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Innovative two-step isolation of Ni prior to stable isotope ratio measurements by MC-ICP-MS: application to igneous geological reference materials

Hugues Beunon, ^(D)*^a Stepan M. Chernonozhkin, ^(D)^b Nadine Mattielli,^a Steven Goderis, ^{(D) c} Luc-Serge Doucet,^d Vinciane Debaille^a and Frank Vanhaecke ^{(D) b}

Nickel stable isotope ratios have attracted a growing interest across the (bio)geochemical and environmental sciences since the late 2000s. Accuracy and precision of Multi-Collector Inductively Coupled-Plasma Mass Spectrometry (MC-ICP-MS) measurements depend crucially on efficient chemical purification of the target analyte to avoid spectral and non-spectral interferences and artificial oncolumn fractionation. In the case of Ni, this has been previously achieved by cumbersome chemical isolation protocols involving non-aqueous media, Ni-specific resin or complexing agent and up to five successive chromatographic columns. Since the advent of MC-ICP-MS, sample throughput in isotopic analysis has increased significantly, but the Ni isolation procedures do not allow for large numbers of samples to be processed. Advances in Ni isotope geochemistry have thus been relatively slow compared to those of other transition elements (e.g., Cu, Zn, Fe). Here, we present an innovative and straightforward two-step procedure for quantitative isolation of Ni from igneous silicate matrix prior to MC-ICP-MS analysis to help bridge that gap. Nickel is purified taking advantage of the selective adsorption of chemical elements from hydrochloric and acetic acids onto the widespread AG1-X8 (200-400 mesh) anion exchange resin, without using Ni-specific compounds nor pH-tuning. A single pass through the two successive columns results in a quantitative recovery (\geq 96%) of Ni as a pure Ni fraction, reducing preparation costs and time, eluent volumes and total procedural blank contribution (<0.25 ng). A set of 14 - both new and well-documented - igneous geological reference materials were processed and measured for their Ni isotopic composition using a Thermo Scientific™ Neptune™ MC-ICP-MS unit to consolidate and expand the pre-existing database of rock standards. All $\delta^{60/58}$ Ni data reported as the per mille deviation of ⁶⁰Ni/⁵⁸Ni from the NIST SRM 986 standard obtained in our study are in excellent agreement with those previously documented, indicating accurate determination of Ni isotope ratios. The overall precision of our method is estimated to be ca. $\pm 0.032\%$ (2SD) on $\delta^{60/58}$ Ni based on repeated analyses of the NIST SRM 986 and geological reference materials MUH-1 and JP-1.

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1. Introduction

Nickel is one of the most abundant element by mass in the solar system and exists in the form of five stable isotopes ⁵⁸Ni, ⁶⁰Ni, ⁶¹Ni, ⁶²Ni and ⁶⁴Ni with respective natural abundances of 68.1%, 26.2%, 1.1%, 3.6% and 0.9%.^{1,2} Initial work on Ni stable isotope ratios was confined to mass-independent fractionation

inherited from the short-lived and long extinct 60Fe-60Ni radioactive decay pair, as this system is a potentially powerful chronometer ($t_{1/2}$ of ⁶⁰Fe = 2.62 Myr (ref. 3)) and might have been an important heat source in the nascent Solar System.⁴⁻¹² Nickel mass-dependent stable isotope variations, on the other hand, have provided insights into a range of cosmochemical processes such as condensation, metal-silicate segregation and early planetary differentiation.13-21 Due to its siderophile tendency, ~93% of the terrestrial inventory of Ni is alloyed with iron in Earth's core.²² Yet, Ni is ubiquitous in the silicate Earth,²³ oceans24 and atmospheric system - where anthropogenic inputs are the dominant emission source.25 In this context, Ni stable isotope ratios have proven to be promising tracers of various low-temperature (bio)geochemical and environmental processes including ore deposit mineralization,26 weathering of



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^aLaboratoire G-Time, DGES, Université Libre de Bruxelles (ULB), Av. Roosevelt 50, CP 160/02, 1050 Brussels, Belgium. E-mail: hbeunon@ulb.ac.be

^bAtomic and Mass Spectrometry – A&MS Research Group, Department of Chemistry, Ghent University, Krijgslaan, 281 – S12, 9000 Ghent, Belgium

^cAnalytical, Environmental, and Geochemistry, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussels, Belgium

^dEarth Dynamics Research Group, TIGeR, Department of Applied Geology, Curtin University Perth, WA 6148, Australia

rocks at the Earth's surface,^{27–29} methanogenesis and the progressive rise of atmospheric oxygen,^{30–33} anthropogenic pollution^{34,35} and plant–soil interaction.^{36,37} Although stable isotope fractionation theoretically decreases proportional to 1/T,^{2,38} preliminary studies suggest that Ni isotope ratios are also sensitive to high-temperature processes such as magmatic differentiation and mantle metasomatism.^{16,39,40}

All of these applications demand highly accurate and precise determination of Ni isotope ratios by Multi-Collector Inductively Coupled-Plasma Mass Spectrometry (MC-ICP-MS). Isotope ratio measurements, however, can be dramatically affected by a number of spectral interferences (i.e., isobaric, polyatomic or doubly-charged ions with mass-to-charge ratios similar to those of the nuclides of interest) on top of matrix effects or nonspectral interfering species.41 Efficient and quantitative isolation of Ni from the sample matrix is thus a critical prerequisite for high-precision MC-ICP-MS analysis. This has been previously achieved by cumbersome chemical purification methodologies impaired by the very similar anion and cation exchange distribution coefficients of Ni, alkali and earth alkali elements in classic HCl-HNO3-HF-HBr media.42 Hence, existing Ni isolation techniques involve up to five successive ion exchange chromatographic steps and make use of a specific Ni resin or dimethylglyoxime (DMG) as a Ni-specific complexing agent, non-aqueous solvents (e.g., acetone) and/or organic reagents requiring careful pH tuning (e.g., ammonium oxalate and ammonium citrate).^{8,14,15,40,43-46} Relatively high blank contribution (up to 12 ng (ref. 43-45)) and significant Ni loss (i.e., 8-19% (ref. 40, 43-45)) are common issues introduced as a result of the multitude of isolation stages and reagents used. Double-spiking has been increasingly used to by-pass the incomplete recovery of Ni from the sample matrix, while correcting for the bias caused by instrumental mass discrimination in MC-ICP-MS. Although allowing to control unwanted on-column isotope fractionation, the double-spike technique only provides information on a single Ni isotope ratio and requires preliminary determination of optimal mixing proportions of the sample with carefully calibrated enriched isotope tracers.⁴⁷ Critically, the use of the mass-spectrometer for nucleosynthetic or geochronology applications may thus be compromised.

Here, a simple and alternative technique for quantitative extraction of Ni from igneous silicate matrix in just two successive chromatographic steps is reported. The proposed protocol exploits the selective adsorption of chemical elements from hydrochloric and acetic acid on the AG1-X8 (200-400 mesh) anion exchange resin and does not necessitate additional chemicals (e.g., Ni-specific resin or complexing agent, organic reagents, non-aqueous solvents). Blank contribution, chemical isolation efficiency, Ni recovery yields and on-column fractionation were carefully assessed and found fit-for-purpose in view of high-precision MC-ICP-MS Ni stable isotopic analysis. The method developed here is appropriate for high-precision Ni stable isotope analysis by MC-ICP-MS using a combination of Cu as an added internal standard and sample-standard bracketing for instrumental mass bias correction. Alternatively, this isolation method can be used with the double-spike technique. A set of 14 both new and well-documented igneous geological reference materials were processed and measured for their Ni stable isotopic composition to validate the methodology and consolidate the pre-existing database of rock standards.

2. Materials and methods

2.1 Reagents and standards

All laboratory work was carried out in a class-100 laminar flow hood of the class-1000 clean room facility at the Laboratoire G-Time (Université Libre de Bruxelles, Belgium). Concentrated reagents (HCl, HNO₃ and HF) were purified by double subboiling distillation in two-bottle Teflon stills, except for glacial acetic acid (hereafter referred as CH₃COOH), which was purchased from Sigma Aldrich™ as Emsure® grade and used as such. Specifically, laboratory work involving the use of CH₃-COOH was peformed in a class-100 laminar flow hood ducted to the outside atmosphere to ensure a well-ventilated workspace. Appropriate dilutions for ion exchange chromatography and MC-ICP-MS analyses were carried out with 18.2 M Ω cm grade Milli-Q (MQ) water. All consumable components (e.g., tips, centrifuge tubes and chromatography columns) were acidcleaned in 10% v/v HNO3 for 24 h and rinsed twice with MQ water before use. Teflon beakers (SavillexTM) were subjected to reflux cleaning with 6 M HCl and 14 M HNO₃ (two times).

Nickel isotope ratios are reported relative to the internationally accepted NIST SRM 986 standard acquired from the National Institute of Standards and Technology (NIST, U.S. Department of Commerce). An in-house Ni isotopic standard solution prepared by digestion of high-purity Ni metal from Sigma Aldrich[™] was also processed alongside samples to verify the reproducibility of all the measurement sessions throughout this work.

