Formation of Rare Earth Deposits in Carbonatites

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Carbonatites and related rocks are the premier source for light rare earth element (LREE) deposits. Here, we outline an ore formation model for LREE-mineralised carbonatites, reconciling field and petrological observations with recent experimental and isotopic advances. The LREEs can strongly partition to carbonatite melts, which are either directly mantle-derived or immiscible from silicate melts. As carbonatite melts evolve, alkalis and LREEs concentrate in the residual melt due to their incompatibility in early crystallising minerals. In most carbonatites, additional fractionation of calcite or ferroan dolomite leads to evolution of the residual liquid into a mobile alkaline "brine-melt" from which primary alkali REE carbonates can form. These primary carbonates are rarely preserved owing to dissolution by later fluids, and are replaced in-situ by monazite and alkali-free REE-(fluor)carbonates.

KEYWORDS: brine-melt; burbankite; critical metals; rare earths; alkaline complexes

INTRODUCTION

Carbonatites are one of the most prospective rock types on Earth. Almost 10% of carbonatite occurrences host an active or former mine and a further 10% are defined as a mineral resource (Simandl and Paradis 2018). The principal commodities mined from carbonatites include phosphate, niobium, fluorite, rare earth elements (REEs), vermiculite, iron, and zirconium, as well as their (often underappreciated) use as a limestone source for aggregate, cement, and agricultural purposes. Despite this abundance of commodities, carbonatites are probably best known for REE mineralisation. The REEs continue to be topical owing to their requirement in the production of high-strength permanent magnets for electric vehicles and wind turbines, among a myriad of other high-tech uses. Carbonatites host most REE mines and are the focus of many exploration projects due to exceptional ore enrichment, with the REEs commonly contained in minerals with well-established extraction methods. Nearly all carbonatites are dominated by the four lightest REEs (the light rare earth elements, LREEs: La, Ce, Pr, and Nd), of which Nd and Pr are particularly marketable. The remaining REEs (the heavy rare earth elements, HREEs: Sm to Lu) are more valuable, but typically comprise less than 1% of the REE content in these rocks.

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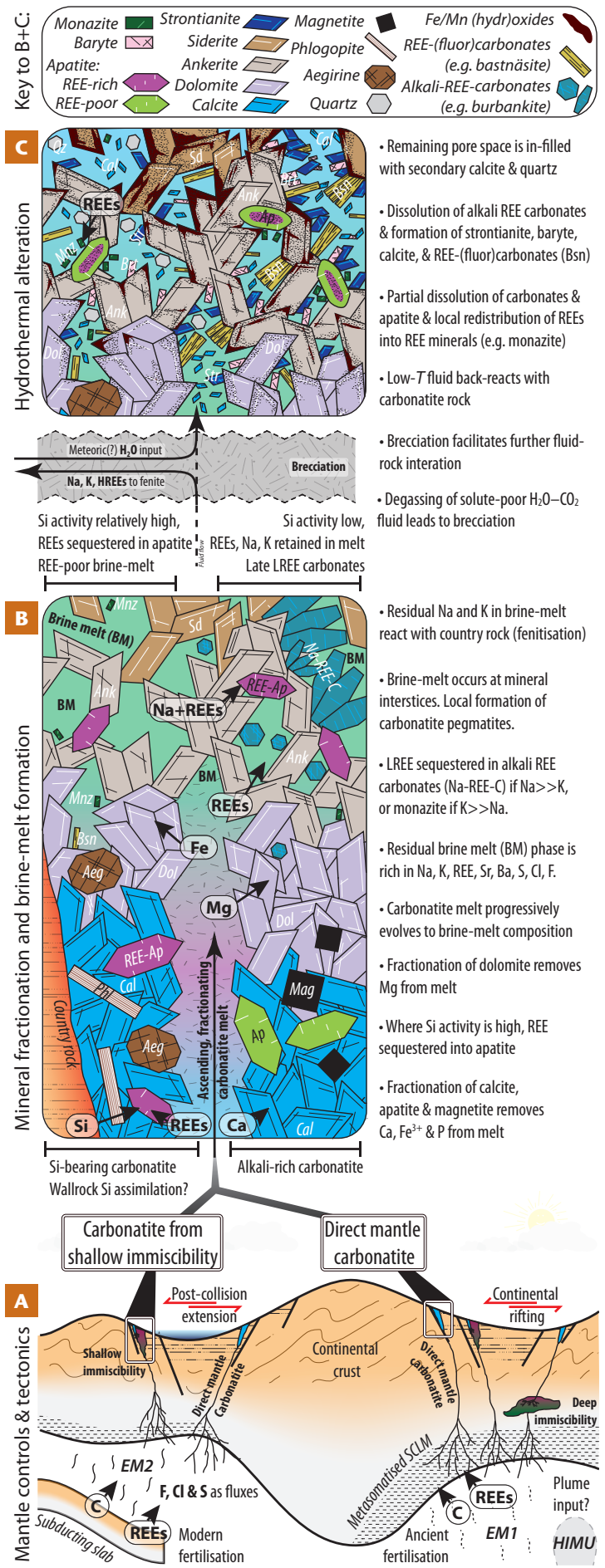   E-mail: Michael.Anenburg@anu.edu.au

