Enrichment of heavy REE and Th in carbonatite-derived fenite breccia

Sam Broom-Fendley, Holly AL Elliott, Charles D Beard, Frances Wall, Paul EB Armitage, Aoife E Brady, Eimeady Deady and William Dawes

Cite this article: Broom-Fendley S, Elliott HAL, Beard CD, Wallace F, Armitage PEB, Brady AE, Deady E, and Dawes W (2021) Enrichment of heavy REE and Th in carbonatite-derived fenite breccia. Geological Magazine 158: 2025–2041. https://doi.org/10.1017/S0016756821000601

Abstract

Enrichment of the heavy rare earth elements (HREE) in carbonatites is rare as carbonatite petrogenesis favours the light (L)REE. We describe HREE enrichment in fenitized phonolite breccia, focusing on small satellite occurrences 1–2 km from the Songwe Hill carbonatite, Malawi. Within the breccia groundmass, a HREE-bearing mineral assemblage comprises xenotime, zircon, anatase/rutile and minor huttonite/thorite, as well as fluorite and apatite. A genetic link between HREE mineralization and carbonatite emplacement is indicated by the presence of Sr-bearing carbonate veins, carbonatite xenoliths and extensive fenitization. We propose that the HREE are retained in hydrothermal fluids which are residually derived from a carbonatite after precipitation of LREE minerals. Brecciation provides a focusing conduit for such fluids, enabling HREE transport and xenotime precipitation in the fenite. Continued fluid–rock interaction leads to dissolution of HREE-bearing minerals and further precipitation of xenotime and huttonite/thorite.

At a maximum Y content of 3100 μg g⁻¹, HREE concentrations in the presented example are not sufficient to constitute ore, but the similar composition and texture of these rocks to other cases of carbonatite-related HREE enrichment suggests that all form via a common mechanism linked to fenitization. Precipitation of HREE minerals only occurs where a pre-existing structure provides a focusing conduit for fenitizing fluids, reducing fluid – country-rock interaction. Enrichment of HREE and Th in fenite breccia serves as an indicator of fluid expulsion from a carbonatite, and may indicate the presence of LREE mineralization within the source carbonatite body at depth.

Highlights

- HREE mineralization occurs in fenitized phonolite breccia, related to carbonatite.
- Mineralization consists of xenotime, zircon, anatase/rutile and minor huttonite/thorite.
- Mineralization shares textural and compositional similarity to higher-grade HREE occurrences in carbonatite and lower-grade occurrences in fenite.
- Carbonatite-derived, HREE-rich residual fluids are focused through high-permeability fenite breccia pipes.
- HREE and Th in fenite breccias may indicate the presence of LREE mineralization in a carbonatite at depth.

1. Introduction

The rare earth elements (REE) exhibit magnetic and spectroscopic properties useful in a number of technological and industrial applications, and demand for REE is increasing (Goodenough et al. 2018). Carbonatites host some of the largest metallurgically-favourable REE resources (Wall, 2014; Verplanck et al. 2016), yet the REE minerals commonly extracted from carbonatites (REE fluorcarbonates, monazite) are typically light (L)REE-rich (La–Sm) and heavy (H)REE-poor (Eu–La + Y; Wall, 2014). With the exception of Nd and Pr, they are, therefore, deficient in many REE which are of economic importance but at risk of supply disruption, such as Dy and Tb (European Commission, 2020: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52020DC0474). The supply imbalance between LREE and HREE is termed the ‘balance problem’ (Binnemans et al. 2018), and is a major cause of undersupply of HREE and, thus, the high price of these elements.

The high value of the HREE makes carbonatites with some degree of HREE enrichment particularly attractive for exploitation. Only a few examples of carbonatite-related HREE...
enrichment are known, and include: Lofdal, Namibia (Wall et al. 2008; Bodeving et al. 2017); Chilwa Island, Kangankunde, Songwe and Tundulu, Malawi (Ngwenya, 1994, Wall & Mariano, 1996; Broom-Fendley et al. 2016a, b, 2017a, b, c; Dowman et al. 2017a); Salpeterkop, South Africa (Verwoerd et al. 1995); Pivot Creek, New Zealand (Cooper et al. 2015); Huanglongpu and Huayangchuan, China (Xu et al. 2007, 2010; Song et al. 2016; Smith et al. 2018; Cangelosi et al. 2020a); and Bear Lodge, USA (Andersen et al. 2016, 2017). These examples vary from mineral-scale enrichment of academic interest, to deposits of sufficient size to potentially constitute ore.

One of the best-known examples of carbonatite-related HREE enrichment is the Lofdal deposit, Namibia. Here, the principal REE ore mineral is xenotime-(Y) ([Y, HREE]PO₄), which occurs in albite-feldspar-rich fault zones radiating from a central carbonatite complex (Wall et al. 2008; HS Swinden & P Siegfried, unpub. technical report, 2011; Do Cabo, 2013; Loye, 2014; Bodeving et al. 2017). While the nature of the carbonate units in the fault zones is debated (e.g. Wall et al. 2008; Do Cabo, 2013; Williams-Jones et al. 2015; Bodeving et al. 2017), the coeval nature of the xenotime with the surrounding carbonate rocks indicates a genetic relationship (Wall et al. 2008). Similarly, at the Bear Lodge carbonatite complex, USA, HREE minerals occur c. 2 km from the main intrusion centre at the Cole high-field-strength elements (HFSE) (+HREE) occurrence (Andersen et al. 2016). Here, xenotime-(Y) (and anatase) occur in recrystallized quartz and K-feldspar-rich breccia, along the contacts of sedimentary units. Based on mineral textures, Andersen et al. (2016) interpret the xenotime-(Y) to be causally linked to carbonatite emplacement. While mineral-scale fractionation of the REE has been demonstrated at many carbonatites (Broom-Fendley et al. 2016a, 2017a; Andersen et al. 2017), the occurrences at Lofdal and Bear Lodge show that fractionation of the REE also occurs on the deposit scale. However, it remains unclear if these examples are an exception, or if HREE mineralization around carbonatites is a common, previously overlooked, feature.

Alkali metasomatism is present at both the Cole occurrence (Bear Lodge) and the Lofdal deposit. At the Cole occurrence, HREE and HFSE minerals are associated with abundant K-feldspar growth, while xenotime at Lofdal is associated with albite. Alkali metasomatic aureoles, termed fenserts, are common around carbonatites, as bodies of carbonatite expel alkali-rich fluids as they cool (Hogarth, 2016). Such fluids metasomatize country rock, removing sodic amphibole or clinopyroxene veins in the country-rock host (see Elliott et al. 2018 and references therein). Many fenserts contain localized HREE enrichment resulting from the transport of these elements from the carbonatite melt by fenitizing fluids. For example, fenite at the Alnö Complex, Sweden, is REE-enriched by 49–354 ppm in the potassic zone and 0–807 ppm in the sodic zone, compared to the original magmatic protolith (Morogran, 1989). REE-enriched micro-mineral assemblages (fine-grained mineral assemblages containing micron-scale REE minerals) occur in fenite at Meech Lake, Québec (Holgarth, 2016), and Chilwa Island, Malawi (Dowman et al. 2017a). The micro-mineral assemblages are predominantly limited to LREE minerals, but these exhibit elevated HREE contents compared to their carbonatite-hosted counterparts. Extremely fenitized rocks can host xenotime in small amounts (Dowman et al. 2017a).

In this contribution, we describe HREE-enriched occurrences of fenitized phonolite breccia from the Chilwa Alkaline Province, Malawi, which share textural and geochemical similarities to the Lofdal deposit and Cole occurrence. The breccias reported here occur on the periphery of the Songwe Hill carbonatite and are directly adjacent to the Maze nepheline syenite complex. We also present data on breccias from the Nkalonje carbonatite complex which are similar in terms of their texture and major element composition, but do not exhibit HREE enrichment.

