxene field, but cannot be constrained in detail. The trace elemental chemistry of particle WF1801-AC5 is marked by a very large enrichment of incompatible elements (e.g., Y, Zr, Nb, REE, Hf, Ta, Th) (Table S1). In contrast, some of the more volatile incompatible elements (e.g., Cs, Na₂O, K₂O) tend to be depleted, although this is not the case for Rb and Ba. In light of these observations, it is plausible that the enrichment of refractory, incompatible elements was caused by evaporation of (moderately) volatile elements during atmospheric entry heating. The REE pattern of particle WF1801-AC5 does not resemble reference values of achondritic spherules but resembles the pattern and enrichment levels observed in apatite from acapulcoites, ordinary chondrites, and the KREEP component of lunar rocks, with exception of the minor, negative Ce anomaly (Fig. 6D). The KREEP component of lunar rocks mostly resides within Caphosphate mineral phases including apatite and whitlockite (Lucey et al., 2006). Consequently, the precursor material of particle WF1801-AC5 likely sampled a Ca-phosphate mineral phase, hosting the vast majority of REEs and superimposing the REE signature of silicate mineral phases. Ward et al. (2017) and Chernonozhkin et al. (2021) compiled refractory elemental ratios (Lu/Hf vs. Sm/Nd) of phosphate minerals in a large variety of meteorites, which is useful for this particular study since the effects of volatilization and passive enrichment are largely negated. Particle WF1801-AC5 (Lu/Hf \approx 0.07, Sm/Nd \approx 0.31) is located slightly below the cluster of basaltic achondrites (see Fig. 12 in Chernonozhkin et al., 2021), which supports the previous observations of extreme volatilization. The corrected oxygen isotope composition of particle WF1801-AC5 is not located within a known meteorite field but plots relatively close to the corrected oxygen isotope composition of particle WF1801-AC3 (Fig. 10). As such, we are unable to specify the precursor body of particle WF1801-AC5, most likely as a result of extreme volatilization, except for a clear contribution of a Ca-phosphate mineral phase based on its REE signature.

4.4. The abundance of achondritic cosmic spherules within the Widerøefjellet sedimentary trap

A total of five achondritic cosmic spherules were recovered from the Widerøefjellet sedimentary trap, which represents ca. 1-2% of all vitreous cosmic spherules and ca. 0.5% of all micrometeorites recovered to date in the 2000–200 µm size range. These numbers are comparable to those reported from other Antarctic micrometeorite collections, including the SPWW and TAMs. For instance, Taylor et al. (2007) found that ca. $0.5 \pm 0.4\%$ of the SPWW micrometeorites could be affiliated to achondritic parent bodies, while Cordier et al. (2012) have reported a number of ca. 2.1% (of which 1.6% is related to 4-Vesta or vestoids) for achondritic micrometeorites from the TAMs. Finally, Badjukov et al. (2010) estimate that ca. 0.25% of the micrometeorites recovered from the Novaya Zemlya glacier have sampled achondritic parent bodies. The abundance of achondritic micrometeorites is thus significantly lower than that of HED meteorites in the meteorite record (ca. 5%, http://www.lpi.usra.edu/meteor/metbull.php, accessed June 2021). This is rather surprising since the surface of many achondritic asteroids and planetary bodies is predominantly covered by fine-grained regolith material, mostly consisting of mineral fragments from ultramafic and basaltic rocks (Papike et al., 1982). Regolith material may thus form an important source to the micrometeorite flux to Earth. However, Taylor et al. (2002b, 2007) argued that physical strength and grain size of regolith material does not favor their development into micrometeorites. In addition, dust particles should exceed the escape velocity associated to its precursor body during collisional events. The potential of achondritic dust particles to contribute to the extraterrestrial dust flux also depends on the orbital parameters of its precursor body, including the

amount and strength of orbital resonances that dust particles need to surpass (Gounelle et al., 2009). Future studies should also focus on non-vitreous type spherules since the texture of cosmic spherules is not solely determined by the composition of its precursor particle, but rather a combination of its physicochemical properties (e.g., chemistry, density, size) and entry parameters (e.g., entry angle, entry velocity) (Love and Brownlee, 1991). As such, given the right circumstances, achondritic micrometeorites could also occur among non-vitreous type spherules, and even scoriaceous or unmelted micrometeorites (e.g., Gounelle et al., 2009; Badjukov et al., 2010). The Fe/Mg vs. Fe/Mn systematics have previously been proven successful to identify the presence of achondritic micrometeorites, and this is furthermore supported by this study.

5. CONCLUSION

We have presented new major, trace elemental and oxygen isotope data for five vitreous achondritic cosmic spherules (341–526 µm) recovered from the Widerøefjellet sedimentary trap in the Sør Rondane Mountains (East Antarctica). We have also introduced the first iron isotope data for four achondritic micrometeorites. Differentiated cosmic spherules were identified based on various chemical parameters, including their Fe/Mg vs Fe/Mn ratio, siderophile element contents (e.g., Co and Ni), and REE abundances and signatures. The data presented here extends the compositional ranges previously documented in achondritic micrometeorites from the SPWW and TAMs. The major, trace elemental and REE chemistry records both the mineralogical variety among achondritic micrometeorites as well as the intensity of atmospheric entry heating. Our observations suggest that achondritic micrometeorites, although accessory mineral phases (e.g., apatite) may also provide an important contribution with regards to the REE content. Atmospheric entry heating results in the volatilization of (moderately) volatile elements (e.g., Na, Cs, Si) and passively enriches the more refractory elements (e.g., Zr, Hf, REE) in a similar manner as observed in chondritic micrometeorites.

The oxygen isotope composition of achondritic micrometeorites cannot be linked to achondritic precursor bodies due to oxygen isotope fractionation processes during atmospheric entry heating, including mass-dependent fractionation, mixing with atmospheric oxygen and kinetic isotope effects. We have roughly estimated that ca. 2–73% of the total oxygen content was lost due to mass-dependent fractionation processes assuming a bulk eucrite oxygen isotope composition. To correct for these effects, we have measured and combined oxygen and iron isotope data following the observations by Lampe et al. (submitted). The corrected oxygen isotope composition of two particles were comparable to HED meteorites and could thus have sampled a HED(-like) precursor body. Yet, two particles could not be linked a known type of achondritic precursor body and may have sampled a new type of asteroidal material. This study thus supports previous observations, which argue that the parent body identification of (a)chondritic parent bodies should mostly be based on their major and trace elemental chemistry.

The abundance of achondritic micrometeorites (ca. 0.5%) in the Widerøefjellet sedimentary trap is comparable to that observed in the SPWW, TAM and Novaya Zemlya micrometeorite collections, emphasizing their rarity and unique nature. The study of achondritic micrometeorites is thus an essential step to document the large variety of asteroidal and cometary bodies, including their source region, within the Solar System.

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FIGURES

Figure 1. Distribution of achondritic cosmic spherules in Fe/Mn versus Fe/Mg space. Achondritic (micro)meteorites generally display higher Fe/Mg ratios at Fe/Mn ratios comparable to those of chondritic (micro)meteorites (grey circles). This can be attributed to a range of planetary scale differentiation processes. The vast majority of achondritic spherules is positioned along the 4-Vesta/Mars reference line, with the exception of particle WF1801-AC3. The latter particle displays Fe/Mn ratios comparable to lunar rocks. In addition, the Fe/Mg ratios can provide information regarding the precursor lithology (mantle vs. crust). Reference values reproduced from Taylor et al. (2007), Cordier et al. (2011a, 2012), Goderis et al. (2020) and Brase et al. (2021).



Figure 2. Distribution of achondritic cosmic spherules in the Si-Fe-Mg ternary diagram. The compositional range of achondritic spherules partly overlaps with the compositional field of chondritic micrometeorites (Rochette et al., 2008). However, the majority of achondritic spherules display elevated Si contents compared to chondritic micrometeorites. Australasian microtektites previously recovered from the SRMs display significantly higher Si contents (Soens et al., 2021), while the meteoritic condensation spherules reported by van Ginneken et al. (2021) have lower Si contents and tend to be slightly enriched in Mg.



Figure 3. Distribution of achondritic cosmic spherules in CaO+Al₂O₃ vs. Fe/Si (atomic) space. Achondritic spherules are separated into two groups, i.e. 'normal chondritic' and 'high Ca-Al', based on the classification scheme of Cordier et al. (2011b), which indicates the extent of evaporation experienced by micrometeorites during atmospheric entry heating. The majority (n = 17 or 71% - datapoints from this study included) of achondritic'. This diagram thus suggests that the position of achondritic cosmic spherules is predominantly determined by their mineralogical precursors, as well as the total extent of volatilization during atmospheric entry heating. Reference values for achondritic spherules reproduced from Taylor et al. (2007), Cordier et al. (2011a, 2012) and Brase et al. (2021). The reader is referred to figure 1 for the full legend.



Figure 4. Distribution of achondritic cosmic spherules in Al/Si vs. Ca/Si space. The following diagram is useful to determine the mineralogical control on achondritic spherules. For instance, pyroxene phases have generally low Al/Si ratios, but their Ca/Si ratio may fluctuate depending on the pyroxene variety. Plagioclase is characterized by high Al/Si ratios and moderately high Ca/Si ratios. See text for further discussion. Reference values for plagioclase from Gooley (1972), Lovering (1975), Wilkening and Anders (1975), Gomes and Keil (1980), Floran et al. (1981), Fredriksson (1982), Christophe Michel-Levy et al. (1987), Mittlefehldt (1994), Metzler et al. (1995), Buchanan and Reid (1996), Warren et al. (1996), Cordier et al. (2011a). Reference values for maskelynite reproduced from Papike et al. (2009). Reference values for pyroxene from Lovering (1975), Harlow et al. (1979), Takeda and Mori (1985), Christophe Michel-Levy et al. (1987), Warren et al. (1990), Mittlefehldt and Lindstrom (1993), Mittlefehldt (1994), Fowler et al. (1994), Takeda et al. (1994), Pun and Papike (1995) and Cordier et al. (2011a). Reference values for achondritic spherules from Taylor et al. (2007), Cordier et al. (2011a, 2012) and Brase et al. (2021). The reader is referred to figure 1 for the full legend.



Figure 5. Trace element chemistry of the achondritic spherules. See text for further discussion. Reference values for 'eucrites' from McCarthy et al. (1973), Cleverly et al. (1986), Mittlefehldt and Lindstrom (1993, 2003), Kitts and Lodders (1998), Barrat et al. (2000, 2007), Buchanan et al. (2000), Patzer et al. (2003, 2005) and Yamaguchi et al. (2009). Reference values for 'mare basalts' from Haskin and Warren (1991). Reference value for 'Nakhla' from Lodders and Fegley (1998). Reference values for NWA7533 (Martian regolith breccia) from Humayun et al. (2013). Reference values for achondritic spherules from Taylor et al. (2007), Cordier et al. (2011a, 2012) and Brase et al. (2021).



Figure 6. Rare earth element pattern of achondritic cosmic spherules. The SRM particles have been separated into different diagrams depending on their REE pattern. We have also included the average REE pattern of 'normal chondritic' TAM cosmic spherules for comparison. A) Particles WF1801-AC1 and WF1801-AC3 have REE-enriched, but relatively flat patterns, similar to Type 1 spherules reported by Cordier et al. (2012) and bulk eucrites (Kitts and Lodders, 1998; Barrat et al., 2007). Both particles display slightly negative Eu anomalies. Due to the compatibility of particle WF1801-AC3 with lunar basalts based on the Fe/Mn ratio (see Fig. 1), we have included the REE pattern observed for Apollo basalts (Meyer, 2016). B) Particle WF1801-AC2 displays a LREE-depleted and HREE-enriched pattern with a large Eu anomaly. This is comparable to the REE pattern of Type 2 spherules (Cordier et al., 2012), pigeonite and augite (Floss et al., 2000) in HED meteorites. This does not match the REE pattern of nakhlites (Treiman, 2005) despite the similarity in Ca/Si and Al/Si ratios of particle WF1801-AC2. C) Particle WF1801-AC4 displays a roughly flat REE pattern with a moderately high, positive Eu anomaly. However, this does not match the REE pattern of plagioclase phases from HED meteorites (Floss et al., 2000). D) Particle WF1801-AC5 displays a LREE-enriched pattern with a minor, negative Ce anomaly and a moderately large, negative Eu anomaly. Its pattern is not compatible with Type 1, Type 2 or Type 3 achondritic spherules, but strongly matches the KREEP component of mare basalts (Meyer, 2016), the REE signature of apatite in a variety of meteorite types (Crozaz et al., 1989; Ward et al., 2017) and the martian meteorite NWA 7034 (Agee et al., 2013). Normalization values for CI chondrites reproduced from McDonough and Sun (1995).



Figure 7. Triple-oxygen (Δ^{17} O vs. δ^{18} O) isotope diagram of achondritic cosmic spherules. All achondritic spherules are positioned between the Eucrite Fractionation Line (Δ^{17} O = -0.242 ± 0.016‰ – Scott et al., 2009) and Martian Fractionation Line (Δ^{17} O = 0.301 ± 0.013‰ – Franchi et al., 1999) within error. The abbreviation 'SLAP' stands for 'Standard Light Antarctic Precipitation'. The oxygen isotopic composition of the atmosphere was reproduced from Thiemens et al. (1995). Analytical error for TAM achondritic spherules is smaller than the symbol size. Reference values for TAM achondritic spherules from Cordier et al. (2012).



Figure 8. δ^{57} Fe vs. δ^{56} Fe diagram for S- and I-type spherules. The positive correlation (R² = 0.9977) observed between the measured δ^{56} Fe and δ^{57} Fe ratios in cosmic spherules results from mass-dependent fractionation during atmospheric entry heating. The standard error of the δ^{56} Fe and δ^{57} Fe ratios are smaller than the particle symbols unless indicated. Reference values for S-type and I-type spherules from Lampe et al. (submitted), and Engrand et al. (2005) and Pack et al (2017) respectively.



Figure 9. FeO vs. δ^{57} Fe diagram for S-type (chondritic and achondritic) and I-type spherules. We observe that the FeO content of S-type spherules roughly decreases as the δ^{57} Fe ratio increases. Additionally, the δ^{57} Fe ratio appears to increase for spherules displaying petrographic textures which reflect increasing heating temperatures (i.e., from porphyritic to barred olivine to cryptocrystalline to vitreous to CAT). This does not appear to be the case for the achondritic spherules reported here: particle WF1801-AC2 and particle WF1801-AC3 display vitreous textures but δ^{57} Fe ratios comparable to barred olivine and cryptocrystalline spherules. In contrast, particle WF1801-AC4 and particle WF1801-AC5 are heavily fractionated based on their δ^{57} Fe ratios. I-type spherules display similar FeO contents for varying degrees of iron isotope fractionation. The standard error is smaller than the symbol size.



Figure 10. Triple-oxygen (δ^{17} O vs. δ^{18} O) isotope diagram for achondritic micrometeorites. The measured oxygen isotope compositions are denoted by filled symbols, while the primary (calculated) oxygen isotope compositions are denoted by hollow symbols. Two particles (WF1801-AC2 and WF1801-AC4) show primary oxygen isotope compositions similar to HED meteorites and may thus originate from HED or HED-like parent bodies. The primary oxygen isotope compositions of particles WF1801-AC3 and WF1801-AC5 are not compatible with known (a)chondritic fields and may thus represent new types of achondritic parent bodies. See text for further discussion.



TABLE CAPTIONS

 Table 1. Overview of particle selection. *van Ginneken et al. (2016). n.o.: not observed. Particle WF1801-AC1 could not be analyzed for Fe isotope analysis

 due to the limited amount of surface area available.

Particle	Size (µm)	Colour	Weathering scale*	Major & trace elements	O isotopes	Fe isotopes
WF1801-AC1	341	n.o.	1a-b	\checkmark	\checkmark	
WF1801-AC2	388	black	0a	\checkmark	\checkmark	\checkmark
WF1801-AC3	377	black/brown	1a-b	\checkmark	\checkmark	\checkmark
WF1801-AC4	526	n.o.	1a-b	\checkmark	\checkmark	\checkmark
WF1801-AC5	369	dark green/grey	1a-b	\checkmark	\checkmark	\checkmark

Table 2. Oxygen isotope data of the Widerøefjellet achondritic spherules. We have calculated the fraction of oxygen that was presumably lost during atmospheric entry heating based on the Rayleigh fractionation law $R/R_0 = (1 - f)^{(1/\alpha - 1)}$, where *R* is the δ^{18} O composition of the cosmic spherule, R_0 is the δ^{18} O composition of a hypothetical parent body (here bulk eucrites – 3.59‰, see Greenwood et al., 2005), α is the isotopic fractionation factor (1.0237 – Wang et al., 2001), and *f* is the amount of oxygen that was lost as a result of evaporation/mass-dependent fractionation. We have also calculated f*, which represents the fraction of oxygen lost when the effects of atmospheric oxygen mixing (ca. 8‰, see Clayton et al. 1986) are considered.

Particle	δ ¹⁷ Ο (‰)	2SE (‰)	δ ¹⁸ Ο (‰)	2SE (‰)	Δ ¹⁷ Ο (‰)	2SE (‰)	R ₀ (‰)	f	f*
WF1801-AC1	8.92		17.90		-0.47	_		0.45	0.23
WF1801-AC2	5.76		12.09		-0.53	-		0.30	0.02
WF1801-AC3	10.97	0.55	21.85	0.53	-0.39	0.62	3.59	0.53	0.35
WF1801-AC4	11.92		24.38		-0.76	•		0.58	0.41
WF1801-AC5	21.93		43.44		-0.65	•		0.81	0.73

Table 3. Iron and corrected oxygen isotope data of the Widerøefjellet achondritic spherules. *The corrected value was calculated by compensating for mass-dependent fractionation processes following the equation $\delta^{18}O_{corr} = (\delta^{18}O_{meas} - 0.6986 * \delta^{57}Fe_{meas}) - 8$, where $\delta^{18}O_{corr}$ is the $\delta^{18}O$ ratio corrected for mass-dependent fractionation effects, $\delta^{18}O_{meas}$ is the $\delta^{18}O$ ratio measured for the cosmic spherule, and $\delta^{57}Fe_{meas}$ is the $\delta^{57}Fe$ ratio measured in the cosmic spherule (Lampe et al., submitted). An additional correction factor of 8‰ was subtracted to compensate for mixing processes with atmospheric oxygen and/or kinetic isotope effects following the observations by Clayton et al. (1986). Since there is no Fe isotope data available for particle WF1801-AC1, we have only applied the correction factor to compensate for mixing processes with atmospheric oxygen and/or kinetic isotope effects.

^{**}The corrected value was calculated using the equation for the terrestrial fractionation line: $\Delta^{17}O = \delta^{17}O - 0.52^* \delta^{18}O_{corr}$, where we assumed that the $\Delta^{17}O$ did not change given the limited $\Delta^{17}O$ range observed in achondritic meteorites.

Particle	δ ⁵⁶ Fe	2SE	δ ⁵⁷ Fe	2SE	δ ¹⁸ Ο	$\Delta^{17}\mathbf{O}$	Atmospheric	δ ¹⁸ Ο	δ ¹⁷ Ο
	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	mixing (‰)	corrected [*] (‰)	corrected ^{**} (‰)
WF1801-AC1	/	/	/	/	17.90	-0.47		9.90	4.68
WF1801-AC2	0.43	0.14	0.71	0.24	12.09	-0.53		3.59	1.34
WF1801-AC3	1.28	0.22	1.87	0.10	21.85	-0.39	8	12.54	6.13
WF1801-AC4	11.53	0.12	17.19	0.40	24.38	-0.76		4.37	1.51
WF1801-AC5	21.65	0.12	32.42	0.20	43.44	-0.65		12.79	5.70

Appendix A. Supplementary Material

The Supplementary Material file contains a table of the major and trace elemental data obtained using LA-ICP-MS, as well as a backscatter electron-scanning electron microscope image (BSE-SEM) of a single achondritic cosmic spherule.

Element	WF1801-AC1	WF1801-AC2	WF1801-AC3	WF1801-AC4	WF1801-AC5
	(<i>n</i> = 3)	(n = 3)	(n = 3)	(n = 3)	(n = 3)
SiO ₂ (wt%)	44.90	54.10	40.90	43.09	44.03
TiO ₂	0.67	1.21	0.71	0.85	3.28
Al ₂ O ₃	13.75	0.98	11.59	25.53	14.78
FeO*	19.64	21.19	21.43	9.40	6.65
MnO	0.65	0.66	0.27	0.39	0.29
MgO	7.52	6.93	13.58	5.55	7.79
CaO	12.86	14.71	11.45	15.18	23.16
Na ₂ O	0.0040	0.0063	0.0031	<lod< th=""><th><lod< th=""></lod<></th></lod<>	<lod< th=""></lod<>
K ₂ O	<lod< th=""><th>0.0014</th><th>0.0020</th><th>0.0015</th><th><lod< th=""></lod<></th></lod<>	0.0014	0.0020	0.0015	<lod< th=""></lod<>
Li (µg/g)	6.11	20.86	<lod< th=""><th>9.25</th><th><lod< th=""></lod<></th></lod<>	9.25	<lod< th=""></lod<>
Be	4.45	0.44	0.80	0.96	0.53
Sc	34.59	161.74	38.62	39.02	71.05
V	34.93	49.98	75.78	6.44	2.05
Cr	112	1461.58	263.76	13.07	0.47
Со	4.94	4.70	18.72	0.85	<lod< th=""></lod<>
Ni	3.12	75.19	10.71	6.57	5.28
Cu	<lod< th=""><th>0.29</th><th>0.18</th><th>0.65</th><th>0.33</th></lod<>	0.29	0.18	0.65	0.33
Zn	<lod< th=""><th>1.15</th><th>1.91</th><th>3.75</th><th>1.03</th></lod<>	1.15	1.91	3.75	1.03
Ga	1.62	0.64	0.42	0.95	1.34
Ge	0.60	0.17	<lod< th=""><th>0.31</th><th>0.21</th></lod<>	0.31	0.21
Rb	<lod< th=""><th>0.07</th><th><lod< th=""><th>0.36</th><th>0.13</th></lod<></th></lod<>	0.07	<lod< th=""><th>0.36</th><th>0.13</th></lod<>	0.36	0.13
Sr	92.72	8.10	85.87	162.82	121.25
Y	20.45	56.91	14.63	15.63	88.41
Zr	72.19	88.56	44.69	32.41	466.65
Nb	3.66	6.27	2.80	2.87	29.34
Мо	<lod< th=""><th>0.24</th><th><lod< th=""><th>0.56</th><th><lod< th=""></lod<></th></lod<></th></lod<>	0.24	<lod< th=""><th>0.56</th><th><lod< th=""></lod<></th></lod<>	0.56	<lod< th=""></lod<>
Sn	<lod< th=""><th>0.17</th><th>0.18</th><th>0.26</th><th><lod< th=""></lod<></th></lod<>	0.17	0.18	0.26	<lod< th=""></lod<>
Sb	<lod< th=""><th>0.08</th><th>0.10</th><th>0.54</th><th><lod< th=""></lod<></th></lod<>	0.08	0.10	0.54	<lod< th=""></lod<>
Cs	<lod< th=""><th>0.04</th><th>0.009</th><th>0.25</th><th><lod< th=""></lod<></th></lod<>	0.04	0.009	0.25	<lod< th=""></lod<>
Ba	43.36	1.37	25.42	46.51	48.13
La	3.95	1.12	2.91	2.60	17.23
Ce	11.55	5.02	6.82	4.63	33.61
Pr	1.68	1.16	1.02	1.02	6.79
Nd	7.12	8.28	5.39	4.12	36.12
Sm	2.57	4.27	1.88	1.71	11.13
Eu	0.69	0.11	0.54	1.69	1.14
Gd	3.33	5.86	2.52	2.37	14.72
Tb	0.43	1.24	0.46	0.53	2.46
Dy	3.53	10.24	2.76	2.67	15.71
Ho	0.88	2.09	0.62	0.63	3.10
Er	2.38	6.64	1.64	1.86	8.62
Tm	0.36	1.00	0.24	0.43	1.15
Yb	2.29	7.39	1.63	1.90	7.34
	0.39	1.11	0.24	0.40	0.98
HI T	2.13	4.99	1.36	0.99	13.28
	0.20	0.47	0.15	0.40	5.55
	<lud< th=""><th>0.049</th><th>0.32</th><th>0.42</th><th></th></lud<>	0.049	0.32	0.42	
ГО Ть		0.036	0.059	0.30	0.016
10	0.44	0.24	0.33	0.30	5.50

Table S1. Major and trace element chemistry determined by LA-ICP-MS.
U	0.0065	0.27	0.036	0.25	0.0054
Fe/Mg (atomic)	1.47	1.72	0.89	0.95	0.48
Fe/Mn	30	32	78	24	22
Al/Si	0.36	0.021	0.33	0.70	0.40
Ca/Si	0.31	0.29	0.30	0.38	0.56
(La/Yb) _N	1.18	0.10	1.21	0.93	1.59
Average REE _N *	15.78	29.93	11.29	12.02	61.80
ΣREE^{**}	40.41	55.39	28.16	24.91	158.86
Eu*-anomaly	0.72	0.07	0.76	2.56	0.27

*Eu was not included.

^{**}The Σ REE was determined by calculating the sum of the individual REE concentrations, excluding Eu.

Figure S2. Backscatter electron – scanning electron microscope (BSE-SEM) image of particle WF1801-AC4. The vitreous core of particle WF1801-AC4 has largely remained pristine, while its outer edge has presumably been altered due to the interaction with Antarctic precipitation, producing secondary, lower density mineral phases.



An extraterrestrial trigger for the mid-Ordovician ice age: Dust from the breakup of the L-chondrite parent body

by Schmitz et al. (2019). Sci. Adv. 5, eaax4184.

This article presents new insights into the abundance and types of chromite and Cr-rich spinel phases encountered within the Walnumfjellet micrometeorite collection, and compares this to the chromite and Cr-rich spinel content of middle Ordovician deposits prior, during and after the L-chondrite parent body breakup event. This information is relevant to track differences in the cosmic dust flux to Earth throughout geological time, assess its impact on past climates, and re-evaluate the significance of chromite and Cr-rich spinel phases in micrometeorite investigations. This study is part of a research project that was planned to be incorporated in this PhD dissertation, but was postponed and ultimately carried over to another doctoral student (see the 'Future outlook' section for more information).

BS has assisted Birger Schmitz by processing numerous sedimentary deposits from the Sør Rondane Mountains to extract a large number (>2000) of micrometeorites. BS has also provided the SEM image for Figure 5 in the manuscript.

The supplementary materials related to this manuscript are available on the following website: https://doi.org/10.1126/sciadv.aax4184.

