Apatite in carbonatitic rocks: Compositional variation, zoning, element partitioning and petrogenetic significance

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Abstract

Apatite-group phosphates are nearly ubiquitous in carbonatites, but our understanding of these minerals is inadequate, particularly in the areas of element partitioning and petrogenetic interpretation of their compositional variation among spatially associated rocks and within individual crystals. In the present work, the mode of occurrence, and major- and trace-element chemistry of apatite (*sensu lato*) from calcite and dolomite carbonatites, their associated cumulate rocks (including phoscorites) and hydrothermal parageneses were studied using a set of 80 samples from 50 localities worldwide. The majority of this set represents material for which no analytical data are available in the literature. Electron-microprobe and laser-ablation mass-spectrometry data (~600 and 400 analyses, respectively), accompanied by back-scattered-electron and cathodoluminescence images and Raman spectra, were used to identify the key compositional characteristics and zoning patterns of carbonatitic apatite. These data are placed in the context of phosphorus geochemistry in carbonatitic systems and carbonatite evolution, and compared to the models proposed by previous workers. The documented variations in apatite morphology and zoning represent a detailed record of a wide range of evolutionary processes, both magmatic and fluid-driven. The majority of igneous apatite from the examined rocks is Cl-poor fluorapatite or F-rich hydroxylapatite (≥ 0.3 apfu F) with 0.2-2.7 wt.% SrO, 0-4.5 wt.% LREE₂O₃, 0-0.8 wt.% Na₂O, and low levels of other cations accommodated in the Ca site (up to 1000 ppm Mn, 2300 ppm Fe, 200 ppm Ba, 150 ppm Pb, 700 ppm Th and 150 ppm U), none of which show meaningful correlation with the host-rock type. Silicate, (SO₄)²⁻ and (VO₄)³⁻ anions, substituting for (PO₄)³⁻, tend to occur in greater abundance in crystals from calcite carbonatites (up to 4.2 wt.% SiO₂, 1.5 wt.% SO₃ and 660 ppm V). Although (CO₃)²⁻ groups are very likely present in some samples, Raman micro-spectroscopy proved inconclusive for apatites with small P-site deficiencies and other substituent elements in this site. Indicator REE ratios sensitive to redox conditions (δ Ce, δ Eu) and hydrothermal overprint (δ Y) form a fairly tight cluster of values (0.8-1.3, 0.8-1.1 and 0.6-0.9, respectively) and may be used in combination

with trace-element abundances for the development of geochemical exploration tools. Hydrothermal apatite forms in carbonatites as the product of replacement of primary apatite, or is deposited in fractures and interstices as euhedral crystals and aggregates associated with typical late-stage minerals (e.g., quartz and chlorite). Hydrothermal apatite is typically depleted in Sr, REE, Mn and Th, but enriched in F (up to 4.8 wt.%) relative to its igneous precursor, and also differs from the latter in at least some of key REE ratios [e.g., shows $(\text{La/Yb})_{\text{cn}} \leq 25$, or a negative Ce anomaly]. The only significant exception is Sr($\pm$ REE,Na)-rich replacement zones and overgrowths on igneous apatite from some dolomite(-bearing) carbonatites. Their crystallization conditions and source fluid appear to be very different from the more common Sr-REE-depleted variety. Based on the new evidence presented in this work, trace-element partitioning between apatite and carbonatitic magmas, phosphate solubility in these magmas, and compositional variation of apatite-group minerals from spatially associated carbonatitic rocks are critically re-evaluated.

Keywords: Apatite; Trace-element composition; Element partitioning; Raman micro-spectroscopy; Carbonatites; Phoscorites; Magma evolution

1. Introduction

Apatite is the most common non-carbonate phase in both intrusive and extrusive carbonatites (see Section 4), but its modal content varies greatly from trace levels to > 50% in cumulate rocks commonly also enriched in magnetite, ferromagnesian silicates, zircon and Nb oxides (e.g., Andersen, 1986; Ray et al., 2010; Chakhmouradian et al., 2015). As can be expected, published apatite analyses number in the hundreds. However, most of these data are either incomplete (i.e. lack information on such key substituent elements as lanthanides), or suffer from analytical problems (e.g., unrealistic levels of certain elements), which often translate into unfeasible chemical formulae. For example, Manthilake et

al. (2008) reported up to 0.34 wt.% MgO at very low Ca and high Si in apatite from Eppawala, Sri Lanka; formulae derived from their data show as much as 10% cation deficiency at the Ca site, although no explanation is provided for these deviations from the expected stoichiometry (see Section 2). The importance of apatite as a tracer of magma evolution in carbonatite complexes was first recognized by Le Bas and Handley (1979), and further explored by Hogarth (1989), Hornig-Kjarsgaard (1998) and Böhn et al. (2001), who examined the composition of carbonatitic apatite from a number of localities, and provided first reliable trace-element data for this mineral. Other noteworthy recent contributions are those by Brigatti et al. (2004), Brassinnes et al. (2005), Wang et al. (2014) and Zaitsev et al. (2014), where the chemical variation of apatite from carbonatites and associated rocks was regarded in the context of their petrogenesis. At present, accurate assessment of the role played by apatite in the evolution of carbonatites is hindered by the poor understanding of trace-element partitioning between this mineral and carbonate-rich liquids. The available literature is limited to a few experimental and modeling studies that produced overall contradictory results (Section 7.1). Another poorly understood aspect of the crystal chemistry of carbonatitic apatite is zoning. Although its crystals commonly exhibit striking intragranular compositional variations in cathodoluminescence (CL), back-scattered-electron (BSE) and, in some cases, transmitted-light images (e.g., Hayward and Jones, 1991; Ahijado et al., 2005; Chakhmouradian et al., 2008), only a few published studies provided quantitative data and interpretations for the observed variations.

In the present work, we summarize information available for carbonatitic apatite in the literature, provide a large volume of new paragenetic and analytical data, and put observations stemming from this synthesis in the context of carbonatite petrogenesis. The principal variations in composition and zoning among the studied samples are discussed from the standpoint of magma evolution and trace-element partitioning.

2. Background information on the crystal chemistry, compositional variation and formula of apatite

The collective term *apatite* refers to a series of hexagonal and monoclinic phosphates whose idealized formula can be expressed as $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{OH}, \text{Cl})$. Prefixes *fluor-*, *hydroxyl-* or *chlor-* are added to the root name to indicate the predominant anion located in structural channels parallel to [0001] (Hughes et al., 1989; 1990). High- and low-symmetry members of this series, designated with suffixes *-H* and *-M* respectively, can be distinguished from each other only on the basis of high-precision diffraction studies (Hughes et al., 1990, 1993; Chakhmouradian and Medici, 2007). We are not aware of any reports of natural *oxyapatite* incorporating O^{2-} in place of monovalent anions; however, such compounds can be readily synthesized (e.g., Serret et al., 2000). The lack of published evidence for channel-hosted O^{2-} in natural material may simply reflect difficulties involved in the quantification of O and H in small samples and poorly constrained stoichiometric variations (see below). Apart from biogenic samples (Pasteris et al., 2014), channel H_2O has been detected in sedimentary apatite (Mason et al., 2009) and should probably be expected to occur also in hydrothermally precipitated material.

The structure of apatite is tolerant to a wide range of substitutions (Table 1). Some of the large substituent cations are accommodated preferentially either in the ninefold-coordinated Ca1 site, or the Ca2 site coordinated by six oxygens and F ($\pm \text{OH} \pm \text{Cl}$). Element partitioning between Ca1 and Ca2 in chlorapatite differs from that in fluor- and hydroxylapatite owing to an increase in polyhedral volumes with Cl incorporation (Fleet et al., 2000; Luo et al., 2009); extensive substitution of Ca by Sr has a similar effect (Chakhmouradian et al., 2005). These ordering phenomena place constraints on the extent of certain substitutions, and are ultimately responsible for the existence of mineral species distinct from fluorapatite in symmetry and in that cations other than Ca^{2+} dominate in one of the large sites, even though Ca^{2+} may still be the preponderant cation overall (Chakhmouradian et al., 2005; Pasero et al., 2010).

The apatite structure can also accommodate vacancies in the Ca positions, and deficiency or excess of channel anions (Hata et al., 1980; Serret et al., 2000; Fleet and Liu, 2008; Zhang et al., 2012). However, the detection of non-stoichiometry in natural apatites is complicated by (1) the common presence of H in their composition; (2) the presence of $(\text{CO}_3)^{2-}$ groups in some samples; and (3) uncertainties sometimes associated with the measurement of F and Cl by electron-microprobe analysis (EMPA). Hydrogen cannot be detected by EMPA, whereas accurate C measurements by this method are challenging (Reed, 1995). The CO_2 content is rarely reported for non-biogenic samples, but even when it is, the partitioning of carbonate between the tetrahedrally coordinated and channel sites (i.e., the formula) cannot be constrained without structural or spectroscopic studies (Fleet et al., 2004; Yi et al., 2013). Apatites are susceptible to halogen diffusion induced by an electron beam, particularly when the channels hosting these anions are oriented parallel to the beam (Stormer et al., 1993). Hence, EMPA data obtained in random orientations with a focused ($< 5 \mu\text{m}$) beam may be subject to errors and should be treated with caution (Stock et al., 2015). In the literature, there are numerous reports of natural fluorapatite containing $> 3.8 \text{ wt.}\%$ (i.e. $> 1.0 \text{ apfu}$) F (e.g., Bühn et al., 2001; Cao et al., 2011; Luo et al., 2011). Apatites synthesized from a melt or by replacement also show up to 1.2 apfu F+Cl (Prowatke and Klemme, 2006; Kusebauch et al., 2015). In the absence of structural data, it is unclear whether such anomalous values, in some cases exceeding 1.6 apfu (Edgar, 1989), stem from F excess in the structure, or are merely an artefact arising from halogen diffusion during the analysis. There is compelling evidence that excess F can be accommodated in apatite via the following substitution (Binder and Troll, 1989; McArthur, 1990; Fleet and Liu, 2008; Yi et al., 2011):

At least 0.2 apfu of “surplus” F, raising the total F content to $\sim 4.5 \text{ wt.}\%$, can occur in natural fluorapatite according to spectroscopic studies (Mason et al., 2009).

Conclusive identification and assignment of molecular and ionic species to specific sites require advanced techniques that may not be applicable to microscopic samples. Given the uncertainties described above, there is no single “failsafe” way of calculating apatite formulae from EMPA data. Recasting weight percentages of individual elements to apfu values on the basis of eight cations, a fixed positive charge, or the total of 13 anions will give spurious results for samples containing appreciable $(\text{CO}_3)^{2-}$ or $(\text{OH})^-$ groups (supplementary Fig. SF1). For this reason, the data discussed below were recalculated to five Ca-site cations and assuming no vacancies in these sites.

Both Ca1 and Ca2 sites can accommodate significant proportions of REE depending on the composition of the host crystal (Fleet et al., 2000). Owing to this flexibility, samples from different rock types exhibit dramatic variations in the distribution of individual REE (supplementary Fig. SF2), reflecting fractionation within the lanthanide series driven by differences in cation size and charge, or poorly understood decoupling between nearly isometric Y^{3+} and Ho^{3+} . Variations in rare-earth budget are reflected in the shape of chondrite-normalized profiles, their tilt with respect to the abscissa axis, quantified as $(\text{La/Yb})_{\text{cn}}$, and deviations of the measured concentrations of Ce, Eu and Y from the expected values. In the present work, the magnitude of such deviation was measured with respect to the values interpolated from the chondrite-normalized abundances of the nearest smaller and larger REE³⁺ cations: $\delta\text{Ce} = \text{Ce}_{\text{cn}}/[0.5 \times (\text{La}_{\text{cn}} + \text{Pr}_{\text{cn}})]$; $\delta\text{Eu} = \text{Eu}_{\text{cn}}/[0.5 \times (\text{Sm}_{\text{cn}} + \text{Gd}_{\text{cn}})]$; $\delta\text{Y} = \text{Y}_{\text{cn}}/[(0.25 \times \text{Dy}_{\text{cn}}) + (0.75 \times \text{Ho}_{\text{cn}})]$. In addition to $(\text{La/Yb})_{\text{cn}}$, we use the chondrite-normalized ratio of Dy to Yb to determine whether the REE profile maintains a uniform slope, or shows “sagging” in the middle, as observed in some igneous rocks (Fig. SF2).

3. Research material and methodology

In order to determine the extent of compositional variation in carbonatitic apatite, we examined some 120 samples, eventually choosing 80 samples from 50 localities worldwide for further analysis.

Most of this material (~70%) represents apatites, for which little or no data is available in the literature. We also examined several samples from some “classic” localities, where apatite had been reported by previous workers to have unusual compositional characteristics (e.g., Oka in Canada, Kaiserstuhl in Germany, Kovdor in Russia). To study the partitioning of selected elements between apatite and carbonatitic magma, we chose three rocks of different modal mineralogy, all of which form shallow intrusions, are not accompanied by any alkaline silicate lithologies, and contain a significant proportion of non-carbonate material, including early-crystallizing apatite and silicate minerals. Among the studied samples, these three are most likely to approach their parental magmas in composition: calcite carbonatite from the Zibo diatreme (Shandong, China), calcite-dolomite carbonatite from Paint Lake (Manitoba, Canada) and dolomite carbonatite from Upper Fir (British Columbia, Canada). The detailed petrographic descriptions of these samples are provided in supplementary Appendix A1. The chemical variation of apatite within a series of genetically related rocks was investigated using a suite of 15 carbonatite samples from the Aley intrusion (British Columbia, Canada), four carbonatites from Paint Lake, and six samples of phoscorites and associated hydrothermal “staffelite” from Kovdor. Their petrography is detailed in Appendix A1, whereas the compositions of rock-forming carbonate minerals from these rocks were reported by Chakhmouradian et al. (2016a) and Zaitsev et al. (2014).

Apatite crystals in polished thin sections were analyzed by EMPA and laser-ablation inductively-coupled-plasma mass-spectrometry (LA-ICPMS). The concentrations of major and some minor elements were determined by wavelength-dispersive spectrometry (WDS) using a Cameca SX 100 electron microprobe operated at 15 kV and 20 nA. The following standards were employed in the analysis: fluorapatite (F, P, Ca), albite (Na), diopside (Si), barite (S), tugtupite (Cl), fayalite (Fe), SrTiO₃ (Sr), REE orthophosphates (Y, La, Ce, Pr, Nd, Sm) and ThO₂ (Th). Aluminum was sought, but found not to be present at detectable levels (> 200 ppm) in any of the samples. The electron beam was defocused to 10 µm and, wherever possible, only crystals oriented with their [0001] axis perpendicular to the beam were

analyzed to minimize anion diffusion (see Section 2). The only exceptions were thin late-stage zones in some apatite grains, whose orientation could not be ascertained (see Section 5.1). To test the effect of crystal orientation on F content, we analyzed several crystals of apatite from Fuerteventura (Canary Islands), Clay Howells, Argor and Paint Lake (Canada) in sections parallel and perpendicular to the pathways of preferential halogen diffusion. These measurements show that the two sets of values for all elements, including F, are essentially within the estimated standard deviation of each other and, hence, diffusion-induced effects can be neglected under the chosen instrumental parameters. One of the apatites from Kovdor (P5), which locally showed low analysis totals and enrichment in elements not observed in the other samples, was re-analyzed using a JEOL 8900 electron microprobe at the University of Tübingen (Germany) and following the procedure described by Wang et al. (2014). A total of ~600 WDS analyses were obtained; selected data discussed in detail below are presented in supplementary Tables ST1-ST3 (available online).

Transmitted-light, CL and BSE images were used for the selection of homogeneous areas suitable for trace-element analysis by LA-ICPMS. Because electron bombardment enhances halogen diffusion (Wang et al., 2014), all CL images were acquired after the WDS measurements, using a Reliotron VII instrument (Relion Ind.) operated at 8.5 eV and 400-450 mA and an electronically cooled Nikon DS-Ri1 camera. The abundances of selected trace elements were measured in 43 samples from 17 localities using a 213-nm Nd-YAG Merchantek laser connected to a Thermo Finnigan Element 2 sector-field mass-spectrometer. To match specific CL patterns to trace-element variations, several samples covering essentially the entire range of luminescence colors were selected and analyzed by carefully positioning the beam over each distinct area within the crystal. Laser-operation parameters were selected individually for each sample, taking into account its thickness, as well as the size and homogeneity of crystals. The data were collected using spot analysis with a 30-40 μm beam at a repetition rate of 5-10 Hz and power level of 80-85%. The incident pulse energy was 0.03-0.07 mJ, yielding a surface energy-density of 4.0-5.6 J/cm². The

ablation was performed in Ar (plasma and auxiliary) and He (sample) atmospheres. The rate of oxide production was monitored during instrument tuning by measuring the ThO/Th ratio and kept below 0.2%. Synthetic glass standard NIST SRM 610 was employed for calibration and quality control. After taking into account potential spectral overlaps and molecular interferences, the following isotopes were chosen for analysis: ^{43}Ca , ^{51}V , ^{55}Mn , ^{85}Rb , ^{88}Sr , ^{89}Y , ^{90}Zr , ^{93}Nb , ^{137}Ba , ^{139}La , ^{140}Ce , ^{141}Pr , ^{143}Nd , ^{147}Sm , ^{151}Eu , ^{155}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{167}Er , ^{169}Tm , ^{172}Yb , ^{175}Lu , ^{208}Pb , ^{232}Th and ^{238}U . The Ca contents determined by WDS served as an internal standard. All analyses were performed in a low-resolution mode (~ 300) using Pt skimmer and sample cones. Data reduction was carried out online using the GLITTER software (van Achterbergh et al. 2001) and an in-house Excel-based program. Quality control was ensured by keeping the fractionation at less than 10% and fractionation/error ratio at less than three. Data affected by subsurface inhomogeneities were discarded, bringing the number of analyses in the reduced dataset to ~ 400 (supplementary Tables ST4-ST6).

Representative whole-rock samples of the Zibo, Paint Lake and Upper Fir carbonatites used for partitioning calculations were crushed to 80% passing a 100-mesh sieve, pulverized in an agate mortar to > 85% passing a 200-mesh sieve and homogenized. The homogenized powders were analyzed for major elements by X-ray fluorescence and for trace constituents by inductively-coupled-plasma mass-spectrometry following four-acid digestion (for non-refractory elements) and $\text{Li}_2\text{B}_4\text{O}_7$ fusion for REE. The analyses were performed at Inspectorate (Vancouver, Canada).

Raman spectra were recorded using a HORIBA Scientific LabRAM ARAMIS instrument equipped with a multichannel electronically cooled charge-coupled device detector, motorized x-y-z stage and solid-state 532-nm laser (mpc6000 by Laser Quantum) with a nominal output power of 50 mW. The instrument was operated in confocal mode; an Olympus microscope coupled to the spectrometer was used to focus the laser beam on the sample surface and collect the generated Raman signal with a spatial resolution of $\sim 1 \mu\text{m}$. The spectra were collected with a diffraction grating of 1800 gr/mm; other

instrumental parameters (data-collection times, slit width, etc.) were optimized by performing multiple measurements on the same area. The spectrometer was calibrated using the 520.7 cm^{-1} signal produced by a mirror-polished synthetic Si standard.