2.2 Sample preparation and digestion

A set of 14 igneous geological reference materials from the United States Geological Survey (USGS), the Geological Survey of Japan (GSJ), the Centre de Recherches Pétrographiques et Géochimiques (CRPG), the International Association of Geoanalysts (IAG), the Council for Mineral Technology (MINTEK), the Smithsonian Institute (SI) and Natural Resources of Canada (NRCAN) were selected for Ni isotopic analysis. The selected geostandard materials display a wide range of silicate matrix compositions and Ni concentrations ranging from 119 μ g g⁻¹ to 1.42 wt% (GeoReM⁴⁸ recommended values). These include: four peridotites (PCC-1, USGS; JP-1, GSJ; MUH-1, IAG; WPR-1, NRCAN); three dunites (DTS-1 and DTS-2b, USGS; SARM6, MINTEK); one pyroxenite (SARM5, MINTEK); two serpentinites (UB-N, CRPG; SARM47, MINTEK); two basalts (BHVO-2, BIR-1, USGS); one kimberlite (SARM39, MINTEK); and one carbonaceous chondrite (Allende, SI).

For each material, ~100 mg of powdered sample was dissolved using a 1 : 1 mix of concentrated HF and HCl in a closed square-bodied screw-top Teflon beaker (SavillexTM) on a hotplate at 160 °C for 5 days. Samples were then dried down and further attacked with a 3 : 1 mix of concentrated HCl and HNO₃ (*aqua regia*) for 3 days at 150 °C. This procedure ensures complete dissolution of refractory phases (*e.g.*, spinel) and/or Ca, Mg fluoride complexes. After total digestion, samples were evaporated to dryness and converted into the chloride form by treating the digest with 1 mL of 6 M HCl at 100 °C, followed by evaporation to dryness at 90 °C. The Cl-converted rock residues were allowed to equilibrate with 1 mL of 6 M HCl overnight at 90 °C on a hotplate, ready for chromatographic isolation of Ni.

2.3 Chemical purification of Ni

Quantitative separation of Ni from the rock matrix was achieved by an innovative two-step anion exchange chromatographic procedure (Table 1). The two successive elution stages use the same 0.8×4 cm Bio-Spin® polypropylene column filled with 1 mL of AG1-X8 (200–400 mesh) strongly basic anion exchange resin in chloride form obtained from Bio-RadTM. The entire Ni isolation scheme can be carried out using one and the same column, as long as the resin is thoroughly rinsed in-between the two consecutive steps.

2.3.1 First stage. In the first ion exchange stage, Ni is separated from Cu, Fe, Zn and Cd \pm Co within the sample matrix. These are potential parent elements of isobaric, polyatomic or doubly-charged ions interfering with ⁵⁸Ni, ⁶⁰Ni, and/ or ⁶⁴Ni. The first isolation step follows the protocol described by Sossi et al. (2015)49 and relies on differences in partition behavior between the anion exchange resin and the HCl medium used as mobile phase as determined experimentally.50 The AG1-X8 resin (200-400 mesh) was pre-cleaned by rinsing with, successively, 5 mL volumes of MQ H₂O, 3 M HNO₃, MQ H₂O, 3 M HNO₃ and MQ H₂O. The resin was further rinsed and pre-conditioned with 5 mL of 6 M HCl. Then, the 1 mL sample solution in 6 M HCl matrix was loaded onto the column, following centrifugation in a polypropylene test tube. Nickel is eluted immediately and was quantitatively stripped from the column with an additional 4 mL of 6 M HCl. The total loading volume plus the rinsing elution cut were collected into a clean

Teflon vial and dried down at 90 °C. The residue was treated by two cycles of addition of 100 μ L of 14 M HNO₃ and evaporation at 90 °C (two times) to expel potential organic species originating from the resin and to ensure the reduction of Cr(vi) to Cr(m) (ref. 51) for subsequent Ni purification. Finally, the remaining sorbed elements were washed off the resin bed with 10 mL of 3 M HNO₃. Alternatively, Cu, Fe and Zn can be recovered for combined isotopic measurements with 15 mL 6 M HCl, 10 mL 0.5 M HCl and 10 mL 3 M HNO₃, respectively.⁴⁹

2.3.2 Second stage. In the second ion exchange stage, the Ni fraction is further purified from matrix elements which are eluted alongside Ni during step one (e.g., Ca, K, Al, Mg, Sn, Co, Ti, Sc, P, V, Cr, Mn) by exploiting the selective sorptivity of the anion exchange resin in CH₃COOH media as determined experimentally.^{52,53} The column packed with 1 mL AG1-X8 resin (200-400 mesh) used to perform the first stage was cleaned by alternatingly passing 5 mL volumes of MQ H₂O, 3 M HNO₃, MQ H₂O, 6 M HCl, MQ H₂O and pre-conditioned with 5 mL of 100% v/v CH₃COOH. The dried Ni fraction obtained after stage one was taken up in 1 mL of 100% v/v CH₃COOH and placed in an ultrasonic bath for 30 minutes to promote sample dissolution. In some cases, a white, insoluble residue was still present after centrifugation - likely due to the difficulty to obtain solutions for certain elements (e.g., Ti, V) in acetic acid.52,53 However, this insoluble residue was found to contain no Ni (see Section 3.1.3 on recovery yields). Then, the 1 mL sample solution in 100% v/v CH₃COOH matrix was transferred into a polypropylene test tube, centrifuged and loaded onto the column. The resin was subsequently rinsed with 24 mL of 100% v/v CH₃COOH, eluting most matrix elements of the sample. Nickel was then quantitatively collected in a clean Teflon beaker by passing 15 mL of 95% v/v CH₃COOH. Remaining matrix elements (i.e., V, Co) sorbed onto the resin were washed off with 5 mL of 3 M HNO₃ and the column was rinsed following the same cleaning steps aforementioned in Section 2.3.1 for future re-use. Nickel cuts

Table 1 Two-step elution scheme for Ni using the strongly basic AG1-X8 (200-400 mesh) anion exchange resin in chloride form

		Volumo
Step I	Eluent	(mL)
Resin cleaning	MQ H ₂ O-3 M HNO ₃ -MQ H ₂ O-3 M HNO ₃ -MQ H ₂ O	5×5
Equilibration	6 M HCl	5
Sample load, Ni elution	6 M HCl	1
Ni elution	6 M HCl	4
Cu elution	6 M HCl	15
Fe elution	0.5 M HCl	10
Zn elution	3 M HNO ₃	10
Step II	Eluent	Volume (mL)
Pagin algoning		
Equilibration	$MQ H_2O-3 M HNO_3-MQ H_2O-6 M HOI-MQ H_2O$	5 × 5 F
	100% V/V CH ₃ COOH	5
Sample load	100% V/V CH ₃ COOH	1
Matrix elution	100% v/v CH ₃ COOH	24
Ni elution	95% v/v CH ₃ COOH	15
Resin rinsing	3 M HNO ₃	5

were dried down, re-dissolved in 100 μ L of concentrated HNO₃ to oxidise and remove any potential organic compounds leached from the resin and evaporated to dryness again. Finally, the Ni fraction was brought into solution in 3% v/v HNO₃ ready for MC-ICP-MS measurements.

2.4 Mass spectrometry

All mass spectrometry measurements were performed at the A&MS research group facility (Ghent University, Belgium). Determination of element concentrations was achieved using a Thermo ScientificTM Element XRTM sector field ICP-MS. Quantification was accomplished *via* internal standardization and external calibration, correcting for matrix effects and signal instability. When needed, spectral interferences were resolved using medium and high mass resolution modes (*i.e.*, $m/\Delta m = 4000$ and 10 000, respectively).

Nickel isotopic analysis was carried out using a Thermo ScientificTM NeptuneTM MC-ICP-MS unit equipped with a PfiefferTM OnToolTM Booster 150 dry interface pump (130 m³ h⁻¹ pumping speed) and high transmission "jet" interface, following the modified method of Chernonozhkin *et al.* (2015).⁴⁵ Samples and standards were diluted to 500 ng mL⁻¹ in 3% v/v

⁵⁷Fe

HNO3 and introduced into the ICP using a combination of a 200 μ L min⁻¹ pneumatic nebulizer and a double-pass spray chamber with cyclonic and Scott-type sub-units ("wet plasma" mode). High mass resolution mode was used, resulting in a beam intensity of *ca.* 12–15 V for ⁵⁸Ni. As the peak shoulder plateau is typically not observed when measuring pure Ni solutions, accurate determination of the m/z position for measurements was best achieved using a 500 ng mL⁻¹ NIST SRM 986 standard solution doped with 3 μ g mL⁻¹ of Mg, Ca and Ti (*i.e.*, in a X : Ni ratio of 6) before each analysis sequence. All Ni and Cu masses of interest (⁵⁸Ni, ⁶⁰Ni, ⁶¹Ni, ⁶²Ni, ⁶³Cu and ⁶⁵Cu) were monitored in static multicollection mode, as well as ⁵⁷Fe to correct for the overlap of the ⁵⁸Fe and ⁵⁸Ni signals. The bias caused by instrumental mass discrimination was corrected for by combination of internal correction using admixed Cu and external correction relying on sample-standard bracketing with NIST SRM 986.45,54 A summary of Neptune™ MC-ICP-MS instrument settings, data acquisition parameters and the multi-collector detector configuration used is provided in Table 2. Mass-dependent Ni isotope ratio variations are expressed in the delta notation ($\delta^{i/58}$ Ni in per mille, where i =60, 61, 62 or 64) relative to the NIST SRM 986 standard and following the conventional equation from Hoefs (2018):41