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In the last ten years, continued interest in REE deposits has led to an increase in published descriptions of carbonatite-hosted REE mineralisation. In this paper, we reconcile some of the field and petrological observations with recent experimental and isotopic advances to outline a conceptual model for the formation of carbonatite-associated rare earth deposits (FIG. 1).

MANTLE FORMATION AND INITIAL REE PARTITIONING

Most carbonatites trace their origins to mantle melting (FIG. 1A). Radiogenic isotopic compositions of carbonatite-associated REE deposits suggest an origin from enriched mantle domains (enriched mantle type 1, EM1; enriched mantle type 2, EM2; and HIMU type, i.e., high "μ", where μ = $^{238}U/^{204}Pb$). Carbonate melts enriched in REEs originate from mantle sources that were previously refertilised by different components. For instance, it has been suggested that North American carbonatites, such as Bear Lodge (Wyoming, USA), derive from an asthenospheric mantle plume that was composed of depleted mantle refertilised by a subduction-derived EM1 component (Moore et al. 2015). In another example, the Mianning-Dechang REE deposits in China are derived from previously metasomatised subcontinental lithospheric mantle: prior to carbonatite formation, this mantle domain was enriched by REE-rich and CO_2-rich fluids that were themselves derived from subducted marine sediments, leading to a final radiogenic isotope signature intermediate between the EM1 and EM2 end members (Hou et al. 2015). Continental rift zones, such as the East African Rift, are another tectonic setting which is conducive to the formation of REE deposits associated with carbonatites and that derive from mantle having radiogenic isotope compositions intermediate between the EM1 and HIMU end members (Bell and Simonetti 2010).

This apparent variety in mantle sources and tectonic settings indicates that there is no single source for carbonatites and that these REE-rich melts can form in any CO_2-enriched mantle, regardless of how the enrichment occurred. Fertilisation of that mantle with other chemical constituents (e.g., Na, K, P, S, and F) does not have to immediately precede the partial melting that generates carbonatite magmas. In fact, these two events can be separated by hundreds of millions of years (Anenburg et al. 2020a). Carbonatite melts are typically emplaced during continental rifting (Bell and Simonetti 2010), although a number of complexes are associated with syn- to post-collisional tectonic environments (Hou et al. 2015).

Carbonatite melts are most commonly thought to form either by direct mantle melting or to evolve from carbonate-bearing alkaline silicate melts by immiscibility or fractionation (Fig. 1A). All of these processes potentially lead to REE-enrichment. Carbonatites formed by very-low degrees of melting of carbonated mantle will concentrate LREEs relative to siliceous higher-degree melts generated from the same source (Foley et al. 2009). Immiscible separation of carbonatite and silicate melts from carbonated silicate melts can also lead to partitioning of LREEs to carbonatite melts. Carbonatite–silicate partition coefficients for the LREEs, Ba, Sr, F, P, and Cl are highest when the immiscible silicate melt is highly polymerised, Ca-poor, and hydrous (Nabyl et al. 2020). Carbonatite–silicate partition coefficients are low for the LREEs in deep mantle–derived alkali-silicate melts, substantial REE partitioning to conjugate carbonatites being only achieved after prolonged fractionation. Strong LREE enrichment of carbonatites, thus, requires immiscibility to occur very late in the evolution of an alkaline magma batch when the conjugate silicate melt is phonolitic (Nabyl et al. 2020). The common spatial association of the plutonic chemical equivalent of phonolite (nepheline syenite) with REE-mineralised carbonatites (e.g., Moore et al. 2015; Doroshkevich et al. 2016) circumstantially supports their petrogenetic link. The two immiscible melts are unlikely to rise together due to their differing physical properties; thus, the close association between carbonatite and nepheline syenite indicates that their emplacement was immediately preceded by immiscibility, temporally and spatially. Nevertheless, the immiscibility origin for some carbonatite–silicate rock associations is questionable (Gittins and Harmer, 2003), while others are not accompanied by cogenetic silicate rocks (e.g., Kangankunde in Malawi; Nkombwa in Zambia). Therefore, liquid immiscibility may not always be a prerequisite for carbonatite melt formation and, by extension, economic mineralisation.