4. Occurrence and paragenesis

4.1. Phosphorus in carbonatites: general observations

Carbonate melts produced by low-degree melting of dolomite-bearing peridotite in the mantle can incorporate up to ~24 wt.% P_2O_5 (Fig. 1a); the solubility of apatite increases with T, but is relatively independent of alkali content (Baker and Wyllie, 1992; Ryabchikov and Hamilton, 1993). The experimentally determined solubilities are significantly higher than the P_2O_5 contents of natural dolomitic melts equilibrated with apatite in a similar P-T range and covering a similar compositional range: 7.6-10.8 wt.% P_2O_5 (Guzmics et al., 2008). With very few exceptions, extrusive and shallow intrusive carbonatites of unquestionable mantle provenance contain even lower levels of P_2O_5 (0.6-6.6 wt.%). Well-preserved calciocarbonatitic melt inclusions in perovskite from the Kerimasi volcano (Tanzania) also show lower P_2O_5 values (Guzmics et al., 2012; our Fig. 1a).

Carbonatitic magmas can also derive from “mixed” carbonate-alkali-silicate melts – e.g., of (mela)nephelinitic composition – by liquid immiscibility or crystal fractionation (Watkinson, 1970; Hamilton et al., 1979). In experiments, phosphorus partitions consistently into a carbonate liquid (CL) relative to its immiscible silicate conjugate, SL ($^{CL/SL}D_P = 1.1\text{-}13.5$; Martin et al., 2013). It is noteworthy that these experimental melts are extremely rich in alkalis (10-19 wt.% $\text{Na}_2\text{O}+\text{K}_2\text{O}$; $\text{Na}_2\text{O} \leq \text{K}_2\text{O}$). Their closest natural analogues are carbonate globules documented at the Kerimasi and Oldoinyo Lengai carbonatite volcanoes (Tanzania), which were interpreted to have evolved from carbonated nephelinitic magma by immiscibility (Guzmics et al., 2012; Sharygin et al., 2012). In both instances, phosphorus

shows a clear preference for the carbonate phase (3.2-7.7 wt.% P_2O_5) relative to the associated silicate melt (≤ 2.3 wt.% P_2O_5).

Virtually nothing is known about the behavior of phosphorus in fractionating carbonate-alkali-silicate melts. The few published studies, where crystal fractionation was proposed as the primary driving force in carbonatite petrogenesis (e.g., Cooper and Reid, 1998; Böhn et al., 2001; Brassinnes et al., 2005; Verhulst et al., 2005), do not show consistent P_2O_5 evolutionary trends linking consanguineous silicate and carbonate rocks. This lack of consistency probably owes to the fact that the fate of phosphorus will depend, most of all, on whether apatite is part of the fractionating assemblage or not. In addition to the solubility of P_2O_5 in carbonate-silicate melts and its changes with T, P and melt composition, such factors as fluid regime and the activity of F will determine if phosphate is precipitated out as cumulus apatite or concentrated in a residual liquid. Some carbonatite complexes were reported to comprise rocks containing up to 70 vol.% apatite associated with magnetite, (tetra-ferri)phlogopite, forsterite, baddeleyite and pyrochlore, and variably referred to as *phoscorite*, *nelsonite* and *camaforite* (Russell et al., 1955; Borodin et al., 1973; Krasnova et al., 2004; Cordeiro et al., 2011). There are also rare examples of essentially anchimonomineralic cumulate lithologies termed *apatitite* by Yegorov (1993). Whereas some of these rocks are clearly related to carbonatites, thus justifying the use of the name *phoscorite* (sensu Russell et al., 1955), this association is not evident at other occurrences (e.g., unit P1 of Cordeiro et al., 2011). It is entirely feasible that apatite-rich lithologies may form by fractionation of apatite and other heavy minerals from both silicate and carbonatitic magmas that may not necessarily share a lineage. Note that the term *nelsonite* (e.g., Yegorov, 1993; Cordeiro et al., 2011) is erroneous in this context and should be avoided. Nelsonites, initially described from Nelson County in Virginia (USA), are apatite-ilmenite $\pm$ rutile rocks related to tholeiitic gabbroids (Herz and Force, 1987) and having no kinship whatsoever to carbonatitic or alkaline magmatism.

Average P_2O_5 values calculated for 151 calcite and 72 dolomite carbonatites worldwide in the present work are relatively low and essentially identical (2.4 wt.%, equivalent to ~6 wt.% apatite). Histograms for both rock types show a lopsided data distribution with a median P_2O_5 content of ~2 wt.% and most of the data trailing off toward higher values (Fig. 1b). In the absolute majority of cases, apatite is the only or the principal phosphate constituent. Primary monazite ($LREEPO_4$) and bradleyite [$Na_3Mg(PO_4)(CO_3)$] are much less common (Figs. 2a-d), whereas daqingshanite [$(Sr,Ca)_3LREE(PO_4)(CO_3)_3(PO_4)$] and xenotime [$(Y,HREE)PO_4$] are restricted in occurrence to just a few localities worldwide (e.g., Cooper and Paterson, 2008; Wall et al., 2008). Early-crystallizing bradleyite and monazite are usually succeeded by apatite (Fig. 2a), although some carbonatites are characteristically devoid of the latter (Figs. 2b, c). More commonly, monazite forms at the expense of apatite (Fig. 2e) or REE carbonates by reaction of carbonatites with hydrothermal fluids of various provenance (Chakhmouradian et al., 1998; Moore et al., 2015). According to published (Wu et al., 1996; Castor, 2008) and our own data, carbonatite deposits that have produced REE on a commercial scale contain monazite as the principal phosphate mineral. For example, apatite is scarce at Maoniuping (China) and absent from the Mountain Pass ore (USA). At Mountain Pass (Fig. 2f), occasional apatite xenocrysts derived from syenitic wall-rocks underwent resorption in the carbonatite, and the assimilated phosphate was deposited as monazite alongside REE fluorocarbonates [predominantly, bastnäsite $LREE(CO_3)F$] and Ba-Sr sulfates, implying that apatite was not stable in this magma system. In a humid environment, carbonatites weather to saprolites and laterites containing a plethora of secondary phosphate minerals, which develop largely at the expense of igneous apatite (e.g., Lottermoser, 1987); their discussion is beyond the scope of the present work.

4.2. Apatite occurrence in carbonatites

Igneous apatite is one of the earliest minerals to precipitate from carbonatitic magma, as evidenced by (i) the intimate association of many plutonic carbonatites with cumulate rocks composed of apatite, magnetite, ferromagnesian silicates, Nb and Zr minerals (pyrochlore, columbite, baddeleyite or zircon; Figs. 3a-f); (ii) the common presence of apatite inclusions in its associated cumulus minerals (Figs. 3d, e); and (iii) the presence in apatite of primary Na-rich melt and carbonate inclusions, implying crystallization prior to the loss of alkalis to fenitization (Figs. 3g, 4a, 4b). As can be expected, cumulate rocks, including phoscorites (Figs. 3a-c), commonly show very high P_2O_5 contents reaching, in some cases, economically viable levels (Mariano, 1989).

In extrusive and shallow intrusive rocks, apatite may be present as euhedral prismatic or hopper-shaped phenocrysts (Figs. 4c, 4d) and/or groundmass crystals (Figs. 4e-g). Note that relatively large apatite grains in these rocks may not necessarily all be phenocrysts, and macrocrysts (i.e. high-P phenocrysts, disaggregated autoliths, or xenocrysts) may also be present; it is advisable to examine such samples with CL, which will usually enable their distinction (Fig. 4d). Groundmass apatite is acicular, with aspect ratios ranging from 5 to 11 (Fig. 4e), whereas phenocrysts are less elongate in habit. In one case (Prairie Lake, Canada), we observed peculiar atoll-textured grains comprising a resorbed hydroxylapatite core and a thin fluorapatite rim (Fig. 4h). The 5-10 μm hiatus is filled with the same material that makes up the surrounding matrix (mostly, dolomite). This texture formed by disaggregation of calcite carbonatite xenoliths incorporated in dolomitic carbonatite breccia. It is noteworthy that carbonatites containing apatite phenocrysts (e.g., Figs. 4c, 4d) show unremarkable P_2O_5 contents similar to the calculated global average values (i.e., 1.5-3.5 wt.%), i.e. far below the saturation levels inferred from high-pressure experiments of Ryabchikov and Hamilton (1993) (Fig. 1a).

In contrast to (sub)volcanic rocks, igneous apatite from plutonic carbonatites and associated cumulate assemblages typically lacks any recognizable crystal faces (although maintaining its prismatic

habit) and can be best described to have a tapered rod- or pill-like shape, with smooth to embayed contours (Figs. 5a-c). This morphology is in striking contrast to euhedral cumulus apatite from gabbros, syenites and other plutonic rocks (e.g., Drinkwater et al., 1990; Andrews, 1996; Warner et al., 1998). Apatite crystals grown experimentally from melts also show a well-developed prismatic habit (e.g., Prowatke and Klemme, 2006). Clearly, the pill-like morphology, so ubiquitous in our samples, results either from interaction of euhedral cumulus apatite with its host melt and other crystals and erosion of sharp crystal edges in the process, or from unusual growth mechanisms specific to plutonic carbonatites. Apatite grains of similar shape have been synthesized from a P_2O_5 -saturated, but silica-undersaturated, melt in the system $MgO-CaO-SiO_2-P_2O_5$ (Shyu and Wu, 1991, cf. their Fig. 16), where their unusual morphology was explained in terms of dendritic growth under the condition of growth-rate anisotropy (Shyu and Wu, 1994). It is tempting to suggest that similar mechanisms may operate in P_2O_5 -saturated carbonate melts, facilitating entrapment of inclusions (like those shown in Figs. 3g, 4a and 4b) in igneous apatite, and its subsequent recrystallization into optically coherent grains. There is no doubt that recrystallization is a potent texture-modifying process in intrusive carbonatites (Chakhmouradian et al., 2016b), but its significance for non-carbonate minerals remains to be ascertained.

Many carbonatites contain a large proportion of minerals formed at late evolutionary stages by either direct precipitation from fluids, or metasomatic reworking of the primary igneous paragenesis by such fluids (e.g., Chakhmouradian and Zaitsev, 2012). Overall, hydrothermal apatite is not particularly common in these late-stage environments and does not show a consistent association with any specific mineral(s). In this study, we examined colloform aggregates from “staffelite” ores developed at the expense of stage-III phoscorites (P3) at Kovdor, prismatic crystals associated with quartz, fluorite and secondary dolomite from Aley, and spherulites of acicular crystals associated with chlorite, prehnite, thorite and secondary calcite from Afrikanda, Russia (Figs. 5d-g). Notably, hydrothermal crystals from both Aley and Afrikanda differ from igneous apatite from the same localities by their sharp euhedral

morphology, whereas spherulites of Kovdor “staffelite” comprise slender fibrous crystals with lengthwise zoning not seen in any other of the samples (cf. Chakhmouradian et al., 2002).

5. Compositional variation of carbonatitic apatite

5.1. EMPA data

In accord with the previously published data, the majority of samples studied in the present work correspond to fluorapatite (≥ 2 wt.% F; supplementary Fig. SF3a) with Cl levels at or below detection by WDS (< 140 ppm). A few samples from calcite carbonatites correspond to F-rich hydroxylapatite (e.g., 0.34-0.36 apfu F at Magnet Cove, USA), or show zoning straddling the hydroxylapatite-fluorapatite boundary (see Section 5.4). All samples from the Kovdor phoscorites are hydroxylapatite (≤ 0.47 apfu F); their average F content increases from ~ 0.3 apfu in P1-P2 to ~ 0.4 apfu in P4 and then drops to 0.2-0.3 apfu in the core of crystals from P5 (Section 5.4). Thin reaction-induced zones in apatite crystals from dolomite carbonatites at Lesnaya Varaka (Russia), Albany Forks and Chipman Lake (Canada), and dolomitized calcite carbonatite at Sokli (Finland) show F contents exceeding the stoichiometric value (up to 1.36 apfu at Lesnaya Varaka). Notably, the primary cores of these anomalous grains show “normal” F values (< 1 apfu), implying that the measured excess F is real and incorporated in the structure (cf. Mason et al., 2009), rather than arising from F diffusion during the analysis. This conclusion is consistent with the absence of any detectable variation between the F content of crystals analyzed parallel and perpendicular to the pathways of preferential F diffusion (Section 3). Comparably high F values were reported for apatite from carbonatites in Bühn et al. (2001, their Table 4) and elsewhere for other rock types (Section 2). The only sample containing appreciable Cl (up to 1 wt.% or 0.14 apfu) is fluorapatite from Yousuobao (China), which is described below (Section 5.4).

The principal substituent cations detectable in carbonatitic apatite by WDS are Sr, REE, Na, Si and S (Tables ST1-ST3). Strontium is ubiquitous, but its content can range over one order of magnitude in the

same sample (e.g., 1.1-14.6 wt.% SrO at Lesnaya Varaka and 0.7-9.3 wt.% SrO at Chipman Lake); the majority of analyses fall between 0.2 and 2.7 wt.% SrO (Fig. SF3b). Rare-earth elements are invariably dominated by light lanthanides ($Ce > La \approx Nd > Pr$). Their content also varies from nil to several wt.% within our sample suite and, in some cases, across individual grains. The highest levels of LREE enrichment are observed in the rim of fluorapatite from calcite carbonatites of Eden Lake (Canada), Kerimasi and Fuerteventura: 7.3, 8.1 and 8.8 wt.% $LREE_2O_3$, respectively; the majority of data show < 4.5 wt.% $LREE_2O_3$. In dolomite carbonatites, the maximum $LREE_2O_3$ values (up to 6.7 wt.%) were measured in reaction-induced mantles on fluorapatite from Chipman Lake, which also show high Na levels (up to 1.6 wt.% Na_2O). Comparably high Na contents occur locally in hydroxylapatite from the Kovdor dolomite phoscorite (Section 5.4), but in the other samples, the Na_2O content does not exceed 0.8 wt.%. There is no clear systematic variation in Sr, REE or Na between the calcite and dolomite carbonatites (Fig. SF3b); however, extremely Sr-rich compositions (> 5 wt.% SrO) appear to be exclusive to the latter, whereas igneous apatite with > 4.5 wt.% REE_2O_3 was only observed in the calcite rocks. Silicon and S are generally higher in crystals from calcite carbonatites (up to 4.2 wt.% SiO_2 at Kerimasi and 1.5 wt.% SO_3 at Eden Lake) in comparison with dolomite carbonatites (≤ 0.2 and 0.1 wt.%, respectively; Fig. SF3c). Iron was detected in only a few samples; consistently elevated levels of this element (0.2-0.3 wt.% FeO) are found in the core of fluorapatite phenocrysts from the Zibo calciocarbonatite, and in the rim of phenocrysts from dolomite carbonatites at Wekusko Lake (Canada). The late-stage Sr-rich zones in fluorapatite from Chipman Lake, Albany Forks and Sokli show up to 1.7 wt.% FeO, but the measured values lack consistency; i.e., the presence of Fe-oxide micro-inclusions in these samples cannot be ruled out. For a discussion of Mn and Ba variations, see Section 5.3. The $(La/Nd)_{cn}$ ratios of carbonatitic apatite calculated from the WDS analyses range from 0.2 to 15; however, most of the data fall in the range of 0.5-6.2 (Fig. SF3d).

5.2 Raman micro-spectroscopy

Appreciable CO₂ has been reported in carbonatitic apatite in several studies (e.g., Liu and Comodi, 1993; Nadeau et al., 1999), most of which, however, employed bulk techniques for quantitative analysis. The reliability of the published data is unclear, given the common presence of carbonate and other inclusions in this mineral (Figs. 4a, b). Such inclusions could certainly explain discrepancies between the measured CO₂ contents and those derived from structure refinements (Liu and Comodi, 1993, their Table 2), or the extreme variability of $\delta^{13}\text{C}$ and CO₂ values in the same sample (Nadeau et al., 1999, their Fig. 5b). According to the published structural and spectroscopic evidence, data, carbonate anions substitute predominantly for (PO₄)³⁻ in the structure of carbonatitic apatites (Liu and Comodi, 1993; Nadeau et al., 1999). To determine if Raman micro-spectroscopy could be used to detect relatively low concentrations of (CO₃)²⁻ in microscopic samples and be potentially developed into a (semi)quantitative technique, we collected spectra of fluorapatite from Eden Lake and hydroxylapatite from Prairie Lake, which show consistently low cation totals in the P site (min. 2.83 and 2.88 apfu P+Si+S, respectively), and compared them with a stoichiometric reference material (Fig. 6). Assuming that the cation deficit is due to the presence of C undetectable by WDS (Section 2), the corresponding CO₂ content should not exceed 1.4 and 1.0 wt.%, respectively, in the two samples. These values are well within the variation of EMPA totals observed for stoichiometric apatites (e.g., 99.2 ± 1.2 wt.% for the Aley samples), which means a slightly lower total does not necessarily imply the presence of undetected carbonate in the mineral.

In addition to P–O vibration modes at 432–447, 582–616 and 965 cm⁻¹ (Kravitz et al., 1968), the spectra of Eden Lake fluorapatite (≤ 0.26 apfu Si, 0.10 apfu S) show strong signals corresponding to S–O (640, 1114–1186 cm⁻¹) and Si–O vibrations (395, 811–838 cm⁻¹). In contrast, the Prairie Lake hydroxylapatite (< 0.11 apfu Si, S below detection) does not show these features. The asymmetric stretch modes (ν_3) of PO₄ group between 1020 and 1080 cm⁻¹ are sensitive to carbonate substitution in the tetrahedrally coordinated site owing to their overlap with an intense C–O symmetric stretch mode

(ν_1) at $1070 \pm 1 \text{ cm}^{-1}$ (Penel et al., 1998; Awonusi et al., 2007). In synthetic apatites, the 1070-cm^{-1} signal becomes discernible at CO_2 contents around 2 wt.%, and even then it is expressed merely as broadening of the 1081 cm^{-1} phosphate mode (Awonusi et al., 2007, their Fig. 2). The ν_1 mode of $(\text{CO}_3)^{2-}$ anions accommodated in the structural channels is found at higher wavenumbers ($1102\text{-}1107 \text{ cm}^{-1}$: Penel et al., 1998) and was not observed in the present work. In the acquired spectra, the ν_3 cluster is indeed significantly different in the Eden Lake and Prairie Lake apatites relative to the carbonate-free reference sample and can be deconvoluted to a number of vibrations, including one at $1071 \pm 1 \text{ cm}^{-1}$, whereas no signals are present between 1089 and 1114 cm^{-1} (Fig. 6). The only other C–O vibrations identified in synthetic and biological samples are ν_4 modes between 675 and 765 cm^{-1} (Penel et al., 1998; Awonusi et al., 2007), but there is no consensus on how individual peaks within that range should be assigned. Although our samples with deficiency in the P site all show a signal at 737 cm^{-1} , it does not match any of the carbonate ν_4 modes reported in the literature. Alternatively, weak signals in this spectral region could be assigned to O–H libration that is sensitive to the substitution of F in the structural channels (Freund and Knobel, 1977). Because such interpretation would be satisfactory for the Prairie Lake hydroxylapatite (0.39–0.44 apfu F), but may not be applicable to the essentially water-free Eden Lake fluorapatite (0.97–1.09 apfu F), the assignment of the 737-cm^{-1} signal remains uncertain. An O–H libration mode at lower wavenumbers, characteristic of apatites with a low-to-intermediate F:OH ratio, is clearly visible in the Prairie Lake sample, but is masked by the S–O vibrations in the Eden Lake spectra (Fig. 6). Overall, Raman micro-spectroscopy does not provide conclusive evidence for the presence of carbonate in natural apatites with small P-site deficiency, particularly if other substituents are also present in this site.