PLANETARY SCIENCE

An extraterrestrial trigger for the mid-Ordovician ice age: Dust from the breakup of the L-chondrite parent body

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The breakup of the L-chondrite parent body in the asteroid belt 466 million years (Ma) ago still delivers almost a third of all meteorites falling on Earth. Our new extraterrestrial chromite and ³He data for Ordovician sediments show that the breakup took place just at the onset of a major, eustatic sea level fall previously attributed to an Ordovician ice age. Shortly after the breakup, the flux to Earth of the most fine-grained, extraterrestrial material increased by three to four orders of magnitude. In the present stratosphere, extraterrestrial dust represents 1% of all the dust and has no climatic significance. Extraordinary amounts of dust in the entire inner solar system during >2 Ma following the L-chondrite breakup cooled Earth and triggered Ordovician icehouse conditions, sea level fall, and major faunal turnovers related to the Great Ordovician Biodiversification Event.

INTRODUCTION

During the past 500 million years (Ma), Earth has experienced three major ice ages (1). We live in the latest ice age that began in the Late Eocene, ~35 Ma ago, after more than 230 Ma of ice-free high-latitude continental regions. The preceding major ice age lasted from the Late Devonian to the mid-Permian, leaving behind extensive glacial deposits over ancient Gondwanaland. The oldest major Phanerozoic ice age peaked in the Late Ordovician, as indicated by glacial deposits in, e.g., North and South Africa and South America (2, 3), but sea level records indicate that ice age conditions may have started already in the mid-Ordovician (4–7). Although much of Earth's short-term climate variability is astronomically paced, as expressed by the Milankovitch cycles, the fluctuations on a 10- to 100-Ma scale between greenhouse and icehouse climates are generally explained in terms of Earth-bound causes, such as the closing or opening of seaways, uplift of mountain chains, or changes in atmospheric CO₂ concentrations (1).

Here, we focus on an interval of the geological record that has been proposed to represent the onset of the Ordovician ice age and

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where important faunal turnovers occurred worldwide (4, 8). The interval has been studied in particular detail in Baltoscandia where many well-preserved sedimentary sections are exposed. In these sections, shortly following the transition between the regional Volkhov and Kunda stages (~466 Ma ago), one of the major steps in the so-called Great Ordovician Biodiversification Event (GOBE) is registered (4). Similar biodiversity changes are seen in coeval Laurentian sections, indicating a global event (8). The GOBE concept refers to a stepwise change over ~30 Ma from a world with relatively low marine invertebrate biodiversity in the Cambrian and Early Ordovician to near-modern levels at the end of the Ordovician (9). The literature discusses two seemingly opposing explanations for the faunal and climatic changes in the earliest Kundan (4, 10). Schmitz et al. (10) showed that the changes appear to coincide with the breakup of the L-chondrite parent body (LCPB; diameter, ~150 km) in the asteroid belt, the largest documented breakup during the past 3 billion years. Besides the abundant L-chondritic meteorites still falling on Earth from this event, common fossil meteorites (1 to 20 cm large) in mid-Ordovician sediments attest to the breakup (11). Schmitz et al. (10) argued that recurrent asteroid impacts on Earth after the LCPB breakup may have spurred increases in biodiversity. This is consistent with the "intermediate disturbance hypothesis" that explains biodiversity increases in recent rain forests under mild stress (12). This proposed GOBE-LCPB relation has been challenged on the basis of oxygen-isotope temperature records, interpreted to indicate that the Ordovician biodiversity expansion, including the mid-Ordovician biota turnover, instead relates to a gradual cooling of Earth, culminating with the icehouse conditions in the Late Ordovician (4, 13). Over the past decade, further evidence has accumulated in support of an increase in asteroid impacts during the extended period when the main phase of the GOBE took place (14). The craters from these impacts, however, are typically small (diameter, <10 km), and no direct links between these craters and faunal turn-

overs have been found. The debate about a possible causal connec-

tion between the LCPB breakup and GOBE has suffered from a lack

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of data concerning the precise, high-resolution timing of the breakup in relation to terrestrial biotic and climatic events (10). Our previous less detailed chrome-spinel data placed the breakup at a stratigraphic level somewhere in the lower part of the *Lenodus variabilis* Conodont Zone, corresponding to an age of ~466 Ma ago according to the 2012 Geologic Time Scale (15). This age agrees with ~470-Ma Ar-Ar isotopic ages for shocked, recently fallen L chondrites [e.g., (16)].

The abundant fossil meteorites in mid-Ordovician limestone are associated with the conspicuous Täljsten interval that represents a unique episode of eustatic sea level lowstand (Fig. 1 and fig. S3) (11, 17–19). The Täljsten has been interpreted as a lowstand systems tract of the Kunda depositional cycle (18, 19) and is traceable over most of Baltoscandia but also in Laurentia, Siberia, Gondwana, and the Yangtze platform (fig. S3). To resolve whether the LCPB breakup directly affected Earth's climate and biota, we here use new highresolution, multiparameter data (chrome spinel and He and Os isotopes) to locate the precise level in the sedimentary strata that corresponds to the LCPB event. We compare these data with previous noble gas data for chromite grains from large fossil meteorites (20, 21) that can be used for an independent assessment of the timing of the LCPB breakup. A multiparameter approach is required because of the potentially different transport mechanisms and routes to Earth for different size fractions of asteroid breakup products, as well as uncertainties in sedimentation rates. As will be discussed, it is not simple to relate the first signal of L-chondritic material in a stratigraphic column to the precise time of the breakup of the LCPB in the asteroid belt.

A multiparameter approach

We investigated marine limestone exposed in the composite Hällekis-Thorsberg section at Kinnekulle in southern Sweden and in the Lynna River section near St. Petersburg in Russia. These are two "classical" sections studied in detail from many paleontological and sedimentological aspects [see (4, 11)]. The abandoned Hällekis Quarry encompasses also the interval of limestone that has yielded >130 fossil meteorites in the active Thorsberg Quarry 4 km to the southeast (Fig. 1) (11, 22). The meteorites are all (except one) L chondrites, and they have been found over the entire 5-m stratigraphic interval quarried at Thorsberg, starting at the base of the bed informally named Arkeologen by quarry workers (Fig. 2). Measurements of ²¹Ne in chromite grains from meteorites at different levels in the quarry have yielded consecutively longer cosmic ray exposure (CRE) ages, from ca. 0.1 to 1.2 Ma, with increasing stratigraphic height (20, 21). This progression is best explained by all the meteorites originating from a single breakup event and reaching Earth after different exposure times to cosmic rays in space. The age succession is consistent with generally accepted average sedimentation rates for the strata (2 to 4 mm ka⁻¹) [e.g., (23)]. The ²¹Ne data place the LCPB breakup at a stratigraphic level between ~0.4 and 1.2 m below the base of the Arkeologen bed (Fig. 3; see Supplementary Text regarding the uncertainties of this dating approach).

Shortly after the LCPB breakup, the flux of L-chondritic material to Earth may have increased gradually, a change that would be difficult to determine with confidence because a constant meteorite flux during a period when sedimentation rates decrease would yield the same grain abundance signal in the limestone as a gradually increasing flux. We can circumvent this problem by studying the change in the ratios between grains from L chondrites and other meteorite groups. Existing chrome-spinel data show that the meteorite flux to Earth before and after the LCPB breakup was very different (*24*). Studies of sediments that formed about 1 Ma before the breakup show that different types of, today very rare, achondritic



Fig. 1. The mid-Ordovician Hällekis section in southern Sweden. The red line represents the stratigraphic level (at –1 m in this study) that corresponds to the time of the breakup of the LCPB in the asteroid belt. At this level, there is a change in the strata in abundance and types of extraterrestrial chrome-spinel grains. A low-abundance, mixed micrometeorite assemblage is replaced by a high-abundance assemblage completely dominated by L-chondritic grains. At the same level, the grain size of bioclastic limestone fragments begins to increase, indicating onset of a gradual sea level fall that culminates with the conspicuous Täljsten lowstand deposit traceable over most of Baltoscandia and likely also globally. Asteroid breakup artwork by Don Davis. (Photo credit: Birger Schmitz, Lund University)

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Fig. 2. Stratigraphic scheme for the composite Hällekis-Thorsberg section and distribution of equilibrated ordinary chondritic chromite (EC) grains through the section. The stratigraphic interval is marked over which >130 fossil meteorites have been found in the Thorsberg Quarry. In 18 samples studied representing 791 kg of rock spanning the interval from -9 to -1 m relative to the base of the Arkeologen bed, we found only 15 EC grains >63 μ m, i.e., 2 grains per 100 kg, which is about the same number of grains that we find per kilogram in samples in the overlying ca. 7 m of section. At -1 m, we also see a change in the abundance ratios of H, L, and LL chondritic grains from an evenly mixed assemblage to one completely dominated by L-chondritic grains. The results in the figure build on a total of 1320 kg of limestone dissolved in acids and searched for chrome spinels (see also fig. S1). TS, Täljsten lowstand deposit.

micrometeorites made up ~15 to 34% of the flux. In the same beds, the three different groups of ordinary chondrites, H, L, and LL, make up about a third each of the ordinary chondritic micrometeorites. After the LCPB breakup, the total flux of extraterrestrial chromite grains (>63 μ m) increased by two to three orders of magnitude, and >99% of the chromites found are L chondritic (Figs. 1 and 2).

We know that Ordovician sediment-dispersed chromite grains originate from micrometeorites because of their high concentrations of solar wind–implanted Ne and He (21, 25). Solar wind ions only penetrate a few nanometers; hence, our chromite grains must, at some time, have shared surface with the enclosing silicate micrometeoroid. Large micrometeoroids (>0.1 mm) containing >32- μ m chromite grains would normally require on the order of 0.3 to 2 Ma to reach Earth through Poynting-Robertson light drag from a breakup in the inner asteroid belt (table S5) (21). Their first appearance in the strata may thus not reflect the precise time of the LCPB breakup. The most fine-grained, micrometer-sized dust from a breakup will have much shorter transfer times, in the order of 10 thousand years (ka).



Fig. 3. The ²¹Ne CRE ages (T_{21}) of fossil L chondrites from the Thorsberg Quarry inversely correlate with sediment ages. Solid symbols are ages with cosmogenic ²¹Ne production rates from Heck *et al.* (20), and open symbols are ages with production rates determined by Heck *et al.* (21) (see Supplementary Text). The interval between linear regressions on the lower and upper limits, respectively, of the two data sets is shaded orange and sets the LCPB breakup at $T_{21} = 0$ Ma between -0.4 and -1.2 m relative to the base of the Arkeologen bed.

The ³He content in sediments has been shown to be a reliable and robust indicator of this fine-grained dust (*26*). Thus, we have established a detailed extraterrestrial ³He profile across the extended stratigraphic interval in which the first arrival of dust from the LCPB likely is registered. In another approach, we have performed refined, high-resolution Os isotope analyses over the same strata. Previously, ¹⁸⁷Os/¹⁸⁸Os isotope ratios in the Hällekis section were shown to drop markedly after the LCPB breakup, reflecting abundant extraterrestrial matter in the sediment (*10*). Here, we try to find the precise (centimeter resolution) stratigraphic level where this change starts.

It is not known in what state the abundant, relict L-chondritic chromite grains reached the Ordovician seafloor. In an attempt to clarify this, we have here separated 2792 melted and 190 scoriaceous and unmelted micrometeorites in the size range of 80 to 2000 μ m from recent micrometeorite-rich deposits in Antarctica. All the micrometeorites were dissolved in hydrofluoric (HF) acid, and residual chrome-spinel grains were recovered and analyzed.

RESULTS

The results of all the parameters studied across the Hällekis section show that the first signal of the LCPB breakup occurs 1 m below the base of the Arkeologen bed, in the *L. variabilis* Conodont Zone (Figs. 2 and 4). At this level, we see the gradual onset of a marked rise in the number of extraterrestrial chromite grains. There is also a sharp change at -1 m in the ratios between different meteorite groups toward complete dominance of L-chondritic grains (Fig. 2). Extremely high numbers of extraterrestrial chromite grains continue upward through the section for at least 8 m, corresponding to 2 to 4 Ma. Extraterrestrial ³He shows a marked and sudden rise at the -1-m level, which indicates that the first fine-grained dust arrived on Earth at the same (±50 ka) time as the first abundant LCPBrelated micrometeorites (Fig. 4). Osmium isotopes also show a major shift at this level, indicative of increased delivery of extraterrestrial matter to the seafloor. Both the He and Os isotopes indicate elevated abundances of extraterrestrial matter for some meters upward through the section, in concordance with the chromite data. It is clear from our detailed studies that the sudden increase in extraterrestrial material at -1 m reflects the arrival of the first LCPB dust on Earth and cannot be explained by a stratigraphic hiatus (fig. S2).

In the almost 3000 Antarctic micrometeorites dissolved in HF, we only found a single ordinary chondritic chromite grain of $>32 \,\mu m$, an angular grain of $\sim 60 \ \mu m$ in diameter, and two chrome-spinel grains ~20 µm large from other meteorite types (see data file S4 for details). The grains were found in the melted micrometeorites, which is consistent with chromite and other chrome-spinel types being among the minerals in meteorites with the highest melting temperatures. Chromite apparently can survive atmospheric passage when most other minerals melt or recrystallize (Fig. 5). From other studies of recent micrometeorite assemblages, we can deduce that about one-fifth of the micrometeorites that we dissolved were ordinary chondrites (27, 28). This means that about 1 in 600 ordinary chondritic micrometeorites contains a chromite grain of >32 µm. Thus, the up to ~50 chromite grains >32 μ m kg⁻¹ in post–LCPB breakup limestone represent the residue on the order of 30,000 micrometeorites (>0.1 mm) per kilogram of sediment.

DISCUSSION

On the basis of our new results, we place the breakup of the LCPB at a time corresponding to the -1-m level in the section, consistent with previous²¹Ne CRE ages for the fossil meteorites (Fig. 3). As Poynting-Robertson transfer times to Earth increase with increasing particle size, ³He hosted primarily in the fine fraction would be expected to increase in the strata ~1 to 2 m below the level where abundant large chromite grains first appear. The simultaneous appearance on Earth of fine dust and coarser micrometeorites can be reconciled in light of the low ²¹Ne CRE ages for the fossil meteorites. Recent ordinary chondrites typically have CRE ages in the range of 3 to 60 Ma, compared to ~0.1 to 1.2 Ma for the Ordovician fossil L chondrites (20, 21). The latter short durations have been explained by positioning the LCPB breakup close to an orbital resonance that would have sent dust and meteoroids to Earth at much shorter time scales than normal Poynting-Robertson drag would alone (29). Considering the very short (~100 to 200 ka)²¹Ne CRE ages of the oldest recovered L-chondritic fossil meteorites (from the Arkeologen bed) (Fig. 3), we argue that also millimeter-sized micrometeoroids had very short travel times. This would explain why the fine-grained and coarser dust arrived to Earth at about the same time. We note that our ²¹Ne data have been used by others to place the LCPB breakup at 0.2 m below the base of the Arkeologen bed (30), an interpretation that we dispute because it is impossible that the breakup took place 200 to 400 ka after the first arrival of extraordinary amounts of L-chondritic micrometeorites on Earth.

On the basis of comparisons of the content of extraterrestrial chromite in the post-LCPB breakup sediments with similar condensed sediments from the Late Silurian, Middle and Late Devonian, Early and Late Cretaceous, and the Early Paleocene, we know that the chromite flux in the >32- μ m fraction during >2 Ma after the disruption of the LCPB was two to three orders of magnitude higher than the background flux through the rest (or most) of the Phanerozoic [e.g., (*31, 32*)]. There is a size dependency in the flux of extraterrestrial material to Earth after a breakup event. In agreement with modeling scenarios, our empirical data indicate that the post–LCPB breakup



Fig. 4. The lower part of the Hällekis section with plots of bulk-rock concentrations of equilibrated ordinary chondritic chromite (EC) grains, ³He and Al₂O₃, and ¹⁸⁷Os/¹⁸⁸Os ratios. In the far-right column, skeletal grain abundance according to (41, 42) is shown. The chromite and He and Os isotopes indicate a sudden increase in extraterrestrial material in the sediment at -1 m, whereas the Al₂O₃ and skeletal grain abundances illustrate the change to a more clean and coarse-grained limestone that can be used for production of industrial limestone slabs. The coarsening of the sediment reflects stronger hydrodynamic forcing with shallowing, leading to winnowing of the fine fraction.

increase in the flux of 100-m-sized asteroids, decimeter-sized meteoroids, and millimeter-sized micrometeoroids, was one, two, and two to three orders of magnitudes, respectively (11, 14, 31, 32). The increase in the flux of the most fine-grained, micrometer-sized material was certainly even higher, but our Ordovician ³He data cannot resolve the magnitude because gas loss from the 466-Ma-old sediment has occurred (33). However, on the basis of the ³He versus chromite relation in ³He anomalies in much younger sediments (~36 and ~91 Ma old) (32, 34), we are confident about a three to four orders of magnitude increase in the fine-fraction flux after the LCPB breakup.

We argue here that ice age conditions in the mid-Ordovician, postulated by other groups [e.g., (4-7)], were triggered or intensified by the LCPB breakup. We hypothesize that the origin of the prominent Täljsten lowstand deposit (Fig. 1) that has puzzled regional geologists for more than a century (35) can be explained by a eustatic sea level fall related to global cooling triggered by the dust from the LCPB breakup. In Earth's atmosphere today, extraterrestrial dust represents about 1% of the total stratospheric dust and has no direct climatic significance (36, 37). However, cooling is to be expected if the amount of extraterrestrial dust in the atmosphere for several 100 ka or longer increases by more than three orders of magnitude. Following the LCPB breakup, not only Earth's atmosphere but also much of interplanetary space in the inner solar system became dusty, further shading Earth from sunlight [see e.g., 38, 39]. Dust from the LCPB breakup may also have fertilized large areas of the ocean, which could have led to drawdown of CO_2 from the atmosphere (40). The

mechanisms leading to cooling are complex and are influenced by the character of the dust, e.g., size, albedo, mineralogy, and chemical composition. Further research is needed to explore the full parameter space that connects enhanced dust delivery to climate cooling.

Previous studies of the Täljsten sea level fall have placed its onset, in both the Hällekis and the Lynna sections, at the precise level where our new data show arrival of the first LCPB dust (Fig. 4 and fig. S5) (4, 41, 42). In the Hällekis section, the bioclastic particles (from invertebrate skeletal material) making up the limestone are generally coarser in the Täljsten interval than through the rest of the section. The coarser grain size indicates stronger (i.e., with shallower water) hydrodynamic forcing that preferentially removes finer particles from the seafloor sediments. This change to coarser grain size starts at the -1-m level (Fig. 4) (41, 42). The Al₂O₃ profile, which reflects the amount of fine-grained clay in the limestone, shows a drop at the -1-m level, illustrating the onset of the change toward more coarse-grained and cleaner limestone (Fig. 4). Quarry workers have known for centuries that, in the ~54-m section of Ordovician limestone exposed at Hällekis, only a ~3-m interval of the strata, with the Täljsten at its core, is sufficiently clean to be used for the production of commercial limestone slabs (35). We note that, if the LCPB breakup had not led to a change in Ordovician seafloor hydrodynamics, then there would have been no rocks to quarry for limestone slabs and no fossil LCPB meteorites would have been found. Another argument is based on the detailed studies by Rasmussen et al. (4) of brachiopod faunas in the Lynna River valley section and our chromite reconstructions for the same section (fig. S5). The first LCPB



Fig. 5. A chromite grain in an Antarctic micrometeorite. Back-scattered electron image of a porphyritic olivine spherule with large (>63 μ m) chromite relict grain (light gray). This grain is not included in the present study but is shown here to illustrate the distribution of relict grains in cosmic spherules, often found near the particle edge. This relict chromite grain is angular, with limited indication of melting during atmospheric passage.

dust in the strata occurs close to the stratigraphic level where a shallowwater fauna of brachiopods replaces deeper-water faunas. This faunal change then culminates with the low-stand deposits ca. 2 m higher in the section, which are coeval with the Täljsten in Sweden. The shallowing recorded at Lynna is attributed by Rasmussen *et al.* (4) to ice buildup on continents at the onset of the Ordovician ice age. In another mid-Ordovician section that we previously studied at Puxi River in China, we observe a similar trend. There, unusual biogenic micromounds, which may reflect shallowing, formed at the seafloor shortly after the first abundant chromite grains from the LCPB event arrived on Earth (11).

Establishing sea level curves from sedimentary sections is a difficult task involving also subjective considerations. Therefore, various sea level curves for Darriwilian deposits in Baltoscandia are sometimes contradictory. In particular, the magnitude of a sea level change is often very difficult to quantify. However, the prominent sea level lowstand associated with the Täljsten is a very obvious feature [e.g., *17–19, 41–44*]. The 1.4-m thick, gray Täljsten in the middle of a ca. 27-m-thick section of otherwise red Ordovician limestone starts ca. 0.8 m above the base of the Arkeologen bed. Besides the coarser grain size, the Täljsten shows many other features indicative of marked shallowing, such as anomalous shallow-water fossil faunas of gastropods, echinoderms, and ostracods. In some beds, centimetersized echinoderm fossils build the rock (fig. S4). Oncoids and stromatolites, both clear shallow-water indicators, have also been reported (*44*).

The Täljsten lowstand occurred simultaneously over Baltoscandia (e.g., Fig. 1 and fig. S3) consistent with a eustatic origin (18, 19). The setting on the interior of a large, stable craton also supports a eustatic signal (4). Detailed studies of the mid-Ordovician sea level evolution on the Siberian craton, which at the time represented a separate paleocontinent from Baltica, place the most prominent sea level lowstand at the base of the Mukteian-Vikhorevian regional stage, which correlates with the base of the Baltic Kunda stage (45). A coeval major sea level fall has been proposed for other paleocontinents, including Gondwana and Laurentia [(6); see fig. S3], although the biostratigraphic correlations have uncertainties related to the provincialism in mid-Ordovician invertebrate faunas. Future studies using chromespinel grains as a precise global correlation tool will refine our understanding of the age relations between sediment sections on different paleocontinents.

Our revised "astrogeobiological" explanation for the conspicuous faunal diversifications observed in the mid-Ordovician involves breakup of an ~150-km large asteroid in the asteroid belt (16, 46), which flooded the inner solar system with dust. The sudden global change from an equable greenhouse situation to a climatically more heterogeneous icehouse world spurred the GOBE. The cooling increased latitudinal temperature gradients, requiring adaptions by the biota acclimatized to a warm climate. Faunal changes are therefore expected to be more pronounced at mid-to-high latitudes, such as in mid-Ordovician Baltoscandia, than in low-latitude regions. The prominent Täljsten sea level fall may reflect the sudden onset of a continuous, mid-to-late Ordovician ice age, or it may only represent a shorter, intensified icehouse period superimposed on a general cooling trend that culminated in the Late Ordovician (13). The dust from the LCPB could have been the tipping factor triggering an icehouse world. Some oxygen isotope data indicate very warm oceans in the Early Ordovician, and authors have been puzzled by the apparently sudden evolution of icehouse conditions in the mid-Ordovician (7, 47). The enigma could be an artifact of the many difficulties in interpreting Early Paleozoic oxygen isotope data (48), but an alternative explanation links sudden cooling to dust from the LCPB.

In an effort to mitigate ongoing global warming, it has been suggested to capture a large near-Earth asteroid and position it at the first Lagrange point as a source of dust that could help to reduce solar insolation on Earth (39). Gravitationally "anchoring" such a dust cloud at this point would reduce dust particle dispersion and create a prolonged cooling effect. Such an anchored cloud can lead to insolation reductions to Earth three times larger than the reduction required to offset a CO2-induced increase of 2°C in mean global temperature. The >2 Ma of strongly enhanced dust flux to Earth after the LCPB breakup must reflect a complex series of events, including secondary collisions of asteroid fragments from the LCPB, greatly enhanced numbers of near-Earth asteroids, and, speculatively, even dust clouds anchored at unusual gravitational locations. In any case, studies of the extraterrestrial fraction of mid-Ordovician sediment provide new empirical knowledge that is relevant in the context of present-day climate mitigation.

MATERIALS AND METHODS

Separation of chrome-spinel and chemical analyses

The present study builds on the results from previous chrome-spinel studies of the Hällekis-Thorsberg and Lynna River sections, as well as new samples prepared for this study (see data files S1 and S5) for further details. A total of 1320 and 188 kg of limestone at Hällekis-Thorsberg and Lynna River, respectively, have been dissolved in acids and searched for chrome-spinel. The method description here discusses only the treatment of the new samples. The sample preparations were conducted at the Astrogeobiology Laboratory at Lund University (www.astrogeobiology.org) especially built for the separation and extraction of extraterrestrial minerals from sediments. The laboratory has a capacity to dissolve 5 to 10 metric tons of limestone in

hydrochloric (HCl) and HF acid per year. The samples were thoroughly cleaned with a high-pressure washer to remove the weathered material and detritus and then placed in 500-liter plastic barrels with 6 M HCl acid. After ca. 48 hours, the insoluble residue was neutralized with sodium hydroxide and sieved through a 32-µm mesh. The residue was once again treated with HCl for ca. 24 hours and then neutralized with sodium hydroxide and sieved. The resulting residual >32-µm fraction was treated with 11 M HF acid for 48 hours to dissolve the siliciclastic material. After neutralization of the HF acid by means of repeated water decanting, the remaining mineral residue was treated with 18 M sulfuric acid for 12 hours to dissolve hydroxide minerals. After neutralization with sodium hydroxide and sieving through a 32-µm mesh, most of the samples were further treated with undiluted high-density LST (lithium heteropolytungstate) liquid to remove the organic material. The heavy residues in the two size fractions 32 to 63 µm and 63 to 355 µm were recovered and searched beneath a stereo microscope for opaque and transparent spinel grains that were picked with a fine brush. The grains were mounted in epoxy resin, together with analytical standard UWCr-3 (49), and polished with 1- μ m diamond paste. The polished grains were then coated with carbon and quantitatively analyzed at Lund University for chemical composition with a calibrated Oxford INCA X-Sight energy-dispersive spectrometer with a Si detector, mounted on a Hitachi scanning electron microscope (SEM-EDS). Cobalt was used as a standard to monitor instrumental drift. An acceleration voltage of 15 kV, a sample current of ~1 nA, and a counting live time of 80 s was used. Precision of the analyses was typically better than 1 to 4%. Typically, three spots were analyzed on each grain, and the average result is used here. Analysis spots were selected away from grain fractures or rims with signs of diagenetic alteration.