Table 2 Summary of Thermo Scientific[™] Neptune[™] MC-ICP-MS instrument settings, data acquisition parameters and multi-collector detector configuration

Instrument settings										
RF power, W		1200								
Gas flow rates, $L \min^{-1}$	Sample	1.025								
	Auxiliary	0.85								
	Cooling	15.0								
Interface	Interface pumping	High-efficiency dry interface pump (130 m ³ h ⁻¹ pumping speed)								
	Sampler cone	Jet type Ni cone: 1.0 mm actual aperture ϕ								
	Skimmer cone	X-type Ni cone: 0.7 mm actual aperture ϕ								
Sample uptake		Pumped via	peristaltic pump	, approximatel	y 0.1 mL min ^{-1}	1				
Nebulizer	Concentric. 100 μ L min ⁻¹									
Spray chamber		Double-pass	Double-pass, with cyclonic and Scott-type sub-units							
Resolution mode	High ^a									
Concentration	500 ng mL^-	¹ of both Ni and	Cu, fitted to th	e bracketing st	andards within	$\pm 3\%$				
Typical sensitivity		12–15 V of ⁵⁸ Ni for 500 ng mL ^{-1} Ni solution								
Data acquisition										
Mode		Static, multi	-collection							
Idle time, s		3								
Integration time, s		4.194								
Number of integrations		1								
Number of blocks		4								
Number of cycles per block	12									
Baseline	300 s baseline every 20 samples									
Instrumental mass fractionation correction		Baxter's internal correction using $Cu + SSB^b$								
Cup configuration for Ni is	otope ratio measurements									
Cup	- L4	L2	L1	С	H1	H2	H4			
Amplifier	$10^{12}\Omega$	$10^{11}\Omega$	$10^{11}\Omega$	$10^{12}\Omega$	$10^{11}\Omega$	$10^{11}\Omega$	$10^{11}\Omega$			

 $a^{a} \Delta m$ for pseudo-high resolution in MC-ICP-MS is defined as the mass difference between $m_{5\%}$ and $m_{95\%}$, corresponding to 5% and 95% of the signal intensity level on the plateau, respectively. A resolving power of ~10 000 is achieved in HR mode. Such a definition of resolving power exceeds that based on atomic mass difference by more than a factor of two.⁷² ^b Correction of instrumental mass fractionation is performed following a revised exponential model of Baxter *et al.* (2006),⁵⁴ using the isotope ratio of admixed Cu as an internal standard, followed by sample standard bracketing with NIST SRM 986, as described previously in Chernonozhkin *et al.* (2015).⁴⁵

⁶⁰Ni

⁶¹Ni

⁵⁸Ni, ⁵⁸Fe

Nuclide

⁶³Cu

⁶⁵Cu

⁶²Ni

$$\delta^{i/58} \mathrm{Ni} = \left(\frac{({}^{i}\mathrm{Ni}/{}^{58}\mathrm{Ni})_{\mathrm{Cu\ corr,\ sample}}}{({}^{i}\mathrm{Ni}/{}^{58}\mathrm{Ni})_{\mathrm{Cu\ corr,\ NIST\ SRM\ 986}}} - 1 \right) \times 1000 \quad \text{(I)}$$

3. Results and discussion

3.1. Two-step separation of Ni

Geological materials typically exhibit subtle, but resolvable Ni isotope ratio variations on the 1/10 000 level relative to the NIST SRM 986 standard. To achieve the required level of analytical precision, (1) a low blank contribution, (2) high-purity Ni fractions and (3) quantitative target element recovery are crucial features that must be assessed prior to MC-ICP-MS analysis.^{41,55}

3.1.1 Blank contribution. The total procedural blank contribution for the procedure presented here is <0.25 ng. Such blank levels are substantially lower than those reported for previous Ni isolation schemes (0.4–12 ng (ref. 40, 43–45)) and negligible compared to the total amount of Ni loaded on the columns (\sim 5 to 100 µg, blank contribution \ll 1%). Hence, the procedure presented here is found to be suitable even for samples with low Ni contents.

3.1.2 Chemical isolation efficiency. Ni isotopic analysis can be subject to a number of spectral interferences (caused by isobaric, polyatomic or doubly charged ions) and other matrixbased effects^{41,56} (Table 3). The ⁵⁷Fe beam intensity was monitored to apply a mathematical correction for the contribution of the ⁵⁸Fe isobaric interference on ⁵⁸Ni based on the natural ⁵⁷Fe/⁵⁸Fe ratio and the ⁶⁵Cu/⁶³Cu fractionation exponent derived



Fig. 1 (a and b) Experimentally determined elution profiles for MUH-1 (peridotite, USGS) for the first (a) and second (b) AG1-X8 (200–400 mesh) anion exchange stages of the Ni isolation scheme presented here. Note that relative eluted fractions (%) are displayed as a ridgeline plot.

from Russel's exponential law.⁵⁴ However, the ⁵⁷Fe signal intensity was found to be comparable in samples and pure artificial Ni standard solutions, indicating nearly complete Fe removal from the analyzed solutions and thus insignificant contribution of ⁵⁸Fe on ⁵⁸Ni (*e.g.*, ⁵⁸Fe : ⁵⁸Ni ~10⁻⁵ to 10⁻⁶). High-precision measurements of ratios involving ⁶⁴Ni are hampered by the large isobaric

Table 3	Representative matrix removal efficiency for MUH-1 (peridotite, USGS) and spectral interferences potentially affecting the measurement
of Ni isc	otope ratios. ⁴⁵ Initial concentrations X _{initial} (μ g g ⁻¹) and X : Ni _{initial} ratios in MUH-1 are from GeoRem. ⁴⁸ X : Ni _{x1 col} and X : Ni _{x2 col} are
element	t-to-Ni mass ratios after one and two passes of the second purification step in CH_3COOH medium, respectively

Element	$X_{initial}\left(\mu g \; g^{-1}\right)$	X : Ni initial	X : Ni <i>x</i> 1	X : Ni, <i>x</i> 2 col	Potential spectral interferences ^a
Ni	2104	_	_	_	60 Ni ¹ H ⁺ , 61 Ni ¹ H ⁺
Mg	230672	$1 imes 10^2$	$5 imes 10^{0}$	$1 imes 10^{-1}$	${}^{26}Mg^{32}S^{+}, {}^{25}Mg^{33}S^{+}, {}^{24}Mg^{34}S^{+}, {}^{36}Ar^{24}Mg^{+},$ ${}^{26}Mg^{34}S^{+}, {}^{36}Ar^{25}Mg^{+}, {}^{38}Ar^{24}Mg^{+},$ ${}^{36}c, {}^{26}c, {}^{+}40, {}^{24}c, {}^{+}b, {}^{38}a, {}^{26}c, {}^{+}b,$
Fe	60 083	$2 imes 10^1$	$4 imes 10^{-2}$	$2 imes 10^{-2}$	⁵⁸ Fe, ⁵⁷ Fe ¹ H ⁺
Ca	8669	$4 imes 10^{0}$	$8 imes 10^{-1}$	$6 imes 10^{-2}$	${}^{42}\text{Ca}^{16}\text{O}^+, {}^{40}\text{Ca}^{18}\text{O}^+, {}^{44}\text{Ca}^{14}\text{N}^+, {}^{43}\text{Ca}^{15}\text{N}^+, \\ {}^{44}\text{Ca}^{16}\text{O}^+, {}^{43}\text{Ca}^{17}\text{O}^+, {}^{42}\text{Ca}^{18}\text{O}^+, {}^{46}\text{Ca}^{14}\text{N}^+, \\ {}^{44}\text{Ca}^{17}\text{O}^+, {}^{43}\text{Ca}^{18}\text{O}^+, {}^{46}\text{Ca}^{16}\text{O}^+, {}^{44}\text{Ca}^{18}\text{O}^+, \\ {}^{48}\text{Ca}^{14}\text{N}^+, {}^{48}\text{Ca}^{16}\text{O}^+, {}^{46}\text{Ca}^{18}\text{O}^{+b} $
Al	7060	$3 imes 10^{0}$	$6 imes 10^{-2}$	$2 imes 10^{-3}$	${}^{27}\text{Al}{}^{31}\text{P}^+$, ${}^{27}\text{Al}{}^{34}\text{S}^+$, ${}^{27}\text{Al}{}^{37}\text{Cl}^+$
Cr	2710	$1 imes 10^{0}$	$4 imes 10^{-2}$	$5 imes 10^{-4}$	${}^{50}\mathrm{Cr}^{14}\mathrm{N}^{+b}$
Na	772	$4 imes 10^{-1}$	<d.l.< td=""><td><d.l.< td=""><td>$^{38}Ar^{23}Na^{+}$</td></d.l.<></td></d.l.<>	<d.l.< td=""><td>$^{38}Ar^{23}Na^{+}$</td></d.l.<>	$^{38}Ar^{23}Na^{+}$
Ti	206	1×10^{-1}	$3 imes 10^{-2}$	$3 imes 10^{-3}$	${}^{46}\text{Ti}^{14}\text{N}^+, {}^{47}\text{Ti}^{14}\text{N}^+, {}^{46}\text{Ti}^{15}\text{N}^+, {}^{46}\text{Ti}^{16}\text{O}^+, \\ {}^{48}\text{Ti}^{14}\text{N}^+, {}^{47}\text{Ti}^{15}\text{N}^+, {}^{48}\text{Ti}^{16}\text{O}^+, {}^{b}{}^{46}\text{Ti}^{18}\text{O}^+, {}^{b}, \\ {}^{47}\text{Ti}^{17}\text{O}^+, {}^{b}{}^{50}\text{Ti}^{14}\text{N}^+, {}^{b}{}^{49}\text{Ti}^{15}\text{N}^{+b}$
Со	107	$5 imes 10^{-2}$	$6 imes 10^{-4}$	$7 imes 10^{-6}$	⁵⁹ Co ¹ H ⁺
К	100	$5 imes 10^{-2}$	$3 imes 10^{-3}$	$7 imes 10^{-5}$	${}^{41}\text{K}{}^{17}\text{O}^+, {}^{4}\text{K}{}^{18}\text{O}^+$
Zn	45	$2 imes 10^{-2}$	$2 imes 10^{-2}$	$6 imes 10^{-3}$	64 Zn ^b
v	41	$2 imes 10^{-2}$	$5 imes 10^{-4}$	$6 imes 10^{-6}$	${}^{50}\mathrm{V}^{14}\mathrm{N}^{+b}$
Cu	19	$9 imes 10^{-3}$	$1 imes 10^{-2}$	$5 imes 10^{-3}$	⁶³ Cu ¹ H ⁺ , ^b ⁴⁷ Ti ¹⁶ O ⁺ , ^c ⁴⁶ Ti ¹⁶ O ¹ H ⁺ , ^c ⁴⁸ Ti ¹⁶ O ¹ H ⁺ , ^c ⁴⁹ Ti ¹⁶ O ^{+c}
Cd	0.051	$2 imes 10^{-5}$	$3 imes 10^{-3}$	$1 imes 10^{-3}$	$^{116}Cd^{2+}$