2. Geological background and field observations

The late Jurassic – early Cretaceous Chilwa Alkaline Province of southern Malawi and Mozambique consists of alkali granite, nepheline syenite and numerous carbonatite complexes (Fig. 1; Woolley & Garson, 1970; Woolley, 1991, 2001). Of the carbonatites, Kangankunde, Tundulu and Songwe Hill host REE deposits of economic interest (Ngwenya, 1994; Wall & Mariano, 1996; Broom-Fendley et al. 2017a, b). At present, however, only Songwe Hill is being developed and has a combined measured and indicated mineral resource estimate of 21 Mt, grading 1.41 % TREO (total rare earth oxides; C Witley et al., unpub. technical report, 2020). At many Chilwa carbonatite complexes, the carbonatite itself is a minor part of an exposed complex. Instead, these complexes are distinguished by large, near-circular, breccia units composed of heavily altered K-feldspar-rich rock, termed feldspathic breccia (Garson, 1965). Feldspathic breccias from the Songwe Hill / Maze and Nkalonje complexes are the focus of this work.

2.1 The Songwe Hill carbonatite and the Maze nepheline syenite complexes

The Songwe Hill carbonatite complex abuts the larger Maze nepheline syenite (Fig. 2a). Songwe Hill predominantly comprises fertilized, and locally, extensively brecciated fine-grained alkali silicate rock, into which at least three different carbonatite stages have been emplaced (Broom-Fendley et al. 2017a). The different carbonatite stages principally consist of fine-grained calcite carbonatite (C2) and a more Sr- and REE-rich ferroan variety (C3); coarse-grained calcite carbonatite (C1) is volumetrically insignificant at surface but occurs as clasts in later carbonatite units. Late-stage Fe- and Mn-rich veins and apatite fluorite veins cut all carbonatite stages, and the complex has undergone several stages of hydrothermal alteration and recrystallization (Broom-Fendley et al. 2016b). Notably, apatite at the complex is abnormally HREE-rich, for a carbonatite, and apatite–fluorite veins contain minor xenotime-(Y) (Broom-Fendley et al. 2017b). Both the HREE-enriched apatite and xenotime are considered to be late hydrothermal phases based on fluid inclusion microthermometry of associated fluorite (Broom-Fendley et al. 2016b, 2017b).

Recent mapping has focused on the wider relationship between Songwe and the surrounding Maze nepheline syenite (Fig. 2a). Several small breccia units occur at the contact between Maze and the surrounding basement gneiss, and these are the main focus of this study. The breccia units to the south of Songwe are colloquially termed ‘Mantrap’, while those to the west are termed the ‘School vents’ and those to the northeast are the ‘North vents’. Both the School vents and those at Mantrap correspond to areas
of high Th counts in radiometric surveys (Fig. 2b), which aided their discovery.

The breccia units at the Songwe Hill / Mauze complex are located at, or close to, the contact between nepheline syenite and the surrounding country rock (Fig. 2a). They are small, the largest comprising an area no more than \(\sim 125 \times 125\) m, and occur at the top of small hills abutting the larger, steeper, Mauze mountain (Fig. 3). Exposure is poor, but the boundaries of the breccia units can be roughly demarked by the extent of reddish-brown, slightly radioactive, soils.

Owing to sparse outcrop, many of the available samples are float (Fig. 2a). On the weathered surface, the rocks are buff–pink in colour, with local black Mn-oxide staining (Fig. 4a). Most samples are heavily altered and composed predominantly of clay minerals, after K-feldspar, and Fe- and Mn-oxide phases (Fig. 4b). The rocks contain varying proportions of sub-rounded clasts of various protoliths. Clasts range from small, mm-scale fragments to c. 50 cm across. A K-feldspar-rich variety, akin to fenite, is most common (Fig. 4c). Other clearly identifiable clasts include nepheline syenite (Fig. 4d), phonolite (Fig. 4e) and basement gneiss (Fig. 4f), reflecting the surrounding units through which the breccia was emplaced. In addition, the breccia also features many fragments of coarse-grained, magnetite-bearing, calcite carbonatite (Fig. 4g), which is mineralogically similar to the C1 carbonatite described at Songwe Hill (Broom-Fendley et al., 2017b). Locally, the rocks are clast-poor and have a groundmass which is conspicuously K-feldspar-phryic, with the phenocrysts exhibiting a trachytic texture. Some of the feldspar is euhedral, but many grains are fragmented and broken (Fig. 4c).

2.2 The Nkalonje carbonatite complex

Nkalonje is located c. 10 km NW of the Songwe Hill / Mauze complex (Fig. 1b). The complex consists of several small hills that largely consist of fenitized basement with only a few dyke rocks. Most of the complex is focused on Nkalonje/Nyama Hill, which consists of a nepheline syenite plug, minor carbonatite dykes and a large round breccia unit (Garson, 1965).

The main breccia unit at Nkalonje is c. 800 m wide and consists of trachyte, melanephelinite, metamorphic basement and K-feldspar-rich fenite fragments in a comminuted matrix. Fragments of breccia commonly contain vesicular patches of fluorite. Locally, the matrix exhibits a trachytic texture, consisting of phenocrysts of K-feldspar and accessory zircon and apatite, thought to represent recrystallized comminuted matrix (Garson, 1965; Woolley, 2001; Fig. 4b).

3. Petrography of the breccias

Crystal phases and their petrographic relationships were determined on polished thin-sections at Camborne School of Mines, University of Exeter, using conventional transmitted light microscopy, CITL Mk3 and Mk5 cold-cathodoluminescence (CL) imaging equipment and a FEI Quanta 650 FEG scanning electron microscope (SEM) with energy-dispersive spectrometers (EDS).
Fig. 2. (Colour online) (a) Geological map of the Songwe/Mauze complex, showing the location of the altered breccia vents and samples. (b) Radiometric colour map of Th concentration, courtesy of Mkango Resources. Red: higher Th; blue: lower Th (arbitrary units). Note the elevated Th contents at the altered breccia vents. Coordinate system is UTM 36S, WGS1984 datum.

Fig. 3. (Colour online) Annotated field photo showing the morphology of the breccia, and its association with the Mauze nepheline syenite. Photo location indicated in Figure 2.
3.1 Breccias associated with the Songwe–Mauze complex

The breccias at Mauze are fenitized xenolith-rich, porphyritic phonolites, the groundmass of which contains an assemblage of fluorite, apatite, Fe- and Mn-(hydr)oxides, HREE- and HFSE minerals. Fenitization is evident from the buff–pink colour of the rocks, their high alkali contents and an absence of quartz.

Samples from the School vents form the basis for interpreting the textures of more strongly mineralized and altered samples from Mantrap and the North vents. K-feldspar is abundant and forms large (1–25 mm), unbroken euhedral phenocrysts (Fig. 5a), with a trachytic texture in some samples. Pseudomorphs after nepheline occur as a subordinate phase and similarly form large euhedral phenocrysts. Accessories include subhedral zircon and euhedral apatite. Mafic phenocrysts are absent; however, minor Fe-(hydr) oxide-rich trapezoids may represent amphibole pseudomorphs. The groundmass is made up of microcrystalline K-feldspar, with abundant patches of Fe-/Mn-(hydr)oxides and clay minerals. Minor flow banding occurs in some fresher samples (Fig. 5b).

