Geochemical and spectroscopic investigation of apatite in the Siilinjärvi Carbonatite Complex: keys to understanding apatite forming processes and assessing potential for rare earth elements

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Geochemical and spectroscopic investigation of apatite in the Siilinjärvi 1 Carbonatite Complex: keys to understanding apatite forming processes and 2 assessing potential for rare earth elements 3 4 Sophie Decrée^{1,*}, Mikko Savolainen², Julien Mercadier³, Vinciane Debaille⁴, Stefan Höhn⁵, 5 Hartwig Frimmel⁵ and Jean-Marc Baele⁶ 6 ¹ Royal Belgian Institute of Natural Sciences-Geological Survey of Belgium, Brussels (Belgium) 7 * Corresponding author: sophie.decree@naturalsciences.be 8 ² Yara Suomi Oy, Siilinjärvi (Finland). E-mail: mikko.savolainen@yara.com 9 ³ Université de Lorraine, CNRS, CREGU, GeoRessources, F-54000 Nancy (France). E-mail: 10 julien.mercadier@univ-lorraine.fr 11 ⁴ Vinciane Debaille, DGES – Laboratoire G-Time (CP 160/02), Université Libre de Bruxelles (ULB), Brussels, 12 13 Belgium. E-mail: vinciane.debaille@ulb.ac.be ⁵ Bavarian Georesources Centre, Dept. of Geodynamics and Geomaterials Research, Institute of Geography and 14 Geology, University of Würzburg (Germany). E-mail: hartwig.frimmel@uni-wuerzburg.de 15 ⁶ Department of Geology and Applied Geology, University of Mons, Mons (Belgium). E-mail: jean-16 marc.baele@umons.ac.be 17 18

19 Abstract

The Siilinjärvi phosphate deposit (Finland) is hosted by an Archean carbonatite complex. The main 20 body is composed of glimmerite, carbonatite and combinations thereof. It is surrounded by a well-21 22 developed fenitization zone. Almost all the rocks pertaining to the glimmerite-carbonatite series are 23 considered for exploitation of phosphate. New petrological and in-situ geochemical as well as spectroscopic data obtained by cathodoluminescence, Raman and laser-induced breakdown 24 25 spectroscopy make it possible to constrain the genesis and evolution of apatite through time. Apatite in 26 the glimmerite-carbonatite series formed by igneous processes. An increase in rare earth elements 27 (REE) content during apatite deposition can be explained by re-equilibration of early apatite (via subsolidus diffusion at the magmatic stage) with a fresh carbonatitic magma enriched in these elements. 28 29 This late carbonatite emplacement has been known as a major contributor to the overall P and REE endowment of the system and is likely connected to fenitization and alkali-rich fluids. These fluids -30 enriched in REE - would have interacted with apatite in the fenite, resulting in an increase in REE 31 content through coupled dissolution-reprecipitation processes. Finally, a marked decrease in LREE is 32 33 observed in apatite hosted by fenite. It highlights the alteration of apatite by a REE-poor fluid during a late-magmatic/hydrothermal stage. Regarding the potential for REE exploitation, geochemical data 34 35 combined with an estimation of the reserves indicate a sub-economic potential of REE to be exploited as by-products of phosphate mining. Spectroscopic analyses further provide helpful data for 36 exploration, by determining the P and REE distribution and the enrichment in carbonatite and within 37 38 apatite.

39

40 Keywords: Carbonatite-related ore deposits, Fennoscandian Shield, Archean, rare earth elements,

41 cathodoluminescence, Raman spectroscopy, LIBS, LA-ICPMS

42

43 **1. Introduction**

44 Phosphate is one of the main commodities mined from alkaline complexes and carbonatites. It has 45 been exploited - mainly to produce fertilizer - in South Africa, Zimbabwe, Brazil, Finland, and Sri Lanka (Verwoed, 1986; Pell, 1996; van Straaten, 2002). Beside phosphate, it has been shown that 46 47 numerous critical raw materials - as defined by the European Commission (EC, 2014) - could be 48 recovered from phosphate deposits of this type, namely the rare earth elements (REE), fluorine 49 (fluorspar), and vanadium (Ihlen et al., 2014; Goodenough et al., 2016; Decrée et al., 2017). For 50 instance, magmatic apatite usually contains more than 0.35% REE (Ihlen et al., 2014), in exceptional cases reaching as much as 21 wt. % REE₂O₃ (e.g., Roeder et al., 1987; Hughes et al., 1991; Hoshino et 51 al., 2015). With a theoretical maximal content of 3.73 wt% F in apatite, phosphate rocks can contain 52 53 up to 3-4% F (Notholt et al., 1979). Phosphate formation and accumulation in these rocks can result 54 from various processes that range from magmatic to hydrothermal (metasomatic) to supergene 55 alteration (e.g., Walter et al., 1995; Broom-Fendley et al., 2016, 2017; Chakhmouradian et al., 2017; Decrée et al., 2015, 2016, 2020). These processes also affect the content of other elements (such as F 56 57 and REE) in apatite, leading locally to significant enrichment and economic potential of these resources as by-product of phosphate production (Ihlen et al., 2014; Decrée et al., 2016). The spatial 58 superimposition of these processes can make the understanding of the genesis of a given phosphate 59 deposit, and its enrichment in critical raw materials, fairly complex. The objective of this work is to 60 assess the relative importance of each individual crystallization stage in the various facies of the 61 62 Neoarchean Siilinjärvi Carbonatite Complex (Finland), through a careful petrographic and 63 geochemical study of apatite.

The Siilinjärvi deposit is related to a carbonatite complex dated at ~2610 Ma (Bayanova, 2006; GTK 64 unpublished report in O'Brien et al., 2015). The complex is of lenticular shape, comprises intermixed 65 carbonatite and glimmerite, and dips steeply into a gneissic basement (O'Brien et al., 2015). Fenite is 66 well developed all around the complex. Almost all the glimmerite-carbonatite rocks constitute 67 phosphate ore, with an apatite content of about ~10 vol%. Apatite-rich carbonatite and glimmerite 68 contain up to 30 vol% apatite, and apatite veins are essentially monomineralic (~80 vol% apatite; 69 70 O'Brien et al., 2015). The Siilinjärvi mine produces about 11 Mt/yr, with ore reserves of 234 Mt at an average grade of 4 wt% P₂O₅ (data for January 2014; O'Brien et al., 2015). The Siilinjärvi deposit has 71 a potential for recovering REE and F. The REE content in apatite was estimated at 0.3-0.4 wt% REE 72 (based on analyses on mineral separates; Puustinen, 1971; Hornig-Kjarsgaard, 1998), though the REE 73 74 content in whole rock samples varies significantly (from 0.05 to 0.16 wt%; Hornig-Kjarsgaard, 1998). 75 The fluorine content reported for the apatite typically ranges from 2.3 to 3.5 wt% (based on electron 76 microprobe analyses; Puustinen and Kauppinen, 1989; Al Ani, 2013).

77 Studies focusing on the mineralogy and chemistry of apatite from Siilinjärvi are scarce. Apart from the 78 analyses referred to above, a microthermometric study by Poutiainen (1995) corroborated a primary 79 igneous origin of the apatite and the involvement of an aqueous fluid during fracturing and 80 recrystallization of this mineral. A few isotopic studies on apatite separates from Siilinjärvi have given more information about the origin of this mineral. Based on Nd, δD and $\delta^{13}C$ isotope data, it appears 81 that apatite retained its primary mantle-derived signature and formed from relatively undegassed 82 magmas (Nadeau et al., 1999; Tichomirowa et al., 2006; Zozulya et al., 2007), whereas Sr isotope 83 84 signatures tend to suggest sub-solidus exchange during late magmatic stages (Tichomirowa et al., 85 2006). Uranium-Pb isotope data signal the Svecofennian metamorphic overprint and resetting of the 86 Pb-Pb isotope system in apatite at that time (Tichomirowa et al., 2006).