^{*a*} Non-exhaustive list. ^{*b*} Spectral interferences potentially affecting ⁶⁴Ni; this nuclide is not considered in this study. ^{*c*} Spectral interferences potentially affecting the ⁶⁵Cu/⁶³Cu ratio used for instrumental mass bias correction.⁷³

Table 4 Summary of Ni isotopic compositions ($\delta^{i/58}$ Ni, ∞) of the geological reference materials analyzed in this work compared to previous studies. All Ni isotope ratios are expressed relative to the NIST SRM 986 standard. Uncertainty is given as 2SD (see Section 3.3 for details). Also provided are the number of replicates (*n*) for the isotopic analyses, Ni concentrations from GeoRem⁴⁸ (μ g g⁻¹) and recovery yields (∞) from this study

Allende Carbonaceous chondrite 14 200 93.3 $+0.349 \pm 0.032$ $+0.392 \pm 0.048$ $+0.479 \pm 0.064$ 3 This study Carbonaceous chondrite $+0.249 \pm 0.078$ $+0.322 \pm 0.078$ $+0.322 \pm 0.078$ $+0.329 \pm 0.064$ 3 This study BiR-1 166 96.5 $+0.149 \pm 0.032$ $+0.323 \pm 0.048$ $+0.329 \pm 0.064$ 2 Rhis study Basalt 166 96.5 $+0.149 \pm 0.032$ $+0.323 \pm 0.048$ $+0.329 \pm 0.064$ 2 Rhis study HIVO-2 119 97.1 $-0.021 + 0.032$ $+0.022 + 0.044$ $+0.028 \pm 0.048$	Sample	Ni ($\mu g g^{-1}$)	Yield (%)	$\delta^{60/58}$ Ni (‰, 2SD)	$\delta^{61/58}$ Ni (‰, 2SD)	$\delta^{62/58}$ Ni (‰, 2SD)	n	References ^{<i>a</i>}
Carbonaccous chondrine 9.0242 0.018 8.8 Rever. <i>i.d.</i> , 2010 BIR-1 166 9.5 0.019 0.003 10.323 ± 0.048 40.329 ± 0.04 2 Summerical value Basah 10.10 ± 0.058 -0.119 ± 0.058 -0.214 ± 0.303 10.323 ± 0.048 40.329 ± 0.041 2 Summerical value BirN-1 10.01 ± 0.051 -0.010 ± 0.071 -0.051 -0.010 ± 0.071 -0.010 ± 0.071 -0.010 ± 0.071 -0.010 ± 0.071 -0.010 ± 0.071 -0.010 ± 0.071 -0.008 ± 0.060 -0.010 ± 0.071 -0.010 ± 0.071 -0.008 ± 0.060 -0.010 ± 0.071 -0.008 ± 0.061 -0.008 ± 0.061 -0.008 ± 0.061 -0.008 ± 0.061 -0.008 ± 0.061 -0.008 ± 0.061 -0.008 ± 0.061 -0.008 ± 0.061 -0.008 ± 0.061 -0.008 ± 0.061 -0.008 ± 0.061 -0.008 ± 0.011 -0.008 ± 0.011 -0.018 ± 0.013 -0.018 ± 0.018 -0.018 ± 0.018 -0.018 ± 0.018 -0.018 ± 0.018 -0.018 ± 0.018 -0.018 ± 0.018 -0.018 ± 0.018 -0.018 ± 0.018 -0.018 ± 0.018 -0.018 ± 0.018 -0.018 ± 0.018 -0.018 ± 0.018 -0.018 ± 0.018 -0.018 ± 0.018 -0.018 ± 0.018 -0	Allende	14 200	99.3	+0.240 \pm 0.032	+0.392 \pm 0.048	+0.479 \pm 0.064	3	This study
BIR-1 16 9-242 + 0.078 +0.219 + 0.030 9-0.33 ± 0.048 +0.232 ± 0.048 40.32 ± 0.048 +0.232 ± 0.048 40.32 ± 0.048 +0.22 ± 0.048 40.32 ± 0.048 +0.32 ± 0.048 40.32 ± 0.048 +0.32 ± 0.048 10.30 ± 0.071 +0.019 ± 0.035 +0.019 ± 0.035 Bissalt 119 0.71 0.021 ± 0.032 +0.030 ± 0.071 +0.106 ± 0.071 40.32 ± 0.048 +0.022 ± 0.048 40.32 ± 0.048 +0.022 ± 0.048 40.32 ± 0.048 +0.022 ± 0.048 60 Gall, 201 Bissalt 119 0.71 0.012 ± 0.032 +0.005 ± 0.071 40.054 +0.005 ± 0.071 60 Gall, 201 Bissalt 10.00 ± 0.017 +0.005 ± 0.071 -0.010 ± 0.042 +0.005 ± 0.018 40.32 ± 0.054 +0.028 ± 0.014 60 Gall, 201 Bissalt 10.00 ± 0.017 +0.005 ± 0.017 -0.010 ± 0.042 +0.015 ± 0.068 -0.012 ± 0.028 +0.015 ± 0.068 11 ± 6.12 +0.015 ± 0.068 11 ± 6.12 +0.014 ± 0.018 11 ± 6	Carbonaceous chondrite			$+0.243 \pm 0.018$			8	Klaver <i>et al.</i> , 2020
BIR-1 160 10-20 ± 0.073 -0.23 ± 0.030 -0.23 ± 0.040 2.0 This study Basalit 160 -0.14 ± 0.050 -0.23 ± 0.040 2.0 Chernonochkin et al., 2015 Basalit -0.16 ± 0.051 -0.16 ± 0.051 -0.16 ± 0.051 -0.16 ± 0.051 BirV0-2 119 7.1 0.021 ± 0.030 -0.060 ± 0.048 4.028 ± 0.064 2.0 Chernonochkin et al., 2015 BirV0-2 119 7.1 0.021 ± 0.030 -0.060 ± 0.048 4.028 ± 0.064 2.0 Chernonochkin et al., 2015 BirV0-2 119 7.1 0.021 ± 0.033 -0.060 ± 0.048 4.028 ± 0.064 2.0 Chernonochkin et al., 2015 BirV0-2 119 7.1 0.021 ± 0.033 -0.060 ± 0.048 4.028 ± 0.064 2.0 Chernonochkin et al., 2015 BirV0-2 119 7.0 0.011 ± 0.033 -0.060 ± 0.014 0.023 ± 0.014 2.0 Chernonochkin et al., 2015 BirV0-2 119 0.012 ± 0.013 0.017 ± 0.018 0.230 ± 0.014 10.21 ± 0.018 3.0 10.21 ± 0.018 BirV0-2 2.0019 0.012 ± 0.013 0.021 ± 0.018 10.21 ± 0.018 10.21 ± 0.018 10.21 ± 0.018 10.21 ± 0.018 10.21 ± 0.018 10.21 ± 0.018 10.21 ± 0.018 10.21 ± 0.018<				$+0.242 \pm 0.078$			9	Gall et al., 2017
BIR-1H0.241 + 0.030H0.252 ± 0.048H0.232 ± 0.048<				$+0.210 \pm 0.078$			_	Gall, 2011
BIR-1 166 96.5 40.147 ± 0.053 40.323 ± 0.048 40.329 ± 0.064 2 Statistudy Basalt -61.91 ± 0.055 -0.120 ± 0.061 -8 Chernonzokine et al. 2015 HVD-2 119 97.1 -0.021 ± 0.032 40.066 ± 0.048 40.28 ± 0.064 2 Statistudy Basalt -0.010 ± 0.071 -0.021 ± 0.032 40.066 ± 0.048 40.28 ± 0.064 2 Statistudy Basalt -0.010 ± 0.071 -0.021 ± 0.032 -0.010 ± 0.071 3 Gall et al., 2012 Basalt -0.030 ± 0.075 -0.021 ± 0.032 -0.010 ± 0.071 3 Gall et al., 2013 Basalt -0.020 ± 0.076 -0.021 ± 0.032 -0.171 ± 0.048 -0.230 ± 0.064 3 Statistudy Basalt -0.020 ± 0.076 -0.023 ± 0.064 -0.230 ± 0.064 3 Statistudy Hirzburgite -0.010 ± 0.074 -0.023 ± 0.064 -0.230 ± 0.064 -0.230 ± 0.064 -0.230 ± 0.064 -0.230 ± 0.064 -0.230 ± 0.064 -0.230 ± 0.064 -0.230 ± 0.064 -0.230 ± 0.064 -0.230 ± 0.064 -0.230 ± 0				$\textbf{+0.241} \pm \textbf{0.030}$				Recommended value
Basalt 10.17 ± 0.063 2 Saunders, 2018 H191 ± 0.054 2 Chernonzlkin et al., 2013 BHVO-2 119 97.1 -0.021 ± 0.061 80.9 Basalt 10.160 ± 0.071 40.060 ± 0.048 40.028 ± 0.064 8 Basalt -0.021 ± 0.032 40.060 ± 0.048 40.028 ± 0.064 6 Wat et al., 2015 Basalt -0.021 ± 0.032 40.060 ± 0.041 6 Wat et al., 2019 8 Basalt -0.010 ± 0.071 -0.010 ± 0.076 3 16 8 6 9.001 8 10.020 ± 0.076 3 16 8 10.010 ± 0.011 10.010 ± 0.011 10.010 ± 0.011 10.010 ± 0.011 10.010 ± 0.011 10.010 ± 0.011 10.010 ± 0.011 10.010 ± 0.011 10.010 ± 0.011 10.010 ± 0.011 10.010 ± 0.011 10.010 ± 0.011 10.011 ± 0.018 10.010 ± 0.011 10.010 ± 0.011 10.010 ± 0.011 10.010 ± 0.011 10.010 ± 0.011 10.010 ± 0.011 10.010 ± 0.011 10.010 ± 0.011 10.010 ± 0.011 10.010 ± 0.011 10.010 ± 0.011 10.010 ± 0.011 10.010 ± 0.011 10.010 ± 0.011 10.010 ± 0.011 10.010 ± 0.013 10.0101 ± 0.013	BIR-1	166	96.5	+0.169 \pm 0.032	+0.323 \pm 0.048	+0.329 \pm 0.064	2	This study
HWO-211997.1 -0.21 ± 0.051 -0.61 ± 0.054 -0.028 ± 0.064 -0.029 ± 0.064 -0.19 ± 0.064 -0.19 ± 0.064 -0.19 ± 0.064 -0.19 ± 0.054 -0.103 ± 0.075 -0.023 ± 0.064 $-0.113 \pm 0.023 \pm 0.064$ -0.103 ± 0.063 $-0.113 \pm 0.023 \pm 0.064$ -0.103 ± 0.048 -0.104 ± 0.048 -0.1	Basalt			+0.147 \pm 0.085			22	Saunders, 2018
BHV0-2 19 97.1 -0.021 ± 0.032 +0.060 ± 0.048 +0.028 ± 0.04 2 Geommended value Basalt 119 97.1 -0.021 ± 0.032 +0.060 ± 0.048 +0.028 ± 0.048 2 This study Basalt -0.01 ± 0.071 -0.03 ± 0.078 -0.010 ± 0.071 6 W et al., 2013 Basalt -0.010 ± 0.071 -0.030 ± 0.078 -0.010 ± 0.071 6 W et al., 2013 -0.021 ± 0.078 -0.030 ± 0.078 -0.030 ± 0.078 -0.030 ± 0.078 1 I at al., 2013 -0.021 ± 0.078 -0.020 ± 0.078 -0.021 ± 0.048 +0.230 ± 0.064 1 Recommended value -0.012 ± 0.078 -0.072 ± 0.078 - - Gall, 2011 Recommended value -0.012 ± 0.078 +0.127 ± 0.048 +0.230 ± 0.060 +0.197 ± 0.072 4 This study Harzburgite 2460 92.2 +0.127 ± 0.048 +0.230 ± 0.061 1 This study Harzburgite 2460 93.3 +0.127 ± 0.048 +0.227 ± 0.061 3 This study				$+0.191 \pm 0.058$			2	Chernonozhkin <i>et al.</i> , 2015
				$+0.120 \pm 0.061$			3	Gueguen <i>et al.</i> , 2013
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$				$+0.130 \pm 0.078$			68	Gall, 2012
BrVO-2 119 9'.1 -0.001 ± 0.032 *0.003 ± 0.043 *0.003 ± 0.044 2 Ims study Basalt -0.001 ± 0.052 -0.0071 6 Firstad et al., 2015 6 Wu et al., 2015 Basalt +0.003 ± 0.078 -0.014 ± 0.058 5 Chernonezkhin et al., 2015 6 Wu et al., 2015 Harden et al., 2012 +0.005 ± 0.078 -0.014 ± 0.058 5 Permoneckhin et al., 2015 +0.005 ± 0.078 +0.016 ± 0.005 -0.078 1 I at al., 2012 1 I at al., 2015 +0.015 ± 0.089 +0.0171 ± 0.048 +0.023 ± 0.064 -0.033 I is study - Gall, 2011 Recommended value IP-1 2460 99.2 +0.171 ± 0.048 +0.230 ± 0.064 - This study - Gall, 2011 - Gall, 2019 + + 1.13 ± 0.032 +0.171 ± 0.048 +0.230 ± 0.064 - I is study' Harzburgite +0.134 ± 0.058 +0.171 ± 0.048 +0.127 ± 0.072 4 This study PCC-1 2380 93.3	DIN/O A	110	07.1	$+0.160 \pm 0.054$			•	Recommended value