Helium isotope analyses

Helium isotope concentrations were measured using standard practices at Caltech (50). Briefly, each sample of sedimentary rock was dried at 90°C for several hours and crushed in a jaw crusher to ~250-µm chips. Several grams of crushate were then leached of carbonate in 10% acetic acid until no CO₂ evolution was observed even after agitation, and the residue was centrifuged and transferred into a tin sample cup. After drying at 90°C, the amount of residual mass was determined. This provided the operationally defined noncarbonate fraction estimate. Multiple samples were transferred simultaneously into the vacuum system and pumped for at least several hours. Helium was extracted sequentially from each sample by heating to 1200°C in a double-walled resistance furnace for 30 min. Evolved helium was purified and cryo-focused and then analyzed using a simultaneous detection mode on a GV-SFT mass spectrometer. Typical blank levels were 0.75×10^{-15} cm³ at standard temperature and pressure (STP) ³He and 0.2×10^{-9} cm³ STP ⁴He. With the exception of a few samples, these blank levels were less than a few percent on 3 He and $\ll 1\%$ of ⁴He. For the least ³He-rich samples, the blank makes up as much as 10% of the total ³He measured. Estimated uncertainties were derived from the uncertainty in the blank correction and the reproducibility of standards of size comparable to the sample.

Osmium analyses

Here, we used the results of previous osmium (Os) analyses across the Hällekis section, described in (10), as well as new analyses of nine samples collected at a high resolution between 0.54 and 1.1 m below the base of the Arkeologen bed. For the Os analyses, whole-

rock samples were ground into a fine powder with an agate mortar. Between 3 and 10 g of powdered sample were mixed with an isotopically enriched spike (containing ⁹⁹Ru, ¹⁰⁵Pd, ¹⁹⁰Os, ¹⁹¹Ir, and ¹⁹⁸Pt), dried at room temperature overnight, and then mixed with a flux consisting of borax, nickel, and sulfur powder. The typical sample/ flux weight ratio used was 2. After fusing the mixture for 90 min at 1000°C in a glazed ceramic crucible, the melt was allowed to cool and the NiS bead was separated from the glass. The bead was then dissolved in HCl acid (6.2 M HCl), and the residue was filtered through 0.45-µm cellulose filter paper. Insoluble platinum group element-containing particles on the filter paper were dissolved together with the filter paper in 1 ml of concentrated nitric acid (HNO₃) in a tightly closed Teflon vial at ~100°C for about 60 min immediately before Os isotope analysis. After dissolution of the filter paper and oxidation of Os, the Teflon vial was chilled in ice water to minimize the escape of volatile OsO4. Osmium was then extracted from this vial with the sparging method (51) that relies on purging dissolved OsO4 with inert Ar carrier gas and by transferring directly the gas mixture into the torch of a multicollector inductively coupled plasma mass spectrometer (ThermoFinnigan Neptune) and analyzing Os isotopes and potential interferences with a multidynamic data acquisition procedure using three continuous dynode electron multipliers. The details of the method are described in (52). The accuracy and precision of the analytical data have been evaluated in detail by (52) and (53) using various international reference materials and community standards.

Bulk-rock Al₂O₃ analyses

The Al₂O₃ results in Fig. 4 are for ground whole-rock samples that were fused with LiBO₂ and dissolved in HNO₃. Analyses were made with an inductively coupled plasma atomic emission spectrometer. The relative reproducibility (2σ) of the analyses is better than 5% [see further details in (54) and references therein].

Division of chrome-spinel grains

The interpretation of the origin of recovered chrome-spinel grains follows practices developed in a number of studies over the past decade [see, e.g., (11, 24, 31, 32, 49, 55, 56)]. Below is given the full description of how grains are divided into different groups, but in the present study, with focus on the consequences of dust from the LCPB breakup on Earth's climate and biota, only the results for the equilibrated ordinary chondritic chromite (EC) grains are relevant. We deal with the abundance variations of EC grains through the section and how the ratios between H, L, and LL grains among the EC grains vary through the section. Other aspects of the results, such as the high numbers of achondritic grains in pre-LCPB sediments (24), or the variations in terrestrial chrome-spinel grains through the section, will be dealt with elsewhere, although all data are presented in data file S1.

Division into main groups

1) EC: Grains from equilibrated ordinary chondrites (petrological types 4 to 6) with oxide weight percentages within the ranges of ~53.0 to 62.0 Cr_2O_3 , ~23.0 to 32.0 FeO, ~4.5 to 8.5 Al_2O_3 , ~1.3 to 4.5 MgO, ~0.55 to 0.95 V_2O_3 , and ~1.40 to 4.50 TiO₂ [for more detailed discussions, see (11), p. 127]. The FeO values of EC grains can sometimes be lower than 23% because of replacement by MnO and/or ZnO [see (57)].

2) OtC-V: Other chrome-spinel, i.e., grains that do not have the typical equilibrated ordinary chondritic composition but contain

 ${\geq}0.45$ weight % (wt %) V_2O_3 and a Cr_2O_3/FeO ratio of ${\geq}1.45,$ indicating a likely meteoritic origin.

3) OtC: Other chrome-spinel grains but with V₂O₃ < 0.45 wt % or V₂O₃ \ge 0.45 wt % together with a Cr₂O₃/FeO ratio of <1.45. Most or all the OtC grains are likely of terrestrial origin.

The type of grains here referred to as OtC grains have, in our previous studies, been referred to as OC grains, but we have changed the acronym to avoid confusion with OC being used for "ordinary chondrites" in other research.

Division of EC grains in H, L, and LL groups

The EC grains can be further divided into the three groups H, L, and LL based on their oxygen isotope and TiO₂ contents, but here, we used only the latter parameter [see (24, 31, 32, 55, 56)]. The three groups of ordinary chondrites, H, L, and LL, have different average values of Δ^{17} O (0.73, 1.07, and 1.26‰) and TiO₂ (2.2, 2.7, and 3.4 wt %, respectively) (56, 58, 59). Around these averages, the Δ^{17} O and TiO₂ values are spread following a Gaussian distribution, but the distributional tails overlap (56). Although the distinction between the equilibrated ordinary chondritic groups can be done with oxygen-3-isotopic analysis, separating them with TiO₂ has been proven as effective (55, 56). The exact definitions of the ranges for dividing grains based on TiO₂ can, in principle, be arbitrarily set but must be used consistently when comparing different time periods. We used the following ranges in TiO₂ concentration: $H \le 2.50$ wt %, L = 2.51 to 3.39 wt %, and LL \geq 3.40 wt % (55). The TiO₂ content of each group follows a Gaussian distribution with about 10% overlap between the groups. This overlap is insignificant when each of the three groups has similar abundances, but when one group strongly dominates, such as the L chondrites after the LCPB, the overlap creates false high numbers of grains in the other groups. We therefore present our data in two ways: corrected for a 10% overlap between groups and uncorrected for overlap in TiO₂ concentration ranges (Fig. 2, fig. S1, and tables S2 and S3).

Separation of Antarctic micrometeorites

A total of 2.8 kg of micrometeorite-rich sediment from Antarctica (see fig. S6 and Supplementary Text for collection sites) was processed by washing in Milli-Q H₂O and sieving at the Vrije Universiteit Brussel (Brussels, Belgium) to separate size fractions of <125 µm, 125 to 200 µm, 200 to 400 µm, 400 to 800 µm, 800 to 2000 µm, and >2000 μ m, while the remaining half is kept for reference and other research purposes. All size fractions were subjected to magnetic separation using hand magnets. Using optical microscopy and micro x-ray fluorescence spectrometry, 2039 cosmic spherules and 190 partially melted (scoriaceous) and unmelted micrometeorites were handpicked from the four magnetic fractions between 125 and 2000 µm. On the basis of the inspection of multiple small subsamples, no significant number of residual micrometeorites remained in the nonmagnetic fractions. Surficial textural characteristics and diameters were determined for these particles using a FEI ESEM Quanta 200 environmental scanning electron microscope at the Royal Belgian Institute of Natural Sciences (Fig. 5 and figs. S7 and S8). Additional but smaller subsamples of sediment (<150 g) were processed at the Astrogeobiology Laboratory at Lund University following a protocol similar to the one described above. Here, the studied size fractions of 80 to 200 µm, 200 to 300 µm, 300 to 500 µm, and 500 to 700 µm led to the recovery of an additional 753 cosmic spherules. The total of 2982 micrometeorites was dissolved in HF acid at Lund University. All residual mineral grains were collected

on filter paper and analyzed by SEM-EDS for elemental composition (data file S4).

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/5/9/eaax4184/DC1

Supplementary Text

Fig. S1. Distribution of equilibrated ordinary chondritic chromite (EC) grains through the Hällekis-Thorsberg section.

Fig. S2. High-resolution ¹⁸⁷Os/¹⁸⁸Os isotope profile across a proposed discontinuity surface.

- Fig. S3. The gray Täljsten in the Degerhamn Quarry, southern Öland.
- Fig. S4. Cystoid echinoderms in the Likhall bed of the Täljsten.
- Fig. S5. Distribution of extraterrestrial chromite across the Lynna River section.
- Fig. S6. Map of Antarctic micrometeorite localities.
- Fig. S7. Back-scattered electron images of Antarctic micrometeorites.
- Fig. S8. Size distribution of Antarctic micrometeorites. Table S1. Chrome-spinel distribution through the Hällekis-Thorsberg section.
- Table S1. Extraterrestrial chromite division below reference level in Hällekis section.
- Table 52. Extraterrestrial chromite division above reference level in Hallekis section.
- Table S4. Published abundances of micrometeorite types from different collections.
- Table S5. Poynting-Robertson transfer times (Ma) from the outer solar system to Earth.
- Data file S1. Hällekis-Thorsberg section—chrome-spinel chemical results.

Data file S2. Helium isotope data.

. Data file S3. Osmium isotope data.

Data file S4. Spinels in Antarctic micrometeorite.

Data file S5. Lynna River section—chrome-spinel chemical results.

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Australasian microtektites across the Antarctic continent: Evidence from the Sør Rondane Mountain range (East Antarctica)

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Microtektites are SiO₂-rich, vitreous particles that solidified from molten, upper crustal rocks shortly after the hypervelocity impact of an asteroidal or cometary body with the Earth's surface (e.g., Koeberl, 1994; Artemieva et al., 2002). Four major strewn fields have currently been identified and linked to impact structures in North-America, Ivory Coast and Central Europe (Glass and Simonson, 2013). Yet, the Australasian strewn field is the largest and most recent tektite strewn field (e.g., Schwarz et al., 2016; Jourdan et al., 2019; Di Vincenzo et al., 2021), extending from South-East Asia to the TAM (e.g., Folco et al., 2008; 2009; 2016; Brase et al., 2021). Here, we present new major, trace element and Sr-Nd isotope data for 33 microtektite-like particles recovered from sedimentary deposits in the SRM in an attempt to verify their microtektite-nature and potentially affiliate them to one of the four known strewn fields. Such affiliation may have important implications with regard to the distribution pattern of impact ejecta and may provide a minimal age constraint for the sedimentary deposits from the SRM. The latter is crucial to reconstruct and understand the regional deglaciation history. In addition, the preservation and abundance of microtektite-like particles is compared among different sedimentary deposits from the SRM to assess their accumulation potential.

BS is first author of this manuscript and has performed sample acquisition; sample preparation; sample imaging (SEM); acquisition and processing of the major and trace elemental dataset (LA-ICP-MS); and dataset interpretation.

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Australasian microtektites across the Antarctic continent: Evidence from the Sør Rondane Mountain range (East Antarctica)



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ABSTRACT

The ~790 ka Australasian (micro)tektite strewn field is one of the most recent and best-known examples of impact ejecta emplacement as the result of a large-scale cratering event across a considerable part of Earth's surface (>10% in area). The Australasian strewn field is characterized by a tri-lobe pattern consisting of a large central distribution lobe, and two smaller side lobes extending to the west and east. Here, we report on the discovery of microtektite-like particles in sedimentary traps, containing abundant micrometeorite material, in the Sør Rondane Mountain (SRM) range of East Antarctica. The thirty-three glassy particles display a characteristic pale yellow color and are predominantly spherical in shape, except for a single dumbbell-shaped particle. The vitreous spherules range in size from 220 to 570 µm, with an average diameter of ~370 µm. This compares relatively well with the size distribution (75-778 µm) of Australasian microtektites previously recovered from the Transantarctic Mountains (TAM) and located ca. 2500-3000 km from the SRM. In addition, the chemical composition of the SRM particles exhibits limited variation and is nearly identical to the 'normal-type' (i.e., <6% MgO) TAM microtektites. The Sr and Nd isotope systematics for a single batch of SRM particles (n = 26) strongly support their affiliation with TAM microtektites and the Australasian tektite strewn field in general. Furthermore, Sr isotope ratios and Nd model ages suggest that the target material of the SRM particles was composed of a plagioclase- or carbonate-rich lithology derived from a Paleo- or Mesoproterozoic crustal unit. The affiliation to the Australasian strewn field requires long-range transportation, with estimated great circle distances of ca. 11,600 km from the hypothetical source crater, provided transportation occurred along the central distribution lobe. This is in agreement with the observations made for the Australasian microtektites recovered from Victoria Land (ca. 11,000 km) and Larkman Nunatak (ca. 12,000 km), which, on average, decrease in size and alkali concentrations (e.g., Na and K) as their distance from the source crater increases. The values for the SRM particles are intermediate to those of the Victoria Land and Larkman Nunatak microtektites for both parameters, thus supporting this observation. We therefore interpret the SRM particles as 'normal-type' Australasian microtektites, which significantly extend the central distribution lobe of the Australasian strewn field westward. Australasian microtektite distribution thus occurred on a continent-wide scale across Antarctica and allows for the identification of new, potential recovery sites on the Antarctic continent as well as the southeastern part of the Indian Ocean. Similar to volcanic ash layers, the ~790 ka distal Australasian impact ejecta are thus a record of an instantaneous event that can be used for time-stratigraphic correlation across Antarctica.

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1. Introduction

Tektites (and their submillimeter analogues microtektites) are natural, SiO_2 -rich glasses that form during oblique hypervelocity impact of

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asteroidal or cometary bodies with the Earth's surface (e.g., Koeberl, 1994; Artemieva et al., 2002). They are distributed over large geographical areas (>100–1000 km) commonly referred to as 'strewn fields', which have previously been linked to large-scale impact cratering events in North America, Ivory Coast and Central Europe (Glass and Simonson, 2013).

The Australasian strewn field is among the largest (>10% of the Earth's surface) and most recent (788.1 \pm 3.0 ka; Schwarz et al., 2016;

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Jourdan et al., 2019) impact events on Earth in terms of ejecta material, but no source crater has yet convincingly been identified. The existence of such impact crater is nevertheless supported by the presence of melt layers in Australasian tektites, shock-metamorphic features observed in Australasian tektites, microtektites and microscopic ejecta particles recovered from Australasian ejecta layers, and high pressuretemperature mineral phases, including coesite and reidite in Muong Nong-type tektites (e.g., Walter, 1965; Glass and Wu, 1993; Folco et al., 2010b; Cavosie et al., 2017; Glass et al., 2020; Masotta et al., 2020). Furthermore, a detailed investigation of the moderately (e.g., Ni, Co, Cr) and highly (e.g., Os, Ir, Pt, Pd, Rh, Ru, Re) siderophile element concentrations in Australasian impact ejecta has revealed that their geochemistry is consistent with upper continental crust material to which chondritic or primitive achondritic material was admixed (Goderis et al., 2017; Folco et al., 2018; Ackerman et al., 2019). Based on the distribution and physicochemical properties (i.e., size distribution, composition) of Australasian impact ejecta, it has been suggested that the hypothetical source crater is located on the northern or central parts of the Indochina peninsula (Barnes, 1964; Glass and Pizzuto, 1994; Ma et al., 2004; Prasad et al., 2007; Folco et al., 2010a, 2010b). Based on geophysical evidence, Sieh et al. (2020) have argued that the Australasian impact crater is buried beneath the Bolaven volcanic field in southern Laos. Australasian (micro)tektites are distributed along a trilobed pattern consisting of a large, central (SE Asia, Australia) SSE orientated ejecta ray, which is flanked by two smaller, western (Indian Ocean, SE Africa) and eastern (Pacific Ocean) side lobes (Fig. 1). This distinctive lobe pattern was reconstructed through multiple (>60) ocean drilling program (ODP) campaigns and other oceanographic studies, revealing the location of Australasian (micro)tektites distributed on the seafloor of the Indian and Pacific Oceans (Glass and Simonson, 2013).

Microtektites have previously been recovered from sediment traps on nunataks (e.g., Miller Butte, Pian delle tectiti, etc. – Victoria Land) and glacial moraines (e.g., Larkman Nunatak) in the TAM (Folco et al., 2008, 2009, 2016; van Ginneken et al., 2018) (Fig. 1). Due to the isolated nature and high altitude ca. 2600–2800 m.a.s.l.) of these sampling sites, the accumulation of material is restricted to surrounding basement rock and direct atmospheric infall, including micrometeorites, volcanic glass shards, meteorite ablation debris, and microtektites (e.g., Folco et al., 2008, 2009; Rochette et al., 2008; van Ginneken et al., 2010). Major and trace element compositions of the Victoria Land microtektites are consistent with those of microtektites at other sites within the Australasian strewn field. However, their volatile compounds (e.g., Na₂O, K₂O) are strongly depleted and presumably record a high degree of vaporization, which is compatible with large-scale translation from the source crater (Artemieva et al., 2002; Folco et al., 2010a; van Ginneken et al., 2018). Isotopic tracers (⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd) have provided an unequivocal link to the Australasian impact event, demonstrating that the Victoria Land and Australasian microtektites have sampled similar target rocks (Folco et al., 2009). Fission track dating also confirms similar formation ages (ca. 0.85 ± 0.17 Ma) that match the Australasian impact event (Folco et al., 2011), effectively extending the central distribution lobe of the Australasian strewn field approximately 3000 km southward.

Here, we report the discovery of thirty-three microtektite-like particles from sedimentary traps in the Sør Rondane Mountain range (East Antarctica). We present major, trace element and Sr–Nd isotope data to determine the nature of the SRM particles and compare them to other Antarctic microtektites, previously affiliated to the Australasian strewn field. The implications of such potential affiliation are threefold: (1) the geographical distribution of Australasian microtektites can be refined and allows for new, potential recovery sites to be identified, (2) this information, in turn, is relevant to reconstruct the collisional parameters (e.g., entry angle, direction) of the hypervelocity bolide impact and refine the target stratigraphy, and (3) the abundance and



Fig. 1. Geographical distribution (contour) of the recovery sites (ODP - black filled circles) of Australasian (micro)tektites with indication of the Sør Rondane (SRM) and Transantarctic Mountain ranges, including the Victoria Land and Larkman Nunatak sampling sites. Note that continental recovery sites (e.g., Indonesia, Laos, Australia, etc.), except for those on the Antarctic continent, are not shown here. The SRM and TAM chains are separated approximately 2500–3000 km from one another. The hypothetical crater location (star symbol) is based on previous suggestions by Barnes (1964), Glass and Pizzuto (1994), Ma et al. (2004), Prasad et al. (2007), Folco et al. (2010a, 2010b), Sieh et al. (2020). Figure modified from Folco et al. (2009, 2016).

preservation potential of microtektites in Antarctic sedimentary traps can be evaluated to increase the chances of success during future sampling campaigns.

2. Materials and methods

A limited number (n = 33) of microtektite-like particles has been recovered from sedimentary traps (e.g., exposed cracks, fissured surfaces, moraines) in the SRM, Queen Maud Land, East Antarctica (Figs. 1 and 2; Goderis et al., 2020). These sedimentary deposits were collected during the 2018 Belgian Antarctic Meteorites and Micrometeorites (BAMM!) expedition. Based on the bedrock exposure ages and general glacial history for the western part of the SRM, accumulation of extraterrestrialand impact-related material presumably occurred over a time span of ~1–3 Ma at the respective sampling sites (Suganuma et al., 2014). Accumulation appears to be directly controlled by atmospheric infall as demonstrated for the Mt. Widerøe cosmic spherule collection, based on the structural, textural, chemical, and isotopic characteristics of this collection (Goderis et al., 2020).

Bulk sedimentary deposits were weighed and wet-sieved into six different size fractions ranging from $<125 \,\mu\text{m}$ up to $>2000 \,\mu\text{m}$. The deposit was subsequently dried in an oven for 12 h at a temperature of ca. 60 °C. Microtektites were mainly searched for in the non-magnetic size fractions between 200 and 800 µm. The separation of magnetic particles was performed by repeatedly moving a hand magnet over the respective size fractions until no additional material remained attached to the magnet. Potential microtektite particles were then manually extracted using a set of titanium tweezers and binocular microscope. Semi-quantitative geochemical compositions were determined using a JEOL JSM IT-300 scanning electron microscope (SEM), coupled to an Oxford energy dispersive spectrometer (EDS) at the SURF department of the Vrije Universiteit Brussel (Brussels, Belgium). Operating conditions for SEM analysis were 15 kV acceleration voltage and a 10 nA beam current. Given the vitreous nature of the particles, a defocused beam with a ca. 10 µm spot size was used for chemical analysis. The first seven particles, with major element compositions comparable to those of Victoria Land microtektites, were embedded in epoxy resin and polished for further analysis. An additional 26 particles were placed on a separate glass slide, characterized for major and trace element compositions, and finally combined for Sr and Nd isotope analysis.

Following a short pre-ablation run to clean the exteriors of the particles, the major and trace element compositions of 34 possible microtektites were measured using a Teledyne Cetac Technologies Analyte G2 excimer-based laser ablation system equipped with HelexII double volume cell and ARIS aerosol introduction system and coupled to a Thermo Scientific Element XR sector field inductively coupled plasma - mass spectrometer (LA-ICP-MS) at the Department of Chemistry of the Ghent University (Ghent, Belgium) using an external calibration by USGS and MPI-DING glass reference materials and established sum normalization data processing approach (see Das Gupta et al., 2017; Appendix A, Supplementary Data). Two replicate analyses with a spot size of ca. 35 µm were performed on the first seven microtektite candidates, while the remaining 26 bulk particles were analyzed two to three times using a 40 µm circular spot size, depending on their size. During these analyses, a single vitreous cosmic spherule was identified among the selected particles and excluded from the following analyses. In addition, a single green, irregularshaped vitreous particle was discovered that was subsequently identified as volcanic glass. The accuracy of the LA-ICP-MS analysis was determined by comparing the average bias between the experimentally obtained values and the reference values and was found to be less than 10% for all reported elements. To determine the reproducibility of the applied procedure, the relative standard deviation (RSD) was calculated for the MPI-DING ATHO-G reference glass. For most elements, the reproducibility was ≤5% RSD, except in the case of Li, Ge, As, Mo, Cs, Tb, Tm (5%-10% RSD), and Be, Cr, Co, Ni, Sb, U (>10% RSD). The slightly worse reproducibility of the latter elements can be attributed to their lower concentration in the ATHO-G reference glass. This is furthermore supported by their good reproducibility (<10% RSD) in other USGS and MPI-DING reference glasses such as BHVO-2G and ML3B-G, where these respective elements are more concentrated



Fig. 2. Overview of the sampling locations in the Sør Rondane Mountains. (A) Overview of the Mt. Widerø summit with indication of the Mt. Widerø #1 sampling location (window – S72.14458°, E23.27798°). (B) Detailed view upon the Mt. Widerø #1 sedimentary trap with compass for scale. (C) Moraine deposits near the Mt. Walnum summit. (D) Detailed view upon the Walnumfjellet Moraine sedimentary trap (S72.13632°, E23.84309°) illustrating the incorporation of moraine deposits in the ice sheet. The dashed line indicates the transition from the sediment to ice. (E) Detailed view upon the Mt. Walnum #1 sedimentary trap (S72.10801°, E24.22434°) with scoop for scale. The sedimentary traps are located at elevations between ca. 2500–2800 m.a.s.l. and are continuously subjected to frosty conditions.

For Sr–Nd isotope measurements, 0.8 mg of combined microtektites, alongside with USGS international standards BCR-2 (2 mg) and BHVO-2 (1 mg), was dissolved using subboiled 3:1 HNO₃ : HF for 2 days at 120 °C, and subboiled HCl after evaporation for one day at 120 °C at the Laboratoire G-Time at the Université Libre de Bruxelles (Brussels, Belgium). Cationic resin has been used to separate Sr in 1.5 N HCl from rare earth elements (REE) in 6 N HCl. Strontium has subsequently been purified, notably from Rb, by using Sr.Spec resin in combination with 7 N HNO₃, while Nd has been purified from other REE, and notably Sm, using HDEHP resin with 0.16 and 0.27 N HCl. Both Sr and Nd isotope compositions have been measured on the Nu-Plasma2 multi-collection inductively coupled plasma-mass spectrometer at Laboratoire G-Time using a desolvating nebulizer Aridus 2 system. For Sr, the NBS987 standard was measured at 50 ppb, and provided an average value of 87 Sr/ 86 Sr = 0.710372 \pm 0.000019 (2 σ , *n* = 20), and values were subsequently corrected with the accepted value by standard-bracketing at ${}^{87}\text{Sr}/{}^{86}\text{Sr} = 0.710248$ (Weis et al., 2006). Internal reproducibility based on repeated measurement of an in-house carbonate standard (n = 4) is better than 35 ppm (2 σ). For Nd, the Rennes standard was measured at 10 ppb and yielded an average value of 143 Nd/ 144 Nd = 0.511951 ± 0.000035 (2 σ , n = 15), and values were corrected for the accepted value by standard-bracketing at 143 Nd/ 144 Nd = 0.511963 (Chauvel and Blichert-Toft, 2001). Internal reproducibility based on repeated analysis of the IMC quality control standard (n = 3) is better than 35 ppm and is identical to the value obtained for 15 Rennes standards. In both cases, BCR-2 and BHVO-2 values overlap within error with published values (e.g. Weis et al., 2006).

3. Results

In total, thirty-three glassy spherules were identified as microtektites in the SRM deposits using SEM-EDS and LA-ICP-MS analysis based on their Si-Al-enriched composition (SiO₂ = 65.2–76.1 wt.%, $Al_2O_3 = 12.2-20.1$ wt.%), which distinguishes them from chondritic (vitreous) cosmic spherules (Figs. 3 and 4 and Appendix A, Supplementary Data). Additionally, their volatile element concentrations (e.g., Na₂O, K₂O) are significantly higher than those of (a)chondritic micrometeorites, but lower than those of Victoria Land volcanic glass shards and the single volcanic glass particle recovered during this study (Fig. 3). The SRM particles therefore discriminate themselves from all types of (extra)terrestrial materials recovered from Antarctic micrometeorite traps, except for the TAM microtektites (Folco et al., 2009). Their major element compositions also fall within the compositional range defined by 'normal-type' (<6 wt.% MgO) Australasian microtektites and, more specifically, overlap with the compositions of the 'normal-type' Victoria Land microtektites (Glass et al., 2004; Folco et al., 2008, 2009, 2016; see Figs. 3 and 4). No other chemical microtektite types (i.e., intermediate, high-Mg, high-Al, or high-Ni, Fe-type; Glass et al., 2004; Folco et al., 2016, 2018) have been recovered from the SRM collection so far.