Carbonatites are fully endowed with their REE budget during the initial short-lived magmatic intrusion event and do not accumulate additional REEs over time via

FIGURE 1 Schematic illustration of the key steps to form a rare earth element (REE)-rich carbonatite. (**A**) Modern or ancient metasomatism transfers carbon, REEs, and other large ion lithophile elements (LILEs), high field-strength elements (HFSEs) and volatile elements into the subcontinental lithospheric mantle (SCLM), with a contribution from a range of mantle reservoirs depending on tectonic setting. The enriched mantle type 1 (EM1) and enriched mantle type 2 (EM2) isotopic signature associated with the resulting hybrid mantle likely reflects recently metasomatised lithosphere rather than ancient asthenospheric EM1 and EM2 components sampled by ocean island basalts. The HIMU-like source [HIMU = high 'μ', i.e., high $^{238}U/^{204}Pb$] may reflect deeper contributions from recycled oceanic crust. Elevated F, Cl, and S act as fluxes and promote melting and the transfer of REEs into carbonatite or carbonated silicate melt(s), which coalesce and rise to the crust during extension. Shallow immiscibility promotes the transfer of REEs from a carbonated silicate melt into carbonatite melt. (**B**) An ascending and fractionating carbonatite melt having (**LEFT**) high SiO_2 activity or (**RIGHT**) low SiO_2 activity. Both melts crystallise calcite, dolomite, and, locally, Fe-bearing carbonates. In a low-Si melt, alkalis (Na, K) and REEs are retained in the melt, evolving to a brine-melt composition. The REEs precipitate as alkali–REE-carbonates (K/Na–REE-C), such as burbankite. In a high-Si melt, alkalis are sequestered in silicate minerals, and the REEs predominantly substitute into apatite plus minor REE-fluorcarbonate or monazite crystallisation. These high-Si carbonatites tend to have a greater proportion of calcite to dolomite and ankerite, as Mg and Fe are sequestered in silicates. The cooling brine-melt boils, leading to brecciation and further dilution with H_2O. (**C**) Low-T hydrothermal fluids back-react with the crystallised carbonatite, dissolving alkali–REE-carbonates, as well as apatite and carbonate minerals. The REEs are then redistributed as REE-(fluor)carbonates and monazite. The Fe-bearing carbonates breakdown, leaving Fe and Mn (hydr)oxides. Mineral abbreviations: Cal = calcite; Dol = dolomite; Ank = ankerite; Sd = siderite; Str = strontianite; Ap = apatite; Phl = phlogopite; Aeg = aegirine; Mag = magnetite; Bsn = bastnäsite (illustrative of any REE-[fluor]carbonate); Na–REE-C = alkali–REE-carbonate minerals (such as burbankite); Mnz = monazite, Brt = baryte; Qz = quartz.

Key to B+C:
Monazite, Baryte, Apatite: REE-rich, REE-poor, Strontianite, Siderite, Ankerite, Dolomite, Calcite, Magnetite, Phlogopite, Aegirine, Quartz, Fe/Mn (hydr)oxides, REE-(fluor)carbonates (e.g. bastnäsite), Alkali-REE-carbonates (e.g. burbankite)

C — Hydrothermal alteration

- Remaining pore space is in-filled with secondary calcite & quartz
- Dissolution of alkali REE carbonates & formation of strontianite, baryte, calcite, & REE-(fluor)carbonates (Bsn)
- Partial dissolution of carbonates & apatite & local redistribution of REEs into REE minerals (e.g. monazite)
- Low-T fluid back-reacts with carbonatite rock
- Brecciation facilitates further fluid-rock interaction
- Degassing of solute-poor $H_2O–CO_2$ fluid leads to brecciation

Meteoric(?) H_2O input
Na, K, HREEs to fenite
Brecciation

Si activity relatively high, REEs sequestered in apatite REE-poor brine-melt

Si activity low, REEs, Na, K retained in melt Late LREE carbonates

B — Mineral fractionation and brine-melt formation

Brine melt (BM)
Na+REEs

- Residual Na and K in brine-melt react with country rock (fenitisation)
- Brine-melt occurs at mineral interstices. Local formation of carbonatite pegmatites.
- LREE sequestered in alkali REE carbonates (Na-REE-C) if Na>>K, or monazite if K>>Na.
- Residual brine melt (BM) phase is rich in Na, K, REE, Sr, Ba, S, Cl, F.
- Carbonatite melt progressively evolves to brine-melt composition
- Fractionation of dolomite removes Mg from melt
- Where Si activity is high, REE sequestered into apatite
- Fractionation of calcite, apatite & magnetite removes Ca, Fe^{3+} & P from melt