- 87 These studies constitute important steps towards the understanding of apatite genesis in the Siilinjärvi88 Carbonatite Complex. However, apatite is typically characterized by small-scale heterogeneities that
- reveal the complexity of the processes involved in its formation (e.g., Chakhmouradian et al., 2017;
- 90 Broom-Fendley et al., 2016, 2017; Decrée et al., 2016, 2020). Thus, a careful petrographic study and
- 91 in-situ geochemical analyses are needed to document these textural and chemical variations and to
- better constrain the sequence of processes in the apatite's genesis explaining the variability of P and
- 93 REE contents observed within the deposit.

94 This is the aim of the present study in which we conducted (i) a thorough petrographic characterization 95 under cathodoluminescence (CL), which is a useful tool highlighting textures in minerals and their 96 associated geochemical/structural heterogeneities (e.g., Chakhmouradian et al., 2017; Baele et al., 97 2019), (ii) *in-situ* chemical analyses by electron microprobe analyses (EMPA) and laser ablation-98 inductively coupled plasma-mass spectrometry (LA-ICP-MS), and (iii) a careful study of the CL and 99 Raman spectra that can help to detect the presence and the level of REE-enrichment in apatite (e.g., 100 Kempe and Götze, 2002, Decrée et al., 2016).

101 The second objective of this study is to unlock the potential of carbonatite-related deposits for REE 102 recovery. For this purpose, the REE contents of the different lithotypes constituting the Siilinjärvi Complex were determined based on whole rock analyses and laser induced breakdown spectroscopy 103 (LIBS). This became necessary after the few previous studies on the geochemistry of the Siilinjärvi 104 rocks (Puustinen, 1971; Hornig-Kjarsgaard, 1998) had provided incomplete datasets. LIBS provides 105 106 fast and spatially-resolved, multi-element imaging and constitutes an emerging tool for mineral 107 exploration (Harmon et al., 2019). It is ideally suited for investigating the P and REE distribution in the rocks, irrespective whether or not mineralized. 108

109

110 2. Geological Context

The Neoarchean Siilinjärvi Carbonatite Complex is located in the Karelian Province in eastern 111 112 Finland. The complex forms a roughly subvertical lenticular body that is about 16 km long with a maximal width of 1.5 km (O'Brien et al., 2015; Fig. 1). It was emplaced into Archean tonalite, gneiss, 113 syenite, and quartzdiorite at around 2610 Ma (2610 ± 4 Ma, zircon U-Pb ages, GTK unpublished 114 115 report in O'Brien et al., 2015; 2613 ± 18 Ma, U-Pb ages on baddeleyite, Bayanova, 2006). A N-S structure likely controlled its emplacement (Puustinen, 1969). Contacts between the Siilinjärvi 116 117 Carbonatite Complex and the country rocks are either primary magmatic or sheared (O'Brien et al., 118 2015). Several episodes of deformation affected the Siilinjärvi Carbonatite Complex, including multiphase compressional and metamorphic events related to the Svecofennian orogeny between ~ 1.9 119 and 1.7 Ga (Niiranen et al., 2015; O'Brien et al., 2015). 120

Carbonatite and glimmerite form the central part of the body. The glimmerite-carbonatite series ranges 121 from pure glimmerite (with dominant tetraferriphlogopite) to carbonate glimmerite, silicocarbonatite 122 and carbonatite (with >50 vol% carbonate) (O'Brien et al., 2015). These rock types are intimately 123 mixed, varying from pure glimmerite to pure carbonatite, with carbonate glimmerite and silica 124 125 carbonatite among intermediate facies (Fig. 2a-e). Most of the carbonatite is present as subvertical 126 veins concentrated towards the center of the intrusion, cutting across glimmerite, whereas glimmerite 127 is located more at the margin of the central core (Puustinen and Kauppinen, 1989; O'Brien et al., 2015). The intrusion of carbonatite magma occurred in several stages (Tichomirowa et al., 2006) and 128 129 silicocarbonatite formed from later intrusions (Puustinen and Kauppinen, 1989). Carbonatite represents roughly 1.5 vol % of the main intrusion and the final stage of magmatic influx in the system 130 131 (O'Brien et al., 2015). Tetraferriphlogopite and calcite are the dominant minerals in the glimmerite-

carbonatite series. Apatite and richterite are other minerals that are ubiquitous in these lithotypes(Puustinen, 1971; Puustinen and Kauppinen, 1989).

Fenite developed within the country rocks surrounding the glimmerite-carbonatite body and comprises 134 a variety of facies. These are mainly related to the (proportion of) minerals forming the fenites, mostly 135 microcline, amphibole, pyroxene, but also carbonate and quartz (O'Brien et al., 2015). Amphibole-rich 136 137 fenite (Fig. 2f,g; abbreviated as fenite (amph)) and pyroxene-rich fenite (Fig. 2h,I; abbreviated as 138 fenite (pyrox)) are distinguished. Fenite occurs as megaxenoliths in glimmerite, implying that at least part of the fenite formed early in the history of the complex (O'Brien et al., 2015). According to 139 140 Poutiainen (1995), fenitization resulted from the circulation of H₂O- and alkali (Na,K)-rich fluids during the pre-emplacement evolution of the carbonatite at mid-crustal conditions. 141

Ultramafic dikes cut the whole complex (including the fenitized zone) and country rocks. They could 142 also originate from the parental magma of the complex (O'Brien et al., 2015). Based on isotopic 143 144 evidence, the parent magma of the Siilinjärvi carbonatite and glimmerite was derived from a moderately enriched mantle source (Nadeau et al., 1999; Tichomirowa et al., 2006; Zozulya et al., 145 2007). Isotope studies further point to an increase of the Sm/Nd ratio of the source domain in the 146 147 mantle (Tichomirowa et al., 2006), which was also characterized by a high δ^{13} C component during the 148 Archean (Demeny et al., 2004). The magmatic system is thought to have been large and well-mixed. 149 The composition of calcite and apatite further speaks for a moderate level of fractionation of the source magma, which was likely not very REE-enriched (O'Brien et al., 2015). Strontium isotope data 150 point at sub-solidus exchange with aqueous fluids during emplacement and cooling of the carbonatites 151 (Tichomirowa et al., 2006). Further perturbation of the isotopic systems was induced by the 152 Svecofennian orogeny, which caused resetting of the isotope systems (Tichomirowa et al., 2006), in 153 spite of a rather low grade of metamorphism (Puustinen and Kauppinen, 1989). 154

155

3. Material and methods

Eleven samples were taken from the Siilinjärvi mine (Table 1). The petrographic analysis was 157 based on optical microscopy and scanning electron microscopy (SEM) using a Quanta 20 ESEM 158 (FEI), with energy-dispersive spectroscopy (Apollo 10 Sillicon Drift EDS detector; EDAX) at the 159 Royal Belgian Institute of Natural Sciences (RBINS). Cathodoluminescence (CL) studies were 160 161 performed at the University of Mons (UMONS) using a cold-cathode CL unit model Mk5 operated at 15 kV beam voltage and 500 µA current (Cambridge Image Technology Limited). The surface area of 162 the unfocused electron beam on the sample was 12 x 4 mm, resulting in a current density of about 10 163 μ A/mm². CL spectra were recorded with a CITL optical spectrometer model OSA2 allowing 164 acquisition from 350 to 1100 nm at 3.7 nm spectral resolution. Spectra were acquired and processed 165 using Spectragryph optical spectroscopy software (https://www.effemm2.de/spectragryph/). A dark 166 spectrum, i.e. a spectrum of the stray light in the CL chamber, was systematically subtracted from the 167 experimental spectrum. However, this procedure was not always successful in suppressing the two 168 artifact peaks that are sometimes observed on both sides of the Eu²⁺ emission around 410 nm. These 169 artifact peaks, which sometimes appear negative due to over-correction, are due to the spurious 170 emission of some excited species (probably nitrogen) from the atmosphere in the electron gun. 171 Spectral CL images of the Nd³⁺ emission were collected by inserting an optical bandpass filter with a 172 transmission curve centered at 880 nm and 50 nm wide (full width at half maximum) in the light path. 173 Such spectral CL imaging enhances the details of the distribution of the apatite activated by light REE. 174 which is especially useful when apatite luminescence is overwhelmed by the intense luminescence of 175 calcite and feldspars. In addition, Nd³⁺ emits in the near infrared region of the spectrum and is 176