The trace element compositions, including the refractory elements Zr and Hf, are consistent with 'normal-type' Victoria Land microtektites (Fig. 5). Zinc is the sole exception and appears to be notably depleted in the SRM particles. Additionally, three samples, which are indistinguishable from the other SRM particles based on major element geochemistry, extend the known ranges in V, Cs, Pb and U contents. The multi-element diagram displays the range of elemental concentrations observed in the characterized particles and are normalized to upper continental crust values (Taylor and McLennan, 1995) (Fig. 6). Their geochemical composition strongly resembles the pattern defined by 'normal-type' Victoria Land microtektites, with concentrations similar to those of the upper continental crust, except for Na, K, V, Zn, Cs, Pb and U, which are strongly depleted relative to crustal values.

The 143 Nd/ 144 Nd ratio (0.512073 \pm 10, 2 σ) of the SRM particles is identical (within error) to that measured for Victoria Land microtektites $(0.512086 \pm 29, 2\sigma)$, and is fully consistent with the Australasian strewn field. In contrast, the 87 Sr/ 86 Sr ratio (0.716664 \pm 12, 2 σ) is within range of the values observed for Victoria Land microtektites (0.716215 ± 10) , and 0.716372 ± 10 , 2σ), but offset to slightly higher values in the direction of Australasian tektites from Malaysia, China and the Philippines. Isotopic ratios in Fig. 7A are expressed in the ε notation, where $\varepsilon = [(R_{sample} - R_{standard})/R_{standard}] \times 10,000$. The reference material used for comparison of the Sr and Nd isotopes are Uniform Reservoir (UR) and Chondritic Uniform Reservoir (CHUR), respectively. This translates to $\epsilon^{87}Sr_{UR}$ and $\epsilon^{143}Nd_{CHUR}$ values of 173 and - 11.0, respectively, for the SRM particles. This compares well with the values observed for Victoria Land microtektites ($\epsilon^{87}Sr_{UR} = 166-168$, ε^{143} Nd_{CHUR} = -10.8) (Table 1; Folco et al., 2009). The single and twostage Nd model ages, calculated with respect to the Depleted Mantle (DM) reservoir, are consequently also highly comparable between the SRM particles and Victoria Land microtektites (Table 1), and are



Fig. 3. Ternary diagrams discriminating chondritic and achondritic micrometeorites, Australasian microtektites and volcanic rocks-tephra from Victoria Land (Antarctica) based on the distribution of Si-Fe-Mg (A) and Al-Ca-Na-K (B). Values are calculated based on the atomic abundances of elements (see Appendix A, Supplementary Data). In both instances, the SRM particles are positioned within the range defined by 'normal-type' Australasian microtektites from the Transantarctic Mountains (TAM). A single, green irregular-shaped glass particle is presumably linked to volcanic activity in Victoria Land and is referred to as 'SRM – Volcanic Glass'. Reference values for Australasian microtektites, (a)chondritic micrometeorites and volcanic rock-tephra reproduced from Perchiazzi et al. (1999), Taylor et al. (2007), Curzio et al. (2008), Rochette et al. (2008), Folco et al. (2009), Cordier et al. (2011, 2012) and van Ginneken et al. (2018), Figure modified from Folco et al. (2009).



Fig. 4. Major element chemistry of the SRM particles (including a single volcanic glass particle – VG) determined by LA-ICP-MS (see Appendix A, Suplementary Data). The geochemical range of the particles is largely indistinguishable from reference values for Victoria Land (TAM) microtektites and is clearly distinguished from the volcanic glass particle. Reference values for North American, Ivory Coast and Australasian (micro)tektites (DSS – Deep Sea Sediment) were reproduced from Glass et al. (2004), Folco et al. (2009, 2016) and van Ginneken et al. (2018).

consistent with reference values for Australasian tektites (Folco et al., 2009; Ackerman et al., 2020). This age indicates the time at which the parent material of the respective particles physicochemically separated from the DM reservoir. However, the single-stage model assumes that the parent material of the SRM and TAM particles directly separated from the DM reservoir, while the two-stage model assumes that the crustal unit is composed of recycled, well-mixed sedimentary strata.

The single-stage model age for the SRM particles indicates a possible Mesoproterozoic age, while the two-stage model age is slightly older suggesting a Paleo- or Mesoproterozoic age. Furthermore, on a diagram of ⁸⁷Sr/⁸⁶Sr versus 1/Sr, which indicates a mixing of Sr-rich and Sr-poor isotopically distinct components, the SRM particles and Victoria Land microtektites plot within the 'normal and intermediate australites' field (Fig. 7B). Both groups of particles also display ⁸⁷Sr/⁸⁶Sr ratios



Fig. 5. Trace element geochemistry of the SRM particles (including a single volcanic glass particle – VG) determined by LA-ICP-MS (see Appendix A, Supplementary Data). Particles are predominantly positioned within the geochemical range defined by the Victoria Land (TAM) microtektites, except for Zn. Three samples within the SRM suite are characterized by higher Cs and U contents. The reader is referred to Fig. 4 to observe the legend of this figure. Reference values for North American, Ivory Coast and Australasian (micro)tektites are from Glass et al. (2004), Folco et al. (2009, 2016) and van Ginneken et al. (2018). Figure modified from van Ginneken et al. (2018).

similar to those observed in splash-form Australasian tektites from Indonesia and the Philippines, but at lower K_2O/CaO values (Fig. 7C).

from Larkman Nunatak (ca. <300 μm) and Victoria Land (ca. 500 μm) (Folco et al., 2008, 2009, 2016; van Ginneken et al., 2018).

The pale yellow, transparent SRM particles range in size between ca. 224 and 568 µm and are predominantly spherical in shape (ca. 97%) (Fig. 8). A single particle displays a more irregular and flattened morphology. We refer to this particle as 'dumbbell-shaped'. The major and trace element composition of the dumbbell-shaped particle does not exhibit notable differences compared to its spherical counterparts. No vesicles were observed during petrographic and SEM analysis. The size distribution of the SRM particles is not well constrained due to the relatively limited sample set (n = 33). The peak area is distributed between ca. 300 and 500 µm with an average size of ca. 378 µm. This is positioned in between the average sizes of Australasian microtektites recovered

4. Discussion

4.1. Nature of the Sør Rondane Mountain particles

The physicochemical properties and Sr–Nd isotopic compositions of the SRM particles bear a strong resemblance with 'normal-type' Victoria Land microtektites (Folco et al., 2008, 2009, 2016), and Australasian tektites as a whole (Glass et al., 2004). The Australasian impact event has previously been dated to ca. 788.1 \pm 2.8 ka (Schwarz et al., 2016; Jourdan et al., 2019), which is considerably younger than the final



Fig. 6. Geochemical plot of major and trace element chemistry normalized against average compositions of the upper continental crust. The light grey envelope represents the compositional range of the SRM particles (see Appendix A, Supplementary Data), while the dark grey envelope represents the compositional range of 'normal-type' microtektites from the Victoria Land (TAM) (Folco et al., 2009). The three distinct lines represent individual SRM microtektites that slightly extend the range for V, Pb, U, and Cs. Reference values for upper continental crust and Victoria Land microtektites are from Taylor and McLennan (1995) and Folco et al. (2009), respectively. Figure modified from Folco et al. (2009).

deglaciation stages of the SRM (ca. 1–3 Ma; Suganuma et al., 2014). As such, there is a possibility that the SRM sedimentary traps were able to collect Australasian microtektites. To confirm the nature of the SRM particles as (Australasian) microtektites, several key properties need to be verified (Koeberl, 1994; Montanari and Koeberl, 2000; Glass and Simonson, 2013): (i) distribution over a large geographical area, (ii) aerodynamic shapes due to the molten state of the precursor material during atmospheric transportation, (iii) major and trace element geochemistry resembling average compositions of the upper continental crust, (iv) the presence of high SiO₂ (lechatelierite) inclusions, and (v) relatively low H₂O contents.

(i) Large impact cratering events commonly produce an ejecta curtain consisting of e.g., tektites, microtektites, clinopyroxene-bearing spherules, which are transported ca. 100 s to 1000 s of kilometers from the source crater (Glass et al., 2004). Despite the substantial distance between the SRM and TAM ranges (ca. 2500–3000 km), we have observed nearly identical physicochemical features between both types of particles, suggesting they have shared a common source lithology. A contribution of volcanic rock or tephra can be excluded based on their major and trace element chemistry, which is characterized by higher CaO, Na₂O, K₂O and LREE contents with respect to the SRM particles and Victoria Land microtektites (Figs. 3–5).

The sampling sites of the Victoria Land and Larkman Nunatak microtektites are located at ca. 11,000 and 12,000 km from the hypothetical source crater in Indochina, respectively. Following the distribution of Australasian impact ejecta (Fig. 1), the SRM particles may have travelled along the central or western distribution lobe. However, this would greatly affect the total travel distance of the SRM particles. If transportation occurred along the central distribution lobe, then the estimated great circle distance would amount ca. 11,600 km. Alternatively, the estimated great circle distance would exceed ca. 13,000 km if transportation occurred along the western distribution lobe instead.

Folco et al. (2010a) observed that the concentration of volatile compounds (e.g., Na₂O, K₂O) in Australasian (micro)tektites is inversely correlated with distance from the hypothetical source crater (Fig. 9A). They have attributed this observation to high-temperature vaporization of crustal target rocks during oblique hypervelocity impacts. According to Artemieva et al. (2002), heating temperatures systematically increase closer to the point of impact, severely depleting volatile components, reducing the overall size of microtektites due to a reduction in surface tension processes, and limiting the presence of high SiO₂ inclusions and vesicles. This hypothesis is consistent with mathematical models of Melosh (1989), who suggested that impact ejecta, which originated closer to the contact surface, are subjected to more extreme pressure-temperature conditions and are thus ejected further away from the source crater. This would imply that the translational history of Australasian (micro)tektites is possibly correlated to a number of criteria including volatile element depletion, size-frequency distribution, and the presence of high SiO₂ inclusions and vesicles.

The concentration of volatile compounds (Na₂O = 0.15–0.41 wt.%; $K_2O = 0.49-1.10$ wt.%) in the SRM particles are intermediate between the Victoria Land (Na₂O = 0.15–0.63 wt.%; $K_2O = 0.38-1.54$ wt.%) and Larkman Nunatak (Na₂O = 0.07–0.39 wt.%; $K_2O = 0.10-0.81$ wt.%) microtektites (Folco et al., 2008, 2009, 2016; van Ginneken et al., 2018) (Fig. 9A). The geochemical signatures of the Larkman Nunatak microtektites are more refractory and display greater volatile element depletions compared to 'normal-type' Victoria Land microtektites (van Ginneken et al., 2018), therefore extending the volatilization trend previously established by Folco et al. (2010a). While inconclusive, the intermediate values observed in the SRM particles are supportive of transportation along the central distribution lobe since the extent of volatile element depletion does not exceed that observed in the more refractory Larkman Nunatak microtektites (Fig. 9A).

Following mathematical models (Melosh, 1989; Artemieva et al., 2002) and previous observations (Folco et al., 2009; van Ginneken et al., 2018) regarding the physicochemical properties of microtektites, the size-frequency distribution of microtektites may provide additional insight into the trajectory path followed by the SRM particles. Van Ginneken et al. (2018) have, on average, reported smaller particle sizes (mean diameter of ca. 275 µm) and a narrower size-frequency distribution compared to the Australasian microtektites recovered from Victoria Land (mean diameter of ca. 500 µm). The latter authors



Fig. 7. Strontium and neodymium isotope plot. (A) ϵ^{87} Sr_{UR} versus ϵ^{143} Nd_{CHUR} diagram for (micro)tektites from the four major strewn fields. Values are expressed in the ε notation, CHUR = Chondritic Uniform Reservoir. The ε values of the SRM particles are consistent with literature values for the Australasian strewn field (Table 1). Reference values for Ivory Coast, North American, Central European and Australasian (micro)tektites from Shaw and Wasserburg (1982), Blum et al. (1992), Deutsch and Koeberl (2006), and Folco et al. (2009). Figure modified from Folco et al. (2009). (B) The Sr elemental and isotopic compositions of the SRM and Victoria Land particles appear to be consistent with reference values for normal- and intermediate-type australites. Reference values for Muong Nong-type and splash-form Australasian tektites from Compston and Chapman (1969), Shaw and Wasserburg (1982), Blum et al. (1992) and Lee et al. (2004). Figure modified from Ackerman et al. (2020). (C) ⁸⁷Sr/⁸⁶Sr versus K₂O/CaO diagram linking the respective (micro)tektites to a specific component within the target material. Australasian tektites displaying higher ⁸⁷Sr/⁸⁶Sr and K₂O/CaO presumably sampled a large proportion of K-feldspar, mica, and to a lesser extent plagioclase, due to the incorporation of radiogenic ⁸⁷Rb and K in the aforementioned mineral phases (Ackerman et al., 2020). In contrast, the lower abundances of ⁸⁷Rb and preferential incorporation of Ca and Sr in plagioclase and carbonate mineral phases consequently result in lower ⁸⁷Sr/⁸⁶Sr and K₂O/CaO ratios. Muong Nong-type tektites predominantly appear to have sampled the former lithology, while splash-form tektites are linked to both lithologies. The SRM and Victoria Land particles are positioned in a distinct location on the diagram, but have also suffered severe volatilization resulting in lower K₂O/CaO values, despite a similar ⁸⁷Sr/⁸⁶Sr ratio compared to splash-form tektites from Indonesia and the Philippines (Ackerman et al., 2020). The SRM and Victoria Land particles may therefore have sampled a plagioclase- and carbonate-rich target material assuming that the ⁸⁷Sr/⁸⁶Sr ratio did not change extensively as a result of volatilization. Figure modified from Ackerman et al. (2020).

suggested that average particle sizes may decrease as their distance from the source crater increases. The SRM particles range in size between 220 and 570 μ m with an average size of ca. 370 μ m, which also favors a trajectory path along the central, rather than the western,

distribution lobe. Due to low counting statistics for the SRM particles and Victoria Land microtektites of less than 400 µm in diameter, this interpretation should be considered with care. Potential effects from weathering processes can be excluded due to the lack of physicochemical alteration in the SRM particles across the entire size range (Fig. 8B– D). Significant sorting effects can also be discarded based on the physicochemical properties of the cosmic spherules extracted from the SRM sedimentary traps (cfr. See cumulative size distribution in Goderis et al., 2020) and TAM micrometeorites and microtektites (Suavet et al., 2009; Suttle and Folco, 2020).

(ii) Despite the substantial range of aerodynamic morphologies (e.g., spherical, dumbbell, teardrop, etc.) observed in Cenozoic microtektites (Glass et al., 2004), the vast majority of Victoria Land microtektites exhibits spherical shapes (ca. 98%; Folco et al., 2008, 2009). Folco et al. (2009) consequently suggested that the proportion of spherical tektites is positively correlated with distance from the source crater. This appears to be validated by the Larkman Nunatak microtektites where all 52 characterized microtektites exhibit spherical shapes (van Ginneken et al., 2018). The SRM particles also support these observations as 97% (32 out of 33) is spherical, with the exception of a single dumbbell-shaped particle (Fig. 8A-D). The latter displays a similar extent of volatile element depletion compared to its spherical counterparts, which suggests that the vaporization of volatile compounds occurs within the impact plume, rather than during atmospheric reentry, and is consistent with previous numerical models (e.g., Melosh, 1989; Artemieva et al., 2002).

(iv) The major and trace element geochemistry of the SRM particles is consistent with average compositions of upper continental crust, except for a number of elements including Na, K, V, Zn, Cs, Pb and U (Fig. 6). Volatile elements (i.e., Na, K, Cs, Pb, U) are partially vaporized during high thermal regimes and their loss passively enriches the more refractory elements (e.g., Zr, Hf, REE), as previously observed by Folco et al. (2009). The depletion of moderately volatile (e.g., Zn) and redox-sensitive elements (e.g., V, U) is more difficult to explain. These variations are likely primary in nature and may relate to target rock heterogeneity or variable redox conditions in the impact plume, but this cannot be further constrained based on the limited sample set. Given the pristine nature of the SRM particles, alteration processes are unlikely to have significantly affected the geochemical composition of the SRM particles.

(v) While seven polished sections were analyzed and imaged using SEM-EDS, no high SiO₂ inclusions have been observed in these particles. Folco et al. (2009) only reported a single lechatelierite inclusion among hundreds of Victoria Land microtektites, which Folco et al. (2010a) have argued to be a consequence of the high-temperature regime experienced by the Antarctic Australasian microtektites during the impact event (see discussion above). In addition, no vesicles have been observed in the SRM microtektites, which is consistent with the overall low number of vesicles observed in the Victoria Land and Larkman Nunatak microtektites (Folco et al., 2010a, 2016; van Ginneken et al., 2018).

(v) The H₂O content of (micro)tektites can also be utilized to discriminate the respective strewn fields (Glass et al., 2004). However, no water content was analyzed during this study due to the relative low number of particles recovered and priority to analyze the Sr–Nd isotopic compositions instead.

Based on the observations and arguments provided above, we propose that the SRM particles are microtektites affiliated to the Australasian strewn field. All recovered microtektites classify as 'normal-type' since the measured MgO concentrations are lower than 6 wt.% (Glass et al., 2004; Fig. 4 and Appendix A, Supplementary Data). Although the absence of the 'high-Mg' and 'intermediate-type' microtektites in the SRM collection may reflect a sampling or extraction bias, their abundance in other Australasian microtektite collections (5% to 10% by number; Glass et al., 2004; Folco et al., 2009) that were processed following comparable protocols, suggests that at least one such particle should be expected among the 33 SRM particles reported here. Their absence

Table 1

Rb-Sr and Sm-Nd elemental and isotopic compositions of the SRM-Victoria Land microtektites and Australasian tektites.

	$Rb~(\mu g/g)$	$Sr~(\mu g/g)$	$({}^{87}\mathrm{Sr}/{}^{86}\mathrm{Sr})_m\pm2\sigma$	$\epsilon^{87} Sr_{UR}$	Nd ($\mu g/g$)	$Sm~(\mu g/g)$	$(^{143}\text{Nd}/^{144}\text{Nd})_m\pm2\sigma$	$\epsilon^{143} Nd_{CHUR}$	$T_{\rm DM}^{\rm Nd}({\rm Ga})$	T ^{№d} (Ga)
SRM ($n = 33$)	32 ± 8	206 ± 19	0.716664 ± 12	173	43 ± 5	8.59 ± 1	0.512073 ± 10	-11.0	1.55	1.66
TAM – Sample A ($n = 11$)	38 ± 14	207 ± 35	0.716215 ± 10	166	42 ± 5	8.33 ± 1	0.512086 ± 29	-10.8	1.51	1.64
TAM – Sample B ($n = 11$)			0.716372 ± 10	168						
AAT – Muong Nong ($n = 12$)	116 ± 10	133 ± 12	0.717361-0.720206	183-223	33 ± 4	6.37 ± 1	0.512031-0.512062	-11.2	1.49-1.57	1.67-1.71
								-11.8		
AAT – Splash form $(n = 10)$	110 ± 9	132 ± 7	0.716361-0.718569	173-200	33 ± 2	6.31 ± 1	0.512035-0.512049	-11.5	1.51-1.56	1.69-1.70
								-11.8		

Note: Elemental concentrations and isotopic ratios are reported in ± 1 SD and $\pm 2\sigma$, respectively. The 87 Sr/ 86 Sr and 143 Nd/ 144 Nd ratios of the SRM particles were measured on a batch of 26 particles (excluding WF-MT01–01 – WF-MT01–07). Average elemental concentrations (Rb, Sr, Nd, Sm) were calculated from all 33 SRM particles. Values reported for Muong Nong-type tektites include light-dark layers and bulk samples. The 87 Sr_{UR} values were calculated using the contemporary 87 Sr/ 86 Sr ratio (0.7045) of the Uniform Reservoir (Faure, 1986). The 81 AVd_{CHUR} values were calculated using the contemporary 143 Nd/ 144 Nd ratio (0.512638) of the Chondritic Uniform Reservoir (Wasserburg et al., 1981). ¹Single-stage Nd model age calculated using the 147 Sm/ 144 Nd (0.222) and 143 Nd/ 144 Nd (0.513114) reference values for the DM reservoir, and the 147 Sm/ 144 Nd (0.219) and 143 Nd/ 144 Nd (0.513151) reference values for the DM reservoir, and the 147 Sm/ 144 Nd (0.219) and the continental crust (Liew and Hofmann, 1988). Reference values for Tansantarctic Mountain (TAM) and Australasian tektites (AAT) reproduced from Folco et al. (2009) and Ackerman et al. (2020), respectively.

among the SRM microtektites may thus reflect initial compositional heterogeneity in the impact vapor plume or, alternatively, biases during transport from the impact site. Furthermore, we suggest that transportation of the SRM microtektites occurred along the central distribution lobe of the Australasian strewn field, which is supported by the extent of volatile element depletion and their size-frequency distribution (Figs. 8 and 9). This would extend the central distribution lobe toward the west and encompass the vast majority of the eastern Antarctic continent as well as the southeastern part of the Indian Ocean. These observations are also in agreement with previous studies, which position the hypothetical source crater on the Indochina peninsula (Barnes, 1964; Glass and Pizzuto, 1994; Ma et al., 2004; Prasad et al., 2007; Folco et al., 2010a, 2010b; Sieh et al., 2020).

4.2. Implications of the Sør Rondane Mountain microtektites

4.2.1. Revised distribution pattern of Australasian (micro)tektites and identification of potential recovery sites

The occurrence of microtektites in sediment traps from the SRM range is unique for the eastern Antarctic continent and substantially increases the total surface area of the Australasian strewn field up to 15% of the Earth's surface, verifying its status as one of the largest and most recent impact events on Earth. We have demonstrated that the Australasian strewn field extends west of the established field (Folco et al., 2008, 2009, 2016; van Ginneken et al., 2018) based on the physicochemical characteristics of the SRM microtektites, which presumably link these particles to the central distribution lobe of the Australasian strewn field. This may imply that additional sites in the southeastern Indian Ocean and on the eastern Antarctic continent can now be identified where the recovery of Australasian microtektites is plausible (Fig. 9B). This could potentially be tested by examining future ODP cores obtained from the southeastern Indian Ocean, or ice cores from the EPICA Dome C (or similar) ice record since their age has been demonstrated to be older (ca. 800 ka) than the Australasian impact event (e.g., Jouzel et al., 2007). Furthermore, due to the average smaller size and refractory nature of microtektites recovered from the Larkman Nunatak moraine, there is a possibility that similar types of these refractory microtektites can be recovered south of the SRM range. New sampling campaigns in surrounding (e.g., Mhlig-Hofmann) or western Antarctic (e.g., Ellsworth Mountains) mountain ranges may clarify whether this is the case. As such, the Australasian strewn field may encompass the whole Antarctic continent and Australasian microtektites could thus be used as a time-stratigraphic tracer in Antarctic ice cores. Furthermore, Australasian impact ejecta can provide a minimal age constraint of microtektite-bearing sedimentary traps (see e.g., Folco et al., 2008; Rochette et al., 2008; Genge et al., 2018). This may be useful to reconstruct the local/regional evolution of ice sheets on the Antarctic continent, as demonstrated by a case study in the Alan Hills by Folco et al. (2016). The revised distribution pattern of Australasian (micro)tektites suggested in Fig. 9B maintains the established tri-lobe pattern, but is ultimately limited by the amount of ODP cores available (Glass and Simonson, 2013). As future ODP campaigns acquire new sediment cores from the southern Indian Ocean, the true extent of the Australasian strewn field can be constrained.

4.2.2. Abundance and preservation potential of Australasian microtektites in the Sør Rondane Mountains

Microtektite abundance in sedimentary traps from the SRM is surprisingly low. Here, we will use the Mt. Widerøe #01 sediment trap as example since the vast majority (ca. 82%) of microtektites were collected from this deposit. We estimate that <10 microtektites were recovered per kg of bulk detritus. In comparison, van Ginneken et al. (2018) estimate that the moraine deposits near Larkman Nunatak produced microtektite abundances on the order of ca. 200 per kg of sediment, while Folco et al. (2009) report even higher numbers of up to 400 per kg of sediment, which vary considerably between the different types of deposits. Even at some sites within the TAM, less than 1–2 microtektites were extracted per kg of sediment. Previous work has argued that the concentration of microtektites is mainly controlled by the erosion rate of the surrounding host rock and local environmental parameters, which may possibly affect sedimentary traps (Folco et al., 2009). The SRM sediment traps were sampled at altitudes ranging between ~2500 and 2800 m above sea level, which have not been affected by thaw throughout the year. Hence, we suggest that microtektites in the SRM deposits were predominantly diluted by variable erosion rates of the surrounding host rocks, rather than being subjected to weathering processes, or receiving lower numbers of Australasian microtektites. The deposits from the Mt. Widerøe #01 sediment trap are relatively coarse-grained and composed of gneissose biotitehornblende metatonalite, which appear to be resilient to weathering in the cold and relatively dry Antarctic weather conditions (Goderis et al., 2020). In contrast, sediment traps from the Mt. Walnum #01 sampling site are more fine-grained and substantially weathered, and therefore only produce <1 microtektite per kg of bulk detritus. To maximize microtektite yields, sedimentary deposits should preferably be coarsegrained and resistant to alteration processes. This should prevent the dilution of microtektites through weathering of surrounding host rocks.

4.2.3. Target stratigraphy of the Sør Rondane and Transantarctic Mountain microtektites

Isotopic tracers, including the ⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd ratios, are commonly used within impact cratering studies since (micro)tektites retain the isotopic signature of their target material. Consequently, these isotopic tracers are able to discriminate the respective (micro)tektite strewn fields (Fig. 7), but also allow to characterize their target material (Compston and Chapman, 1969; Shaw and Wasserburg, 1982;



Fig. 8. Stereomicrograph (A) and BSE-SEM (B–D) images of the SRM microtektites. All particles display a typical pale yellow color and spherical shape, except for a single dumbbell-shaped particle (second particle in A, not shown in B). Particles are pristine and show only minor surficial fractures as observed from (B). Size-frequency distribution (E) of the SRM particles (this study), the Victoria Land microtektites (Folco et al., 2009), and Larkman Nunatak microtektites (van Ginneken et al., 2018). The frequency of the SRM particles and Larkman Nunatak microtektites is displayed on the left side of the y axis. The frequency of Victoria Land microtektites (curve) is displayed on the right side of the y axis. Despite the limited number of samples collected, the average size of the SRM particles (n = 33, size range of 220–570 µm) appears to be positioned in between those of Larkman Nunatak (n = 52, size range of 107–388 µm) and Victoria Land (n = 456, size range of 75–778 µm) (Folco et al., 2009; van Ginneken et al., 2018). Note that the size-frequency distribution of the SRM particles is biased for particles less than 200 µm, and less than 400 µm for Victoria Land microtektites due to limited sampling of these respective size fractions. Data reproduced from Folco et al. (2009) and van Ginneken et al. (2018).

