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Carbonatite and Alkaline Intrusion-Related Rare Earth Element Deposits—A Deposit Model

By Philip L. Verplanck and Bradley S. Van Gosen

The rare earth elements (REEs) are not as rare in nature as their name implies, but economic deposits with these elements are not common and few deposits have been large producers. In the past 25 years, demand for REEs has increased dramatically because of their wide and diverse use in high-technology applications. Yet, presently the global production and supply of REEs come from only a few sources. China produces more than 95 percent of the world's supply of REEs. Because of China's decision to restrict exports of these elements, the price of REEs has increased and industrial countries are concerned about supply shortages (Tse, 2011). As a result, understanding the distribution and origin of REE deposits, and identifying and quantifying our nation's REE resources have become priorities.

Carbonatite and alkaline intrusive complexes, as well as their weathering products, are the primary sources of REEs (Long and others, 2010). The general mineral deposit model summarized here is part of an effort by the U.S. Geological Survey's Mineral Resources Program to update existing models and develop new descriptive mineral deposit models to supplement previously published models for use in mineral-resource and mineral-environmental assessments. We are discussing carbonatite and alkaline intrusion-related REE deposits together because of their spatial association, common enrichment in incompatible elements, and similarities in genesis. A wide variety of commodities have been exploited from carbonatites and alkaline igneous rocks, such as rare earth elements, niobium, phosphate, titanium, vermiculite, barite, fluorite, copper, calcite, and zirconium. Other enrichments include manganese, strontium, tantalum, thorium, vanadium, and uranium.

The REEs are defined as the elements from lanthanum to lutetium (atomic numbers 57 to 71) and yttrium (atomic number 39). Yttrium is typically included as a REE with the "lanthanides" (lanthanum to lutetium) because of its similarity in chemical properties and applications. The elements from lanthanum to gadolinium are referred to as light REEs (LREEs); the elements from terbium to lutetium are referred to as heavy REEs (HREEs). Overall, the REEs have similar geochemical properties, because they all form stable 3^+ ions of similar size. Slight differences in their geochemical behavior occur because, with increasing atomic number, there is a steady decrease in ionic size. Cerium and europium can exist in oxidation states other than 3^+ , with cerium also occurring as 4^+ and europium as 2^+ . Yttrium only occurs as 3^+ and has an ionic radius similar to holmium (1.019 compared to 1.015 angstroms, respectively); thus, yttrium is grouped with the HREEs. Although the geochemical properties of REEs are similar, their metallurgical, chemical, catalytic, electrical, magnetic, and optical properties vary, and these unique properties and differences have led to their prominence in a variety of emerging technologies.

Whereas no REE deposit models have been published, some deposits are described in the literature. In particular, extensive work has been done on the petrology of carbonatites and alkaline intrusive complexes. Understanding the petrology and petrogenesis of carbonatites and alkaline

intrusive complexes is essential in unraveling the complexities of REE deposits associated with these rock types. General descriptions of a variety of types of REE deposits can be found in Neary and Highley (1984), Mariano (1989a, b), Wall and Mariano (1996), Castor and Hedrick (2006), Castor (2008), and Long and others (2010). Orris and Grauch (2002) provide a worldwide compilation of data on rare earth mines, deposits, and occurrences. Berger and others (2009) compiled tonnage and grade data for niobium and REE-bearing carbonatite deposits. Bell (1989) and chapters within provide an excellent geologic framework for carbonatites; Fitton and Upton (1987) and chapters within provide an excellent framework for alkaline intrusive complexes.