Si-bearing carbonatite Wallrock Si assimilation?
Alkali-rich carbonatite

Carbonatite from shallow immiscibility
Direct mantle carbonatite

A — Mantle controls & tectonics

Post-collision extension
Continental rifting
Shallow immiscibility
Continental crust
Direct mantle carbonatite
Deep immiscibility
Metasomatised SCLM
Subducting slab
F, Cl & S as fluxes
EM2
REEs Modern fertilisation
Ancient fertilisation
EM1
Plume input?
HIMU

metamorphic or hydrothermal processes, although these may modify mineral assemblages or chemical signatures (overprinting) and result in local REE redistribution. A particularly extreme example is the Bayan Obo deposit (China) where Nd isotope compositions of monazite crystals reflect initial Mesoproterozoic carbonatite magmatism, followed by protracted 1 Gy history of later fluids recording recrystallisation and locally limited remobilisation of REEs (Song et al. 2018). Owing to the fact that carbonatites can seemingly be derived via more than one route, yet all routes can lead to a REE deposit, we consider processes that modify carbonatite melts after their generation to be the dominant controls for generating most carbonatite-associated REE deposits. That is, enrichment of REEs in the carbonatite source is needed, particularly for the largest economic deposits, but must be accompanied by one or more key processes during carbonatite evolution.

IGNEOUS FRACTIONATION (>600 °C)

Crystallisation of REE-poor minerals from a carbonatite melt is crucial for REE enrichment in the residual melt. Field relationships and experimental evidence on carbonate minerals indicate that a carbonatite melt typically first crystallises calcite, followed by dolomite, then Fe-rich dolomite (sometimes referred to as ankerite in the carbonatite literature, even if not always strictly ankerite according to its composition), and, locally, siderite (FIG. 1B). This crystallisation sequence is manifested in the concentric rings of many carbonatite complexes, where an Fe-rich and REE-rich dolomite carbonatite occupy a central position which is enveloped by REE-barren Fe-poor dolomite or calcite carbonatite (e.g. Chilwa Island in Malawi; Karasug in Russia) (Prokopyev et al. 2016; Dowman et al. 2017). The observed sequence of calcite followed by dolomite followed by ankerite is consistent with carbonatite differentiation experiments (Anenburg et al. 2020b) and with the predicted stability ranges of Ca-, Mg-, and Fe-carbonates derived from thermodynamic data.

It is important to be aware that the compositions of different carbonatite rocks (calcite carbonatite, dolomite carbonatite, siderite carbonatite) are not representative of a carbonatite melt. Rather, these are crystal cumulates of an alkali- and volatile-bearing carbonatite melt. The most compelling evidence for the high alkali content of carbonatite melts is the presence of fenites—metasomatised rocks predominantly composed of Na–K-silicates (Elliott et al. 2018)—which occur around almost all carbonatite complexes. In addition, Na-rich carbonatite melt inclusions are common in minerals hosted in Na-poor carbonatite rocks (e.g., Prokopyev et al. 2016), with experimental evidence further supporting alkali-rich carbonatite melts in equilibrium with alkali-poor cumulates (Weidendorfer et al. 2017; Anenburg et al. 2020b).

The REEs are incompatible (i.e., they partition into the liquid rather than solid) during high-temperature igneous crystallisation of carbonatite melts. The principal early crystallising minerals are magnetite, olivine, and clinopyroxene, all of which exclude REEs, and particularly the LREEs, from their crystal structures. Once the melts are calcite-saturated and voluminous carbonatite cumulates form, the REEs are strongly enriched in the liquid owing to their incompatibility in calcite (Chebotarev et al. 2019). Additionally, fluorapatite is common throughout the entire crystallisation sequence of carbonatite liquids. Although REEs can be compatible in (i.e., partition into) fluorapatite, with REE uptake controlled by coupled substitutions with either Na^+ or Si^{4+}, formation of REE-fluorapatite is unlikely in high-temperature carbonatite systems. Experimental evidence indicates that high-temperature fluorapatite will not concentrate REEs regardless of Na contents in the melt (Anenburg et al. 2020b). Furthermore, silica activities in high-temperature carbonatite melts are not typically high enough to allow REEs + Si substitution into fluorapatite. Only in rare circumstances, such as carbonatite intrusion into silica-saturated rocks (e.g., granites) and exceptional silica assimilation efficiency, can substantial incorporation of REEs into early high-temperature fluorapatite occur. In these unusual cases, fluorapatite can be the REE ore in its own right (e.g., the Nolans Bore fluorapatite vein deposit in the Northern Territory, Australia) (Anenburg et al. 2020a).