177 therefore not visible in color CL images. Raman spectroscopy was performed at the Royal Belgian 178 Institute of Natural Sciences to investigate the fluorescence induced by the REE. We used a 785 nm 179 (red) laser Raman spectrometer (Senterra, Olympus BX51, Bruker optics). The spectra were acquired 180 using a 1 mW excitation power, 5x30 s integration time and with a 50 μ m spectrometer slit. They were 181 processed using Spectragryph optical spectroscopy software. The Raman shift has been transformed 182 into wavelengths according to the following formula: Wavelength (nm) = (Laser wavelength⁻¹ -183 Raman shift x 10⁻⁷)⁻¹. Here, the laser wavelength is 785 nm and the Raman shift is given in cm⁻¹.

Laser-Induced Breakdown Spectroscopy (LIBS) was performed with a system under development at 184 185 UMONS, which comprises a flashlamp-pumped Q-switched Nd:YAG laser (Quantel-Lumibird OSmart 450, France) with frequency doubling and quadrupling crystals (266 nm wavelength) and a 9-186 channel optical CCD spectrometer with integrated delay electronics (Avantes ULS2048, The 187 Netherlands). The spectral range and resolution of the spectrometer were 190-1100 nm and 0.05 to 0.2 188 nm (from ultraviolet to infrared), respectively. LIBS maps were recorded by moving the sample with a 189 190 motorized XY stage (Zaber Technologies, Canada) that was synchronized with the laser Q-switch 191 using a digital pulse/delay generator (Quantum Composers, USA). The surface of the sample was ground on an ultra-flat lapping plate using grit 600 silicon carbide abrasive in order to achieve a flat 192 surface with an even rugosity. A constant lens-to-sample distance, which is critical in LIBS 193 194 spectroscopy, was ensured by finely adjusting the horizontality of the surface using laser pointers. Laser pulse duration and energy were 5 ns and 15 mJ, respectively. The laser pulses were focused onto 195 the sample surface with a 150 mm focal distance silica planoconvex lens. With these settings, the 196 diameter of the ablation craters was about 200 µm, which yields a fluence of 48 Jcm⁻² and an 197 irradiance (power density) of 9.5 GWcm⁻². The plasma light was collected by a 6 mm focal distance 198 199 planoconvex lens and injected into multi-furcated optical fibers connected to the spectrometer. The 200 delay between laser shots and start of the integration was 1 µs to avoid the intense initial continuum radiation of the plasma and the integration time was set to 1 ms. The energy of the laser pulses was 201 202 continuously monitored by sampling the beam with a silica window and measuring the energy with a pyroelectric sensor (Thorlabs ES220C). The measured relative standard deviation of pulse energy 203 fluctuation at 10 Hz repetition rate was found to be 4.1% after thermal stabilization of the frequency-204 205 quadrupling crystals. Acquisition and processing of the LIBS spectra were achieved with Spectragryph spectroscopy software. Jython and Java scripting under Fiji/ImageJ free image analysis software 206 207 (Rueden et al., 2017) were used to build the hyperspectral data cube and to extract the LIBS maps. 208 Elemental lines were identified based on both experimental LIBS spectra of internal reference 209 materials and the NIST atomic emission database. The LIBS maps show the intensity of selected ionic (II), atomic (I) or molecular emission lines without calibration. Therefore, they are qualitative 210 geochemical maps. The following emission lines were used for the LIBS maps presented in this study: 211 Ca I (458.59 nm), Si I (390.55 nm), P I (255.33 nm), CaF (~543 nm), Na I (819.48 nm), K I (766.49 212 nm). La II (412.32 nm) and Ce II (416.46 nm). The selection of the wavelengths was based on the 213 following criteria: maximizing intensity while avoiding those lines that obviously suffer from 214 autoabsorption and minimizing interference from other elements. The CaF molecular emission is a 215 216 good means of detecting F because this element is extremely difficult to excite under common experimental LIBS conditions due to its very high first ionization potential. However, when Ca is 217 present together with F, both elements form a transient CaF molecule in the plasma as it cools and the 218 associated intense emission band is easily detected. The only drawback of this method is that fluorine 219 is not detected if no Ca is present in the sample, which could, however, be mitigated by nebulizing 220 some Ca solution into the plasma (Alvarez Llamas et al., 2017). 221

In all the samples zoned apatite grains were investigated in-situ for their composition. Where possible, the different types of analyses (EMPA and LA-ICPMS) have been performed on the same spot or

224 nearby spots. Quantitative microanalyses of the chemical composition for major elements (Table 1S (Supplementary Material)) were acquired using a JEOL JXA 8800L electron microprobe at the 225 Institute of Geography and Geology, University of Würzburg (Germany). It was operated at 15 kV and 226 4 nA, with a beam diameter of 10 μ m. This microprobe is equipped with four wavelength-dispersive 227 (WDS) spectrometers and standard LDE1, TAP, PET and LIF crystals (LiF for F, Fe₂O₃ for Fe, SrSO₄ 228 for Sr, MnTiO₃ for Mn, MgO for Mg, BaSO₄ for S and Ba) and mineral standards (albite for Na, 229 vanadinite for Cl, apatite for P and Ca, and andradite for Si) supplied by CAMECA (SX Geo-230 Standards) were used as a reference. The L α line was used for the measurements of Sr and Ba, and the 231 Ka line for all other elements. The lower limit of detection is typically better than 0.05 wt%. For each 232 233 mineral spot, the relatively mobile elements F and Na were analyzed first in order to prevent their potential loss over the course of the analysis. The analytical data acquired are provided in Table 1S 234 235 (Supplementary Material). A correction for excess F due to third-order interference of P K α on F K α was applied. Excess F was estimated at about 0.35% based on 15 measurements of F K α in a 236 phosphate that does not contain F (reference monazite at Univ. Würzburg). The measurements yielded 237 a mean of 0.040 % "fake" F per % P. A similar value (0.045 %) was obtained by Potts and Tindle 238 (1989). Note that grain orientation and anisotropic ion diffusion can also have a substantial influence 239 240 on the quantification of F with the electron microprobe (e.g., Stormer et al., 1993; Goldoff et al., 2012). For the compositional maps of apatite grains, an acceleration voltage of 15 kV and a beam 241 current of 40 nA were used with a spot size of 5 µm. 242

