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# Rare Earth Mineralization in Igneous Rocks: Sources and Processes

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**D**eposits of rare earth elements (REEs) in igneous rocks have played an instrumental role in meeting the growing industrial demand for these elements since the 1960s. Among the many different igneous rocks containing appreciable concentrations of REEs, carbonatites and peralkaline silicate rocks are the most important sources of these elements, both historically and for meeting the anticipated growth in REE demand. The contrasting geochemical and mineralogical characteristics of REE mineralization in carbonatites, peralkaline feldspathoid rocks, and peralkaline granites reflect different sources and evolutionary pathways of their parental magmas, as well as differences in the extent of postmagmatic reworking of primary REE minerals by hydrothermal fluids.

**KEYWORDS:** rare earth elements, lanthanides, yttrium, mineral deposits, carbonatites, nepheline syenites, granites

## INTRODUCTION

Out of some 50 advanced rare earth exploration projects currently active outside China, 20 target carbonate igneous rocks (carbonatites) or their weathering products, whereas at least 13 other projects are focused on various alkaline silicate rocks. These statistics reflect the importance of igneous deposits in the economics of rare earth elements (REEs). Indeed, between the 1960s and 1995, these deposits accounted for over 50% of the global REE production. In the early 1990s, 30–35% of the total production of ca 50,000 tonnes of total rare earth oxides (REOs) came from the carbonatite-hosted Mountain Pass deposit in California, USA, 5–10% from Chinese carbonatites, and 10–15% from loparite mines in nepheline syenites at Lovozero, Russia. The present paper introduces the most significant types of igneous REE deposits and provides an overview of their sources, their evolution, and their geological, geochemical, and mineralogical characteristics.

Rare earth deposits in igneous rocks can be grouped into five distinct categories differing in the provenance and evolution of the magma and in the rock types hosting mineralization: (1) carbonatites, (2) peralkaline silica-undersaturated rocks, (3) peralkaline granites and pegmatites, (4) pegmatites associated with sub- to metaluminous granites, and (5) Fe oxide–phosphate deposits. We will

place emphasis on the first three categories because they are far more important from a practical standpoint. To complement the information provided elsewhere in this issue by Kynicky et al. (2012), Mariano and Mariano (2012), and Williams-Jones et al. (2012), we will focus on localities outside China and North America.

## TECTONIC SETTINGS, SOURCES, AND EVOLUTION OF REE-RICH MAGMAS

The majority of igneous REE deposits occur in intracontinental, anorogenic, extensional settings formed by pull-apart tectonics or asthenospheric upwelling. Here, thinning of the continental lithosphere facilitates decompressional melting of the mantle and emplacement of a wide spectrum of magmas, including alkali-rich, silica-undersaturated types relevant to the present discussion (carbonatite, nepheline, and phonolite). These magmas often form extensive igneous provinces associated with rifts, grabens, crustal lineaments, and transcurrent fault systems (see Figure 5 in Chakhmouradian and Wall 2012 this issue). In some cases, these structures were activated episodically, giving rise to deposits of very different age within the same province; for example, the western branch of the East African Rift comprises carbonatite-hosted deposits of Mesoproterozoic, Ediacaran, and Cretaceous age (Woolley 2001).

Comparison with oceanic basalts (FIG. 1) shows that silica-undersaturated rocks from extensional settings are significantly enriched in light lanthanides and characterized by a greater degree of light REE (LREE)–heavy REE (HREE) fractionation  $[(La/Yb)_N \geq 20]$ , as compared to  $\leq 20$  in basalts, where values are normalized to primitive mantle, implying that their parental magmas were derived by very low-degree (<1%) partial melting of the subcontinental upper mantle. Element-partitioning models show that the geochemical characteristics of anorogenic magmas require



Mines at Khibiny (north-western Russia) have produced over 620 million tonnes of apatite concentrate since 1929. Historically, REEs have not been recovered from this concentrate, and 50,000–60,000 tonnes of REEs wind up in fertilizer-plant tailings annually. The current market situation has stimulated interest in the Russian mining industry to develop a commercially viable technology for extracting REEs from the Khibiny ore.