In all samples the primary phenocrysts are broken down to some degree, and in many cases are altered such that only a pseudomorph remains. Most K-feldspar phenocrysts are turbid and, in CL images (Fig. 6), exhibit distinct red luminescence, characteristic of fenitization (Mariano & King, 1975; Finch & Klein, 1999; Mariano & Mariano, 2014; Elliott et al. 2018; Bael et al. 2019), becoming progressively browner with higher degrees of alteration to fine-grained clay minerals. Mineralized samples are typically brecciated (Fig. 6b–c), and are clast-supported with angular to sub-angular rotated clasts (chaotic/float breccia; Woodcock & Mort, 2008), and a matrix consisting of comminuted potassic fenite. Within the comminuted groundmass is an assemblage of

![Fig. 4.](https://doi.org/10.1017/S0016756821000601)

Fig. 4. [Colour online] Field photos of breccia from around Mauze (a–g) and Nkalonje (h). (a) Typical float sample of a xenotime-rich breccia from Mantrap, showing characteristic knobby texture and buff–pink colour. (b) Fresh surface of the same sample (a) exhibiting substantial breakdown of the primary minerals to clay. (c) Characteristic weathered surface of a mineralized breccia, with abundant clasts and K-feldspar. (d–g) Examples of different clasts, including (d) nepheline syenite, (e) phonolite, (f) gneiss and (g) carbonatite. Note the presence of a 2–3 cm alteration rim on the phonolite clasts in (e). (h) Similar breccia sampled from Nkalonje, exhibiting a clast of nepheline syenite(?), hosted in a K-feldspar phryic groundmass. K-fsp = K-feldspar; N-Sy = nepheline syenite; Phon = phonolite; carb = carbonatite.
Mn-, Fe- and Ba-bearing (hydr)oxides, such as hollandite, as well as non-luminescent low-Mg calcite, fluorite, apatite, HFSE-bearing minerals, comminuted K-feldspar, illite, quartz and a substantial amount of pore space (Fig. 5b–c). Small veins of calcite carbonatite also occur locally in a limited number of samples and can envelop fragments of fenite.

3.2 HREE and HFSE mineralization at the Songwe–Mauze complex

The predominant HREE and HFSE minerals in the mineralized assemblage are xenotime-(Y), Nb- and V-bearing rutile/anatase and zircon, as well as minor amounts of Th-rich monazite, thorite/huttonite, an unidentified Th–Si–P mineral and LREE fluoro-carbonates. The growth of these phases is intimately associated with the breakdown and recrystallization of apatite, zircon and Fe-oxides.

Mineralization occurs in two different habits. Where present, pre-existing zircon grains have epitaxial overgrowths of isostructural xenotime-(Y) (Fig. 7a–b), as well as Nb- and Fe-bearing rutile/anatase (Fig. 7b–c). In these cases, zircon is clearly broken down, as demonstrated by the rounding of the original grain boundaries, as well as fracturing, fragmentation, embayment, local development of porosity and a darkening in BSE images (Fig. 7a–c). Xenotime overgrowths exhibit complex zoning, with porous dissolution zones and precipitation of Th-rich horizons (Fig. 7a–b). Rutile/anatase overgrowths are similarly highly porous and zoned.

Xenotime and rutile/anatase on pre-existing zircon grains accounts for most of the mineralization in samples with relatively low Y contents. However, in samples where Y contents are higher, these phases occur as stringers of euhedral to subhedral grains within the comminuted groundmass of the most brecciated samples (Fig. 6b–c, 7d–h). Very small (1–5 μm) euhedral zircon is disseminated throughout the mineralized zones, akin to the ‘nanozircons’ described by Dowman et al. (2017b). Commonly, such zircons form the core of xenotime-(Y) grains (Fig. 7b), which can reach up to 50 μm in size, but are most commonly c. 10–20 μm. These xenotime grains cathodoluminesce a distinct teal-blue colour (Fig. 7g). Xenotime is typically overgrown by Nb- and V-bearing anhedral rutile/anatase, which, in turn, is overgrown by Mn–Fe-(hydr)oxides (Fig. 7c, f). Locally, xenotime is also overgrown by a REE-absent, Th–Si–P phase, and is associated with the growth of euhedral Th-rich monazite and gorceixite (Fig. 7e).

Apatite occurs in all samples, in two distinct habits. Early apatite forms large, rounded grains with luminescence colours ranging from buff–pink to yellow (Fig. 6c, 7i). Early apatite is partially to completely broken down, and replaced by complex porous and, locally, skeletal violet-luminescent apatite (Fig. 7i–l); 1–10 μm huttonite/thorite and monazite grains occur within these porous horizons (Fig. 7i). In xenotime-rich samples, euhedral xenotime post-dates the breakdown of apatite (Fig. 7j).

3.3 Breccias associated with the Nkalonje complex

The field relationships and hand-specimen-scale characteristics of breccias associated with the Nkalonje complex are similar to those surrounding the Mauze nepheline syenite. The Nkalonje breccias are predominantly composed of brecciated feldspar-rich fenite, with clasts of nepheline syenite and basement gneiss. However,
the matrix of these breccias is composed of quartz, fluorite, Fe oxides and weathered pseudomorphs likely to be after siderite. REE-bearing minerals are rare, and HFSE minerals are limited to small grains of zircon and rutile/anatase.

4. Whole-rock composition of the breccia rocks

Nineteen samples were analysed for major and trace element compositions (Table 1), carried out in three tranches. The first six samples were analysed by Intertek-Genalysis, Australia, by inductively coupled plasma optical emission spectrometry (ICP-OES) and mass spectrometry (ICP-MS), with powdered samples prepared as sodium peroxide fusions (see Broom-Fendley et al. 2017a for details). The second tranche of an additional four analyses was also analysed at Intertek-Genalysis, using the same instrumentation, but with samples instead prepared as Li metaborate fusions. The remaining nine analyses were undertaken at ALS Loughrea, Ireland, again by ICP-OES and ICP-MS, following technique code CCP-01. Sample powders were prepared by dissolution of Li metaborate fusions and by four-acid digestion on unfused powders, the latter technique being used for analysis of Li, Ag, As, Cd, Co, Cu, Mo, Ni, Pb, Sc, Ti and Zn. C and S were analysed using
a LECO furnace. Owing to the visibly altered and, locally, weathered nature of the samples, as well as the inherent heterogeneity when analysing breccia samples, caution is warranted when interpreting the major element data, especially in respect to elements which are mobile in the weathering environment, such as Na.

Chondrite-normalized REE distributions for unmineralized Mauze breccia samples exhibit a steep negative slope from La to Gd and then a relatively flat distribution to Lu (Fig. 8a). This distribution matches that of unaltered phonolite dykes and nepheline syenite from Mauze but with a greater REE content.

Fig. 7. (Colour online) BSE (a–f, h, j, l) and CL (g, i, k) images of HREE and HFSE mineralization. (a–c) Xenotime and rutile/anatase (Rt/Ant) overgrowing zircon. Note the presence of fine fractures, embayments and locally porous nature of the zircons, and the zoning and small huttonite/thorite (Th–Si) minerals in the xenotime overgrowths. (d–h) disseminated zircon, xenotime, Th-rich monazite (Th-Mnz), a REE-deficient Th–Si–P mineral (Th-P-Si), rutile/anatase and gorceixite (Gcx) in breccia. (i–l) Partially (i–j) and fully (k–l) broken-down apatite grains. Note in (i) the thin zone of partial dissolution around the edge of the large grain, and the presence of fine, violet-luminescent apatite disseminated throughout the groundmass, as well as xenotime. Note in (l) the presence of small grains of monazite and huttonite/thorite in the porous apatite.
| Smpl #  | School vent | Mantrap | Nkalonje |
|--------|-------------|---------|----------|
| SoS132 | 57.10       | 57.90   | 53.30    |
| SoS133 | 53.30       | 54.60   | 59.30    |
| SoS134 | 57.11       | 59.10   | 56.20    |
| HTAC1549 | 54.12   | 56.20   | 39.30    |
| HTAC1551 | 51.20   | 57.24   | 54.98    |
| T0135  | 52.74       | 57.10   | 54.98    |
| T0136  | 57.11       | 57.10   | 58.30    |
| T0137  | 54.60       | 57.11   | 57.12    |
| T0155  | 1.05        | 1.07    | 0.79     |
| T0157  | 0.58        | 0.60    | 0.80     |
| T0159  | 0.58        | 1.07    | 0.79     |
| T0311  | 1.00        | 0.59    | 1.05     |
| U4910  | 1.93        | 0.92    | 0.92     |
| U4911  | 1.89        | 0.92    | 0.92     |
| H0214  | 1.93        | 0.92    | 0.92     |
| H0215  | 1.89        | 0.92    | 0.92     |
| H0217  | 1.93        | 0.92    | 0.92     |
| 1008   | 1.93        | 0.92    | 0.92     |
| T0304  | 1.93        | 0.92    | 0.92     |

**Table 1.** Major and trace element composition of whole-rock samples from breccias around Mauze and Nkalonje. Blank cells denote elements not analysed. Elements below the limit of detection are denoted by '<'.