Basin -0.000 ± 0.073 0.000 ± 0.078 0.000 ± 0.0078 0.001 ± 0.006 0.002 ± 0.006 0.002 ± 0.0060 0.002 ± 0.0060 0.002 ± 0.0060 0.002 ± 0.0060 0.101 ± 0.0064 0.101 ± 0.0044 0.103 ± 0.018 0.002 ± 0.0060 0.107 ± 0.0072 4 This studyHarzburgite 0.078 0.078 0.012 ± 0.0660 0.197 ± 0.077 4 This study 1 1 1 0.012 ± 0.018 1 </td <td>BHVO-2 Recelt</td> <td>119</td> <td>97.1</td> <td>-0.021 ± 0.032</td> <td>$\pm 0.060 \pm 0.048$</td> <td>$\pm 0.028 \pm 0.064$</td> <td>2</td> <td>Fistrada at al. 2015</td>	BHVO-2 Recelt	119	97.1	-0.021 ± 0.032	$\pm 0.060 \pm 0.048$	$\pm 0.028 \pm 0.064$	2	Fistrada at al. 2015
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Dasan			-0.010 ± 0.071 $\pm 0.030 \pm 0.078$			6	$\frac{1}{2019}$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				$+0.030 \pm 0.078$ $+0.083 \pm 0.058$			5	Chernonozhkin <i>et al</i> 2015
PCC-1 2360 93.3 0.032 0.042 3 11 et al., 2013 JP-1 2460 92.2 0.012 0.012 0.012 0.020 0.013 10 et al., 2015 Harzburgite 2460 92.2 0.012 0.012 0.012 0.020				$+0.050 \pm 0.078$			31	Gall <i>et al.</i> , 2012
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				$+0.006 \pm 0.061$			8	Gueguen <i>et al.</i> , 2013
P1-1 2460 9.2 40.015 ± 0.089 +0.028 ± 0.085 +0.079 ± 0.078 +0.012 ± 0.032 40.171 ±±0.048 +0.222 ± 0.055 +0.203 ± 0.036 +0.111 ± 0.022 40.230 ± 0.064 +0.121 ± 0.048 +0.121 ± 0.018 +0.121 ± 0.022 This study (average) +0.120 ± 0.060 +0.197 ± 0.072 4 This study +0.111 ± 0.022 +0.120 ± 0.060 10.171 ±±0.048 +0.222 ± 0.055 +0.102 ± 0.056 40.233 ± 0.033 +0.120 ± 0.078 4 This study +0.130 ± 0.078 +0.130 ± 0.078 +0.130 ± 0.078 3 11 ± d. 2.015 +0.100 ± 0.084 +0.124 ± 0.018 +0.124 ± 0.018 +0.124 ± 0.018 +0.124 ± 0.018 +0.124 ± 0.018 +0.120 ± 0.078 +0.110 ± 0.061 +0.120 ± 0.078 +0.110 ± 0.061 +0.120 ± 0.078 +0.110 ± 0.078 +0.110 ± 0.061 +0.050 ± 0.078 +0.110 ± 0.061 +0.120 ± 0.06				$+0.020 \pm 0.078$			3	Li <i>et al.</i> , 2020
JP-1 2460 90.2 +0.075 ± 0.089 - 5 Pasava et al., 2019 Harzburgite 2460 92.2 +0.072 ± 0.032 +0.171 ±±0.048 +0.230 ± 0.064 This study Harzburgite 2460 92.2 +0.171 ±±0.048 +0.230 ± 0.056 +0.263 ± 0.038 3 This study Harzburgite +0.143 ± 0.018 +0.222 ± 0.056 +0.263 ± 0.037 4 This study +0.143 ± 0.018 +0.127 ± 0.032 +0.127 ± 0.036 +0.197 ± 0.072 4 This study +0.143 ± 0.018 +0.127 ± 0.035 1 Chernonzhkin et al., 2010 1 Chernonzhkin et al., 2010 +0.127 ± 0.035 +0.127 ± 0.035 1 Chernonzhkin et al., 2010 1 Kalver et al., 2020 PCC-1 2380 9.3 +0.132 ± 0.018 +0.273 ± 0.064 3 This study Harzburgite +0.166 ± 0.058 +0.211 ± 0.048 +0.273 ± 0.064 3 Chernonzhkin et al., 2010 Harzburgite +0.166 ± 0.058 +0.141 ± 0.078 -0.138 ± 0.048 +0.273 ± 0.064 3 Chernonzh				$+0.010 \pm 0.042$			12	Ratié <i>et al.</i> , 2015
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				$\textbf{+0.015} \pm \textbf{0.089}$			5	Pasava et al., 2019
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				$+0.028 \pm 0.085$			39	Saunders, 2018
$ \begin{array}{ c c c c c c } & +0.013 \pm 0.058 & +0.232 \pm 0.056 & +0.263 \pm 0.034 & -0.171 \pm 0.048 & +0.230 \pm 0.064 & -1015 \operatorname{study} \operatorname{rearge} \\ & +0.143 \pm 0.018 & +0.232 \pm 0.056 & +0.263 \pm 0.038 & 3 & This \operatorname{study}^{h} \\ & +0.160 \pm 0.078 & +0.197 \pm 0.072 & 4 & This \operatorname{study}^{h} \\ & +0.160 \pm 0.078 & +0.197 \pm 0.072 & 4 & This \operatorname{study}^{h} \\ & +0.160 \pm 0.078 & -1 & 1 & Chernonozhkin et al., 2019 \\ & +0.130 \pm 0.078 & -1 & 1 & Chernonozhkin et al., 2019 \\ & +0.130 \pm 0.078 & -1 & 1 & Chernonozhkin et al., 2019 \\ & +0.124 \pm 0.018 & -1 & 1 & Chernonozhkin et al., 2010 \\ & +0.124 \pm 0.018 & -1 & 1 & Chernonozhkin et al., 2010 \\ & +0.124 \pm 0.018 & -1 & 1 & Chernonozhkin et al., 2011 \\ & +0.124 \pm 0.018 & -1 & 1 & Chernonozhkin et al., 2011 \\ & +0.124 \pm 0.018 & -1 & 1 & Chernonozhkin et al., 2011 \\ & +0.124 \pm 0.018 & -1 & 1 & Chernonozhkin et al., 2011 \\ & +0.124 \pm 0.018 & -1 & 1 & Chernonozhkin et al., 2011 \\ & +0.124 \pm 0.018 & -1 & 1 & Chernonozhkin et al., 2011 \\ & +0.124 \pm 0.018 & -1 & 2 & Chernonozhkin et al., 2011 \\ & +0.124 \pm 0.018 & -1 & 2 & Chernonozhkin et al., 2011 \\ & +0.124 \pm 0.018 & -1 & 2 & Chernonozhkin et al., 2012 \\ & +0.124 \pm 0.018 & -1 & 2 & Chernonozhkin et al., 2012 \\ & +0.124 \pm 0.018 & -1 & 2 & Chernonozhkin et al., 2012 \\ & +0.124 \pm 0.018 & -1 & 2 & Chernonozhkin et al., 2012 \\ & +0.124 \pm 0.018 & -1 & -1 & 6 & Chernonozhkin et al., 2012 \\ & +0.124 \pm 0.018 & -1 & -1 & 6 & Chernonozhkin et al., 2012 \\ & +0.124 \pm 0.018 & -1 & -1 & 6 & Chernonozhkin et al., 2012 \\ & +0.124 \pm 0.018 & -1 & -1 & 6 & Chernonozhkin et al., 2012 \\ & -0.071 \pm 0.061 & -0.068 & -0.068 & -0.068 & -0.061 \\ & -0.069 \pm 0.058 & -0.068 & -0.068 & -0.061 & -0 & 6 & Chernonozhkin et al., 2012 \\ & -0.071 \pm 0.078 & -1 & -0 & Chernonozhkin et al., 2012 \\ & -0.071 \pm 0.078 & -1 & -1 & 6 & Chernonozhkin et al., 2012 \\ & -0.067 \pm 0.078 & -1 & -1 & 6 & Chernonozhkin et al., 2012 \\ & -0.071 \pm 0.078 & -1 & -1 & 6 & Chernonozhkin et al., 2012 \\ & -0.063 \pm 0.035 & -0 & -1 & 6 & Chernonozhkin et al., 2012 \\ & -0.063 \pm 0.035 & -1 & -1 & 6 & Chernonozhkin et al.$				$+0.070 \pm 0.078$			—	Gall, 2011
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Harzburgite+0.143 \pm 0.018+0.223 \pm 0.056+0.263 \pm 0.0383This study+0.111 \pm 0.032+0.120 \pm 0.060+0.197 \pm 0.0724This study ^b +0.130 \pm 0.078-0.161 \pm 0.078-0.197 \pm 0.0724This study+0.130 \pm 0.078-0.130 \pm 0.078-0.197 \pm 0.0724This study+0.130 \pm 0.078-0.134 \pm 0.058-0.161 \pm 0.044-0.109 \pm 0.020 \pm 0.060-0.197 \pm 0.0724PCC-1238099.3+0.133 \pm 0.032+0.241 \pm 0.048+0.273 \pm 0.0643This studyHarzburgite-0.166 \pm 0.058-0.166 \pm 0.0588Chermonozhkin <i>et al.</i> , 2015+0.110 \pm 0.078-0.132 \pm 0.0188Klaver <i>et al.</i> , 2020+0.120 \pm 0.078-0.138 \pm 0.048-0.161 \pm 0.0643This studyDTS-1236099.3-0.039 \pm 0.032-0.138 \pm 0.048-0.161 \pm 0.0643This studyDunite-0.069 \pm 0.058-0.018-0.611 \pm 0.0643This studyDunite-0.069 \pm 0.035-0.161 \pm 0.0643Klaver <i>et al.</i> , 2015-0.071 \pm 0.051-0.073-0.622 \pm 0.018-0.611 \pm 0.0643-0.071 \pm 0.051-0.073-0.611 \pm 0.0643Klaver <i>et al.</i> , 2017-0.082 \pm 0.018-0.159 \pm 0.048+0.277 \pm 0.0643This study-0.012 \pm 0.068 \pm 0.032+0.192 \pm 0.048+0.192 \pm 0.0643Klaver <i>et al.</i> , 2017-0.083 \pm 0.035-0.161 \pm 0.0643 <td>JP-1</td> <td>2460</td> <td>99.2</td> <td>+0.127 \pm 0.032</td> <td>+0.171 ±±0.048</td> <td>+0.230 \pm 0.064</td> <td></td> <td>This study (average)</td>	JP-1	2460	99.2	+0.127 \pm 0.032	+0.171 ±±0.048	+0.230 \pm 0.064		This study (average)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Harzburgite			$+0.143 \pm 0.018$	$+0.222 \pm 0.056$	$+0.263 \pm 0.038$	3	This study
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				$+0.111 \pm 0.032$	$+0.120 \pm 0.060$	$+0.197 \pm 0.072$	4	This study
$\begin{array}{c c c c c c c c c c c c c c c c c c c $				$\pm 0.180 \pm 0.078$ $\pm 0.120 \pm 0.078$			6	Wu et al., 2019
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $				$+0.130 \pm 0.078$ +0.134 ± 0.058			3 1	Chernonozhkin <i>et al</i> 2015
$\begin{array}{c c c c c c c c c c c c c c c c c c c $				$+0.134 \pm 0.038$ +0.100 ± 0.084			54	Steele <i>et al</i> 2011
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SARM6 2050 98.5 +0.077 ± 0.032 +0.114 ± 0.048 +0.145 ± 0.064 5 This study	Pyroxenite	300	99.0	0.100 ± 0.032	0.009 ± 0.040	0.110 ± 0.004	5	1113 Study
	SARM6	2050	98.5	+0.077 \pm 0.032	+0.114 \pm 0.048	+0.145 \pm 0.064	5	This study