Alkaline rocks form an expansive category of igneous rocks. Using a broad definition, alkaline rocks are deficient in SiO_2 relative to Na_2O , K_2O , and CaO (Winter, 2001). Two of the most important subclasses of alkaline rocks with respect to REE deposits are carbonatites and peralkaline rocks. Carbonatites are defined by the International Union of Geological Sciences (IUGS) system of igneous rock classification as having more than 50 modal percent primary carbonate minerals, such as calcite, dolomite, and ankerite, and less than 20 percent SiO_2 (Le Maitre, 2002). Most identified carbonatites are intrusive bodies, but a few extrusive examples are known, most prominently an active carbonatite volcano in northern Tanzania (Oldoinyo Lengai volcano; Woolley and Church, 2005). Recent work has shown that carbonatites can be quite diverse and likely originate from multiple processes (Woolley, 2003; Mitchell, 2005). Alkaline intrusive rocks also contain elevated concentrations of REEs; these rock types tend to be spatially associated with carbonatites, but not in all examples. Alkaline rocks can be further classified based on their chemistry. Peralkaline rocks are one subset of alkaline rocks, defined by $(\text{Na}_2\text{O} + \text{K}_2\text{O})/(\text{Al}_2\text{O}_3) > 1$, and they commonly are enriched in REEs.

Mineral deposits associated with carbonatites account for the greatest production of REEs. Important deposits are the Bayan Obo deposit in Inner Mongolia (China), and the Sulphide Queen carbonatite of the Mountain Pass district, California. Until the late 1980s, the Mountain Pass mine was the largest global producer of REEs, subsequently supplanted by the Bayan Obo deposit, which is currently the largest producer of REEs. Carbonatite REE deposits are extremely enriched in light REEs, particularly lanthanum, cerium, and neodymium. The origin of the Bayan Obo deposit has been debated, but recent work by Yang and others (2011) demonstrates that the deposit fits into the carbonatite class of REE deposits.

Although there are no alkaline intrusion-related deposits currently being mined for REEs, many are in various stages of exploration because these peralkaline igneous rocks contain relatively high concentrations of heavy REEs. Deposits of interest include those at Bokan Mountain, southeastern Alaska; Thor Lake, Strange Lake and Kipawa Lake in Canada; Kola Peninsula, Russia; and Ilímaussaq, Greenland.

Common characteristics of carbonatite and alkaline intrusion-related REE deposits are: (1) they tend to be enriched in high field strength elements (REEs, Y, Nb, Zr, and U); (2) REE-rich carbonatites tend to be enriched in the LREEs; (3) REE-rich alkaline intrusion-related deposits have variable REE enrichments, but are not as enriched in LREEs as carbonatites; (4) REE deposits can contain a variety of ore minerals that are usually either REE-bearing carbonates, phosphates, or fluorates; (5) significant REE-bearing ore minerals include bastnäsite, monazite, and xenotime; (6) ore minerals can be coarsely crystalline to fine grained and can have complex replacement textures; (7) the origin of the REEs is commonly crystallization through magmatic processes, but economic enrichment of REEs may also be because of precipitation of minerals from a magmatic hydrothermal solution or redistribute of magmatic REEs by the hydrothermal fluid; (8) many carbonatite occurrences include breccias; and (9) the intrusive bodies generally have alteration halos derived from alkali-rich fluids (fenitization) that migrated into and reacted with the surrounding rock.

Carbonatites and peralkaline igneous rocks associated with REE deposits tend to occur within stable continental tectonic units, in areas defined as shields, cratons, and crystalline blocks; they are generally associated with intracontinental rift and fault systems (Berger and others, 2009). These igneous rocks formed from the cooling of silica-undersaturated, alkaline magmas, which were derived by small degrees of partial melting of rocks in the Earth's mantle. The evolution of these initial mantle melts to form REE mineral deposits is not fully understood. Although carbonatites and alkaline intrusions are spatially associated, a definitive genetic association is not agreed upon. As summarized by Winter (2001), petrogenetic discussions focus on these questions:

Are carbonatite and alkali magmas developed separately by partial melting within the mantle or do carbonatites evolve from parental alkali magmas?

If carbonatites evolve from parental alkali magmas, then is it by fractional crystallization or by liquid immiscibility? At what depths does this occur?

If carbonatites are derived directly from a carbonatite magma, then what is the nature of the parental carbonatite magma?