Downloaded from https://www.cambridge.org/core. IP address: 207.241.231.83 on 08 Dec 2021 at 03:35:10, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms.

HREE and Th in fenite breccia
| Smpl # | School vent | Mantrap | Nkalonje |
|--------|-------------|---------|---------|
|        | SoS132 | SoS133 | SoS134 | HTAC1549 | HTAC1551 | T0135 | T0136 | T0137 | T0155 | T0157 | T0159 | T0311 | U4910 | U4911 | H0214 | H0215 | H0217 | T0304 | 1008 |
| La     | 790   | 587   | 762    | 581   | 197   | 391   | 456   | 456   | 262   | 278   | 652   | 710   | 365   | 316   | 1205  | 535  | 392  | 214   | 222   |
| Ce     | 848   | 979   | 1590   | 1140  | 414   | 488   | 742   | 702   | 467   | 504   | 993   | 1380  | 617   | 552   | 1976  | 950  | 756  | 479   | 396   |
| Pr     | 167   | 97    | 167    | 111   | 40    | 82    | 63    | 86    | 51    | 48    | 88    | 127   | 68    | 52    | 202   | 98   | 74   | 50    | 52    |
| Nd     | 612   | 319   | 633    | 375   | 152   | 311   | 189   | 297   | 175   | 159   | 275   | 422   | 236   | 166   | 709   | 327  | 261  | 194   | 194   |
| Sm     | 80    | 36    | 106    | 44    | 29    | 78    | 23    | 46    | 25    | 23    | 34    | 46    | 47    | 23    | 146   | 63   | 67   | 39    | 38    |
| Eu     | 21    | 9.2   | 29     | 11    | 9.0   | 33    | 7.5   | 15    | 7.2   | 6.3   | 9.0   | 12    | 21    | 6.1   | 57    | 5   | 30   | 12    | 16    |
| Gd     | 65    | 26    | 81     | 28    | 23    | 137   | 25    | 49    | 22    | 18    | 28    | 92    | 18    | 202   | 109  | 132  | 38    | 55    |
| Tb     | 7.9   | 3.2   | 13     | 4.3   | 4.2   | 40    | 8.6   | 14    | 4.7   | 3.7   | 4.2   | 3.5   | 31    | 3.7   | 51    | 42   | 45   | 6.1   | 12    |
| Dy     | 45    | 20    | 97     | 33    | 28    | 309   | 81    | 128   | 36    | 28    | 30    | 19    | 255   | 27    | 352   | 412  | 409  | 36    | 77    |
| Ho     | 8.9   | 3.8   | 22     | 7.3   | 6.5   | 66    | 20    | 30    | 8.8   | 6.3   | 7.3   | 4.3   | 57    | 5.5   | 74    | 102  | 97   | 6.3   | 17    |
| Er     | 24    | 12    | 75     | 23    | 18    | 184   | 62    | 88    | 26    | 19    | 25    | 13    | 161   | 16    | 200   | 307  | 287  | 16    | 44    |
| Tm     | 3.5   | 1.5   | 13     | 3.3   | 2.6   | 25    | 9.3   | 12    | 3.9   | 2.8   | 3.2   | 1.9   | 22    | 2.2   | 27    | 42   | 38   | 1.5   | 4.9   |
| Yb     | 22    | 12    | 21     | 91    | 19    | 143   | 59    | 69    | 26    | 19    | 23    | 12    | 117   | 14    | 157   | 240  | 216  | 7.9   | 26    |
| Lu     | 3.1   | 1.7   | 13     | 3.0   | 3.5   | 17    | 7.9   | 9.0   | 3.5   | 2.6   | 3.5   | 1.7   | 14    | 2.0   | 19    | 31   | 26   | 1.1   | 3.5   |
| Y      | 290   | 127   | 690    | 231   | 181   | 1859  | 554   | 910   | 265   | 186   | 228   | 119   | 1584  | 154   | 1991  | 3100 | 2942 | 167   | 455   |
| REE    | 2987  | 2234  | 4380   | 2615  | 1126  | 4162  | 2308  | 2910  | 1384  | 1304  | 2400  | 2899  | 3686  | 1354  | 7368  | 6384 | 5772 | 1268  | 1612  |

*S measured as total S, recalculated to SO\(_3\); C measured as total C, recalculated to CO\(_2\); † S measured by ICP OES, after LiBO\(_2\) fusion. Fe\(_2\)O\(_3\)\(_t\) = total Fe as Fe\(_2\)O\(_3\)
Sample T0311 contains more than 10 wt % CO₂. This elevated CO₂ content correlates with increased Sr and LREE, demonstrating that this sample is composed, in part, of carbonatite (Fig. 9f). Importantly, however, there is no correlation between CO₂ and the HREE or HFSE contents.

5. Discussion

5.1 Evidence for carbonatite at depth

The breccias around Mauze are 1–2 km away from the Songwe Hill carbonatite (Fig. 2a), and a direct link between these bodies is not apparent. Nonetheless, the presence of calcite carbonatite xenoliths (Fig. 4g), and minor amounts of fluorite- and apatite-bearing carbonatite veins (e.g. T0311; Table 1) clearly demonstrates the small-scale presence of carbonatite at the present level of erosion, and supports the notion of further carbonatite at depth. Moreover, the composition and texture of the fenitized phonolite is similar to the equivalent fenitized phonolite at Songwe Hill (Broom-Fendley et al. 2017a). We suggest that the breccia occurrences around Mauze represent small satellite vents to the main Songwe Hill carbonatite (Fig. 10).

5.2 Order of brecciation and mineralization

Cross-cutting textures indicate that brecciation, fenitization and crystallization of HREE minerals at Mauze occur after the initial emplacement of the xenolith-rich phonolite bodies (Fig. 10). Based on the angular nature of the clasts and the comminuted groundmass, the breccia formed by in situ rapid volume expansion (Jébrak, 1997), most likely as a result of subsurface explosive release of volatiles from the proposed underlying carbonatite bodies. The result is a vertical breccia pipe which likely grades down into an underlying carbonatite body at depth. The groundmass of the breccia contains xenotime associated with late carbonate minerals, fluorite and apatite (Fig. 6a–b). These apatite- and fluorite-bearing carbonate veins are similar to veins at Songwe Hill and the adjacent fenitized breccia on Chenga Hill (Broom-Fendley 2017a). Similar features include the violet-coloured apatite luminescence, presence of fluorite, xenotime, zircon, rutile/anatase and Mn- and Fe oxides, as well as the heavily altered nature of the fenite host rocks. Combined, these features further support the notion that a carbonatite-derived fluid is responsible for the HREE mineralization, and that the emplacement of such a fluid post-dates the formation of the vent rocks.