BRINE-MELT STAGE (600–400 °C)

As carbonatite melts evolve to more Mg- and Fe-rich compositions, several components are retained in the melt, such as Na^+, K^+, H_2O, sulfate, chloride, and fluoride, and these act as fluxes (Prokopyev et al. 2016; Weidendorfer et al. 2017). These fluxes strongly depress the solidus and the melt transitions to a Na,K-carbonate ± chloride ± sulfate brine with no clear boundary or distinct exsolution of fluids, as evident by a lack of immiscible carbonatite melts and REE-rich alkali brines in studies of fluid and melt inclusions (Xie et al. 2015; Walter et al. 2021). Limited fluid and melt inclusion homogenisation data point to a transition from 650 °C down to ~400 °C (Prokopyev et al. 2016; Walter et al. 2021). This stage is commonly referred to as the "magmatic–hydrothermal transition", but here we prefer the term "brine-melt", originally introduced by Prokopyev et al. (2016), to emphasise the lack of solute-rich volatile exsolution at this stage and to avoid the magmatic/hydrothermal dichotomy inherited from silicate magmatic systems. This continuous transition of high-temperature carbonatitic magma to a lower-temperature brine-melt does not preclude the presence of an additional commonly observed immiscible aqueous fluid phase, which at sufficiently high pressures and temperatures can be highly saline (Walter et al. 2021). However, REEs do not significantly partition into this aqueous phase and remain dissolved in the brine-melt (Song et al. 2016).

At this stage, REEs are sufficiently concentrated in the residual brine-melt to form REE-minerals (top of FIG. 1B), such as monazite and alkali REE carbonates from the burbankite and carbocernaite groups (Zaitsev et al. 2002; Anenburg et al. 2020b). These alkali REE carbonate minerals are not in the lexicon of the average mineralogist for good reason—they are extremely ephemeral. However, in a few localities, they are preserved as euhedral or subhedral phases, associated with carbonate, or as inclusions in dolomite, fluorapatite, and perovskite (Zaitsev et al. 2002; Moore et al. 2015). Similar carbon and oxygen isotope values for burbankite and its host carbonate minerals demonstrate that they are derived from the same source (Zaitsev et al. 2002). Burbankite also occurs in REE-rich dolomite-carbonatite pegmatites, forming large euhedral hexagonal crystals exhibiting spectacular unidirectional crystallisation. These pegmatites locally form some of the highest REE concentrations found anywhere on the planet and can reach up to several metres in width (FIG. 2A).

In cases where a carbonatite melt is silica-rich, perhaps through melt–wall rock interaction (Xie et al. 2015; Giebel et al. 2019), crystallisation of alkali-silicates, such as phlogopite or aegirine, can suppress the formation of alkali REE carbonate minerals, leading to high-temperature pseudomagmatic bastnäsite or monazite instead (Anenburg et al. 2020b). Fluorapatite forming at the brine-melt stage can incorporate substantial LREE contents owing to the greater availability of charge-balancing Na^+ from the alkaline brine-melt. Furthermore, the low temperature leads to an increase in silica activity, permitting substitution of the Si + REE "britholite" component into fluorapatite (Chakhmouradian et al. 2017; Anenburg et al. 2020b). Often, this brine-melt fluorapatite has a texture suggesting that it forms by hydrothermal replacement of earlier
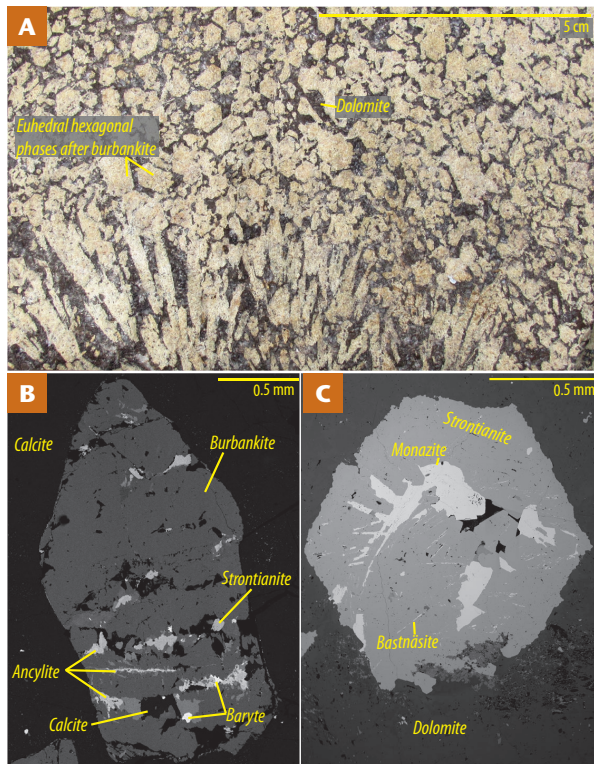
FIGURE 2 Euhedral burbankite formation and replacement. (**A**) Radiating hexagonal pseudomorphs after burbankite, composed of polycrystalline aggregates of bastnäsite, baryte, strontianite, synchysite, dolomite, and quartz. From Wigu Hill (Tanzania). PHOTO: PETE SIEGFRIED. (**B**) Back-scattered electron image of burbankite, partially pseudomorphed to an assemblage of REE carbonates, strontianite, and baryte. From Shaxiongdong (China). SAMPLE COURTESY OF JINDRICH KYNICKY. (**C**) Back-scattered electron image of a fully altered hexagonal pseudomorph, likely to be after burbankite, composed of monazite, strontianite, and baryte. From Kangankunde (Malawi).