Blum et al., 1992; Deutsch and Koeberl, 2006; Folco et al., 2009; Ackerman et al., 2020). The Nd isotope data observed in the SRM microtektites are intermediate between reference values of Australasian tektites and the Victoria Land microtektites (Fig. 7 and Table 1). This similarity, in conjunction with comparable ¹⁴⁷Sm/¹⁴³Nd values, has

been interpreted to reflect a fairly homogeneous target material for Australasian tektites with respect to the REE (Ackerman et al., 2020). The opposite pattern is observed for Sr isotopic ratios, which display a much larger range compared to the Nd isotope ratios. The distribution of Sr was likely controlled by variable proportions of both plagioclase



Fig. 9. (A) Distribution of volatile compounds (i.e., K₂O and Na₂O) in (micro)tektites across the Australasian strewn field (see Appendix A, Supplementary Data). On average, volatile element contents systematically decrease as distance from the hypothetical source crater increases. This is predominantly explained by high-temperature volatilization of target rock material during the impact event (Folco et al., 2010a), and was previously suggested for other volatile compounds (e.g., H₂O) by Artemieva et al. (2002). The source crater is assumed to be located on the Indochina peninsula following the observations of Barnes (1964), Glass and Pizzuto (1994), Ma et al. (2004), Prasad et al. (2007), Folco et al. (2010b), Sieh et al. (2020). The range of measured volatile element contents of the SRM particles fall in between those from the Victoria Land and Larkman Nunatak microtektites. This is consistent with large-scale translation along the central distribution lobe of the Australasian strewn field. Figure modified from Folco et al. (2010a) and van Ginneken et al. (2004), Glass and Koeberl (2006), Folco et al. (2010a), and van Ginneken et al. (2018). We argue that an extension of the central distribution lobe is more likely compared to the western distribution lobe as great circle distances along the latter trajectory path would exceed 13,000 km. This has also been suggested by Folco (2020) based on preliminary data reported in Soens et al. (2019). This would imply (on average) a more narrow size distribution and microtektite sizes, as well as extensive volatile compound depletion compared to the Larkman Nunatak microtektites. A global distribution so pervisos ODP campaigns.

and K-feldspar (Ackerman et al., 2020). However, carbonates (calcite, dolomite) have also been detected in rock fragments from microtektite layers (Glass and Fries, 2008) and are also suggested based on high CaO contents (up to 10 wt.%) in a number of Australasian tektites from northern Australia (Compston and Chapman, 1969). Indeed, australites display the lowest ⁸⁷Sr/⁸⁶Sr values due to less radiogenic ingrowth from lower Rb/Sr values in the target lithologies.

Following discrete trends on a plot of 87 Sr/ 86 Sr versus K₂O/CaO, Ackerman et al. (2020) argued that splash-form tektites with slightly higher CaO contents reflect larger contributions of carbonate or plagioclase relative to Muong Nong-type tektites, and were derived from melting of the upper layers of a stratified sedimentary target at the Australasian impact site. Conversely, the Muong Nong-type tektites were thought to originate from melting of deeper, more heterogeneous parts of the target. Vertically stratified sediments deposited by a highflux fluvial system capable of transporting and delivering silt-sized, rather well-homogenized sedimentary material, have previously been suggested and are both consistent with an impact site in the Gulf of Tonkin (e.g., Ma et al., 2004; Rochette et al., 2018; Whymark, 2018; Ackerman et al., 2019) or beneath the Bolaven volcanic field in Southern Laos (Sieh et al., 2020). Both Antarctic data points fall within the cluster of splash-form australites and may suggest larger surficial target rock contributions (Fig. 7). This is consistent with ¹⁰Be data for Victoria Land microtektites, which suggest that TAM microtektites were mainly sampled from the surface of the target material (i.e., soil, sediment) (Rochette et al., 2018, 2019). Based on the ⁸⁷Sr/⁸⁶Sr versus K₂O/CaO plot (Fig. 7C), this target material appears to be relatively plagioclaseand carbonate-rich. However, the K₂O/CaO ratio of the SRM and TAM microtektites is noticeably lower compared to splash-form tektites from Indonesia and the Philippines. This can presumably be attributed to volatilization where K (50% condensation temperature – $T_c \approx 1006$ K; Lodders, 2003) is predominantly vaporized over Ca (50% $T_c \approx 1517$ K). A plagioclase- and carbonate-rich target material is also consistent with the relatively CaO- and Sr-rich nature of the SRM and Victoria Land microtektites (Figs. 4, 6 and 7; Appendix A, Supplementary Data). Additionally, the moderately high condensation temperature of Sr (50% $T_c \approx 1464$ K; Lodders, 2003) suggests that potential effects of volatilization and mass-dependent fractionation should be minimal, thus reflecting the original target material composition. The correspondence in Sr and Nd isotope data for two geographical distinct Antarctic sites therefore implies that the sedimentary target material was likely more effectively mixed during the generation of the Australasian microtektites.

5. Conclusions

Thirty-three microtektites were recovered from sedimentary traps in the SRM range (Queen Maud Land, East Antarctica). These particles are characterized by a typical pale yellow, transparent color and predominant spherical shapes (>97%). Microtektites range in size between ca. 224 and 558 µm with an average size of ca. 370 µm.Major and trace element chemistry largely overlaps with compositional data for 'normal-type' Australasian microtektites from Victoria Land, and strongly resembles average compositions of upper continental crust, except for a number of volatile elements. The physicochemical properties of the SRM microtektites, including the degree of volatile element depletion and its size-frequency distribution, are consistent with volatilization and particle size trends previously observed in the Victoria Land and Larkman Nunatak microtektites (Folco et al., 2009, 2010a, 2016; van Ginneken et al., 2018). The SRM microtektites thus appear to be affiliated to the Australasian strewn field, which is further supported by matching Nd and Sr isotope ratios falling on a mixing line typical for Australasian tektites. The central distribution lobe of the Australasian strewn field should therefore encompass a significantly larger geographical area including parts of the southeastern Indian Ocean and East Antarctica. The Australasian strewn field may extend across the entire Antarctic continent although this requires verification through dedicated sampling campaigns. If so, the presence of Australasian microtektites in sediments or ice layers can be used for timestratigraphic correlation, as they display a unique geochemical composition and record of an instantaneous geological event across Antarctica. The SRM and Victoria Land microtektites display a remarkable similarity with Australasian tektites in terms of their Nd isotopic ratios, suggesting that the target material was homogenous in terms of the REE contents and was incorporated into a crustal unit of Paleo- or Mesoproterozoic age. Strontium isotopic ratios are more variable and suggest a contribution of plagioclase- or carbonate-rich target material. The abundance of microtektites in sedimentary traps from the SRM range appears to be controlled by the surrounding host rock lithology and its resistance to weathering. A higher contribution of microtektites is observed in coarse-grained lithologies, whereas fine-grained lithologies principally dilute microtektite abundances.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.gsf.2021.101153.

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Convoluted Fe isotope fractionation during Australasian microtektite formation

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Tektites and microtektites are ejected along ballistic trajectories following oblique hypervelocity impact events at the Earth's surface (e.g., Koeberl, 1994; Artemieva et al., 2002). During their flight, (micro)tektites are quenched from hot, molten rock that was subjected to evaporation based on the analysis of volatile compounds (e.g., Na₂O and K₂O) and water contents (e.g., Beran and Koeberl, 1997; Folco et al., 2010). Recent studies have demonstrated that the abundance of volatile compounds in Australasian (micro)tektites progressively decreases as distance from the hypothetical source crater increases (e.g., Folco et al., 2010; van Ginneken et al., 2018). Yet, the nature of chemical and isotopic fractionation processes is currently not well constrained despite their significant role within (micro)tektites, and by the extension the Solar System. In this study, we analyze the iron isotope compositions of a representative number (n = 62) of Australasian tektites and microtektites, collected from various locations at various distances of the hypothetical source crater, due to its potential as a key tracer for high-temperature atmospheric and Solar System processes. This information provides additional insight into the physicochemical processes occurring during the atmospheric flight of Australasian (micro)tektites, and can to some degree be compared to the atmospheric entry stage of micrometeoroids.

BS has assisted Stepan Chernonozhkin with the sample acquisition of the Sør Rondane Mountains microtektites; and the acquisition and processing of the major and trace elemental dataset (LA-ICP-MS).

The supplementary materials related to this manuscript are available below.

Title

- Long title: Convoluted Fe isotope fractionation during Australasian microtektite formation
- Short title: Fe isotopic composition of microtektites

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Teaser: Australasian microtektites reveal among the strongest Fe isotope fractionations observed on Earth, a result of a convoluted sequence of evaporation and condensation events

Abstract

Isotope fractionation of volatile elements takes place in rocks and tektites formed or modified during hypervelocity impact events. Evaporative isotope fractionation is observed in tektites for Cu, Zn, Cd, and Sn. Here, we expand these observations to more refractory Fe, by studying 12 Australasian tektites and 43 microtektites. While the macroscopic tektites exhibit no $\delta^{56/54}$ Fe variations, microtektites differ over nearly 5‰, both in negative and positive direction. This range extends the signatures of typical terrestrial rocks by a factor of four, and can only be explained by melt expulsion, evaporation, and condensation of isotopically light components in the impact plume and mixing between these reservoirs, followed by variable ablative evaporation during atmospheric re-entry. The isotope fractionation pathways demonstrated here apply to all solid planetary surfaces in the Solar

System and call for a revision of our understanding of the effects of impact processing on the isotopic evolution of planetary crusts.

Introduction

Tektites are distal impact glasses formed by melting of terrestrial rocks upon hypervelocity meteoroid impacts (1). Such impacts are characterized by extreme heat and pressure, generating ejected silicate melt with broadly upper crustal compositions. Microtektites are the sub-millimeter analogues of tektites, generally thought to have solidified from smaller droplets of melt. Both tektites and microtektites are ejected from the source crater, travel ballistically, are quenched in the upper atmosphere, and are subsequently deposited hundreds to thousands of kilometers from the source crater, in so-called strewn fields. A key feature of tektites is their depletion in water as well as volatile and moderately volatile elements (2). Of the four usually recognized strewn fields, the Australasian tektite/microtektite strewn field is the largest and most recent example. The geochemical compositions and absence of primary minerals in Australasian tektites and microtektites, together with the presence of lechatelierite and shocked mineral grains in some Muong Nong-type tektites and microtektites (3) link Australasian tektites and microtektites to a hypervelocity impact event. The occurrence of high-pressure mineral phases in Muong Nong type tektites (4), and the recovery of shock metamorphosed rock and mineral unmelted fragments in microtektite layers found in the South China Sea (5) further support the impact origin of Australasian tektites and microtektites. Australasian microtektites have been collected from deep-sea sediment cores from the Ocean Drilling Program (ODP) and Deep Sea Drilling Project (DSDP), as well as from piston cores by a variety of oceanographic institutes in over sixty locations in the Indian and western Pacific Oceans and adjacent seas (5, 6), as well as from several sediment accumulation traps in Antarctica (7-10).

Iron is a major rock-forming element in most planetary reservoirs with variable geochemical behavior following an assortment of contexts. Fe isotope ratios have been used as a key tracer of high-temperature Solar System processes, but also as a useful tool to study the geochemical cycle of Fe in low-temperature environments. The isotopic composition of Fe in most terrestrial igneous and sedimentary rocks spans a narrow range close to the bulk Fe signatures of CI-type carbonaceous chondrites ($\delta^{56/54}$ Fe = $-0.008 \pm 0.095\%_0$, n = 47 (11)). With a 50% condensation temperature of 1334 K (12) under typical nebular conditions, Fe is relatively refractory and thus energetic events are required for evaporation to play a significant role in the Fe isotope budgets of planetary bodies. As such, the role of evaporation on the Fe isotope budget during different stages of the Solar System evolution remains the topic of considerable debate (13). The process of thermal evaporation of a target rock is typically associated with a loss of volatile components, shifting the residual melt towards heavier isotopic compositions. Because lighter isotopes of the volatilized element have incrementally higher evaporation rates than their heavier counterparts, any vapor phase is enriched in the lighter isotopes, while the residual fraction is progressively enriched in the heavier isotopes.

Isotope fractionation due to partial distillation at high temperatures (>1870-2270 K) during impact processes has a direct bearing on our understanding of key processes in the planetary sciences, such as asteroid or planetary collisions, for example during accretion or the Moon-forming impact. Tektite glass represents a natural laboratory, which might be used to study the behavior of Fe isotopes following impact-related fractionation. The isotopes of several moderately volatile elements have previously been shown to fractionate in tektites as the result of extreme conditions during hypervelocity impacts. Of these elements, Cu, Zn and Sn systematically display heavy isotopic signatures (~ 10 % variation for $\delta^{65/63}$ Cu, ~ 3 % variation for $\delta^{66/54}$ Zn and ~ 2.5 % variation for $\delta^{122/118}$ Sn), correlated with the extent of element depletion as a result of evaporative loss (14–18). The Cd isotopic composition of a single Muong-Nong layered tektite from Laos (19) displayed an isotopic composition 0.76 ‰ per a.m.u. heavier than the average terrestrial composition. At the same time, volatile Li and K exhibit no isotope fractionation due to evaporation in macroscopic tektites, and their recorded isotopic variation has been interpreted to reflect mixing of the reservoirs of an inhomogeneous target (16, 20–22). Due to their sub-millimeter size, microtektites have different surface-to-volume ratios and heating histories as a function of time, as compared to macroscopic tektites. While several elements have been tested for potential evaporative isotope fractionation in macroscopic tektites, only a single study so far has focused on microtektites, reporting K isotope ratio data for twenty-eight Australasian microtektites (23). The observation of extreme K isotope fractionation implies that microtektites may be a more sensitive proxy of evaporation in hypervelocity impact processes than their macroscopic analogues, for which previous studies showed no significant variations in K isotope ratios (16).

The main aim of this work is to evaluate the Fe isotopic composition of microtektites from different locations within the Australasian strewn field to assess the effects of evaporative isotope fractionation processes during hypervelocity impact events and ejecta distribution. The goal is to evaluate the effect of collisional processing on the Fe isotopic evolution of planetary bodies in the early Solar System. Microscopic ejecta particles may thus play a critical role in our understanding of the isotopic evolution of primary planetary crusts.

Results

We studied a collection of forty-eight microtektites from fourteen locations in the Indian and Pacific Oceans and Antarctica, and thirteen macroscopic tektites from Thailand, Vietnam, Philippines, Indonesia, Australia, distributed across the Australasian strewn field (Fig. 1). All microtektites analyzed in this work are glassy spherules with a diameter in the range of 60 and 600 μ m. Petrographic observations suggest that all particles studied are relatively unaltered, with no cracks or any signs of alteration. The concentrations of all major and trace elements are within the range previously reported for Australasian macroscopic tektites and microtektites (Fig. 2). Iron isotope ratios, expressed as $\delta^{56/54}$ Fe, range from +2.19 to -2.85 ‰, with an average uncertainty of 0.1 ‰

(1SD). A frequency distribution of the Fe isotope variation is presented in figure 1. Iron isotopic signatures show a correlation with the average distance from the presumed impact crater to the site location, with the most distal Antarctic microtektites containing isotopically heavier Fe (Fig. 3). Note that a crater location at 22° N and 104° E, as suggested by ref. (5), was used here to calculate great circle distances, although other suggested locations (including the recently proposed Bolaven volcanic field, (24)) would provide nearly equal distances. Contrary to expectation, smaller microtektites tend to display isotopically lighter Fe isotopic signatures (Fig. 3). Microtektites 137-4 from RC9-143 and 17 from ODP 769A exhibit FeO contents of 9.01 and 8.29 wt%, respectively, nearly twice as high as the average value for normal-type Australasian microtektites (8, 25). This may reflect a distinct endmember composition within the target lithologies or an immiscible Fe rich melt known to occur within specific tektites (7, 26). These particles are not discussed together with the other microtektites, as they likely represent distinct endmember compositions in the precursor material. For the numerical data, the reader is referred to the electronic supplementary materials.

Discussion

Fe isotope fractionation due to evaporation

Evaporative isotope fractionation has long been suggested as the dominant process that governs the isotopic signatures of moderately volatile elements (Zn, Cu, Cd, Sb) in macroscopic tektites, without additional details on the exact mechanism (14, 17). For macroscopic tektites, previous studies as well as the results of this work ($\delta^{56/54}$ Fe = -0.30 to +0.14 ‰) show no significant variation in Fe isotopic composition, suggesting that evaporation did not play a significant role in the evolution of their Fe isotopic signatures. The $\delta^{56/54}$ Fe values and FeO concentrations in microtektites, found in Ocean Drilling Program sediment cores drilled in the South China and the Sulu Seas, cluster near average continental crustal values, indicating only marginally significant Fe isotope ratio variability ($\delta^{56/54}$ Fe = -0.46 to +0.29 %). The measured data for the microtektites from these sites are also not consistent with the trends expected for evaporative fractionation. Relative to the other microtektites analyzed in this work, the microtektites from the South China and the Sulu Seas were deposited at the shortest distance from the hypothetical impact crater location (1300-2350 km, ref. (5)). Their trace element signatures indicate minimal, if any, evaporation following their residence in the impact plume and ballistic transfer (Fig. 2). Further away from the putative crater are the Antarctic microtektites from Widerøefjellet in the Sør Rondane Mountains (SRM), which traveled up to 12000 km from the crater site. These microtektites display the highest $\delta^{56/54}$ Fe values between +0.77 and +2.19 ‰, correlated with lower FeO contents (Fig. 4). The Fe isotope ratio data of the SRM microtektites linearize in 1000 ln((⁵⁶Fe/⁵⁴Fe)/(⁵⁶Fe/⁵⁴Fe)₀) versus -ln(FeO/FeO₀) coordinates, with an intercept described by a $\delta^{56/54}$ Fe starting composition of ~0 and FeO of 6.9 wt% (average crust). This is consistent with a system that follows a Rayleigh relationship with f = 0.71 - 0.58 and a fractionation factor α between 0.995 and 0.997. However, the Fe isotopic signatures of Australasian microtektites do not simply depend on the distance from the crater (Fig. 3). For example, the Australasian microtektites from RC9-143, one of the most remote locations from the putative crater evaluated in this work, do not demonstrate heavy Fe isotopic signatures, which might be assigned to evaporation. The isotopic variability at a particular site (and distance) from the crater may be caused by the analysis of an unrepresentative number of particles, preventing the derivation of evaporation trends. On the other hand, the restriction of heavy Fe isotope ranges to the more distally deposited Australasian microtektites provides clear evidence that evaporative Fe isotope fractionation does take place during hypervelocity impact events, while the magnitude of fractionation is among the largest observed for Fe in silicate materials from natural environments. The microscopic size thus plays a critical role in the isotope fractionation mechanism of microtektites, as compared to their macroscopic analogues, microtektites experienced different temperature profiles over time.

The distinct Fe isotopic signatures of microtektites between more proximal (light) and distal (heavy) collection sites, with Antarctic microtektites having experienced the largest degree of evaporation, hints towards Fe isotope fractionation in the hotter and cooler areas of the impact plume. It has previously been shown that impact glass particles that form during the earliest stages of the impact cratering process, in the hottest and fastest part of the impact plume closer to the growing transient cavity, undergo progressively more evaporation and homogenization, are smaller, and contain less vesicles and mineral inclusions (3). Particles originating from hotter zones in the impact plume have experienced more evaporation and have at the same time been accelerated to higher velocities, leading to their deposition farther from the impact crater. This evaporation mechanism, previously demonstrated for a collection of Australasian microtektites and confirmed for microtektites from the Larkman Nunatak (10), in which the abundances of the volatile alkali elements decrease progressively with the flight distance (27), appears to be similarly applicable to the Fe isotope fractionation observed in this work.

While the extreme conditions of hypervelocity impact events are likely the primary factor controlling the evaporation and isotope fractionation in microtektites, we have also evaluated the potential for evaporation during their ablative flight and interaction with the atmosphere. Microtektites have cooled quickly after the pressure release and the plume expansion, so by the time they reach space, the evaporation ceases. Gas drag cannot contribute to heating over most of their ballistic trajectories, as they escape the atmosphere. However, our model based on standard equations for a meteoroid entry with drag and ablation (see Materials and Methods) indicates that the most remote Australasian microtektites, which reach Antarctica, must have experienced velocities and trajectory angles that could lead to partial vaporization and mass loss during atmospheric re-entry. As shown in figure 5, the temperature and mass loss due to vaporization depend on the particle velocity and size. Particles with a diameter of 150-300 µm that reach Antarctica may lose 40 to 80% of their initial size during atmospheric re-entry (Fig. 5, blue curves), while particles smaller than 150 µm experience nearly no

evaporation. At the same time, proximal Australasian microtektites have lower velocities when they re-enter the atmosphere, are decelerated more quickly due to their small masses, and are therefore not reheated to evaporation temperatures. As such, they are not vaporized by friction in the atmosphere and preserve their initial volatile contents and Fe isotopic compositions, acquired during the impact event itself.

Whilst most Antarctic microtektites are fractionated towards heavier Fe isotopic signatures, a small number of microtektites from the Transantarctic Mountains (TAM) and Larkman Nunatak (LN) do not exhibit positively fractionated values. This may suggest that the SRM microtektites underwent slightly different processes during the impact event compared to the TAM and LN Antarctic microtektites. Alternatively, TAM and LN microtektites could contain a higher proportion of an isotopically light Fe component, relative to those from the SRM. However, the major and trace element geochemistry of these groups do not record such processes or otherwise these processed led to a similar range of concentrations. Similarly, the variation of nearly ~1 per mil in $\delta^{56/54}$ Fe observed for ODP microtektites must be related to a heterogeneously distributed isotopically light phase during the turbulent impact plume stage. Turbulence is an important property inherent to the structure of impact plumes, and thus perfect geochemical trends with distance are not to be expected in general.

Mechanism behind light Fe isotopic signatures in microtektites

Surprisingly light Fe isotopic signatures down to $\delta^{56/54}$ Fe = -2.85 ‰, observed for microtektite 137-8 from the V19-153 location in the Eastern Indian Ocean, cannot be explained based on a continuously evaporating melted reservoir. To account for the Fe isotopic compositions of all Australasian microtektites from a single evaporation trend, fractionation factors a from 0.986 to 0.998 and a non-natural initial composition with approximate values of $\delta^{56/54}$ Fe = -3 ‰ and FeO = 9 wt% are required. Such scenario leaves isotopically heavy and high-FeO areas of the diagram underrepresented. The light signatures found in some microtektites are also unlikely to represent initial isotopic heterogeneity in the target material (28), because most terrestrial (igneous) rocks are characterized by $\delta^{56/54}$ Fe values close to 0 (11). Although some sulfides (29) and carbonates (30, 31) may be characterized by light Fe isotopic values, a $\delta^{56/54}$ Fe of -2.85 % constitutes an exceptionally low value, which would require unrealistically large contributions of such mineral phases to the target based on mass balance considerations. Although the crater associated to the Australasian field is yet to be found, a sulfur- or carbonate-rich target has not been suggested based on the geochemistry and Fe isotopic signatures of macroscopic tektites. The light Fe isotopic composition in Australasian microtektites can also not result from equilibration with sea water ($\delta^{56/54}$ Fe = 0 to +1 ‰ (32)), because lower $\delta^{56/54}$ Fe values would be expected for Fe-poor particles in the case of a diffusive kinetic control. The major and trace element concentrations measured in this work and in literature (5, 9, 10, 27)reflect the heterogeneous composition of a stratified target and suggest that limited to no alteration affected the microtektites studied here. Antarctic microtektites are in general highly pristine and only in a few exceptional cases, pits filled with palagonite are observed at the surface of the spherules, which cannot affect the Fe isotope ratios measured *in situ* in the inner parts of the particles. Australasian microtektites also show no evidence of hydration rinds, as observed in obsidian, which would be the first alteration step. The concentrations of the LREE, Sr and Ba, elements which are mobilized easily, reveal linear trends that suggest only limited alteration during residence in pelagic or other surface environments (Fig. 2). The observed trends based on REE patterns, Eu anomalies and Zr/Hf ratios relate all Australasian microtektites and macroscopic tektites to a single non-homogeneous target with a complex stratigraphy, *i.e.* variable Rb/Sr ratios, figure 2.

On the other hand, melts with an extremely light isotopic composition are characteristic for condensation processes. Isotopically light melts may be formed in the impact plume as instant condensates from the gas phase, which progressively evolves towards isotopically light signatures when condensate is removed following a Rayleigh condensation process. Light isotopic signatures may also result from low degrees of thermal volatilization of the target followed by rapid nearly complete re-condensation of the vapor. For example, assuming ideal Rayleigh evaporation and condensation of FeO from a normal crustal target, the instantly evaporated gaseous phase can have a $\delta^{56/54}$ Fe as light as -14 ‰, while a 50 % re-condensed melt would display a $\delta^{56/54}$ Fe of -4.5 ‰. The extremely light Fe isotopic signatures of the microtektites down to $\delta^{56/54}$ Fe = -2.85 ‰ thus likely result from interaction of the ejected melt of the target with isotopically light re-condensed melts. The occurrence of Fe,Ni,Cr-Ti-rich spinel grains observed on the external surface of some Australasian microtektites found near Indochina has previously been interpreted to indicate a late accretion process taking place during flight through a plume enriched in vaporized components of the target and potentially the projectile (25). Interaction with isotopically light condensed melts has also been advocated for Australasian microtektites based on their K isotopic compositions (23). The K isotope ratio data for thirteen Australasian microtektites displayed variations of up to a percent (down to δ^{41} K = -10.6 ‰), also in positive and negative direction, in full agreement with the Fe isotope fractionation observed here. The observation that microtektites closer to the source location contain slightly less K relative to macroscopic textites (21, 27) may be consistent with the incorporation of a re-condensed component in those microtektites. Overall, these observations form strong evidence that condensation processes during the impact event played an important role in the formation of at least a fraction of the Australasian microtektites. Potentially, the condensation of a hot over-saturated gas phase starts during the expansion of the impact plume when the pressure and temperature are rapidly reduced. In the case of macroscopic tektites, condensation is likely insignificant as a result of their low surface-to-volume ratios.