Mineral overgrowths demonstrate that the crystallization order of the REE- and HFSE-bearing minerals is consistent in each of the three mineralized fenite vents associated with the Songwe–Mauze complex. After brecciation, pre-existing zircon and apatite grains underwent dissolution, as reflected by fracturing, embayments and locally porous textures (Figs 7a–c, i–l, 10b). Simultaneously, or not long thereafter, zircon recrystallized as micron-sized euhedral grains and apatite formed needle-like and skeletal grains within the groundmass of the breccia. Partially dissolved and recrystallized micron-sized zircon both serve as a seed for isostructural growth of xenotime, which is subsequently overgrown by Nb- and V-bearing rutile and, later, Mn-, Fe- and Ba-bearing (hydr)oxides (Fig. 10c). Localized dissolution and reprecipitation of xenotime is evident from the presence of porous growth bands, formation of Th silicates and monazite, and complex zoning (Figs 7a, g, 10d).

![Graph showing chondrite-normalized whole-rock REE distributions](https://www.cambridge.org/core)

**Fig. 8.** (Colour online) Chondrite-normalized (after McDonough and Sun, 1995) whole-rock REE distributions of (a) samples from this study, compared to nepheline syenite and phonolite from Mauze (Broom-Fendley, 2015 and unpub. data; Chiwona et al. 2020) and carbonatite from Songwe Hill (Broom-Fendley et al. 2017a); and (b) comparison samples from the Cole HREE deposit (Andersen et al. 2016), Lofdal (Loye, 2014; Namibia Rare Earths, unpub. data), and ‘high-grade’ fenite from Chilwa Island (Dowman et al. 2017a). HREE-poor samples are excluded from (b) for clarity.
5.3 A conceptual model for HREE mineralization in fenite breccia

A wide range of processes have been proposed to account for HREE enrichment in carbonatites. Such processes include: (1) melting of eclogitic garnet from the mantle source region during the ascent or stalled ascent of a carbonatite melt (Song et al. 2016); (2) precipitation of a LREE-rich mineral, such as bastnäsite or monazite, from a carbonatite melt/fluid, thus depleting LREE in the residual melt phase and therefore relatively enriching it in HREE (Xu et al. 2007; Andersen et al. 2017; Anenburg et al. 2020); and (3) redistribution of REE during late-stage hydrothermal alteration, owing to the preferential stability of REE-chloride complexes (Broom-Fendley et al. 2016a, 2017b). All three processes, or a combination thereof, can occur at a given locality (e.g. Huanglongpu and Huayangchuan, China; Smith et al. 2018; Cangelosi et al. 2020a). Major source contributions from eclogitic garnet can be discounted as these would result in regional-scale HREE enrichment. While Songwe Hill does exhibit whole-rock HREE grades that are slightly elevated when compared to other REE deposits in southern Africa (Harmer & Nex, 2016), most carbonatites and alkali silicate rocks in the Chilwa Alkaline Province are LREE-rich.

The textural and field evidence discussed above clearly demonstrates that the HREE, Ti, Zr and Th mineralization is a hydrothermal process relating to brecciation peripheral to intrusive carbonatite bodies. As such breccias are characterized by a high initial porosity of 20–30 % and high permeability (Stripp et al. 2006), we propose that the breccia acted as a conduit for a carbonatite-derived mineralizing fluid (Fig. 10b). Some degree of REE transport occurs in and around REE-mineralized carbonatites, and Songwe Hill is no exception (Broom-Fendley et al. 2016a, 2017a). REE can be transferred from carbonatite into the surrounding fenite aureole (Dowman et al. 2017a; Elliott et al. 2018) or as small-scale (in situ) dissolution and reprecipitation of REE-bearing phases within carbonatite bodies (Broom-Fendley et al. 2016a; Benaouda et al. 2017; Cangelosi et al. 2020b). Here, we propose that mineralization encompasses both of these mechanisms and occurs as a two-step process. Initial mineralization forms due to the transport of HREE away from a LREE-mineralized...
carbonatite by a fenitizing fluid. Subsequently, HREE contents are locally upgraded by later, lower-temperature, fluid-mediated, dissolution–reprecipitation processes.

5.3.1 HREE transport and precipitation

The initial mineralization step proposed here presumes (1) prior precipitation of LREE-rich minerals in a cooling, crystallizing carbonatite at depth, or (2) a direct relationship between the breccia vents at Mauze and the LREE-mineralized Songwe Hill carbonatite. Neither interpretation can be proved on the basis of the evidence presented, but each may be justified considering the evolution of the Songwe Hill carbonatite and the recent experimental results of Anenburg et al. (2020). These authors demonstrate that alkali–LREE–carbonate minerals precipitate from a Na–K–carbonate±chloride±sulphate-brine phase which itself represents the residuum from crystallization of a carbonatitic melt (Prokopyev et al. 2016). During crystallization of the carbonatitic melt, the HREE are incompatible in the crystallizing assemblage so are retained in the residual Na- and K-rich fluid phase (Anenburg et al. 2020). Similar alkali-rich fluids have been proposed as the origin of fenite alteration aureoles adjacent to carbonatites, as supported by the presence of alkali carbonate daughter minerals in fluid inclusions (Bühn & Rankin, 1999; Williams-Jones & Palmer, 2002; Dowman et al. 2017a; Prokopyev et al. 2020).
The field and mineralogical evidence presented here is consistent with the model for HREE mineralization proposed by Annenburg et al. (2020). Here, a carbonatite intrusion undergoes extensive differentiation and small amounts of HREE become concentrated in the residual liquid phase. This liquid is localized into the overlying permeable structure of vent breccias. Alteration of the breccia rocks to a fenite assemblage coincides with the precipitation of the HREE minerals from this liquid. Xenotime evidently forms as a euhedral phase during, or not long after, the initial brecciation (Fig. 7a–h). Apatite, too, is introduced during this initial fenitization, but is considerably altered by subsequent hydrothermal fluids (Fig. 7i–j). Thus, we propose that the HREE-rich mineralization in fenite breccia is the result of prior crystallization of LREE minerals, either from an unexposed carbonatite body intruded into the fenite breccia vent at depth, or from the nearby Songwe Hill carbonatite (Fig. 10).

5.3.2 Local dissolution–reprecipitation
In addition to early xenotime precipitation, several features indicate that a subsequent hydrothermal fluid mediates dissolution and reprecipitation of REE- and HFSE-bearing minerals in the fenite breccias. Fluid-mediated dissolution–reprecipitation is common in carbonatites whereby cooling hydrothermal fluids back-react with a parent mineral, forming new phases from the trace element contents of the parent phase (Putnis, 2009). Such a process is common in phases that contain REE as minor components, such as apatite and calcite (Broom-Fendley et al. 2016a, b; Cangelosi et al. 2020a; Ying et al. 2020). It is evident that dissolution–reprecipitation has occurred in xenotime, apatite and xenotime at several stages of the Mauze fenite breccias. In all cases, the principal evidence is the volume reduction in the parent phase, as indicated by porosity and fractures (e.g. zircon: Fig. 7a; xenotime: Fig. 7c; and apatite: Fig. 7f). Additionally, the product phase crystallizes in close proximity to the parent, such as the isostructural overgrowths of xenotime on zircon (Fig. 7a) and the local formation of huttonite/thorite on xenotime (Fig. 7c). Where dissolution–reprecipitation has occurred in xenotime and zircon, the HREE- and Th phases are retained close to the original mineral (Fig. 7a, c), while LREE minerals form new euhedral phases, in close proximity (Fig. 7c). The substantially larger size and higher abundance of the xenotime grains indicates that zircon breakdown is not the sole source of the HREE in these rocks.

While the proximity of the product phases indicates that REE transport is probably not substantial, the difference in Th content and LREE/HREE contents of the reprecipitated minerals indicates that the altering fluid was capable of fractionating the REE. Experimental work demonstrates that both chloride and fluoride are capable of fractionating the REE, under acidic conditions, owing to the different stabilities of the LREE and HREE chloride and fluoride complexes (Migdisov et al. 2009). However, the low solubility of REE fluorides means the capacity for F to transport the REE is limited (Migdisov et al. 2016). We speculate that after crystallization, xenotime is altered by a Cl-bearing hydrothermal fluid and this fluid redistributes the LREE to a new LREE phase, while retaining the HREE and Th in close proximity to the parent mineral (Fig. 10d). Such a mechanism was proposed by Williams-Jones et al. (2015) to have led to the HREE mineralization at Lofdal, although here we only consider the transport and fractionation to occur on a scale of a few metres.

5.4 Comparing the Chilwa Province fenite breccias with other carbonatite-associated HREE and HFSE mineralization
The vent breccias described here are not as HREE-rich as peralkaline-related HREE deposits (Dostal, 2017) or unconformity-related xenotime mineralization (Nazari-Dehkordi et al. 2018), but they far exceed the HREE contents of most examples of carbonatite and fenite. As a basis for comparison, Figures 8b and 9a–e include data from the Cole occurrence (Andersen et al. 2016) and the Lofdal deposit (Do Cabo, 2013; Loye, 2014; Namibia Rare Earths, unpub. data), as well as high-grade fenite breccia from Chilwa Island (Downman et al. 2017a).

All of these examples are located adjacent to intrusive carbonatite complexes and are HREE-enriched when compared to these adjacent complexes and to typical carbonatite compositions. All are associated with brecciated rocks which have been metamorphosed to increase their alkali content: those at the Cole occurrence are composed predominantly of K-feldspar (Andersen et al. 2016), while at Lofdal (Area 4), mineralization is associated with albite (HS Swinden & P Siegfried, unpub. technical report, 2011). In both occurrences xenotime occurs as a mixture of disseminated fine grains and overgrowths on older zircon cores, and is associated with fluorite.

The REE pattern of mineralized Mauze vent breccias broadly matches the REE distribution of all three comparison examples (Fig. 8b), with an injection to elevated HREE contents occurring between Nd–Eu, depending on the LREE content of the sample. Yttrium contents (as a proxy for total HREE) are much lower in the Mauze vent breccias than those at the Cole occurrence and also typically lower than samples from Lofdal (Figs 8b, 9a). The HREE contents of the most HREE-rich fenite sample from Chilwa Island correspond to the least-mineralized Mauze breccia samples (Fig. 8b). The Mauze breccias share elevated HFSE contents, similar to those reported from the Lofdal Deposit and the Cole occurrence. Samples from Lofdal define a similar correlation between Y, Ti and U to the mineralized Mauze samples (Fig. 9a, c). Thorium contents also increase with Y in Lofdal samples, but not as steeply as those from Mauze breccia. While Zr and Nb contents from Lofdal are correlated in the data presented here (Loye, 2014; Fig. 9b–c), this relationship is not apparent when considering all analyses of drillcore from Lofdal (Namibia Rare Earths, unpub. data).

In addition to the few carbonatite localities where xenotime-(Y) or HREE enrichment has been documented, there are also examples of carbonatite-related alteration with elevated Ti, Zr, Th or Nb contents. These include: the Christy deposit of the Magnet Cove complex, USA (Flohr, 1994); Salpeterkop and Goudini, South Africa (Verwoerd et al. 1995; Verwoerd, 2008a, b) and Gross Brukkaros, Namibia (Werner & Cook, 2001). Many of these examples share textural and geochemical features with the mineralization at Mauze. Of particular note are the Christy deposit and Salpeterkop. Both of these localities host Ti in brookite, with grades sufficiently high at the Christy deposit to warrant extraction on a small scale between 1934 and 1944 (Flohr, 1994). At the Christy deposit, Ti minerals predominantly occur in highly altered alkali-rich country rock associated with clay-rich dykes with abundant relict K-feldspar. At Salpeterkop, mineralization is hosted in highly altered breccia, associated with abundant K-feldspar and trachyte (Verwoerd et al. 1995). These associated rocks bear some similarity to the deposits discussed above, and of particular note is that the Christy clay-rich dykes and the Salpeterkop breccia are both locally HREE-enriched.
While the REE grades in fenite are typically low (Fig. 8b; Elliott et al. 2018), REE mineralization can still occur in this rock up to several kilometres from the parent carbonate intrusion (Dowman et al. 2017a). REE mineralization in fenite is limited to small vein networks and pockets, which can also include monazite, xenotime, bastnäsite, parsite, ancylite, as well as Th and Nb minerals. In particular, xenotime and Th-rich minerals can occur in the highest-grade fenites found at the Chilwa Island complex, Malawi (Dowman et al. 2017a). While they contain far lower HREE contents than the samples described here, these xenotime-bearing micro-mineral assemblages bear strong textural and petrographic similarities to the mineralization at Mauze. The host rocks are near-identical and the late-stage nature of the mineralization is highly similar. Dowman et al. (2017b) also note that zircon in the most intensely fenitized rocks exhibits dissolution textures and forms the nucleus for later REE mineral precipitation, features we also report from the Mauze breccias (Fig. 7a).

Based on the similarities to the relatively HREE-rich micro-mineral assemblages present in the Chilwa Island fenite, we suggest that some degree of HREE transport occurs in all fenite assemblages – particularly high-grade K-rich fenite. The substantially higher HREE contents of the fenitized vent rocks at Mauze, however, may be caused by the focusing of fluids through highly permeable breccia, which would lead to a greater degree of HREE input than the comparatively lower-grade fentes studied by Dowman et al. (2017a). We propose that similar HREE mineralization at Lofdal and the Cole HFSE/HREE deposit represents extreme focusing of a similar residual fluid, and that all examples of HREE mineralization in fentes peripheral to carbonatites share a similar causal link.

5.5 HREE-rich fenite breccias as an exploration indicator for LREE mineralization

The mineralization reported here is not of sufficiently high grade or large enough to be economic in its own right. Moreover, the HREE enrichment is intimately associated with an increase in Th, the processing of which provides environmental and social challenges (Findeiß & Schäffer, 2017). Nonetheless, enrichment of HREE and Th in fenite breccias serves as a record of fluid expulsion from a REE-rich carbonate, and may indicate the presence of LREE mineralization in carbonatite at depth. The Chilwa Alkaline Province features at least 13 breccia vents similar to those investigated in this study. Many of these are associated with carbonatite (Garson, 1965), but have not yet been studied with respect to their REE mineralization potential. Minor carbonate veins, and a proximity to other carbonatite complexes, suggest that these vents may be related to the emplacement of carbonatite intrusions below the present level of erosion. In particular, if HREE mineralization occurs due to the prior formation of LREE minerals, then a HREE-enriched vent may be an exploration indicator for a LREE deposit at depth (Dowman et al. 2017a; Elliott et al. 2018). Importantly, the link between HREE and Th contents (Figs 2b, 9d) demonstrates that radiometric surveys may be used to locate near-surface enrichment of HREE and, therefore, any potentially associated LREE mineralization.

Vent breccias at the Nkalonje complex and the small Malagani vent, to the northwest of Songwe (Fig. 1), were investigated in this study as a comparison to mineralized vents around Mauze. These share superficial similarities to the mineralized vents (Fig. 4b), but both laboratory whole-rock analyses and field analyses using a portable X-ray fluorescence instrument do not indicate HREE mineralization. HFSE minerals are limited to localized occurrences of anatase/rutile. Carbonatite is scarce at Nkalonje, with only minor REE-rich dykes, and is absent at Malagani, so we speculate that the lack of HFSE and HREE minerals in their fentes reflects the low REE content of their parent carbonatites.