REE-poor fluorapatite (Chakhmouradian et al. 2017), but it can also form as thin veins and stringers (Broom-Fendley et al. 2017).

In contrast to LREEs, HREEs are still largely incompatible during the brine-melt stage, and remain dissolved in the residual brine-melt (Anenburg et al. 2020b). The highly evolved brine-melt has extremely low viscosity and low wetting angles and can infiltrate wall rock. This process removes HREEs from the carbonatite body, further contributing to the extreme fractionation of LREEs from HREEs typical of carbonatites. These alkali fluids are highly corrosive and, once in contact with the surrounding silicate rocks, will strongly alter them into fenite (Elliott et al. 2018). Fenite alteration zones can extend up to several kilometres from their host carbonatites, and occasionally contain sub-economic amounts of REE-bearing minerals, such as xenotime, Y-enriched fluorapatite, and REE-(fluor) carbonates with elevated HREE/LREE ratios (Andersen et al. 2016; Broom-Fendley et al. 2017; Dowman et al. 2017).

HYDROTHERMAL FLUID

During late-stage evolution of carbonatite systems, the brine-melt evolves into something resembling a more conventional hydrothermal fluid, with salinity diluted by an increasing H_2O content. Fluid inclusions and stable isotope data point to a diverse range of evolutionary paths, depending on carbonatite emplacement depth, as well as the effects of cooling, mixing, and fluid–rock reaction (Walter et al. 2021). Carbonatite-derived fluids show a temperature of up to 400 °C, whereas externally derived fluids are typically cooler (up to 250 °C). In particular, the aqueous and carbonic components may exsolve, or boil, from the carbonatite melt, possibly many times, leading to a complex mixture of low-density and high-density inclusions ("vapour" and "liquid", respectively). Boiling can lead to fracturing of the surrounding country rock, facilitating further dilution of the carbonatite-derived fluid by meteoric water (Walter et al. 2021).

Whether wholly derived from the carbonatite brine-melt or mixed with a meteoric component, hydrothermal fluids can back-react with alkali–REE-carbonates, such as burbankite and carbocernaite. In this process, alkalis are removed and the original minerals are replaced by an assemblage of less-soluble REE-(fluor)carbonates (ancylite, synchysite, parisite, bastnäsite) or monazite, accompanied by strontianite, baryte, and, locally, low-Sr calcite and quartz (FIGS. 2B, 3A–B) (Andersen et al. 2017; Giebel et al. 2017). This replacement reaction results in a significant reduction in volume, propagating further hydrothermal input and dissolution of alkali–REE-carbonates. Preservation of alkali–REE-carbonates is scarce and only observed in a handful of localities. In most cases, evidence for the formation of burbankite is indicated only by the preservation of hexagonal pseudomorphs, now containing a variety of Ca, REE, Ba, and Sr minerals (FIG. 2B–C). If burbankite, carbocernaite, or any other alkali–REE-carbonates did not form euhedral phases during the brine-melt stage, then evidence for their former presence is often erased, with only scarce mineral inclusions offering any hint to the former presence of these minerals (FIG. 3C). The local abundance of quartz in hydrothermal assemblages attests
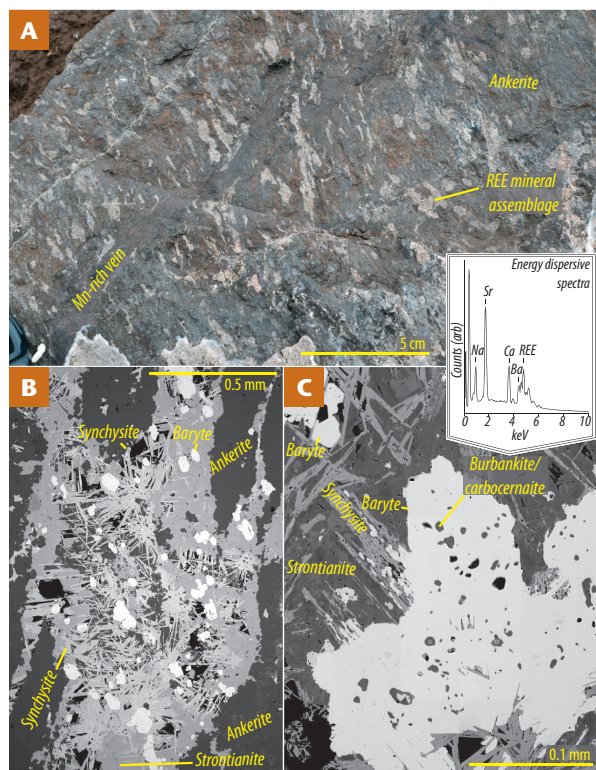