Mechanisms of Fe isotope fractionation overprinting

The relation between the Fe isotopic signatures and FeO contents of the Australasian microtektites, including those from Antarctica, implies more convoluted processes driving their Fe isotope

fractionation, beyond single Rayleigh-style evaporation or mixing with an isotopically light component in the impact plume. Evaporation is not restricted to Antarctic microtektites only, as one microtektite from ODP 769A, another particle from ODP 1144A and a third one from V20-138 also display slightly positive $\delta^{56/54}$ Fe values. However, most microtektites from the Indian and Pacific Oceans demonstrate signatures approximating zero or display negative $\delta^{56/54}$ Fe values, suggesting more complex fractionation histories. The microtektites from the V20-138 and V19-153 locations in the Pacific and Indian Ocean, respectively, both show weakly negatively correlated $\delta^{56/54}$ Fe and FeO contents. The Fe isotopic compositions for each of these two geographic locations can loosely be explained by Rayleigh distillation expected for thermal evaporation. However, compared to the putative target composition, these trends suggest that the starting material was characterized by extremely light Fe isotopic signatures, as low as $\delta^{56/54}$ Fe = -2.61 to -2.85 ‰ at elevated FeO contents of 7.19 to 7.32 wt%. Such compositions are in agreement with the lightest isotopic signatures preserved among the microtektites. If only evaporation was responsible for these signatures, this implies fractionation factors (α) equal to 0.998 to 0.9935 and up to 80 % FeO loss due to evaporation. In addition, these microtektites indicate stronger scatter along the Rayleigh curve. Such signatures are thus best explained by a combination of i) isotope fractionation of the melt towards heavier values due to evaporation and ii) mixing with variable amounts of a re-condensed, isotopically light component.

However, the mixed Fe isotopic signatures cannot be explained by assuming that all microtektites form within the plume as fractional condensates that subsequently underwent partial evaporation during atmospheric re-entry in the case of sufficiently high velocities. Based on the presence of abundant vesicles and the occurrence of mineral inclusions displaying some indications of melting in particular specimens (3), the involvement of condensation in the formation of all microtektites is unlikely.

Although evaporation during ballistic transport and interaction with the atmosphere cannot be excluded in the case of the most distally deposited (Antarctic) microtektites, evaporation must also take place earlier on, in the impact plume. In this case, the evaporation and condensation regimes must coexist in the rapidly expanding impact plume. Within the first few seconds after the impact molten, shocked and partially vaporized materials from the upper target layers are ejected. The resulting impact plume is a turbulent mixture of vapor, melt and solid fragments with wide compositional and thermal ranges. The temperature of the ejected materials is mainly defined by the melt-vapor transition of quartz and does not exceed ~4000 K. As the plume expands, the temperature and pressure of the ejected materials start to drop quickly along the pressure release pattern on the phase diagram (Fig 6A). Depending on the initial shock level of the ejected materials, this material may enter the two-phase area as vapor or liquid. As a result, materials shocked above ~300 GPa start to condense, whereas materials shocked below 300 GPa commence to boil, resulting in dissimilar
isotopic compositions. In addition to distinct pressure release patterns, the ejected materials display dissimilar cooling rates in different parts of the plume (Fig. 6B). The part of the impact plume expanding downrange initially has the highest temperature and velocity (>10 km·s⁻¹) and cools down faster than the central part of the plume, which is characterized by lower velocities and a higher density. In this context, the cooling rates are known to be an important factor affecting the final isotopic composition of the condensed material (*33*).

As a final alternative scenario, the isotope fractionation mechanisms may be overprinted in the impact plume when the microtektites initially form as expulsed melt that is partially vaporized. These droplets may then serve as nucleation seeds on which an isotopically light component starts to recondense as the temperature and pressure drop, allowing for condensation (fig. 6A). Such mechanism of heterogeneous nucleation on the surface on pre-existing particle has previously been demonstrated to occur in volcanic eruption plumes (34). Similarly, a thin layer enriched in volatile elements has been observed on the surface of lunar volcanic glasses, suggesting heterogeneous condensation in volcanic plumes (35). As no isotopically light microscopic glass (36, 37) was found in the vicinity of the crater, homogeneous condensation may not have been a prevailing mechanism in the plume. Because the impact event produces relatively little material (see ref. (37) for details) with extremely high compression >300 GPa (Fig. 6) that allows for condensation, the isotopically light reservoir potentially existed only in the form of condensate at the surface of nucleation seeds, and was later mixed and diluted in these seeds. Large scatter around the Rayleigh evaporation trend for microtektites from the V20-138 and V19-153 locations might be explained by individual microtektites incorporating variable proportions of condensate diluted in the evaporated melt. The latter could take place when their ballistic paths pass through turbulent heterogeneous parts of the condensing impact plume. The Antarctic microtektites, with the heaviest Fe isotope signatures, appear to have experienced the least interaction with this isotopically light Fe component and/or underwent an additional episode of evaporation during atmospheric re-entry. Among the Antarctic microtektites, the lowest $\delta^{56/54}$ Fe values and the largest within-site variation are found for LN, the collection site most remote from the postulated crater location.

Non-ideal Rayleigh evaporation

It should be noted that all fractionation factors α fitted to the microtektite data sub-sets differ significantly from that predicted by ideal distillation to vacuum for both Fe (0.982) and FeO (0.986) species. This implies non-equal evaporation coefficients γ for the Fe isotopes in microtektites, in agreement with a diffusion-limited evaporation regime, as previously proposed for Cu and Zn in macroscopic tektites (*17*, *18*, *38*). Alternatively, a model of evaporation from a supercritical fluid during rapid cooling soon after the impact may be invoked, the so-called "bubble-stripping" evaporation mode suppressed at high pressures (*16*, *39*). In the past, local partial re-condensation in the thin layer above the surface of the microtektite during evaporation was often used to explain non-

ideal Rayleigh distillation (40). However, microtektites move fast relative to the surrounding gas and are expected to lose such vaporized shell very quickly. Additionally, the mean free path of an evaporated species in the vapor is likely to be large compared to the particle size, making it unlikely for these species to re-condense. Finally, the deviations of the actual fractionation factors found in this work to best fit the microtektite data from that predicted by ideal evaporation to vacuum may be explained in terms of the Hertz-Knudsen theory (*33*) by Fe partial pressures that are 64 to 93% of the saturation pressure during evaporation. As ideal Rayleigh fractionation factors ($\alpha = 0.995$ to 0.999) fitted for Fe isotope fractionation in microtektites may be used as a first order estimate to interpret volatilityrelated Fe isotope fractionation in natural systems.

Effect of evaporation on elements more volatile than Fe

Different to the relations between $\delta^{56/54}$ Fe and FeO, which can be explained by Rayleigh evaporation trends and mixing of heavy and light re-condensed melt components, the Australasian microtektites that have the lowest concentrations of volatile elements are characterized by both the lightest and the heaviest Fe isotopic compositions (Fig. 7). Here, the measured ratio of Na₂O+K₂O normalized to refractory TiO_2 is taken as a measure of volatile retention. While progressive evaporation results in a decreased content of volatiles and an enrichment of the heavier Fe isotopes in the melt, the condensed component with isotopically light Fe displays significantly depleted concentrations of Na and K. This is because at the temperatures typical for partial condensation of Fe, alkali elements largely remain in the gaseous phase. Both the most evaporated and re-condensed melts experienced the hottest conditions in the impact plume and are depleted in alkali elements. The microtektites with an Fe isotopic composition close to that of the target rock either did not undergo intense heating, or their initial isotope fractionation by evaporation was balanced out by mixing with condensate enriched in the lighter Fe isotopes. The latter results in microtektites that are characterized by Fe isotopic signatures near the starting value but with strong depletions in the alkali elements. In general, volatile elements are expected to have significantly higher magnitudes of isotope ratios compared to Fe (23) because they experience more evaporation in the impact plume. Isotopic signatures of volatile elements in microtektites have a high potential to unravel the volatilities of elements in realistic impact conditions, different from that of early Solar nebula.

Implications for Solar System processes

The observation of condensed, isotopically light melts is not unique to impact-related evaporation/condensation materials on Earth, and confirms that earlier observations of light isotopic signatures of Fe, Cu, Zn and Cd (41, 42) in orange glass beads contained in lunar samples may result from condensation following (micro)meteoroid impacts. This makes terrestrial microtektites analogue materials to gas-associated spheroidal precipitates (GASP), and their genetically related

counterpart, the so-called high-Al, Si-poor precipitates (HASP) that are glassy microscopic spheroids found in lunar regolith breccias. These glassy spheroids are thought to have formed from lunar crustal materials as condensates (GASP) and partial evaporates (HASP) within impact plumes on the Moon (36). Although no isotopic data have been reported, based on their geochemical compositions these lunar phases are likely to be characterized by strongly fractionated isotopic ratios for a range of (moderately) refractory and volatile elements. Impact materials with Fe isotopic signatures both lighter and heavier than the target are thus produced during impact cratering events on all planetary bodies. The observed condensed isotopically light materials present in impact ejecta stand in stark contrast to most current models, where the evaporated reservoir with a light isotopic signature is assumed to irreversibly have been lost. Such considerations affect our view onto mass-balance constraints of the evaporative loss of moderately volatile elements in planetary collisions in the Solar System, such as the Moon-forming impact (43), as these processes can affect the bulk compositions of disrupted bodies. The observation of a spatial disconnection between the isotopically heavy evaporated and light condensed components has significant implications for the formation of primary planetary crusts. Although the average Fe isotopic composition of the microtektites approximates that of the Bulk Silicate Earth, with a near-Gaussian frequency distribution (Fig. 1), the spatial displacement between the isotopically heavy and light ejecta (Fig. 3) implies that microtektite-like material might be lost to space disproportionally. If the isotopically heavy material sampling the most energetic zones of the impact plume and experiencing higher accelerations is preferentially lost to space, hypervelocity impacts on planetary surfaces may lead to lighter isotopic signatures of primary planetary crusts. This may affect our estimates of the isotopic compositions of their mantles and cores following the differentiation. The multi-stage, convolute process by which tiny distal ejecta particles evolve, therefore, may be a fundamental control on the isotopic composition of primary crusts of entire planets.

Materials and Methods

Materials

The SRM#1-7 Antarctic microtektites from Sør Rondane Mountains, Widerøefjellet, were collected by SG and characterized by BS (9). A collection of microtektites from ODP 769 (particles 17, 15) and ODP 1144A cores (particles 35-38), as well as the Antarctic microtektites from Transantarctic Mountains (particles 4.6, 20.3, 20.14, 23.01, 20.17, 7.04) were provided by LF (7, 8, 27). The Antarctic microtektites from Larkman Nunatak are from the collection of MG (10). The microtektites collected from the sea sediments V19-153 (137-7 to 137-12), V16-76 (137-5 and 137-6), RC9-143 (137-1, 137-2 and 137-4), V20-138 (197-1 to 197-6 and 463-3 to 463-6) and V28-238 (188-3), as well as the microtektites from the ODP 768B core (ODP#1, ODP#3, ODP#4), are part of the collection of BG (44). Several of these microtektites were characterized in terms of their petrology and geochemistry in previous studies (7–10, 27, 44). The macroscopic tektites are collected within the Australasian strewn field in Philippines (PMJ-20 - Paracale), Indonesia (JAV-32 - Sangiran, JAV1.1, JAV1.5, JAV-1.8, JAV0.9 - Kaliosso), Thailand (FT-598 - Ubon Ratchathani, FT-118 - Muang Loei, T18A,B - Khorat Plateau), Vietnam (Saigon BT-2) and Australia (MA-142) (26). The macroscopic Javanites JAV1.1, JAV1.5 JAV1.8, JAV0.9, Saigon BT-2 and a single Philippinite are from the VUB collection (26). The macroscopic Philippinite PMJ-20 and MA-142 Australite flanged button were purchased from a commercial vendor. The Muong Nong tektites FT-598 and FT-118, tumbled Indochinites TI8A and TI8B and the Javanite JAV-32 are from the collection of Darryl Futrell. The latitudes and longitudes for the collection sites are presented in the ESI.

Fe isotopic analysis

Fe isotope ratios of the Australasian macroscopic tektites and microtektites were measured at A&MS-UGent *in situ* by coupling a Teledyne CETAC Technologies Analyte G2 laser ablation system, based on a 193 nm ArF*excimer laser with a pulse duration <5 ns and equipped with a HelexII double-volume ablation cell, to a Thermo Scientific Neptune MC-ICP-MS unit, equipped with a large volume jet interface pump and high-efficiency jet interface. The instrumental mass discrimination was corrected for by a combination of internal standardization using a co-nebulized Ni standard solution and sample standard bracketing with USGS BHVO-2G or BCR-2G glass reference material as the external standard. MPI-DING glass reference materials ML3B-G, ATHO-G, GOR128-G and StHS6/80-G were used for daily validation of isotope ratio accuracy and precision. For further details on the method, the reader is referred to Gonzalez de Vega et al. (*45*).

Element concentration measurements

Concentrations of the major elements in microtektites were measured at A&MS-UGent by coupling the Analyte G2 laser ablation system to an Agilent Technologies 8800 tandem ICP-MS instrument. The mass spectrometer was operated in MS/MS mode and the collision/reaction cell was pressurized with H_2 to minimize spectral interferences otherwise hampering accurate measurements of elements in the low mass range. Quantification of the major elements was performed relying on external calibration against MPI-DING and USGS glass reference materials combined with normalization of element oxides to 100% (46). Trace element compositions were measured in a separate LA-ICP-MS run with the collision/reaction cell operated in vented mode (as spectral interferences are known to be less severe for the heavy part of the spectrum) and by focusing the laser beam to a larger spot with a diameter of 80 µm in order to achieve higher sensitivity. The trace elements were quantified relying on external calibration against MPI-DING and USGS glass reference materials. One of the major elements (Cr or Mn), quantified in a previous run, was used as internal standard. Such approach allows for an *in situ* analysis without preliminary knowledge of the concentration of an internal standard.

Calculation of isotope fractionation due to evaporation

In process of evaporation, the isotopic compositions of the remaining melt and instant gaseous phase are calculated using the Rayleigh fractionation equation: $\delta^{56/54}$ Fe_{melt}=($\delta^{56/54}$ Fe₀+1000) $f^{(\alpha-1)}$ -1000 and $\delta^{56/54}$ Fe_{vapor}=($\delta^{56/54}$ Fe₀+1000) $\alpha f^{(\alpha-1)}$ -1000, where the delta notation reflects the relative difference between the 56 Fe/ 54 Fe isotope ratios of the melt, vapor and the initial phase from that of an internationally accepted IRMM014 standard in per mil: $\delta^{56/54}$ Fe=((56 Fe/ 54 Fe)/(56 Fe/ 54 Fe)_{IRMM014}-1)·1000. *f* is the fraction of the 54 Fe evaporated and α is a fractionation factor that scales to the square root of the masses (40). The fractionation factor α between the residue and the gas in the case of evaporation to vacuum is defined by the Hertz-Knudsen equation $\alpha = (\gamma_{56}/\gamma_{54})(m_{56}/m_{54})^{0.5}$, where m represents the masses of the Fe isotopes and γ the corresponding evaporation coefficients. At first estimation, the ratio of the evaporation coefficients for different isotopes of the same element approximates unity.

Numeric model of the impact event

The impact event is modeled with 25 m resolution (50x50 m cell), the equation of state is based on pure quartz (47) and includes phase transitions. Radiative energy transfer and kinetics of vaporization/condensation are not included. Shock physics code SOVA (48) was used to model the early stage of impact cratering and ejection of potential tektites and microtektites. The code is coupled with the ANEOS (49) package for quartz target material (47) and a dunitic projectile. A projectile 2 km in diameter with an impact velocity of 22 km·s⁻¹ at 45° to the horizon and porous material at the upper 100m of the target (sand) were used to model the Australasian impact, which results in a diameter of the transient cavity of about 18-22 km. The initial stage modelled here can easily be scaled to any crater size. Moreover, ejection velocities and shock pressures do not depend on the projectile size. Tracer particles are used to track the ejection of tektites.

Numeric model of the re-entry of microtektites

A standard set of differential equations was used to model re-entry of high-velocity particles into the atmosphere (50, 51). The drag equation was modified for a molecular flow regime:

$$m\frac{dV}{dt} = -\rho_a S V^2 \ (1)$$

where m is particle mass, V – velocity, S – particle cross-section, and ρ_a is density of the atmosphere. The incoming energy $E_{in}=0.5\rho_aSV^3$ is balanced by radiation and vaporization. Assuming that particles are small enough to be isothermal with temperature T and emissivity ε , radiative energy is $E_{rad}=4S\sigma\varepsilon T^4$, where the Stephan-Bolzmann constant $\sigma=5.67\cdot10^{-8}$ W/m²/K⁴. Evaporation into a vacuum can be described by the Langmuir equation:

$$\frac{dm}{dt} = 4SCP_{\nu}\sqrt{\mu/T}$$
(2),

where C=4.377·10⁻³, μ is molecular weight, P_v is vapor pressure provided by the Antoine equation P_v=A-B/T. Finally, temperature was calculated from a non-linear equation:

$0.5\rho_a V^3 = 4(\sigma\epsilon T^4 + H_v CP_v \sqrt{\mu/T}) \ (3).$

If vaporization is neglected, the temperature definition is straightforward (52). However, such simplification leads to a substantial temperature overestimate. Although there is no obvious dependence for temperature on the particle size, the particle velocity dependence on altitude (and hence, the atmospheric density) is a function of the particle size. An emissivity of 0.95 is used in all simulations. Atmospheric density is defined by the ATMCIRA data. A list of constants used for numeric modeling is provided in table 1.

H2: Supplementary Materials

The Fe isotope ratio data together with a compilation of major and trace element concentrations measured in this work and in earlier studies (7–10, 27, 44) are provided in tabular form in the electronic supplementary material.

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Author contributions: SCh and SG designed the concept of the research. SCh wrote the initial manuscript, processed, analyzed and visualized the data, modelled the evaporation/condensation fractionation and performed Fe isotopic and multi-elemental analyses. CGdV performed Fe isotopic analysis and processed the raw isotope ratio data. NA performed numerical modeling and visualization of the impact event and the atmospheric entry, wrote part of the manuscript, took part

in conceptualization of the research. JB performed Fe isotopic analysis and analyzed the data concerning the weathering of glass. EBF performed multi-elemental LA-ICP-MS analysis together with SCh and took part in conceptualization of the research. LF, BG, MG, MVG and BS took part in sample selection, preparation, managed the microtektite collections and took part in conceptualization of the research. FV, PhC and SG ensured funding and reviewed the manuscript. FV supervised the measurements at A&MS-UGent. SG supervised the project, took part in sample selection, data processing, visualization, analysis, conceptualization and manuscript writing. All authors contributed to the discussion and interpretation of the results and proofread the manuscript.

Competing interests: authors declare no competing interests.

Data and materials availability: all numeric data is provided in tabular form in the electronic supplementary material.

Figures and Tables

Fig. 1. Locations of the Australasian tektites and microtektites studied in this work. The microtektites are collected from the sea sediments and sedimentary traps in Antarctica. *n* corresponds to the number of microtektites studied from each location. Top right – frequency distribution plot for $\delta^{56/54}$ Fe values of the microtektites. *22° N and 104° E is one of the proposed crater locations based on the abundance of unmelted ejecta and microtektites (5). **A location of the impact crater anywhere within the yellow oval explains the distribution of the microtektites and impact ejecta equally well (5). ***Australasian strewn field after Folco *et al.* extended to the Transantarctic Mountains (5, 53). The blue dashed line suggests an extention of the central lobe to the Widerøefjellet, SRM (9).



Fig. 2. Composition of the microtektites collected in different locations of the Australasian strewn field. REE concentrations are normalized to CI-chondrite values (*54*). LN – Larkman Nunatak, Antarctica; TAM – Transantarctic Mountains; SRM – Sør Rondane Mountains, Widerøefjellet; ODP – microtektites from ocean sediments collected during Ocean Drilling Programs 768B, 769A and 1144A, Ocean Sediments – microtektites collected from piston cores during oceanographic studies.





Fig. 3. Iron isotopic signatures of the Australasian microtektites *versus* their distance to the hypothetical crater location and the diameter. Macroscopic tektites are shown with grey circles.

Fig. 4. $\delta^{56/54}$ Fe versus FeO diagram. The shaded horizontal area indicates the Fe isotopic composition in macroscopic Australasian tektites. The average composition of the upper continental crust (FeO = 6.9 wt%, $\delta^{56/54}$ Fe = -0.263 ‰) suggested to be the starting composition for the Australasian strewn field. A range of Rayleigh evaporation trends predicted by different fractionation factors α are shown. The Rayleigh fractionation trend under ideal conditions of evaporation to vacuum predicted by Hertz–Knudsen equation is shown as a thick line. The downward shift of certain microtektites from the upper crust $\delta^{56/54}$ Fe – FeO composition is best explained by a mixing line between the pristine melt and condensed components.



Fig. 5. Heating and ablation of particles entering the atmosphere with different velocities and angles. Upper panes are for a 300 μ m radius particle, bottom panes for a 150 μ m radius particle. Black: velocity of 7.4 km·s⁻¹, re-entry angle of 15°; red: 7.4 km·s⁻¹, angle of 27°; blue: 8 km·s⁻¹, angle of 42°. All combinations of angle/velocity result in deposition at ~11000 km from the source crater.



Fig 6. Temperature and density of the materials within the Australasian impact plume. (A) black and blue lines show the phase boundaries of quartz as calculated by the ANEOS package. The black branch represents saturated liquid and the grey branch saturated vapour. Red lines show release adiabats after shock compression to 110, 205, and 400 GPa. Thin horizontal lines correspond to the atmospheric pressure at sea level (10^{-4} GPa) and at an altitude of 30 km (10^{-6} GPa). The ejected materials with shock pressures below ~300 GPa, start to boil when the pressure is released. When the shock compressions are above ~300 GPa, the ejected material condenses during pressure release. Fraction of vapour remaining after the release is 0.1, 0.28, and 0.45, respectively. (**B**, **C**, **D**) – Temperature cross-sections of the plume through the plane of symmetry XZ at time frames of 0.5 to 5 seconds following the impact at 45 degrees. (**E**, **F**, **G**) – density cross sections of the impact plume at the same timeframes. Target materials are shown in green, projectile in gray and the atmosphere in blue.



Fig. 7. Effect of evaporation and condensation on volatile elements in microtektites. The Australasian microtektites which experienced the hottest conditions in the impact plume display the lowest concentrations in the alkali elements and simultaneously the highest magnitudes of $\delta^{56/54}$ Fe, both in positive and negative direction. The Antarctic microtektites experienced additional evaporation during atmospheric re-entry.



 Table 1. Constants used for numeric modeling. These parameters are used for numeric modeling of the atmospheric re-entry of the microtektites.

	Microtektites (fused silica)	
Α	12.856	
В	24 824	
μ	60	
$H_v, kJ \cdot g^{-1}$	6.4	
Density, kg·m ⁻³	2300-2800	

A large meteoritic event over Antarctica ca. 430 ka ago inferred from chondritic spherules from the Sør Rondane Mountains

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The frequency and magnitude of meteoritic events on Earth is mainly determined by the size and composition of meteoritic fragments (e.g., Bland and Artemieva, 2006). Large asteroids (>200 m) are estimated to impact the Earth's surface every ca. 100 ka producing large impact craters (>1 km) and potentially hazardous tsunamis. In contrast, meteorites (ca. 2–1000 mm) and micrometeorites (ca. 10–2000 μ m) represent the vast majority of (hazardless) extraterrestrial material accumulating on Earth on a daily basis (e.g., Love and Brownlee, 1993; Zolensky et al., 2006). Intermediate-sized objects (ca. 10's up to 150 m), such as those related to the Tunguska and Chelyabinsk airburst events, occur on a time span of ca. 100 a to 100 ka. However, their contribution to the accretion of extraterrestrial material on Earth is not well constrained. In this study, we present major, trace elemental and oxygen isotope data of 17 spherulitic aggregate particles recovered from the Walnumfjellet sedimentary deposit, which are potentially linked to a meteoritic airburst event over Antarctica ca. 430 ka (Narcisi et al., 2007; Misawa et al., 2010; van Ginneken et al., 2010). This information is useful to understand the formation of meteoritic spherules related to airburst events and identify these events in the geological record to estimate their frequency, scale and hazard. Additionally, a minimum age constraint for sedimentary deposits can be acquired if the age of such events can be linked within a time-stratigraphic framework.

BS has assisted Matthias van Ginneken with processing a number of sedimentary deposits from the SRM to extract meteoritic condensation spherules.

The supplementary materials related to this manuscript are available on the following website: https://doi.org/10.1126/sciadv.abc1008.

PLANETARY SCIENCE

A large meteoritic event over Antarctica ca. 430 ka ago inferred from chondritic spherules from the Sør **Rondane Mountains**

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Large airbursts, the most frequent hazardous impact events, are estimated to occur orders of magnitude more frequently than crater-forming impacts. However, finding traces of these events is impeded by the difficulty of identifying them in the recent geological record. Here, we describe condensation spherules found on top of Walnumfjellet in the Sør Rondane Mountains, Antarctica. Affinities with similar spherules found in EPICA Dome C and Dome Fuji ice cores suggest that these particles were produced during a single-asteroid impact ca. 430 thousand years (ka) ago. The lack of a confirmed crater on the Antarctic ice sheet and geochemical and ¹⁸O-poor oxygen isotope signatures allow us to hypothesize that the impact particles result from a touchdown event, in which a projectile vapor jet interacts with the Antarctic ice sheet. Numerical models support a touchdown scenario. This study has implications for the identification and inventory of large cosmic events on Earth.

INTRODUCTION

Remnants of hypervelocity impact on Earth's surface are mainly preserved as impact craters, generally circular depressions resulting from asteroids large and/or dense enough to reach ground level without suffering substantial atmospheric disruption (1). Crater formation is accompanied by the production of a characteristic set of shockmetamorphic effects (e.g., shocked quartz or shatter cones) and formation of high-pressure mineral phases (e.g., coesite and stishovite) in target rocks, resolvable geochemical anomalies, and ejection of target/projectiles materials with high velocity (e.g., tektites and microtektites) (2). Identifying hypervelocity impacts in the geological record is relatively straightforward if one or several of these features are identified. However, impactors several tens up to 150 m in size are totally fragmented and vaporized during atmospheric entry, resulting in a low-altitude airburst, similarly to the Tunguska and Chelyabinsk events over Russia in 1908 and 2013, respectively (3-5). Observation by direct eye witness accounts and indirect infrasound, seismic, video cameras, and numerical modeling of medium-sized airbursts have shown that these impacts represent a notable fraction of the extraterrestrial material accreted to Earth, with Tunguska-like

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RESULTS

The igneous particles studied in this work (N = 17) are dark black, subrounded to perfectly spherical. About half the particles are compound spherules consisting of two or more coalesced spherules (Fig. 2 and fig. S1). Scanning electron microscopy observations of polished sections of the particles indicate quench textures similar to S-type cosmic spherules (10). The mineralogy of the particles mainly consists of olivine and iron spinel, with minor interstitial glass. We subdivided the particles into four groups on the basis of their textures and spinel content: (i) spinel-rich (SR) particles (N = 9) characterized by abundant octahedral, cruciform and/or dendritic spinel ($\geq 17\%$ volume), and skeletal and/or euhedral olivine (Fig. 2, A and C, and fig. S1, A to F); (ii) spinel-poor (SP) particles (N = 5) characterized by large (>10 µm) skeletal or euhedral crystals of olivine with minor

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events occurring once every 100 to 10,000 years, which is orders of magnitude more frequent than large crater-forming impacts (6). However, evidence of these events is scarce in the geological record, principally due to difficulty in identifying and characterizing potential residues (7). Finding evidence of these low-altitude meteoritic events thus remains critical to understanding the impact history of Earth and estimating hazardous effects of asteroid impacts. In recent years, meteoritic ablation debris resulting from airburst events have been found in three different locations of Antarctica. The material found at Miller Butte (Northern Victoria Land), Dome Concordia, and Dome Fuji all appears to have been produced during a Tunguska-like airburst event 480 thousand years (ka) ago (7-9). Here, we present the discovery of extraterrestrial particles formed during a significantly larger event recovered on the summit of Walnumfjellet (WN) within the Sør Rondane Mountains, Queen Maud Land, East Antarctica (Fig. 1). The characteristic features of the recovered particles attest to an unusual type of touchdown event, intermediate between an airburst and a crater-forming impact, during which the high-velocity vapor jet produced by the total disruption of an asteroid reached the Antarctic ice sheet.