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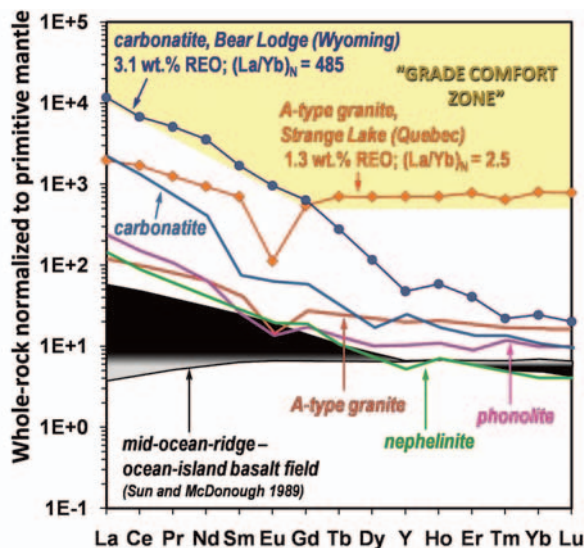


**FIGURE 1** Average compositions of various anorogenic magmas (see online supplementary data at [www.elementsmagazine.org](http://www.elementsmagazine.org) for data sources) compared with the data for oceanic basalts (normalized to the primitive mantle of McDonough and Sun 1995). To demarcate the “comfort zone” for desirable grades in igneous REE deposits (yellow field), we used the average compositions of ore (with a cutoff grade of 1 wt% REO) from Bear Lodge (Wyoming) and Strange Lake (Québec), both of which are North American deposits with recognized economic potential (Mariano and Mariano 2012). The data are derived from assessment reports posted at [www.questrareminerals.com/strangelakeproject.php](http://www.questrareminerals.com/strangelakeproject.php) and [www.rareelementresources.com/s/Home.asp](http://www.rareelementresources.com/s/Home.asp). REO = rare earth oxide

sources metasomatically enriched in incompatible elements (including REEs) relative to “run-of-the-mill” mantle peridotites that produce mid-ocean ridge basalt, for example (Arzamastsev et al. 2001). At present, it is not clear whether the REE budget of these enriched sources is controlled by such common silicate constituents of metasomatized mantle as amphibole (Arzamastsev et al. 2001) or by ephemeral phosphate and Ti oxide phases capable of incorporating high levels of incompatible elements (e.g. Ionov et al. 2006).

The origin of anorogenic (A-type, *sensu lato*) granitic rocks and their relation to geodynamics are a matter of considerable debate, which is reflected in the diverse terminology applied to these rocks by different authors. Their parental magmas may descend from a more primitive basaltic precursor, or they may form by partial melting of a subcrustal mafic underplate and deep crustal sources, possibly metasomatized by mantle-derived fluids (see Bonin 2007; Nardi and Bitencourt 2009 for discussion and references). Petrographically similar (but geochemically distinct) carbonate and silicate igneous rocks also occur in the (post)orogenic environment, where their emplacement is controlled by transtensional pull-apart tectonics. However, only carbonatites emplaced in such settings are known to host economic REE mineralization (Hou et al. 2009).

Regardless of their provenance, none of the magma types mentioned above are sufficiently rich in REEs to form a deposit if they reach the surface and erupt; some sort of evolutionary process is always required to generate the levels of enrichment observed in igneous REE deposits (Fig. 1). For example, precipitation of a mineral S with a lower REE content than its parental magma, L (i.e.  $S/L D_{REE} < 1$ , where  $D$  is the partition coefficient), will drive the residual liquid toward enrichment in REEs (Fig. 2). Differences in partition coefficient among these

elements will modify the rare earth budget of the derivative melt, causing changes in its normalized pattern; for example, the slope will increase if LREEs are fractionated from HREEs, and a negative Eu anomaly will appear if feldspars crystallize and are segregated out. This process of *fractional crystallization* can yield evolved melts showing a large increase in REE content relative to the original magma and capable of producing rare earth mineralization. The level of REE enrichment required for this to occur depends on the composition of the melt and physical parameters. For example, the solubility of monazite in silicic melts increases with decreasing alumina saturation index and increasing temperature (Wolf and London 1995), but remains low (<1 wt% LREE) in comparison with the solubility of  $LREE(OH)_3$  in carbonate systems ( $\geq 20\%$ ; Wyllie et al. 1996).

Separation of a homogeneous melt into two or more liquids of different composition, structure, and rheology can also contribute to the concentration of REEs in igneous systems. If one of the liquids (melt or fluid, L1) has a lower affinity for REEs than its conjugate phase, L2 (i.e.  $L1/L2 D_{REE} < 1$ ), the REEs will concentrate in the latter. In *liquid immiscibility* experiments (Veksler et al. 2012), the partitioning behavior of REEs ranges from strongly in favor of the nonsilicate fraction in fluoride–silicate and phosphate–silicate systems ( $L1/L2 D_{REE} \gg 1$  and  $> 100$  for some elements) to completely the opposite in carbonate–silicate systems (Fig. 2). Carbonate–silicate immiscibility is also more effective in separating LREEs from HREEs because the latter are less compatible in the carbonate melt.