Laser ablation inductively coupled mass spectrometry (LA-ICPMS) was performed at GeoRessources 243 (Nancy, France), with a GeoLas excimer laser (ArF, 193 nm, Microlas) coupled to a conventional 244 transmitted and reflected light microscope (Olympus BX51) for sample observation and laser beam 245 focusing onto the sample and an Agilent 8900 triple quadrupole ICP-MS used in no-gas mode. The 246 247 LA-ICPMS system was optimized to have the highest sensitivity for all elements (from 7Li to 238U), ThO/Th ratio < 0.5% and Th/U ratio of ~ 1 . Samples were ablated with a laser spot size of 32 µm to 248 avoid mixing between the different zones observed in the apatite crystals. A fluence of ~ 7 J.cm⁻² and a 249 repetition rate of 5 Hz were used. The carrier gas used was helium (0.45 l/min) which was mixed with 250 argon (0.5 l/min) gas before entering the ICP-MS. The ICP-MS settings were the following: ICP RF 251 252 Power at 1550 W, cooling gas (Ar) at 15 l/min, auxiliary gas (Ar) at 0.97 l/min, make-up gas (Ar) at 0.5 l/min and dual detector mode was used. For each analysis, acquisition time was 30 s for 253 254 background, 40 s for external standards (NIST SRM 610, NIST SRM 612 and NIST SRM 614 silicate 255 glasses (Jochum et al., 2011 for concentrations)) and 40 to 50 s for apatite. The analytical procedure 256 for the two sessions was the following: 2 analyses of NIST SRM 614, 2 analyses of NIST SRM 612, 2 analyses of NIST SRM 610, analyses of the apatites (series of ~ 20 analyses separated by the analysis 257 of a series of 1 NIST SRM 614, 1 NIST SRM 612 and 1 NIST SRM 610), 2 analyses of NIST SRM 258 614, 2 analyses of NIST SRM 612 and 2 analyses of NIST SRM 610. The external standard was NIST 259 SRM 610 and ⁴⁴Ca was used as internal standard. NIST SRM 614 and NIST SRM 612 silicate glasses 260 were analyzed and considered as cross-calibration samples to control the quality of the analyses 261 (precision, accuracy, repeatability) and to correct the possible drift during the analytical session. The 262 263 Ca contents in apatite were measured before LA-ICP-MS analyses using an electron microprobe (Cameca SX-50, University of Würzburg, Germany), to check the overall homogeneity of the apatite 264 grains. A Ca concentration of 39.54 wt.% was used for internal standardization. The following 265 isotopes were measured: ²⁹Si, ⁴⁴Ca, ⁴⁵Sc, ⁵¹V, ⁸⁵Rb, ⁸⁸Sr, ⁸⁹Y, ⁹⁰Zr, ⁹³Nb, ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, 266 ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷²Yb, ¹⁷⁵Lu, ¹⁷⁸Hf, ¹⁸¹Ta, ²⁰⁸Pb, ²³²Th, ²³⁸U. 267 Acquisition times were 0.01 s for all the isotopes except rare earth elements, which were measured 268 with 0.02 s. Total cycle time was 531 ms. The precision was better than 10% for all the rare earth 269

elements. Data treatment was done using the software "Iolite" (Paton et al., 2011), following
Longerich et al. (1996) for data reduction. Data are provided in Tables 2S (Supplementary Material).

Finally, major and trace element analyses (Tables 3S and 4S (Supplementary Material)) were carried 272 out on the 11 samples at the Laboratoire G-Time (ULB). For measuring the major and trace element 273 contents, ~50 mg of powdered samples were melted by alkaline fusion after adding 0.8 g of lithium 274 275 metaborate and 0.2 g of lithium tetraborate in a graphite crucible. After 5 minutes at 1000 °C, the 276 beads were re-dissolved in a stirring solution of HNO₃. Major elements were measured on the ICP-277 OES Thermofischer Scientific iCAP at ULB, using Y as internal standard. Two USGS standards were 278 used (BHVO-2 and AGV-2) and the total reproducibility was better than 2% for each element. Loss on ignition was measured on a 0.5 g aliquot after 5 h at 800 °C. Trace elements were measured on an 279 280 Agilent 7700 ICP-MS, also at ULB, by adding In as internal standard. The same USGS standards were 281 used. The total reproducibility was systematically better than 5%.

282

283 **4. Results**

284 4.1. Petrography

285 *4.1.1. Apatite in glimmerite and carbonatite*

In rocks of the glimmerite and carbonatite series (including silica carbonatite and carbonate
glimmerite), apatite is mostly present as isolated elongated euhedral to anhedral crystals (from about 1
mm to a few centimeters in size) or as clusters of crystals (Figs. 3, 4).

In these lithotypes, apatite is mostly associated with tetraferriphlogopite and calcite in variable 289 290 proportions. K-feldspar, clinopyroxene and amphibole (richterite) are also locally abundant. REE are 291 concentrated in mm- to cm-sized apatite crystals and small (< 200 µm) REE-rich grains that are scattered in the carbonatite matrix but not included within apatite (see LIBS image and spectra of the 292 apatite rock ore; Fig. 3a,b). In the apatite-rich carbonatite (exploited in the Siilinjärvi mine, sample 293 Si11), apatite seems to be associated with a conspicuous Na- and K-rich zone within the carbonatite 294 295 matrix, which could be related to a separate carbonatite generation (see Fig. 3). The blue luminescence 296 of apatite is dominant in the observed facies (Fig. 4a,c,e,g). The link between a CL color and 297 activation by a specific element can be deduced from cathodoluminescence spectra (Fig. 7a-c). This 298 blue CL color is due to REE activation, mostly Eu²⁺ (e.g., Marshall, 1988; Mitchell et al., 1997; Blanc et al., 2000; Kempe and Götze, 2002; Mitchell et al., 2014, 2020). A stronger activation by Sm³⁺ 299 produces violet shades in the earliest zones (cores) of the crystals (Fig. 4c,e,g), whereas Dy³⁺ induces 300 greenish shades (as illustrated in cathodoluminescence spectra; Fig. 7a). The Nd³⁺ emission lines 301 (multiplet in the 850-930 nm range) are well visible when the Raman shift is converted back to the 302 303 absolute emission wavelength. This method, already used by Decrée et al. (2016), makes it possible to directly compare REE fluorescence (here Nd³⁺) with cathodoluminescence (Fig. 7d). 304

In the glimmerite-carbonatite series, apatite shows a range of CL colors, with violet CL within earlyformed cores to greenish CL inside later generations. In the apatite rock (an apatite-rich carbonatite, sample Si11), a blue-green-luminescent apatite replaced massively a blue-violet apatite as a dense network (Fig. 4a). The greenish CL is accompanied with an increase in Nd³⁺ activation (Fig. 4b). In glimmerite, silica carbonatite and carbonate glimmerite, this replacement occurs preferably along the walls of fissures and cleavage planes. Replacement or overgrowth at the rim of apatite crystals are also commonly observed (Fig. 4c,e,g). The green CL is again coupled with an increase in Nd activation

312 from early- to late-formed apatite (Fig. 4d,f,h).

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314 *4.1.2. Apatite in fenite*

In the fenite, apatite is mostly present as stubby anhedral crystals (a few hundreds of micrometers in 315 size; Fig. 5) associated with a mineral paragenesis comprising K-feldspar, amphibole (actinolite), 316 clinopyroxene (aegirine-augite), calcite and albite. Minor phases are magnetite and REE-minerals 317 (britholite and monazite). The latter are preferentially clustered in the vicinity of apatite crystals (see 318 LIBS image; Fig. 6). Red luminescence of K-feldspar (Fig. 5a) is due to Fe³⁺-activation. This is 319 common in feldspars from fenitized rocks (Marshall, 1988). As mentioned for the apatite in the 320 glimmerite-carbonatite series, the blue, violet-reddish and greenish CL of apatite in fenite (Fig. 5a,c,e) 321 are related to activation by Eu^{2+} , Sm^{3+} and Dy^{3+} , respectively (see cathodoluminescence spectra, Fig. 322 7b,c). A notable exception is a bright green-luminescent apatite observed in a pyroxenite-rich fenite. 323 Spectroscopic data show that this apatite is Mn²⁺-activated, as illustrated by its intense broad band 324 325 emission centered at about 570 nm in cathodoluminescence spectra (Fig. 7b). As for apatite hosted by glimmerite and carbonatite, transformed Raman spectra emphasize the role of Nd³⁺-induced 326 327 fluorescence/luminescence in these rocks (Fig. 7e,f)

Whether it is in pyroxenite- or amphibole-rich fenite, apatite always shows a complex texture under 328 329 CL. Its luminescence is blue-violet in the primary apatite with irregular blue-green-luminescent zones 330 highlighting replacement (Fig. 5a,c) or overgrowth, locally after corrosion/resorption of the primary apatite (as the green-luminescent rim in Fig. 5a,e). Replacement and overgrowth zones are mostly 331 characterized by a stronger Nd-activation compared to early-formed apatite (Fig. 5b,d). In contrast, in 332 several pyroxenite-rich samples (Si5 and Si6), bright green and dark green-luminescent rim and outer 333 replacement zones of apatite grains are associated with a strong decrease in Nd activation (Fig. 5e-g) 334 and REE contents (the decrease in Ce is illustrated in Fig. 5g). Locally, britholite is found lining these 335 grains (Fig. 5h). Note that these episodes of overgrowth/replacement with contrasting chemistry can 336 occur in successive phases, with first the deposition of a blue-luminescent apatite (with strong Nd-337 activation) after a violet-luminescent core, before an overgrowth of a more greenish apatite that is 338 overall less activated by Nd^{3+} (Fig. 5c,d). 339

340

341 **4.2.** Mineral chemistry

Apatite from Siilinjärvi shows a large range of CaO (50.96-55.77 wt.%) and P₂O₅ concentrations (38.04-42.43 wt.%, see Table 1S (Supplementary Material)). These analyses suggest that substitutions (with F, Si, Sr and REE, for instance; Pan and Fleet, 2002) are significant at Ca and P sites.