FIGURE 3 'Typical' rare earth element (REE) mineralisation in ankerite carbonatite. (**A**) Ankerite carbonatite from Songwe Hill (Malawi). Note the striped texture, consisting of pinkish aggregates of synchysite, strontianite, and baryte, hosted in a dark groundmass of ankerite. Veins of Mn-rich material cross-cut the sample, where the REEs are residually enriched through carbonate dissolution. (**B**) Back-scattered electron image from sample in FIGURE 3A, composed of REE-(fluor)carbonates, in this case synchysite-(Ce), with strontianite and baryte. (**C**) Preserved burbankite/carbocernaite inclusions in baryte, demonstrating the prior importance of a Na–REE-carbonate phase. (**INSET**) Energy dispersive spectra of a burbankite/carbocernaite inclusion.

to the substantial involvement of externally derived fluids, as silica solubility is low in earlier carbonatite magmas and brine-melts.

It is the REE-(fluor)carbonate ± monazite mineral assemblage that is most typical in mineralised carbonatites, commonly occurring as stringers or vug-like accumulations (Fig. 3). The vug-like mineralisation habit, in particular, has led many authors to interpret such REE mineralisation as the result of direct precipitation from a hydrothermal fluid. Although it is possible for REE-carbonates to form without an alkali precursor, carbonatite liquids are invariably alkaline and crystallisation of alkali-free carbonates as primary precipitates is unlikely to be the principal mineralisation process in nature. Therefore, we propose that such mineralisation results from the in situ replacement of the alkali–REE-carbonates (such as burbankite and carbocernaite), which were formed during the brine-melt stage, by a less-briny and more mixed hydrothermal fluid that existed during the post-magmatic stages of the carbonatite system, diluted by external fluids (Fig. 1C). In other words, low-temperature fluids do not directly precipitate REE minerals but re-crystallise existing, highly soluble, alkali–REE-carbonates into less soluble, often calcic, phases.

Although we propose here that REE enrichment reaches its apex during the brine-melt stage, it is evident that REEs can be mobilised on the local scale by low-temperature hydrothermal fluids, resulting in further redistribution of the REEs (Broom-Fendley et al. 2016). Rare earth element minerals can be related to the dissolution of other primary REE-bearing minerals, such as fluorapatite or calcite (Chakhmouradian et al. 2017; Giebel et al. 2017; Cangelosi et al. 2020; Ying et al. 2020). The REEs contained within these minerals are then reprecipitated as REE minerals in close proximity to the original host (Fig. 4). Depending on the composition of the low-temperature fluid, protracted fluid fluxing can lead to fractionation of the light from the heavy REEs owing to the preferential stability of LREE–chloride complexes in the fluid (Migdisov et al. 2016). Dissolution–reprecipitation of REE-bearing minerals is likely to occur on a small scale in all cases of carbonatite-hosted REE mineralisation, especially where breakdown of magmatic calcite is evident. However, as carbonates only contain trace amounts of REEs, even dissolution of large amounts of calcite can only account for a small volume of REE mineralisation (Ying et al. 2020).