5.3. LA-ICPMS data

The abundances of most trace elements detectable by LA-ICPMS vary over two-three orders of magnitude (Tables ST4-ST6). The Ba contents are very low (nil to 60 ppm) in the majority of samples; relatively elevated levels of this element are observed in fluorapatite from calcite carbonatites at Eden Lake (50-170 ppm), Turiy Mys, Russia (50-190 ppm), dolomite carbonatite at Albany Forks (locally, up to 130 ppm), and in hydrothermal “staffelite” at Kovdor (180-1070 ppm). Anomalously high Ba concentrations were detected in the peripheral part of crystals from phoscorite P5 (Kovdor), which is also enriched in Mn; LA-ICPMS measurements show up to 1400 ppm Ba and 1300 ppm Mn in these areas, whereas microprobe analyses gave a maximum value of 0.26 wt.% respective oxides for both elements (Tables ST3, ST5). Back-scattered-electron imaging indicates micron-scale variations in heavy elements across the apatite crystals from P5 (Section 5.4), which explains some discrepancy between the maximum Ba and Mn values measured by WDS and LA-ICPMS. In the rest of the samples, the Mn content of igneous apatite ranges from 50-60 ppm (Vishnevye Gory, Russia) to 1000 ppm (Oka); the Aley, Afrikanda and Kovdor hydrothermal samples are all poor in Mn (35-57 ppm at Aley and < 10 ppm at the other two localities). The highest Pb content (~120-150 ppm) was recorded in the fresh material from Yousuobao, whereas the rest of our samples are much poorer in Pb (≤ 30 ppm). With a few exceptions, Th is more abundant in the examined apatite than U (up to 700 and 150 ppm, respectively), particularly in samples from pyrochlore-bearing carbonatites. The latter exhibit very low levels of U (commonly, ≤ 1 ppm) coupled with very high Th/U ratios (> 70 and in some cases, > 500), whereas in the absence of pyrochlore, the Th/U ratio typically ranges from 3 to 30. Crystals from magnesiocarbonatites of Paint Lake are characterized by consistently low Th/U values (0.1-0.7) at low Th and U contents. Hydrothermal apatite from Kovdor (Fig. 5d, e) is even more unusual in showing very low Th, but high U levels (≤ 0.1 and 40-230 ppm, respectively). The absence of correlation between the Th ($\pm$ U) and Pb abundances in carbonatitic apatite suggests that the bulk of Pb in this mineral is non-radiogenic (cf.

Chakhmouradian et al., 2013). Vanadium concentrations are low (< 40 ppm) in the majority of our samples; the two exceptions are fluorapatite from calcite carbonatites of Kaiserstuhl (400-600 ppm) and Oka (440-660 ppm). Notably, both Zr and Nb are present in very low concentrations (up to 15 and 7 ppm, respectively, with $>90\%$ of the values not exceeding 2.5 ppm), whereas Rb levels are below the limit of detection (1.5 ppm) in all analyzed samples.

The LA-ICPMS data show consistent enrichment in light REE (La ... Eu) relative to heavy REE (Gd ... Lu), with $(\text{La/Yb})_{\text{cn}}$ ratios ranging from 30-500 in igneous apatite to ≤ 25 in hydrothermal varieties. The two varieties show overlapping $(\text{La/Nd})_{\text{cn}}$ and $(\text{Dy/Yb})_{\text{cn}}$ ratios (0.1-4.1 and 2-11, respectively). Chondrite-normalized profiles of the samples from Paint Lake show the most convex LREE section, as reflected in their low $(\text{La/Nd})_{\text{cn}}$ values (0.47 ± 0.06 in calcite-dolomite units and 0.15 ± 0.07 in sövites). With a few exceptions, the absolute majority of profiles lack any discernible Ce or Eu anomalies (Fig. 7). Samples from Yousuobao, Zibo (China) and some of the Kovdor phoscorites (P1, P3) are slightly enriched in Ce ($\delta\text{Ce} \approx 1.2 \pm 0.1$), whereas alteration zones in apatite from Turiy Mys (see Section 5.4) show consistently low δCe values (0.77 ± 0.06). The colloform hydrothermal aggregates from Kovdor are characterized by negative Ce and Eu anomalies ($\delta\text{Ce} = 0.2\text{-}0.8$; $\delta\text{Eu} = 0.7\text{-}0.8$, where measurable), coupled with extreme depletion in Mn (< 7 ppm). Igneous apatite is variably depleted in Y relative to the values expected from ionic radius considerations; the measured Y/Ho ratios range from 20.0 ± 0.7 ($\delta\text{Y} = 0.61 \pm 0.02$, sövite from Carb Lake, Canada) to 29.0 ± 0.3 ($\delta\text{Y} = 0.95 \pm 0.01$, Kovdor P5), which is expressed as a “dent” in the chondrite-normalized profiles between Dy and Ho (Fig. 7). The hydrothermal samples from Aley and Kovdor show no Y anomaly (Fig. 7b), whereas those from Afrikanda and Albany Forks, on the contrary, feature the lowest Y/Ho ratios recorded in the present work (~ 19 ; $\delta\text{Y} = 0.57 \pm 0.02$ and 0.53 ± 0.01 , respectively).

5.4. Zoning

Igneous apatite commonly appears homogeneous in transmitted light, but shows striking zoning in BSE and CL images. If we neglect gradual and often subtle variations in composition within texturally distinct areas, the zoning patterns observed in BSE images can be generalized as follows (see Tables ST1-ST5 for selected examples):

- (1) A low-AZ core (AZ = average atomic number) with an ellipsoidal to irregular, embayed outline rimmed by higher-AZ material of uneven thickness (35% of the samples). The volumetric ratio between the high- and low-AZ material varies greatly among the samples (Figs. 4f, 5a, 5b, 8a). The core-rim boundary is invariably sharp, but in some carbonatites, the core or rim exhibit an outward increase in AZ. Groundmass crystals in extrusive calciocarbonatite from Kerimasi are unusual in showing subtle oscillatory variations in AZ within the rim (Fig. 4f);
- (2) A low-AZ core and rim separated from each other by a high-AZ intermediate zone (18% of the samples). This pattern could be viewed as the above-described type (1) modified by the development of a peripheral low-AZ zone (Figs. 5c, 8b, 8c), but CL observations indicate further intricacies that cannot be resolved with BSE imaging (see below);
- (3) Zoned apatite of type (1) or (2), or compositionally homogeneous crystals replaced pervasively by cavernous low-AZ material along their grain boundaries and fractures (18% of the samples; Figs. 5a, 8a, 8d-f). These textural characteristics of low-AZ areas and their association with hydrothermal minerals (secondary rhombohedral carbonates, quartz, chlorite and goethite) indicate that they formed by alteration of igneous apatite. Altered patches may show appreciable variation in AZ (Fig. 8e);
- (4) Zoned crystals of type (1) or (2) locally replaced and overgrown by high-AZ material (Figs. 8c, 8g). This pattern was observed in dolomite carbonatites from Lesnaya Varaka, Chipman Lake and Albany Forks, and one sample of dolomitized sövite from Sokli (i.e., 5% of the samples). The

high-AZ areas within these apatites are discontinuous, have an irregular or embayed outline and delineate fractures and dissolution microcavities. In common with pattern (3), we interpret these high-AZ zones to represent the product of apatite re-equilibration with a fluid;

- (5) A complex pattern observed in a single sample of dolomite phoscorite from Kovdor (P5) and comprising a fragmented and resorbed medium-AZ core, surrounded by a low-AZ zone of variable thickness, and a series of concentric medium- to high-AZ zones with a euhedral outline, ranging from < 10 to 50 μm in width (Fig. 8h).

The type (1) zoning invariably involves enrichment of the rim in LREE relative to the core (in some cases, by one order of magnitude), which is commonly accompanied by an increase in Si content (Fig. 9). Other elements do not show a consistent rim-ward trend. Sodium and Sr levels may be higher in the rim or remain constant; a few samples also show appreciable enrichment in F (e.g., from a hydroxylapatite core to a fluorapatite rim at Prairie Lake and Valentine Township, Canada). The most complex pattern is observed in phenocrysts from the Zibo diatreme (Fig. 4c), where the concentrations of LREE, Sr, Si, S and F increase, whereas the Fe content decreases from the hydroxylapatite core to the fluorapatite rim at essentially constant Na levels. The $(\text{La}/\text{Nd})_{\text{cn}}$ ratio typically increases toward the rim (see below).

Trace-element variations in patterns of type (1) were studied on the example of Eden Lake sövite (Figs. 5a, 10a) and cumulate apatite from Aley (Fig. 10b) because none of the other apatites have rims sufficiently thick for LA-ICPMS. Apart from confirming much higher levels of REE in the rim of the Eden Lake fluorapatite, our data record rim-ward enrichment in Th, U and, to a lesser extent, Mn (Table ST4). The $(\text{La}/\text{Yb})_{\text{cn}}$ and Th/U ratios decrease, whereas the $(\text{La}/\text{Nd})_{\text{cn}}$ value increases slightly toward the rim; none of the other element ratios exhibit any consistent changes. In the Aley sample, the rim is enriched in REE and Sr, but lower in Mn with respect to the core. Both $(\text{La}/\text{Nd})_{\text{cn}}$ and $(\text{La}/\text{Yb})_{\text{cn}}$ are higher in the rim, whereas the rest of the REE ratios do not change perceptibly across the crystal.

Zoned crystals of type (2) show enrichment in REE, accompanied by an increase in Na or Si (to provide charge-balance) and commonly also Sr content in their high-AZ intermediate zone. The levels of these elements then decrease in the low-AZ rim (Figs. 9b, c). With few exceptions (e.g., Table ST1, nos. 20-22), F and other elements do not exhibit any systematic variation among the three zones. Preliminary CL studies suggest that intracrystalline element variations in type (2) apatite are far more complex than can be gleaned from WDS analyses constrained by areas of different brightness in BSE images (see below).

Zoning of type (3) involves the loss of LREE, Sr, Si and S and, in some cases, Fe in low-AZ areas in comparison with the precursor primary apatite (Fig. 9). Within the altered areas, the REE, Si, S and Fe contents typically drop by one order of magnitude or more, to levels close to, or below, their detection limits by WDS, whereas a decrease in Sr is less dramatic (by a factor of 1.5 to 7). The Na content decreases in the low-AZ zones in all cases but one (Turiy Mys), where the altered patches are enriched in this element about threefold relative to the unaltered material. The only apatite with high levels of Cl (Yousuobao) also exhibits total loss of this element (0.8-1.0 to < 0.01 wt.%) in the lowest-AZ areas (Figs. 8d, e). All samples show an increase in F content in the low-AZ zones (by as much as ~0.4 wt.% at Yousuobao). Trace-element variations in zoned crystals of type (3) were examined on the examples of apatite from Turiy Mys and Yousuobao. These data confirm depletion of the altered zones in all REE (especially LREE) and Sr, and show a concomitant decrease in Th and U contents (Table ST4). The Mn concentration is not affected by alteration in the Turiy Mys sample, but drops threefold in the Yousuobao apatite. Preferential removal of LREE leads to lower $(La/Yb)_{cn}$ ratios in the altered areas relative to the fresh material. The Turiy Mys apatite also shows a decrease in δCe and δY from the typical igneous values in the core (0.91-0.97 and 0.74-0.93, respectively) to 0.69-0.84 and 0.66-0.76, respectively, in the low-AZ zones. The rare earths, Fe, Th and U released from the primary apatite are deposited, at least partially, in situ in the form of monazite, LREE fluorocarbonates, hematite and thorite

conspicuous as bright minute ($\leq 30 \mu\text{m}$) inclusions in BSE images (Figs. 8e, f). Altered apatite of type (3) commonly lacks transparency and is stained red owing to the presence of these inclusions.

Zoning pattern (4) involves a two- to eleven-fold increase in Sr content in the high-AZ areas, which in some samples reaches levels not previously recorded in carbonatitic apatite (9.3 and 14.6 wt.% SrO at Chipman Lake and Lesnaya Varaka, respectively), and typically also enrichment in F (supplementary Table ST2), often above the stoichiometric limit (1 apfu). With the exception of the Lesnaya Varaka fluorapatite (Figs. 8g), the Na and LREE abundances are also elevated locally in the Sr-rich zones, reaching their maximum values (1.6 and 6.7 wt.% respective oxides) in the Chipman Lake sample (Figs. 8c, 9c, 9d). However, the distributions of these substituent elements and F is extremely heterogeneous even on a short scale (note the scatter of data in Figs. 9b-d). Only fluorapatite from Albany Forks was amenable to LA-ICPMS measurements, which showed that the hydrothermally reworked high-Sr-REE material is also enriched (by about one order of magnitude) in Ba, Pb and Th, and has higher $(\text{La/Yb})_{\text{cn}}$ ratios, but comparable levels of Mn relative to the precursor crystal (Table ST4). The late-stage zones also have the lowest δY value observed in the present work (0.53 ± 0.01), but are indistinguishable from the precursor apatite in δCe and δEu values.

The zoned apatite of type (5) shows a one-order-of-magnitude increase in Na, Mg, Mn and Fe, coupled with a sharp drop in F content (from 0.6-1.1 wt.% to nil) from its core, which is broadly similar in composition to samples P1-P4, to the low-AZ anhedral mantle (Table ST3). The Na content then decreases, whereas the Sr and F levels increase in the medium-AZ and, especially, high-AZ inner-rim zones of euhedral morphology. The 10-15- μm innermost high-AZ zone is characterized by the highest Ba concentrations recorded in this work (0.21-0.26 wt.% BaO). Outwards from this zone, the concentrations of Na, Mn, Sr, Ba and F generally decrease (although displaying some oscillatory variations), whereas Mg and Fe remain essentially unchanged. Trace-element data (Table ST5) confirm the enrichment in Mn and Ba not seen in any other samples, and also indicate a significant drop in REE and Th (but not U)

concentrations in the rim relative to the core. The $(\text{La}/\text{Nd})_{\text{cn}}$ value decreases rim-ward, but other REE ratios do not show much change.

The examined apatites exhibit a bewildering range of colors and zoning patterns in CL images (see Fig. 10 for representative examples). According to the published data (Waychunas, 2002; Mitchell, 2014, and references therein), most of the observed variations can be explained by the prevalence of Mn^{2+} emission (yellow to greenish-yellow luminescence) in REE-poor material, emission arising from a variety of REE^{3+} species in Mn-poor apatites (violet-blue to purple), or energy transfer from Ce^{3+} to other LREE³⁺ species in some REE-rich crystals (dark maroon). Reddish plum to olive-green colors, common in the low-AZ core of zoned crystals, appear to arise from combined Mn- and LREE-induced CL. Areas showing these types of CL cannot always be distinguished based on their Mn and REE contents, indicating that other, as yet unidentified, luminophores may be responsible for these variations. Relatively Fe- and Mn-rich apatites (e.g., from Zibo and Oka, respectively) are inert, possibly due to (self-)quenching phenomena (Kempe and Götze, 2002; Waychunas, 2002). Some of the observed CL colors, however, cannot be adequately explained on the basis of published spectroscopic evidence, and merit further investigation.

The zoning recorded in CL images is often very complex and cannot always be directly correlated to the patterns identified from BSE micrographs (see above) because the concentration of Mn, which strongly influences CL, is typically below the limit of detection by WDS (~600 ppm) in carbonatitic apatites and will have little effect on their AZ. This is illustrated in Figure 10c, where crystals from dolomitized sövite at Carb Lake (Canada) exhibit at least 18 (!) subconcentric bands differing in CL color within their low-AZ, relatively Mn-rich core, and four or five subzones within both the high-AZ, REE-enriched intermediate zone and REE-depleted rim. Apart from some hydrothermally altered apatites (Figs. 10b, 10e, 10f), the most complex patterns are observed in zoned crystals classified as type (2) above and derived from calcite carbonatites affected by dolomitization (e.g., Figs. 10c, 10d). In the

majority of these apatites, we are unable to correlate variations in their luminescence to trace-element distributions because individual zones visible in CL images are too narrow for analysis. For this reason, we will not discuss the intricacies of type-(2) zoning in the present paper. A detailed study of complexly zoned apatites, involving high-resolution LA-ICPMS and CL spectroscopy, is currently underway.

5.5. Compositional variations among apatite samples from associated carbonatitic rocks

To study variations of the chemical composition of apatite among different rocks within the same carbonatite complex, we studied two samples of each sövite and calcite-dolomite carbonatite from Paint Lake, five phoscorite units and associated hydrothermal apatite from Kovdor, plus five samples of sövite, eight samples of dolomite carbonatite and hydrothermal dolomite-fluorite-apatite-quartz veinlets from the Aley complex (Appendix A1). These data are compared with the compositional variations determined in zoned apatites (see above) and with published data further below (Section 7.3).

At Paint Lake, fluorapatite from the calcite-dolomite carbonatite is richer in Cl (0.16 ± 0.04 wt.%) and Sr (0.44 ± 0.04 wt.% SrO), but poorer in F (2.64 ± 0.19 wt.%), Na (below detection in most grains), Si (0.16 ± 0.03 wt.% SiO₂) and S (0.07 ± 0.02 wt.% SO₃) relative to that from calcite carbonatite (3.59 ± 0.21 wt.% F, 0.06 ± 0.01 wt.% Cl, 0.35 ± 0.04 wt.% SrO, 0.06 ± 0.03 wt.% Na₂O, 0.34 ± 0.13 wt.% SiO₂, 0.34 ± 0.12 wt.% SO₃). The abundances of LREE are similar in the two sets of samples (i.e. they cannot be distinguished based on the WDS data), but fluorapatite from sövite is appreciably richer in HREE (by over one order of magnitude for the heaviest lanthanides), which is reflected in its much lower (La/Yb)_{cn} ratio (2.5 ± 2.0) in comparison with the calcite-dolomite carbonatite (54 ± 12). The (La/Nd)_{cn} ratio is also lower, whereas the δY value is higher in the sövitic fluorapatite (0.15 ± 0.07 vs. 0.47 ± 0.06 , and 0.82 ± 0.03 vs. 0.67 ± 0.03 , respectively). Other trace elements that are relatively enriched in the latter include Th and U, whereas Mn is much higher in the calcite-dolomite sample (361 ± 33 vs. 139 ± 22 ppm) (Table ST4; Fig. 11).