Fluorine contents range from 2.34 to 3.35 wt% (which are below the theoretical maximum of 3.73 wt% in apatite), whereas Cl contents are always below the detection limit (<0.05 wt%). The SiO₂ and SO₃ contents are low to moderate (\leq 0.14 wt%). Strontium oxide contents vary between 0.61 and 1.20 wt%, whereas FeO (\leq 0.16 wt%) and Na₂O (\leq 0.25 wt.%) contents are low to moderate. Barium oxide and MnO contents do not exceed 0.09 wt% and 0.12 wt%, respectively. Magnesium oxide content is above the detection limit (0.07 wt% MgO) in only four analyses.

351 The analyzed apatite grains display similar slightly curved chondrite-normalized REE patterns in

352 general (Table 2S (Supplementary Material)), except those hosted by two pyroxene-rich fenite (Fig.

8a-d). Apatite from the glimmerite-carbonatite series has high total REE contents (3195 - 6665 ppm),

with a strong enrichment in LREE ($La_N/Yb_N = 97 - 129$) and a slightly negative Eu anomaly (0.82-0.87; Fig. 8a,b).

- 356 Similar trends are observed for apatite from several studied fenite samples (samples Si4 and Si10). In
- the latter, apatite exhibits REE and LREE enrichment ($\Sigma REE = 3835 6665$ ppm; $La_N/Yb_N = 97$ -
- 200), with a negative Eu anomaly of about 0.82-0.86 (Fig. 8c; Table 2S (Supplementary Material)).
- Apatite in other fenite samples is generally less rich in REE and LREE ($La_N/Yb_N = 12-103$; $\Sigma REE = 663-4567$), with a more significant negative Eu anomaly (Eu/Eu* = 0.73-0.84). The most extreme
- values (low La_N/Yb_N , low ΣREE and significant negative Eu anomaly) were measured in apatite that is
- 362 hosted by two pyroxene-rich fenite (Fig. 8d). The corresponding REE patterns are moderately curved
- 363 (Fig. 8d).

The primitive mantle (PM)-normalized spidergrams (Fig. 9a) highlight this enrichment in REE and the depletion in Pb, V and high-field-strength elements (HFSE), i.e. Nb, Ta, Hf and Zr. These latter are, however, less depleted in the fenites. The same trends are overall observed when apatite analyses are normalized to their P_2O_5 content (as determined by EMPA analyses; Fig. 9b). A notable difference is the relative enrichment in Pb compared to U and Th.

- 369 Geochemical intra-grain variability can be important in apatite, consistent with the complex texture revealed by Nd³⁺ emission under CL. A correlation between CL intensity/color and REE content is 370 observed in most of the samples. In the glimmerite-carbonatite series, the early-formed violet-blue-371 luminescent apatite (or apatite core) is less enriched in REE than the blue-green-luminescent rims and 372 373 alteration zones (Fig. 8a,b). Similar correlations are also observed in pyroxene- and amphibole-rich fenite (samples Si2 and Si4; Fig. 8c,d). By contrast, (dark) green-luminescent overgrowths/rims in 374 375 apatite from other pyroxene-rich fenite samples are significantly depleted in (L)REE compared to the violet-luminescent early-formed apatite (samples Si5 and Si6; Fig. 8d). Finally, apatite hosted by 376 amphibole-rich fenite (samples Si1 and Si10; Fig. 8c) shows more complex textures, with (i) an early 377 378 enrichment in REE compared to the violet-luminescent core; this enrichment is overall correlated with 379 a blue luminescence of apatite; and (ii) secondary overgrowth (or replacement) by a greenish-380 luminescent apatite is characterized by a slight decrease in REE (Fig. 8c).
- 381 382

4.3. Whole rock chemistry

The analyzed carbonatite has a CaO content of about 54.5 wt% (54.09 and 54.69 wt%), with little 383 384 MgO (~1 wt%). The P₂O₅ contents vary between 11.42% in a typical carbonatite and can reach 34.18 385 wt% in a portion of the carbonatite body that can be considered an apatite rock (Table 3S 386 (Supplementary Material)). In the other rocks pertaining to the glimmerite-carbonatite series, the P_2O_5 content ranges from 0.23 wt% (in the carbonate glimmerite) to 14.01 wt% (in the glimmerite), and 387 2.32 wt% in the silica carbonatite. The CaO content is strongly variable (from 4.10 to 18.60 wt%) in 388 glimmerite-carbonatite. These rocks are rich in SiO₂ (27.24-36.94 wt%), MgO (14.92-21.51 wt%), 389 Fe₂O₃ (6.96-9.91 wt%), Al₂O₃ (5.32-8.07 wt%) and K₂O (4.91-6.89 wt%). All other element contents 390 are below 1 wt%. 391

Some fenite samples are slightly enriched in phosphates (0.55-2.95 wt% P_2O_5) and contain mainly silicates (44.97-56.77 wt% SiO₂). The content in the other major elements varies significantly, with 3.73-12.87 wt% Al₂O₃, 6.39-19.08 wt% CaO, 2.68-11.34 wt% Fe₂O₃ and 2-67-10.61 wt% MgO. They also contain a few percent of Na₂O and K₂O (2.01-3.66 wt% and 2.02-7.66 wt%, respectively). One of the amphibole-rich fenites contains more carbonates (sample Si10). Its SiO₂ content is consequently lower (26.65 wt%), as are the other major elements apart from CaO (28.03 wt%), MgO (11.77 wt%) and Fe₂O₃ (5.68 wt%).

399 The chondrite-normalized REE patterns of rocks of the glimmerite-carbonatite series (Fig. 10a) show 400 an enrichment in LREE (La_N/Yb_N from 60 to 119), with high Σ REE contents (396-3176 ppm) and low

401 negative Eu anomalies ($0.90 < Eu^*/Eu < 0.93$). An exception is the carbonate glimmerite, which 402 contains only 0.23 wt% P_2O_5 and is also particularly poor in REE (68 ppm in total). Though displaying similarly shaped REE patterns, the fenites are in general less enriched in REE and LREE (116 $< \Sigma$ REE 403 <454 ppm; $22 < La_N/Yb_N < 85$), with low negative Eu anomalies (0.86 < Eu*/Eu < 0.95). A notable 404 405 feature shared by a few samples of the glimmerite-carbonatite series and fenites is an enrichment in 406 the heaviest REE (Yb-Lu). The shape of these REE patterns is overall similar to those obtained on apatite (LA-ICPMS measurements; Fig. 10a). Moreover, a good positive correlation between the total 407 408 REE content and the P_2O_5 content indicates that apatite is an important REE-host (Fig. 10b).