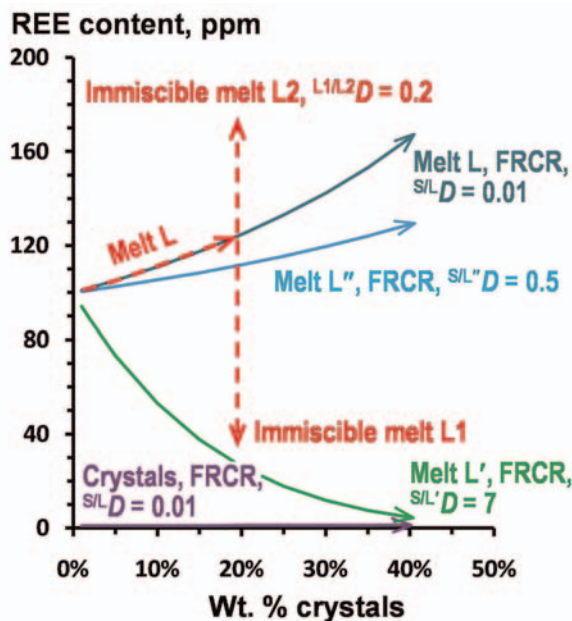


**FIGURE 2** Effect of fractional crystallization and liquid immiscibility (for different partition coefficients) on REE abundances in magmas. Melt L becomes progressively enriched in REEs because it precipitates crystals with a very low  $S/L D$  value ( $\approx D_{LREE}$  in clinopyroxenes and feldspathoids). Melt L undergoes depletion because  $S/L D$  is high ( $\approx D_{Eu}$  in feldspars or  $D_{HREE}$  in garnet). Melt L represents an intermediate case ( $\approx D_{HREE}$  in clinopyroxenes or amphiboles). If Melt L unmixes to produce two fractions, one of which (L1) has much lower affinity for REEs than the other (L2), the resulting trends would replicate the effect of carbonate–silicate immiscibility on most REEs (where L1 = carbonate and L2 = silicate). FRCR = fractional crystallization



**FIGURE 3** Schematic maps of the Khibiny, Ozerny, and Lovozero REE deposits of Russia, showing their location, geology, and mineralization (neighboring countries with active REE exploration programs are indicated in capital letters). Hand-specimen photos show (in the order they are discussed): (A) primary burbankite (Brb) in dolomite carbonatite, (B) complex carbocernaite–bastnäsite–calcite–monazite pseudomorphs after primary burbankite (Brb) in dolomite carbonatite, (C) loparite-bearing urtite, (D) eudialyte lujavrite (pink = eudialyte), (E) apatite (Ap)–nepheline (Ne) rock with titanite (Ttn), and (F) aggregate of shomiokite crystals (pinkish orange) from a low-temperature hydrothermal vein. Geological maps are from Bussen and Sakharov (1972), Epshtein et al. (1972), and Yakovenchuk et al. (2005). AR = Archean; PR = Proterozoic

## REE MINERALIZATION IN IGNEOUS ROCKS: KEY EXAMPLES

### Carbonatites

By definition, carbonatites are *igneous rocks* containing >50% of primary carbonate minerals. However, most carbonatites are actually *polygenetic* and show evidence of hydrothermal and metasomatic reworking; that is, they comprise early magmatic phases and products of crystallization from orthomagmatic and externally derived fluids. The most abundant carbonates in these rocks are calcite and dolomite, whereas ankerite, siderite, magnesite, and rhodochrosite are relatively rare. Other typical rock-forming constituents include apatite, magnetite, and ferro-magnesian silicates.

The current view of carbonatite petrogenesis, supported by voluminous isotopic evidence, is that their parental magmas ultimately come from lithospheric and asthenospheric mantle sources. Relatively few carbonatites crystallize directly from mantle-derived melts generated by low-degree melting of metasomatized peridotite. The

majority of carbonatites occur in association with broadly coeval ultramafic and alkaline silicate rocks (FIG. 3), which is commonly interpreted to indicate a genetic relationship between them. Carbonate melts may evolve from alkali-rich carbonate–silicate magma of mantle provenance by either liquid immiscibility or fractional crystallization (Lee and Wyllie 1998), which has implications for the origin of REE mineralization (see below).