Fig. 1. Location of the sampling site in WN, Sør Rondane Mountains, Queen Maud Land, Antarctica. (A) Landsat image of the sampling site on the summit of WN, where the particles studied here were recovered, along with the Princess Elisabeth Antarctica (PEA). Inset shows the locations of Dome Fuji (DF), Dome Concordia (DC), and BIT-58 for comparison (8, 9, 24). The ages of the various horizons can be found in Table 1. (B) The flat glacially eroded summit of WN on the border of the Antarctic plateau. ¹⁰Be exposure age of glacially eroded surfaces of WN range from 870 to 1740 ka (25). (C) The 30 × 30 × 10 cm sampling site on top of WN. Landsat 7 image courtesy of the Landsat Image Mosaic of Antarctica (LIMA) project. Photo credit: Matthias van Ginneken, University of Kent.

cubic spinel content (<10% volume) (Fig. 2, B and D, and fig. S1, G and J); (iii) barred olivine (BO) particles (N = 3) that contain minor spinel content (<10% volume; fig. S1, H and K); and (iv) one cryptocrystalline (CC) compound particle consisting of two fused spherules exhibiting identical CC textures and moderate spinel content (~15% volume; fig. S1, I and L). The size of the particles does not vary significantly from one group to the other: 131 µm for the CC particle, 203 ± 115 µm for SR particles, 289 ± 93 µm for SP particles, and 308 ± 117 µm for BO particles.

The major element bulk composition of the individual particles obtained by electron probe microanalysis are reported in table S1 and plotted in Fig. 3. Elemental patterns show consistent and broadly chondritic compositions, albeit with variable depletions in alkali and in Cr, and severe depletion in S in all particles. Refractory elements Al, Ti, and Ca are depleted in SP particles WN-IP#8 (Walnumfjellet impact particle #8) and WN-IP#9 (WN-IP, Walnumfjellet Impact Particle; Fig. 3 and table S1). Focused beam electron microprobe

analyses show that olivine in SR particles is mostly iron poor (i.e., Fa₁₀₊₃), whereas it is iron rich in SP and BO particles (i.e., Fa₂₂₊₄ and $Fa_{21\pm5}$, respectively; table S2). The nickel content in olivine is always high and consistent throughout all particle types, with NiO = $2.78 \pm$ 0.46 weight % (wt %) (table S2). In SR particles, spinel exhibits high-Mg and high-Ni concentrations (MgO = 8.12 to 12.26 wt %, NiO = 3.28 to 4.84 wt %; table S3), indicating important magnesioferrite and trevorite components, and minor magnetite. Conversely, spinel crystals exhibit lower Mg and Ni concentrations in SP particles (MgO = 1.77 to 1.99 wt %, NiO = 0.73 to 1.16 wt %). The bulk trace element composition of the particles, determined using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), is reported in table S4 and fig. S2, along with the bulk compositions of sediments from which they were extracted. Similarly to the major element chemistry, the CI-normalized flat pattern exhibited by most particles is suggestive of chondritic material. Enrichments up to ca. an order of magnitude of U, Th, and La (gray dashed lines in fig. S2) are observed and likely due to contamination by the local sediment. Conversely, we observe depletions in Zn and Pb to various extents, suggesting evaporative loss at high temperature. The oxygen isotopic compositions of the particles are characterized by highly negative δ^{18} O, ranging from -35 to -52‰ (Fig. 4 and table S5). Similarly to the textural and chemical properties, the SR and SP particles display distinct δ^{18} O values, ranging from -44 to -28‰ and -52 to -45‰, respectively. The BO particles show a narrower range in δ^{18} O values, from -51 to -50%. The CC particle displays the highest δ^{18} O value at -40‰. The Δ^{17} O is constant throughout all groups and ranges from -0.3 to -1.2%.

DISCUSSION

Spherules resulting from a major meteoritic event on the East-Antarctic ice sheet

The chondritic bulk major and trace element chemistry and high Ni content demonstrate the extraterrestrial nature of the recovered particles (Fig. 3, fig. S2, and tables S1 and S4). The particles resemble S-type cosmic spherules, which are essentially composed of olivine, minor iron spinel, and interstitial glass (10). However, WN particles differ from cosmic spherules on several crucial properties. The high Ni concentrations of olivine (NiO = 2.00 to 3.31 wt %) record high oxidizing conditions relative to those determined for cosmic spherules (11). Compound spherules are not observed among cosmic spherules, as the probability for these spherules to coalesce during flight while still molten is negligible. Iron spinel in S-types cosmic spherules is mainly composed of magnetite ($Fe^{2+}Fe^{3+}{}_{2}O_{4}$), due to the relatively limited oxidizing conditions in the upper atmosphere (10, 12, 13). Increasing oxidizing conditions result in a higher Fe³⁺/Fe_{tot} ratio (77 to 89) and, thus, a major magnesioferrite component, as observed in SR spherules [>80 wt %; Mg(Fe³⁺)₂O₄], whereas magnetite is a minor component (<10 wt %). Present spinel compositions are consistent with impact or meteoritic ablation spherules (2, 14-20). The spinel composition of SR spherules is also consistent with that of impact debris formed during an airburst event in the lower layers of the atmosphere (7). Sodium content is also higher than that observed in S-type spherules [Na₂O < 1 wt %; (11)] and consistent with impact spherules forming in a dense chondritic gas and/or in the pressured gas due to the presence of a bow shock during atmospheric entry (7). The SR spherules must have resulted from the atmospheric entry of a chondritic body large enough to reach the lower atmosphere. SP spherules exhibit low Fe³⁺/Fe_{tot} values with



Fig. 2. Scanning electron backscattered images of WN particles. (A) WN-IP#12 (SR), which consists in skeletal Fe-poor olivine (Fa < 10), Fe spinel, and minor interstitial glass. (B) WN-IP#6 (SP), which consists of large skeletal Fe-rich olivine (Fa > 10), and minor Fe spinel and interstitial glass. (C) and (D) represent polished section of WN-IP#12 and WN-IP#6, respectively. Insets in (C) and (D) are close-ups showing the morphology of olivine and Fe spinel crystals. Scale bars, $100 \mu m$.



Fig. 3. Major element bulk compositions of the impact WN particles (WN-IP), normalized to CI-chondrite bulk composition (46). Bulk compositions of impact particles from BIT-58 (average), L1 from EPICA Dome C ice core (average), and DF2641 from Dome Fuji ice core (range for individual analyses) are shown for comparison. Elements are arranged in order of increasing volatility from left to right (47).

respect to cosmic spherules (i.e., $Fe^{3+}/Fe_{tot} = 60$ to 62 and 66 to 72, respectively). The bulk chemistry and unique petrologic properties of SR and SP particles suggest a paired origin. We will show below how SR and SP spherules can form simultaneously.

The WN particles share structural, textural, and chemical properties with microkrystites, which are spherules that condense from large impact plumes (2, 19). Their mafic chemistry suggests high contributions from the impactor, while the spherical and/or subspherical shapes and lack of vesicles suggest that they condensed within a vapor saturated impact plume. These characteristics contrast those of the more common microtektites, which are melt products mainly composed of target material that display aerodynamic shapes (e.g. teardrops, dumbbells) typical of ballistic flight (2, 21-23). Formation through condensation in a dense plume is thus favored for the WN particles, as opposed to formation as melt products rapidly ejected along ballistic trajectories from the impact area.

In the Antarctic ice record, several occurrences of microkrystitelike dust layers have been recognized: the ~2.8-Ma-old BIT-58 dust horizon close to Allan Hills [76°43′0″S, 159°40′0″E; (24)] and two extraterrestrial dust horizons in the EPICA (European Project for Ice Coring in Antarctica) Dome C [i.e., L1 and L2; 75°06′S to 123°21′E; (8)] and Dome Fuji ice cores [i.e., DF2641 and DF2691;



Fig. 4. δ^{17} O versus δ^{18} O diagram (values in ‰ versus V-SMOW) for WN particles, DF2641 particles from the Dome Fuji ice core (9), and L1 particles from the EPICA Dome C ice core (48). Antarctic inland ice values from (26) and tropospheric oxygen values from (32). Bulk isotopic compositions of chondritic meteorites are represented in rounded colored shaded areas, including carbonaceous chondrites [i.e., below the terrestrial fractionation line (TFL)], ordinary and Rumuruti chondrites (i.e., above the TFL), and enstatite chondrites (i.e., on the TFL) (27–29). The blue/red shaded areas represent hypothetical mixing area between a carbonaceous chondritic impactor, Antarctic inland ice (blue), and atmospheric oxygen (red). Trend lines for SR and SP WN particles are in red and black, respectively, and broadly represent mixing lines pointing to increasing mixing with ice. A larger deviation from the TFL means less interaction with atmospheric oxygen. Inset: The effects of oxygen isotopic exchange of a chondritic impactor with Antarctic ice and atmospheric air.

77°19'S to 39°42'E; (9)]. The dust horizons in the EPICA Dome C and Dome Fuji ice cores form the two pairs L1/DF2641 and L2/DF2691, which record two distinct cosmic events that occurred ca. 430 and 480 ka ago, respectively (8, 9). The BIT-58 particles formed during a single meteoritic event and exhibit a range in mineralogy and textures similar to those of our particles, albeit with some metals and sulfides in the glassy mesostasis (Table 1 and fig. S3) (24). These observations strongly support formation of WN particles during a single event. An absolute age for WN particles could not be determined. However, the ¹⁰Be exposure ages of glacially eroded surfaces of the WN mountains range from 870 to 1740 ka old (25). The altitude of the WN particle collection surface suggests an exposure age of at least 870 ka and likely closer to 1740 ka. Therefore, the age and slight mineralogical incompatibilities prevent pairing with BIT-58, suggesting that both events are distinct.

The WN particles also bear remarkable resemblance to L1/ DF2641 particles, whereas they are clearly distinct from L2/DF2691 particles (Table 1) (8, 9). Figure 3 and fig. S4 show that the observed chemical patterns of WN particles match well with the patterns exhibited by the L1/DF2641 particles. The bulk major compositions of WN particles do not appear to be controlled by the modal mineralogy of the particles, except for marked depletions in Na, K, Al, Ti, and Ca in two SP particles. These two particles are characterized by the largest olivine grains (up to 100 μ m) and olivine modal abundance (~75% volume). Similar elemental depletions are observed in L1 particles and in some DF2641 particles (8, 9). Particles from the EPICA ice core show a relatively high modal abundance of olivine,

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similar to SP particles. The observed depletions in these particles are likely due to the overabundance of olivine, which is not a carrier for these elements, thus favoring Mg, Fe, and Si. The high Si content in iron spinel in DF2641 particles suggests an overlap with surrounding silicate phases, preventing a precise calculation of Fe^{3+}/Fe_{tot} values and, thus, comparison with spinels in WN particles.

DF2641 particles exhibit negative δ^{18} O ranging from -27 to -47‰, similar to WN particles. The concentrations of grains, several orders of magnitude higher than the normal flux of cosmic spherules, coupled with their coeval age and chemistry indicate that L1 and DF2641 formed during a single large impact over the East Antarctic ice sheet (7–9). Negative δ^{18} O values in DF2641 particles are thought to result from the interaction of the particles with vapor characterized by Antarctic ice values at high temperature (9). As mentioned above, WN particles were deposited over the last 870 ka ago, which is compatible with the deposition time of L1 and DF2641 particles. The common petrological, chemical, and isotopic characteristics of the WN particles and L1/DF2641 particles, coupled with their age compatibility, suggest that they formed during the same event, thereby documenting a major meteoritic event over most of the Antarctic continent that occurred ca. 430 ka ago.

Nature of the impactor

Figure 4 shows that the oxygen isotopic signatures of WN particles plot between chondritic and inland Antarctic ice values along the terrestrial fractionation line (TFL) (26). This negative δ^{18} O is outside the range of chondritic materials and suggests that they have exchanged oxygen with ice during either formation or subsequent weathering (27–29). The silicate fraction of the particles does not show evidence of leaching and/or topotactic mineral replacement typical of terrestrial alteration, indicating no notable interaction with liquid water during weathering (30). In addition, oxygen isotopic compositions of cosmic spherules recovered from the summits of nunataks exposed for ca. 3 to 4 Ma ago show no evidence of isotopic exchange with seasonal snow (23, 31). This indicates that WN particles cannot have inherited their unique oxygen isotopic signatures during their storage in the Antarctic environment but rather during the impact event responsible for their formation.

The oxygen isotope compositions of WN particles exhibit several important characteristics (Fig. 4): (i) All values are close to the TFL, (ii) all values are below TFL (negative Δ^{17} O, which represents the deviation from the TFL), and (iii) all values are within δ^{18} O values of Antarctic inland ice (26). These characteristics allow several interpretations on the original composition of the precursor extraterrestrial material and the degree of mixing involved. We assume three discrete sources of oxygen as end members in the mixing occurring during the impact: (i) the chondritic impactor, (ii) Antarctic ice, and (iii) atmospheric air. Since Antarctic ice and atmospheric oxygen both have values very close to TFL (26, 32), the negative Δ^{17} O of the WN particles can only be produced by mixing between ice and/or air with a starting chondritic material having even lower Δ^{17} O. Consequently, a carbonaceous chondrite impactor rather than an ordinary chondrite body can be preferred as shown by the blue shaded area in Fig. 4. It is also possible to discount a CI chondrite precursor.

The oxygen isotope compositions also allow the degree of mixing between ice, air, and the impactor to be constrained. The low δ^{18} O values of the WN particles are close to Antarctic inland ice and demonstrate that ice-derived oxygen predominates over impactor or air-derived oxygen. We infer the degree of mixing from their

Sample	Locality	Coordinates	Age (ka ago)	Types	Size (µm)	Shape
WN	Walnumfjellet	72°07′S, 24°12′E	<870	SR, SP, BO, and CC	93 to 473	Spherical + subspherical
L1*	Dome Concordia	75°06′S, 123°21′E	434	SR and SP	Up to 100 µm	Angular (SP) + spherical (SR)
DF2641 [†]	Dome Fuji	77°19′S, 39°42′E	434 ± 6	SR and SP	Up to 100 s µm	Subspherical
L2*	Dome Concordia	75°06′S, 123°21′E	481	DM	Submicrometer: 25 μm	Spherical
DF2691 [†]	Dome Fuji	77°19′S, 39°42′E	481 ± 6	DM	Submicrometer: 15 μm	Spherical
MB [‡]	Miller Butte	72°42'S, 160°14'E	481	Mainly DM	Submicrometer: 65 μm	Spherical
BIT-58 [§]	Allan Hills	76°43'S, 159°40'E	2.8×10^{3}	SR, SP, BO, and DM	Up to 100 µm	Angular (SP) + spherical (SR)
Sample		Mineralogy	Spinel morphology	Olivine morphology	Fa (olivine)	δ ¹⁸ Ο (‰)
WN		Olivine + glass + Fe spinel	Cruciform + dendritic + cubic	Porphyritic + skeletal + barred	7 to 69	-51 to -32
L1*		Olivine + glass + Fe spinel	Cruciform + dendritic	Porphyritic + skeletal	~10 to 50	-38 to -21^{\parallel}
DF2641 [†]		Olivine + glass + Fe spinel	Cruciform + dendritic	Porphyritic + skeletal + barred	26 to 85	−47 to −27
L2*		Glass + Fe spinel	Dendritic	-	-	$-17 \text{ to } -10^{\parallel}$
DF2691 [†]		Olivine + glass + Fe spinel	Dendritic	Dendritic	~10 to 50	-
MB [‡]		Olivine + glass + Fe spinel	Cruciform + dendritic + cubic	Skeletal + barred	14 to 21	3 to 6
BIT-58 [§]		Olivine + glass + Fe spinel + Fe metal	Cruciform + dendritic + cubic	Porphyritic + skeletal + barred	17 to 24	-

Table 1. Main properties of impact spherules from Antarctica. SR, spinel-rich; SP, spinel-poor; BO, barred olivine; CC, cryptocrystalline; DM, glassy dominated by dendritic magnesioferrite.

range at ~95 to ~50% by mass ice-derived oxygen. SR spherules have the highest δ^{18} O and thus have experienced less exchange with Antarctic ice. The more negative Δ^{17} O of WN particles than air and ice testifies to the impactor-derived fraction of oxygen in the particles. The relative fraction of air/impactor oxygen is difficult to conclusively specify since it depends on the initial impactor composition. If we assume an impactor having carbonaceous chondrite isotopic compositions (i.e., Δ^{17} O < 0‰), then a mixture of ice and impactorderived oxygen will result in WN particles plotting in the blue shaded area in Fig. 4. The mixing line for SR spherules (i.e., red dashed trendline) falls above the mixing line formed by SP spherules (i.e., black dashed trendline), suggesting a lower Δ^{17} O impactor contribution in the former with respect to the latter and, thus, more mixing with air. Conversely, the lowest δ^{18} O WN particles (i.e., SP) exhibit larger Δ^{17} O deflections from TFL, providing some evidence, albeit at the limits of analytical certainty, that mixing with air decreases as mixing with ice increases. We discuss the large degree of ice-derived oxygen compared with impactor or air below in terms of the physical conditions of the impact scenario.

A touchdown event leading to the formation of the WN impact spherules

The discovery of unusual impact particles covering such a large area in Antarctica is anomalous. Known impact spherule layers in the geological record are usually associated with impact-cratering events (2). Examples of particles produced during airbursts events are rare, with the notable exceptions being the 480-ka-old event over Antarctica mentioned earlier (7, 9). DF2641 impact spherules recovered in the Dome Fuji ice core were also supposedly produced during a large airburst event over Antarctica ca. 430 ka ago (9). However, none of the proposed scenarios can account for the anomalous oxygen isotopic signature. The purely chondritic composition of WN particles precludes mixing with target rocks and thus implies the impact was not associated with a crater penetrating into crustal rocks (fig. S5). An event that generated a crater on the ice sheet may also be excluded, since no structure several hundreds of meters in diameter has yet been identified. Conversely, an airburst scenario implies no interaction with Earth's surface, and thus only mixing with atmospheric oxygen (33). An alternative to these two scenarios is an

intermediate "touchdown event," in which a jet of melted and vaporized meteoritic material reaches the surface at high velocity, whereas its density is too low to form an impact crater.

The petrological and geochemical properties of WN particles provide important clues about their mode of formation. Particularly, cosmic spinel is a good recorder of the ambient oxygen fugacity at the time of its crystallization as characterized by the ratio $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ (15). SR spherules have a $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ [76 to 88 atomic percent (at %)] similar to fusion crusts of meteorites (75 to 90 at %) and higher than micrometeorites (<75 at %). This is consistent with their formation in the lower atmosphere at high oxygen fugacity [<40 km; $\text{fO}_2 > 10^{-6}$ atmosphere (atm)] rather than the high atmosphere (i.e., >80 km; $\text{fO}_2 < 10^{-6}$ atm). In contrast, SP spherules exhibit $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ (60 to 62 at %) that imply formation under more reducing conditions.

The quenched textures of SR and SP spherules indicate cooling in a matter of seconds, similar to both cosmic spherules and meteorite ablation spheres. These particles could not, therefore, have formed as cosmic spherules in the upper atmosphere since they would have cooled long before reaching Antarctic ice and would not have experienced isotopic exchange of oxygen with ice.

Formation in an impact plume could explain the occurrence of both SR and SP spherules at the same locality and is the simplest explanation for their morphological, mineralogical, and isotopic properties. Approximately half the particles are compound spherules, which necessitates formation in a dense and turbulent plume in which interparticle collisions are common, and precludes formation as cosmic spherules. Although we might expect some composite particles among meteorite ablation debris, lower abundances would be expected owing to their rapid liberation and distribution over the meteoroid trail.

Experimental synthesis of cosmic spinel by melting chondritic material shows that changing fO2 during spinel formation essentially results in Mg²⁺ and Ni²⁺ replacing Fe²⁺, and Fe³⁺ replacing Al³⁺ and Cr³⁺. Figure S6 shows that the compositional trend observed for spinels in SR and SP spherules fits a scenario involving the condensation of pure chondritic material within a plume having extremely heterogeneous oxidizing conditions. The higher abundance of spinel in SR spherules compared with SP spherules is consistent with higher oxidizing conditions in the former, as spinel abundance is mainly controlled by oxygen fugacity (14). Spinel in SR spherules implies interaction at high oxygen fugacity (> 10^{-2} atm) similar to meteorite fusion crusts and thus infer oxidation by air. Certainly, the intrinsic oxygen fugacity of carbonaceous chondrite gas is too low to account for such a degree of oxidation in spinel (i.e., $\log fO_2 \approx -9$ at 1200°C) (34). Conversely, the lower oxidizing conditions (i.e. $fO_2 < 10^{-6}$ atm) responsible for the formation of spinel in SP spherules implies a more limited interaction with atmospheric oxygen. In case of a touchdown event on ice, however, vaporization will inject pure H₂O vapor into the impact plume. At low temperatures, the abundance of free oxygen in H₂O vapor is small [0.16% dissociation at 1600 K and 0.1 MPa; (35)]. However, this abundance increases with temperature owing to thermal dissociation (6.1% dissociation of H₂O at 2200 K). The oxidizing potential of high-temperature water vapor is moderated by the production of H2 and, at the highest temperatures, 2H. Given a sequestration of large amounts of free oxygen from high-temperature gas, for example, by condensation of silicate droplets, the remaining hydrogen is likely to cause reduction.

An increased interaction with atmospheric O_2 during the formation of SR spherules can explain their oxygen isotopic compositions

with respect to SP spherules. The δ^{18} O of SP spherules suggest almost complete (~80 to 95%) exchange with ice vapor, while exchange is lower (~50 to 80%) in SR spherules. The consistent Na₂O content in SR and SP spherules (table S1) implies that both spherule types experienced a similar degree of evaporation. Thus, their differences in δ^{18} O are unlikely to result strongly from mass-dependent fractionation [i.e., that shifts toward higher δ^{18} O, as observed in cosmic spherules; (31)]. A more likely scenario is a dominant isotopic exchange between SR spherules and atmospheric oxygen, similarly to meteorite ablation spheres resulting from an airburst (33). Such an exchange accounts for an approximately 8‰ increase in δ^{18} O in meteorite fusion crusts (13). The relatively large available surface area available for isotopic exchange in impact spherules compared to fusion crusts may partly explain the large degree of isotopic exchange and account for the δ^{18} O difference observed between SR and SP spherules (~20‰). More significantly, silicates vaporize as SiO and O₂ molecules in the vapor phase (36); thus, large-scale exchange of oxygen is possible as vapor cools and condenses to form silicate melt spherules.

A touchdown event may reconcile both the spinel compositions and oxygen isotopes in SR and SP spherules. Assuming that SR spherules interacted early during their formation with atmospheric oxygen, as suggested by their spinel composition and oxygen isotopic signatures, a formation in the periphery of an impact plume seems likely. Conversely, the relatively low degrees of oxidation of spinel in SP spherules, coupled with a near total isotopic exchange with ice vapor, are consistent with formation at the core of the plume. Furthermore, although all spherules exhibit skeletal olivine, the substantial crystal size in SP spherules with respect to SR spherules suggests relatively slower cooling rate in the former, consistent with the slowly cooling interior of the plume.

Numerical simulations of a rocky projectile with a diameter of 100 to 150 m entering Earth's atmosphere at a velocity of 20 km s⁻¹ and an impact angle from 15° to 90° show that these objects are entirely disrupted and vaporized before reaching ground level (37). Figure S7 represents a model of the thermal conditions before impact on ice of a 100-m projectile displaying the physical properties of dunite (ρ of 3.3 g cm⁻³), which is a close analog to chondritic material. The projectile is entirely vaporized before reaching ground level by shock-heated air at ~30,000 K. However, contrary to smaller events (e.g., Tunguska), the vapor jet that is almost an order of magnitude wider than the initial body does not lose momentum and reaches the ground with a velocity of ~ 6 to 10 km s⁻¹, resulting in a touchdown event. At this time, its density is too low (0.1 to 0.01 g/cm³; fig. S7) to form a regular impact crater. Instead, a major effect of a touchdown event is the interaction of a superheated vapor jet with the ground surface (fig. S8). Thermal radiation is also produced by fragmentation in airbursts and has been estimated from the energy release in atmosphere using a constant (independent of altitude and observational point) luminous efficiency of 5% (38). This burst of thermal radiation will reach the ground before the arrival of the vaporized object, potentially causing a first stage of ice vaporization. Assuming that all radiation is absorbed by the surface (albedo of 0) and that vaporization is instantaneous (i.e., we did not consider propagation of the vaporization front through ice and any other sources of energy dissipation), the ice density is 0.92 g cm⁻³, and its heat of vaporization is 2270 J/g, we find that the maximum depth of vaporization is near the impact point (>1 cm and up to 50 cm), but in a large area, this depth does not exceed 1 mm (fig. S8, C and D). The total volume of vaporized ice is about 0.01 km³, which is equivalent

to 12 km³ of vapor (at atmospheric pressure and a temperature of 373 K) or to a 150-m-thick layer of vapor within 5-km radius near the impact point. If the ice albedo is 0.5 (39), the vaporized volume and layer thickness would be twice as small. A more accurate numerical model (38) shows that the thermal flux is similar to simple estimates near the impact point but drops much quicker with increasing distance (fig. S8D). As a result, the total volume of vaporized ice is six times smaller. This produces a mass of water vapor of 9.2×10^9 to 1.6×10^9 kg, releasing 4.1×10^9 to 0.71×10^9 kg of O₂ at 3000 K (50% dissociation), compared to 7.0×10^8 kg of O₂ released by vaporization of the chondritic impactor (assuming 50 wt % O) (35). Thus, vaporization by the thermal pulse alone produces sufficient water vapor to explain the large degrees of mixing observed.