Sample	Ni ($\mu g g^{-1}$)	Yield (%)	$\delta^{60/58}$ Ni (‰, 2SD)	$\delta^{61/58}$ Ni (‰, 2SD)	$\delta^{62/58}$ Ni (‰, 2SD)	n	References ^a
Dunite							
WPR-1	2900	98.1	-0.040 ± 0.032	-0.061 ± 0.048	-0.080 ± 0.064	5	This study
Altered peridotite							·
UB-N	2000	99.1	+0.128 \pm 0.032	+0.203 \pm 0.048	+0.257 \pm 0.064	3	This study
Serpentinite							
SARM47	2221	99.4	+0.214 \pm 0.032	+0.355 \pm 0.048	+0.489 \pm 0.064	5	This study
Serpentinite							
MUH-1	2104	99.0	+0.137 \pm 0.032	+0.185 \pm 0.048	+0.276 \pm 0.064		This study
Serpentinized harzburgite			$\textbf{+0.137} \pm \textbf{0.008}$	+0.185 \pm 0.005	+0.277 \pm 0.011	3	This study
			+0.124 \pm 0.052	$\textbf{+0.188} \pm \textbf{0.052}$	$+0.255 \pm 0.064$	5	This study ^b
Bulk reconstructed			$+0.130 \pm 0.092$	$+0.238 \pm 0.097$	$+0.010 \pm 0.116$	—	This study
Aliquot #1		5.5	$+1.271 \pm 0.019$	$\textbf{+2.041} \pm \textbf{0.006}$	$+2.551 \pm 0.059$	2	This study
Aliquot #2		31.9	$+0.458 \pm 0.076$	$+0.742 \pm 0.108$	$+0.891 \pm 0.088$	5	This study
Aliquot #3		35.7	$+0.003 \pm 0.088$	$+0.045 \pm 0.117$	$+0.025 \pm 0.130$	5	This study
Aliquot #4		19.2	-0.284 ± 0.117	-0.376 ± 0.065	-0.553 ± 0.090	3	This study
Aliquot #5		7.8	-0.419 ± 0.127	-0.702 ± 0.026	-0.897 ± 0.200	3	This study

^{*a*} New recommended values are calculated as error-weighted average of previously published $^{6,16,27,34,39,40,43-45,64-67}$ and newly acquired $\delta^{60/58}$ Ni data (using IsoplotR⁵⁸). For consistency, all uncertainties from other studies were re-calculated as discussed in Section 3.3 encompassing the intermediate precision obtained from both pure Ni solution and real samples. ^{*b*} Samples processed twice on the second chromatographic column.

interference from ⁶⁴Zn on this isotope and its monitoring would require a dynamic mode of acquisition; hence, ⁶⁴Ni/⁵⁸Ni ratios are not reported in this study. Most other interferences can be resolved in high mass resolution mode ($m/\Delta m = 10\ 000$) of the Neptune[™] MC-ICP-MS when analyte/matrix isolation is properly addressed.45 Conservatively, the presence of matrix elements should not affect $\delta^{i/58}$ Ni measurements as long as their X : Ni ratios are kept below one.39,44,45 After the first and second ion exchange stages, \geq 90% of the Ti, 93% of the Ca, 98% of the Mg and K, 99% of th Cr, V and Co and virtually 100% of the Na, Zn, Fe, Cu and Cd contents originally present are removed from the Ni fraction (Fig. 1a and b). Consequently, for almost all matrix elements X : Ni < 1 in the purified fraction, with the exception of Mg (X:Ni \sim 5, Table 3). However, even such relatively high Mg: Ni ratio was found to be suitable for Ni isotopic analysis under our instrument operating conditions. To further discern potential biases arising from incomplete removal of matrix elements during Ni isotope ratio measurements, a duplicate of peridotite MUH-1 was processed twice on the second ion exchange stage (Table 3). The $\delta^{60/58}$ Ni values for the samples processed once (+0.137 \pm 0.008%, 2SD) and twice (+0.124 \pm 0.052%) are indistinguishable within uncertainty, highlighting the validity of the isolation procedure described here.

3.1.3 Recovery yields and ion exchange fractionation. The Ni recovery yields for the entire chemical separation were \geq 96% for all reference materials presented here (Table 4), implying minimal Ni loss (\leq 4%) in comparison with previously reported procedures (*i.e.*, 8–19% Ni loss^{40,43–45}). Since different isotopic species may show distinct ion exchange rates, however, even small losses of Ni may shift the isotope ratio of the eluted Ni to erroneous values relative to the original samples.^{45,57} To further investigate any on-column fractionation potentially arising from incomplete recovery in the second isolation stage, a digest of peridotite MUH-1 was loaded onto the column and five successive

Ni elution splits of 3 mL 100% v/v CH₃COOH were collected for MC-ICP-MS measurements (Table 4 and Fig. 2a and b). The $\delta^{60/5}$ Ni composition decreases gradually from +1.271 \pm 0.019‰ (2SD) in the leading fraction to $-0.419 \pm 0.127\%$ in the tailing fraction, corresponding to a total range of 1.690‰ within the Ni elution band. Given the apparent stronger affinity of the light isotopes of Ni for the AG1-X8 anion resin in CH₃COOH medium, quantitative yields are primordial to avoid ion exchange related fractionation of the Ni isotopes. The integrated $\delta^{60/58}$ Ni



Fig. 2 (a) Cumulated fraction of Ni eluted (%) and (b) associated $\delta^{60/58}$ Ni value (%) in individual 3 mL elution cuts for MUH-1 (peridotite, USGS) as a function of the total eluted volume of 95% v/v CH₃COOH (mL). Uncertainty is given as the repeatability of *n* replicate measurements on the MC-ICP-MS (2SD). Also shown is the error-weighted average $\delta^{60/58}$ Ni of *n* = 3 replicates of MUH-1 and associated intermediate precision (2SD) from this study (light grey field).

composition (+0.130 ± 0.092‰, 2SD; Fig. 2a and b), calculated from the relative amount of Ni eluted and $\delta^{60/58}$ Ni of each Ni elution cut, is in excellent agreement with the error-weighted average of n = 3 duplicate digestions of MUH-1 ($\delta^{60/58}$ Ni = +0.137 ± 0.027‰, 2SD calculated using IsoplotR⁵⁸), which indicates ~100% recovery for the two-step isolation procedure presented here. Chernonozhkin *et al.* (2015)⁴⁵ conducted similar experiments and found no on-column Ni isotope fractionation for the strongly basic AG1-X8 anion-exchange resin in HCl medium, which is similar to the first isolation step in this work.

3.2. Instrumental mass bias correction

The analytical mass bias resulting from preferential transmission of isotopes as a function of their mass (instrumental mass discrimination) is commonly described by equilibrium, kinetic or power mass fractionation laws. Each fractionation law can be quantified by a mass bias factor β , linking the isotope fractionation factors α of two paired isotope ratios⁵⁹ (here, ⁵⁸Ni-⁶⁰Ni and ⁵⁸Ni-⁶²Ni):

$$\alpha_{62/58} = \alpha_{60/58}{}^{\beta} \tag{II}$$

Theoretical equilibrium, kinetic and power law fractionation factors can be calculated using the general equations from Wombacher and Rehkämper (2003),⁵⁹ where m_{58} , m_{60} and m_{62} are the atomic weights of ⁵⁸Ni, ⁶⁰Ni and ⁶²Ni, respectively:

$$\beta_{\text{equilibrium}} = \left(\frac{1}{m_{58}} - \frac{1}{m_{62}}\right) / \left(\frac{1}{m_{58}} - \frac{1}{m_{60}}\right)$$
(III)

$$\beta_{\text{kinetic}} = \ln\left(\frac{m_{58}}{m_{62}}\right) / \ln\left(\frac{m_{58}}{m_{60}}\right) \tag{IV}$$

$$\beta_{\text{power}} = (m_{58} - m_{62})/(m_{58} - m_{60})$$
 (V)

To verify the accuracy of the mass bias correction method based on the use of Cu as an admixed internal standard and external correction on a sample-standard bracketing approach, adopted from Chernonozhkin *et al.* (2015),⁴⁵ a three-isotope diagram of $\delta^{60/58}$ Ni and $\delta^{62/58}$ Ni data for all samples analyzed in this study is provided in Fig. 3. Results are mass-dependent and the slope of the mass fractionation line ($\beta_{inferred} = 1.981$ ± 0.048 , York regression analysis^{58,60}) closely matches those calculated theoretically according to equilibrium ($\beta_{equilibrium} =$ 1.937), kinetic ($\beta_{kinetic} = 1.968$) and power law ($\beta_{power} = 2.001$) mass discrimination factors, indicating effective isolation of Ni and appropriate correction for instrumental mass bias.