Despite significant differences in their mineralogy (Krasnova et al., 2004; Zaitsev et al., 2014), the five phoscorite samples from Kovdor cover a relatively limited range of apatite compositions (Tables ST3, ST5; Fig 11). These rocks contain hydroxylapatite with low Na, Sr, REE, Fe, Si, S and Cl contents. In common with the Paint Lake samples, apatite from dolomite phoscorite P5 is enriched in Sr and Mn relative to its counterparts from the calcite-bearing units (P1–P4). However, other elements or their ratios do not form any consistent trends across this sample set; for example, the $(\text{La}/\text{Nd})_{\text{cn}}$ and δY values are appreciably higher in P5 than in the calcite-bearing rocks, whereas the $(\text{La}/\text{Yb})_{\text{cn}}$ ratio is comparable in P5 and P2, but much higher in the other three phoscorites (Fig. 11). The hydrothermal colloform variety developed after hydroxylapatite in P3 (Figs. 5d, e) is strongly enriched in F (0.55–0.99 vs. 0.40–0.48 apfu), Ba (180–1070 vs. 7–15 ppm) and U (35–230 vs. 0.2–0.6 ppm), but depleted in Na (< 0.02 vs. 0.05–0.15 wt.% Na_2O), Sr (0.1–0.2 vs. 0.3–0.5 wt.% SrO) and, especially, Mn (≤ 7 vs. 100–140 ppm), REE (≤ 110 vs. 1000–2300 ppm) and Th (≤ 0.1 vs. 2–25 ppm) relative to its igneous precursor. As noted above, the hydrothermal variety is also characterized by a negative Ce anomaly absent in the phoscoritic material.

The Aley complex is a large (~ 700 ha) intrusion composed almost entirely of dolomite and subordinate calcite carbonatites, where cross-cutting relations are essentially impossible to work out (Chakhmouradian et al., 2015). However, major carbonates from these rocks form well-defined trends in terms of their REE and $(\text{La}/\text{Yb})_{\text{cn}}$ values, which could potentially arise from fractionation of a mineral scavenging REE and showing preference for LREE vs. HREE (Chakhmouradian et al., 2016a). In this work, we analyzed fluorapatite from a carefully selected series of calcite and dolomite carbonatites with carbonate $(\text{La}/\text{Yb})_{\text{cn}}$ ratios ranging from 44 to 6, and from 76 to 3, respectively (Appendix A1). The compositions of igneous fluorapatite from these rocks form two closely overlapping fields with respect to the majority of substituent elements and element ratios (Fig. 11). One exception is Th enrichment (140–320 ppm) in apatite from the supposedly most evolved dolomite carbonatite – as indicated by the

very low $(\text{La/Yb})_{\text{cn}}$ of its constituent dolomite – which is not seen in the other Aley samples (Fig. 11b). The very limited extent of variation in REE ratios across the dataset [e.g., $\delta\text{Eu} = 0.89\text{--}1.00$, $(\text{La/Nd})_{\text{cn}} = 1.5\text{--}2.1$] is particularly remarkable, given the appreciable variation in REE content among these apatites. Even the $(\text{La/Yb})_{\text{cn}}$ value, ranging from ~ 60 to ~ 130 in both rock types, shows *less* variation than seen *within individual crystals* from dolomitized sövite at Carb Lake, or within hydrothermally altered apatite from Turiy Mys and Yousuobao, for example (Fig. 11d). Importantly (see Section 7), apatite from the carbonatites containing calcite/dolomite with the lowest $(\text{La/Yb})_{\text{cn}}$ values has somewhat lower $(\text{La/Nd})_{\text{cn}}$ ratios (< 1.8) than that from the less-evolved carbonatites, although no consistent trend could be established within either of the datasets. Hydrothermal apatite in dolomite carbonatites (Figs. 5f, 10g) is much poorer in Sr, REE and Mn than its igneous counterparts; its REE budget is also significantly different, featuring lower $(\text{La/Yb})_{\text{cn}}$ and $(\text{La/Nd})_{\text{cn}}$, but appreciably higher δEu and δY values.

As can be seen from Figure 11, apatite from mineralogically and texturally diverse phoscorites (Kovdor) and carbonatites (Paint Lake, Aley) shows less variation in such trace elements as Sr, REE, Th and Mn than some of the zoned crystals from a *single sample*. Strongly zoned crystals of type (1) from Eden Lake exhibit little variation in REE ratios, whereas crystals of types (2), (3) and (4) exhibit as much – and in some cases, more – variation in $(\text{La/Yb})_{\text{cn}}$, δEu and δY as samples from a wide spectrum of carbonatitic rocks from the same complex.

6. Trace-element partitioning

Because it cannot be established conclusively whether apatite in the Zibo, Paint Lake and Upper Fir carbonatites maintained equilibrium with the host melt, we modeled the distribution of trace elements between this mineral and its host magma using a modified equation for Rayleigh fractionation:

$$C_X^{\text{Ap}} = C_X^0 \times (1 - F^{\text{Ap/crb} D_X}) / (1 - F)$$

where C_X^{Ap} and C_X^0 are the concentrations of element X in the apatite and parental magma, respectively; F is the mass proportion of melt remaining after apatite fractionation; and $^{Ap/crb}D_X$ is the apatite-carbonatite partition coefficient for element X. The C_X^{Ap} values were determined by LA-ICPMS, and melt fractions (F) calculated from the whole-rock P_2O_5 concentrations on the basis of mass-balance considerations, given that apatite is the only phosphate mineral in all three carbonatites. The whole-rock element abundances were assumed to be equal to C_X^0 and elements that are likely to have been flushed from the magma by fenitization or degassing during the carbonatite emplacement (in particular, Na, K, Ba, F and Cl) were excluded from consideration. The $^{Ap/crb}D_X$ calculations were straightforward for the Paint Lake and Upper Fir magnesiocarbonatites, but somewhat more challenging for the Zibo calciocarbonatite because of type (1) zoning in apatite crystals, whose rims were too narrow for trace-element measurements. To address this problem, we performed image analysis on multiple high-contrast BSE images of this rock taken at different magnifications to calculate the relative mass proportions of phenocrysts and groundmass crystals, and of low-AZ material confined to crystal cores and high-AZ apatite deposited later. Obviously, the $^{Ap/crb}D_X$ values could only be calculated for the low-AZ core material in this case. (The possible cause of zoning in the Zibo sample is addressed in Section 7.4.)

Competitive partitioning of trace elements between two or more co-crystallizing minerals is an obvious hindrance in those cases where apatite is not the only early fractionating phase. In the examined samples, such minerals are phlogopite at Zibo, forsterite at Paint Lake and richterite at Upper Fir (Appendix A1). Both phlogopite and richterite host appreciable Na, V, Mn and Fe, but are virtually devoid of detectable REE (< 6 ppm) and have two-order-of-magnitude lower levels of Sr relative to the associated apatite (Reguir et al., 2009; 2012). Taking into account their potential contributions to the whole-rock REE and Sr budget, removal of the REE and Sr contained in these silicate minerals from the whole-rock data will increase the calculated $^{Ap/crb}D_{REE}$ and $^{Ap/crb}D_{Sr}$ values in the third decimal place, which is well within the estimated standard deviations of our method anyway. The (co)precipitation of olivine

at Paint Lake would have no perceptible effect on $^{Ap/crb}D_{REE}$ or $^{Ap/crb}D_{Sr}$ either, but could affect the partitioning of V, Mn and Fe. Because the major-element compositions of the Zibo phlogopite, Upper Fir richterite and Paint Lake forsterite are known (authors' unpubl. data), the effect of their fractionation from the parental carbonatitic magma on its Mn budget can be calculated and taken into account. To achieve this, we calculated two sets of $^{Ap/crb}D_{Mn}$ values for each of the three samples: one assuming that the silicate minerals fractionated prior to apatite, and the other that apatite preceded the silicates. Because in all three cases, the MnO contents of the silicate phases are comparable to the whole-rock values (~0.1-0.3 wt.%), fractionation of these minerals would actually have little effect on the Mn budget and, hence, on $^{Ap/crb}D_{Mn}$ values (all within the standard deviation of the mean).

The calculated $^{Ap/crb}D_x$ values for Mn decrease, whereas those for Sr and REE increase with decreasing Ca/(Ca+Mg+Fe+Mn) ratio (i.e. increasing proportion of normative dolomite) in the carbonatite (Table 2). These changes can be explained in terms of structural differences between Mg-poor and Mg-rich carbonate melts: those with low Ca/(Ca+Mg+Fe+Mn) ratios are characterized by shorter cation-oxygen and cation-cation distances (Kono et al., 2014) making the melt less tolerant to the incorporation of such large cations (relative to Mg^{2+}) as Sr^{2+} or REE^{3+} . As a result, these cations will partition into the apatite structure more readily in dolomite carbonatites. For the same reason, the relatively small Mn^{2+} cation will show the opposite trend.

Although the partition coefficients for Si and S could not be calculated because of the presence of silicate minerals in all three samples and lack of data on their sulfate content, we infer that both these elements are significantly more compatible with respect to apatite in calcite carbonatites relative to dolomite carbonatites. This is suggested by the overall lower levels of Si and S in apatites from the latter rock type and a twofold increase in Si and S values in fluorapatite from the Paint Lake sövite in comparison with the calcite-dolomite carbonatite from the same locality (Section 5.5). The higher affinity of apatite in Ca-rich magmas for Si may also explain the occurrence of exceptionally REE-rich

compositions (> 4.5 wt.% REE_2O_3) in these systems to compensate charge imbalance induced by the $\text{P}^{5+} \Rightarrow \text{Si}^{4+}$ substitution (Fig. 9a).

7. Discussion

7.1. Rare-earth partitioning between apatite and carbonatitic magma

The importance of apatite as a petrogenetic indicator, with primary emphasis placed on its REE budget, has been demonstrated in a large number of studies, including several focused on carbonatites (Bühn et al., 2001; Brassinnes et al., 2005; Costanzo et al., 2006; Wang et al., 2014; Zaitsev et al., 2014; Xu et al., 2015; Broom-Fendley et al., 2016). Assessment of the role played by apatite in carbonatite evolution is hindered by the poor understanding of element partitioning between this mineral and carbonate(-rich) liquids. The available experimental studies are limited to Klemme and Dalpé (2003) and Hammouda et al. (2010), which gave contradictory results. In the former study, REE were found to be incompatible in fluor- and hydroxylapatite, with crystal-melt partition coefficients ($^{S/L}D_{\text{REE}}$) fitted to a single Onuma curve with a crest at Pr ($^{S/L}D_{\text{Pr}} = 0.6$), whereas Hammouda et al. (2010) reported $^{S/L}D_{\text{REE}}$ in excess of 1.4 and reaching maximum values between Dy and Er (Fig. 12a). Importantly, REE in apatite substitute in *two cation sites* of different geometry: the average cation-anion distance in the ninefold-coordinated Ca1 site is 0.09-0.10 Å longer than that in the sevenfold-coordinated Ca2 site (Hughes et al., 1989, 1991; Fleet and Pan, 1995, 1997). This implies that the affinity of REE for a specific site will depend on their ionic radius, which has been proven experimentally (Fleet and Pan, 1995, 1997). Also, the elastic properties of the two Ca sites should be expected to differ from each other significantly (but are as yet unknown). For reference, the Young's moduli of M1 and M2 sites in the structure of orthopyroxene differ by a factor of 1.5-2.5 for trivalent substituent cations (Frei et al., 2009). In our opinion, fitting the calculated or experimentally measured partitioning data for REE in apatite to a *single* curve (see Fig. 4 in Klemme and Dalpé, 2003, and Fig. 7 in Hammouda et al., 2010) is misleading. The REE partition

coefficients presented in this and some previous publications (e.g., Klemme and Dalpé, 2003; Brassinnes et al., 2005; Arzamastsev et al., 2009) clearly do not conform to a simple unimodal pattern (Fig. 12a). We interpret these deviations to arise from the preferential uptake of LREE and HREE by the Ca1 and Ca2 sites, respectively. The lanthanides of intermediate size (Sm-Tb) are accommodated equally well in both sites, which will further complicate the shape of a cumulative partitioning curve. This is illustrated schematically in Figure 12b, where the data for the Zibo hydroxylapatite fit reasonably well a model based on two overlapping partitioning curves, one corresponding to the Ca1 site with a crest between Pr and Nd, and the other to the more rigid (i.e. characterized by a higher Young's modulus) Ca2 site with a crest between Dy and Ho. Atomic substitutions involving elements other than REE and other crystallographic sites (in particular, P and structural channels) will obviously affect the rigidity and dimensional characteristics of Ca1 and Ca2, and hence the tightness and position of partitioning parabolae on the Onuma diagram (for details, see Blundy and Wood, 2003).

Note that Figure 12b is a demonstration of concept, rather than an “ironclad” quantitative model: experimental data for the entire lanthanide series and melt compositions approaching natural carbonatitic magmas are required to develop such models. The currently available experimental studies (Klemme and Dalpé, 2003; Hammouda et al., 2010) are based on the oversimplified system $\text{CaCO}_3\text{--Ca}_5(\text{PO}_4)_3(\text{F,OH})$, whose relevance to carbonatites is questionable (see, e.g., Chakhmouradian et al., 2016a). The abundance of Mg and Fe in mantle-derived magmas will most certainly affect the partitioning behavior of REE, Sr, Na and other elements that readily substitute for Ca, but not for the smaller divalent cations (Table 2). Our data are in agreement with the estimates of Brassinnes et al. (2005), i.e. show that REE are compatible with respect to apatite in carbonatites, with the highest $^{Ap/crb}D_x$ values observed between Pr and Ho. Interestingly, similar geometry is seen in the patterns of REE distribution between fluorapatite and melilitite from Kaiserstuhl (Arzamastsev et al., 2009) and synthetic nepheline-normative basaltic melt (Prowatke and Klemme, 2006). That there is no well-defined peak in

any of these models, and the curves are nearly flat across a wide range of ionic radii (Figs. 12a and SF4) lends further support to the two-site partitioning concept discussed above. Atomic substitutions in Ca1, Ca2 and elsewhere in the structure (Sr, Na, Si, S, OH) probably explain why the maximum $^{Ap/crb}D_x$ is not constrained to the same ionic radius value for apatites from different rocks and experimental systems (see above).

The coefficients calculated in the present work are at variance with the $^{Ap/crb}D_x$ values of Bühn et al. (2001). Although incremental fractionation models proposed by these authors reproduced some of the variations in the REE budget of apatite from Otjisazu (Namibia) and Homa Mt. (Kenya), these models were based on too many poorly constrained parameters (including $^{Ap/crb}D_x$, which “were chosen between those published for the silicate melt system ... and for the synthetic phosphate-fluoride system”, p. 586), to be of practical value. It is also noteworthy that the Otjisazu apatite exhibits unusual compositional characteristics that set it well apart from any igneous apatite examined in this or other published studies (see below).

7.2. Apatite fractionation and its effects on carbonatite evolution

Given the extremely low viscosity of carbonatitic melts (Kono et al., 2014), and a large density difference between these melts ($\leq 2.8 \text{ g/cm}^3$; Sykes et al., 1992) and apatite ($3.1\text{-}3.2 \text{ g/cm}^3$), there is no doubt that, provided a favorable emplacement regime, this mineral will readily separate from its parental magma by gravitational settling (Costanzo et al., 2006). Even the most conservative estimates for apatite crystals measuring a few hundred μm (Figs. 3d-g) suggest Stokes’ settling velocities ranging from $\sim 1 \text{ mm/s}$ in dolomitic magmas to twice as fast in natrocarbonatites. The presence of apatite phenocrysts in extrusive and hypabyssal carbonatites showing only moderate P_2O_5 contents (1.5-3.5 wt.%) indicates that carbonatitic magmas reach apatite saturation well below the experimentally determined high-P limit of P_2O_5 solubility (Ryabchikov and Hamilton, 1993). Our empirical upper limit of

~6.5 wt.% P_2O_5 (Fig. 1a) is, however, within the apatite solubility range in primary carbonatitic melts measured by Baker and Wyllie (1992), i.e. 9-18 wt.% at 1120-1430 °C. The discrepancy between the extremely P-rich melts of Ryabchikov and Hamilton (1993) and naturally occurring carbonatites remains to be explained; however, it is clear from the evidence presented in this work that there is no need for carbonatitic magma to precipitate large quantities of calcite or silicate phases to reach apatite saturation.

Early crystallization of apatite and its effective isolation into phoscorites and other types of cumulate rocks (Figs. 3, 10b) will have a profound effect on the geochemistry of evolving carbonatitic systems and, in particular, their REE budget. The data presented above imply that REE are compatible with respect to apatite in a wide range of carbonatite compositions, and La is less compatible than Nd. Apatite fractionation should then result in depletion of the residual melt in REE and its relative enrichment in La with respect to Nd. Fractionating crystals will show a similar trend, but stronger depletion in REE, in particular in Mg-rich systems (Fig. 13a). The $^{Ap/crb}D_{La}$ and $^{Ap/crb}D_{Yb}$ values are similar in the Zibo and Paint Lake carbonatites, but differ appreciably in the Upper Fir sample (Table 2), implying that apatite fractionation will have a variable effect on the $(La/Yb)_{cn}$ ratio and may, in some cases, generate strong depletion of the carbonatite in La. Most of the published and our own data agree that Y is subtly less compatible in apatite than Ho, resulting in subchondritic Y/Ho ratios in most igneous compositions. The decoupling between these two elements is variable and typically small ($\delta Y = 0.6-0.9$; mean $\delta Y = 0.74 \pm 0.09$). It is unlikely to manifest itself in primary growth zoning, for example, but may raise the initially chondritic Y/Ho ratio of carbonatitic magma precipitating a significant volume of apatite (Fig. 13b). The above-described variations in $^{Ap/crb}D_x$ values and fractionation trends controlled by apatite-carbonatite element partitioning can be explained in terms of the structural flexibility of apatite and the potential effects of atomic substitutions on the partitioning curves representing the two REE-hosting sites (Section 7.1). For example, preferential incorporation of the large Sr^{2+} cation in the Ca2 site

(Table 1) can be expected to shift the position of the Ca2 curve to larger ionic radii (Fig. 12b), thus lowering $^{Ap/crb}D_X$ values for the heaviest lanthanides and enhancing the effect of apatite crystallization on the $(La/Yb)_{cn}$ ratio of Sr-rich carbonatites. Anion substitutions in the structural channels also affect REE partitioning (e.g., Fleet and Pan, 2000), but in the absence of detailed experimental data, their outcome is difficult to predict for mixed F–OH±Cl apatites.

In conclusion, we would also like to comment on the partition coefficients for Rb and high-field-strength elements (HFSE) derived by Hammouda et al. (2010) from their high-P apatite-calcite experiments. If these coefficients were indeed as high as reported in that study (i.e., $^{Ap/crb}D_{Rb} = 1.5-2.2$, $^{Ap/crb}D_{Zr} = 1.6-2.2$ and $^{Ap/crb}D_{Nb} \approx 0.1$), apatite fractionation would lead to appreciable changes in the Rb and HFSE budget of the evolving carbonatitic magma. Simple calculations based on the composition of primitive carbonatitic magmas worldwide (Rilley et al., 1998; Ying et al., 2004; Chakhmouradian et al., 2009; Eby et al., 2009; Stoppa and Schiazza, 2013) show that apatites with tens of ppm Rb and Nb and a few hundred ppm Zr should be common in these rocks, which is clearly not the case (Mao et al., 2016; this work). Thus, our data indicate that apatite has a negligible effect on the fate of Rb or HFSE in natural magmas and that the $^{Ap/crb}D_{Rb}$ and $^{Ap/crb}D_{HFSE}$ values of Hammouda et al. (2010) are overestimated and should not be used to model natural systems.