The condensation of spherules releases additional (latent) heat into the system. On the other hand, mixing and heat exchange between melt droplets and ice are much less efficient. Subsequently, this hot mixture rises along the atmospheric wake while cooling proceeds (Fig. 5). Within 3 to 4 min, the plume, which is now a mixture of projectile material, water, and air, reaches its maximum altitude of ~400 km, by which point impact spherules have condensed (fig. S9). Last, the plume collapses back to the lower dense layer of the atmosphere, forming a spherule-rich cloud with a radius of thousands of kilometers (*37*). Such a scenario may account for a continental distribution including the Sør Rondane Mountain chain, Dome Concordia (i.e., approximately 2700 km away), and Dome Fuji that is located along a line between these two locations.

Implications for the impact cratering record and hazard

A unique characteristic of the touchdown event described here is that it occurred over the Antarctic ice sheet. The difficulty in linking a precise age to WN particles cannot exclude that the occurrence of

WN, DC, and DF results from multiple touchdown events taking place within a short time window. However, the rate of impact of an asteroid ca. 10⁶ kt in mass has been calculated as approximating one every 10⁵ years, which strengthens our scenario of a single impact and may explain the paucity of such touchdown events in the geological record. However, should the particles represent the products of several events, this stresses the necessity for reassessing the threat of medium-sized asteroids even more. Examples of impact-derived material found in the geological record that are not associated with known craters remain rare (2). These include the Dakhla desert glasses, which are thought to have been produced by melting of desert surface by thermal radiation resulting from a large airburst event (40). The spherules described here are further unequivocal examples of impactites produced during a unique touchdown event in the geological record (9). It is likely that similar touchdown events vaporizing the surface of an ocean will produce similar spherules exhibiting purely meteoritic compositions [albeit with possible contamination from Na and Cl; e.g., (20)] and heterogeneous redox conditions producing SR and SP spherules, which are not observed in airburst residues (7). As a result, WN spherules may prove useful for the identification of these events in deep sea sediment cores and, if plume expansion reaches landmasses, the sedimentary record. Furthermore, cosmic spinel is known to be particularly resistant to terrestrial weathering and has long been used to characterize impact spherules. However, oxygen isotope signatures of these particles may not be distinguishable from those of airburst residues, as the target (i.e., oceanic water) δ^{18} O overlaps with that of chondrites (41). To complete Earth's asteroid impact record, future studies should focus on the identification of similar events on different targets (e.g., rocky or shallow oceanic basements), as the Antarctic ice sheet only covers ca. 9% of Earth's land surface.



Fig. 5. Temperature and density distribution in the impact plume after the contact. (A) and (**B**) represent temperature and density after 10 s, respectively; (**C**) and (**D**) represent temperature and density after 36 s, respectively. Shortly after the impact of vapor jet into ice, temperature near the impact point (from –4 to 0 km along the *X* axis and up to 2-km altitude) remains extremely high. Mixing with vaporized ice (i.e., steam) occurs at this point. Thirty-six seconds after the contact, temperature drops below 3000 K; it is likely that impact spherules have condensed by that point (note, however, that the process of condensation and formation of particles is not included into the model). (B) and (D) show relative density (the ratio of the current density to the density of undisturbed atmosphere). Shock waves (dark gray areas) propagate outward from the impact point; density within the wake is below normal (vapor and air are hot). Blue/red contours show ice/projectile materials respectively. Intensive mixing takes place immediately after the impact (B); this mixture subsequently moves upward along the rarefied wake and reaches the upper troposphere during the first minute.

The impact hazards resulting from the atmospheric entry of an asteroid that are currently being addressed by impact mitigation programs depend mainly on whether the impactor reaches the ground or is entirely disrupted in the atmosphere (i.e., airburst). For smallto medium-sized impactors (50- to 150-m diameter) producing airbursts, the main hazard is limited to blast effects resulting in strong overpressures over areas of up to 100,000 km² (37). Thermal radiation may also result in fires over an area of 10 to 1000 km^2 wide (38). The effects of a touchdown event resulting from a projectile with a diameter of 100 m remain relatively poorly studied. Figure 5 shows that in addition to shockwaves and thermal radiation covering the aforementioned areas, these events are potentially entirely destructive over a large area, corresponding to the area of interaction between the hot jet and the ground. Touchdown events may not threaten human activity, apart from the formation of a large plume and the injection of ice crystals and impact dust in the upper atmosphere, if these occur over Antarctica. However, if a touchdown impact event takes place above a densely populated area, this would result in millions of casualties and severe damages over distances of up to hundreds of kilometers (5).

MATERIALS AND METHODS

Major element chemistry

Major element analyses were carried out using a JEOL JXA-8500F electron microprobe at the Museum für Naturkunde Berlin, Germany. The electron microprobe is equipped with a field emission cathode and five wavelength-dispersive spectrometers. The following experimental conditions were used:

1) 15-kV acceleration voltage, 15-nA beam current, and defocused beam of $20 \,\mu\text{m}$ for glass and whole-rock analyses. Bulk major analyses were determined averaging several analyses (table S1).

2) 15-kV acceleration voltage, 15-nA beam current, and spot size of 1 μ m for olivine and spinel analyses.

All measured intensities were calibrated against natural minerals of the Smithsonian international standard suite and pure metals of the Astimex metal standard. Analyses were processed by the ZAF routine by the JEOL series operating system to minimize matrix effects. In addition, accuracy and reproducibility were checked regularly before and after each analysis session by measurements of minerals of the Smithsonian international standard suite.

Trace element chemistry

Uncoated sections of the particles embedded in epoxy resin were analyzed by LA-ICP-MS using the Electro Scientific Instruments New Wave UP-193FX ArF excimer (193 nm) Laser Ablation System coupled to a Thermo Electron Element XR ICP-MS at Florida State University, USA (42-44). Together, 76 peaks for major and trace elements and their interferences were monitored. Spot sizes of 50 µm were used, and the laser repetition rate was 50 Hz, with a fluence of >2 GW cm⁻². Laser dwell times on a spot were 10 s, resulting in a pit depth of \sim 50 μ m. USGS glasses (BHVO-2g, BCR-2g, and BIR-1g) were used as the external standards for elements that have been precisely determined in these glasses, for example, major elements, Rb, Sr, Nb, Zr, Ba, Rare Earth Elements, Th, and U. For elements that were poorly constrained in USGS glass, such as some chalcophile and siderophile elements, NIST SRM 610 was used as the external standard. The reproducibility of major elements and most of the trace lithophile elements obtained using this technique is better than 5%.

Quantitative data for trace element concentrations of the bedrock residues from which the particles were extracted were acquired for sample powders at the Laboratoire G-Time of the Université Libre de Bruxelles (ULB), using ICP-MS. Bulk subsamples were cleaned, crushed manually, and homogenized in an agate mortar at the Analytical, Environmental and Geo-Chemistry (AMGC) laboratory of the Vrije Universiteit Brussel (VUB). Around 50 mg of powdered samples was mixed with ~1 g of a 4:1 ultrapure metaborate-tetraborate mixture. The mixture was heated in a graphite crucible at 1000°C for 10 min. After cooling down, the bead was dissolved in 50 ml of 2N HNO3 with a stirring magnet for 5 hours. The solution was diluted accordingly for major and trace element measurements. Indium was used as internal standard for trace elements analyses, performed on an Agilent 7700 ICP-MS at Laboratoire G-Time at ULB. Yttrium was used as internal standard for major element analyses performed on a Thermo Scientific ICaP also at ULB. In both cases, the calibration curves were obtained on solutions of artificial multielement standards, while solutions prepared from natural reference material from the USGS (BHVO-2 and AGV-2) were used for quality control. The external reproducibility expressed as relative SD (RSD) is better than 5% (based on six replicates of BHVO-2) for trace elements (except Rb and Lu, 7 and 10%, respectively). The external reproducibility for major elements is better than 5% RSD (based on eight replicates of BHVO-2), except for K that is better than 10% RSD. Loss on ignition was determined after 1 hour at 500°C followed by 1 hour at 1000°C.

Oxygen isotope ratios

We measured the oxygen isotopic compositions of geochemically characterized olivine crystals with a CAMECA IMS 1270 E7 at the Centre de Recherches Pétrographiques et Géochimiques (Nancy, France). ¹⁶O⁻, ¹⁷O⁻, and ¹⁸O⁻ ions produced by a Cs⁺ primary ion beam (~10 µm and ~2 nA) were detected in multicollection mode using two off-axis Faraday cups (FCs) for ¹⁶O⁻ and ¹⁸O⁻ and the axial FC for ¹⁷O⁻. To remove the ¹⁶OH⁻ interference on the ¹⁷O⁻ peak and to obtain maximum flatness on the top of the ${}^{16}O^{-}$ and ${}^{18}O^{-}$ peaks, entrance and exit slits were adjusted to acquire a mass resolving power (MRP) of \approx 7000 for ¹⁷O⁻ on the central FC. The multicollection FCs were set on slit 1 (MRP = 2500). The total measurement time was 270 s (180-s measurement + 90-s presputtering). We used four in-house terrestrial standard materials (San Carlos olivine, CLDR01 MORB glass, Charroy magnetite, and JV1 diopside) to (i) define the instrumental mass fractionation line for the three oxygen isotopes and (ii) to correct the instrumental mass fractionation due to the matrix effect in samples. Typical count rates obtained on the San Carlos olivine standard were 1×10^9 cps for 16 O, 3.5×10^5 cps for 17 O, and 1.8×10^6 cps for ¹⁸O. The 2 σ errors were $\approx 0.4\%$ for δ^{18} O, $\approx 0.7\%$ for δ^{17} O, and $\approx 0.8\%$ for Δ^{17} O (Δ^{17} O representing the deviation from the TFL, $\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$.

Impact model

To model the impact of a 100-m asteroid, we use the SOVA hydrocode (45) coupled with the ANEOS equations of state for dunite (projectile) and ice (target). First, the atmospheric entry of a cosmic body was modeled in 2D (the atmospheric stratification was changed to imitate an oblique impact). Second, interaction of the projectile remnants with ice and atmosphere was modeled in 3D. Details of this approach are described in (35). Mixing of two materials (ice and projectile vapor) is not included in the model. The SOVA code was built to prevent mixing and numerical diffusion between different materials. Thus, we can only hypothesize ice melting within an impact plume that is formed after the impact. There are three possible ways to vaporize the icy surface: (i) by thermal radiation emitted during the entry, (ii) by shock compression of ice during the impact, and (iii) by thermal conduction/convection/radiation within a rising plume. The main text evaluates the input from each of these processes.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/ content/full/7/14/eabc1008/DC1

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Summary

- This work has presented a detailed inventory of extraterrestrial- and impact-related dust particles, including micrometeorites, microtektites and meteoritic condensation spherules, that were recovered from the Widerøefjellet and Walnumfjellet sedimentary traps in the Sør Rondane Mountains (Dronning Maud Land, East Antarctica). Based on a statistical analysis of the petrographic, chemical and isotopic properties of cosmic spherules from the WMC, as well as a comparison with the SPWW and TAM micrometeorite collections, it was demonstrated that the WMC is representative of the cosmic dust flux to Earth over the last ca. 1-3 Ma (Suganuma et al., 2014; Goderis et al., 2020) for particles >240 µm in size. Since the majority of extraterrestrial- and impact-related dust particles examined during this study exceed this size threshold, we can exclude potential sorting effects such as wind sorting or aqueous alteration. This is furthermore supported by the abundance and preservation of (Mg-rich) vitreous cosmic spherules, which are prone to weathering (van Ginneken et al., 2016) and do not display significant alteration features. The physicochemical and isotopic properties of extraterrestrialand impact-related dust particles are thus mainly determined by their precursor bodies (e.g., parent asteroid or comet, upper continental crust, etc.) and potential secondary effects (e.g., atmospheric entry or transit, interaction with Antarctic precipitation, etc.). In conclusion, the SRM sedimentary deposits, and specifically the WMC, represent a unique and pristine collection from the eastern Antarctic continent suited to monitor the contemporary flux of extraterrestrial matter to Earth and document major meteoritic events over the Antarctic continent, and potentially even on a global scale.
- The atmospheric entry of meteoroids and micrometeoroids is associated with significant modifications of their original physicochemical and isotopic properties. Melting experiments using alkali basalt and ordinary chondrite samples in a high enthalpy facility suggest that (micro)meteoroids are subjected to a complex interplay of redox processes, where iron is ultimately oxidized to form magnetite (Pittarello et al., 2019; Helber et al., 2019). Additionally, a series of microscopic structures (e.g., skeletal olivine and magnetite grains, olivine zoning patterns), observed within vitreous residues of the ordinary chondrite sample, show a strong resemblance with petrographic features previously reported in cosmic spherules and the fusion crust of ordinary chondrite meteorites. Volatile alkali metals including Na and K have largely been vaporized and are depleted in the residue material, similarly to cosmic spherules. The melting experiments have thus successfully reproduced the textural and chemical observations in cosmic spherules and the fusion crust of meteorites. This information can subsequently be used to quantify the extent of chemical fractionation processes and reconstruct the chemical composition of micrometeorite precursor bodies. Yet, chemical fractionation trends seemingly

appear to be decoupled from oxygen isotope fractionation processes. This observation was determined based on a detailed chemical and oxygen isotopic analysis of fifty-eight chondritic cosmic spherules spanning a wide textural range (Lampe et al., submitted), and suggest that both processes occur (in large part) independently from each other, or that the extent of chemical fractionation processes cannot be discerned accurately due to varying mineralogical contributions in the precursor body of micrometeorites. Consequently, we have measured the iron isotope compositions of the chondritic cosmic spherules to correct for oxygen isotope fractionation processes. These results suggest that kinetic fractionation is predominantly responsible for mass-dependent oxygen and iron fractionation processes in micrometeoroids during atmospheric entry heating. Based on the correlation between oxygen and iron isotopes, a correction factor was designed to calculate the original oxygen isotope fractionation. This method has proven to be successful for ordinary chondrite-, and to a lesser extent, carbonaceous chondrite-related micrometeorites, which may imply that oxygen isotope fractionation is largely controlled by the mineralogical components of micrometeorite precursor bodies.

- This work has provided additional evidence to support that the micrometeorite population samples new types of asteroidal and cometary bodies. First, we have presented textural and chemical data for a chondrule- and CAI-bearing micrometeorite (particle WF1202A-001) with highly anomalous oxygen isotope compositions that are inconsistent with meteoritic or asteroidal bodies known to date (Soens et al., 2020). Based on the entry parameters of micrometeorite WF1202A-001, it was concluded that this particle likely originated from the Jupiter Family Comets. This is in agreement with dynamical models, which suggest that the vast majority of the cosmic dust flux to Earth originates from these particular bodies (Nesvorný et al., 2010). In addition, we have discovered at least two achondritic cosmic spherules displaying unique chemical and oxygen isotopic compositions, next to 3 HED-like micrometeorites (Soens et al., submitted). These observations are consistent with those of Cordier and Folco (2014) who argued that cosmic dust essentially samples different types of precursor bodies than macroscopic meteorites, and emphasizes the importance of micrometeorite investigations to document the large variety of asteroidal and cometary bodies present within the Solar System.
- A small number (*n* = 33) of microtektite-like particles were recovered in the non-magnetic size fractions of sedimentary deposits from the SRM (Soens et al., 2021). The physicochemical properties of the microtektite-like particles strongly resemble 'normal-type' Australasian microtektites previously identified from the TAM (e.g., Folco et al., 2008; 2009; 2016; Brase et al., 2021). Other chemical subtypes (e.g., 'high-Mg', 'high-Al', 'high-Ni', etc.) have currently not been recovered. The Sr-Nd isotope systematics of the SRM microtektites are consistent with the Australasian strewn field and indicate that the target material was presumably composed of a plagioclase- or carbonate-rich lithology derived from a Paleo- or Mesoproterozoic crustal unit.

The SRM microtektites likely extend the central distribution lobe of the Australasian strewn field based on their average alkali metal concentrations (e.g., Na₂O and K₂O) and their sizefrequency distribution. Previously, it has been demonstrated that both parameters correlate with distance of the hypothetical Australasian impact site (e.g., Folco et al., 2010; van Ginneken et al., 2018). Based on these observations, the distribution of Australasian microtektites likely occurred across the entire Antarctic continent and significantly extends the size of the Australasian strewn field up to ca. 15% of the Earth's surface. This area includes a large portion of the south-eastern Indian Ocean, which has barely been examined during previous ODP campaigns. Furthermore, iron isotopic data has revealed that the generation of microtektites during large impact events is significantly more complex than originally was considered (Chernonozhkin et al., in press). Specifically, molten target rock material appears to be subjected to a range of processes including condensation, varying degrees of mixing with isotopically distinct reservoirs, and ablative evaporation during its atmospheric re-entry. As a result, we have observed both isotopically light and heavy impact ejecta, which display a δ^{56} Fe range of ca. 5‰. Iron isotope studies of impact ejecta on Earth can thus provide a more thorough understanding on the isotopic evolution of planetary crusts due to impact processes.

We have reported on the discovery of spherulitic aggregates, similar to those found in Dome Fuji, Dome Concordia and the TAM, recovered from the Walnumfjellet sedimentary deposit in the Sør Rondane Mountains (van Ginneken et al., 2021). Four different types of particles were identified, which appear to resemble the petrographic and chemical properties of chondritic micrometeorites. Yet, the spherulitic aggregates are clearly distinct from micrometeorites based on the relatively high concentration of NiO in olivine mineral phases, the occurrence of compound particles, the presence of magnesioferrite previously observed in impact debris during airburst events and indicative of condensation processes (van Ginneken et al., 2010), and the relatively high concentration of Na compared to cosmic spherules. These parameters indicate that the spherulitic aggregates were formed in a more oxidizing environment, presumably in the lower atmosphere. Oxygen isotope data are comparable to Antarctic ice (Dome Fuji Ice Core Project, 2017) and suggest that oxygen isotopes of the spherulitic aggregates were mainly inherited from its precursor body, Antarctic ice and atmospheric oxygen. It is estimated that roughly ca. 95–50% of the oxygen isotopes were inherited from Antarctic ice. As such, these observations are interpreted to represent a touch-down event where a hot projectile vapor jet interacted with the Antarctic sheet ca. 430 ka and subsequently condensed to form spherulitic aggregates which were dispersed across the Antarctic continent. These observations are supported by numerical models and may assist the identification of similar events in the geological record.

• Finally, a comprehensive analysis of chromite and Cr-rich spinel phases in thousands of micrometeorites from the Walnumfjellet micrometeorite collection has suggested that the former mineral phases are relatively rare (i.e., 4 chromite and Cr-rich spinel phases out of 2792 cosmic spherules or ca. 0.14%) (Schmitz et al., 2019). As such, the accumulation of extraterrestrial chromite and Cr-rich spinel phases on Earth during and after the L-chondrite parent body breakup event can only be explained by a significant increase of cosmic dust to Earth in order to explain their abundance in middle Ordovician pelagic sediments. This study thus re-emphasizes the importance and relevance of the aforementioned mineral phases in the reconstruction of past climatic regimes and the cosmic dust flux to Earth throughout geological time.

Future outlook

- While the majority of large (>400 μ m) micrometeorites from the Widerøefjellet sedimentary deposit has been investigated during the course of this PhD research, most small-sized (<200 μ m) particles still require further examination. Goderis et al. (2020) demonstrated that particles <240 µm have possibly been subjected to wind sorting or alteration processes based on their cumulative size distribution. To discriminate both possibilities, two strategies can be considered. First, an oxygen isotope study (e.g., SIMS, SHRIMP) could be performed on a large, representative number of small-sized micrometeorites. Since recent isotopic and modelling studies have shown that small-sized micrometeorites predominantly sample carbonaceous chondrite precursors (e.g., Flynn et al., 2009; Suavet et al., 2009; Cordier and Folco, 2014; Goderis et al., 2020), a potential deviation from these observations could indicate whether sorting processes at Widerøefjellet can mainly be attributed to wind activity or aqueous alteration. Wind activity should retain the relative proportions of micrometeorite precursor bodies since sorting is predominantly controlled by size. Particles with similar sizes should thus have an equal opportunity to be transported by wind, irrespective of their precursor bodies. In contrast, aqueous alteration may possibly target specific textural or chemical types of micrometeorites due to their precursor properties (e.g., van Ginneken et al., 2016; 2017). Secondly, a detailed petrographic examination of small-sized particles can be performed to investigate whether they have been affected more extensively by weathering processes compared to their larger analogues.
- Furthermore, it is plausible that a limited amount of microtektites can be recovered from the smaller size-fractions, which would provide a more detailed and accurate size-frequency distribution of Australasian microtektites from the SRM. This information is important to understand the distribution mechanisms of Australasian impact ejecta, reconstruct the extent of the Australasian strewn field and identify potential preservation biases in the SRM sedimentary deposits. Special attention should be given to the recovery of different microtektite subtypes, including 'high-Mg', 'high-Ni', 'high-Al', which have not been identified in the SRM sedimentary deposits thus far. Based on the abundance of microtektite subtypes at other Antarctic collection sites, these subtypes should also be present within the SRM sedimentary deposits. A new search effort could thus verify whether these microtektite transportation mechanisms, and preservation or sampling biases between the respective recovery sites. Future ODP campaigns should concentrate on potential recovery sites in the south-eastern Indian Ocean. In parallel, Antarctic expeditions south of the SRM may verify whether the distribution of Australasian microtektites occurred on a continent-wide scale.

- This PhD research mainly focused on the characterization of extraterrestrial- and impact-related dust particles from the Widerøefjellet and Walnumfjellet sedimentary deposits. Yet, many deposits (e.g., Svindland, Vikinghøgda, etc.) have not been investigated thoroughly or even processed (see Fig. 1 in Goderis et al., 2020). Preliminary tests have indicated that the latter deposits commonly contain lower micrometeorite (and microtektite) abundances. As such, it would be worthwhile to characterize every single deposit in terms of their physical (e.g., colour, size), textural (e.g., abundance), chemical and isotopic properties to compare and discuss their productivity and preservation potential. This should improve our general understanding of the glaciological evolution of the SRM and environmental conditions, which in turn allows future expeditions to target new sedimentary deposits more accurately to obtain a higher micrometeorite and -tektite yield. Alternatively, future expeditions may target new sampling sites in the surrounding mountain chains, such as the Belgica and Yamato Mountains, or possibly even Greenland.
- Despite the plenitude of anthropogenic dust particles, a recent study demonstrated the possibility to collect micrometeorites from densely populated areas in an attempt to incentivize and introduce the broader public to the field of meteoritics (Genge et al., 2017b). During a recent test, a single cosmic spherule was successfully retrieved from a local roof gutter. As such, a simplistic social media campaign could be launched providing tips to successfully hunt urban micrometeorites, thereby extending the project across Belgium.
- Since the chemical and mineralogical properties can vary considerably among micrometeorite precursor bodies, and thus affect atmospheric heating processes, new heating experiments could focus on a diverse selection of meteorite samples or analogous materials, which are representative of other common micrometeorite groups (e.g., carbonaceous chondrites). For instance, the potential affiliation of 'Group 4' ¹⁶O-poor micrometeorites with the newly classified CY chondrites (Ikeda, 1992; King et al., 2019) could be tested by using a CY chondrite fragment. In addition, a thorough oxygen isotope study, possibly in combination with iron isotopes, of the molten meteoritic material could provide more insight into oxygen isotope fractionation processes for each specific meteorite group.
- The recent addition of a X-ray photoelectron spectrometer (XPS) by the SURF Department at the Vrije Universiteit Brussel provides an excellent opportunity to quantitively analyse the surface of micron-sized particles including micrometeorites, microtektites or meteoritic condensation particles. The method is particularly interesting to investigate scoriaceous or unmelted micrometeorites since the instrument is capable of detecting the bonding state of chemical elements. As scoriaceous and unmelted micrometeorites may contain relict mineral

phases, this method may potentially be useful to identify the mineralogy of micrometeorites more accurately.

Finally, in light of the recent scientific interest into chromite and Cr-rich spinel phases, a series of experiments was conducted throughout this PhD research to detect and characterize the aforementioned mineral phases in a large number of Antarctic micrometeorites from the SRM and TAM. Since geological samples are commonly dissolved into acid to concentrate chromite and Cr-rich spinel phases, all information regarding their micrometeorite hosts is lost. As such, a novel procedure was developed to detect chromite and Cr-rich spinel phases within micrometeorites in a non- or semi-destructive manner. This information is pivotal to understand the textural-chemical relationship between chromite and Cr-rich spinel phases on one hand, and their silicate- and/or metal-rich host bodies on the other hand. Furthermore, we are able to document the precursor bodies of chromite-bearing micrometeorites and better constrain their source region within the Solar System. This concept was accomplished by scanning a large number of micrometeorites using the Tornado M4 micro X-Ray Fluorescence Spectrometer (micro-XRF) at the AMGC Department (Vrije Universiteit Brussel) to produce 2D elemental (including Cr) maps of each particle (Fig. 2). We hypothesized that Cr-rich zones within the elemental map of individual particles corresponded with a chromite or Cr-rich spinel phase. These particles were consequently selected for further analysis. In addition, we included particles that displayed a global Cr-enrichment. Initially, a series of line scans was measured with micro-XRF to verify whether the Cr-rich zones within micrometeorites were authentic. Next, a small number of micrometeorites was selected representing both groups of Crsignatures. Particles were embedded in epoxy resin and polished for further analysis with a JEOL JSM IT-300 SEM, coupled to an Oxford Energy Dispersive Spectrometer (EDS) at the SURF Department (Vrije Universiteit Brussel). We successfully identified 7 chromite and Crrich spinel phases within 10 micrometeorites, demonstrating the possibility to detect and identify these mineral phases while retaining its context within micrometeorites. As a result of the pandemic, additional experiments were initially postponed and ultimately cancelled. Consequently, these results have not been published or were not included into this PhD dissertation. However, the project was carried over to doctoral researcher Flore Van Maldeghem who continued the experiments. Recently, a selection of chromite- and Cr-rich spinel-bearing micrometeorites were analysed with a JEOL JXA-8200 electron probe micro analyzer (EPMA) at the National Institute of Polar Research (Tokyo, Japan). In a later stage, oxygen isotope analyses will be conducted on the chromite and Cr-rich spinel phases and micrometeorite hosts.


Figure 2: Overview of chromite experiment for sample 50 bis 800-400 A. (A) Micro-XRF map, (B-D) BSE-SEM images of three selected particles.

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