Regardless of the petrogenetic debates, at some point carbonatite magma is generated, which contains anomalous concentrations of REEs and other incompatible elements. The source of REEs is the initial magma, and with decreasing pressure and temperature the magma evolves, which leads to further enrichments in REEs. Crystallization is one process that drives the evolution of the magma. The REE mineralization can be associated with primary magmatic minerals, as has been interpreted for the Mountain Pass carbonatite (Mariano, 1989a); however, more commonly, the REE mineralization is associated with fluid phases expelled from the carbonatite magmas. The carbonatites can vary laterally and vertically from calcic to dolomitic to iron-rich across a district and within a single carbonatite mass, and there will be associated major variations in accessory minerals. Following primary crystallization, alteration by magmatic, or less commonly meteoric, fluids can produce complex assemblages of minerals, accounting for some of the mineralogical and geochemical variation between carbonatite units (Castor, 2008). Carbonatite masses and dikes of differing mineralogy and chemistry within a single district can represent separate intrusive episodes.

The principal REE-bearing minerals associated with carbonatites are fluocarbonates (bastnäsite, parasite, and synchysite), hydrated carbonates (ancylite), and phosphates (monazite and apatite) (Zaitsev and others, 1998). Other REE phases are less common, such as britholite and burbankite. Because most carbonatites experienced complex petrogenetic evolution, which included hydrothermal overprinting of primary magmatic phases, the resulting mineralogical and textural characteristics can be quite varied and intricate, and thus difficult to summarize. For this reason, limited published information is available regarding paragenesis, zoning patterns, and structure.

Similar to carbonatites, the parental magma for alkaline intrusive complexes that host REE mineralization is generated as a partial melt of metasomatized mantle material; likewise, this initial melt is the source of the REEs. How and where these magmas evolve is not well understood. In general, REE deposits associated with peralkaline intrusive complexes fall into two categories: (1) deposits in peralkaline, layered complexes, and (2) deposits in veins or dikes associated with peralkaline intrusions. Examples of the first category include Thor Lake and Ilímaussaq. An example within the United States of the second type is Bokan Mountain. The REE-rich alkaline complexes associated with large, layered complexes display evidence of magmatic evolution by fractional crystallization and magma chamber processes including the formation of roof and floor cumulates. Rare earth element mineralization is associated with individual layers which are rich in REE-bearing mineral phases such as eudialyte (Salvi and Williams-Jones, 2005). At Bokan Mountain, Thompson

and others (1982) and Thompson (1988) invoke fractional crystallization of an already evolved magma at shallow crustal levels to explain the observed lithologies. Rare earth element bearing minerals are identified in veins or dikes in the groundmass of larger silicate minerals (Warner and Barker, 1989). A variety of REE-bearing minerals are associated with alkaline intrusion-related REE deposits, in part because secondary processes tend to overprint the primary mineralogy. Important REE-bearing mineral phases include apatite, eudialyte, loparite, gittinsite, xenotime, gadolinite, monazite, bastnäsite, kainosite, mosandrite, britholite, allanite, and zircon.

A common feature of most carbonatite and alkaline intrusion-related deposits is that the surrounding rocks have been hydrothermally altered because of alkali metasomatism. This style of alteration is known as fenitization, so-named because it was first described at the Fen alkaline complex in southern Norway. Alkali-rich fluids are released into the country rock from the crystallizing magma, and reactions convert the host rock minerals to an assemblage of alkali-bearing minerals. Fenites can be classified as sodium or potassium rich. Sodium-rich fenites are characterized by the presence of alkaline feldspar with alkali amphibole or sodic pyroxene, and potassium-rich fenites contain potassium feldspar (Le Bas, 2008).