Carbonatites are characteristically enriched in REEs relative to other igneous rocks; about 90% of the published analyses fall in the 250–8000 ppm range (cf ≤1600 ppm in alkaline volcanics rocks; FIG. 1). However, these values can fluctuate wildly even within a single carbonatite intrusion (e.g. from <0.2 to 20.4 wt% REO at Khibiny, Kola; Zaitsev et al. 1998). Typically, carbonatites show strong enrichment in LREEs relative to HREEs (FIG. 1); the chondrite-normalized (La/Yb)<sub>CN</sub> ratio ranges from 20 to 1200, reaching 9500 at some localities (e.g. Sallanlatvi, Kola). Despite the highly fractionated nature of their parental magmas, a few carbonatites host minor HREE mineralization; examples include late-magmatic xenotime at Lofdal in Namibia (Wall et al. 2008) and carbohydrothermal parageneses with mckelveyite-group carbonates in Kola (Wall and Zaitsev 2004). A significant share of the rare earth budget of carbonatites is dispersed among their major constituent minerals (principally calcite, dolomite, apatite, and amphibole-group minerals; e.g. Reguir et al. 2012), whereas the remainder is incorporated in a plethora of REE-rich carbonate, phosphate, oxide, and silicate phases.

Carbonatites with appreciable REE mineralization have been reported at Khibiny and Vuoriyarvi (Kola, Russia), Ozerny and Arshan (Siberia, Russia), Fen (Norway), Khanneshin (Afghanistan), Amba Dongar (India), Barra

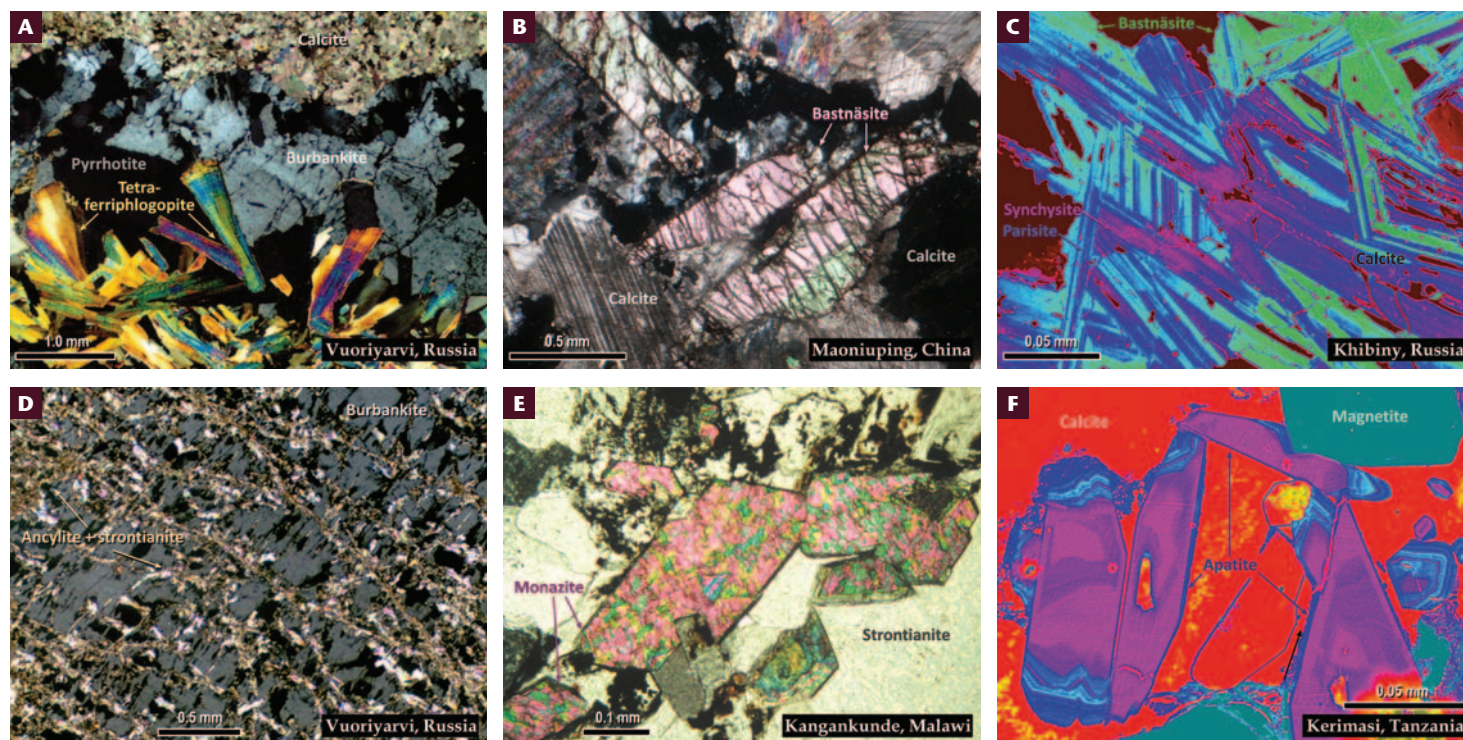


**FIGURE 4** Typical REE host phases in carbonatites. (A) Primary burbankite decorating a contact between clinopyroxene and calcite carbonatite, (B) prismatic bastnaesite in calcite carbonatite, (C) syntactic intergrowths of REE fluorocarbonates, (D) partial replacement of primary burbankite by ancylite and strontianite, (E) monazite-rich hydrothermal paragenesis, (F) zoned apatite in calcite carbonatite, with strong REE enrichment (up to 8.5 wt% REO) in the oscillatory-zoned rim. (A), (B), (D), and (E) = micrographs (crossed polars); (C) and (F) = false-color back-scattered electron images. PHOTO E COURTESY OF HARALD DILL