6. Conclusions

- HREE mineralization occurs in fenitized xenolith-rich phonolite breccia, peripheral to the Songwe Hill carbonatite and adjacent to the Mauze nepheline syenite, Malawi.
- Fenitization and brecciation post-date the emplacement of phono- lite and minor carbonatite, with possible further carbonatite present at depth.
- Mineralization predominantly consists of xenotime, with zircon, anatase/rutile and minor huttonite/thorite hosting other HFSE. Zircon formed both from the mineralizing fluid as well as providing the seed for further epitactic xenotime growth.
- The mineralization at Mauze is texturally and compositionally similar to higher-grade HREE-bearing rocks at the Cole occurrence (USA) and the Lofdal deposit (Namibia), as well as minor HREE enrichment in fenite at the Chilwa Island carbonatite (Malawi).
- The formation of HREE-rich fenite may reflect the passage of liquids derived from an intrusive carbonatite body that have undergone extensive fractional crystallization. Experimental evidence suggests that during this crystallization the LREE cargo of the carbonatite is deposited as mineralization at depth. HREE-rich fenite may therefore represent an exploration indicator for LREE deposits in the associated intrusive carbonatite body.
- We suggest that HREE transport and fractionation occurs in most cases of fenitization, but enrichment to the concentrations occurring in the Mauze breccia requires the focusing of fenite fluid through pre-existing structures.
- The link between HREE and Th contents demonstrates that radiometric surveys may be used to locate near-surface enrichment of HREE in fenite breccias.

Acknowledgements. We are grateful to James Mtenga, Ansel Zabula, Innocencia Nkumila and Chikondi Micheka (Mkango Resources) for their contributions to Figure 2b and constructive field discussions, and to Enoch Chitsulo for assisting with fieldwork – including important snake and buffalo bean identification. Scott Swinden kindly provided unpublished data on the Lofdal deposit and comments on an early version of the manuscript. We also thank two anonymous reviewers for their comments. This work was funded by a Natural Environment Research Council (NERC) Industrial Innovation Fellowship to S.B-F. (NE/R013403/1), supported by contributions from Mkango Resources, the NERC SoS RARE consortium (NE/M011429/1) and the EU H2020 HiTech AlkCarb program grant agreement no. 689909.

Conflicts of interest. None.

References

- Andersen AK, Clark JG, Larson PB and Donovan JJ (2017) REE fractionation, mineral speciation, and supergene enrichment of the Bear Lodge carbonates, Wyoming, USA. Ore Geology Reviews 89, 780–807.
- Andersen AK, Clark JG, Larson PB and Neill OK (2016) Mineral chemistry and petrogenesis of a HFSE (+ HREE) occurrence, peripheral to carbonatites of the Bear Lodge alkaline complex, Wyoming, American Mineralogist 101, 1604–23.
- Annenb M, Mavrogenes JA, Frigo C and Wall F (2020) Rare earth element mobility in and around carbonatites controlled by sodium, potassium, and silica. Science Advances 6, eabb6570.
Baele JM, Decréev S and Rusk B (2019) Cathodoluminescence applied to ore geology and exploration. In Ore Deposits: Origin, Exploration, and Exploitation (eds S Decrée and L Robb), pp. 131–161. New York: Wiley.

Beniouda R, Devey CW, Badra L and Ennaciri A (2017) Light rare-earth element mineralization in hydrothermal veins related to the Jebi Bobo alkaline igneous complex, AntiAtlas/Morocco: the role of fluid–carbonate interactions in the deposition of synchysite-(Ce). Journal of Geochimical Exploration 177, 28–44.

Binnemans K, Jones PT, Müller T and Yurramendi I (2018) Rare earths and the balance problem: how to deal with changing markets? Journal of Sustainable Metallurgy 4, 126–46.

Bodeving S, Williams-Jones AE and Swinden S (2017) Carbonate–silicate melt immiscibility, REE mineralizing fluids, and the evolution of the Lofdal Intrusive Suite, Namibia. Lithos 268–271, 383–98.

Broom-Fendley S (2015) Targeting heavy rare earth elements in carbonatite complexes. PhD thesis, Camborne School of Mines, University of Exeter, UK. Published thesis.

Broom-Fendley S, Brady AE, Wall F, Gunn G and Dawes W (2017a) REE minerals at the Songwe Hill carbonatite, Malawi: HREE-enrichment in late-stage apatite. Ore Geology Reviews 81, 22–41.

Broom-Fendley S, Brady AE, Horstwood MSJ, Woolley AR, Miegha J, Wall F, Dawes W and Gunn G (2017b) Geology, geochemistry and geochronology of the Songwe Hill carbonatite, Malawi. Journal of African Earth Science 134, 10–23.

Broom-Fendley S, Wall F, Spiro B and Ullmann CV (2017c) Deducing the source and composition of rare earth mineralising fluids in carbonatites: insights from isotopic (C, O, 87 Sr/86 Sr) data from Kangankunde, Malawi. Contributions to Mineralogy and Petrology 172, 96.

Broom-Fendley S, Styles MT, Appleton JD, Gunn G and Wall F (2016a) Evidence for dissolution–reprecipitation of apatite and preferential LREE mobility in carbonatite-derived late-stage hydrothermal processes. American Mineralogist 101, 596–611.

Broom-Fendley S, Heathon T, Wall F and Gunn G (2016b) Tracing the fluid source of heavy REE mineralisation in carbonatites using a novel method of oxygen-isotope analysis in apatite: the example of Songwe Hill, Malawi. Chemical Geology 440, 275–87.

Bühn B and Rankin AH (1999) Composition of natural, volatile-rich Na-Ca-REE–Sr carbonatite fluids trapped in fluid inclusions. Geochimica et Cosmochimica Acta 63, 3781–97.

Cangelosi D, Smith M, Banks D and Yardley B (2020a) The role of sulfate-rich fluids in heavy rare earth enrichment at the Dashigou carbonatite deposit, Huanglongpu, China. Mineralogical Magazine 84, 65–80.

Cangelosi D, Broom-Fendley S, Banks D, Morgan D and Yardley B (2020b) Light rare earth element redistribution during hydrothermal alteration at the Okorusu carbonatite complex, Namibia. Mineralogical Magazine 84, 49–64.

Chiwona AG, Cortés JA, Gaulton RG and Manning DAC (2020) Petrology and geochemistry of selected nepheline syenites from Malawi and their potential as alternative potash sources. Journal of African Earth Sciences 164, 103769.

Cooper AF, Collins AK, Palin JM and Spratt J (2015) Mineralogical evolution and REE mobility during crystallisation of anclite-bearing ferrocarbonatite, Haast River, New Zealand. Lithos 216-217, 324–37.

Do Cabo VN (2013) Geological, mineralogical and geochemical characterisation of the heavy rare earth-rich carbonatites at Lofdal, Namibia. PhD thesis, Camborne School of Mines, University of Exeter, UK.

Dostal J (2017) Rare earth element deposits of alkaline igneous rocks. Resources 6, 34. Doi: 10.3390/resources6030034.

Downman E, Wall F, Trelor PJ and Rankin AH (2017a) Rare-earth mobility as a result of multiple phases of fluid activity in fenite around the Chilwa Island Carbonatite, Malawi. Mineralogical Magazine 81, 1367–95.

Downman E, Wall F, Jefferies T, Trelor P, Carter A and Rankin A (2017b) Granatoid zircon forms the nucleus for minerals precipitated by carbonatite-derived metasomatic fluids at Chilwa Island, Malawi. Gondwana Research 51, 64–77.

Elliott HAl, Wall F, Chakhmouradian AR, Siegfried PR, Dahlgren S, Weatherley S, Finch AA, Marks MAW, Downman E and Deady E (2018) Ore Geology Reviews 93, 38–59.

Finch AA and Klein J (1999) The causes and petrological significance of cathodoluminescence emissions from alkali feldspars. Contributions to Mineralogy and Petrology 135, 234–45.