409 The primitive mantle (PM)-normalized spidergrams for the Siilinjärvi carbonatite (Fig. 10c) display an enrichment in REE (which is quite similar to that measured in-situ in apatite) and several large-ion 410 lithophile elements (LILE), such as Sr, Ba and Th, but a depletion in K, Ti, V. The contents of other 411 HFSE generally conforms to those of the primitive mantle. The glimmerite and carbonate glimmerite 412 exhibit enrichment in LILE, REE and HFSE. The Hf and Zr concentrations of the carbonate 413 glimmerite are nevertheless as low as in the PM. The fenites are all enriched in elements presented in 414 the spidergram, except for Ti, Y, Yb,V and Sc, which are only slightly depleted or enriched (Fig. 10d). 415 416 The enrichment in REE of fenites is less important than in apatite, whereas their enrichments in Pb and 417 HFSE strongly contrast with the signature of apatite (LA-ICPMS measurements). The Post Archean Australian Shale (PAAS)-normalized spidergrams are overall comparable to the PM-normalized ones 418 (Fig. 10e,f). However, most of the elements are depleted compared to PAAS, except for Sr, LREE, P 419 and Sc that are enriched in all rock types. Another notable discrepancy is the more pronounced 420 421 depletion in LILE of the fenites.

422

423 **5.** Discussion

424 5.1 Apatite forming processes at Siilinjärvi and related REE content and distribution

425 5.1.1 Glimmerite and carbonatite series

426 The magmatic origin of apatite in the glimmerite-carbonatite series is confirmed by the blue cathodoluminescence of this mineral (e.g., Broom-Fendley et al., 2016; Decrée et al., 2016, 2020; 427 428 Waychunas, 2002), the enrichment in LREE and the lack of complex textures such as turbid or conversion textures under CL (e.g., Broom-Fendley et al., 2017; Zirner et al., 2015). LIBS images of 429 430 the investigated apatite ore (an apatite-rich carbonatite exploited for its very high P content; Fig. 3) 431 show that apatite crystals could be associated with a distinct carbonatitic intrusion enriched in Na-K. This leads to the following inferences: (i) there were probably multiple pulses of carbonatite magma 432 intrusion at Siilinjärvi, as already suspected by Tichomirowa et al. (2006), with significant differences 433 434 in magma chemistry; (ii) apatite was preferentially associated with discrete intrusions of Na- and K-435 rich carbonatite melts. Such enrichment could relate to the fenitization processes and the circulation of Na-K-rich fluids during mid-crustal pre-emplacement evolution of the carbonatite, as suggested by 436 437 Poutiainen (1995) based on the microthermometric study of apatite.

A major evolution trend regarding the distribution of REE in apatite is revealed by CL imaging and
LA-ICPMS analyses. An overall increase in REE content – concomitant with an increase in Sr and Y
(Fig. 9a,b) – is observed during apatite deposition in glimmerite and carbonatite. Early-formed violetluminescent apatite was replaced by a blue-green-luminescent apatite that is more strongly activated
by Nd and enriched in REE compared to the former (Fig. 3 and Fig. 8a,b). Similarly, the blueluminescent outer part of apatite crystals (rims or overgrowths) has a CL that is more strongly

444 activated by Nd than in early apatite (Fig. 3 and Fig. 8a,b). An increase in REE uptake from early-445 formed to later-formed apatite can be reached by two processes:

(i) The fractionation of a large amount of co-precipitating minerals - here calcite and phlogopite -446 could theoretically influence the REE budget of the residual melt (e.g., Bühn et al., 2001; 447 Chakmouradian et al., 2017). However, this possibility can be largely discarded in our case for the 448 449 following reasons. First, the removal of REE hosted by phlogopite should not significantly affect the 450 REE distribution and content in later formed apatite because the REE content of this mineral is very 451 low, that is, hardly above the detection limits (Chakhmouradian et al., 2017). Moreover, an increase of 452 the (La/Yb)_N ratio of the residual melt is expected after crystallization of a large quantity of calcite (Bühn et al., 2001). Such a trend is not observed in the late generations of apatite, which supposedly 453 crystallized in equilibrium with the residual melt. 454

(ii) Alternatively, the REE enrichment during apatite deposition could be due to a more evolved 455 456 magmatic/metasomatic input. Such an input could come via the intrusion of a fresh magma enriched in REE (as the one observed on the LIBS images). This intrusion would lead to the re-equilibration of 457 earlier-formed apatite with the intruding magma, likely through sub-solidus diffusion at the magmatic 458 459 stage (e.g., Harlov et al., 2005; Chakhmouradian et al., 2017). This was already suggested for zircon 460 close to warm and thick calcite veins at Siilinjärvi (Tichomirowa et al., 2013). Moreover, Tichomirowa et al. (2006) noticed a change of apatite CL color from purple to blue in contact with the 461 latest generation of carbonatite. We have shown here that this change in color is associated with an 462 increase in REE. All these arguments suggest that a late carbonatite pulse associated with the 463 development of alkali-rich fluids that caused widespread fenitization could be responsible for a 464 465 significant input of P and REE into the system, affecting all the previously emplaced rocks of the glimmerite-carbonatite series. This is consistent with the fact that REE are typically found in more 466 467 evolved magmas (e.g., Mariano, 1989; Elliott et al., 2018; Simandl and Paradis, 2018).

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469 *5.1.2 Fenite*

In amphibole- and pyroxene-rich fenites, apatite displays a complex zonation (alteration and conversion textures), which can be regarded as the product of apatite re-equilibration with highly evolved melts and/or fluids (e.g., Zirner et al., 2015; Broom-Fendley et al., 2017; Chakhmouradian et al., 2017; Decrée et al., 2020). Late-stage interactions with water-rich fluids were already assumed at Siilinjärvi, based on the general tendency of decreasing Sr concentrations with increasing δ^{18} O ratios (Tichomirowa et al., 2006). The REE content and distribution follow two major evolution trends in the investigated apatite within fenite:

477 (i) Apatite grains can exhibit an increasing Nd activation under CL towards their outer rim, as
478 overgrowths after resorption, and in the inner part of the grains, while replacing early-formed violet479 luminescent apatite. Both overgrowth and replacement zones show a blue-green luminescence and an
480 increase in REE content (samples Si2 and Si4; Fig. 5a,b and Fig. 8c,d).

(ii) The second trend is characterized by a strong decrease in Nd-activation in green-luminescent rims
and overgrowths (in samples Si5 and Si6; Fig. 5e-g). This decrease in REE is coupled with a
substantial LREE loss (and a stronger Eu negative anomaly) that modifies the shape of the REE
patterns (Fig. 8d) and a loss in other elements, such as Sr and Y (Fig. 11a,b). It is worth mentioning
that several apatite grains record both trends, with a first phase of growth/replacement characterized by
a REE-enrichment and a second phase of growth recording a slight depletion in REE (samples Si1 and
Si10; Fig. 5c,d and Fig. 8c).

Considering the above contrasting trends, at least two types of melt/fluid-rock interactions could 488 explain the observed phenomena. The REE enrichment could involve Na-K-rich fluids during early 489 (pre-emplacement) evolution of the carbonatite. These fluids are likely enriched in P and REE, as 490 already evoked in section 5.1.1. Interacting with them, the early formed apatite would have been 491 enriched in REE through coupled dissolution-reprecipitation processes (e.g., Zirner et al., 2015). 492 493 Other elements – namely, Nb, Th, Pb (and U to some extent) – could be concentrated when interacting with these fluids. Their contents in apatite hosted by fenite are higher than those in apatite from the 494 carbonatite-glimmerite series (Fig. 11c-e). 495

496 Conversely, the decrease in LREE in apatite is commonly attributed to the mobilization of these elements during fluid flow through the rock (e.g., Harlov et al., 2002). The LREE are more easily 497 498 mobilized than M/HREE during fluid-rock interactions and show greater stability as chloride or 499 fluoride complexes (e.g., Broom-Fendley et al., 2016; Elliot et al., 2017; Krneta et al., 2018). The more pronounced negative Eu anomalies (0.73<Eu/Eu*<0.83) are likely due to the extraction of 500 divalent Eu via a high-temperature aqueous fluid evolving from the magma (Bühn et al., 2001). The 501 502 assemblage of green-luminescent apatite (which is less enriched in REE) and REE mineral phases as 503 britholite and monazite at the apatite rim would have formed at the expense of the REE-rich apatite through coupled substitution and mass transfer (e.g., Zirner et al., 2015; Giebel et al., 2017). 504