7.3. Compositional diversity of apatite in carbonatites: driving factors

Figures 13c-d summarize the apatite evolutionary trends proposed in the literature (Bühn et al., 2001; Brassinnes et al., 2005) and identified in the present work (thick arrows), including the key examples of zoning discussed earlier and in the next section. Estimated changes in the REE budget of fractionating apatite (see above) are shown schematically by thin arrows in the corner. The trend of REE enrichment postulated for Otjiszazu, Homa Mt. and Vuoriyarvi (Bühn et al., 2001; Brassinnes et al., 2005) cannot be explained exclusively by apatite fractionation because: (a) given the overall compatible nature

of REE with respect to this mineral, their content should *decrease* with fractionation (Fig. 13a), not increase; (b) other elements show variations inconsistent with either the REE trend (e.g., Sr, Ba and Th at Otjisazu) or their partitioning behavior (e.g., an increase in compatible Sr at Vuoriyarvi); and (c) key REE ratios do not follow a consistent pattern of variation among the three localities (e.g., Y/Ho value decreases at Homa Mt., varies erratically at Otjisazu and increases at Vuoriyarvi). Böhn et al. (2001) developed a model involving incremental fractionation of apatite, accompanied by calcite and clinopyroxene, to address some of these issues (in particular, the enrichment in REE), but their model cannot reproduce the seemingly erratic behavior of Sr, Ba, Th and Y (with respect to Ho) within the Otjisazu sample suite. We believe it is significant that their samples shows variations in δY and δEu values (0.27-1.45 and 0.44-0.78, respectively) unparalleled by any other carbonatitic apatite described in the literature or present work (Fig. 13e). None of our 40 igneous samples examined by LA-ICPMS show a detectable, unequivocal Eu anomaly ($\delta Eu = 0.78-1.12$; mean $\delta Eu = 0.93 \pm 0.07$), or extreme variations in Y recorded by Böhn et al. (2001). Although hydrothermal apatite from Aley and Kovdor does differ in δY and δEu from its igneous counterparts from the same locality (Fig. 11e), the magnitude of departure is nowhere near what is observed at Otjisazu. Hydrothermal apatites from the Tundulu and Kangankunde carbonatites in Malawi (Broom-Fendley et al., 2016) plot essentially in the same field as the Aley sample, i.e. at $\delta Eu = 1.06-1.30$ and $\delta Y = 0.84-1.00$. As illustrated by Figures SF2 and 13e, low δEu values are common in apatites from igneous rocks that underwent feldspar fractionation, and in hydrothermal-metasomatic rocks (such as greisens and skarns), where redox processes and ligand-specific complexing become potent vehicles of Eu^{2+}/Eu^{3+} decoupling (e.g., Bao et al., 2008; Chu et al., 2009; and references therein). We agree with Böhn et al. (2001, p. 589) that the trace-element variations documented at Otjisazu require some form of fluid-carbonatite interaction at all stages of apatite crystallization.

It is pertinent to the present discussion that the REE enrichment vectors suggested for the Homa Mt. (Böhn et al., 2001) and Vuoriyarvi (Brassinnes et al., 2005) apatites are speculative because they are

883 based on circumstantial evidence, rather than on demonstrated genetic relations among the apatite
884 host rocks. For example, sample HC34, inferred to mark the climax of apatite evolution at Homa Mt., is
885 composed almost entirely of apatite and pyrochlore (Bühn et al., 2001, p. 583), i.e. could actually
886 represent a *primitive*, cumulate unit (Section 4.2). Perhaps the most convincing argument against the
887 existence of a “universal” evolutionary trend is that the Otjisazu, Homa Mt. and Vuoriyarvi apatites do
888 not show a *consistent* variation in the content of substituent elements or their ratios. Likewise, our data
889 reveal no recognizable evolutionary pattern for the large suites of spatially associated carbonatites
890 (Aley), or phoscorites (Kovdor). For example, samples P2, P3 and P4 show a gradual increase in F content
891 and appear to form a Sr-REE covariation trend (Fig. 11a), but their $(La/Nd)_{cn}$ values are essentially
892 identical, whereas the earlier-emplaced P2 has much lower $(La/Yb)_{cn}$ than either P3 or P4 (Figs. 11c, d),
893 effectively ruling out derivation of these rocks from the same parental magma by apatite fractionation.
894 Other heavy minerals present in phoscorites P2-P4 (forsterite, magnetite, baddeleyite $\pm$ phlogopite) do
895 not concentrate REE sufficiently to balance out the increase in $(La/Nd)_{cn}$ ratio, or reverse the $(La/Yb)_{cn}$
896 trend, caused by apatite precipitation. In the closely overlapping fields for the Aley calcite and dolomite
897 carbonatites, apatites associated with the most and least HREE-enriched carbonates have similar REE
898 ratios (cf. empty and solid squares and diamonds in Figs. 11 c-e). Apatites from the calcite-dolomite and
899 calcite carbonatites at Paint Lake form two distinct compositional fields with little overlap. However,
900 although some of the recorded differences between these fields [i.e., decreasing Sr and $(La/Yb)_{cn}$ values
901 at increasing δY] can be accounted for by apatite fractionation, the trend of decreasing $(La/Nd)_{cn}$ at
902 stable LREE levels requires an alternative explanation (Figs. 13a, b). The interpretation of the Paint Lake
903 trend is further complicated by the much higher $Ca/(Ca+Mg+Fe+Mn)$ ratio in the sövite in comparison
904 with the calcite-dolomite carbonatite (0.93 and 0.66, respectively), implying significant differences in
905 trace-element partitioning between their parental magmas. The compositions of macro- and
906 phenocrysts from Wekusko Lake (Fig. 4d) define a trend toward lower REE, Mn, Ba, Th, U and $(La/Nd)_{cn}$,

but higher $(\text{La/Yb})_{\text{cn}}$ values at a constant Sr level (supplementary Table ST4). Their δCe , δEu and δY values are essentially identical, suggesting that these apatites derive from the same magma, but the observed trace-element variations, again, depart significantly from the predicted trends.

From the above summary, it is clear that even in seemingly simple systems – such as the calcite carbonatites from Aley (Chakhmouradian et al., 2016a), phoscorites P1-P4 from Kovdor (Zaitsev et al., 2014), Wekusko Lake, or Paint Lake rocks – the documented trace-element variations in apatite cannot be adequately modelled exclusively by fractionation of this mineral. Syn-emplacement hydrothermal processes, proposed by Bühn et al. (2001) for Otjisazu, should be expected to produce a recognizable δEu , δY or δCe signature, at least in some members of the compositional series (Fig. 13e). No such signature is observed in the igneous samples from Aley, calcite-bearing phoscorites from Kovdor, Paint Lake, or Wekusko Lake carbonatites. In fact, all igneous samples examined in the present work exhibit remarkably little variation in δEu , δY or δCe , especially in comparison with the Otjisazu suite. Hence, we conclude that processes other than magma-fluid interaction are responsible for the inconsistencies and the lack of identifiable “universal” trends discussed above.

Discrete carbonatite units occurring within the same complex may derive from different magma batches that explored the same system of lithospheric conduits and derive from broadly similar sources, but do not share a lineage (Fig. 14a). Multiple juxtaposed magmatic events have been documented even for such small-volume and rapidly ascending melts as kimberlites (e.g., the 15-ha Victor cluster in Canada: Webb et al., 2004). Hence, there is no a priori reason why similar juxtaposition and composite structures could not result from more voluminous carbonatitic magmatism that gave rise to the 70-ha Kovdor phoscorite-carbonatite stock or ~700-ha Aley complex (Krasnova et al., 2004; Chakhmouradian et al., 2015). Under this scenario, apatites from individual carbonatite units will not follow any specific trend, but may form overlapping compositional fields if their parental magmas were sufficiently similar.

In those cases where fractionating apatite is accompanied by other minerals (Fig. 14b), their effect on the REE budget of the melt can be quite significant not only if they have a large capacity for REE (e.g., perovskite or pyrochlore: Chakhmouradian and Williams, 2004; Chakhmouradian et al., 2015), but also if they precipitate in voluminous proportions. We agree with Böhn et al. (2001) that crystallization of cumulus carbonates will significantly affect the compositional evolution of apatite, but the lack of reliable data on element partitioning between carbonates and melts precludes any meaningful analysis at this point. To demonstrate the importance of coprecipitating cumulus phases, we will use clinopyroxene that, although showing relatively low REE levels (≤ 150 ppm), is very common and locally forms cumulate layers in carbonatites (Requir et al., 2012; our Fig. 3f). Owing to the greater affinity of this mineral for HREE in comparison with LREE and to their overall low partition coefficients, clinopyroxene fractionation will effectively “reroute” apatite evolution, causing higher REE and $(\text{La/Yb})_{\text{cn}}$ values in later-crystallized generations of this mineral (Fig. 14c). Co-precipitation of apatite with large quantities of another mineral (mn), or the release of a fluid phase (fl) will result in the enrichment of late apatite generations in REE, as long as $^{mn/crb}D_{\text{REE}} < 1$ (or $^{fl/crb}D_{\text{REE}} < 1$), but any changes in REE ratios will be governed by element partitioning within the lanthanide series, including redox- and complexing-driven processes (see above), specific to the co-precipitating mineral (e.g., Fig. 14c) or released fluid (e.g., Böhn et al., 2001). Further implications of these processes for apatite zoning are discussed below.

7.4. The origin of zoning in carbonatitic apatite

The prevalent type of primary zoning in carbonatitic apatite, involving a rim-ward increase in REE content, is contrary to what could be expected from the partitioning behavior of these elements (Figs. 13c, d); the sharp and often irregular core-rim boundary (Figs. 5a, b) also indicates that a process other than apatite fractionation is responsible for this pattern (cf. Chakhmouradian et al., 2013). As illustrated by Figure 14c, it may develop if the formation of early apatite (crystal cores) is followed by the

precipitation of a rock-forming non-phosphate mineral (or minerals) with low $^{mn/crb}D_{REE}$, which will raise the P_2O_5 and REE contents in the melt until the level of apatite saturation is reached again and a younger, REE-enriched generation is deposited as crystal rims (Figs. 15a, b), with Si-for-P substitution typically providing the balance of charge. As discussed above, a variety of rock-forming minerals can produce the REE-enrichment trends shown in Figures 9 and 11, but the core-to-rim variations in REE ratios and the content of other trace elements among carbonatites will vary greatly depending on the nature of fractionating phases (cf. Eden Lake and Aley fields in Figs. 13c, d). For the majority of minerals that may co-precipitate with apatite (calcite, dolomite, amphiboles, zircon, pyrochlore, columbite, monticellite, andradite, titanite), the partitioning behavior of REE and other trace elements in carbonatitic systems is unknown and, hence, no detailed predictions of apatite evolution can be made at this point. The typically irregular and embayed contours of apatite cores (Figs. 5a, 8a-c) suggest that the mineral undergoes abrasion ($\pm$ resorption) during the hiatus in crystal growth, possibly through erosion of the cumulate material and its transport by moving magma (Figs. 15c-e). Variations in composition within the REE-rich rim may reflect multiple growth episodes, each associated with the deposition of a specific rock-forming mineral (Fig. 5a), or changes in crystallization conditions (Fig. 4f).

Without sufficient high-resolution trace-element data, patterns of type (2) are difficult to interpret conclusively because of the significant variations in their morphological and compositional characteristics, in particular: the boundary between the REE-rich intermediate zone and low-AZ rim may be sharp or, less commonly, diffuse; the rim may be relatively homogeneous in BSE and CL images, or consist of subzones (cf. Figs. 8b, c, g); the Na, Sr, REE and F contents in the rim may be similar to, or very different from, those in the core (Figs. 9b, d). The REE-rich zone is typically discontinuous and, in some luminescent samples, the rim was observed to truncate both the core and intermediate zone (Fig. 10c), as if the crystal were abraded or resorbed prior to the rim formation. Carbonatites containing this type of apatite are often mineralogically complex and contain both calcite and dolomite, or show

petrographic evidence of disequilibrium. We hypothesize that at least in some cases, this type of zoning develops by re-equilibration of type-(1) crystals with a fresh batch of less-evolved carbonatitic magma (Fig. 15f). Because the latter may approach in composition the magma that precipitated the precursor apatite, or differ from it, we see a variety of zoning trends. A detailed study of type-(2) apatites and their associated mineralogical peculiarities is currently underway.

Based on textural evidence (cf. our Figs. 8d-f to Figs. 2c-e of Kusebauch et al., 2015), both type-(3) and type-(4) zoning patterns are produced by reaction of igneous apatite with fluids percolating along fractures and grain boundaries (Figs. 15g, h). The more common type (3) involves leaching of the majority of substituent cations (with the exception of Na at Turiy Mys) from the primary apatite and F uptake at the expense of OH and Cl. These processes are accompanied by the deposition of typical hydrothermal minerals (e.g., quartz) in the fractures and sequestration of the less-mobile, high-charge cations released from the precursor (REE, Th and U) in secondary monazite, LREE($\pm$ Ca) fluorocarbonates and thorite (Figs. 8e, f). A large drop in $(La/Yb)_{cn}$ and, to a lesser extent, $(La/Nd)_{cn}$ values in the altered apatite (Figs. 13c, d) implies that REE mobility in the fluid decreases with atomic number. This observation is in agreement with the experimental data and models of Migdisov et al. (2009) and Williams-Jones (2015). Replacement of Cl-rich ternary apatite by essentially Cl-free fluorapatite (i.e. analogous to the Yousuobao sample) was achieved experimentally in a NaF solution at 500-700 °C by Kusebauch et al. (2015). Contrary to previous studies, these authors concluded that the apatite-fluid partition coefficient for F is independent of T and inversely correlates with the concentration of this element in the fluid. Because of this compositional dependence, it is impossible to estimate the concentration of F in the fluid based on its content in the secondary apatite. However, it is noteworthy that extremely F-rich synthetic compositions comparable to those observed in this work (e.g., no. 4 in Table ST1) required very high F levels in the fluid (15 mg/g: Kusebauch et al., 2015).

The apatite of type (4), which is fairly uncommon and appears to be restricted to dolomite carbonatites or those affected by dolomitization, differs from type (3) in showing generally *higher* levels of substituent elements (especially, Sr) than in the precursor apatite. The extreme variations in Sr, Na, REE, Fe and F observed in the type-(4) apatites over a scale of tens of μm (Figs. 9b-d) indicate that their composition was controlled by the concentration of these elements in the local crystallization environment (e.g., inside a dissolution microcavity) and precipitation of “competitor” minerals in that environment (e.g., monazite and goethite: Fig. 8c). Hence, it is difficult to draw any conclusions about the chemistry of their parental fluid from such cursory evidence. The only sample studied by LA-ICPMS (Albany Forks) is characterized by consistently elevated $(\text{La}/\text{Yb})_{\text{cn}}$ ratios and Th abundances relative to its igneous precursor, which seems to indicate a radically different type of fluid relative to that responsible for the type-(3) zoning. This conclusion is consistent with the absence of carbonatites where these two types of secondary apatite would co-exist.

Type (5), observed in the dolomite phoscorite (P5) from Kovdor, exhibits textural and compositional characteristics not seen in any other carbonatitic samples from either the present work or the literature. The resorbed shape of apatite cores and striking euhedral morphology of their rim are reminiscent of hydrothermal samples from Malawi (Broom-Fendley et al., 2015; cf. their Fig. 3a and our Fig. 8h). The rim of the Kovdor crystals is depleted in REE and enriched in elements typically present at low levels in primary carbonatitic apatite (Na, Mn and Ba), which also seems to suggest a non-igneous origin. However, the Malawian apatites, as well as the hydrothermal samples examined here, are associated with quartz and other typical hydrothermal minerals, show unremarkable levels of Mn, Ba and Mg, and $(\text{La}/\text{Yb})_{\text{cn}}$ values ≤ 25 (Broom-Fendley et al., 2015; this work), i.e. much lower than in the Mn-Ba-rich variety from P5. The latter is also very different in composition from the Mn-Ce-poor, F-rich aggregates of unquestionably hydrothermal origin mantling apatite P3 from the same deposit (Figs. 5d, e; Tables ST3, ST5). Although it is feasible that the Kovdor phoscorites could be overprinted by chemically distinct

fluids derived from two (or more) different sources, the currently available mineralogical evidence is inconclusive and further work is desirable.

7.5. Implications for mineral exploration

Although the applicability of apatite as an indicator mineral for exploration was not the focus of the present work (interested readers are referred to Belousova et al., 2002; Mao et al., 2016), we consider it worthwhile to reflect on the potential implications of our findings for the development of geochemical vectoring tools for carbonatite-hosted rare-metal deposits. The following observations should be viewed as complementary to, and will address only the points not raised in, the study by Mao et al. (2016).

- (1) Apatite zoning (as revealed by BSE and CL imaging) may be useful for recognizing a carbonatitic source and even specific evolutionary processes of relevance to exploration (e.g., leaching of REE by fluids and their deposition as secondary mineralization in fractures);
- (2) Apatite is rare or absent in carbonatites hosting economic REE mineralization (fluorocarbonates + monazite), but may be common in their associated syenitic rocks (Fig. 2f). A detailed trace-element study of the latter apatites is desirable to determine whether they can be used as a proxy indicator;
- (3) Abundant detrital apatite, accompanied by magnetite, baddeleyite, pyrochlore or columbite, suggests early removal of rare earths from carbonatitic magma and, hence, is an indicator of low REE potential of the substrate rock;
- (4) Igneous apatite from carbonatites and other rock types can be distinguished reliably using a variety of criteria (i.e., ≤ 1000 ppm Mn, > 2000 ppm Sr, $\delta\text{Eu} \approx 1$, $\delta\text{Y} = 0.6\text{--}0.9$ in the former; see Fig. 13e); detrital apatite with this type of signature and high Th/U ratios (> 70) is indicative of pyrochlore mineralization in its source;

(5) Sr-bearing and low-Mn fluorapatite with $\delta\text{Eu} \neq 1$ and $\delta\text{Y} < 0.6$ or > 0.9 is suggestive of a hydrothermally reworked carbonatitic rock and possible late-stage mineralization associated with such environments.

8. Conclusions and recommendations for future work

Apatite-group minerals are a nearly ubiquitous accessory constituent of calcite and dolomite carbonatites and their cogenetic cumulate rocks. These apatites vary greatly in morphology and zoning, which not only reflect the place of these minerals in the paragenetic sequence (macrocryst, phenocryst, groundmass, cumulate, or hydrothermal phase), but also record a wide range of evolutionary processes (from early magmatic fractionation to interaction of carbonatites with hydrothermal fluids). The majority of igneous apatite from carbonatites is Cl-poor fluorapatite or F-rich hydroxylapatite with Na, Sr, REE and low levels of other cations accommodated in the Ca site; no meaningful correlation was observed between the abundances of these elements and their host-rock type. In the P site, Si and S are the principal, and V is a minor, substituents that are both more common and greater in abundance in samples from calcite carbonatites. Hydrothermal apatite occurs as zones of replacement in primary apatite and as euhedral crystals, spherulitic and colloform aggregates with a number of distinctive compositional characteristics. This late-stage apatite tends to be depleted in Sr, REE, Mn and Th, but enriched in F relative to its igneous precursor that served as a source of phosphorus; it is generally poorer in LREE relative to HREE in comparison with igneous samples, and commonly falls outside the igneous range of δCe , δEu and δY values. One notable exception is Sr($\pm$ Na, REE)-rich hydrothermal apatite observed in several dolomite(-bearing) carbonatites, whose extremely variable composition appears to have been controlled by the availability of these cations on microscopic spatial scales. Some of the textural and chemical characteristics identified in this study may be used to enhance the application of detrital apatite in surface sediments to mineral exploration targeting rare-metal deposits.

1072 However, a better understanding of the compositional variation in apatite from alkaline silicate rocks
1073 associated with these deposits (e.g., syenites) is critical to the development of such exploration tools.

1074 Contrary to the published experimental results, our data indicate that in common with
1075 undersaturated silicate melts (Prowatke and Klemme, 2006; Arzamastsev et al., 2009), REE are
1076 compatible with respect to apatite in carbonatitic systems (those in the middle of the lanthanide series
1077 more so than either La or Yb), and their compatibility increases with the normative content of dolomite
1078 in the melt. Given the high limits of P_2O_5 solubility in such melts (at least 6.5 wt.%), fractionation of
1079 apatite will have a profound effect on the trace-element budget of evolving phosphate-rich carbonatitic
1080 magma (e.g., cause its depletion in rare earths). However, the calculated fractionation trends do not
1081 replicate the variations in trace-element composition (in particular, REE distribution and ratios) actually
1082 observed in natural apatites in the present and previously published work. We interpret these
1083 discrepancies as evidence that intrusions the size of Kovdor or Aley ($n \times 10^{1-2}$ ha) comprise rocks
1084 representing multiple magma pulses, rather than derived by protracted differentiation in a single
1085 magma chamber. The composition of apatite in individual carbonatite units is strongly affected by other
1086 rock-forming minerals that may have a limited capacity for REE, but are capable of “rerouting” apatite
1087 evolution when precipitated in voluminous quantities. At present, any attempt at modeling specific
1088 carbonatites would be hindered by the lack of understanding of element partitioning in such common
1089 rock-forming minerals as calcite, dolomite, phlogopite and amphiboles. Comprehensive studies of
1090 mineral-melt partitioning in undifferentiated carbonatites, other carbonate-rich mantle-derived rocks,
1091 and their synthetic analogues are clearly desirable.

1092 One of the most intriguing unresolved issues is the origin of complex growth zoning patterns
1093 observed in apatite from some carbonatites and phoscorites, which involve multiple changes in element
1094 abundances and ratios across the crystal. Detailed studies of the host-rock mineralogy and, where

present, melt and fluid inclusions in such apatites, will provide clues to the causes of these variations and their implications for carbonatite evolution.

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References

Ahijado, A., Casillas, R., Nagy, G., Fernández, C., 2005. Sr-rich minerals in a carbonatite skarn, Fuerteventura, Canary Islands (Spain). *Mineralogy and Petrology* 84, 107–127.

1117 Andersen, T., 1986. Magmatic fluids in the Fen carbonatite complex, S.E. Norway: Evidence of mid-
 1118 crustal fractionation from solid and fluid inclusions in apatite. *Contributions to Mineralogy and*
 1119 *Petrology* 93, 491–503.

1120 Andrews, O.E.G., 1996. Apatite in the Kensington and Sainte-Véronique plutons, near Mont-Laurier,
 1121 Québec: an indicator of magmatic and hydrothermal processes. Unpublished MSc Thesis, McGill
 1122 University, Montreal, Canada, 93 pp.

1123 Arzamastsev, A.A., Arzamastseva, L.V., Bea, F., Montero, P., 2009. Trace elements in minerals of the
 1124 evolution of alkaline ultrabasic dike series: LA-ICP-MS data for the magmatic provinces of
 1125 Northeastern Fennoscandia and Germany. *Petrology* 17, 46–72.

1126 Awonusi, A., Morris, M.D., Tecklenburg, M.M.J., 2007. Carbonate assignment and calibration in the
 1127 raman spectrum of apatite. *Calcified Tissue International* 81, 46–52.

1128 Baker, M.B., Wyllie, P.J., 1992. High-pressure apatite solubility in carbonate-rich liquids: implications for
 1129 mantle metasomatism. *Geochimica et Cosmochimica Acta* 56, 3409–3422.

1130 Bao, S., Zhou, H., Peng, X., Ji, F., Yao, H., 2008. Geochemistry of REE and yttrium in hydrothermal fluids
 1131 from the Endeavour segment, Juan de Fuca Ridge. *Geochemical Journal* 42, 359–370.

1132 Belousova, E.A., Griffin, W.L., O'Reilly, S.Y., Fisher, N.I., 2002. Apatite as an indicator mineral for mineral
 1133 exploration: trace-element compositions and their relationship to host rock type. *Journal of*
 1134 *Geochemical Exploration* 76, 45–69.

1135 Binder, G., Troll, G., 1989. Coupled anion substitution in natural carbon-bearing apatites. *Contributions*
 1136 *to Mineralogy and Petrology* 101, 394–401.

1137 Blundy, J., Wood, B., 2003. Partitioning of trace elements between crystals and melts. *Earth and*
 1138 *Planetary Science Letters* 210, 383–397.

1139 Bonyadi, Z., Davidson, G.J., Mehrabi, B., Meffre, S., Ghazban, F., 2011. Significance of apatite REE
1140 depletion and monazite inclusions in the brecciated Se-Chahun iron oxide-apatite deposit, Bafq
1141 district, Iran: Insights from paragenesis and geochemistry. *Chemical Geology* 281, 253–269.

1142 Borodin, L.S., Lapin, A.V., Kharchenkov, A.G., 1973. Rare-metal Camaforites. Nauka, Moscow (in
1143 Russian).

1144 Brassinnes, S., Balaganskaya, E., Demaiffe, D., 2005. Magmatic evolution of the differentiated ultramafic,
1145 alkaline and carbonatite intrusion of Vuoriyarvi (Kola Peninsula, Russia). A LA-ICP-MS study of
1146 apatite. *Lithos* 85, 76–92.

1147 Brigatti, M.F., Malferrari, D., Medici, L., Ottolini, L., Poppi, L., 2004. Crystal chemistry of apatites from
1148 the Tapira carbonatite complex, Brazil. *European Journal of Mineralogy* 16, 677–685.

1149 Broom-Fendley, S., Styles, M.T., Appleton, J.D., Gunn, G., Wall, F., 2016. Evidence for dissolution-
1150 reprecipitation of apatite and preferential LREE mobility in carbonatite-derived late-stage
1151 hydrothermal processes. *American Mineralogist* 101, 596–611.

1152 Bühn, B., Wall, F., Le Bas, M.J., 2001. Rare-earth element systematic of carbonatitic fluorapatites and
1153 their significance for carbonatite magma evolution. *Contributions to Mineralogy and Petrology* 141,
1154 572–591.

1155 Cao, M., Li, G., Qin, K., Seitmuratova, E.Y., Liu, Y., 2011. Major and trace element characteristics of
1156 apatites in granitoids from central Kazakhstan: implications for petrogenesis and mineralization.
1157 *Resource Geology* 62, 63–83.

1158 Castor, S.B. (2008) The Mountain Pass rare-earth carbonatite and associated ultrapotassic rocks,
1159 California. *Canadian Mineralogist* 46, 779–806.

1160 Chakhmouradian, A.R., Hughes, J.M., Rakovan, J., 2005. Fluorocaphite, a second occurrence and detailed
1161 structural analysis: simultaneous accommodation of Ca, Sr, Na, and LREE in the apatite atomic
1162 arrangement. *Canadian Mineralogist* 43, 735–746.

1163 Chakhmouradian, A.R., Medici, L., 2006. Clinohydroxylapatite: a new apatite-group mineral from
 1164 northwestern Ontario (Canada), and new data on the extent of Na-S substitution in natural apatites.
 1165 European Journal of Mineralogy 18, 105–112.

1166 Chakhmouradian, A.R., Mitchell, R.H., 1998. Lueshite, pyrochlore and monazite-(Ce) from apatite-
 1167 dolomite carbonatite, Lesnaya Varaka complex, Kola Peninsula, Russia. Mineralogical Magazine 62,
 1168 769–782.

1169 Chakhmouradian, A.R., Mumin, A.H., Demény, A., Elliott, B., 2008. Postorogenic carbonatites at Eden
 1170 Lake, Trans-Hudson Orogen (northern Manitoba, Canada): Geological setting, mineralogy and
 1171 geochemistry. Lithos 103, 503–526.

1172 Chakhmouradian, A.R., Reguir, E.P., Couëslan, C., Yang, P., 2016a. Calcite and dolomite in intrusive
 1173 carbonatites. II. Trace-element variations. Mineralogy and petrology 110, 361–377.

1174 Chakhmouradian, A.R., Reguir, E.P., Kamenetsky, V.S., Sharygin, V.V., Golovin, A.V., 2013. Trace-element
 1175 partitioning in perovskite: Implications for the geochemistry of kimberlites and other mantle-derived
 1176 undersaturated rocks. Chemical Geology 353, 112–131.

1177 Chakhmouradian, A.R., Reguir, E.P., Kressall, R.D., Crozier, J., Pisiak, L., Sidhu, R., Yang, P., 2015. Carbonatite-hosted
 1178 niobium deposit at Aley, northern British Columbia (Canada): Mineralogy, geochemistry and
 1179 petrogenesis. Ore Geology Reviews 64, 642–666.

1180 Chakhmouradian A.R., Reguir E.P., Mitchell R.H., 2002. Strontium-apatite: new occurrences, and the
 1181 extent of Sr-for-Ca substitution in apatite-group minerals. Canadian Mineralogist 40, 121–136.

1182 Chakhmouradian, A.R., Reguir, E.P., Zaitsev, A.N., 2016b. Calcite and dolomite in intrusive carbonatites.
 1183 I. Textural variations. Mineralogy and Petrology 110, 333–360.

1184 Chakhmouradian, A.R., Williams, T.C., 2004. Mineralogy of high-field-strength elements (Ti, Nb, Zr, Ta,
 1185 Hf) in phoscoritic and carbonatitic rocks of the Kola Peninsula, Russia, in: Wall, F., Zaitsev, A.N.

1186 (Eds.), Phoscorites and Carbonatites from Mantle to Mine: the Key Example of the Kola Alkaline
 1187 Province. Mineralogical Society of Great Britain and Ireland, London, pp. 293–340.
 1188 Chakhmouradian, A.R., Zaitsev, A.N., 2012. Rare earth mineralization in igneous rocks: sources and
 1189 processes. *Elements* 8, 347–353.
 1190 Chen, W.T., Zhou, M.F., Zhao, T.P., 2013. Differentiation of nelsonitic magmas in the formation
 1191 of the ~1.74 Ga Damiao Fe–Ti–P ore deposit, North China. *Contributions to Mineralogy and*
 1192 *Petrology* 165, 1341–1362.
 1193 Chu, M.F., Wang, K.L., Griffin, W.L., Chung, S.L., O'Reilly, S.Y., Pearson, N.J., Iizuka, Y., 2009. Apatite
 1194 composition: tracing petrogenetic processes in Transhimalayan granitoids. *Journal of Petrology* 50,
 1195 1829–1855.
 1196 Cooper, A.F., Paterson, L.A., 2008. Carbonatites from a lamprophyric dyke-swarm, South Westland, New
 1197 Zealand. *Canadian Mineralogist* 46, 753–777.
 1198 Cooper, A.F., Reid, D.L., 1998. Nepheline syenites as parental magmas in carbonatite complexes: evidence
 1199 from Dicker Willem, Southwest Namibia. *Journal of Petrology* 39, 2123–2136.
 1200 Cordeiro, P.F.O., Brod, J.A., Santos, R.V., Dantas, E.L., de Oliveira, C.G., Barbosa, E.S.R., 2011. Stable (C,
 1201 O) and radiogenic (Sr, Nd) isotopes of carbonates as indicators of magmatic and post-magmatic
 1202 processes of phoscorite-series rocks and carbonatites from Catalão I, central Brazil. *Contributions to*
 1203 *Mineralogy and Petrology* 161, 451–464.
 1204 Costanzo, A., Moore, K.R., Wall, F., Feely, M., 2006. Fluid inclusions in apatite from Jacupiranga calcite
 1205 carbonatites: Evidence for a fluid-stratified carbonatite magma chamber. *Lithos* 91: 208–228.
 1206 D'Orazio, M., Innocenti, F., Tonarini, S., Doglioni, C., 2007. Carbonatites in a subduction system: the
 1207 Pleistocene alvikites from Mt. Vulture (southern Italy). *Lithos* 98, 313–334.
 1208 Drinkwater, J.L., Czamanske, G.K., Ford, A.B., 1990. Apatite of the Dufek intrusion: distribution,
 1209 paragenesis, and chemistry. *Canadian Mineralogist* 28, 835–854.

- 1210 Eby, G.N., Lloyd, F.E., Woolley, A.R., 2009. Geochemistry and petrogenesis of the Fort Portal, Uganda,
1211 extrusive carbonatite. *Lithos* 113, 785–800.
- 1212 Edgar, A.D., 1989. Barium- and strontium-enriched apatites in lamproites from West Kimberley, Western
1213 Australia. *American Mineralogist* 74, 889–895.
- 1214 Fleet, M.E., Liu, X., Pan, Y., 2000. Rare-earth elements in chlorapatite $[\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2]$: Uptake, site
1215 preference, and degradation of monoclinic structure. *American Mineralogist* 85, 1437–1446.
- 1216 Fleet, M.E., Liu, X., 2008. Accommodation of the carbonate ion in fluorapatite synthesized at high
1217 pressure. *American Mineralogist* 93, 1460–1469.
- 1218 Fleet, M.E., Liu, X., King, P.L., 2004. Accommodation of the carbonate ion in apatite: An FTIR and X-ray
1219 structure study of crystals synthesized at 2–4 GPa. *American Mineralogist* 89, 1422–1432.
- 1220 Fleet, M.E., Pan, Y., 1995. Site preference of rare earth elements in fluorapatite. *American Mineralogist*
1221 80, 329–335.
- 1222 Fleet, M.E., Pan, Y., 1997. Site preference of rare earth elements in fluorapatite: Binary (LREE+HREE)-
1223 substituted crystals. *American Mineralogist* 82, 870–877.
- 1224 Frei, D., Liebscher, A., Franz, G., Wunder, B., Klemme S., Blundy, J., 2009. Trace element partitioning
1225 between orthopyroxene and anhydrous silicate melt on the Iherzolite solidus from 1.1 to 3.2 GPa
1226 and 1,230 to 1,535°C in the model system $\text{Na}_2\text{O}-\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$. *Contributions to Mineralogy*
1227 and *Petrology* 157, 473–490.
- 1228 Freund, F., Knobel, R.M., 1977. Distribution of fluorine in hydroxyapatite studied by infrared
1229 spectroscopy. *Journal of the Chemical Society Dalton Transactions* 1136–1140.
- 1230 Frietsch, R., Perdahl, J.-A., 1995. Rare earth elements in apatite and magnetite in Kiruna-type iron
1231 ores and some other iron ore types. *Ore Geology Reviews* 9, 489–510.
- 1232 Guzmics, T., Mitchell, R.H., Szabo', C., Berkesi, M., Milke, R., Ratter, K., 2012. Liquid immiscibility
1233 between silicate, carbonate and sulfide melts in melt inclusions hosted in co-precipitated minerals

1234 from Kerimasi volcano (Tanzania): evolution of carbonated nephelinitic magma. Contributions to
 1235 Mineralogy and Petrology 164, 101–122.

1236 Guzmics, T., Zajacz, Z., Kodolányi, J., Halter, W., Szabó, C., 2008. LA-ICP-MS study of apatite- and K
 1237 feldspar-hosted primary carbonatite melt inclusions in clinopyroxenite xenoliths from
 1238 lamprophyres, Hungary: Implications for significance of carbonatite melts in the Earth's mantle.
 1239 Geochimica et Cosmochimica Acta 72, 1864–1886.

1240 Hamilton, D.L., Freestone, I.C., Dawson, J.B., Donaldson, C.H., 1979. Origin of carbonatites by liquid
 1241 immiscibility. Nature 279, 52–54.

1242 Hammouda, T., Chantel, J., Devidal, J.-L., 2010. Apatite solubility in carbonatitic liquids and traceelement
 1243 partitioning between apatite and carbonatite at high pressure. Geochimica et Cosmochimica Acta
 1244 74, 7220–7235.

1245 Harlov, D., Renzulli, A., Ridolfi, F., 2006. Iron-bearing chlor-fluorapatites in crustal xenoliths from the
 1246 Strombolivolcano (Aeolian Islands, Southern Italy): an indicator of fluid processes during contact
 1247 metamorphism. European Journal of Mineralogy 18, 233–241.

1248 Hata, M., Marumo, F., Iwai, S. I., 1980. Structure of a lead apatite $Pb_9(PO_4)_6$. Acta Crystallographica B36,
 1249 2128–2130.

1250 Hayward, C.L., Jones, A.P., 1991. Cathodoluminescence petrography of Middle Proterozoic extrusive
 1251 carbonatite from Qasiarsuk, South Greenland. Mineralogical Magazine 55, 591–603.

1252 Herz, N., Force, E.R., 1987. Geology and mineral deposits of the Roseland District of central Virginia.
 1253 USGS Professional Paper 1371, 56 pp.

1254 Hogarth, D.D., 1989. Pyrochlore, apatite and amphibole: distinctive minerals in carbonatite, in: Bell, K.,
 1255 (Eds.), Carbonatites. Genesis and evolution. Unwin Hyman, London, pp. 105–148.

1256 Hornig-Kjarsgaard, I., 1998. Rare earth elements in sövitic carbonatites and their mineral phases. Journal
 1257 of Petrology 39, 2105–2121.

- 1258 Hughes, J.M., Cameron, M., Crowley, K.D., 1989. Structural variations in natural F, OH, and Cl apatites.
1259 American Mineralogist 74, 870–876.
- 1260 Hughes, J.M., Cameron, M., Crowley, K.D., 1990. Crystal structures of natural ternary apatites: Solid
1261 solution in the $\text{Ca}_5(\text{PO}_4)_3\text{X}$ (X = F, OH, Cl) system. American Mineralogist 75, 295–304.
- 1262 Hughes, J.M., Cameron, M., Crowley, K.D., 1991. Ordering of divalent cations in the apatite structure:
1263 Crystal structure refinements of natural Mn- and Sr-bearing apatite. American Mineralogist 76,
1264 1857–1862.
- 1265 Hughes, J.M., Ertl, A., Bernhardt, H.J., Rossman, G.R., Rakovan, J., 2004. Mn-rich fluorapatite from
1266 Austria: crystal structure, chemical analysis and spectroscopic investigations. American Mineralogist
1267 89, 629–632.
- 1268 Hughes, J.M., Franolet, A.-M., Schreyer, W., 1993. The atomic arrangement of iron-bearing apatite.
1269 Neues Jahrbuch für Mineralogie Monatshefte 11, 504–510.
- 1270 Ito, J., 1968. Silicate apatites and oxyapatites. American Mineralogist 53, 890–907.
- 1271 Kampf, A.R., Steele, I.M., Jenkins, R.A., 2006. Phosphohedyphane, $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}$, the phosphate analog
1272 of hedyphane: Description and crystal structure. American Mineralogist 91, 1909–1917.
- 1273 Kempe, U., Götze, J., 2002. Cathodoluminescence (CL) behaviour and crystal chemistry of apatites from
1274 rare-metal deposits. Mineralogical Magazine, 66, 151–172.
- 1275 Klemme, S., Dalpé, C., 2003. Trace-element partitioning between apatite and carbonatite melt.
1276 American Mineralogist 88, 639–646.
- 1277 Kono, Y., Kenney-Benson, C., Hummer, D., Ohfuji, H., Park, C., Shen, G., Wang, Y., Kavner, A., Manning,
1278 C.E., 2014. Ultralow viscosity of carbonate melts at high pressures. Nature Communications 5, 5091.
- 1279 Krasnova N. I., Petrov T. G., Balaganskaya E. G., Garcia D., Moutte J., Zaitsev A. N., Wall F., 2004.
1280 Introduction to phoscorites: occurrence, composition, nomenclature and petrogenesis, in: Wall, F,

- 1281 Zaitsev, N. (Eds.), Phoscorites and Carbonatites from Mantle to Mine: the Key Example of the Kola
1282 Alkaline Province. Mineralogical Society of Great Britain and Ireland, London, pp. 45–74.
- 1283 Kravitz, L.C., Kingsley, J.D., Elkin, E.L., 1968. Raman and Infrared studies of coupled PO_4^{3-} vibrations.
1284 Journal of Chemical Physics 49, 4600–4610.
- 1285 Kusebauch, C., John, T., Whitehouse, M.J., Klemme, S., Putnis, A., 2015. Distribution of halogens
1286 between fluid and apatite during fluid-mediated replacement processes. *Geochimica et*
1287 *Cosmochimica Acta* 170, 225–246.
- 1288 Le Bas, M.J., Handley, C.D., 1979. Variation in apatite composition in ijolitic and carbonatitic igneous
1289 rocks. *Nature* 279, 54–56.
- 1290 Liu, Y., Comodi, P., 1993. Some aspects of the crystal-chemistry of apatites. *Mineralogical Magazine* 57,
1291 709–719.
- 1292 Livingstone, A., 1994. An apatite high in lead from Wanlockhead, Strathclyde Region, Scotland.
1293 *Mineralogical Magazine* 58, 159–163.
- 1294 Lottermoser, B.G., 1987. Churchite from the Mt Weld carbonatite laterite, Western Australia.
1295 *Mineralogical Magazine* 51, 468–469.
- 1296 Luo, Y., Hughes, J.M., Rakovan, J., Pan, Y.M., 2009. Site preference of U and Th in Cl, F, and Sr apatites.
1297 *American Mineralogist* 94, 345–351.
- 1298 Luo, Y., Rakovan, J., Tang, Y., Lupulescu, M., Hughes, J.M., Pan, Y.M., 2011. Crystal chemistry of Th in
1299 fluorapatite. *American Mineralogist* 96, 23–33.
- 1300 Manthilake, M.A.G.M., Sawada, Y., Sakai, S., 2008. Genesis and evolution of Eppawala carbonatites, Sri
1301 Lanka. *Journal of Asian Earth Sciences* 32, 66–75.
- 1302 Mao, M., Rukhlov, A.S., Rowins, S.M., Spence, J., Coogan, L.A. (2016) Apatite trace element
1303 compositions: A robust new tool for mineral exploration. *Economic Geology* 111, 1187–1222.

1304 Mariano, A.N., 1989, Nature of economic mineralization in carbonatites and related rocks, in: Bell, K.
 1305 (Ed.), Carbonatites: Genesis and Evolution. Unwin Hyman, Boston, p. 149–176.

1306 Martin, L., Schmidt, M.W., Mattsson, H.B., Guenther, D., 2013. Element partitioning between immiscible
 1307 carbonatite and silicate melts for dry and H₂O-bearing systems at 1-3GPa. *Journal of Petrology* 54,
 1308 2301–2338.

1309 Mason, H.E., McCubbin, F.M., Smirnov, A., Phillips, B.L., 2009. Solid-state NMR and IR spectroscopic
 1310 investigation of the role of structural water and F in carbonate-rich fluorapatite. *American*
 1311 *Mineralogist* 94, 507–516.

1312 Mazziotti-Tagliani, S., Angelone, M., Armiento, G., Pacifico, R., Cremisini, C., Gianfagna, A., 2012. Arsenic
 1313 and fluorine in the Etnean volcanics from Biancavilla, Sicily, Italy: environmental implications.
 1314 *Environmental Earth Science* 66, 561–572.

1315 McArthur, J.M., 1990. Fluorine-deficient apatite. *Mineralogical Magazine* 54, 508–510.

1316 Migdisov, A.A., Williams-Jones, A.E., Wagner, T., 2009. An experimental study of the solubility and
 1317 speciation of the rare earth elements (III) in fluoride- and chloride-bearing aqueous solutions at
 1318 temperatures up to 300°C. *Geochimica et Cosmochimica Acta*, 73, 7087–7109.

1319 Mitchell, R.H., 2014. Cathodoluminescence of apatite, in: Coulson, I.M. (Ed.), Cathodoluminescence and
 1320 its Application to Geoscience. Mineralogical Association of Canada Short Course Series 45, 143–168.

1321 Moore, M., Chakhmouradian, A.R., Mariano, A.N., Sidhu, R., 2015. Evolution of rare-earth mineralization
 1322 in the Bear Lodge carbonatite, Wyoming: Mineralogical and isotopic evidence. *Ore Geology Reviews*
 1323 64, 499–521.

1324 Nadeau, S.L., Epstein, S., Stolper, E., 1999. Hydrogen and carbon abundances and isotopic ratios in
 1325 apatite from alkaline intrusive complexes, with a focus on carbonatites. *Geochimica et*
 1326 *Cosmochimica Acta* 63, 1837–1851.

- 1327 Pasero, M., Kampf, A.R., Ferraris, C., Petkov, I.V., Rakovan, J., White, T.J., 2010. Nomenclature of the
1328 apatite supergroup minerals. *European Journal of Mineralogy* 22, 163–179.
- 1329 Pasteris, J.D., Yoder, C.H., Wopenka, B., 2014. Molecular water in nominally unhydrated carbonated
1330 hydroxylapatite: the key to a better understanding of bone mineral. *American Mineralogist* 99, 16–
1331 27.
- 1332 Penel, G., Leroy, G., Rey, C., Bres, E., 1998. MicroRaman spectral study of the PO_4 and CO_3
1333 vibrational modes in synthetic and biological apatites. *Calcified Tissue International* 63, 475–481.
- 1334 Pieczka, A., 2007. Beusite and an unusual Mn-rich apatite from the Szklary granitic pegmatite, Lower
1335 Silesia, southwestern Poland. *Canadian Mineralogist* 45, 901–914.
- 1336 Prowatke, S., Klemme, S., 2006. Trace element partitioning between apatite and silicate melts.
1337 *Geochimica et Cosmochimica Acta* 70, 4513–4527.
- 1338 Ray, J.S., Shukla, A.D., Dewangan, L.K., 2010. Carbon and oxygen isotopic compositions of Newania
1339 Dolomite Carbonatites, Rajasthan, India: implications for source of carbonatites. *Mineralogy and*
1340 *Petrology* 98, 269–282.
- 1341 Reed, S.J.B., 1995. *Electron Microprobe Analysis and Scanning Electron Microscopy in Geology*.
1342 Cambridge University Press.
- 1343 Reguir, E.P., Chakhmouradian, A.R., Halden, N.M., Malkovets, V.G., Yang, P., 2009. Major- and trace-
1344 element compositional variation of phlogopite from kimberlites and carbonatites as a petrogenetic
1345 indicator. *Lithos* 112S, 372–384.
- 1346 Reguir, E.P., Chakhmouradian, A.R., Pisiak, L., Halden, Yang, P., Xu, C., Kynický, J., Couëslan, C.G., 2012.
1347 Trace-element composition and zoning in clinopyroxene- and amphibole-group minerals:
1348 Implications for element partitioning and evolution of carbonatites. *Lithos* 128-131, 27–45.
- 1349 Riley, T.R., Bailey, D.K., Lloyd, F.E., 1998. Extrusive carbonatite from the Quaternary Rockeskyll complex,
1350 West Eifel, Germany. *Canadian Mineralogist*, 34, 389–401.

1351 Rønsbo, J., 1989. Coupled substitutions involving REEs and Na and Si in apatites in alkaline rocks from
 1352 the Ilímaussaq intrusion, South Greenland, and the petrological implications. *American Mineralogist*
 1353 74, 896–901.

1354 Roeder, P.L., MacArthur, D., Ma, X.P. and Palmer, G.R., 1987. Cathodoluminescence and microprobe
 1355 study of rare-earth elements in apatite. *American Mineralogist* 72, 801–11.

1356 Russell, H.D., Hiemstra, S.A., Groeneveld, D., 1955. The mineralogy and petrology of the carbonatite at
 1357 Loolekop, Eastern Transvaal. *Transactions and Proceedings of the Geological Society of South Africa*
 1358 57, 197–208.

1359 Ryabchikov, I.D., Hamilton, D.L., 1993. Interaction of carbonate–phosphate melts with mantle
 1360 peridotites at 20–35 kbar. *South African Journal of Geology* 96, 143–148.

1361 Serret, A., Cabañas, M.V., Vallet-Regí, M., 2000. Stabilization of calcium oxyapatites with lanthanum(III)-
 1362 created anionic vacancies. *Chemistry of Materials* 12, 3836–3841.

1363 Shang, M., Geng, D., Yang, D., Kang, X., Zhang, Y., Lin, J., 2013. Luminescence and energy transfer
 1364 properties of $\text{Ca}_2\text{Ba}_3(\text{PO}_4)_3\text{Cl}$ and $\text{Ca}_2\text{Ba}_3(\text{PO}_4)_3\text{Cl}:\text{A}$ ($\text{A} = \text{Eu}^{2+}/\text{Ce}^{3+}/\text{Dy}^{3+}/\text{Tb}^{3+}$) under UV and low-
 1365 voltage electron beam excitation. *Inorganic Chemistry* 52, 3102–3112.

1366 Sharygin, V., Kamenetsky, V.S., Zaitsev A.N., Kamenetsky, M.B., 2012. Silicate–natrocarbonatite liquid
 1367 immiscibility in 1917 eruption combeite–wollastonite nephelinite, Oldoinyo Lengai Volcano,
 1368 Tanzania: Melt inclusion study. *Lithos* 152, 23–39.

1369 Shyu, J.J., Wu, J.M., 1991. Spherulitic growth of apatite in a $\text{MgO-CaO-SiO}_2\text{-P}_2\text{O}_5$ glass. *Journal of the*
 1370 *American Ceramic Society* 74, 1532–1540.

1371 Shyu, J.J., Wu, J.M., 1994. Growth kinetics of spherulitic apatite in some $\text{MgO-CaO-SiO}_2\text{-P}_2\text{O}_5$ glasses.
 1372 *Journal of Materials Science* 29, 3167–3171.

1373 Stock, M.J., Humphreys, M.C.S., Smith, V.C, Johnson, R.D., Pyle, D.M., EIMF, 2015. New constraints on
 1374 electron-beam induced halogen migration in apatite. *American Mineralogist* 100, 281–293.

1375 Stoppa, F., Schiazza, M., 2013. An overview of monogenetic carbonatitic magmatism from Uganda, Italy,
 1376 China and Spain: Volcanologic and geochemical features. *Jurnal of South American Earth Sciences*
 1377 41, 140–159.

1378 Stoppa, F., Woolley, A.R., 1997. The Italian carbonatites: field occurrence, petrology and regional
 1379 significance. *Mineralogy and Petrology* 59, 43–67.

1380 Stormer, J.C.J., Pierson, M.J., Tacker, R.C., 1993. Variation of F and Cl X-ray intensity due to anisotropic
 1381 diffusion of apatite during electron microprobe analysis. *American Mineralogist* 78, 641–648.

1382 Sykes, D., Baker, M.B., Wyllie, P.J., 1992. Viscous properties of carbonate melts at high pressure, EOS,
 1383 Transactions of the American Geophysical Union 73, 372.

1384 Tappe, S., Foley, S.F., Jenner, G.A., Heaman, L.M., Kjarsgaard, B.A., Romer, R.L., Stracke, A., Joyce, N.,
 1385 Hoefs, J., 2006. Genesis of ultramafic lamprophyres and carbonatites at Aillik Bay, Labrador: a
 1386 consequence of incipient lithospheric thinning beneath the North Atlantic craton. *Journal of*
 1387 *Petrology* 47, 1261–1315.

1388 van Achterbergh, E., Ryan, C.G., Griffin, W.L., 2001. GLITTER on-line interactive data reduction for the
 1389 LA- ICPMS microprobe. Macquarie Research Ltd, Sydney.

1390 Verhulst, A., Balaganskaya, E., Kirnarsky, Y., Demaiffe, D., 2000. Petrological and geochemical (trace
 1391 elements and Sr–Nd isotopes) characteristics of the Paleozoic Kovdor ultramafic, alkaline and
 1392 carbonatite intrusion (Kola Peninsula, NW Russia). *Lithos* 51, 1–25.

1393 Wall, F., Niku-Paavola, V.N., Storey, C., Müller, A. and Jeffries, T., 2008. Xenotime-(Y) from carbonatite
 1394 dykes at Lofdal, Namibia: unusually low LREE:HREE ratio in carbonatite, and the first dating of
 1395 xenotime overgrowths on zircon. *Canadian Mineralogist* 46, 861–877.

1396 Wang, L.X., Marks, M.A.W., Wenzel, T., von der Handt, A., Keller, J., Teiber, H., Markl, G., 2014. Apatites
 1397 from the Kaiserstuhl Volcanic Complex, Germany: new constraints on the relationship between
 1398 carbonatite and associated silicate rocks. *European Journal of Mineralogy* 26, 397–414.

1399 Warner, S., Martin, R., Abdel-Rahman, A-F. M., Doig, R., 1998. Apatite as a monitor of fractionation,
 1400 degassing and metamorphism in the Sudbury igneous complex, Ontario. *Canadian Mineralogist* 36,
 1401 981–999.

1402 Watkinson, D.H., 1970. Experimental studies bearing on the origin of the alkali rock-carbonatite complex
 1403 and niobium mineralization at Oka, Quebec. *Canadian Mineralogist* 10, 350–361.

1404 Waychunas, G.A., 2002. Apatite luminescence. *Reviews in Mineralogy and Geochemistry* 48, 701–742.

1405 Webb, K.J., Scott Smith, B.H., Paul, J.L., Hetman, C.M., 2004. Geology of the Victor Kimberlite,
 1406 Attawapiskat, Northern Ontario, Canada: cross-cutting and nested craters. *Lithos* 76, 29–50.

1407 Williams-Jones, A.E., 2015. The hydrothermal mobility of the rare earth elements. British Columbia
 1408 Geological Survey Paper 2015-3, 119–123.

1409 Woolley, A.R., Barr, M.W.C., Din, V.K., Jones, G.C., Wall, F., Williams, C.T., 1991. Extrusive carbonatites
 1410 from the Uayyah area, United Arab Emirates. *Journal of Petrology* 32, 1143–1167.

1411 Wu, C., Yuan, Z., Bai, G., 1996. Rare earth deposits in China, in: Jones, A.P., Wall, F., Williams, C.T. (Eds.),
 1412 *Rare Earth Minerals: Chemistry, Origin and Ore Deposits*. Chapman & Hall, London, p. 281–310.

1413 Yi, H., Balan, E., Gervais, C., Segalen, L., Fayon, F., Roche, D., Person, A., Morin, G., Guillaumet, M.,
 1414 Blanchard, M., Lazzeri, M., Babonneau, F., 2013. A carbonate- fluoride defect model for carbonate-
 1415 rich fluorapatite. *American Mineralogist* 98, 1066–1069.

1416 Yegorov, L.S., 1993. Phoscorites of the Maymecha–Kotuy ijolite–carbonatite association. *International*
 1417 *Geology Review* 35, 346–358.

1418 Ying, J., Zhou, X., Zhang, H., 2004. Geochemical and isotopic investigation of the Laiwu–Zibo carbonatites
 1419 from western Shandong Province, China, and implications for their petrogenesis and enriched
 1420 mantle source. *Lithos* 75, 413–426.

1421 Yoder, C.H., Pasteris, J.D., Worcester, K.N., Schermerhorn, D.V., 2012. Structural water in carbonated
 1422 hydroxylapatite and fluorapatite: confirmation by solid state ^2H NMR. *Calcified Tissue International*
 1423 90, 60–67.

1424 Zaitsev, A.N., Williams, C.T., Jeffries, T.E., Strekopytov, S., Moutte, J., Ivashchenkova, O.V., Spratt, J.,
 1425 Petrov, S.V., Wall, F., Seltmann, R., Borozdin, A.P., 2014. Rare earth elements in phoscorites and
 1426 carbonatites of the Devonian Kola Alkaline Province, Russia: Examples from Kovdor, Khibina,
 1427 Vuoriyarvi and TuriyMys complexes. *Ore Geology Reviews* 61, 204–225.

1428 Zhang, Y., Su, Z., Azad, A.K., Zhou, W., Irvine, J.T., 2012. Directly imaging interstitial oxygen in silicate
 1429 apatite. *Advanced Energy Materials* 2, 316–321.

1430 Ziemann, M.A., Förster, H.J., Harlov, D., Frei, D., 2005. Origin of fluorapatite–monazite assemblages in a
 1431 metamorphosed, sillimanite-bearing pegmatoid, Reinbolt Hills, East Antarctica. *European Journal of*
 1432 *Mineralogy* 17, 567–579.

1433

1434 **Figure captions**

1435 **Fig. 1.** Phosphorus geochemistry of carbonatites. (a) P_2O_5 content of carbonate melts vs. their
 1436 $\text{Ca}/(\text{Ca}+\text{Mg}+\text{Fe}+\text{Mn})$ ratio: asterisks – high-P experiments of Ryabchikov and Hamilton (1993); empty
 1437 squares – melt inclusions, Kerimasi (Guzmics et al., 2012); solid squares – melt inclusions, Hungary
 1438 (Guzmics et al., 2008); cross – average calcite carbonatite (this work); diagonal cross – average
 1439 dolomite carbonatite (this work); other symbols are extrusive and shallow intrusive carbonatites,
 1440 including Wekusko Lake, Canada (grey circles); Aillik Bay, Canada (solid triangles); Kontozero, Russia
 1441 (solid diamonds); Rockeskyll, Germany (empty triangles); Italy (bricks); Laiwu-Zibo, China (empty
 1442 circles); Uyaynah, UAE (grey square); Fenshuiling, China (grey diamonds) and Fort Portal, Uganda
 1443 (empty diamonds). The diagram was constructed using Woolley et al. (1991), Rilley et al. (1998), Ying
 1444 et al. (2004), Tappe et al. (2006), Chakhmouradian et al. (2009), Eby et al. (2009), Stoppa and

Schiazza (2013), and authors' unpublished data). (b) Histograms of P_2O_5 distribution in intrusive calcite (rear) and dolomite (front) carbonatites (this work).