Findeš M and Schläfer A (2017) Fate and environmental impact of thorium residues during rare earth processing. Journal of Sustainable Metallurgy 3, 179–89.

Flohr MJK (1994) Titanium, vanadium, and niobium mineralization and alkali metasomatism from the Magnet Cove Complex, Arkansas. Economic Geology 89, 105–30.

Garson MS (1965) Carbonatites in southern Malawi. Bulletin of the Geological Survey of Malawi 15.

Garson MS and Walsh R (1969) The geology of the Manje area. Bulletin of the Geological Survey of Malawi 21.

Goodenough KM, Wall F and Merriman D (2018) The rare earth elements: demand, global resources, and challenges for resourcing future generations. Natural Resources Research 27, 201–16.

Harmer RE and Nex PAM (2016) Rare earth deposits of Africa. Episodes 39, 381–406.

Hogarth DD (2016) Chemical trends in the Meech Lake, Québec, carbonatites and fenites. The Canadian Mineralogist 54, 1105–20.

Jebbrik M (1997) Hydrothermal breccias in vein-type ore deposits: a review of mechanisms, morphology and size distribution. Ore Geology Reviews 12, 111–34.

Le Bas MJ (2008) Fenites associated with carbonatites. The Canadian Mineralogist 46, 915–32.

Loye E (2014) The geological controls on the heavy rare earth element enriched alteration zone of Area 4, Lofdal, Khorixas, Namibia. MRes thesis, Camborne School of Mines, University of Exeter, UK. Published thesis.

Mariano AN and King PJ (1975) Europium-activated cathodoluminescence in minerals. Geochimica et Cosmochimica Acta 39, 849–60.

Mariano AN and Mariano A (2014) Cathodoluminescence as a tool in mineral exploration. In Cathodoluminescence and Its Application to Geoscience (ed IM Coulon), pp. 97–111. Ottawa: Mineralogical Association of Canada Short Course No. 45.

McDonough WF and Sun S-S (1995) The composition of the Earth. Chemical Geology 120, 223–53.

Migdisov AA, Williams-Jones AE and Wagner T (2009) An experimental study of the solubility and speciation of the Rare Earth Elements (III) in fluoride- and chloride-bearing aqueous solutions at temperatures up to 300 °C. Geochimica et Cosmochimica Acta 73, 7087–109.

Migdisov A, Williams-Jones AE, Brugger J and Caporuscio FA (2016) Hydrothermal transport, deposition, and fractionation of the REE: experimental data and thermodynamic calculations. Chemical Geology 439, 13–42.

Morogan V (1989) Mass transfer and REE mobility during fenitization at Alnö, Sweden. Contributions to Mineralogy and Petrology 103, 25–34.

Nagari-Dekhordi T, Spandler G, Oliver NHS and Wilson R (2018) Unconformity-related rare earth element deposits: a regional-scale hydrothermal mineralization type of Northern Australia. Economic Geology 113, 1297–305.

Ngwenya BT (1994) Hydrothermal rare earth mineralisation in carbonatites of the Tundulu complex, Malawi: processes at the fluid/rock interface. Geochimica et Cosmochimica Acta 58, 2061–72.

Prokopyev IR, Borisenko AS, Borovikov AA and Pavlova GG (2016) Origin of REE-rich ferrocarbonatites in southern Siberia (Russia): implications based on melt and fluid inclusions. Mineralogy and Petrology 110, 845–59.

Prokopyev I, Kozlov E, Fomina E, Doroshkevich A and Dyomkin M (2020) Mineralogy and fluid regime of formation of the REE-late-stage hydrothermal mineralization of Petyayan–Vara carbonatites (Vuoriyri, Kola Region, NW Russia). Minerals 10, 405.

Putnis A (2009) Mineral replacement reactions. Reviews in Mineralogy and Geochemistry 70, 87–124.

Smith M, Kyника J, Xu C, Song W, Spratt J, Jefrīsz J, Brtnický M, Kopriva P and Cangelosi D (2018) The origin of secondary heavy rare earth element enrichment in carbonatites: Constraints from the evolution of the Huanglongpu district, China. Lithos 308–309, 65–82.

Song W, Xu C, Smith M, Kyника J, Huang K, Wei C, Zhou L and Shu Q (2016) Origin of unusual HREE-Mo-rich carbonatites in the Qinding orogen, China. Scientific Reports 6, 37377. doi: 10.1038/srep37377.
HREE and Th in fenite breccia

Stripp GR, Field M, Schumacher JC, Sparks RSJ and Cressey G (2006) Post-emplacement serpentinization and related hydrothermal metamorphism in a kimberlite from Venetia, South Africa. Journal of Metamorphic Geology 24, 515–34.

Verplanck PL, Mariano AN and Mariano Jr A (2016) Rare earth element ore geology of carbonatites. Reviews in Economic Geology 18, 5–32.

Verwoerd WJ (2008a) The Goudini carbonatite complex, South Africa: a reappraisal. The Canadian Mineralogist 46, 825–30.

Verwoerd WJ (2008b) Kamphaugite-(Y) from the Goudini carbonatite, South Africa. The Canadian Mineralogist 46, 1007–22.

Wall F (2014) Rare earth elements. In Critical Metals Handbook (ed G Gunn), pp. 312–39. New York: John Wiley & Sons.

Wall F and Mariano A (1996) Rare earth minerals in carbonatites: a discussion centred on the Kangankunde Carbonatite, Malawi. In Rare Earth Minerals: Chemistry Origin and Ore Deposits (eds A Jones, F Wall and CT Williams) pp. 193–226. London: Chapman and Hall.

Wall F, Nika-Paavola VN, Storey C, Müller A and Jeffries T (2008) Xenotime-(Y) from carbonatite dykes at Lofdal, Namibia: unusually low LREE:HREE ratio in carbonatite, and the first dating of xenotime overgrowths on zircon. The Canadian Mineralogist 46, 861–77.

Werner M and Cook NJ (2001) Nb-rich brookite from Gross Brukkaros, Namibia: substitution mechanisms and Fe²⁺/Fe³⁺ ratios. Mineralogical Magazine 65, 437–40.

Williams-Jones AE, Wollenberg R and Bodeving S (2015) Hydrothermal fractionation of the rare earth elements and the genesis of the Lofdal REE deposit, Namibia. In Symposium on Strategic and Critical Materials Proceedings, November 13–14, 2015 (eds GJ Simandl and M Neetz), pp. 125–30. Victoria, British Columbia: British Columbia Geological Survey Paper 2015-3.

Woodcock NH and Mort K (2008) Classification of fault brecias and related fault rocks. Geological Magazine 145, 435–40.

Woolley AR (1991) The Chilwa alkaline igneous province of Malawi: a review. In Magmatism in Extensional Structural Settings: The Phanerozoic African Plate (eds AB Kampunzu and RT Lubala), pp. 377–409. Berlin: Springer.

Woolley A (2001) Alkaline Rocks and Carbonatites of the World. Part 3: Africa. London: The Geological Society.

Xu C, Campbell IH, Allen CM, Huang Z, Qi L, Zhang H and Zhang G (2007) Flat rare earth element patterns as an indicator of cumulate processes in the Lesser Qinling carbonatites, China. Lithos 95, 267–78.

Xu C, Campbell IH and Allen CM (2010) Trace-element modeling of the magmatic evolution of rare-earth-rich carbonatite from the Miaoya deposit, Central China. Lithos 118, 145–55.

Ying Y-C, Chen W, Simonetti A, Jiang S-Y and Zhao K-D (2020) Significance of hydrothermal reworking for REE mineralization associated with carbonatite: constraints from in situ trace element and C-Sr isotope study of calcite and apatite from the Miaoya carbonatite complex (China). Geochimica et Cosmochimica Acta 280, 340–59.