Gamma-ray (radiometric), magnetic, gravity, and remote sensing surveys have been used successfully to map REE deposits and in regional reconnaissance surveys to identify targets for more detailed geologic mapping and geochemical sampling (Thomas and others, 2010). Because of the physical properties of the suite of incompatible elements associated with these deposits, including thorium, uranium, tantalum, niobium, titanium, and zirconium, geophysical techniques provide an excellent tool for exploration. Aerial gamma-ray surveys measure the naturally emitted gamma radiation derived from three radioelements (potassium, uranium, and thorium) which reside in soils and rocks within the upper 30 centimeters of the Earth's surface. Regardless of their form or type, REE-bearing deposits contain anomalous concentrations of thorium and uranium, often associated with potassic alteration. The radioactivity inherent to these deposits make them well suited for gamma-ray surveys. Magnetic and gravity surveys can be used to locate carbonatites and alkaline intrusive complexes. Magnetic and gravity anomalies produced by carbonatites and alkaline rocks are because of the magnetic and density characteristics of the intrusions, not the REE mineralization. There are several notable examples of successfully using airborne magnetic and/or ground- or airborne-based gravity surveys to locate REE-bearing carbonatites or alkaline intrusions. The Mount Weld carbonatite, Australia, was discovered during the interpretation of a regional aeromagnetic survey; subsequent detailed surveys showed the concentric zonation in its magnetic pattern (Gunn and Dentith, 1997). In Quebec, the Oka carbonatite-alkaline complex and the St-Honoré carbonatite complex each produce strong gravity anomaly highs, well above the surrounding area at Oka (Gold and others, 1967; Vallée and Dubac, 1970).

The environmental issue raised most often in the development of REE deposits is the elevated radioactivity of the ore material. The magmatic differentiation processes that concentrate the REEs also form minerals containing other incompatible elements, such as thorium and uranium. Thus, anomalous values of thorium and uranium, in particular thorium, are common in carbonatites and REE-bearing alkaline intrusions. For this reason, thorium-rich areas of REE deposits are typically treated as a hazardous material for special handling and treatment, as is the waste in streams generated from processing these rocks. In contrast to the majority of uranium-bearing minerals, the thorium-bearing minerals are generally resistant to chemical breakdown, forming relatively insoluble detrital minerals. Thus, thorium-bearing minerals typically contribute only trace concentrations of thorium (about 1 part per billion) to natural waters (pH 5 to 9). Thorium is insoluble in most natural waters.

References Cited

- Bell, Keith, ed., 1989, Carbonatites—Genesis and evolution: Boston, Mass., Unwin Hyman Ltd., 618 p.
- Berger, V.I., Singer, D.A., and Orris, G.J., 2009, Carbonatites of the world, explored deposits of Nb and REE—Database and grade and tonnage models: U.S. Geological Survey Open-File Report 2009-1139, 17 p. and database, available at <http://pubs.usgs.gov/of/2009/1139/>.
- Castor, S.B., 2008, Rare earth deposits of North America: *Resource Geology*, v. 58, p. 337–347.
- Castor, S.B., and Hedrick, J.B., 2006, Rare earth elements, *in* Kogel, J.E., Trivedi, N.C., Barker, J.M., and Krukowski, S.T. eds., *Industrial minerals and rocks: Society for Mining, Metallurgy and Exploration*, p. 769–791.
- Fitton, J.G., and Upton, B.G.L., eds., 1987, *Alkaline igneous rocks: Blackwell Scientific, Oxford, Geological Society Special Publication 30*, p. 568 p.
- Gold, D.P., Vallée, Marcel, and Charette, J-P., 1967, Economic geology and geophysics of the Oka alkaline complex, Quebec: Montreal, Canadian Institute of Mining and Metallurgy, Canadian Mining and Metallurgical Bulletin, v. 60, no. 666, p. 1131–1144.
- Gunn, P.J., and Dentith, M.C., 1997, Magnetic responses associated with mineral deposits: *AGSO Journal of Australian Geology and Geophysics*, v. 17, no. 2, p. 145–158.
- Le Bas, M.J., 2008, Fenites associated with carbonatites: *Canadian Mineralogist*, v. 46, p. 915–932.
- Le Maitre, R.W., ed., 2002, *Igneous rocks—A classification and glossary of terms: Cambridge, United Kingdom, Cambridge University Press*, 236 p.
- Long, K.R., Van Gosen, B.S., Foley, N.K., and Cordier, Daniel, 2010, The principal rare earth elements deposits of the United States—A summary of domestic deposits and a global perspective: U.S. Geological Survey Scientific Investigations Report 2010–5220, 96 p, available at <http://pubs.usgs.gov/sir/2010/5220>.
- Mariano, A. N., 1989a, Economic geology of rare earth minerals, *in* Lipin, B.R. and McKay, G.A., eds., *Geochemistry and mineralogy of rare earth elements: Mineralogical Society of America, Washington D.C., Reviews in Mineralogy*, v. 21, p. 309–338.
- Mariano, A.N., 1989b, Nature of economic mineralization in carbonatites and related rocks, *in* Bell, Keith, ed., *Carbonatites—Genesis and evolution: Boston, Mass., Unwin Hyman Ltd.*, p. 149–176.
- Mitchell, R.H., 2005, Carbonatites and carbonatites and carbonatites: *Canadian Mineralogist*, v. 43, p. 2049–2068.
- Neary, C.R., and Highley, D.E., 1984, The economic importance of the rare earth elements, *in* Henderson, Paul ed., *Rare earth element geochemistry: Amsterdam, The Netherlands, Elsevier*, p. 423–466.
- Orris, G.J., and Grauch, R.I., 2002, Rare earth element mines, deposits, and occurrences: U.S. Geological Survey Open-File Report 02–189, 174 p.
- Salvi, Stefano, and Williams-Jones, A.E. 2005, Alkaline granite-syenite deposits: *in* Linnen, R.L., and Samson, I.M. eds., *Rare-element geochemistry and mineral deposits. Short Course Notes—Geological Association of Canada*, v. 17, p. 315–341.
- Thomas, M.D., Ford, K.L., and Keating, P., 2010, Exploration geophysics for intrusion-hosted rare earth metals, *in* International workshop—Geology of rare metals, November 9–10, 2010, Victoria, B.C., Canada: British Columbia Geological Survey Open File [Report] 2010–10, p. 59–61.
- Thompson, T.B., 1988, Geology and uranium-thorium mineral deposits of the Bokan Mountain granite complex, southeastern Alaska: *Ore Geology Reviews*, v. 3, p. 193–210.
- Thompson, T.B., Pierson, J.R., and Lyttle, Thomas, 1982, Petrology and petrogenesis of the Bokan granite complex, southeastern Alaska: *Geological Society of America Bulletin*, 93, p. 898–908.

