Nd and Sr isotopic composition of rare earth element mineralized carbonatites

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Summary

For nearly 50 years, carbonatites have been the primary sources of niobium and rare earth elements (REEs), particularly the light REEs including La, Ce, Pr, and Nd. In addition, carbonatites may be enriched in other critical elements and have the potential to be future sources. Currently, only five of the more than 500 known carbonatites in the world are being mined for REEs: Bayan Obo (Inner Mongolia, China); Maoniuping (Sichuan, China); Dalucao (or Daluxiang, Sichuan, China); and Mountain Pass (California, USA), and the carbonatite-derived laterite at Mount Weld (Australia). To achieve ore-grade REE enrichment, initial carbonatitic magmas require an adequate endowment of REEs and need to evolve in ways for these elements to concentrate in REE-bearing mineral phases.

Radiogenic isotope studies of carbonatites clearly point to a mantle origin, but a wide range in isotopic compositions has led to contrasting views about the specific mantle reservoir(s) that sourced carbonatites. In this study we use the neodymium and strontium isotopic compositions of a suite of mineralized carbonatites to establish the nature of the source magmas. We examine samples that span a wide range in age (~23 Ma to 1385 Ma), Nd concentrations (3720 to 32,900 ppm), and Sr concentrations (2290 to 167,900 ppm). Our Nd and Sr isotopic data include multiple samples from Mountain Pass (USA; $\varepsilon_{\mathrm{Nd\,i}}$ = -3.1 to -5.4, $\mathrm{Sr_i}$ = 0.70512 to 0.70594), Elk Creek (USA; ~$\varepsilon_{\mathrm{Nd\,i}}$ = 1.7, $\mathrm{Sr_i}$ = 0.7035), and Maoniuping (China; $\varepsilon_{\mathrm{Nd\,i}}$ = -4.1 and -4.2, $\mathrm{Sr_i}$ = 0.70627 and 0.70645), and one sample each from Bear Lodge (USA; $\varepsilon_{\mathrm{Nd\,i}}$ = 0.1, $\mathrm{Sr_i}$ = 0.70441), Kangankunde (Malawi; $\varepsilon_{\mathrm{Nd\,i}}$ = 3.3, $\mathrm{Sr_i}$ = 0.70310), Adiounedj (Mali; $\varepsilon_{\mathrm{Nd\,i}}$ = -0.1, $\mathrm{Sr_i}$ = 0.70558), and Mushgai Khudag (Mongolia; $\varepsilon_{\mathrm{Nd\,i}}$ = -1.3, $\mathrm{Sr_i}$ = 0.70636). Isotopic data from two producing carbonatite REE deposits (Mountain Pass and Maoniuping) have broadly similar isotopic compositions ($\varepsilon_{\mathrm{Nd\,i}}$ = -3.1 to -5.4 and $\mathrm{Sr_i}$ = 0.7051 to 0.7065), and these compositions point to a carbonated source in the lithospheric mantle. Mineralized but unmined carbonatites have higher Nd initial isotopic compositions ($\varepsilon_{\mathrm{Nd\,i}}$ = -1.3 to 3.3) and a wider range in Sr isotopic compositions ($\mathrm{Sr_i}$ = 0.70310 to 0.70637), but these data are consistent with a lithospheric mantle reservoir.

1. Introduction

Carbonatites are volumetrically rare compared to silicate igneous rocks, but they have become important exploration targets because of their enrichments in critical elements. For nearly 50 years, carbonatites have been the primary source of rare earth elements (REEs), particularly the light REEs (LREEs) that include La, Ce, Pr, and Nd. Although most carbonatites contain elevated concentrations of REEs, only a few have sufficient quantities to warrant economic exploitation. Carbonatites that are currently being mined for REEs are Bayan Obo (Inner Mongolia, China), Maoniuping (Sichuan, China), Dalucao (or Daluxiang, Sichuan, China), and Mountain Pass (California, USA), and the carbonatite-derived laterite at Mount Weld (Australia). Most of the more than 500 carbonatites known worldwide are enriched in REEs but lack economic concentrations (Woolley and Kjarsgaard, 2008). To become producers, targets need to have adequate grade and tonnage, and mineralogical characteristics that would enable economically viable processing.

Carbonatites are composed of greater than 50 vol.% primary carbonate minerals, mainly calcite and/or dolomite. They contain the highest concentrations of REEs of any igneous rocks. Although substantial petrogenetic research has focused on the origin of non-mineralized carbonatites, the origin of carbonatitic magmas remains controversial. Radiogenic and stable isotopic studies show that the parental magmas of carbonatites are derived from mantle melts (Bell and Blenkinsop, 1989), but the nature of the initial melts, the processes responsible for generating carbonatitic magmas, and how the magmas evolve to form the observed rock types are still debated. In general, carbonatite magmas evolve by fractional crystallization and the gravitational separation of early-formed crystals (Twyman and Gittins, 1987). Carbonatite magmas may contain a variety of volatile components including CO_2, H_2O, Cl, F, and S. As crystallization progresses, volatiles become enriched in the residual magma, along with various incompatible elements, and may exolve into a separate fluid phase. Fluid inclusions and fenite alteration (alkali metasomatism) provide clear evidence for the separation of a volatile-rich fluid phase.

To achieve ore-grade REE enrichment, the initial carbonatite magma needs an adequate endowment of REEs and must evolve in ways that REEs are concentrated in REE-bearing mineral phases: fluorocarbonates (bastnäsite, parisite, and synchysite); hydrated carbonates (ancylite); and phosphates (monazite and apatite). The primary ore mineral exploited at carbonatite-hosted REE mines is bastnäsite, which contains approximately 75 wt.% RE_2O. In most economic deposits bastnäsite is coarse grained, which allows for relatively straightforward processing. Bastnäsite can crystallize both directly from magmas and from evolved fluids.

The Mountain Pass REE deposit, the world's leading source of REEs from 1965 to 1995, is hosted by the Sulphide Queen carbonatite, a composite, tabular body made up of REE-bearing sövites and beforsites. Calcite and dolomite, in varying proportions, are the primary mineral phases, with subordinate and variable amounts of barite, celestine, strontianite, cerussite, phlogopite, and fluorite (Castor, 2008; Mariano and Mariano, 2012). Bastnäsite is the primary REE mineral, along with parisite, synchysite, and monazite, and lesser allanite, ancylite, apatite, cerite, florencite, hydroxylbastnäsite, and sahamalite (Castor and Nason, 2004; Castor, 2008; Mariano and Mariano, 2012). Barite and bastnäsite are generally the second, third, or fourth most abundant mineral phases in different parts of the Sulfide Queen carbonatite. Other REE-rich phases are present generally in trace amounts, but locally can make up a few percent of the rock. Bastnäsite at Mountain Pass is commonly coarse grained and displays primary igneous textures (Fig. 1). Textural evidence shows that bastnäsite and parisite crystallized with euhedral morphology with calcite, barite, and dolomite, and thus probably formed as primary magmatic phases (Mariano and Mariano, 2012). Samples used in this study include a suite of ore carbonatite and individual bastnäsite minerals.

Two actively mined carbonatite-related REE deposits (Maoniuping and the Dalucao) are in the Mianning-Dechang REE belt, Sichuan Provence, China. Surpassed only by Bayan Obo, Maoniuping is the second largest REE deposit in China. Unlike the Mountain Pass deposit, where the REE mineralization is in the carbonatite body, the REE mineralization at Maoniuping is mainly in pegmatite and stockwork veins and minor breccias. In drill core, disseminated REE mineralization in the carbonatite has been identified (Xie et al., 2015). Medium- to coarse-grained bastnäsite is the primary ore mineral along with minor brunsite, chevkinite, and cerianite. The pegmatitic veins consist of calcite and barite with coarse-grained bastnäsite, as well as fluorite with local aegirine and augite, and minor amounts of microcline arfvedsonite, biotite, apatite, quartz, and sulfides (Xu et al., 2008, 2012). In this study individual bastnäsite minerals were separated from vein and breccia ores.

Fig. 1. Plane-polarized light photomicrograph of Mountain Pass black ore bastnäsite (Bast) in ferruginous calcite carbonatite displaying primary igneous texture. Field of view is 5 mm wide.

In contrast to coarse-grained bastnäsite as the primary REE mineral in REE ore deposits, many unmined but REE-enriched carbonatites contain late-stage, fine-grained fluorocarbonates (bastnäsite, parisite, and synchysite) and phosphates (monazite and apatite). The fluorocarbonates are generally described as very fine grained (1-100 μm), forming syntaxial intergrowths as bundles, clusters, or aggregates of radiating needles (Fig. 2). The crystals may line miarolitic cavities or form at the expense of primary minerals. These REE mineral phases are commonly attributed to the late-stage magmatic-hydrothermal phase of carbonatite evolution. As carbonatite magmas crystallize, the REEs may behave as incompatible elements that remain in the magma. Late in the magmatic evolution, the residual magma becomes enriched in incompatible elements (including REEs) and volatiles, and a volatile-rich fluid may exsolve. These REE-rich exsolved fluids may be responsible for late-stage REE enrichment, or the enrichment may result from late-stage fluids remobilizing REEs from earlier crystallized minerals.

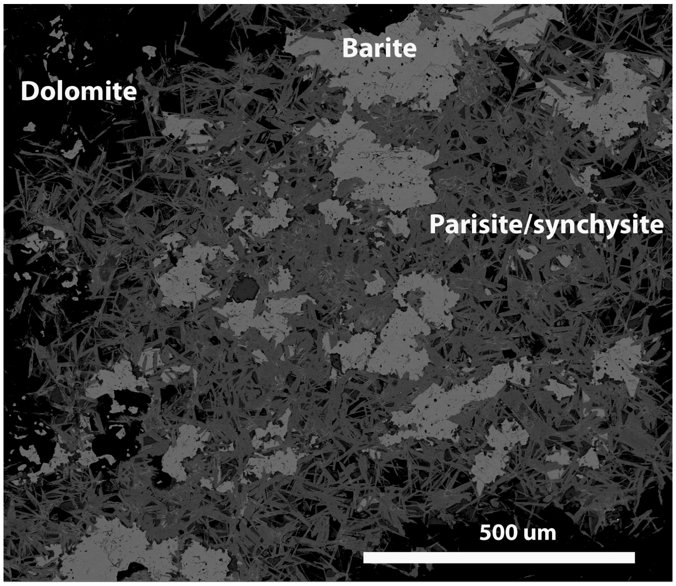

Fig. 2. SEM backscattered electron image of REE fluorocarbonates in barite beforsite unit of Elk Creek carbonatite.

For this study, we analyzed samples from unmined REE-enriched carbonatites at Elk Creek and Bear Lodge (USA), Adiounedj (Mali), Kangankunde (Malawi), and Mushgai Khudag (Mongolia). The Elk Creek samples are a representative suite of carbonatite lithologies including apatite beforsite, magnetite beforsite, and barite beforsite. A drill-core sample from Bear Lodge is from a hydrothermal vein containing ancylite-strontianite pseudomorphs and minor fluorite from the unoxidized zone. The sample analyzed from Adiounedj is a ferrocarbonatite consisting of calcite, fluorite, apatite, Fe-oxide minerals, and synchysite. The sample from Kangankunde is a ferrocarbonatite with strontianite, monazite, apatite, and barite. The sample from Mushgai Khudag, Mongolia was collected from the apatite-magnetite body and can be termed ‘apatitite’ because it consists of >50 vol.% apatite, with celestine, gypsum, and lesser monazite. The fine-grained monazite and celestine appear to be supergene products that crystallized during weathering.

2. Results

Most isotopic studies of carbonatites have focused on constraining the origin of carbonatitic magmas, with only a few recent studies dedicated to the nature of mineralization. Bell and Blenkinsop (1989) and Bell (1998) summarized much of the radiogenic isotopic work conducted to determine the origin of carbonatites and associated alkaline rocks. The radiogenic isotopic data document that the carbonatites are of mantle origin, but the range in isotopic data suggests that the subcontinental upper mantle is inhomogeneous (Bell and Blenkinsop, 1989).

We determined the Nd and Sr isotopic compositions of a suite of carbonatites with varying degrees of REE enrichment (Fig. 3). Mineralized carbonatite samples evaluated in this study are from four continents and span a wide range in age (~23 Ma to 1385 Ma), Nd concentrations (3720 to 32,900 ppm), and Sr concentrations (2290 to 167,900 ppm). Our new Nd and Sr isotopic data include multiple samples for Mountain Pass (USA; $\varepsilon_{\mathrm{Nd}\ i}$ = -3.1 to -5.4, Sr_i = 0.70512 to 0.70594), Elk Creek (USA; ~$\varepsilon_{\mathrm{Nd}\ i}$ = 1.7, Sr_i = 0.7035), and Maoniuping (China; $\varepsilon_{\mathrm{Nd}\ i}$ = -4.1 and -4.2, Sr_i = 0.70627 and 0.70645), and one sample each from Bear Lodge (USA; $\varepsilon_{\mathrm{Nd}\ i}$ = 0.1, Sr_i = 0.70441), Kangankunde (Malawi; $\varepsilon_{\mathrm{Nd}\ i}$ = 3.3, Sr_i = 0.70310), Adiounedj (Mali; $\varepsilon_{\mathrm{Nd}\ i}$ = -0.1, Sr_i = 0.70558), and Mushgai Khudag (Mongolia; $\varepsilon_{\mathrm{Nd}\ i}$ = -1.3, Sr_i = 0.70636). In addition to the mineralized carbonatites, we analyzed the underlying carbonatite at Mount Weld (Australia; $\varepsilon_{\mathrm{Nd}\ i}$ = 0.7, Sr_i = 0.70197) and a carbonatite sample from Kerimasi (Tanzania; $\varepsilon_{\mathrm{Nd}\ i}$ = -0.2, Sr_i = 7.0402).

Our results are similar to previously published data from the same localities. For example, Nelson et al. (1988) report $\varepsilon_{\mathrm{Nd}\ i}$ and Sr_i values of 3.1 and 0.7031, respectively, for a carbonatite sample from Kangankunde, Malawi, whereas we measured $\varepsilon_{\mathrm{Nd}\ i}$ and Sr_i values of 3.3 and 0.70310 for a carbonatite sample from the same locality. Moore et al. (2015) report $\varepsilon_{\mathrm{Nd}\ i}$ (0.5) and Sr_i (0.70462) for an ancylite-carbocernaite sample at Bear Lodge, and we report similar $\varepsilon_{\mathrm{Nd}\ i}$ (0.1) and Sr_i (0.70441) values for a drill-core ancylite vein sample. Xu et al. (2003) published Nd and Sr isotopic data for fluorite gangue minerals from Maoniuping ($\varepsilon_{\mathrm{Nd}\ i}$ = -3.7 to -4.3, Sri = 0.70603 to 0.70624).

Our results, together with a literature compilation, show that most unmineralized carbonatites and mineralized but unmined carbonatites have $\varepsilon_{\mathrm{Nd}\ i}$ values >-1 and Sr_i <0.705. These two groups overlap in values and do not form individual fields on a $\varepsilon_{\mathrm{Nd}\ i}$ - Sr_i diagram. In contrast, samples from two REE carbonatite ore deposits (Mountain Pass and Maoniuping) have distinctly different isotopic compositions, with $\varepsilon_{\mathrm{Nd}\ i}$ values from -3.1 to -5.4 and Sr_i from 0.7051 to 0.7065. These isotopic compositions clearly point to a carbonated source in

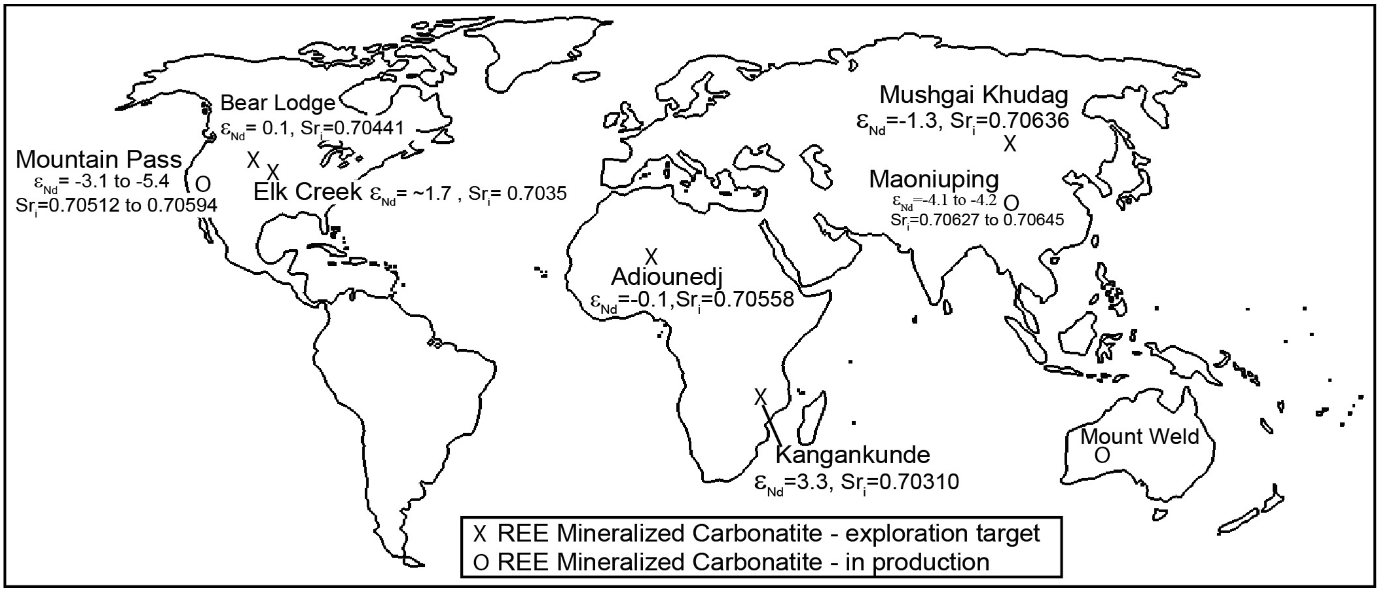

Fig. 3. Map displaying initial neodymium ($\varepsilon_{\mathrm{Nd}}$) and strontium ($\mathrm{Sr}_i$) isotopic compositions for samples analyzed in this study.

the lithospheric mantle. Mineralized but unmined carbonatites have higher Nd initial isotopic compositions ($\varepsilon_{Nd\,i}$ = -1.3 to 3.3) and a wider range in Sr isotopic compositions (Sr_i = 0.70310 to 0.70637), but these data are consistent with the involvement of a lithospheric mantle reservoir as well.

Acknowledgments

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