do Itapirapuã (Brazil), Tundulu and Kangankunde (Malawi), and Wigu Hill (Tanzania), among many others. The most important REE hosts at these localities are carbonates and phosphates (Fig. 4), some containing very high levels of REEs and readily amenable to processing (TABLE 1 in Chakhmouradian and Wall 2012).

Three distinct assemblages of REE minerals have been recognized in carbonatites: (1) primary magmatic, (2) subsolidus hydrothermal-metasomatic, and (3) supergene. Where present, magmatic mineralization may constitute a viable resource (e.g. Mountain Pass; Mariano and Mariano 2012). The earliest phases to crystallize are Na-Ca-Sr-Ba-REE carbonates of the burbankite group, forming crystals up to several centimeters in size (Figs. 3, 4A) and small drop-like inclusions in rock-forming carbonates, and REE(±Ca) fluorocarbonates, occurring as single crystals and syntactic intergrowths (Fig. 4B, C). Isotopic data (Zaitsev et al. 2002) indicate that the primary REE minerals and their host rocks are cogenetic and derived from the same mantle sources. Burbankite-group phases are commonly replaced by complex intergrowths of REE, Sr, and Ba minerals, such as carbocernaite, ancylite, synchysite, bastnaesite, strontianite, and barite (Figs. 3, 4D). These pseudomorphs result from hydrothermal and metasomatic reworking involving low- to medium-temperature fluids of different provenance and chemistry (Wall and Mariano 1996; Wall and Zaitsev 2004). Although hydrothermally overprinted carbonatites are very common, they rarely host REE mineralization of potential economic interest (Fig. 4E). During intense chemical weathering, rare earths are concentrated to weight-percent levels in thick saprolitic and lateritic profiles

developed at the expense of plutonic carbonatites (e.g. Tomtor and Chuktukon in Siberia, Mt. Weld in Australia). However, the market competitiveness of supergene ores, which comprise a very fine-grained mixture of clays and secondary REE phosphates (monazite, xenotime, churchite, rhabdophane, and crandallite-group minerals), remains to be demonstrated.

Assuming carbonatitic magmas originate in the same enriched parts of the mantle as other undersaturated silicate rocks shown in FIGURE 1, how can we explain the extraordinary geochemical signature of carbonatites? In the context of the preceding discussion, is it plausible that their REE enrichment results from immiscible separation of hybrid carbonate-silicate melts tapping metasomatized peridotites? Or do these rocks represent highly evolved melts derived by fractional crystallization? Experimental evidence (Fig. 2) argues against liquid immiscibility as the driving force behind the REE enrichment (Veksler et al. 2012). However,  $D_{\text{REE}}$  values are very high in systems involving salt melts rich in P and F. The highest partition coefficients (215 for La and 94 for Lu) were observed for a fluoride-silicate system, implying that an immiscible carbonate melt strongly enriched in F, for example, may be capable of scavenging REEs from its source magma. A more straightforward mechanism of REE enrichment is fractional crystallization of REE-poor oxide and silicate minerals (forsterite, phlogopite, diopside, magnetite, and ilmenite); this mechanism is supported by the common association of carbonatites with cumulate clinopyroxene-magnetite and olivine-magnetite rocks. The flip side to fractional crystallization is that at high activities of F and  $\text{P}_2\text{O}_5$ , carbonatitic magma will precipitate copious amounts of apatite, which has a gargantuan appetite for REEs (Fig. 4F), but no demonstrated practical value as a source of these elements (e.g. Xu et al. 2010).

### Peralkaline Undersaturated Rocks

These rocks are undoubtedly the most mineralogically exotic and challenging to study among all products of anorogenic magmatism. For example, Yakovenchuk et al. (2005) list 45 (!) rare earth minerals (not including those

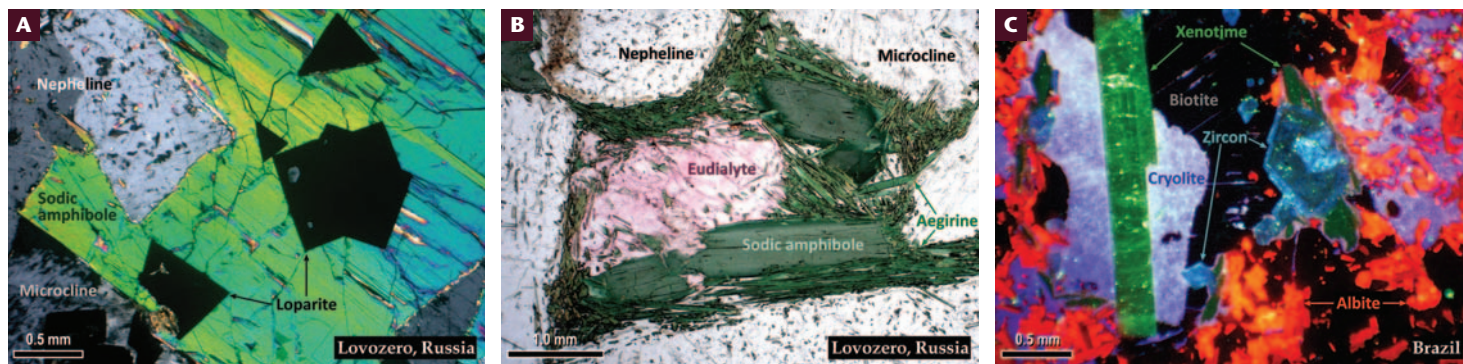


**FIGURE 5** Selected REE host minerals in peralkaline rocks. (A) Loparite in nepheline syenite (crossed polars), (B) eudialyte in eudialyte lujavrite (plane polarized light), (C) cathodoluminescence image of xenotime and associated minerals in peralkaline granite. PHOTO C COURTESY OF ANTHONY N. MARIANO

where REEs substitute for other cations) distributed throughout some 40 different rock types in the Khibiny alkaline complex (FIG. 3). Anyone interested in working with these unusual rocks will first need to learn a new language, because names like lujavrite, melteigite, and ijolite would probably perplex even a seasoned petrographer (and their correct pronunciation, an experienced linguist!). Khibiny, Lovozero (FIG. 3), and similar large composite plutons are products of the protracted evolution of alkali-rich and silica-undersaturated basic melts tapping a colossal volume of metasomatized mantle (e.g. on the order of several million cubic kilometers beneath Kola; Arzamastsev et al. 2001).

The structural and petrologic complexity of these complexes owes much to the differentiation of several compositionally distinct batches of magma emplaced in spatial and temporal proximity to one another (e.g. 377–362 Ma for Khibiny; Kramm and Sindern 2004). Some intrusions (e.g. Ilímaussaq in Greenland) offer compelling geochemical and geophysical evidence for a transient, deep-seated magma chamber where initial differentiation occurred (Sørensen 2006), whereas in other cases (e.g. Lovozero), geochemical data are at odds with geophysical models (cf Arzamastsev et al. 2001; Féménias et al. 2005). Plutonic feldspathoid syenites and their (sub)volcanic counterparts, phonolites, are the most voluminous products of magma evolution. Depending on the volatile content of the parental magma and the magma's ability to retain it, the predominant feldspathoid constituent may be nepheline or, less commonly, sodalite-group minerals. Abundant sodic clinopyroxenes and amphiboles (FIG. 5A, B) reflect the *peralkalinity* of these rocks, i.e. a surplus of Na + K over Al (in atomic terms) in their composition. Common “by-products” of the crystallization of such magmas are feldspar-poor rocks composed essentially of nepheline and ferromagnesian silicates; these rocks are typically referred to as the melteigite–ijolite–urtite series (with urtites being the most nepheline-rich members of the series).

There is a great deal of variation in the relative volumetric contribution and emplacement mode of individual rock types. The Khibiny pluton, for example, is a ring complex consisting predominantly (~60% by volume) of modally and texturally diverse nepheline syenites, some of which contain xenoliths of older alkali-ultramafic rocks. The syenite core and outer “ring” (FIG. 3) are separated by melteigite–ijolite–urtite series rocks whose temporal and structural relations with respect to the other units are a subject

of much debate (Arzamastsev et al. 2001; Yakovenchuk et al. 2005). The urtites host economically important apatite deposits (FIG. 3; see below).

In contrast to Khibiny, the smaller Lovozero complex is a layered intrusion whose lower part (~80% of the estimated volume) consists of a rhythmic sequence of nepheline (± sodalite) syenite, subordinate urtite, and modally transitional layers of variable thickness. Here, meso- to melanocratic trachytoid nepheline syenite (lujavrite) is the most volumetrically significant (~36%) rock type. The upper part of the Lovozero pluton is a crudely stratified package of eudialyte lujavrites reaching a thickness of 700 m and covering 44% of the pluton's exposed area (Bussen and Sakharov 1972).

In contrast to carbonatites, primary magmatic parageneses in peralkaline feldspathoid rocks lack monazite or REE carbonates (but see below). The bulk of their rare earth content is distributed between apatite-group phosphates and accessory zircono- and titanosilicates (e.g. eudialyte- and rinkite-group minerals); early crystallizing perovskite- and pyrochlore-group phases are much less common (Veksler and Teptev 1990; Chakhmouradian and Mitchell 2002). Cumulate rocks containing large concentrations of REE-rich minerals form by gravity settling from extremely evolved magmas probably derived by fractional crystallization of feldspathoids, feldspars, and other minerals characterized by low  $S/L D_{REE}$  (e.g. Dawson et al. 2008). For example, the Na–REE–Ti–Nb oxide loparite (FIG. 5A) is a characteristic accessory constituent of many of the Lovozero rocks, but it is concentrated (2–4 vol%) in urtites and feldspar-bearing rocks transitional to lujavrites (Kogarko et al. 2002). Several of these loparite-rich units have been mined by underground methods since 1951 (FIG. 3 and cover of this issue). Loparite was the major source of LREE, Nb, and Ta for Soviet industry but is currently facing fierce competition from cheaper and easier-to-process ore types available in the global market. A potential alternative to loparite is the REE-bearing zirconosilicate eudialyte, which makes up >10 vol% (locally, up to 80 vol%) of eudialyte lujavrites and related rocks at Lovozero (FIGS. 3, 5B). Although the REE content of this eudialyte (~2.0–2.5 wt% REO) is lower than at some North American localities (Mariano and Mariano 2012), the Lovozero deposit is far superior to its potential rivals in tonnage and accessibility.

Other notable examples of REE-rich products of the protracted differentiation of peralkaline undersaturated magma include steenstrupine-bearing amphibole lujavrite at Ilímaussaq (Sørensen et al. 2011) and apatite–nepheline rocks at Khibiny (Kogarko et al. 1984). The apatite, mined for phosphate since 1929 (FIG. 3), contains ca 0.9 wt% REO with an appreciable proportion of HREEs (Samonov 2008). If these elements were extracted, the currently active mines could supply about 40% of the global rare earth demand.

Although some of the Russian apatite producers have expressed their interest in developing a REE separation technology at their chemical plants, it remains to be seen whether these efforts will materialize into a marketable and competitive product (see photo on p. 347).

Peralkaline feldspathoid rocks are commonly subjected to hydrothermal reworking and autometasomatism, whose effects are most conspicuous in pegmatites (e.g. Yakovenchuk et al. 2005). Such late-stage parageneses have been reported to contain HREE carbonate mineralization (e.g. shomiokite, mckelveyite, and related minerals; Fig. 3) arising from the decomposition of eudialyte and other primary minerals in extremely Na-rich carbothermal fluids (Pekov 2002). Although a mere mineralogical curiosity at present, this type of mineralization could be of practical interest if found in sufficient tonnages.

### Peralkaline Granites

Granitic rocks differing in alumina, alkali, and Ca contents contain distinct, albeit overlapping, assemblages of accessory REE minerals, which account for 70–80% of the whole-rock rare earth budget in amphibole-rich metaluminous granites and >90% in peraluminous and peralkaline types (Bea 1996). The highest concentrations of REEs (commonly, in the 300–800 ppm range) are found in anorogenic peralkaline granites and associated pegmatites; there does not appear to be any consistent correlation between the REE geochemistry of these rocks and their different proposed modes of origin (see above). Extremely evolved systems attain much higher levels of enrichment through a combination of fractional crystallization and concentration of REEs in F-rich residual melts (e.g. Strange Lake, Canada; Boily and Williams-Jones 1994). One remarkable characteristic of peralkaline granites, which makes them an attractive exploration target, is their enrichment in HREEs relative to other igneous rocks (Fig. 1); for example,  $(La/Yb)_N = 2\text{--}10$  and  $Y/Nd \geq 1$ . This peculiar element distribution is usually interpreted in terms of the low solubility of monazite in silicic melts (see above), resulting either in retention of LREEs in their monazite-bearing crustal source or in early removal of LREEs from the magma. The HREE enrichment of evolved granites is likely enhanced by fractional crystallization of feldspars ( $S/L_{D_{LREE}} \gg S/L_{D_{HREE}}$ ; e.g. Dawson et al. 2008), which is also responsible for the conspicuous negative Eu anomaly ( $Eu/Eu^* \leq 0.6$ ) in their normalized patterns (Fig. 1).<sup>\*</sup> It is not surprising, therefore, that in addition to monazite and allanite, which are typical LREE hosts in most granitoids, peralkaline varieties contain such HREE minerals as xenotime (Fig. 5c), fergusonite, samarskite, and gagarinite (Bea 1996; Bastos Neto et al. 2009). Other notable rare earth hosts include primary zirconosilicates (ranging from zircon to eudialyte and elpidite, depending on the activity of Na and silica in the system) and pyrochlore. Hydrothermally modified deposits also contain an assortment of exotic silicate, fluorocarbonate, and mixed-radical phases whose precipitation is controlled by the relative mobility of REEs in fluids of different chemistry and by fluid–rock interactions (Williams-Jones et al. 2012). If proven competitive relative to low-cost “ionic clay” operations in China (Kynicky et al. 2012), REE recovery from the mineralogically complex Strange Lake ore and from xenotime-bearing tailings of the Pitinga Sn–Nb–Ta mine in Brazil will hopefully pave the way for the development of other granite-based polymetallic projects.

### Granitic Pegmatites

In addition to peralkaline granites (see above), their sub- to metaluminous counterparts in post- or anorogenic settings may be associated with pegmatites containing appreciable LREE (allanite–monazite subtype) or HREE (gadolinite subtype) mineralization (Černý 1997). Although pegmatites were the first bedrock source of REEs exploited in the first half of the 1900s to meet an increasing demand for Ce, Y, and actinides, these operations were small and short-lived. Apart from small tonnages, another handicap of these deposits is their “difficult” mineralogy, which incorporates a spectacular variety of REE hosts but is characterized by fairly low concentrations of minerals amenable to easy metal recovery. Interested readers are referred to Linnen et al. (2012) for further information.

### Iron Oxide–Phosphate Deposits

Iron oxide–phosphate ( $\pm$  Ti) deposits are associated with a wide spectrum of igneous rocks (including anorthosites, gabbroids, felsic volcanics, alkaline-ultramafic intrusions, and carbonatites) and undoubtedly have a multiplicity of origins. Their REE budget is dominated by apatite (typically,  $\leq 1$  wt% REOs, but rarely up to 10 wt%) and, at some localities, small (10–150  $\mu$ m) inclusions of monazite and xenotime formed during postmagmatic reequilibration of the apatite with a fluid (Harlov et al. 2002). With the possible exception of Mineville in the USA (Mariano and Mariano 2012), these deposits are not economic to develop exclusively for their rare earth content but may serve as a source of by-product REEs in large-scale iron ore or apatite mining operations.

### PARTING THOUGHTS

Our current understanding of REE deposits is too fragmentary and too “crustal” (i.e. lacking in depth) for the development of an integrated metallogenic model in any foreseeable future. We are just beginning to appreciate the scale and significance of the mantle processes responsible for rare-element transport and enrichment in parts of the lower continental crust and subcontinental lithosphere. Another highly speculative area is the behavior of rare earths in those natural systems whose complexity has thus far thwarted all experimental and thermodynamic attempts at modeling their evolutionary pathways. For example, we still know next to nothing about the relative stability of different REE–Nb–Ta oxides in silicate magmas and REE partitioning between carbonate minerals and melts. Equally obscure (and underappreciated) is the fate of Y and lanthanides in synemplacement contact metasomatism, postmagmatic deformation, and metamorphism. Needless to say, work in any of these or other knowledge-gap areas will offer great intellectual rewards to researchers willing to embrace the challenge.

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<sup>\*</sup> The  $Eu/Eu^*$  ratio stands for the normalized Eu concentration divided by the value interpolated from the abundances of its neighboring elements; i.e.,  $Eu/Eu^* = Eu_N / (0.5Sm_N + 0.5Gd_N)$ .

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# Ultrafast. Contextural. Quantitative.

## SEM-based Petrographic Analyzers



*Image courtesy of Prof. Frances Wall & Dr Gavyn Rollinson, Camborne School of Mines, University of Exeter, UK*

ACROSS THE GLOBE, natural resource companies, service providers, and research organizations are utilizing automated mineralogy and petrography to image and quantify features of commercial interest. Our SEM-based automated solutions, QEMSCAN® and MLA, are essential technologies for mineralogists, geologists, and metallurgists interested in ultrafast, contextual and quantitative analysis of rocks.

The image shows synchysite/parisite (blue), barite (yellow-green), quartz (pink) and iron and manganese oxides/carbonates (black and purple) replacing bastnäsite-(Ce) (orange) in a rare earth ore from Mountain Pass, California, USA.