- Tse, Pui-Kwan, 2011, China's rare-earth industry: U.S. Geological Survey Open-File Report 2011–1042, 11 p.
- Vallée, Marcel, and Dubuc, Fernand, 1970, The St-Honoré carbonatite complex, Quebec: Transactions of the Canadian Institute of Mining and Metallurgy and of the Mining Society of Nova Scotia, v. 73, p. 346–356.
- Wall, Frances, and Mariano, A.N., 1996, Rare earth minerals in carbonatites—A discussion centered on the Kangankunde carbonatite, Malawi, *in* Jones, A.P., Wall, Frances, and Williams, C.T., eds., Rare earth minerals—Chemistry, origin and ore deposits: London, United Kingdom, Chapman and Hall, The Mineralogical Society, Series 7, p. 193–225.
- Warner, J.D., and Barker, J.C., 1989, Columbian- and rare-earth element-bearing deposits at Bokan Mountain, southeast Alaska: U.S. Bureau of Mines Open File Report 33–89, 196 p.
- Winter, J.D., 2001, An introduction to igneous and metamorphic petrology: New Jersey, Prentice Hall, 697 p.
- Woolley, A.R., 2003, Igneous silicate rocks associated with carbonatites—Their diversity, relative abundances and implications for carbonatite genesis: *Periodico di Mineralogia*, v. 72, p. 9–17.
- Woolley, A.R., and Church, A.A., 2005, Extrusive carbonatites: a brief review: *Lithos* 85, p. 1–4.
- Yang, K-F, Fan, H-R., Santosh, M., Hu, F-F., and Wang, K-Y., 2011, Mesoproterozoic carbonatitic magmatism in the Bayan Obo deposit, Inner Mongolia, north China—Constraints for the mechanism of super accumulation of rare earth elements: *Ore Geology Reviews*, v. 40, p. 122–131.
- Zaitsev, A.N., Wall, Frances, and Le Bas, M.J., 1998, REE-Sr-Ba minerals from the Khibina carbonatites, Kola Peninsula, Russia: their mineralogy, paragenesis and evolution: *Mineralogical Magazine*, v. 62, p. 225–250.

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