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5.1.3 Prospect of REE quantitation in apatite using CL and Raman spectroscopy

507 Fluorescence and CL activation can be deduced from the observation of the cathodoluminescence 508 and Raman spectra. At a first glance, it appears that the relative intensity of the emission peak of a specific luminescence activator can be correlated with its concentration. For instance, in carbonatite, 509 the overall luminescence is more intense in the REE-rich green-luminescent apatite of the replacement 510 511 zones than in the early-formed violet luminescing apatite, which is less enriched in REE (Fig. 7a,d). An attempt was made to correlate the luminescence spectra and the REE content of apatite more 512 513 accurately. Neodymium appeared as a good candidate for such a purpose, because the emission multiplet of Nd³⁺ in the near-infrared is free from any interference with other REE and the background 514 signal is low. After subtraction of the background, the area under the peaks was measured between 515 ~850 and ~950 nm. The good correlation between the Nd content as measured using LA-ICPMS and 516 spectroscopic measurements for both fluorescence and cathodoluminescence spectra is presented in 517 518 Figure 12. It shows that the spectral signal of apatite using CL and Raman can be used to estimate the relative content of Nd. These correlations could be undoubtedly improved with more careful 519 acquisition settings, data processing (especially background subtraction) and a more rigorous 520 521 chemometric approach. An absolute concentration could be obtained if a minimum of geochemical 522 data is provided for calibration. Of course, this method should be extended to more types of apatite from other carbonatites and other environments to validate the observed correlation. Nevertheless, the 523 currently available data confirm that spectroscopic analysis of luminescence is a helpful tool to assess 524 525 the REE potential of apatite with relatively little effort.

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5.2. Reassessment of the economic potential regarding strategic elements

The estimation of the ore reserves at Siilinjärvi as per January 2014 was 234 Mt at an average grade of 4 wt% P_2O_5 . Almost all the rocks of the glimmerite-carbonatite series can be considered economic for apatite exploitation (O'Brien et al., 2015). The analyses performed in the frame of this study confirm the enrichment in phosphate of these rocks (2.32< P_2O_5 <34.18 wt%), apart from the carbonate glimmerite that contains only 0.23 wt% P_2O_5 . In the Siilinjärvi mine, fenites are stockpiled separately (O'Brien et al., 2015), though some of these rocks show a promising phosphate content (two samples at 2.4 and 2.9 wt% P_2O_5), close to the average grade of the rocks that are currently mined.

Beside phosphate, numerous commodities can be recovered from deposits associated with carbonatites 536 537 and related alkaline complexes, such as Nb, Zr, Hf and REE (e.g., Pell, 1996). The spidergrams in 538 Figure 10 show that none of these elements are concentrated at Siilinjärvi, apart from the REE. 539 Whether it is in the rocks pertaining to the glimmerite-carbonatite series or in fenites, the REE content 540 of the rocks correlates well with their P_2O_5 concentration (Fig. 10b). These correlations can be used to roughly estimate the REE reserves at Siilinjärvi. Based on the latter and on an average content of 4 541 wt% P_2O_5 in the rocks exploited (O'Brien et al., 2015), two average hypothetical REE contents were 542 543 calculated, depending on the correlation used: (i) 576 ppm, using the equation based on all rock types (Fig. 10b), and (ii) 697 ppm using the equation considering only the rocks currently mined as 544 phosphate (i.e. the glimmerite-carbonatite series; Fig. 10b). As a reserve of roughly 200 Mt remains to 545 546 be exploited, the REE reserve should approximate ~133,000 t of Total Rare Earth Oxide (TREO) 547 (using an average grade of 576 ppm) or ~161,000 t of TREO (using an average grade of 697 ppm) in the phosphate deposit. A large part of the REE must be present in apatite that contains up to 0.66 wt% 548 549 REE, even though other REE-minerals are also present as scattered minute grains in the different rocks 550 (as observed on the LIBS images, Fig. 3,5h,6). The exploitation of REE as a by-product of the apatite could be interesting at Siilinjärvi, and probably in other alkaline complexes as well. In the Khibina 551 552 alkaline massif (Kola Peninsula, Russia), an increase in production of REE would be achieved by extracting the REE from apatite through a hydrochloric acid treatment (with recovery rates of ~80% 553 554 REE; Pereira and Bilal, 2012). Considering the relative ease of REE extraction from apatite (e.g. 555 Emsbo et al., 2015), the potential reserves of REE at Siilinjärvi (133,000-161,000 tons of REE₂O₃) and assuming that a large part of REE is locked into the structure of apatite, the beneficiation of REE as a 556 557 by-product of the Siilinjärvi phosphates could be of economic interest.

558

559 6. Summary and conclusions

Apatite from the Neoarchean carbonatite complex of Siilinjärvi has been investigated for its 560 chemistry and optical spectroscopy (CL, Raman spectroscopy, LIBS). The aim was to decipher the 561 562 processes leading to the formation of apatite and controlling the distribution of REE in this mineral. In the glimmerite-carbonatite series, the blue-violet CL and LREE enrichment corroborate a previously 563 assumed igneous origin of the apatite. The REE enrichment in alteration zones and at the rim of apatite 564 565 crystals reveals re-equilibration of early formed apatite with a REE-rich fresh carbonatite magma. This 566 magma, which is one of the last intruded, caused a significant input of P and REE into the system. The late carbonatite also recorded interactions with alkali-rich fluids, likely in connection with fenitization. 567 In fenite, alteration textures emphasize fluid-rock/magma interactions at various stages of apatite 568 crystallization. A first event led to enrichment in REE of the early formed apatite. This enrichment 569 was likely due to interaction with REE-rich fluids related to fenitization. Local depletion of apatite in 570 571 LREE is ascribed to a late-magmatic or hydrothermal stage.

572 Spectroscopic methods used here constitute powerful and inexpensive tools for exploration. In 573 addition to bringing crucial information about mineralization events, LIBS mapping makes it possible 574 to map elemental distribution (and speciation) of P and REE in the rocks. Raman and CL spectroscopy 575 give clues regarding enrichment in REE of apatite, as illustrated by (i) the spectral CL of the Nd³⁺ 576 emission at 880 nm that quickly reveals the REE distribution and enrichment in apatite, and (ii)

fluorescence (photoluminescence) and cathodoluminescence spectra that enable fast qualitative
assessments of the REE enrichment in apatite based on the observed correlation between spectroscopic
and geochemical data, with some insight into (semi)-quantification.

Finally, the geochemical data obtained on whole rock samples show that part of the fenites could be considered for exploitation, because their phosphate content is close to the average content of the rocks currently mined. In addition, the REE and phosphate contents correlate well in all of the investigated rocks. A rough estimate based on this correlation and the available data on reserves suggests that REE could constitute an economically interesting by-product of the Siilinjärvi phosphates.