Fig. 2. Phosphorus mineralogy in carbonatites: (a) primary equant monazite (Mnz) occurring as inclusions in cumulate apatite (Ap) and columbite (Cb) in dolomite (Dol) carbonatite (Western Sahara; M. Bouabdellah et al., work in progress); (b) acicular monazite in apatite-free norsethite (Nrs)-dolomite carbonatite (Aley, Canada), Sd = siderite; (c) acicular monazite in barite (Brt)-calcite (Cal) carbonatite (Mountain Pass, USA), Phl = phlogopite; (d) primary prismatic bradleyite (Brd) forming inclusions in ilmenite (Ilm) from calcite carbonatite which also contains igneous and hydrothermal apatite (Afrikanda, Russia), Ttn = titanite; (e) late-stage monazite formed at the expense of igneous apatite (Miaoya, China); (f) apatite in a fenitized felsic rock (Kfs = microcline, Ab = albite) at the contact with calcite carbonatite (Mountain Pass); note resorption and peripheral REE loss (yellow CL rim) in the apatite xenocryst in the left lower corner; the assimilated phosphate was deposited as spherulitic monazite associated with bastnäsite (Bst) and celsian (Cls). (a-e) and inset in (f) are false-color BSE images; (f) is a CL image; scale bars are 200 μm for all images, except (d) and (e) (100 μm both).

Fig. 3. Key characteristics of cumulate rocks associated with carbonatites. (a) Layered phoscorite (psc) intersected by carbonatite (crb); Kovdor (Russia). (b) Interlayered package of carbonatite and cumulate rock comprising ~60% magnetite, 15% apatite, 7% columbite and carbonates; Aley (Canada). (c) Typical phoscorite comprising forsterite (Fo), apatite, magnetite (Mgt) and subordinate calcite; Kovdor. (d) Typical Nb-rich cumulate rock comprising magnetite, apatite, phlogopite and columbite; Aley. (e) Apatite inclusions in cumulus columbite and zircon (Zrn); Aley. (f) Weakly layered cumulate rock comprising apatite, diopside (Di), calcite and pyrochlore (Pcl); Firesand River

(Canada). (g) Numerous melt inclusions in cumulus apatite; calcite carbonatite, Kaiserstuhl (Germany). (c) Image in transmitted cross-polarized light (XPL), (d-f) BSE images, (g) image in transmitted plane-polarized light (PPL); scale bar is 500 μm in (c, e, f) and 200 μm in (d, g).

Fig. 4. Key morphological characteristics of apatite in carbonatites. (a) Early-crystallizing apatite hosting inclusions of Na-bearing carbonates, Afrikanda (Russia); note an alteration rim composed of REE silicates (Chakhmouradian and Zaitsev, 2004). (b) Calcite-dolomite-burbankite (Brb) inclusions in apatite set in a matrix of the same composition; Guli (Russia). (c) Apatite phenocrysts set in an andradite-ilmenite-phlogopite-aegirine-calcite groundmass (grms); Zibo (China). (d) Resorbed and fractured apatite macrocryst (Ap_m) associated with a euhedral phenocryst (Ap_p) in dolomite carbonatite (Wekusko Lake, Canada); the two minerals differ in CL, but share some compositional characteristics indicative of their common lineage (further details in Section 7.3). (e) Acicular hopper crystals of apatite in the groundmass of a calcite carbonatite dike; Kaiserstuhl. (f) Acicular zoned apatite crystals (see Section 5.4) in the groundmass of extrusive calcite carbonatite (lava?), Kerimasi (Tanzania). (g) Hopper crystals in a sövite autolith; Kerimasi. (h) Atoll-textured apatite in dolomite carbonatite breccias incorporating clasts of apatite-rich sövite; Prairie Lake (Canada). (a-c, e-h) BSE images; (d) CL image; scale bar is 200 μm in (a, d), 500 μm in (b, c), 50 μm in the rest of the photos.

Fig. 5. Morphology and zoning of igneous and hydrothermal apatite from carbonatite (see Section 5.4 for the explanation of zoning types). (a) Tapering long-prismatic cumulus crystals in sövite, Eden Lake (Canada). (b) Pill-like crystals in dolomite-calcite carbonatite, Schryburt Lake (Canada). (c) Tapering prismatic crystal in sövite; Shaxiongdong, China. (d) Crust of colloform hydrothermal apatite (Ap_h) on brecciated phoscorite; Kovdor. (e) Detail of (d) showing relict grains of igneous apatite (Ap_i) overgrown by zoned colloform apatite. (f) Euhedral crystal of hydrothermal apatite

inside fluorite-quartz (Qtz) veinlets and pockets in dolomite carbonatite; Aley. (g) Spherulitic aggregates of acicular hydrothermal apatite associated with chlorite (Chl) and thorite (Th); Afrikanda. (a-c, e, g) BSE images; (f) PPL image; scale bar is 1 mm in (a, e), 200 μm in (b, g), and 100 μm in (c, f).

Fig. 6. Raman spectra of cation-deficient Prairie Lake hydroxylapatite and Eden Lake fluorapatite (core and rim) compared with the spectrum of reference stoichiometric fluorapatite from Pant Lake (Canada). See Section 5.2 for details.

Fig. 7. Representative chondrite-normalized REE patterns of apatite from calcite carbonatites (a), dolomite carbonatites, phoscorites and hydrothermal arageneses (b).

Fig. 8. Intricacies of zoning in apatite from carbonatites and phoscorites as seen in BSE images (see Section 5.4 for details on individual zoning types and element distribution): (a) type (1), Fuerteventura, Canary Islands (All = allanite); (2) type (2), Carb Lake, Canada; (3) type (4) superposed over type (2), Chipman Lake, Canada; (d) type (3), Yousuobao, China; (e) detail of (d) showing variations in AZ within the altered areas; (f) type (3) superposed over type (1), Eden Lake (note numerous secondary inclusions of hematite and REE fluorocarbonates in the altered areas); (g) type (4) superposed over type (2); Lesnaya Varaka, Russia; (h) type (5), Kovdor (P5). Scale bar is 200 μm in (a, d, f), and 100 μm in the rest of the photos.

Fig. 9. Representative examples of compositional variation in zoned apatite from carbonatites. Type-(1) and -(2) zoning trends are indicated by solid arrows, and type-(3) and -(4) trends by dashed arrows.

To avoid clutter, only mean compositions of individual zones are shown for all types, except type (4), where dramatic compositional variations are observed on short spatial scales.

Fig. 10. Intricacies of zoning in apatite from carbonatites as seen in CL images (see Section 5.4 for further details), with the abundances of principal activator elements (in ppm) indicated in boxes: (a) types (1) and (3), Eden Lake; (2) types (1) and (3), Aley; (3) type (2), Carb Lake; (d) type (2), Borden Twp., Canada (Ae = aegirine); (e) type (3), Yousuobao; (f) type (4) superposed over type (2), Albany Forks, Canada; (g) hydrothermal apatite, Aley (Fl = fluorite); (h) hydrothermal apatite, Afrikanda. Scale bar is 250 μm for all images.

Fig. 11. Variations in the abundances of some substituent elements and key REE ratios in apatites from associated calcite and dolomite carbonatites (Cal crb and Dol crb, respectively) from Paint Lake and Aley, and Kovdor phosphorites. The parenthesized numbers in the legend for Aley carbonatites correspond to the $(\text{La}/\text{Yb})_{\text{cn}}$ ratio of the rock-forming carbonate mineral (calcite or dolomite). Representative samples of zoned apatites from Eden Lake (Figs. 11f, 13a), Yousuobao (Figs. 11d, 13e), Turiy Mys, Carb Lake (Fig. 13c) and Albany Forks (Fig. 13f) are plotted for comparison.

Fig. 12. Onuma diagram showing apatite-carbonatite partition coefficients for REE (plotted in order of their ionic radius in a nine-fold coordination): (a) comparison of the data obtained in present work (Zibo, Upper Fir) with published values for carbonatites from Bhn et al. (2001) (data marked "B"), Brassinnes et al. (2005) ("Br") and synthetic apatite-calcite melts from Klemme and Dalp (2003) ("KD") and Hammouda et al. (2010) ("HP"). Data for nepheline-normative basalts (Prowatke and Klemme, 2006) and melilitites (Arzamastsev et al., 2009) are plotted for reference ("PK" and "A", respectively). (b) $^{A\text{p}/\text{crb}}D_{\text{REE}}$ data for the Zibo calcite carbonatite fitted to two partitioning curves

corresponding to the Ca1 and Ca2 sites, respectively; an inferred single partitioning curve for fluor- and hydroxylapatite in a calcitic melt (Klemme and Dalpé, 2003) is shown for comparison. Comparison between the REE partitioning curves and chondrite-normalized profiles is provided in supplementary Figure SF4.

Fig. 13. Apatite evolutionary trends: calculated, inferred and measured. (a, b) Variations in key REE parameters in the fractionating apatite and residual carbonatitic melt calculated on the basis of $A_{p/crb} D_{REE}$ values determined in the present work; each trend starts at $F = 99.99\%$ and culminates with the fractionation of 15 wt.% apatite. (c, d) Compositional fields and evolutionary trends (thick arrows) identified for carbonatitic apatite from Otjisazu, Homa Mt. (Bühn et al., 2001) and Vuoriyarvi (Brassinnes et al., 2005) compared with selected data from the present work (see Figs. 12 and 14 for further examples), including the trends for Paint Lake (calcite-dolomite carbonatites to sövites), Wekusko Lake (macrocrysts to phenocrysts), Eden Lake sövite and Aley apatite [type-(1) zoning for both], Turiy Mys and Yousuobao [type-(3) zoning for both] and Kovdor phoscorite P5 [type (5) zoning]. (e) Variation in δY and δEu within the dataset examined in the present work (symbols as in Fig. 11), African carbonatites (Bühn et al., 2001) and other rock types: (G) granitoids, (GP) granitic pegmatites, (HM) hydrothermal-metasomatic rocks, (FOA) Fe-oxide-apatite deposits (Frietsch and Perdahl, 1995; Ziemann et al., 2005; Chu et al., 2009; Cao et al., 2011; Bonyadi et al., 2011; Chen et al., 2013; authors' unpublished data).

Fig. 14. Schematic diagrams illustrating possible reasons for the compositional variations (and similarities) in apatite compositions from associated carbonatitic rocks. (a) Multiple discrete batches of carbonatitic magma ascending along the same system of conduits and precipitating cumulus apatite whose compositions will depend on the chemistry of their parental magmas, and not

generally follow a recognizable evolutionary trend. (b) A discrete magma batch precipitating early cumulus apatite until it is no longer saturated with respect to this mineral; further fractionation of other rock-forming minerals (e.g., carbonates or clinopyroxene) may saturate the residual magma in apatite, triggering the deposition of a discrete apatite unit or a peripheral zone on the earlier-deposited crystals. In theory, this process may repeat several times, depending on the number of fractionating phases (cf. Bühn et al., 2001). (c) Compositional evolution of fractionating apatite (calculated using the partitioning data obtained in the present work and provided by Reguir et al., 2012) unaccompanied by any other minerals (thick arrow, terminating at 15 wt.%) and co-precipitating with sodic clinopyroxene (dashed arrow). The tick marks indicate the percentage of fractionated clinopyroxene. See Section 7.3 for further discussion.

Fig. 15. Schematic diagram illustrating the paragenetic role and possible interrelations among the major types of zoning in carbonatitic apatite: (a) deposition of cumulus apatite; (b) precipitation of a rock-forming mineral with low $^{min/crb}D_{REE}$ values, leading to the re-saturation of magma with respect to apatite and deposition of a REE-rich rim on the earlier-crystallized grains [type (1) zoning, see Fig. 17c]; (c) erosion of the cumulate layer, transport and resorption of apatite grains; (d,e) precipitation of other mineral, leading to the re-saturation of magma in apatite and deposition of a REE-rich rim on the resorbed cores [type (1)]; (f) intrusion of fresh carbonatitic magma into the carbonatite containing type-(1) apatite and re-equilibration of the apatite with the magma to form type-(2) crystals; (g) and (h) reaction of carbonatites containing apatite crystals with primary zoning with percolating hydrothermal fluids to form type-(3) or type-(4) crystals depending on the fluid chemistry and crystallization conditions. See Section 7.4 for further discussion.

Figure 1a

Figure 1b

Figure 2a

Figure 2b

Figure 2c

Figure 2d

Figure 2e

Figure 2f

Figure 3a, b

Figure 3c

Figure 3d

Figure 3e

Figure 3f

Figure 3g

Figure 4a

Figure 4b

Figure 4c

Figure 4d

Figure 4e

Figure 4f

Figure 4g

Figure 4h

Figure 5a

Figure 5b

Figure 5c

Figure 5d

d

Figure 5e

Figure 5f

Figure 5g

Figure 6

Figure 7a

Figure 7b

Figure 8a

Figure 8b

Figure 8c

Figure 8d

Figure 8e

Figure 8f

Figure 8g

Figure 8h

Figure 9a

Figure 9b

Figure 9c

Figure 9d

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Figure 10a

Figure 10b
[Click here to download high resolution image](#)

Figure 10c

Figure 10d

Figure 10e

Figure 10f

Figure 10g

Figure 10h

Figure 11a

Figure 11b

Figure 11c

Figure 11d

Figure 11e

Figure 11 (legend)

Figure 12a

Figure 12b

Figure 13a, b

Figure 13c

Figure 13d

Figure 13e
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Figure 14

Figure 15

Table 1 Natural non-biogenic apatites: a summary of element substitutions from the literature

Element	Mass content	apfu ^a	Mineral ^b	Site ^c	Rock type	Reference(s)
Ca sites:						
Na	3.9% Na ₂ O ^d	0.63	mHap	Ca1	Hydrothermally altered tholeiitic gabbro	Chakhmouradian and Medici (2006); Fleet and Pan (1995)
K	0.2% K ₂ O	0.03	Hap	Ca1	Hypabyssal kimberlite	Chakhmouradian et al. (2002); Matsunaga and Murata (2009)
Mg	0.39% MgO	0.05	Fap	Ca1	Metasomatized trachyandesite	Mazziotti-Tagliani et al. (2012)
Mn	31.5% MnO	2.43	Cap	Ca1 ^e	Granitic pegmatite (muscovite – rare-element)	Pieczka (2007); Hughes et al. (1991)
Fe	4.9% FeO	0.36	Cap	Ca2	Hornfels xenoliths in basaltic andesite	Harlov et al. (2006); Hughes et al. (1993)
Sr	62.9% SrO ^f	4.55	Fap-Hap	Ca2	Peralkaline syenitic rocks and associated pegmatites	Chakhmouradian et al. (2002); Hughes et al. (1991)
Ba	12.5% BaO ^g	0.44	Hap	Ca2	Diopside-leucite lamproite	Edgar (1989); Shang et al. (2013)
Pb	23.1% PbO	0.68	Hap	Ca2	Oxidized Pb ore	Livingstone (1994); Kampf et al. (2006)
Y	1.75% Y ₂ O ₃	0.09	Fap	Ca2 ⁱ	Peralkaline syenitic rock	Rønsbo (1989); Fleet and Pan (1995)
Ln ^h	~19% Ln ₂ O ₃	0.64	Fap	Ca2 ⁱ	Peralkaline granite	Roeder et al. (1987); Hughes et al. (1991); Fleet and Pan (1995, 1997)
Th	2933 ppm	n.a.	Fap	Ca2 ⁱ	Carbonatite (unspecified)	Belousova et al. (2002); Luo et al. (2009)
U	318 ppm	n.a.	Fap	Ca2 ⁱ	Kiruna-type Fe-P deposit	Luo et al. (2009, 2011)
P site (+ tunnel site for carbonate anions):						
C	6.3% CO ₂	~0.70	Fap	P/F	Sedimentary phosphorite	McArthur (1990)
Si	8.2% SiO ₂	0.80	Fap	P	Peralkaline syenitic rock	Rønsbo (1989)
As	14.9% As ₂ O ₅	0.71	Fap	P	Metasomatized trachyandesite	Mazziotti-Tagliani et al. (2012)
V	1.6% V ₂ O ₅	0.11	Hap	P	Hypabyssal kimberlite	Chakhmouradian et al. (2002)
S	11.4% SO ₃	0.71	mHap	P	Hydrothermally altered tholeiitic gabbro	Chakhmouradian and Medici (2006)

^a Atoms per formula unit calculated on the basis of five large cations.

^b mHap = monoclinic hydroxylapatite; Hap = hydroxylapatite; Fap = fluorapatite; Cap = chlorapatite.

^c Crystallographic site of preference.

^d Up to 4.2% Na₂O (0.64 apfu Na) was reported in Fap by Bühn et al. (2001), but their data give non-stoichiometric formulae with > 20% unaccounted-for deficiency in the P site.

^e Spectroscopic data suggest that a small proportion of Mn enters the P site as Mn⁵⁺ (Hughes et al., 2004).

^f Maximum values correspond to Sr-dominant members of the continuous (Ca,Sr)₅(PO₄)₃(F,OH) series.

^g These data may be subject to peak-overlap errors (this apatite is reported also to contain 0.7-0.8% TiO₂).

^h Lanthanides (La ... Lu).

ⁱ The partitioning pattern of Y, Ln, Th and U changes in Cl- and Sr-rich apatites (Fleet et al., 2000; Chakhmouradian et al., 2005; Luo et al., 2009).

Table 2. Apatite-carbonatite partition coefficients for selected trace elements

Locality	Zibo		Paint Lake		Upper Fir	
Ca/(Ca+Mg+Fe+Mn)	0.70		0.66		0.60	
	Ap/crb	ESD	Ap/crb	ESD	Ap/crb	ESD
Mn	0.24	0.05	0.16	0.01	0.11	0.02
Sr	1.33	0.19	1.68	0.09	1.88	0.10
Y	3.10	0.25	3.22	0.65	10.50	0.69
La	2.10	0.14	2.34	0.58	9.40	0.74
Ce	3.53	0.34	4.30	1.09	9.76	0.53
Pr	3.83	0.20	5.71	1.48	10.10	0.49
Nd	3.88	0.21	5.67	1.42	11.40	0.61
Sm	3.91	0.27	4.09	0.82	11.20	0.67
Eu	4.21	0.30	4.55	0.93	9.86	0.57
Gd	4.92	0.40	4.12	0.95	13.7	0.97
Tb	3.83	0.29	4.00	0.95	11.40	0.81
Dy	3.87	0.39	3.79	0.98	11.00	0.87
Ho	3.64	0.39	3.92	0.91	10.17	0.75
Er	2.97	0.22	2.83	0.65	8.56	0.63
Tm	2.35	0.26	2.56	0.73	8.33	0.71
Yb	2.26	0.18	2.16	0.59	6.11	0.47
Lu	2.13	0.41	2.49	0.75	6.61	0.41