The C and O isotope composition of primary igneous carbonatite is often considered to fall within ranges of $\delta^{18}O$ from 6‰ to 10‰ (VSMOW, or Vienna Standard Mean Ocean Water) and $\delta^{13}C$ from −8‰ to −4‰ (VPDB, or Vienna Pee Dee Belemnite). Similar values can be obtained for calcite and dolomite associated with REE mineralisation, indicating crystallisation from the carbonatite melt or brine-melt occurs at a sufficiently high temperature that there is minimal isotopic fractionation between these minerals and their parental melt or brine-melt (Zaitsev et al. 2002). Interaction of these minerals with hydrothermal fluids causes complex shifts in C and O isotope compositions, because the carbonates are subject to recrystallisation by circulating low-temperature fluids that post-date the brine-melt stage (Moore et al. 2015; Doroshkevich et al. 2016). This results in a wide spread of isotopic compositions, especially to higher $\delta^{18}O$, attributable to interaction with cooling deuteric or basinal fluids. However, it is rarely clear whether these higher $\delta^{18}O$ values are attributable to REE mineralisation or if they are a result of subsequent recrystallisation: reported C and O isotope data are often overly reliant on bulk analyses that blur together compositions of multiple minerals of different origin. Dissolution of primary carbonates, and the formation of late, Sr-poor calcite is common in carbonatites on a range of scales (e.g., Fig. 4B). Careful analyses of carbonates using in situ
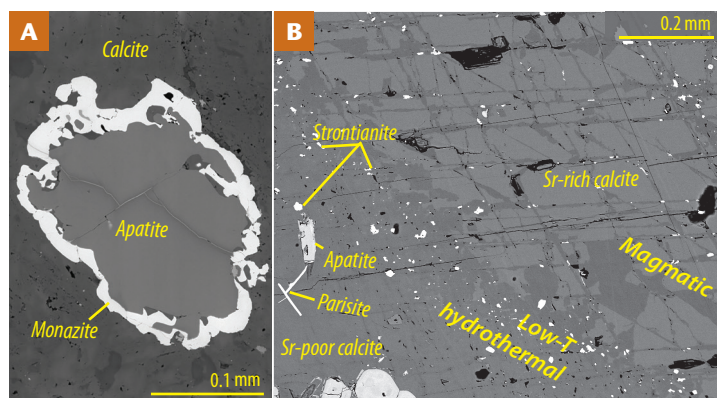
methods on properly mapped minerals (e.g., using cathodoluminescence or high-contrast backscattered electron imaging) (Anenburg et al. 2020a) are crucial to untangle primary magmatic signatures from later recrystallisation.

WEATHERING

As with hydrothermal dissolution–reprecipitation, weathering can also result in the breakdown of primary REE phases and the transport of REEs into newly formed REE phases. Indeed, on a local scale, it can be difficult to differentiate the two processes. Protracted weathering increases REE grade (i.e., whole-rock concentration) through dissolution of carbonate and so chemically removing the bulk of the rock (e.g., Andersen et al. 2017). In some cases, this can make the difference between whether mining is economical or not, such as the case of the Mount Weld (Western Australia), Tomtor (Russia), and Zandkopsdrift (South Africa) carbonatite-derived laterites. While advantageous, protracted weathering can also result in the formation of complex Al–REE-phosphates (e.g., florencite), which are currently not suitable for economic extraction.

UNKNOWNS AND FUTURE STUDY

While we have tried to summarise here the key steps we consider important to forming carbonatite-hosted REE deposits, the model (Fig. 1) is by no means complete. The variables that influence carbonatite evolution predictions are too sensitive and too numerous to find a model that fits perfectly in every case. For every example we can think of where the above mineralisation mechanism fits, it is possible to think of one or two more where it does not.

As an example, crystallisation of alkali–REE-carbonates can also occur in association with calcite carbonatite (e.g., Bear Lodge) (Moore et al. 2015), diverging from the process of late-stage REE concentration in dolomite and ankerite carbonatites we outlined above. Additionally, the calcite–dolomite–ankerite sequence may only be apparent in small carbonatites where the entire crystallisation sequence is visible at the surface.

Owing to the poor preservation of minerals which form during the brine-melt stage, the temperature and composition of such mineralising fluids is challenging to quantify and still represents a significant knowledge gap in our understanding of REE mineralisation. Detailed study of

primary fluid inclusions in LREE-rich apatite linked to the brine-melt stage may be a fruitful avenue to further clarify the fluid temperature and composition.

Consider this paper to be a call to focus greater attention to the brine-melt stage in carbonatites, and on understanding the formation of alkali–REE-carbonates (as well as rare primary monazite and REE-fluorcarbonates), rather than the post-magmatic processes which we consider as mere recrystallisation of alkali–REE-carbonates. Hydrothermal fluids do not transport the LREEs in carbonatites on a significant scale but simply muddy the water with respect to our understanding of how REE-deposits in carbonatite form. The conditions at which a carbonatite melt transitions to a brine-melt and then a hydrothermal fluid, however, remain poorly constrained, as are the finer details regarding which phases are crystallised to make a residual REE-rich ferroan dolomite carbonatite melt. Any future work which promotes the fundamental understanding of REE deposit formation in carbonatites and its regional geological context will likely be useful for exploration and exploitation of these valuable resources, ensuring that metal supply for zero-emission technology is met.

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