3.3. Precision of Ni isotope ratio measurements

The combined uncertainty expressed as the standard deviation (SD) on $\delta^{60/58}$ Ni measurement results can be calculated using the following equation:⁶¹⁻⁶³

$$SD = \sqrt{SD_{MassSpec}}^2 + SD_{sample}^2 + SD_{natural}^2$$
(VI)

where $SD_{MassSpec}$ and SD_{Sample} are the intermediate precision (commonly referred to as "external reproducibility" in



Fig. 3 Nickel three-isotope plot of $\delta^{60/58}$ Ni vs. $\delta^{62/58}$ Ni ($\%_{oo}$). Theoretical fractionation factors β are calculated using equations from Wombacher and Rehkamper (2003)⁵⁹ and atomic weights from Audi and Wapstra (1995).⁷¹ Also shown are the results of York regression analysis computed using IsoplotR.^{58,60} Uncertainty is given as the repeatability of *n* replicate measurements on the MC-ICP-MS (2SD).

geochemistry) obtained for a pure Ni standard solution and a real sample, respectively. The former best reflects the long-term (*i.e.*, \sim 4 months) instrumental intermediate precision while the latter accounts for analytical intermediate precision including potential variations related to the chemical isolation of Ni presented here. The additional SD_{natural} term is the variability related to isotopic heterogeneity within the sample, that is, $SD_{natural} =$ 0 assuming homogeneous material. Accounting for the repeatability over the 48 acquisition cycles during MC-ICP-MS measurements (*i.e.*, "internal precision"), n = 147 analyses of the NIST SRM 986 solution used for sample-standard bracketing provide an error-weighted average $\delta^{60/58}$ Ni value and associated intermediate precision of $-0.005 \pm 0.018\%$ (2SD_{MassSpec} using IsoplotR,58 Fig. 4). Using the same approach, replicate measurements of peridotite reference material MUH-1 (n = 3) and JP-1 (n= 2) yield an error-weighted average $\delta^{60/58}$ Ni value and associated intermediate precision of +0.137 \pm 0.027% (2SD_{sample} using IsoplotR,⁵⁸ Fig. 4) and +0.127 \pm 0.023%, respectively. Consequently, a conservative overall uncertainty (2SD, the expanded combined uncertainty with a coverage factor of 2) of $\pm 0.032\%$ or $\pm 0.016^{\circ}_{\circ\circ}$ per amu (eqn (VI)) is adopted for all $\delta^{60/58}$ Ni measurements presented in this study unless stated otherwise. Notably, the level of precision associated with the method presented here is similar to those achieved in previous studies $(\pm 0.018\%)$ to $\pm 0.089\%_{00}$, $2SD^{6,16,27,39,40,43-45,64-68}$).

3.4. Nickel stable isotope composition of geological reference materials

As part of this work, a set of 14 igneous geological reference materials were subject to Ni isotopic analysis in order (1) to



Fig. 4 Long-term $\delta^{60/58}$ Ni (%) intermediate precision of the NIST SRM 986 standard solution (white dots, n = 147), Sigma Aldrich in-house solution (blue dots, n = 29) and geological reference material MUH-1 (orange dots, n = 3) over a period of ~4 months. Individual uncertainty bars correspond to the repeatability over the 48 acquisition cycles during MC-ICP-MS measurements (2SD) while error-weighted averages are given with their associated intermediate precision (2SD).

test the accuracy of our method and (2) to consolidate and expand the pre-existing database of rock standards. Results are provided in Table 4 and Fig. 5 together with a compilation of published values from the literature. Our $\delta^{60/58} \rm Ni$ value of $+0.240 \pm 0.032\%$ (2SD) for the extra-terrestrial Allende CV3 carbonaceous chondrite is indistinguishable within uncertainty from that of previously published values of +0.241 \pm 0.030%.^{16,39,64} Similarly, new data for the terrestrial basalts BIR-1 (+0.169 \pm 0.032%) and BHVO-2 (-0.021 \pm 0.032%) and ultramafic samples JP-1 (+0.127 \pm 0.032‰), PCC-1 (+0.133 \pm 0.032%), DTS-1 (-0.093 \pm 0.032%) and DTS-2b (+0.140 \pm 0.032‰) all compare consistently with previously reported $\delta^{60/2}$ ⁵⁸Ni values obtained using either a combination of internal and external corrections or double-spiking (+0.151 \pm 0.068%) +0.028 \pm 0.070%, +0.127 \pm 0.036%, +0.133 \pm 0.042%, -0.080 0.036‰ +0.132 \pm and \pm 0.030‰, respectively^{6,16,34,35,39,40,43-45,64-67,69}). Our value of $-0.021 \pm 0.032^{\circ}_{\circ 00}$ for BHVO-2 overlaps with 6 out of the 10 published $\delta^{60/58} \rm Ni$ values

within uncertainty, but is slightly lower than the average $\delta^{60/}$ 58 Ni from previous studies (+0.028 \pm 0.070%, Fig. 5). This potentially relates to the inhomogeneity of this reference material, as suggested by the large range of $\delta^{60/58}$ Ni values spanning from $-0.010 \pm 0.050\%$ (ref. 66) to $+0.190 \pm 0.100\%$ (ref. 4) and already discussed by previous workers.^{16,65} New recommended values for the above-mentioned geological reference materials calculated as error-weighted averages (using IsoplotR⁵⁸) of previously published and newly acquired $\delta^{60/58}$ Ni values are presented in Table 4 and Fig. 5. We also report the first Ni isotopic data for 7 additional geological reference materials including one kimberlite (SARM39, +0.086 \pm 0.032% 2SD), one pyroxenite (SARM5, +0.186 \pm 0.032%), one dunite (SARM6, +0.077 $\pm 0.032\%$), one altered peridotite (WPR-1, -0.040 \pm 0.032%), one serpentinized harzburgite (MUH-1, +0.137 \pm 0.032%) and two serpentinites (UB-N, +0.128 \pm 0.032%; SARM47, +0.214 \pm 0.032%). Interestingly, the pyroxenite SARM5 exhibits a $\delta^{60/58}$ Ni value of $+0.186 \pm 0.032\%$, which is slightly heavier than unaltered peridotites (+0.115 \pm 0.011% (ref. 16)) but in the range of melt-metasomatized peridotites worldwide (+0.108 \pm 0.010%to $+0.215 \pm 0.009\%$ (ref. 16)). Additionally, the serpentinized harzburgite MUH-1 and the two serpentinites UB-N and SARM47 (+0.128 \pm 0.032% to +0.214 \pm 0.032%) are significantly offset from the $\delta^{60/58}$ Ni range of fresh peridotites $(+0.115 \pm 0.011\%$ (ref. 16)) and mineralized serpentinites $(-0.126 \pm 0.035\%$ to $-0.470 \pm 0.020\%$ (ref. 26 and 40)) reported in literature. Although variations in the source compositions cannot be ruled out here, the apparent difference in $\delta^{60/58}$ Ni could suggest the potential of Ni isotope ratios to track ore component mobility and reaction pathways beneath hydrothermal fields as observed for Zn, Cu and Fe isotope ratios.⁷⁰ Although the method is demonstrated to work for igneous rocks, additional tests are needed before expanding it to geological matrices with lower Ni abundances



Fig. 5 Summary of $\delta^{60/58}$ Ni composition (%) of the geological reference materials analyzed in this study (blue dots) compared to previous studies (white dots). Also shown are new recommended values (blue line) calculated as error-weighted average of previously published^{6.16,27,34,39,40,43-45,64-67} and newly acquired $\delta^{60/58}$ Ni data (using IsoplotR⁵⁸). Uncertainty is given as 2SD (see Section 3.3 for details).

and/or high organic contents (*e.g.*, shales), or biological samples.

4. Conclusions

A new and straightforward two-step protocol is presented for isolation of Ni from igneous rock matrices exploiting the selective adsorption of chemical elements from hydrochloric and acetic acids onto the AG1-X8 (200-400 mesh) anion exchange resin. A single pass through the two successive chromatographic stages leads to a quantitative ($\geq 96\%$ recovery yield) and pure Ni isolate, reducing preparation costs and time, eluent volumes and total procedural blank contribution (<0.25 ng). Importantly, our methodology reduces the X : Ni ratios of all potentially interfering elements to negligible levels (including alkali and alkali earth metals that are hardly separated otherwise), no longer affecting the MC-ICP-MS Ni isotopic analysis. A set of 14 geological reference materials was processed for Ni isotope measurements by MC-ICP-MS, where instrumental mass bias was corrected for by a combination of internal correction using admixed Cu solution and external correction in a sample-standard bracketing approach. Our results demonstrate that this method is suited for accurate determination of $\delta^{60/58}$ Ni in rock matrices, with an overall precision of ca. $\pm 0.032\%$ (2SD) similar to those achieved in previous studies. Finally, the Ni isotopic compositions of 7 geological reference materials are reported for the first time with $\delta^{60/58} \rm Ni$ values ranging from $-0.040 \pm 0.032^{\circ}_{\rm loo}$ to +0.214 \pm 0.032‰.

Conflicts of interest

There are no conflicts to declare.

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