586

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751 Figure and Table captions

Fig. 1 Geological sketch map of the Siilinjärvi Carbonatite Complex (modified and redrawn from O'Brien et al., 2015) The second second second state of Siilinjärvi Carbonatite Fields

- 753 2015). The upper insert shows the location of Siilinjärvi in Finland
- Fig. 2 Selected macrophotographs of Siilinjärvi rocks. (a) Carbonatite with green apatite crystals (sample Si8);
- (b) Apatite rock made of carbonatite with abundant green apatite crystals (sample Si11); (c) Glimmerite (sample
- Si9); (d) Silica carbonatite (sample Si7); (e) Carbonate glimmerite (sample Si3); (f) and (g) Amphibole-rich
 fenite (samples Si6 and Si5); (h) and (i) Pyroxene-rich fenite (samples Si1 and Si10)

758 Fig. 3 LIBS analysis of an apatite rock (apatite-rich carbonatite, sample Si11) from Siilinjärvi. Element names 759 are followed by the integer part of the emission wavelength that was used. (a) Selected LIBS maps that show the 760 distribution of both the major minerals (calcite, phlogopite and fluorapatite, as inferred from the distribution of 761 Ca, Si, P, CaF, K and other elements not shown here) and minute REE-minerals (as inferred from the bright 762 spots in La and Ce maps). Although REE are detected in apatite, REE-minerals are scattered throughout the 763 matrix but not included in apatite nor in phlogopite. The map of molecular CaF emission confirms the apatites 764 are all fluorapatites. Note the Na- and K-rich zone within the calcitic groundmass of the carbonatite. (b) Example 765 LIBS spectra of the 411-418 nm range showing the REE lines that were used for mapping elements in the 766 carbonatite sample shown in (a). Each spectrum was obtained by averaging several spectra by selection of a ROI 767 (Region Of Interest) on the maps. The spectra of Na-Poor and Na-rich calcite are identical (except for Na and K, 768 whose emission peaks are observed outside the displayed wavelength range)

769 Fig. 4 Cathodoluminescence (CL) photomicrographs of the Siilinjärvi glimmerite-carbonatite series. Color CL in 770 (a),(c),(e) and (g). Spectral CL (Nd³⁺ emission filtered at 880 nm) in (b),(d),(f) and (h); Cal - calcite, Phl -771 tetraferriphlogopite. The four-pointed stars represent the spots where EPMA and LA-ICPMS analyses were 772 performed. Related REE content (SREE in ppm) is indicated in a black box. (a-b) Apatite crystal in apatite rock 773 (sample Si11) exhibiting a heterogeneous texture; a blue-luminescent apatite is partly altered/replaced by a 774 green-luminescent apatite, which is characterized by a stronger Nd activation; (c-d) Green-luminescent apatite 775 replacing a blue-violet-luminescent apatite towards the outer part of a crystal hosted by a glimmerite. Nd 776 activation increase accordingly towards the crystal rim, suggesting a higher concentration in LREE (sample Si9); 777 (e-f) Violet-luminescent apatite with a more bluish luminescence in the crystal rim and along fissures. These 778 bluish zones correspond to an increased Nd-activation (silica carbonatite, sample Si7); (g-h) Closely-packed 779 cluster of blue-violet-luminescing with more bright/greenish luminescence in the rim of some crystals. 780 Replacement zones inside the grains also present this brighter luminescence. The latter corresponds to a a higher 781 Nd activation (carbonate glimmerite, sample Si3)

782 Fig. 5 Cathodoluminescence (CL) (a-f), EPMA (g,h) and backscattered electron (i) photomicrographs of the Siilinjärvi fenites. Color CL in (a), (c) and (e). Spectral CL (Nd³⁺ emission filtered at 880 nm) in (b), (d), (f) and 783 784 (h); Ab-albite, Ap-apatite, Bri-britholite, Cal - calcite, Cam-clinoamphibole, Cpx-clinopyroxene, Kfs - K-785 feldspar, Mag - magnetite, Phl - tetraferriphlogopite. The four-pointed stars represent the spots where EPMA 786 and LA-ICPMS analyses were performed. Related REE content (SREE in ppm) is indicated in a black box. (a-b) 787 Zoned apatite crystals with a blue-violet CL core and green CL rim in a pyroxene-rich fenite (sample Si4); textures suggest the partial replacement of the early-formed (violet-luminescent) grain by an apatite with 788 789 stronger Nd-activation; (c-d) Stubby crystal of apatite in an amphibole-rich fenite (sample Si10). Apatite exhibits 790 a complex luminescence texture. The primary blue-violet-luminescent apatite is partly replaced by light-blue-791 luminescent apatite (with increased Nd-activation), likely along the direction indicated by the single arrow. It is 792 then overgrown by apatite with a lower Nd activation; (e-g) Closely-packed cluster of apatite crystals in a 793 pyroxene-rich fenite (sample Si5); apatite rim is characterized by a bright green CL, while apatite overgrowth 794 (indicated by arrows) shows a dark blue-greenish luminescence. Interestingly, both are characterized by a 795 decrease in Nd-activation (f) and a decrease in Ce (g), highlighting a global decrease of REE content. The white 796 square presented in (e) corresponds to the zone illustrated in (g); (h) Britholite overgrowth on an apatite grain in 797 a pyroxene-rich fenite (sample Si6)

Fig. 6 Selected LIBS maps of a 38 mm diameter core of pyroxene-rich fenite from Siilinjärvi (sample Si 1).
Elements names are followed by the integer part of the emission wavelength that was used. Here, La and Ce maps do not exactly match together as in the carbonatite, suggesting a more diverse REE-mineral assemblage

Fig. 7 Representative spectra of apatite from various rocks of the Siilinjärvi Complex using
cathodoluminescence (a,b,c) and Raman spectroscopy (d,e,f). (a) and (d) Spectra of apatite from carbonatite and
silica carbonatite (samples Si11 and Si7); (b) and (e) Spectra of apatite from pyroxene-rich fenite (samples Si5
and Si6); (c) and (f) Spectra of apatite from amphibole-rich fenite (sample Si10)

Fig. 8 REE patterns of apatite in the different rock types of the Siilinjärvi Complex; (a) carbonatite and silica
carbonatite, (b) glimmerite and carbonate glimmerite, (c) amphibole-rich fenite and (d) pyroxene-rich fenite;
REE patterns are normalized to chondrite values from McDonough and Sun (1995)

808Fig. 9 Spidergrams generated from LA-ICPMS analyses and normalized to (a) the Primitive mantle809(McDonough and Sun, 1995) and (b) to the P_2O_5 content (in wt. %, electron microprobe analyses)

- **Fig. 10** (a) REE patterns for whole rock data of the Siilinjärvi rocks. REE patterns of apatite (LA-ICPMS data) are given for comparison. Data are normalized to chondrites (McDonough and Sun, 1995), (b) correlation for whole rock analyses between total REE content and P_2O_5 content, (c-f) spidergrams of the Siilinjärvi rocks comparing whole rock analyses and LA-ICPMS analyses of apatite. Normalization to the Primitive mantle
- 814 (McDonough and Sun, 1995) (c-d) and to the Post Archean Australian Shales (PAAS; Condie, 1993) (e-f)
- Fig. 11 Correlations for LA-ICPMS analyses between Sr and total REE content (a), Y and total REE content (b),
 U and Nb (c), U and Th (d) and Pb and Sr (e). Whole rock data are given for comparison
- Fig. 12 Correlation between Nd content and area under curve between 850 and 950 nm for (a) transformed
 Raman spectra (Raman shift converted into wavelength) and (b) CL spectra
- 819 -----
- 820 Table 1. Succinct description of all examined samples from the Siilinjärvi Carbonatite Complex
- 821

Journal Prevention

Sample	Ret. orill core (it available)	Journal Pre- Description
Si1		fenite (amph)
Si2	R713 L-114 513.95-514.45	fenite (amph)
Si3		carbonate glimmerite
Si4		fenite (pyrox)
Si5		fenite (pyrox)
Si6		fenite (pyrox)
Si7	UCS R713 L-128 577-577.60	silica carbonatite
Si8		carbonatite
Si9	UCS R713 L-136 614.85-615.35	glimmerite
Si10		fenite (amph)
Si11		carbonatite (apatite rock)













Wavelength [nm]





Si390









Highlights:

- This study focuses on apatite and its REE content at Siilinjärvi (Finland) -
- Petrological and geochemical study helps deciphering its genesis -
- Igneous processes and metasomatic alteration are evidenced -
- A sub-economic potential of REE to be exploited as by-products is considered _

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Declaration of interests

 \boxtimes 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.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: