

# A Deposit Model for Carbonatite and Peralkaline Intrusion-Related Rare Earth Element Deposits



Scientific Investigations Report 2010–5070–J

**COVER.** Photo 1. Sample of eudialyte (pink) within layered vein consisting of quartz, albite, and sodic amphibole, Dora Bay, Alaska. Size of sample is 11 by 9 cm. Photograph by Philip Verplanck, U.S. Geological Survey. Photo 2. Sample of coarse-grained, tabular bastnäsite within matrix of ferruginous dolomite, Birthday Claim, Mountain Pass, California. Size of sample is 16 by 9 cm. Photograph by Philip Verplanck, U.S. Geological Survey.

# **A Deposit Model for Carbonatite and Peralkaline Intrusion-Related Rare Earth Element Deposits**

By Philip L. Verplanck, Bradley S. Van Gosen, Robert R. Seal, and Anne E. McCafferty

Chapter J of  
**Mineral Deposit Models for Resource Assessment**

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**U.S. Department of the Interior**  
**U.S. Geological Survey**

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## Conversion Factors and Datums

Inch/Pound to SI		
<b>Multiply</b>	<b>By</b>	<b>To obtain</b>
<b>Length</b>		
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
meter (m)	1.094	yard (yd)
<b>Volume</b>		
liter (L)	1.0567	quart (qt)
cubic meter (m <sup>3</sup> )	35.31	cubic foot (ft <sup>3</sup> )
cubic meter (m <sup>3</sup> )	1.308	cubic yard (yd <sup>3</sup> )
<b>Mass</b>		
gram (g)	0.03527	ounce, avoirdupois (oz)
gram (g)	0.03220	ounce, troy (t oz)
tonne (t)	1.10231	ton, short
tonne (t)	2204.62	pound (lb)
<b>Density</b>		
gram per cubic centimeter (g/cm <sup>3</sup> )	62.4220	pound per cubic foot (lb/ft <sup>3</sup> )

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

## Abbreviations Used in This Report

### Units of Measure

°C	degree Celcius
wt%	weight percent
Bq/g	Becquerel per gram
Bt	billion metric tons
cm	centimeter
Eh	redox potential
Eo	Eotvos
g	gram
g/cm <sup>3</sup>	grams per cubic centimeters
kb	kilobar
kg	kilogram
km	kilometer
L	liter
M	meter
Ma	mega-annum (age)
mg	milligram
mg/kg	milligram per kilogram
mGal	milligal
mm	millimeter
MPa	megapascal
mPa	millipascal
mS	millisiemen
Mt	million metric ton
nT	nanotesla
µg	microgram
Pa	pascal
pH	acidity
ppm	parts per million
s	second
t	ton
T, temp.	temperature
vol%	volume percent

**Chemistry**

Ag	silver
Al	aluminum
As	arsenic
Au	gold
B	boron
Ba	barium
Be	beryllium
Bi	bismuth
Br	bromine
C	carbon
Ca	calcium
Cd	cadmium
Ce	cerium
Cl	chlorine
cn	chondrite normalized
Co	cobalt
Cr	chromium
Cs	cesium
Cu	copper
Eu	europium
F	fluorine
Fe	iron
Ga	gallium
Gd	gadolinium
Ge	germanium
H	hydrogen
He	helium
Hf	hafnium
HFSE	high field strength element
Hg	mercury
HREE	heavy rare earth element
In	indium
IOCG	iron-oxide-copper-gold
K	potassium
La	lanthanum
Li	lithium
LILE	large ion lithophile element

LREE	light rare earth element
Lu	lutetium
Mg	magnesium
Mn	manganese
Mo	molybdenum
N	nitrogen
Na	sodium
Nb	niobium
Nd	neodymium
Ni	nickel
O	oxygen
Os	osmium
P	phosphorus
Pb	lead
Rb	rubidium
Re	rhenium
REE	rare earth element
S	sulfur
Sb	antimony
Sc	scandium
Se	selenium
Si	silicon
Sn	tin
Sr	strontium
Ta	tantalum
Te	tellurium
Th	thorium
Ti	titanium
Tl	thallium
Tm	thulium
TREO	total rare earth oxide
U	uranium
V	vanadium
W	tungsten
Y	yttrium
Yb	ytterbium
Zn	zinc
Zr	zirconium

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## Abstract

Carbonatite and alkaline intrusive complexes, as well as their weathering products, are the primary sources of rare earth elements. A wide variety of other commodities have been exploited from carbonatites and alkaline igneous rocks including niobium, phosphate, titanium, vermiculite, barite, fluorite, copper, calcite, and zirconium. Other elements enriched in these deposits include manganese, strontium, tantalum, thorium, vanadium, and uranium. Carbonatite and peralkaline intrusion-related rare earth element deposits are presented together in this report because of the spatial, and potentially genetic, association between carbonatite and alkaline rocks. Although these rock types occur together at many locations, carbonatite and peralkaline intrusion-related rare earth element deposits are not generally found together.

Carbonatite hosted rare earth element deposits are found throughout the world, but currently only five are being mined for rare earth elements: Bayan Obo, Daluxiang, Maoniuping, and Weishan deposits in China and the Mountain Pass deposit in California, United States. These deposits are enriched in light rare earth elements, including lanthanum, cerium, praseodymium, and neodymium. The principal rare earth element-minerals associated with carbonatites are fluocarbonates (bastnäsite, parisite, and synchysite), hydrated carbonates (ancylite), and phosphates (monazite) with bastnäsite being the primary ore mineral. Calcite and dolomite are the primary gangue minerals. At present, the only rare earth element production from a peralkaline intrusion-related deposit is as a byproduct commodity at the Lovozero deposit in Russia. Important rare earth element minerals found in various deposits include apatite, eudialyte, loparite, gittinsite, xenotime, gadolinite, monazite, bastnäsite, kainosite, mosandrite, britholite, allanite, fergusonite, and zircon, and these minerals tend to be enriched in heavy rare earth elements.

Carbonatite and alkaline intrusive complexes are derived from partial melts of mantle material, and neodymium isotopic data are consistent with the rare earth elements being derived from the parental magma. Deposits and these associated rock types 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. Protracted fractional crystallization of the magma leads to enrichment in rare earth elements and other incompatible elements. Rare earth element mineralization associated with carbonatites can occur as either primary mineral phases or as mineralization associated with late stage orthomagmatic fluids. Rare earth element mineralization associated with alkaline intrusive complexes may occur as primary phases in magmatic layered complexes or as late-stage dikes and veins.

The greatest environmental challenges associated with carbonatite and peralkaline intrusion-related rare earth element deposits center on the associated uranium and thorium. Considerable uncertainty exists around the toxicity of rare earth elements and warrants further investigation. The acid-generating potential of carbonatites and peralkaline intrusion-related deposits is low due to the dominance of carbonate minerals in carbonatite deposits, the presence of feldspars and minor calcite within the alkaline intrusion deposits, and only minor quantities of potentially acid-generating sulfides. Therefore, acid-drainage issues are not likely to be a major concern associated with these deposits. Uranium has the potential to be recovered as a byproduct, which would mitigate some of its environmental effects. However, thorium will likely remain a waste-stream product that will require management since progress is not being made towards the development of thorium-based nuclear reactors in the United States or other large scale commercial uses. Because some deposits are rich in fluorine and beryllium, these elements may be of environmental concern in certain locations.

## Introduction

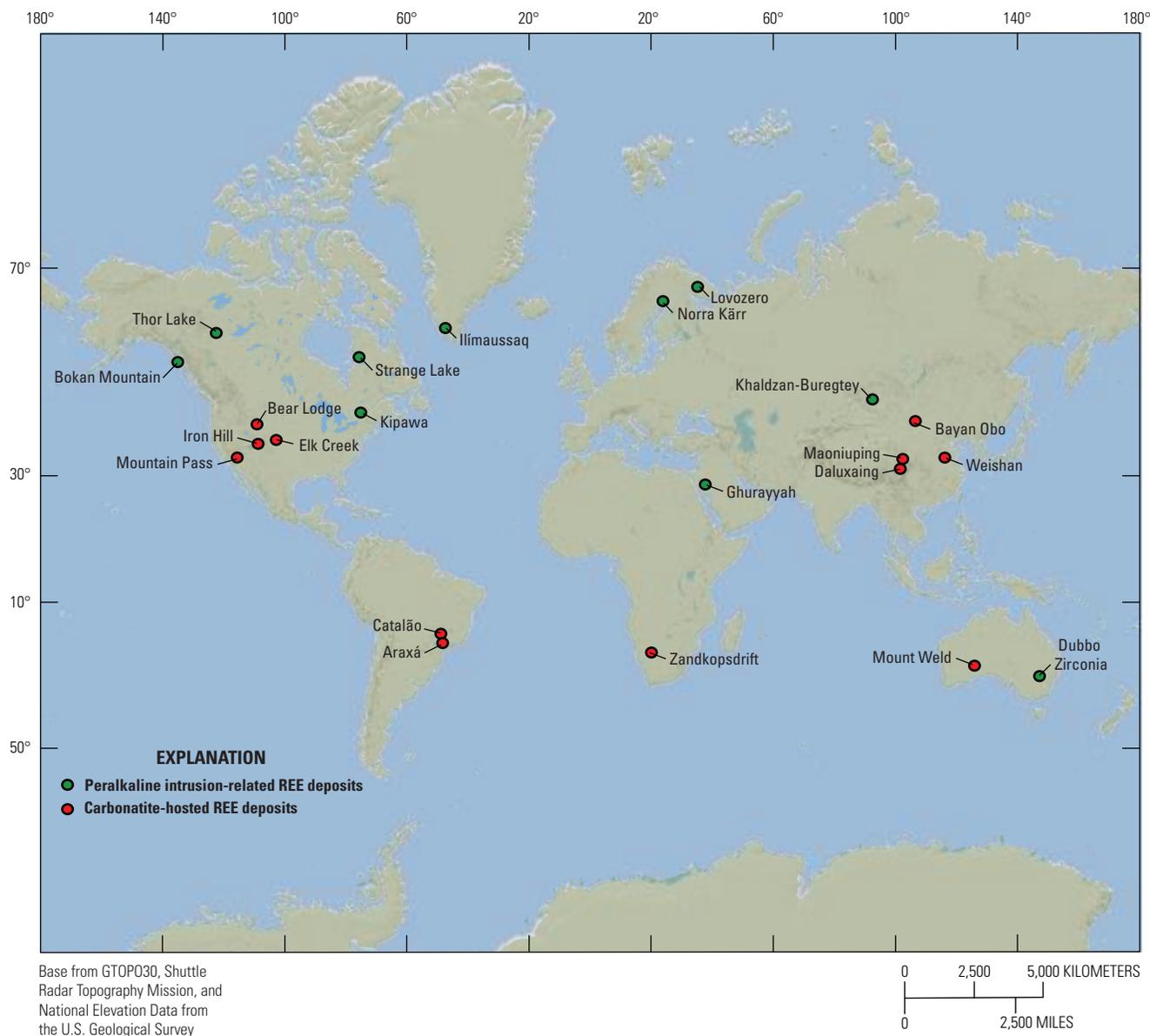
The rare earth elements (REEs) are not as rare in nature as their name implies, but economic deposits with these elements are not common and few deposits have been large REE producers (tables 1 & 2). In the past 25 years, demand for REEs has increased dramatically because of their wide and diverse use in high-technology applications. Yet, the present global production and supply of REEs comes from only a few sources. As of 2012, China produces at least 95 percent of the world's supply of REEs (Tse, 2011). Because of China's

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decision to restrict exports of these elements, the prices of individual REEs have 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), and mineralized bodies are found throughout the world (fig. 1). The general mineral deposit model summarized here is part of an effort by the U.S. Geological Survey (USGS) 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. This report discusses carbonatite and peralkaline intrusion-related REE deposits together because of their spatial association, common enrichment in incompatible elements, and genetic similarities. A wide variety of commodities have been exploited from carbonatites and alkaline igneous rocks, such as REEs, iron (Fe), niobium (Nb), phosphate ( $P_2O_5$ ), titanium (Ti), copper (Cu), calcite, zirconium (Zr), vermiculite, barite, and fluorite. Other common enrichments include manganese (Mn), strontium (Sr), tantalum (Ta), thorium (Th), vanadium (V), and uranium (U).



**Figure 1.** Map showing global distribution of carbonatite and peralkaline intrusion-related rare earth element deposits discussed in this report.

**Table 1.** Rare earth element (REE)-bearing minerals found in rare earth elements deposits.

[Minerals in bold have historically been processed to recover REEs. Small quantities of other minerals may be found in deposits that are or have been mined or in unmined deposits]

Mineral	Formula	Mineral	Formula
Aeschnyrite (Ce)	(Ce,Ca,Fe,Th)(Ti,Nb) <sub>2</sub> (O,OH) <sub>6</sub>	Gorceixite	(Ba,REE)Al <sub>3</sub> [(PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>5</sub> ]·H <sub>2</sub> O
Allanite (Ce)	(Ce,Ca,Y) <sub>2</sub> (Al,Fe <sup>2+</sup> ,Fe <sup>3+</sup> ) <sub>3</sub> (SiO <sub>4</sub> ) <sub>3</sub> (OH)	Gittinsite	CaZrSi <sub>2</sub> O <sub>7</sub>
Allanite (Y)	(Y,Ce,Ca) <sub>2</sub> (Al,Fe <sup>3+</sup> ) <sub>3</sub> (SiO <sub>4</sub> ) <sub>3</sub> (OH)	Goyazite	SrAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>5</sub> ·H <sub>2</sub> O
Anatase	(Ti,REE)O <sub>2</sub>	Hellandite (Y)	(Y,Ca) <sub>6</sub> (Al,Fe <sup>3+</sup> )Si <sub>4</sub> B <sub>4</sub> O <sub>20</sub> (OH) <sub>4</sub>
Ancylite (Ce)	SrCe(CO <sub>3</sub> ) <sub>2</sub> OH·H <sub>2</sub> O	Hingganite (Y)	(Y,Yb,Er) <sub>2</sub> Be <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> (OH) <sub>2</sub>
<b>Apatite</b>	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>3</sub> F	Huanghoite (Ce)	Ba(Ce,La,Nd)(CO <sub>3</sub> ) <sub>2</sub> F
Baddeleyite	ZrO <sub>2</sub>	Imoriite (Y)	Y <sub>2</sub> (SiO <sub>4</sub> )(CO <sub>3</sub> )
<b>Bastnäsite (Ce)</b>	(Ce,La)(CO <sub>3</sub> )F	Joaquinite (Ce)	Ba <sub>2</sub> NaCe <sub>2</sub> Fe <sup>2+</sup> Ti <sub>2</sub> Si <sub>8</sub> O <sub>26</sub> (OH)·H <sub>2</sub> O
<b>Brannerite</b>	(U,Ca,Y,Ce)(Ti,Fe) <sub>2</sub> O <sub>6</sub>	Kainosite (Y)	Ca <sub>2</sub> (Y,Ce) <sub>2</sub> Si <sub>4</sub> O <sub>12</sub> (CO <sub>3</sub> )·H <sub>2</sub> O
Britholite (Ce)	(Ce,Ca) <sub>5</sub> (SiO <sub>4</sub> PO <sub>4</sub> ) <sub>3</sub> (OH,F)	Kamphaugite (Y)	Ca(Y,REE)(CO <sub>3</sub> ) <sub>2</sub> (OH)·H <sub>2</sub> O
Brockite	(Ca,Th,Ce)(PO <sub>4</sub> )·H <sub>2</sub> O	Karnasurite (Ce)	(Ce,La,Th)(Ti,Nb)(Al,Fe <sup>3+</sup> )(Si,P) <sub>2</sub> O <sub>7</sub> (OH) <sub>4</sub> ·3H <sub>2</sub> O
Burbankite	(Na,Ca) <sub>3</sub> (Sr,Ba,Ca,REE) <sub>3</sub> (CO <sub>3</sub> ) <sub>5</sub>	Keiviite (Y)	(Y,Yb) <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>
Calcio-ancylite (Ce)	(Ca,Sr)Ce <sub>3</sub> (CO <sub>3</sub> ) <sub>4</sub> (OH) <sub>3</sub> ·H <sub>2</sub> O	Khanneshite	(Na,Ca) <sub>3</sub> (Ba,Sr,Ce,Ca) <sub>3</sub> (CO <sub>3</sub> ) <sub>5</sub>
Carbocernaite	(Ca,Na)(Sr,REE)(CO <sub>3</sub> ) <sub>2</sub>	Kuliokite (Y)	(Y,Yb) <sub>4</sub> Al(SiO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub> F <sub>5</sub>
Caysichite (Y)	Y <sub>4</sub> (Ca,REE) <sub>4</sub> Si <sub>8</sub> O <sub>20</sub> (CO <sub>3</sub> ) <sub>6</sub> (OH)·7H <sub>2</sub> O	Låvenite	(Na,Ca) <sub>4</sub> (Mn,Fe) <sub>2</sub> (Zr,Ti,Nb) <sub>2</sub> (Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> (O,F) <sub>4</sub>
Cerianite (Ce)	(Ce <sup>4+</sup> ,Th) <sub>2</sub> O <sub>2</sub>	<b>Loparite (Ce)</b>	(Ce,Na,Ca)(Ti,Nb)O <sub>3</sub>
Cerriopyrochlore	Ce(Nb,Ti) <sub>2</sub> O <sub>6</sub>	Miserite	K(Ca,Ce) <sub>6</sub> Si <sub>8</sub> O <sub>22</sub> (OH,F) <sub>2</sub>
Cerite (Ce)	Ce <sub>3</sub> Fe <sup>3+</sup> (SiO <sub>2</sub> ) <sub>6</sub> [(SiO <sub>3</sub> )(OH)](OH) <sub>3</sub>	<b>Monazite (Ce)</b>	(Ce,La,Nd,Th)PO <sub>4</sub>
Cheralite	(Ca,Ce,Th)(P,Si)O <sub>4</sub>	Mosandrite	(H <sub>3</sub> O <sup>+</sup> ,Na,Ca) <sub>3</sub> Ca <sub>3</sub> REE(Ti,Zr)(Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> (O,OH,F) <sub>4</sub>
Chevkinite	(Ca,Ce,Th) <sub>4</sub> (Fe <sup>2+</sup> ,Mg) <sub>2</sub> (Ti,Fe <sup>3+</sup> ) <sub>3</sub> Si <sub>4</sub> O <sub>22</sub>	Nacareniobsite	Na <sub>3</sub> Ca <sub>3</sub> (Ce,La)Nb(Si <sub>2</sub> O <sub>7</sub> )OF <sub>3</sub>
Churchite (Y)	YPO <sub>4</sub> ·H <sub>2</sub> O	Parisite (Ce)	Ca(Ce,La) <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> F <sub>2</sub>
Cordylite (Ce)	NaBaCe <sub>2</sub> (CO <sub>3</sub> ) <sub>4</sub> F	Perovskite	(Ca,REE)TiO <sub>3</sub>
Crandallite	CaAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>5</sub> ·H <sub>2</sub> O	Polycrase (Y)	(Y,Ca,Ce,U,Th)(Ti,Nb,Ta) <sub>2</sub> O <sub>6</sub>
Daqingshanite (Ce)	(Sr,Ca,Ba) <sub>3</sub> (Ce,La)(PO <sub>4</sub> )(CO <sub>3</sub> ) <sub>3-x</sub> (OH,F) <sub>x</sub>	Pyrochlore	(Ca,Na,REE) <sub>2</sub> Nb <sub>2</sub> O <sub>6</sub> (OH,F)
Davidite (Ce)	(Ce,La)(Y,U,Fe <sup>2+</sup> )(Ti,Fe <sup>3+</sup> ) <sub>20</sub> (O,OH) <sub>38</sub>	Rhabdophane (Ce)	(Ce,La)PO <sub>4</sub> ·H <sub>2</sub> O
Doverite	YCaF(CO <sub>3</sub> ) <sub>2</sub>	Rhabdophane (La)	(La,Ce)PO <sub>4</sub> ·H <sub>2</sub> O
Eudialyte	Na <sub>4</sub> (Ca,Ce) <sub>2</sub> (Fe <sup>2+</sup> ,Mn <sup>2+</sup> ,Y)ZrSi <sub>8</sub> O <sub>22</sub> (OH,Cl) <sub>2</sub>	Rinkite (rinkolite)	(Ca,Ce) <sub>4</sub> Na(Na,Ca) <sub>2</sub> Ti(Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> F <sub>2</sub> (O,F) <sub>2</sub>
Euxenite (Y)	(Y,Ca,Ce,U,Th)(Nb,Ta,Ti) <sub>2</sub> O <sub>6</sub>	Rosenbuschite	(Ca,Na,Ce) <sub>2</sub> (Zr,Ti)(Si <sub>2</sub> O <sub>7</sub> )(F,O) <sub>2</sub>
Fergusonite (Ce)	(Ce,La,Y)NbO <sub>4</sub>	Sahamalite	(Mg,Fe)(Ce,La,Nd,Pr) <sub>2</sub> (CO <sub>3</sub> ) <sub>4</sub>
Fergusonite (Y)	YNbO <sub>4</sub>	Samarskite	(REE,Fe <sup>2+</sup> ,Fe <sup>3+</sup> ,U,Th,Ca)(Nb,Ta,Ti)O <sub>4</sub>
Fersmite	(Ca,Ce,Na)(Nb,Ta,Ti) <sub>2</sub> (O,OH,F) <sub>6</sub>	Sphene (titanite)	(Ca,REE)TiSiO <sub>5</sub>
Florencite (Ce)	CeAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	Steenstrupine (Ce)	Na <sub>14</sub> Ce <sub>6</sub> Mn <sub>2</sub> Fe <sub>2</sub> (Zr,Th)(Si <sub>6</sub> O <sub>18</sub> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>7</sub> ·3H <sub>2</sub> O
Florencite (La)	(La,Ce)Al <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	Stillwellite (Ce)	(Ce,La,Ca)BSiO <sub>5</sub>
Fluocerite (Ce)	(Ce,La)F <sub>3</sub>	Synchysite (Ce)	Ca(Ce,La)(CO <sub>3</sub> ) <sub>2</sub> F
Fluocerite (La)	(La,Ce)F <sub>3</sub>	Synchysite (Y) (doverite)	Ca(Y,Ce)(CO <sub>3</sub> ) <sub>2</sub> F
Fluorapatite	(Ca,Ce) <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F	Tengerite (Y)	Y <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> ·2-3H <sub>2</sub> O
Fluorite	(Ca,REE)F <sub>2</sub>	Thalenite (Y)	Y <sub>3</sub> Si <sub>3</sub> O <sub>10</sub> (F,OH)
Formanite (Y)	YTaO <sub>4</sub>	Thorite	(Th,U,REE)SiO <sub>4</sub>
Gadolinite (Y)	Y <sub>2</sub> Fe <sup>2+</sup> Be <sub>2</sub> Si <sub>2</sub> O <sub>10</sub>	Titanite (Y)	(Ca,Y)TiOSiO <sub>4</sub>
Gagarinite (Y)	NaCaY(F,Cl) <sub>6</sub>	Uraninite	(U,Th,Ce)O <sub>2</sub>
Gerenite (Y)	(Ca,Na) <sub>2</sub> (Y,REE) <sub>3</sub> Si <sub>6</sub> O <sub>18</sub> ·2H <sub>2</sub> O	Vitusite (Ce)	Na <sub>3</sub> (Ce,La,Nd)(PO <sub>4</sub> ) <sub>2</sub>

**Table 1.** Rare earth element (REE)-bearing minerals found in rare earth elements deposits.—Continued

[Minerals in bold have historically been processed to recover REEs. Small quantities of other minerals may be found in deposits that are or have been mined or in unmined deposits]

Mineral	Formula
Wöhlerite	$\text{Na}(\text{Ca,Ce,La})_2(\text{Zr,Nb})(\text{Si}_2\text{O}_7)(\text{O,OH,F})_2$
Xenotime (Y)	$\text{YPO}_4$
Yttrialite (Y)	$\text{Y}_2\text{Si}_2\text{O}_7$
Yttriofluorite	$(\text{Ca,Y})\text{F}_2$
Yttrotantalite (Y)	$(\text{Y,Ca,Fe}^{2+})(\text{Ta,Nb})\text{O}_4$
Zircon	$(\text{Zr,REE})\text{SiO}_4$

## Alkaline Igneous Rocks

Alkaline rocks form an expansive category of igneous rocks. As a broad definition, alkaline rocks are deficient in  $\text{SiO}_2$  relative to  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{CaO}$  (Winter, 2001). Two of the most important subclasses of alkaline rocks with respect to REE deposits are *carbonatites* and *peralkaline rocks*. Peralkaline rocks are a subset of alkaline rocks, defined by molar  $(\text{Na}_2\text{O} + \text{K}_2\text{O})/(\text{Al}_2\text{O}_3)$  greater than 1. These rock types host REE deposits and are a primary focus of this report. 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  $\text{SiO}_2$  (Le Maitre, 2002). Most identified carbonatites are intrusive bodies, but a few extrusive examples are known, including the active Oldoinyo Lengai carbonatite volcano in northern Tanzania (Van Straaten, 1989). Carbonatites can be quite diverse and likely originate from multiple processes (Woolley, 2003; Mitchell, 2005). Alkaline intrusive rocks tend to be spatially associated with carbonatites and contain elevated concentrations of REEs; thus, we chose to treat these two subclasses of alkaline rocks together.

## The Rare Earth Elements

The REEs are defined as the elements from lanthanum (La) to lutetium (Lu; atomic numbers 57 to 71) and yttrium (Y; atomic number 39; fig. 2). Yttrium is typically included as a REE with the “lanthanides” (La to Lu) because of its similarity in chemical properties and applications. The elements from lanthanum to gadolinium (Gd; atomic number 64) are referred to as light REEs (LREEs); the elements from terbium (Tb) to Lu are referred to as heavy REEs (HREEs). This split between light and heavy REEs after gadolinium is based on the progressive filling of electrons in the 4f shell. From cerium (Ce) to Gd, the 4f shell is progressively filled by the addition of an unpaired electron. After Gd, each additional

electron that is added is paired with an existing electron. Note that this convention is not universally or consistently applied, and thus care must be taken to determine which elements are included under the terms light and heavy REEs. Also note that promethium (Pm; atomic number 61) does not occur naturally because all of its isotopes are radioactive and all promethium formed during solar system evolution has decayed to other elemental species. However, it can be created as a fission product of uranium.

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 (fig. 3). Cerium and europium (Eu) can exist in oxidation states other than  $3^+$ ; Ce also occurs as  $4^+$  and Eu as  $2^+$ . Yttrium occurs only as  $3^+$  and has an ionic radius similar to holmium (Ho; 1.019 compared to 1.015 angstroms, respectively; Shannon, 1976); thus, Y is grouped with the HREEs. Although the geochemical properties of REEs are similar, the individual elements vary in their metallurgical, chemical, catalytic, electrical, magnetic, and optical properties, and their associated industrial applications. These unique properties and differences have led to their prominence and wide application in a variety of emerging technologies.

The REE concentrations are normally presented as normalized concentration versus atomic number diagrams, with the elements along the x-axis plotted by increasing atomic weight (fig. 4). Along the y-axis, the concentrations are normalized to a reference material, which removes the saw-toothed pattern caused by the even atomic number elements having greater concentrations than the odd number elements. The difference in concentrations between the even and odd atomic number REEs is because the even atomic number elements were more stable than neighboring odd number elements during nucleosynthesis; this relationship is referred to as the Oddo-Harkins effect (North, 2008). For many geologic studies, chondrite meteorite values are used as the reference material for normalization, although composite shale values or seawater concentrations are also commonly used depending on the types of geologic and geochemical processes being investigated.

Unlike many elements, the REEs were not discovered and separated until relatively recently; as a result, there was no early market for these elements and little study of REE ores. Carl Alex Arrhenius is credited with discovering REEs when he collected a black mineral from a feldspar quarry at Ytterby, Sweden in 1787. By 1843, La, Ce, erbium (Er), and Tb had been discovered, and by 1896 the remainder of the REEs had been discovered, with the exception of Pm, which does not occur naturally. The first major industrial application for REEs was the use of Ce in incandescent mantles for gas lanterns in 1890. This was followed by the use of La, Ce, Pr, and Nd in misch metals, primarily used as flints in lighters, in the early 1920s. The first large scale separation of the individual REEs did not occur until the 1940s, when procedures were developed as part of the Manhattan Project during World War II (Gschneidner and Eyring, 1988).

**Table 2.** Carbonatite and peralkaline intrusion-related ore deposits discussed in this report.

	<b>Deposit</b>	<b>Reported resource (metric tons)</b>	<b>Reported ore grade (total REE oxide, in percent)</b>	<b>Comment</b>	<b>Reference</b>
Carbonatites					
Active mines	Bayan Obo, Inner Mongolia, China	800,000,000	6	Tonnage represents estimated mineral resource of the deposit	Berger and others (2009)
	Daluxiang (Dalucao), Sichuan, China	15,200,000	5.0	About 0.76 million metric tons of REE oxide estimated	Hou and others (2009)
	Maoniuping, Sichuan, China	50,200,000	2.89	Reserve of REE oxide is estimated to be more than 1.45 million metric tons (Xu and others, 2008).	Xu and others (2008); Hou and others (2009); Xie and others (2009)
	Weishan, Shandong, China	unavailable	unavailable	Tonnage and grade information not available	
	Mountain Pass, California, USA	16,700,000	7.98	Tonnage represents proven and probable reserves using a cut-off grade of 5 percent	Molycorp, Inc. (2012)
	Mount Weld, Western Australia	23,900,000	7.9	Tonnage represents total mineral resource estimate, as of January 2012, for two deposits at Mount Weld: (1) the Central Lanthanide deposit and (2) the Duncan deposit	Lynas Corporation (2012)
Advanced exploration projects	Bear Lodge Mountains, Wyoming, USA	13,290,000	3.22	Tonnage and grade data represent measured and indicated resources using a cut-off grade of 1.5 percent REE oxide.	Rare Element Resources Ltd. (2013)
	Elk Creek, Nebraska, USA	19,300,000	0.67 percent Nb oxide	Tonnage and grade represent indicated Nb oxide resource estimate. Inferred resources of 83,300,000 metric tons at 0.63 percent niobium oxide. REE resources are not reported.	Quantum Rare Earth Developments Corp. (2012)
Peralkaline intrusions					
Advanced exploration projects	Bokan Mountain, Alaska, USA	5,275,000	0.645	Tonnage and grade represent inferred resources for the combined Dotson and I&L zones using a cut-off grade of 0.4 percent REE oxide.	Robinson and others (2011)
	Kvanefjeld, Ilimaussaq complex, Greenland	437,000,000	1.093	Tonnage and grade represent indicated resources. Inferred resources estimated at 520,000,000 metric tons with a grade of 1.069 percent total REE oxide.	Greenland Minerals and Energy Ltd. (2012)
	Thor Lake (Nechalacho deposit), Northwest Territories, Canada	121,440,000	1.5	Tonnage and grade represents total measured and indicated resources. Total inferred resources reported as 182,010,000 metric tons with a grade of 1.28 percent total REE oxide.	Avalon Rare Metals Inc. (2013)
	Strange Lake, Quebec/Labrador, Canada	36,359,000	1.164	Tonnage and grade represents total indicated resources using a cut-off grade of 0.95 percent REE oxide. Total inferred resources reported as 14,421,000 metric tons with a grade of 1.109 percent total REE oxide, using a cut-off grade of 0.95 percent.	Quest Rare Minerals Ltd. (2012)

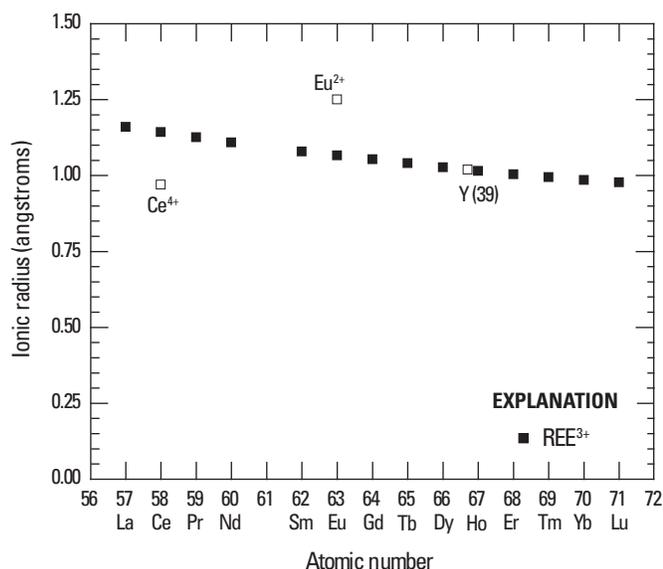
**Table 2.** Carbonatite and peralkaline intrusion-related ore deposits discussed in this report.—Continued

	<b>Deposit</b>	<b>Reported resource (metric tons)</b>	<b>Reported ore grade (total REE oxide, in percent)</b>	<b>Comment</b>	<b>Reference</b>
			Peralkaline intrusions		
Advanced exploration projects	Kipawa, Quebec, Canada	12,472,000	0.512	Tonnage and grade represent total indicated resources using a cut-off grade of >0.30 percent REE oxide. Total inferred resources were reported as 3,842,000 metric tons with a grade of 0.463 percent total REE oxide, using a cut-off grade of >0.30 percent.	Saucier and others (2012, p. 75)
	Norra Kärr, southern Sweden	60,500,000	0.54	Tonnage and grade represent total inferred resources using a cut-off grade of 0.4 percent total REE oxide.	Tasman Metals Ltd. (2012)
	Dubbo Zirconia project, New South Wales, Australia	35,930,000	0.745	Tonnage and grade represent proved and probable resources.	Alkane Resources Ltd. (2011)
	Lovozero, Kola Peninsula, Russia	unavailable	unavailable	Tonnage and grade information not available, REEs are a byproduct of loparite mined for niobium	Zaitsev and Kogarko (2012)

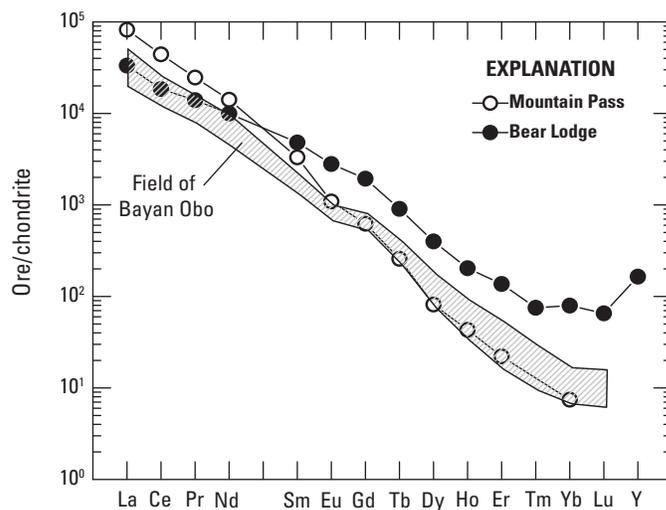
### Periodic Table of the Elements

1																	18																												
1 H 1.01																	2 He 4.00																												
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18																												
11 Na 22.99	12 Mg 24.30	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95																												
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80																												
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (97.91)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.29																												
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (208.98)	85 At (209.99)	86 Rn (222.02)																												
87 Fr (223.02)	88 Ra (226.03)	89 Ac (227.03)	104 Rf (261.11)	105 Ha (262.11)	106 Sg (263.12)																																								
<table border="1" style="width: 100%; border-collapse: collapse; text-align: center;"> <tr> <td>58 Ce 140.12</td> <td>59 Pr 140.91</td> <td>60 Nd 144.24</td> <td>61 Pm (144.91)</td> <td>62 Sm 150.36</td> <td>63 Eu 151.97</td> <td>64 Gd 157.25</td> <td>65 Tb 158.93</td> <td>66 Dy 162.50</td> <td>67 Ho 164.93</td> <td>68 Er 167.26</td> <td>69 Tm 168.93</td> <td>70 Yb 173.04</td> <td>71 Lu 174.97</td> </tr> <tr> <td>90 Th 232.04</td> <td>91 Pa 231.04</td> <td>92 U 238.03</td> <td>93 Np (237.05)</td> <td>94 Pu (244.06)</td> <td>95 Am (243.06)</td> <td>96 Cm (247.07)</td> <td>97 Bk (247.07)</td> <td>98 Cf (251.08)</td> <td>99 Es (252.08)</td> <td>100 Fm (257.10)</td> <td>101 Md (258.10)</td> <td>102 No (259.10)</td> <td>103 Lr (262.11)</td> </tr> </table>																		58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (144.91)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237.05)	94 Pu (244.06)	95 Am (243.06)	96 Cm (247.07)	97 Bk (247.07)	98 Cf (251.08)	99 Es (252.08)	100 Fm (257.10)	101 Md (258.10)	102 No (259.10)	103 Lr (262.11)
58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (144.91)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97																																
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**Figure 2.** Periodic table of the elements. The rare earth elements comprise 15 elements, which range in atomic number from 57 to 71, including lanthanum (La) to lutetium (Lu). The elements are also commonly referred to as "lanthanides." Yttrium (Y, atomic number 39) is also typically included with the rare earth elements group because it shares chemical, physical, and application properties with the lanthanides. Figure from Long and others, 2010.



**Figure 3.** Graph showing variation in ionic radii of rare earth elements.



**Figure 4.** Rare earth elements in selected carbonatite deposits. Concentrations normalized to C1 chondrite values from Anders and Ebihara (1982).

Whereas no comprehensive REE mineral deposit models have been published, deposits such as Bayan Obo, Inner Mongolia, China (Xu and others, 2010a; Yang and others, 2011); Daluxiang and Maoniuping, Sichuan, China (Xu and others, 2008); Mount Weld, Western Australia (Lottermoser, 1990); Mountain Pass, California (Calif.) (Olson and others, 1954; Castor and Nason, 2004; Castor, 2008b); Bokan Mountain, Alaska (Staatz, 1978, Thompson and others, 1982; Thompson, 1988; Warner and Barker, 1989); Nechalacho at Thor Lake, Northwest Territories, Canada (Sheard and others, 2012; Hoshino and others, 2013); and Strange Lake, Quebec, Canada (Salvi and Williams-Jones, 1990, 1996) have been studied in detail. Understanding the petrology and petrogenesis of carbonatites and alkaline intrusive complexes is essential for unraveling the complexities of REE deposits intimately associated with these rock types. Overviews of REE deposit types can be found in Neary and Highley (1984), Mariano (1989a, b), Wall and Mariano (1996), Castor and Hedrick (2006), Castor (2008a), and Long and others (2010). Richardson and Birkett (1996a, b) provided excellent descriptions of carbonatite and peralkaline associated deposits with an emphasis on Canadian occurrences. Orris and Grauch (2002) presented a worldwide compilation of data on rare earth deposits and occurrences. Berger and others (2009) compiled tonnage and grade data for Nb- and REE-bearing carbonatite deposits. Chapters of Bell (1989) provided an excellent geologic framework for carbonatites. The chapters of Fitton and Upton (1987) provided an excellent framework for alkaline intrusive complexes.

## Purpose and Scope

This report is one of a series of USGS Mineral Resources Program publications that present updated deposit models or develop new descriptive mineral deposit models. Because no previous USGS carbonatite and alkaline intrusive REE deposit model exists, this document describes a new effort by the Mineral Resources Program. This descriptive model builds on a strong foundation of previous work on these deposits and is intended to be a summary of the state-of-the-knowledge.

The focus of this report is REE deposits associated with carbonatites and peralkaline intrusions. In many REE deposits, carbonatites and alkaline intrusions are spatially and temporally associated; as such, we have chosen to describe mineral deposits related to these rocks in a single deposit model. These rock types are strikingly different in terms of mineralogy and geochemistry, but REE enrichment, which is characteristic of both, may result from similar source material and similar igneous differentiation and enrichment processes. The vast majority of carbonatites and peralkaline intrusions are not mineralized, and extensive work has been published on these non-mineralized systems compared to mineralized systems. This study uses the published research on non-mineralized systems to constrain many of the attributes of carbonatite and peralkaline magma genesis and evolution. Because of the overlap in geological characteristics, many of the sections

will discuss both types together, but in some sections detailed descriptions will be separated.

## Deposit Type and Associated Commodities

### Name

Carbonatite and peralkaline intrusion-related REE deposits

### Synonyms

Carbonatites and alkaline intrusions are broad categories of igneous rocks, such that numerous subtypes or alternative nomenclatures have been applied to individual deposits. Rocks that fall within the alkaline classification can be subdivided based on their chemistry, mineralogy, and whether they are intrusive or extrusive. General subclasses include peralkaline (molar  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  greater than  $\text{Al}_2\text{O}_3$ ) and ultrapotassic (molar  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  greater than 3), with various rock types in these subclasses being defined based on their mineralogy. Carbonatites are a subclass of the alkaline classification.

Carbonatite is a commonly used term. Few, if any, synonyms are used to refer to these carbonate igneous rocks when mentioned in a general fashion. The use of the term “carbonatite” is similar to the use of “granite”; that is, in the strictest sense the rock type conforms to specific petrologic requirements, but the term can be preceded by numerous descriptive terms (see Woolley and Kempe, 1989). Waldemar C. Brøgger is often credited with originating the concept of magmatic carbonate rocks in 1921, and he used the term karbonatite to describe them in the plural (Heinrich, 1966).

Carbonatites can be classified based on mineralogy or chemistry. A mineralogy-based naming convention includes the following nomenclature (note that the chemistry-based classification uses the same groups as the mineralogy-based classification):

Calcite carbonatite, calciocarbonatite, or sövite: A lithologic term used for calcite-dominant carbonatite; the term sövite originated in the earliest days of carbonatite description.

Dolomite carbonatite, magnesiocarbonatite, or beforosite: A lithologic term used to describe dolomite-dominant carbonatite. The term beforosite was first used in 1928 to describe dolomitic carbonatite.

Ankerite carbonatite or ankerite ferrocarbonatite: A commonly used term to describe an iron-rich carbonatite, such as a carbonatite rich in ankerite  $[(\text{Ca}(\text{Fe},\text{Mg},\text{Mn})(\text{CO}_3)_2]$  or siderite  $(\text{Fe}_2^+\text{CO}_3)$ .

Natrocronatite is a sodium-potassium-calcium carbonatite; this very rare igneous rock is best represented by recent lavas erupted by the Oldoinyo Lengai volcano in northern Tanzania (Fischer and others, 2009).

## Brief Description

Carbonatite and peralkaline intrusive deposits are primary sources of REEs. The Mountain Pass REE deposit in California, hosted by a massive carbonatite body, is the only REE deposit in the United States currently being mined (fig. 5). Carbonatites in the Inner Mongolia Region and Sichuan Province of China are the world's primary REE producers. Deeply weathered horizons atop carbonatites are being mined in Brazil for Nb. At present, the only peralkaline intrusion-related REE deposit that produces REEs is at Lovozero in Russia, but many peralkaline complexes are the focus of ongoing advanced REE exploration activities.

Important characteristics of carbonatite and alkaline intrusive deposits are: (1) they tend to be enriched in high field strength elements (HFSEs), such as REEs, Nb, Zr, Ta, Th, and U; (2) REE-rich carbonatites tend to be light REE-enriched (fig. 4, table 3); (3) REE-rich alkaline intrusive deposits have variable REE enrichments but are not as enriched in LREEs as carbonatites and tend to have higher concentrations of HREE (fig. 6, table 3); (4) REE deposits can contain a variety of ore minerals, particularly carbonates, phosphates, or fluorates; (5) significant REE ore minerals include bastnäsite (or bastnäsite-group minerals), monazite, and xenotime; (6) ore minerals can range in size from coarsely crystalline to fine grained and can have complex replacement textures; (7) the ultimate origin of the REEs is related to magmatic processes, but economic REE enrichments are not always clearly linked with primary magmatic processes, particularly where overprinting hydrothermal processes may redistribute and enrich REEs; (8) many carbonatite occurrences include breccias; and (9) country rocks in contact with the intrusive bodies generally are altered by alkali-rich magmatic fluids (fenitization).

Carbonatites tend to occur with alkaline intrusive rocks, but not all carbonatite districts contain documented alkaline



**Figure 5.** Photograph of the Mountain Pass rare earth element mine.

intrusive rocks. Similarly, REE-rich alkaline intrusions do not necessarily occur with carbonatites. When they do occur together, carbonatites tend to be surrounded by alkaline intrusive rocks, and the carbonatites are generally younger. Although many authors propose a genetic link, recent evaluations question the relationship based on the observation that these rock types are quite different chemically and mineralogically and some carbonatites lack associated alkaline rocks (Gittens and Harmer, 2003). Carbonatites and peralkaline igneous rocks associated with REE deposits tend to occur within stable continental tectonic settings, 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 mantle melting (Fitton and Upton, 1987). The petrogenetic evolution of the initial mantle melts that form carbonatites and peralkaline magmas is not fully understood and the various mechanisms are debated.

Regardless of the petrogenetic debates, carbonatite magmas are generated and contain anomalous concentrations of REEs and other incompatible elements. The term “incompatible elements” refers to elements that preferentially retained in the magma because they do not partition readily into common rock-forming minerals. The source of REEs is the initial magma, and with decreasing pressure and temperature the magma evolves, leading to further REE enrichment. Crystallization is one process that drives magma evolution. 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 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 are accompanied by major accessory mineral assemblage variations. Following primary crystallization, alteration by magmatic fluid (or less commonly, meteoric fluids) can produce complex mineral assemblages responsible for some of the mineralogical and geochemical variation between carbonatite units (Castor, 2008a). Carbonatite masses and dikes of differing mineralogy and chemistry within a single district may represent separate intrusive episodes.

The principal REE-bearing minerals associated with carbonatites are fluorocarbonates (bastnäsite, parisite, and synchysite), hydrated carbonates (ancylite), and phosphates (monazite and apatite) (Zaitsev and others, 1998; table 1). Other REE phases, such as britholite and burbankite, are less common. Because most carbonatites experienced a complex petrogenetic evolution, which included hydrothermal overprinting of primary magmatic phases, the resulting mineralogical and textural characteristics were quite varied and intricate, and thus were difficult to summarize. For this reason, published information regarding paragenesis, zoning patterns, and structure is limited.

## 10 A Deposit Model for Carbonatite and Peralkaline Intrusion-Related Rare Earth Element Deposits

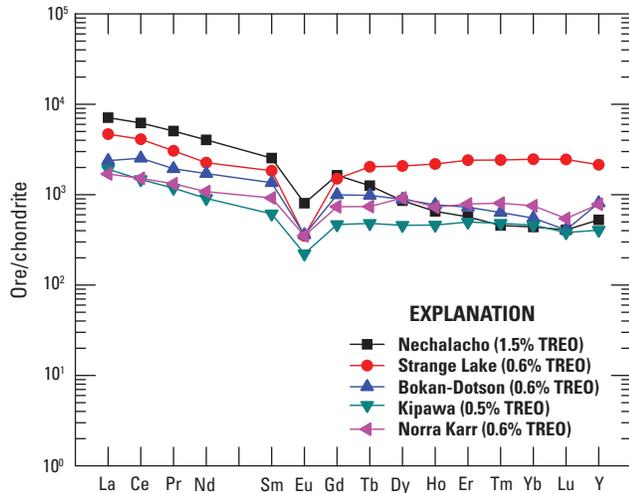
**Table 3.** Whole-rock rare earth element concentration data. In parts per million (ppm).

[Mtn, mountain; >, greater than; FMR, iron oxide, manganese oxide, rare earth element]

Sample number	11PV01	11PV02	11PV04	11PV05	SYMP-1	11BL03A	11BL03A2	11BL06A	11BL11B
<b>Deposit</b>	Mtn Pass	Mtn Pass	Mtn Pass	Mtn Pass	Mtn Pass	Bear Lodge	Bear Lodge	Bear Lodge	Bear Lodge
<b>Unit</b>	carbonatite ore	carbonatite ore	carbonatite ore	shonkinite	syenite	FMR vein	FMR vein	FMR vein	FMR vein
<b>Latitude</b>	35.476	35.476	35.476	35.489	34.459	44.487	44.487	44.489	44.490
<b>Longitude</b>	-115.533	-115.533	-115.533	-115.536	-115.515	-104.451	-104.451	-104.447	-104.445
<b>La</b>	28,800	28,700	28,200	261	207	5,750	4,700	22,800	69,000
<b>Ce</b>	44,100	41,400	42,000	574	463	11,300	9,320	35,200	83,100
<b>Pr</b>	4,010	3,810	3,790	70.3	55.2	1,360	1,170	3,230	8,070
<b>Nd</b>	10,900	10,800	10,200	295	225	5,360	4,720	10,300	26,300
<b>Sm</b>	670	830	640	53	41.2	1,350	1,270	1,390	3,940
<b>Eu</b>	103	148	107	11.1	8.55	411	401	298	1,010
<b>Gd</b>	154	281	158	34	27.4	1,660	1,680	934	3,740
<b>Tb</b>	14	25	14	3.56	2.83	227	238	104	451
<b>Dy</b>	29	68	26	14.8	12.5	1,040	1,130	440	1,610
<b>Ho</b>	4.7	8.5	3.3	2.15	1.93	152	169	62.4	168
<b>Er</b>	11.5	13.3	5.5	4.87	4.61	272	306	117	210
<b>Tm</b>	1.7	1.2	0.5	0.59	0.54	30.6	35.2	15.6	18.2
<b>Yb</b>	14	5.0	3.0	3.2	3.5	139	159	89	75
<b>Lu</b>	2.2	0.7	0.3	0.49	0.52	14.8	17.2	11.5	9.0
<b>Y</b>	111	181	65	63.5	53.6	3,850	4,220	1,350	3,400

Sample number	11BL12A1	11BL02B	11BL02C	11BL13	02-BM10	04-BM10	14-BM10	15-BM10	08-BM10	10B-BM10
<b>Deposit</b>	Bear Lodge	Bear Lodge	Bear Lodge	Bear Lodge	Bokan Mtn	Bokan Mtn				
<b>Unit</b>	FMR vein	trachyte	trachyte	trachyte	Dotson vein	Dotson vein	Dotson vein	Dotson vein	riebeckite granite	aegirine granite
<b>Latitude</b>	44.490	44.474	44.474	44.515	54.910	54.909	54.908	54.908	54.909	54.907
<b>Longitude</b>	-104.444	-104.441	-104.441	-104.446	-132.129	-132.126	-132.122	-132.120	-132.140	-132.139
<b>La</b>	40,000	85.5	121	54.3	266	94.2	532	1,510	40.8	18.9
<b>Ce</b>	61,200	155	223	90.1	600	313	1210	3,090	83	37.2
<b>Pr</b>	6,550	16.7	24.7	11.8	52.6	22.3	123	308	8.99	3.96
<b>Nd</b>	24,300	61.8	94.2	46.6	171	89.6	456	1,150	32.5	14.6
<b>Sm</b>	5,330	10.4	17	9.5	36.2	33	109	272	5.5	3.2
<b>Eu</b>	1,300	2.88	4.79	2.69	3.86	5.08	11.8	33.1	0.48	0.4
<b>Gd</b>	3,740	7.79	13.5	7.67	37.8	68	133	448	4.16	2.57
<b>Tb</b>	273	0.91	1.6	0.93	7.92	22.2	28.3	116	0.99	0.37
<b>Dy</b>	707	4.43	7.94	4.6	54.6	219	206	996	9.17	2.24
<b>Ho</b>	63.2	0.72	1.29	0.73	11.4	64	45.8	248	2.31	0.45
<b>Er</b>	70.9	1.86	3.69	1.93	33.3	258	145	818	9.37	1.43
<b>Tm</b>	6.6	0.26	0.5	0.27	4.96	45.9	22	119	1.83	0.25
<b>Yb</b>	29	1.7	3.1	1.9	30.8	334	139	701	15.3	2.5
<b>Lu</b>	3.6	0.24	0.44	0.29	3.9	47.1	17.5	80.1	2.67	0.59
<b>Y</b>	958	22.1	40.6	22.3	387	>1,000	>1,000	>1,000	39.1	13.5



**Figure 6.** Rare earth elements in selected peralkaline intrusion REE complexes. Concentrations normalized to C1 chondrite values from Anders and Ebihara (1982). (TREO, total rare earth oxide) Percent (%) TREO refers to grade cut off in given deposit.

Similar to carbonatites, the parental magma for alkaline intrusive complexes that host REE mineralization is likely generated as a partial melt of metasomatized mantle material (Platt, 1996); likewise, this initial melt is the REE source. 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 associated with chemically-evolved peralkaline intrusions as either in veins/dikes or disseminated within the intrusive body. Examples of layered complexes include the Nechalacho deposit at Thor Lake, Canada, the Kringlerne deposit at Ilímaussaq, Greenland, and the Lovozero deposit, Kola Peninsula, Russia (fig. 1). Examples of the second category include Bokan Mountain in southerneasternmost Alaska, which is a vein-dike system, and the disseminated deposits at Ghurayyah, Saudi Arabia and at Khaldzan-Buregtey, Mongolia. The REE-rich alkaline intrusions associated with large, layered complexes display evidence of magmatic evolution by fractional crystallization and magma-chamber processes, which include the formation of roof and floor cumulates. Rare earth element mineralization is associated with individual layers that 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) invoked fractional crystallization of an already evolved magma at shallow crustal levels to explain the observed lithologies in structurally controlled vein and dike systems. 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 peralkaline intrusion-related REE deposits, in part because secondary processes tend to overprint the

primary mineralogy. Important REE-bearing minerals include apatite, eudialyte, loparite, gittinsite, xenotime, gadolinite, monazite, bastnäsite, synchysite, iimoriite, euxenite, kainosite, mosandrite, britholite, allanite, fergusonite, and zircon.

## Associated and Transitional Deposit Types

Other deposit types are not typically associated with carbonatite and peralkaline intrusion-related REE deposits, but other commodities can be enriched in these rock types, as described below. Groves and Veilreicher (2001) proposed that the Palabora carbonatite represents an end member of the iron-oxide-copper-gold (IOCG) deposit type because of similarities with the Olympic Dam deposit, Australia, in particular the enrichment in LREEs, P, F, U, and Th. The origin of the world-class Bayan Obo deposit remains controversial, and it too has similarities to the Olympic Dam deposit including enrichment in Fe, LREEs, P, F, U, and Th. Wu (2008) provides a summary of the controversy between a carbonatite and IOCG origin for the Bayan Obo deposit. The Mount Weld REE deposit is a LREE-rich lateritic deposit above a carbonatite and likely formed by similar processes as Ni-Co laterite deposits as described by Marsh and others (2013).

## Primary Commodities

Carbonatite-hosted REE deposits are the world's primary source of LREE. The Sulphide Queen carbonatite of the Mountain Pass district, southeastern California, is the largest known mass of high-grade, LREE ore in the United States. Carbonatite mined from the Bayan Obo deposit, Inner Mongolia, China, as of 2012, the world's primary source of LREE (Long and others, 2010; U.S. Department of Energy, 2010). However, at Bayan Obo, the primary commodity is iron from hematite-magnetite iron-ore, and the REEs are by-product commodities. The Barreiro carbonatite complex near Araxá, Minas Gerais State, Brazil, is currently the world's primary source of Nb (Papp, 2011). Although not currently producing REEs, the Palabora carbonatite-alkaline complex of South Africa (also spelled "Phalaborwa") is mined for copper and apatite. This deposit produced 2.7 million tonnes (t) of copper during the 1960s to 1980s, and as of 2011 produced about 80,000 t of refined Cu per year (Palabora Mining Company, 2011). Phosphate produced from apatites in carbonatites has been a commodity of significant economic importance in northern Europe, Brazil, and South Africa. Apatites in carbonatite systems have higher phosphate and REE content than do marine phosphates.

No alkaline intrusion complex is currently being mined for REEs, but extensive exploration efforts to evaluate numerous peralkaline complexes are underway because of their HREE enrichments. At present, clay deposits in southern China are the primary source of the world's HREEs, but with a limited resource and increasing export limitations, other sources of heavy REEs are being examined, including peralkaline complexes.

## Byproduct Commodities

Carbonatites and peralkaline intrusive complexes can be enriched in a variety of commodities. Carbonatites can contain significant enrichments in barium (Ba), fluorine (F), Fe, Nb, Sr, Th, U, and Zr. Alkaline rocks associated with carbonatites can contain substantial resources of phosphorous (P), titanium (Ti), uranium, zirconium, and (or) vermiculite. The economic mineral deposits associated with carbonatites and associated alkaline igneous rocks have been summarized by Mariano (1989a).

## Trace Constituents

Other constituents potentially enriched in carbonatites include tantalum and titanium. Peralkaline intrusive complexes can also contain potential enrichments of Be, F, Ga, Nb, Ta, Th, V, and Zn (Richardson and Birkett, 1996b).

## Example Deposits

At present, there are five carbonatite-hosted REE deposits being mined: (1) the Bayan Obo deposit, Inner Mongolia, China; (2) the Daluxiang and (3) Maoniuping deposits, Sichuan, China; (4) the Weishan deposit, Shandong, China; and (5) the Mountain Pass deposit, Calif., United States (fig. 1, table 2). The Mount Weld deposit in Australia is scheduled to go into production in 2013. Other carbonatites within the United States include the Bear Lodge deposit in Wyoming, the Elk Creek deposit in Nebraska, and the Iron Hill deposit in Colorado (fig. 1).

At present, the only REE production from a peralkaline intrusion-related deposit is as a byproduct commodity of Nb production at the Lovozero in Russia. Deposits in advanced exploration stages include: Bokan Mountain, Alaska; the Kvanefjeld and Kringlerne deposits within the Ilímaussaq Alkaline Complex, Greenland; the Nechalacho deposit at Thor Lake, Canada; the Strange Lake deposit, Canada; Kipawa, Canada; and the Norra Kärr deposit, Sweden.

## Historical Evolution of Descriptive and Genetic Knowledge and Concepts

Although carbonatites and alkaline intrusive complexes have been studied for nearly 100 years, no mineral deposit model associated with these lithologies has been developed. Brøgger (1921) described the carbonatite and alkaline complex at Fen, Norway, and concluded that the carbonatite was likely of magmatic origin, which sparked the debate on whether these rocks were sedimentary or magmatic (Brøgger, 1921). Scientific and economic interest increased in the late 1950s and early 1960s with (1) the discovery of REE mineralization in carbonate at Mountain Pass in the 1950s (fig. 7);

(2) the discovery of extrusive natrocarbonatite lava at Oldoinyo Lengai, Tanzania in 1960; and (3) the discovery of the carbonatite-hosted Palabora copper deposit in the late 1950s and early 1960s (Heinrich, 1970). The initial report on REE mineralization at Mountain Pass (Olson and others, 1954), called the primary REE-bearing unit the Sulphide Queen *carbonate* and stated that it could be either of sedimentary or magmatic origin.

With increasing interest in carbonatites and advances in analytical techniques, numerous petrologic studies were undertaken, but published accounts concerning the economic geology of REE mineralization are limited. These petrologic studies clearly show that carbonatites are of magmatic origin, but interpretations concerning the genesis of individual occurrences continue to be debated. For example, the origin of the primary mineralized lithology, the H8 dolomite, at the world-class Bayan Obo deposit has been debated for more than 30 years (Yuan and others, 1992). Recently, Yang and others (2011) identified new contact relationships that show that the H8 dolomite intruded its host rock and is therefore magmatic.

Following World War II, exploration efforts focused on uranium and thorium mineralization, which led to the discovery of REE-enriched peralkaline complexes, including Bokan Mountain and Kipawa. Various economic and academic studies of these deposits described enrichments in other HFSEs, such as Nb and Zr, as well as REEs (for example, Thompson and others, 1982; Fitton and Upton, 1987). These studies provided the framework for the recent exploration activity and the general understanding of mineralization style.

Experimental studies have significantly advanced the understanding of alkaline complex petrogenesis. Experimental studies have focused on the processes controlling the generation of carbonatite magmas; both primary mantle melting or immiscibility of alkaline magmas appear to be possible mechanisms. These studies help shed light on the nature of



**Figure 7.** Photograph of the discovery outcrop, the Birthday claim, at Mountain Pass. Coarse-grained, tabular bastnäsite in an iron-rich dolomite vein.

metal sources and processes responsible for their enrichment. To constrain the evolution of fluid phases associated with evolving magmas, fluid inclusion studies have contributed to identification of the aqueous complexes responsible for REE mobility. Rankin (2005) provided a summary of the state of the knowledge for carbonatite systems. Salvi and Williams-Jones (1990) provided an excellent example of the utilization of fluid inclusions to constrain fluid phase evolution at the Strange Lake deposit.

## Regional Environment

### Geotectonic Environment

Carbonatites and peralkaline igneous rocks associated with REE deposits tend to occur within stable continental tectonic settings, in areas defined as shields, cratons, and crystalline blocks; they are generally associated with intracontinental rift and fault systems (Berger and others, 2009). The East African Rift is one of the most studied rift valleys and hosts the well-studied Oldoinyo Lengai volcano and its recent carbonatite lavas. Woolley and Kjarsgaard (2008) compiled data on more than 500 carbonatite occurrences and concluded that carbonatites primarily occur in stable, intra-plate areas and are associated with major faulting and rift-related doming. Carbonatites have also been associated with orogenic activity (Woolley, 1989; Hou and others, 2006). Radiogenic isotopic studies of carbonatites document that some of these magmas were derived from mantle materials with little contamination by crustal interaction (Bell and Blenkinsop, 1989), which is consistent with a rift environment where mantle-derived melts can ascend without substantial crustal interaction.

Castor (2008b) concluded that the ultrapotassic alkaline units spatially associated with carbonatite at Mountain Pass are likely of mantle origin and suggested that these units may be associated with intracontinental rifting. The Elk Creek deposit lies at the eastern margin of the Midcontinent Rift Zone (Van Schmus and others, 1996). Yang and others (2011) concluded that the Bayan Obo deposit was likely part of carbonatite magmatic activity associated with continental rifting. Crustal thinning in rift environments enables magmas derived from the asthenospheric or lithospheric mantle to ascend high in the upper crust because there is a minimal distance to travel and the upper crust is a region of high heat flow.

Although extensive research on the geotectonic setting of alkaline complexes has been published (Fitton and Upton, 1987 and references within), geotectonic studies of their associated REE deposits are limited. Many alkaline complexes are located in continental settings adjacent to rift valleys or major faults. Petrogenetic studies of the Ilímaussaq alkaline complex in Greenland concluded that it formed in a failed rift setting (MacDonald and Upton, 1993). Alkaline magmatism in the Kola Peninsula, including the rocks of the Lovozero intrusive

body, is temporally related to a period of extensive rifting (Kramm and Sindern, 2004).

### Temporal (Secular) Relations

No generalities for temporal relations can be made because of the limited published information on this topic. For a compilation of ages of mineralized carbonatites see Berger and others (2009).

### Duration of Magmatic-Hydrothermal System and/or Mineralizing Processes

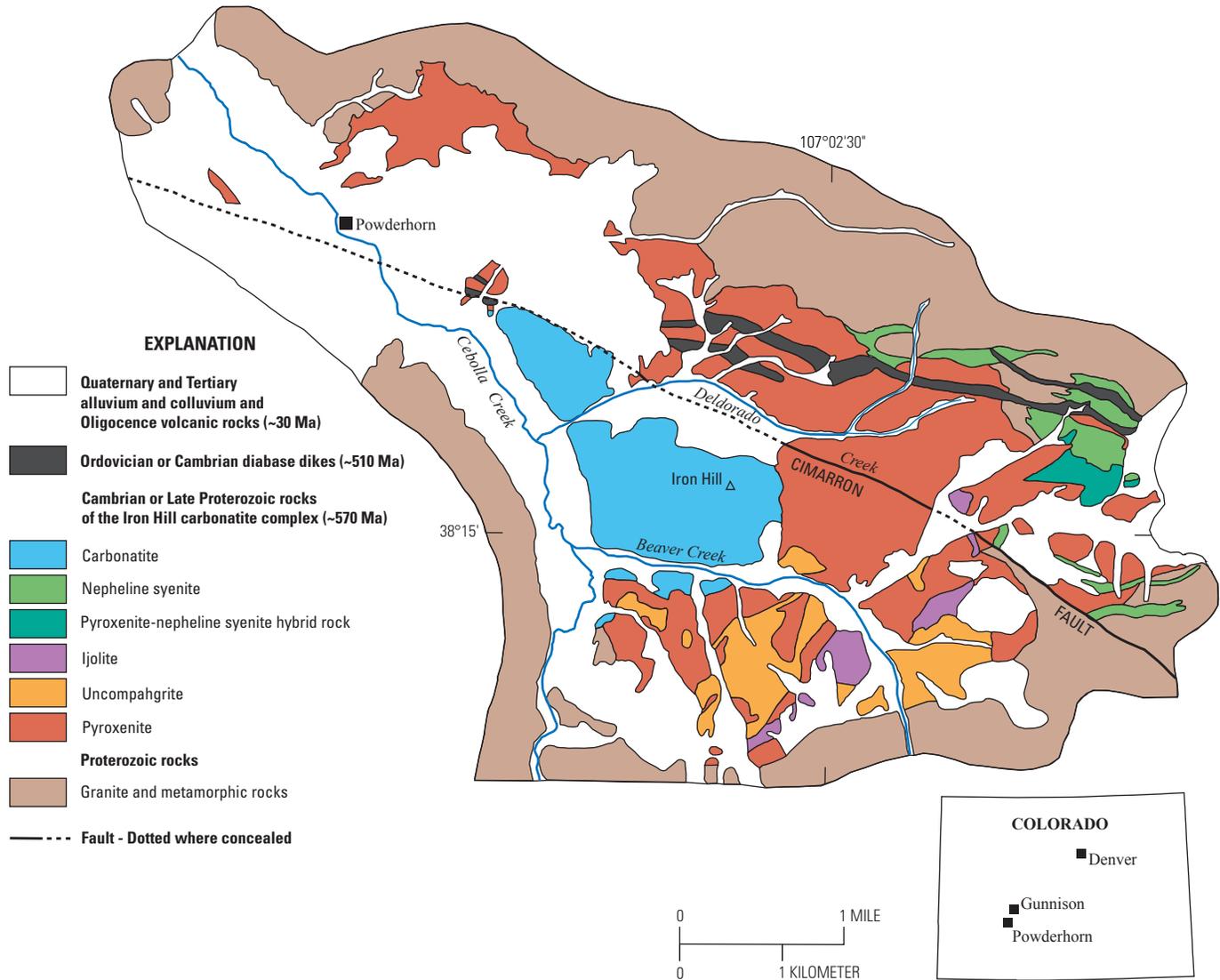
The duration of magmatic and hydrothermal processes responsible for igneous-related REE deposits is unknown because of limited published information.

### Relations to Structures

On a regional scale, these deposit types are linked to continental rifting or major faults, but a detailed evaluation of structural controls is hindered by the limited publications on these deposits. Mineralized rock associated with structurally controlled carbonatites is quite variable and may include REE-rich disseminated zones, breccias, and late-stage veinlets in some carbonatites (Mariano, 1989a, b; Wall and Mariano, 1996). The Dotson vein-hosted REE mineralization at Bokan Mountain (Warner and Barker, 1989; Philpotts and others, 1998) is associated with peralkaline magmatism that is structurally controlled.

### Relations to Igneous Rocks

Igneous rocks play an essential role in the formation of carbonatite and peralkaline intrusion-related REE deposits. In these deposits, carbonatite and peralkaline magmas are the primary sources of the REEs and are generally believed to be the primary sources of fluids that concentrate REEs in mineral deposits. Rare earth element mineralization is hosted in carbonatites and peralkaline intrusions that are typically part of larger magmatic complexes. Examples include the mineralized carbonatite at Mountain Pass, which lies within an ultrapotassic alkaline complex that includes shonkinites, melasyenites, syenites, and quartz syenites (Castor, 2008b). Carbonatite mineralization at the Bear Lodge deposit is within the Bear Lodge alkaline complex, which includes tonalites and phonolites, as well as latites, syenites, and nepheline syenites (Staat, 1983). The Iron Hill carbonatite intruded an alkaline complex, which includes, from oldest unit to youngest: pyroxenite, uncomphgrite, ijolite, and nepheline syenite (fig. 8; Olson and Hedlund, 1981). Crosscutting relations at Mountain Pass, Bear Lodge, and Iron Hill indicate that the carbonatites are younger than surrounding alkaline intrusive units. Age determinations indicate that the Sulphide Queen carbonatite at Mountain Pass



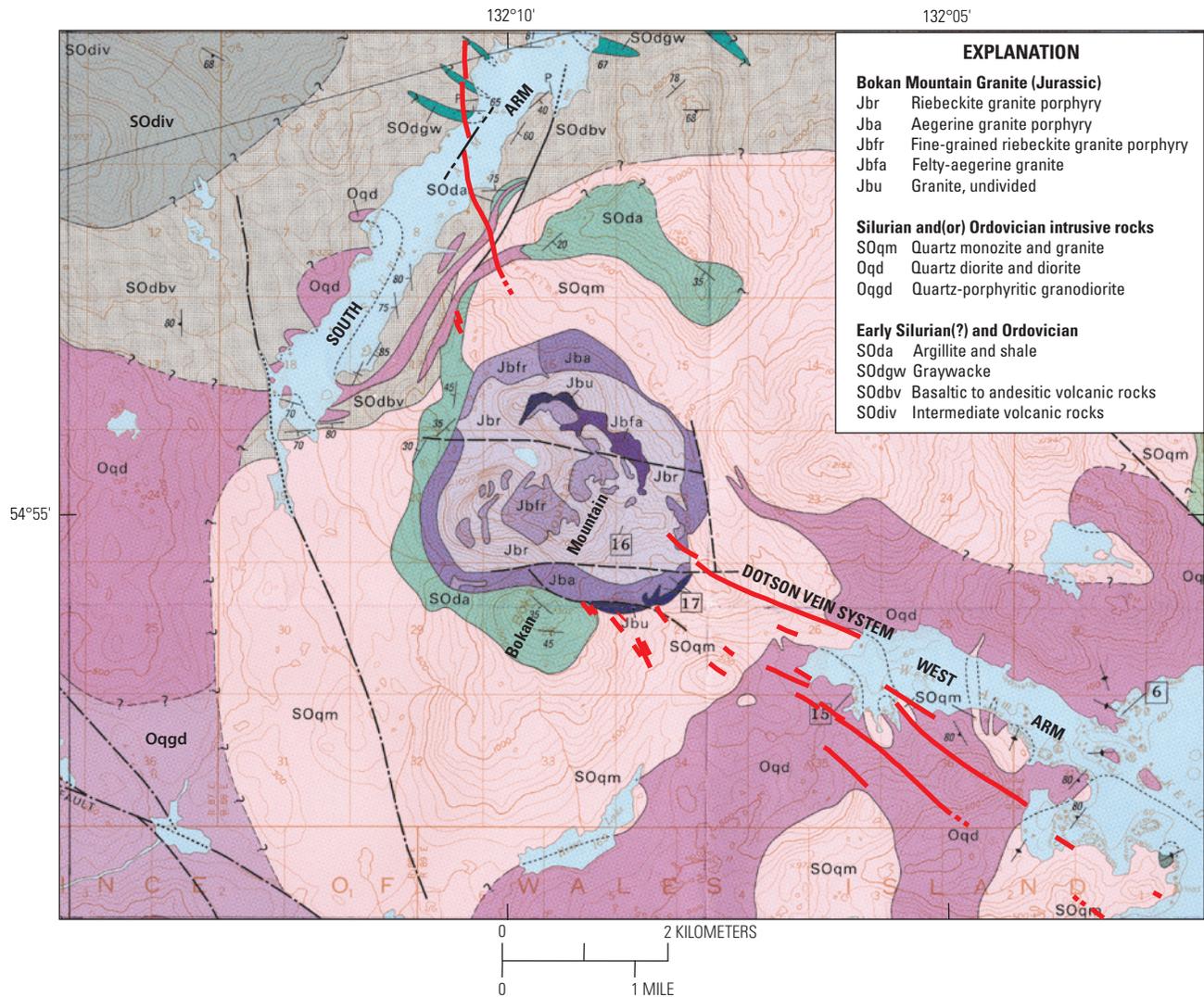
**Figure 8.** Geologic map of the Iron Hill carbonatite complex from Van Gosen (2009). A generalized map from the geologic maps of Olson (1974) and Hedlund and Olson (1975).

was emplaced at  $1375 \pm 5$  Ma (DeWitt and others, 1987), about 25–35 million years after the alkaline igneous intrusions in the district (Castor, 2008b).

Rare earth element deposits associated with alkaline intrusive layered complexes are generally part of larger alkaline complexes. For example, the Nechalacho deposit at Thor Lake lies within the Thor Lake syenite, which is the youngest known intrusive phase of the Blatchford Lake complex, a suite of alkaline to peralkaline rocks (Davidson, 1978). Units within the Blatchford complex include, from oldest to youngest, Caribou Lake gabbro, Whiteman Lake quartz syenite, Hearne Channel and Mad Lake granites, and the Thor Lake syenite (Davidson, 1978; Taylor and Pollard, 1996). The Kvanefjeld and Kringlerne deposits are within the Ilímaussaq Alkaline Complex, which is composed of augite syenite, pulaskite (orthoclase,

soda pyroxene, arfvedsonite, and nepheline), foyaite (potassium feldspar-rich nepheline-syenite), sodalite foyaite, naujaite (sodalite-rich nepheline syenite with microcline), kakortokite (arfvedsonite, nepheline, eudialyte-rich syenite), lujavrite (eudialyte-bearing nepheline-syenite), alkali granite, and quartz syenite (Sørensen, 2001)

At Bokan Mountain, REE mineralization is in narrow veins or dikes that extend out from a peralkaline intrusive complex (fig. 9). The intrusive complex consists of a crudely circular riebeckite- and acmite-bearing peralkaline granite intrusion with a riebeckite granite porphyry core surrounded by an aegirine granite porphyry margin and, in places, a border zone pegmatite-aplite unit (Thompson, 1988). At Ghurayyah, Saudi Arabia, the REE mineralization is disseminated within a porphyritic microgranite stock of peralkaline composition. The



**Figure 9.** Geologic map of the Bokan Mountain area from Barker and Van Gosen (2012). Geology from Gehrels (1992). Red lines delineate dikes and veins. Black lines delineate faults.

granite intrudes metasedimentary and metavolcanic units and is associated with the Jabal Dabbagh alkali granite complex (Drysdall and others, 1984). The mineralization at the Khaldzan Buregtye deposit occurs within peralkaline granitic stocks that are part of the Khaldzan-Buregtye granitoid massif, which is a multiphased intrusive sequence (Kovalenko and others, 1995).

### Relations to Sedimentary Rocks

Sedimentary rocks are not genetically associated with carbonatite and alkaline intrusive REE deposits but may host the intrusion-related deposits.

### Relations to Metamorphic Rocks

Metamorphic rocks are not genetically associated with carbonatite and alkaline intrusive REE deposits but may be the country rock that hosts the intrusion-related deposits.

## Physical Description of Deposit

### Dimensions in Plan View

Carbonatite and peralkaline intrusion-related REE deposits are quite variable in size and shape because of the variable size and geometry of the intrusive rock units and the extent of magmatic hydrothermal system. Although carbonatites vary from plutonic bodies to discrete veins, the mineralized parts of carbonatite bodies can be quite complex. Rare earth element mineralization at Mountain Pass occurs in the Sulphide Queen body, which was about 700 meters (m) by 150 m prior to mining (Olson and others, 1954). Detailed mapping and petrography of the Sulphide Queen carbonatite showed that it is composed of a group of carbonatites having distinct mineralogical or textural characteristics (Castor, 2008b). The Bayan Obo deposits consist of three ore bodies (main, east, and west) within the H8 dolomite marble that are lenticular in shape

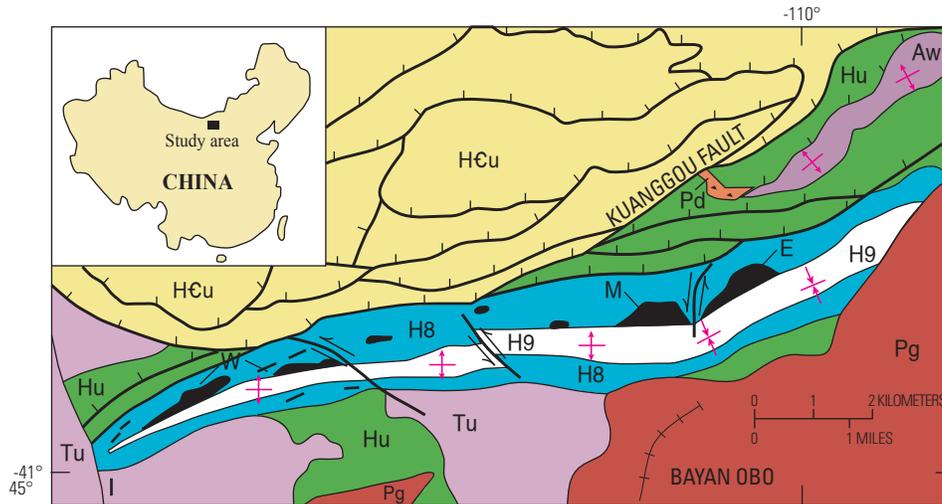
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(fig. 10; Yang and others 2011). The H8 dolomite marble outcrop is 18 kilometers (km) long and as much as 1 km in maximum width (Yuan and others, 1992). The Mauniuping deposit consists of carbonatite sills within a syenite intrusion that is 1,400 m long and 260–350 m wide; individual carbonatite sills are 90–200 m wide (Xu and others, 2008).

Peralkaline intrusion-related REE deposits have variable geometries, either as structurally controlled vein systems associated with peralkaline plutonism (Bokan Mountain), as disseminated deposits within a pluton (Ghurayyah or Khaldzan-Buregtey), or as REE-rich layers within alkaline layered complexes (Ilmaussaqa, Strange Lake, Thor Lake, and Kipawa). Because none of the peralkaline intrusion-related deposits have produced primary REE ore, quantification of ore zone geometry is difficult. At Bokan Mountain, the primary exploration target for REEs is the Dotson vein system, which

has a strike length of 2,140 m and an average width of 50 m; individual veins have a maximum width of 3 m (Robinson and others, 2011). Mineralization associated with layered complexes is quite variable.

Rare earth element mineralization within layered alkaline complexes results from the preferential concentration of various REE-rich minerals within evolving magma chambers, which produce REE-bearing zones that are quite irregular in shape and size. The geometry of mineralized zones is in part controlled by the shape of the magma chamber and the processes responsible for the mineral accumulations. Sheard and others (2012) described the mineralization at the Nechalacho deposit at Thor Lake as occurring within two zones: the 15- to 30-m-thick upper zone and the 15- to 60-m-thick lower zone. The lateral extent of these layers is not reported.



EXPLANATION

(The unit symbols for the Bayan Obo Group are used in accordance with standard Chinese geologic symbols for Middle Proterozoic.)

Bayan Obo Group (Middle Proterozoic)	
Tu	Sedimentary rocks, undivided (Tertiary)
Pd	Diorite (Permian)
Pg	Granite rocks (Permian)
Hcu	Sedimentary rocks, undivided (Proterozoic and Cambrian)
H9	Shale, slate, and schist
H8	Dolostone and limestone marble
Hu	Sedimentary rocks (H1-H7), undivided
Aw	Wutai Group (Archean)—Gneisses

SYMBOLS

Contact	Anticline
Fault (1)—Ticks show direction of dip, where known	Syncline
Other faults—Arrows show relative movement	Orebodies—M, Main Orebody; E, East Orebody, W, West Orebody
Railroad	

Figure 10. Geologic map of the Bayan Obo deposit region from Chao and others (1997).

## Size of Hydrothermal System Relative to Extent of Economically Mineralized Rock

Data on hydrothermal system size relative to the extent of economically mineralized rock associated with carbonatite and alkaline intrusion-related REE deposits are lacking.

## Vertical Extent

Data on the vertical extent of carbonatite and alkaline intrusion related REE deposits are lacking.

## Form and Shape

Carbonatite and alkaline intrusion-related REE deposits are of diverse form and shape. Carbonatite bodies have been described as tabular and moderately dipping (Mountain Pass; Castor, 2008b), lenses (Bayan Obo; Yang and others, 2011), veins (Weishan; Wu and others, 1996), and large stocks (Iron Hill, Colorado; Olson and Hedlund, 1981). Alkaline intrusion-related deposits form vein deposits, disseminated deposits, or layers within alkaline layered complexes. The Dotson vein system at Bokan Mountain forms a series of sub parallel veins, as much as 3 m thick, within a 50-m-wide zone. Mineralization within the Ghurayyah stock is disseminated, occurring within the matrix surrounding quartz and microcline phenocrysts (Drysdall and others, 1984). Mineralization in layered complexes is present as repetitious fine laminations that represent cumulate layers within a magma chamber.

## Host Rocks

Carbonatite REE deposits are hosted in carbonatites. Carbonatites can vary in composition from calcite as the dominant mineral (calciocarbonatite) to dolomite as the dominant mineral (magnesiocarbonatite), as well as to phases that contain variable proportions of calcite and dolomite. Some carbonatites are iron-rich (ferrocarbonatite), typically due to high ankerite content. Across districts and within single carbonatite masses, carbonatites vary laterally and vertically from calcic to dolomitic to iron-rich; these variations may be accompanied by major accessory mineral variations. Alteration that post-dates primary crystallization can yield complex mineral assemblages and accounts for some of the mineralogical and geochemical variation among carbonatite units (Castor, 2008b). Furthermore, cross-cutting relations and geochemical data show that carbonatite masses and dikes that have different mineralogy and composition represent separate intrusive episodes within a single district. These mineralogical and geochemical variations have been related to protracted crystallization differentiation in the source magma (Yang and others, 2010), as well as to complex interactions between magma and crustal host rocks (Fischer and others, 2009).

Detailed mapping and petrographic studies at Mountain Pass have revealed that the ore-bearing carbonatite, or carbonatites, occur within or adjacent to other carbonatite masses (Castor, 2008b). The primary ore minerals at Mountain Pass (bastnäsite, parisite, and monazite) are hosted in carbonatites composed of varying amounts of dolomite, calcite, barite, strontianite, celestite, talc, and quartz (Castor, 2008b). Ore minerals at Bayan Obo, mainly bastnäsite and monazite, are hosted in the H8 dolomite, which consists of dolomite and calcite with feldspar, quartz, Na-tremolite, magnesio-arfvedsonite, phlogopite, apatite, fluorite, and barite (Xu and others, 2008).

Most REE deposits associated with peralkaline intrusive complexes are part of peralkaline layered complexes, are present as veins and dikes associated with the peralkaline intrusions, or are hydrothermal disseminations in peralkaline complexes. Examples of deposits in layered complexes include the Nechalacho deposit at Thor Lake (Canada) and the Kringlerne deposit at Ilímaussaq (Greenland). Bokan Mountain (Alaska) is an example in the United States of a vein- and dike-hosted deposit. As discussed previously, most alkaline systems that contain peralkaline layered complexes with elevated REE concentrations consist of a complex suite of igneous rocks that have evolved by magmatic processes. Mineralization within the Nechalacho deposit at Thor Lake is hosted in an alkaline layered suite that consists primarily of nepheline syenite, termed the Nechalacho syenite (Bakker and others, 2011; Sheard and others, 2012). Layers within this unit include, from the top down, sodalite cumulates; coarse-grained, pegmatitic nepheline aegirine syenite; and a basal zone of foyaitic syenite. The upper sodalite cumulate zone hosts the “upper mineralized zone” and the foyaitic syenite hosts the “basal zone mineralization.” Late-stage hydrothermal processes have overprinted the primary minerals, resulting in complex mineralogical and textural characteristics (Sheard and others, 2012).

Mineralization in the Kvanefjeld and Kringlerne deposits is hosted in the Ilímaussaq alkaline complex, the type locality of agpaite nepheline syenites. The three main rock types that host mineralization are the lujavrite, naujaite, and karkortokite. Lujavrite consists of aegirine or arfvedsonite with nepheline and alkali feldspar; naujaite consists of sodalite, nepheline, aegirine, alkali feldspar, arfvedsonite and locally eudialyte; and karkortokite consists of layers of arfvedsonite, eudialyte, and feldspar (Friis and Mair, 2010).

At Bokan Mountain, REE mineralization forms narrow veins (fig. 11) and linear dikes that extend out from a peralkaline intrusive complex. The mineralized veins are in part hosted by the peralkaline riebeckite granite (the I&L zone), as well as older country rocks of quartz diorite and quartz monzonite (Dotson vein system; Thompson and others, 1982). Disseminated mineralization at Ghurayyah and Khaldzan-Buregtye is hosted in peralkaline granitoids (Drysdall and others, 1984; Kovalenko and others, 1995).



**Figure 11.** Photograph of a vein within the Dotson vein system, Bokan Mountain.

## Structural Setting(s) and Controls

The regional-scale structural setting for these deposit types has been described in the Regional Environment section. Because of the limited publications on individual occurrences, detailed analysis of structural controls is not possible with the exception of the generally northwest-trending faults that control vein and dike mineralization at Bokan Mountain, Alaska.

## Remote Sensing

During the 1980s and 1990s, the USGS researched the use of Airborne Visible-Infrared Imaging Spectrometer (AVIRIS) data to map the mineralogy and rock types of two large, exposed carbonatites at Mountain Pass, Calif., and at Iron Hill, southwestern Colorado (Rowan and others, 1995; Rowan, 1997). At Mountain Pass, Rowan (1997) analyzed AVIRIS and Thermal-infrared Multispectral Scanner (TIMS) data collected from flyovers of the district, compared these data to reference spectra measured from mineral specimens, and produced interpretive mineral maps of the district. Field verification of the mineral maps indicated that this remote sensing spectroscopy method was effective in mapping the distribution of Al-OH, CO<sub>3</sub>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, and Nd<sub>3</sub><sup>+</sup> minerals; spectral properties indicative of Nd<sub>3</sub><sup>+</sup> are coincident with exposed REE-rich carbonatite.

At Iron Hill, Rowan and others (1995) processed and interpreted AVIRIS spectral data to identify and map:

- Dolomite in the Iron Hill carbonatite stock and smaller bodies,
- Calcite in a small carbonatite plug and in travertine spring deposits,

- Illite in sericitized felsite and granite, and
- Kaolinite in hydrothermally altered ash-flow tuff.

Using the full wavelength range of AVIRIS spectra, they mapped the distribution of primary alkaline igneous rock units in the Iron Hill complex that included pyroxenite, uncom-pahgrite, and ijolite. However, some areas of felsite and fenite could not be spectrally distinguished from the alkaline igneous rocks.

Based on the remote sensing studies by the USGS at Mountain Pass and Iron Mountain, Rowan (1997) concluded that TIMS data can be used to map the principal alkalic lithologic units within carbonatite-alkalic rock complexes, but AVIRIS data are needed to map carbonatite, as well as OH- and Fe-bearing minerals.

More recently, another USGS study (Mars and Rowan, 2011) examined the application of Advanced Spaceborne Thermal and Reflection Radiometer (ASTER) data to map lithologies at the Quaternary-age Khanneshin carbonatite volcano in southern Afghanistan. Mars and Rowan (2011) reported that calcic carbonatite could be distinguished from ankeritic carbonatite in the short wave infrared region of ASTER data as indicated by a slight shift in the CO<sub>3</sub> absorption band. Using spectral features, they were also able to map: (1) contact aureole rocks containing muscovite, epidote, and chlorite; (2) the crater rim composed of argillite and sandstone; and (3) iron (Fe<sub>3</sub><sup>+</sup>) and muscovite-illite-rich rocks and iron-rich eolian sands bounding the western side of the volcano. Mars and Rowan (2011) explained in detail how several types of processed ASTER spectral data can be analyzed and used in combination to delineate rock types and mineral mixtures in complex alkaline igneous systems, such as the Khanneshin volcano, which includes carbonatite that varies in composition, along with associated mafic rocks, hornfels, sedimentary rocks, and sediments.

Reflectance spectra can be collected on the ground using a field-portable spectrometer. The reflectance spectra data collected on-the-outcrop can then be compared and correlated with geo-referenced airborne spectral data that are collected from an aircraft. Using a field-portable spectrometer, Bedini and Tukiainen (2009) measured reflectance properties of the primary rock units of the Sarfartoq carbonatite complex in southern West Greenland. An airborne hyperspectral survey was flown over the carbonatite complex with a fixed-wing aircraft at an altitude of 2.5 km. Using the ground and airborne data in concert, the spectral analysis showed success in mapping the three primary rock types that crop out in the complex: carbonatite, fenite, and hematite-rich gneiss (Bedini, 2009). Also, Bedini and Tukiainen (2009) reported positive results in distinguishing two distinct types of carbonatite that form the center of the complex. These included an inner carbonatite core that is fully enclosed by an outer core of carbonatite mixed with fenite.

## Geophysical Characteristics

Airborne surveys now offer the ability to simultaneously acquire gamma-ray, gravity, and magnetic data. This ability provides a valuable exploration tool for locating intrusion-related REE deposits and provides several layers of geo-referenced geophysical data to model and compare. These techniques have been used with success in regional reconnaissance surveys to identify targets for more detailed geologic mapping and geochemical sampling (Thomas and others, 2010). Collection of more tightly spaced geophysical data over target intrusions, whether collected on the ground or from low-flying aircraft, can be modeled to estimate the geometry and structural characteristics of the intrusions in three dimensions. There are several notable examples of successfully using airborne radiometric, magnetic, and (or) ground- or airborne-based gravity surveys to locate REE-bearing carbonatites or alkaline intrusions. Examples of the successful application of these techniques in exploration for REEs are summarized in this section.

As noted earlier, concentrations of the REEs are thought to be genetically linked to alkaline magmas that form from low degrees of partial melting in the upper mantle. These melts can undergo extreme amounts of fractional crystallization as they rise through the crust, during which incompatible elements are concentrated in the magmatic melt phase, rather than vapor phase. Incompatible elements are not readily incorporated into the lattices of the common rock-forming silicate minerals due to their large ionic radius or low valence state. The physical properties of the HFSEs, such as radioactivity or magnetism, enable the intrusions that host these HFSEs to be mapped by geophysical techniques because they provide physical property contrast to the typical country rocks surrounding these intrusions.

### Radioactivity

Gamma-ray (radiometric) surveys have been used successfully to map intrusion-hosted REE deposits. Radiometric surveys measure the natural emission of gamma radiation derived primarily from three radioelements: K, U, and Th. For U and Th, the radiation is via daughter radionuclides. Data can be collected from a helicopter or airplane along flight lines or from the ground along profiles. For all practical purposes, the results are geochemical maps that define the lateral surface distribution of K, U, and Th. Because the method measures the radioactive properties within soils and rock located within the upper 30 centimeters (cm) of the topographic surface (Zotimov, 1971), the host carbonatite or alkaline rock must be at least partly exposed for this method to be successful.

Many REE-minerals contain or are associated with uranium- and thorium-bearing minerals. Rare earth minerals that occur in economic or potentially economic deposits that also contain Th or U include aeschynite, allanite, brannerite, erianite,

cheralite, euxenite, monazite, samarskite, xenotime, yttrantalite, and zircon (Durrance, 1986; Castor and Hedrick, 2006). Hence, gamma-ray surveying can be a direct detection tool for REEs in some deposits. In general, as the silica content of a rock increases, so do the radioelement concentrations.

As described earlier, K enrichment is typically a product of hydrothermal alteration of carbonatites and peralkaline intrusions. Alteration processes can also play an important role in concentrating REE mineralization. Thus, a gamma-ray potassium map can provide important information to understand the lateral extent, ore forming controls, and intensity of alteration.

Many (possibly the majority) of the known REE deposits were originally discovered by prospectors searching for uranium deposits with a scintillometer or Geiger counter that was hand-held, car-mounted, or attached to a low-flying plane or helicopter. The majority of the inadvertent discoveries of REE deposits in the United States occurred during the 1940s and 1950s, when the Atomic Energy Agency financially encouraged the discovery of uranium deposits and, in doing so, created a rush of uranium exploration activity. Examples of REE deposits in the United States that were first discovered by uranium prospectors include the REE-Th-U deposits of:

- the Bokan Mountain (Thompson, 1988; Long and others, 2010) and Salmon Bay (Houston and others, 1955) deposits, both on Prince of Wales Island, Alaska;
- the Mountain Pass deposit in California (Olson and others, 1954);
- the Wet Mountains area, Colorado (Christman and others, 1953, 1959; Armbrustmacher, 1988);
- the Diamond Creek area of Idaho (Anderson, 1958);
- the Lemhi Pass area of Idaho–Montana (Staat, 1972, 1979);
- the Capitan Mountains, south-central New Mexico (Griswold, 1959);
- the Laughlin Peak area, northeastern New Mexico (Staat, 1985); and
- the Lemitar and Chupadera Mountains, west-central New Mexico (McLemore, 1983, 1987; Van Allen and others, 1986).

Similarly, the St-Honoré carbonatite complex in Quebec was discovered when an airborne gamma-ray survey detected the high Th content of the complex. The anomalous REEs were found by follow-up geochemical studies within the area outlined by the most intense total count gamma-ray anomaly (Vallée and Dubac, 1970). The Th-rich Allan Lake carbonatite, Ontario, was discovered in 1977 by a reconnaissance airborne gamma-ray survey conducted by the Geological Survey of Canada's Uranium Reconnaissance Program (Ford and others, 1988).

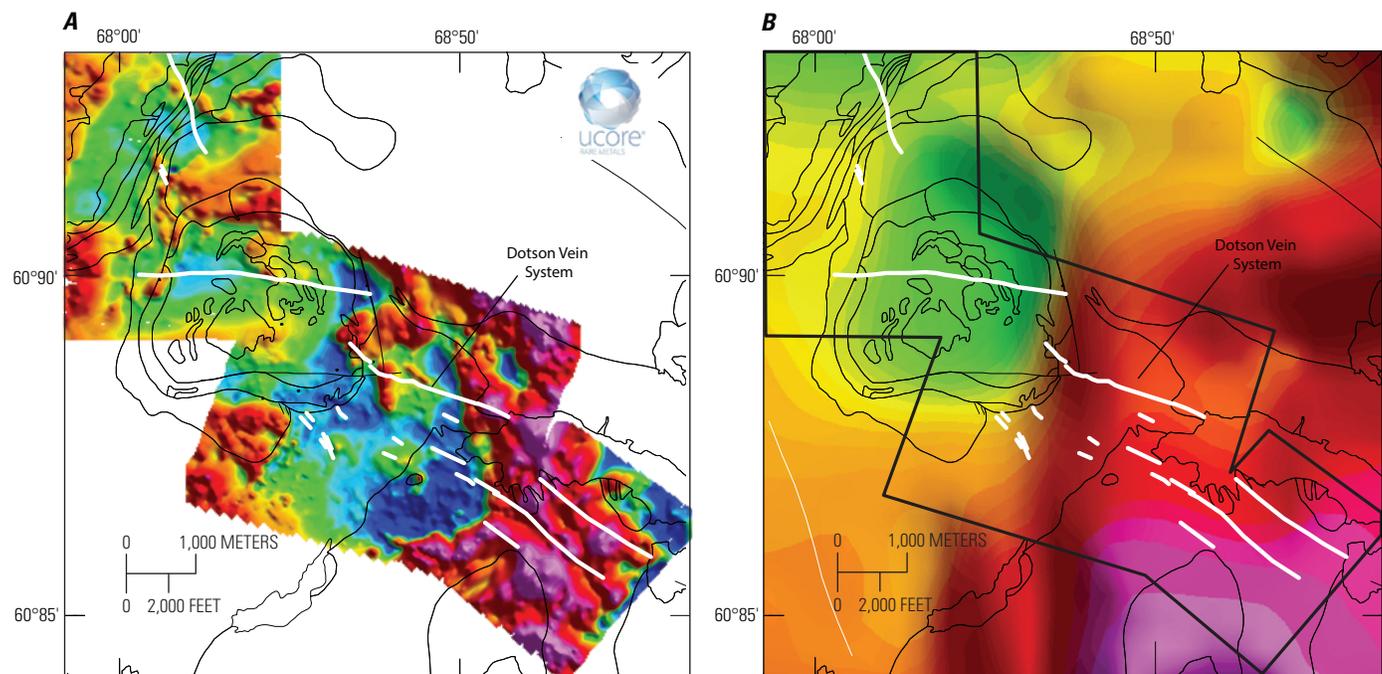
## Magnetic Surveys

Magnetic anomaly surveys measure changes in the Earth's magnetic field as a result of variations in the magnetic mineral content (primarily magnetite) of near surface rocks. In most cases, magnetic anomalies produced by carbonatites and alkaline rocks are due to the magnetic characteristics of the intrusions and surrounding geology, not the REE mineralization. Because sedimentary rocks are mostly nonmagnetic, they are transparent to the magnetic mapping method, which is primarily sensitive to magnetic properties related to crystalline rocks. This makes magnetic surveys useful in mapping REE-bearing carbonatites and alkaline intrusions located under sedimentary cover or unconsolidated material such as glacial till.

Satterly (1970) studied the magnetic anomalies over 43 carbonatites and alkaline complexes in Ontario, Canada. Some complexes are exposed, but most are covered with sedimentary or glacial deposits as much as several hundred meters thick. He noted that the simplest geophysical expression of a carbonatite is an oval to circular-shaped magnetic anomaly low surrounded by a horseshoe-shaped anomaly high. The magnetic high may represent magnetite-bearing carbonatites or mafic alkalic rocks. The Mountain 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).

Magnetic signatures over alkaline complexes can be more complicated. Different phases of emplacement and alteration processes affect the magnetic mineralogy and therefore the magnetic content of alkaline rocks. Complication in magnetic signature also arises with higher resolution data. As an example, regional magnetic data from a survey flown with flight lines spaced every 1,600 m over the Bokan Mountain peralkaline complex in southeastern Alaska (U.S. Geological Survey, 1984) showed the intrusion to be a simple oval magnetic anomaly low approximately 2 km x 3 km. However, comparison with high resolution magnetic data flown in 2010 with flight lines spaced every 100 m over the intrusion (Ucore Rare Metals and Precision GeoSurveys, written commun. 2009) showed the magnetic signature over the complex is much more complex than the regional data suggested (compare figs. 12A and 12B). Rare earth mineralization at Bokan Mountain is hosted in the peralkaline intrusion, but concentrated in northeast-trending vein systems that cut the body. There is no measurable magnetic signature of the vein system. The primary vein system, the Dotson trend, is however, expressed as strong U, Th, and K anomalies in the Ucore gamma-ray survey (not shown).



**Figure 12.** A, High resolution magnetic anomaly map over the Bokan Mountain rare earth deposit, southeast Alaska. Black lines show geologic contacts and white lines show location of mineralized REE-bearing vein systems; B, Regional magnetic anomaly map over same area, which shows the Bokan granite complex as an ovoid magnetic anomaly low (green).

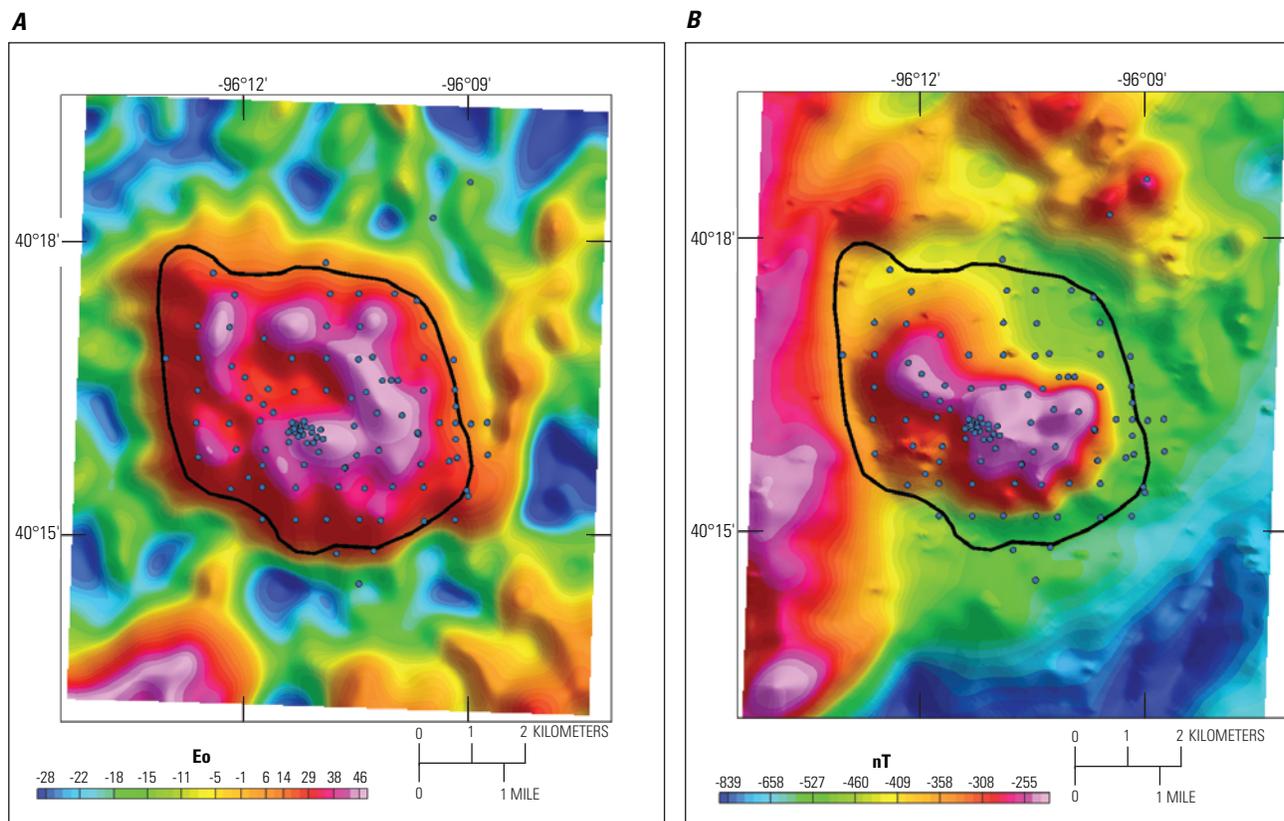
## Gravity Surveys

Gravity surveys measure small variations in rock density expressed as gravity anomalies. Carbonatites and alkaline intrusions tend to have rock densities greater than the average density for crustal rocks, which is 2.67 grams per cubic centimeters ( $\text{g/cm}^3$ ), and thus are reflected by gravity highs. For example, densities for carbonatites and alkaline intrusions in Canada range between 2.84–3.09  $\text{g/cm}^3$  (Thomas and others, 2010) and are typically expressed in the gravity field as ovoid to circular anomaly highs. In Quebec, the Oka carbonatite-alkaline complex and the St-Honoré carbonatite complex each produce strong gravity anomaly highs, 15 milliGals (mGal) above the surrounding area at Oka (Gold and others, 1967; Vallée and Dubac, 1970).

Recent advancements in airborne geophysical survey technology now offer the ability to measure small changes in the earth's gravitational field (gravity gradients) from airborne platforms. This technology maps subtle density contrasts and variations in the gravitational field in much greater detail than would be available from most ground gravity surveys. These small changes in the gravity field coincide with geologic structures, lithologic differences, and contacts that may have importance in regard to establishing controls on REE mineralization.

Regional framework geophysical studies, conducted in southeastern Nebraska in the 1970s, identified a large amplitude gravity anomaly high from a ground survey that was drilled and found to be caused by the Elk Creek carbonatite at a depth of 183 m (Carlson and Treves, 2005). Density studies conducted on core of the carbonatite yielded an average density of 3.28  $\text{g/cm}^3$ . This area of Nebraska is blanketed by loess and glacial till that cover Pennsylvanian marine carbonates and shale.

The gravity anomaly is due to a mostly dolomitic carbonatite (89 percent) with associated fentized basalt, lamprophyre, and syenite (totaling 11 percent) (Xu, 1996). In April 2011, Quantum Rare Earth Developments Corp. commenced a high-resolution airborne gravity and magnetic survey over the buried Elk Creek carbonatite to identify new drilling targets. Figure 13 shows an example of the high resolution airborne gravity gradiometry (fig. 13A) and magnetic anomaly survey (fig. 13B) over the Elk Creek Nb-REE deposit (NioCorp Developments Ltd., formally Quantum Rare Earth Developments, written commun., 2012). This example shows the utility of magnetic and gravity surveys for identifying buried alkaline intrusions, which in this case was in an area that did not exhibit any historic favorability for REE occurrences.



**Figure 13.** A, Vertical gravity gradient map over the Elk Creek carbonatite-hosted Nb-REE deposit, southeastern Nebraska; B, Reduced-to-the-pole magnetic anomaly map. The outline of the carbonatite, which is buried at approximately 183 meters below the surface, is in black. Blue dots are borehole collar locations. (Eo; Eotvoe, nT; nanotesla)

## Hypogene Ore Characteristics

This report focuses on both carbonatite and peralkaline intrusion-related REE deposits because of their spatial association, but detailed examination of the literature leads to the conclusion that the REE ore zones are substantially different in characteristics between the two intrusion types. For this reason, we have chosen to address the hypogene ore and gangue characteristics of carbonatites and peralkaline intrusion-related REE deposits in separate sections.

### Carbonatite Ore Characteristics—Mineralogy, Mineral Assemblages, and Paragenesis

General reviews of carbonatite REE mineralization characteristics include Neary and Highly (1984), Mariano (1989a, b), Richardson and Birkett (1996a), Castor and Hedrick (2006), Castor (2008b), and Long and others (2010). Overall, the ore mineralogy of carbonatite REE deposits is extremely complex. The principal REE-bearing minerals associated with carbonatites are fluocarbonates (bastnäsite, parisite, and synchysite), hydrated carbonates (ancylite), and phosphates (monazite) (Zaitsev and others, 1998), with other REE-bearing phases being less common, such as apatite, britholite, and burbankite (table 1). Because most carbonatites experience complex petrogenetic evolution, including hydrothermal overprinting of primary magmatic phases, the mineralogical and textural characteristics can be quite varied and intricate. For this reason, limited information is available with regards to paragenesis, zoning patterns, and structure. Thus, these topics will not be discussed in detail in this section, but will be summarized in the “Theory of Deposit Formation section” below.

The Mountain Pass deposit is the largest REE deposit in the United States and appears to be a rare example of primary magmatic REE mineralization (Mariano, 1989a). The primary ore minerals of the Sulphide Queen carbonatite at Mountain Pass are bastnäsite and parisite, with monazite as an associated REE-rich phase. In the other carbonatites at the deposit, the REE-bearing minerals are interpreted to have formed by combined magmatic-hydrothermal processes. Mariano (1989a, b) notes that textural evidence shows that bastnäsite and parisite crystallized with calcite, barite, and dolomite and thus likely formed as primary magmatic phases. Olson and others (1954) and Castor (2008b) describe three types of carbonatite within the Sulphide Queen orebody: (1) bastnäsite-barite sövite (calcite-dominant carbonatite), (2) bastnäsite-barite-dolomite carbonatite (beforsite), and (3) a unit that is compositionally between these two (bastnäsite-barite dolomite-sövite). The bastnäsite-barite sövite typically consists of 65 percent calcite, 25 percent strontian barite, and 10 percent bastnäsite (Castor, 2008b). The bastnäsite is coarse grained and forms hexagonal prisms, and the parisite commonly occurs as fan-like intergrowths with bastnäsite (Castor, 2008b). Monazite, a relatively minor phase in the sövite, occurs as small, primary

euohedral grains or as patches of secondary needles (Castor, 2008b). The conclusion that bastnäsite and parisite are of a primary magmatic origin is based on textural evidence that suggests these phases crystallized with the calcite and barite. The bastnäsite-barite-dolomite carbonatite (beforsite) is typically composed of 55 percent dolomite, 25 percent barite, 15 percent bastnäsite, and 5 percent calcite. The bastnäsite is fine grained and typically occurs as interstitial material surrounding the coarser dolomite (Castor, 2008a). Overall, the monazite content is quite variable, but it can be as high as 5 percent and may occur as late stage veinlets (Castor, 2008b).

A second example of primary magmatic REE carbonatite mineralization occurs associated with the Khanneshin carbonatite complex in southern Afghanistan. Tucker and others (2012) describe two types of LREE mineralization, with the type two mineralization as mineralized dikes containing primary magmatic LREE mineralization. Euohedral to subhedral khanneshite, monazite and fluorite in these dikes is evidence for primary magmatic mineralization. In contrast, the other type of mineralization, type one, is likely formed due to the presence of hydrothermal fluids.

More typically, carbonatite-hosted deposits are characterized by REE mineralization derived from magmatic-hydrothermal processes, in which common hypogene REE-bearing ore minerals include bastnäsite, parisite, ancylite, synchysite, and monazite. Bastnäsite is an important source of REEs in most carbonatite-related REE deposits, including Bear Lodge, United States, and at Bayan Obo, Maoniuping, Daluxiang, and Weishan in China. According to Mariano (1989a), bastnäsite of hydrothermal origin typically occurs as fine-grained fibrous or platy masses in vugs, microfractures, and veinlets and is commonly associated with quartz, fluorite, strontianite, barite, and hematite.

Ancylite is described as a minor or trace phase in unweathered carbonatites, including at Bear Lodge (United States), in the Kola region (Russia), and at Araxá and Catalão I (Brazil) (Mariano, 1989a). Ancylite has never been described as a primary magmatic mineral; thus, ancylite is a useful indicator of hydrothermal ore formation (Wall and Zaitsev, 2004). At Bear Lodge, ancylite is a predominant REE-bearing phase and commonly occurs intergrown with strontianite; these intergrowths may be pseudomorphs after an earlier hexagonal mineral (Mariano, 1989a). Similarly, Zaitsev and others (1998) described ancylite in the Khibina carbonatites of the Kola Peninsula, in which ancylite occurs in an alteration assemblage with strontianite replacing the hexagonal crystal form of burbankite. The REE patterns of ancylite from Bear Lodge and Khibina display strong LREE enrichment (Zaitsev and others, 1998).

Similar to ancylite, in the Khibina carbonatite synchysite is present as a pseudomorph of burbankite or as fine syntaxial intergrowths with parisite (Zaitsev and others, 1998). The authors described synchysite as forming porous aggregates, which are enriched in LREEs. Monazite is observed in many

REE mineral deposits and can form as a primary magmatic (Mountain Pass), hydrothermal (Bear Lodge, Kola carbonatites, and Daluxiang), or supergene (Araxá, Catalão, and Mount Weld) phase.

### **Peralkaline Intrusion-Related REE Deposits Ore Characteristics—Mineralogy, Mineral Assemblages, and Paragenesis**

Because peralkaline intrusion-hosted REE deposits tend to be enriched in the highly sought HREEs, Y, and Zr, there are many of these deposits currently in the exploration stage (see fig. 1). Similar to carbonatite-hosted REE deposits, many peralkaline-hosted deposits have undergone complex petrogenetic evolutions that included hydrothermal overprinting of primary magmatic phases, resulting in mineralogical and textural characteristics that are quite varied and intricate. Important REE mineral phases include apatite, eudialyte, loparite, gittinsite, xenotime, gadolinite, monazite, bastnäsite, kainosite, mosandrite, britholite, allanite, and zircon (table 1). Examples of REE deposits associated with peralkaline intrusions include Bokan Mountain (Alaska), Strange Lake (Canada), the Nechalacho deposit at Thor Lake (Canada), Kipawa (Canada), and the Kvanefjeld and Kringlerne deposits within the Ilímaussaq complex (Greenland). Although all of these deposits are associated with peralkaline intrusions, the nature of the REE mineralization at each can be quite different. In addition to REEs, Y, and Zr, the peralkaline mineralized systems may be enriched in Be, Nb, Ta, Th, and U.

At Bokan Mountain, the REEs primarily occur in narrow dikes or veins that radiate from the Bokan intrusion. Rare earth element- and Y-bearing minerals identified at Bokan Mountain include iimoriite, xenotime, allanite, bastnäsite, monazite, synchysite, kainosite, apatite, fergusonite, samarskite, euxenite, and gadolinite (Staatz, 1978; Thompson, 1988; Warner and Barker, 1989; Philpotts and others, 1998). These minerals may be fine grained and occur as pseudomorphs.

At the Ilímaussaq alkaline complex, the REE enrichment is accompanied by anomalous Y, Zr, U, Nb, Th, Li, and Be (Sørensen and others, 2006). Ore mineralogy of this deposit is still being defined. Eudialyte and steenstrupine have been identified as REE phases in the zones of enrichment, and two extremely uncommon minerals, nacareniobsite and vitusite, have been also identified (Pekov and Ekimenkova, 2001). Within the Lovozero complex, Kola Peninsula, the REE-bearing ore mineral is loparite, and it occurs as an accessory phase within the rhythmically layered sequence and can exceed one volume percent (Arzamastsev and others, 2008).

Studies at the Lake Zones of the Thor Lake deposit (now referred to as the Nechalacho deposit at Thor Lake) describe the varied mineralogy of the mineralized zones. The ore minerals in the upper and lower ore zones include zircon, fergusonite, allanite, and bastnäsite (Sheard and others, 2012). In the lower zone, the zircon and fergusonite occur

as pseudomorphs of what was possibly eudialyte (Williams-Jones, 2010). Hoshino and others (2013) evaluated two other cores and identify the major REE-bearing minerals as zircon, bastnäsite-(Ce), fergusonite, parisite-(Ce), synchysite-(Ce), and rare monazite-(Ce) and allanite-(Ce). The drill core that Hoshino and others (2013) evaluated may not have included the lower zone described by Sheard and others (2012).

Many studies of REE mineralization associated with peralkaline intrusions described the REE ore phases as complex assemblages occurring as pseudomorphs of pre-existing phases. Identification of the primary phase and the processes controlling the formation of the replacement phases remains unclear because at many deposits extensive hydrothermal alteration not only overprints the primary REE phases, but also the host rocks. At the Nechalacho deposit, Williams-Jones (2010) and Sheard (2010) tried to unravel the REE mineralization history by comparing core samples from relatively unaltered rock to rocks in the ore zones. The primary magmatic phases are thought to be zircon in the upper zone and eudialyte in the lower zone (Williams-Jones, 2010; Sheard, 2010). Hydrothermal fluids altered the primary phases to form a complex assemblage of secondary phases that included zircon, fergusonite, allanite, and bastnäsite. Compared to the HREEs, the LREEs appear to have been mobilized to a greater extent and distally deposited within bastnäsite (Williams-Jones, 2010).

In contrast to REE deposits associated with peralkaline layered complexes, the Bokan Mountain deposit is primarily hosted within narrow vein-dike systems. Paragenetic studies have not been published for the REE minerals at Bokan Mountain. Thompson (1988) studied the Bokan Mountain complex to evaluate the uranium and thorium deposits, and concluded that the ore was emplaced during a subsidence event associated with devolatilization of the magma chamber. However, he did not specifically evaluate the REE mineralization.

## **Hypogene Gangue Characteristics**

### **Carbonatites—Mineralogy and Mineral Assemblages**

A brief summary of hypogene gangue mineralogy is presented here; some information on this subject was stated above in the “Host Rocks” section of this report. The most common carbonatite hypogene gangue minerals include calcite, dolomite, barite, ankerite, fluorite, fluorapatite, aegerine-augite, phlogopite, strontianite, quartz, magnetite, and hematite. Accessory minerals such as perovskite, pyrochlore, monazite, and thorite are the most common U- and Th-rich phases. As discussed above, the Sulphide Queen ore body at Mountain Pass is generally believed to be a rare example of a carbonatitic REE deposit of magmatic origin. Calcite, dolomite, barite, celestite, strontianite, and quartz are the dominant gangue minerals.

Mineralization at the Bayan Obo deposit is hosted in a massive dolomitic marble. Making general statements about the nature of the mineralization at Bayan Obo is difficult because the nomenclature used in the literature to describe its primary lithologies is quite variable, based on different theories as to the genesis of the deposit. Recent work by Yang and others (2011) delineates four types of Bayan Obo ore: riebeckite type, aegerine type, banded, and massive; however, they do not describe the mineralogy of these ores. The summary of the Bayan Obo deposits by Xu and others (2010a) separated the ore types, based on textural evidence, into disseminated, massive, and banded. They stated that fluorite, apatite, and aegerine are the primary gangue minerals. The primary host mineral for the REE mineralization at the Maoniuping deposit is coarse-grained calcite, with subordinant microcline, aegirine, arfvedsonite, biotite, fluorite, and apatite (Xu and others, 2008). Gangue minerals within the Daluxiang deposit include calcite with subordinate microcline, quartz, arfvedsonite, barium-rich celestite, strontio-barite, fluorite, aegirine, apatite, and sulfides (Xu and others, 2008).

## Peralkaline Hosted REE Deposits—Mineralogy and Mineral Assemblages

Rare earth element deposits associated with peralkaline intrusions can have a wide variety of gangue minerals that can include many uncommon minerals (Richardson and Birkett, 1996b). Bokan Mountain is an example of peralkaline-related REE mineralization in narrow veins or dikes radiating outward from the main intrusive body. Gangue minerals in these dikes include quartz, albite, and aegerine, with variable amounts of barite, biotite, calcite, epidote, fluorite, galena, iron oxides, magnetite, microcline, micropertite, native silver, pyrite, riebeckite, sphalerite, and zircon (Staatz, 1978; Warner and Barker, 1989; Philpotts and others, 1998).

Hydrothermal overprinting of the upper and lower mineralized zones in the Nechalacho deposit at Thor Lake is believed to have further concentrated the REEs and created a complex gangue mineral assemblage (Williams-Jones, 2010; Sheard and others, 2012). The upper zone gangue assemblage includes biotite, magnetite, fluorite, and albite, which occurs within an altered aegerine syenite. Gangue minerals within the lower mineralized zone include magnetite, biotite, and albite (Sheard and others, 2012). Another example of HREE mineralization in a layered alkaline complex is the Strange Lake deposit. Again, hydrothermal overprinting is observed and is interpreted to be important in forming the observed mineralization (Salvi and Williams-Jones, 1990, 1996). Reported gangue phases include quartz, feldspar, amphibole, and pyroxene (Daigle and others, 2011).

## Hydrothermal Alteration

### General Features

A common feature of most carbonatite and alkaline intrusive deposits is that the surrounding rocks have been hydrothermally altered by alkali metasomatism. This style of alteration is known as *finitization* because it was first described at the Fen alkaline complex in southern Norway. Alkali-rich fluids are introduced to the country rock from the crystallizing magma, and reactions convert the host minerals to an assemblage of alkali-bearing minerals. Summary papers that described the nature of finitization include Le Bas (1981, 2008), Woolley (1982), and Morogan (1994). Most studies focused on finitization adjacent to carbonatites and alkaline intrusions that are not highly mineralized. These studies evaluated the alteration products to gain insight into the petrogenesis of the magmatic systems. In addition, experimental work has shown that water solubility in carbonatite melts is quite high, nearly 10 percent at one kilobar pressure, indicating that these magmas can produce the fluid volumes required to develop the hydrothermal alteration aureoles (Keppler, 2003).

Fenites can be classified as sodium- or potassium-rich. Sodium-rich fenites are characterized by the presence of alkali feldspar, as well as alkali amphibole or sodic pyroxene, and potassium-rich fenites contain potassium feldspar (Le Bas, 2008). Intermediate fenites, which are sodium- and potassium-rich, are common. Mineralogy, mineral chemistry, and textures can be complex in fenites because of heterogeneity in the original lithologies, variable proximity to the intrusion, variations in the fluid chemistry, and overprinting of multiple hydrothermal events. Common minerals resulting from finitization include aegerine, alkali-amphibole, nepheline, phlogopite, alkali-feldspar, and carbonates.

Fluid inclusion studies provide direct information on the nature and composition of fluids exsolved from carbonatite and alkali intrusives that were responsible for finitization of surrounding rocks. Gittens and others (1990), Rankin (2005), and Veksler and Lentz (2006) have summarized the state of the knowledge by describing detailed fluid inclusion studies at carbonatites in North America, Asia, and Africa. Fluids released from carbonatite magmas tend to be Na-K-Cl-carbonate/bicarbonate brines with K to Na weight ratios of 0.1–0.6 (Rankin, 2005). Such fluids are consistent with the mineralogy of the altered rocks. Furthermore, experimental work by Keppler (2003) showed that alkali elements are preferentially partitioned into water within the carbonatite melts, providing the appropriate constituents to finitize wallrock.

### Hydrothermal Alteration Associated with Carbonatite REE Deposits

Mountain Pass is one of the few carbonatite REE ore deposits that has a description of hydrothermal alteration. Olson and others (1954) described the wallrock alteration

in the vicinity of the Sulphide Queen orebody. Although the contacts between the carbonatite orebody and the surrounding rock are generally sharp, the syenite and gneissic host rocks are altered. Sodic amphibole (crocidolite) and chlorite are present along and near the contacts, and both the gneiss and syenite near the contact are reddened by hematite (Olson and other, 1954). Crocidolite is commonly fibrous in texture. In some locations, the abundance of potassium feldspar increases near the contacts. Details on the lateral and vertical extent of alteration have not been reported.

Hydrothermal alteration is intense and widespread at Bayan Obo, encompassing an area of approximately 50 square kilometers (km<sup>2</sup>) (Drew and others, 1990). The intensity and complexity of the hydrothermal alteration is one reason that the origin of the deposit has been debated, particularly because primary mineralogy and textures are overprinted by multiple hydrothermal alteration events. Drew and others (1990) described the wallrock alteration assemblage as consisting of aegirine, sodic amphiboles, albite, and potassium feldspar with subordinant barite, apatite, Fe-Nb-Ti-Mn oxides, and monazite. Yang and others (2011) noted that the fenitization at Bayan Obo between the host dolomite (H8) and wallrock slates consisted of the addition of potassium and the occurrence of riebeckite and phlogopite. Within the dolomite, fluorite appeared in the zone of fenitization (Yang and others, 2011)

In addition to fenitization, late-stage oxidizing hydrothermal fluids produced a hematite-calcite-dolomite assemblage referred to as rødberg or “red rock” (Andersen, 1984). The type locality is within the Fen complex, southern Norway, but similar material has been observed in U.S. deposits, such as at Bear Lodge and Elk Creek. At Fen, Andersen (1984) concluded that hematite formed by oxidation of pre-existing magnetite-pyrite without substantial introduction of ferric iron. The Bear Lodge deposit is characterized by an upper oxidized zone (100 to 160 m thick), above a transition zone (roughly 6 m thick) and an unoxidized zone. The oxidized zone is termed “FMR”, with F for abundant iron (Fe) oxides, M for abundant manganese (Mn) oxides, and R for REEs (fig. 14). The REE-bearing minerals (dominantly bastnäsite group minerals and subordinate monazite and cerianite) are hydrothermal or supergene in origin (Laroche and others, 2012). Within the transition zone, 10 to 90 percent of the sulfide minerals, which dominate in the underlying unoxidized zone, have been oxidized to limonite (Laroche and others, 2012).

### Hydrothermal Alteration Associated with Peralkaline Intrusion-Related REE Deposits

Alteration halos surrounding peralkaline plutonic complexes are generally small. They are typically a few hundred meters wide in deeper zones to tens of meters in upper zones (Richardson and Birkett, 1996b). However, hydrothermal fluids can play an important role in concentrating REEs in these systems (Boily and Williams-Jones, 1994; Sheard and others, 2012). In some mineralized areas, such as at Strange Lake, late

stage pegmatitic dikes intrude the country rock. Hydrothermal alteration associated with these late intrusions can extend the zone of alteration beyond the above stated widths.

Salvi and Williams-Jones (1990, 1996) described extensive wallrock alteration at the Strange Lake deposit, which was characterized by the replacement of arfvedsonite by aegirine and/or hematite. They separated the alteration into the replacement of arfvedsonite by aegirine in or near pegmatites, and subsequent hematization and the replacement of alkali minerals by calcic minerals (Salvi and Williams-Jones, 1996). The authors concluded that the first type of alteration was a high temperature (greater than or equal to 350°C) oxidizing event and the second type was a low temperature (less than or equal to 200°C) oxidizing event with Ca-rich fluids. The REE mineralization at Strange Lake occurs in the Ca-metasomatized zones (Salvi and Williams-Jones, 1996, 2005).

Recent work at the Nechalacho deposit, Thor Lake property, has focused on the role that hydrothermal alteration played in the ore-forming processes (Sheard and others, 2012). The hydrothermal alteration at the Nechalacho deposit at Thor Lake is characterized by magnetite and biotite in the upper zone and by magnetite in the lower zone, with widespread albitization and late stage silicification, illitization, and carbonatization. Remobilization of Zr and REEs accompanied the hydrothermal alteration and was characterized by the replacement of the primary cumulate mineral eudialyte by a suite of secondary phases (Sheard and others, 2012).

Hydrothermally altered peralkaline dikes and shear zones host the significant REE deposits within the alkaline intrusive complex at Bokan Mountain. These dikes and structures display late-stage hydrothermal alteration that includes locally intense silicification, albitization, hematization, and chloritization, resulting in enrichments in REEs, Y, Th, U, Zr, Nb, Ta, and Ti (Barker and Van Gosen, 2012). More than 20 REE-Y-, Nb-, and U-Th-bearing minerals have been identified in the deposit in the form of fluorocarbonates, oxides, silicates, and



**Figure 14.** Photograph of the oxidized zone at the Bear Lodge deposit. Field of view approximately 4 feet across with 1.5 foot-wide FMR vein.

phosphates. These ore minerals form complex intergrowths and textures within a groundmass of albite, quartz, minor aegirine, and minor to trace amounts of zircon, chlorite, fluorite, magnetite, calcite, and Fe-Pb-Zn sulfides. The dominant REE-bearing minerals are kainosite, apatite, allanite, xenotime, bastnäsite (often Y-rich), parisite, brannerite, thalenite, iimoriite, fergusonite, synchysite (Y), and monazite.

## **Weathering/Supergene Characteristics and Processes**

Near-surface enrichment of REEs above carbonatite and alkaline intrusions can be an important step for developing economic REE deposits. At present, as of 2012, mining of laterites, a term used to describe highly weathered subsoils that form in tropical or subtropical settings, in southeast China produces much of the world's supply of heavy REEs, but these deposits are not associated with carbonatites or alkaline intrusive complexes. Mount Weld, Australia; Araxá, Brazil; and Zandkopsdrift, South Africa are three examples of significant lateritic deposits associated with carbonatites. Within the United States, no economic lateritic REE resource is currently being exploited (Long and others, 2010).

Outcrop and drill core at the Araxá deposit and the neighboring Catalão deposit provided clear evidence that the parent rock is carbonatite (Mariano, 1989a; Morteani and Preinfalk, 1996). Although these deposits are rich in REEs, they are currently being mined for Nb. At Catalão, the thickness of the laterite varies from 15–250 m, and at Araxá the laterite is as thick as 230 m (Woolley 1987; Morteani and Preinfalk, 1996). The Mount Weld deposit also consists of a well-developed laterite that overlies a carbonatite. The thickness of the laterite is variable, but is as thick as 69 m in places. Another example of a lateritic zone above a carbonatite is at the Mrima Hill deposit, Kenya. The lateritic zone is over 100 m thick in places and is enriched in REEs and Nb. The lateritic zone is locally greater than 100 m thick and is enriched in REEs and Nb. No examples of supergene occurrences of peralkaline intrusion-related REE deposits are recognized.

## **Mineralogical Reactions to Establish Process**

As discussed above, the primary ore mineralogy of carbonatite and alkaline intrusion REE deposits is extremely complex, and, as a result, the ore mineralogy of these secondary deposits can be quite variable. In the weathering environment, some primary REE-bearing phases can be stable; hence the formation of REE placer deposits. Other phases can more easily breakdown due to chemical weathering. As lateritic weathering progresses, the REEs can be released from the more stable phases (Bao and Zhao, 2008). In the lateritic zone, REEs can be present within: (1) primary igneous minerals, such as apatite, monazite, xenotime, and zircon; (2) secondary

minerals that include apatite, monazite, cerianite, churchite, florencite, gorceixite, plumbogummite-group (part of the crandallite subgroup), and rhabdophane; and (3) clays and iron and aluminum oxyhydroxides (Mariano, 1989a, Lottermoser, 1990; Wu and others, 1990; Morteani and Preinfalk, 1996; Bao and Zhao, 2008). Secondary REE minerals formed in this environment are commonly fine grained and occur as polycrystalline aggregates (Mariano, 1989a).

At Mount Weld, gangue minerals include goethite and hematite with minor calcite, cryptomelane, dolomite, hollandite, kaolinite, maghemite, montmorillonite, magnetite, pyrochlore, ilmentite, and rutile, and traces of quartz, barite, anatase, and vermiculite (Lottermoser, 1990). Gangue minerals in laterites of Araxá and Catalão include gorceixite, goethite, hematite, magnetite, gibbsite, kaolinite, quartz, vermiculite, and barite (Morteani and Preinfalk, 1996). Detailed evaluation of clay mineralogy assemblages in the Chinese laterites shows a change from hydromica and montmorillonite, to halloysite and kaolinite, and then to gibbsite downward in the weathering profiles (Bao and Zhao, 2008). This zonation reflects the increased intensity of weathering and the progressive removal of Ca, Mg, Na, and K.

## **Geochemical Processes**

Laterites form by the intense weathering of the underlying bedrock. Factors controlling the degree of laterization include climate, topography, length of time exposed in a stable environment, and bedrock composition (for example, Marsh and others, 2013). Optimal conditions for the formation of substantial lateritic zones include a topography that allows the entrapment of newly formed residual minerals and a tectonically stable region so that denudation rates are low and the weathering profiles are preserved. Detailed descriptions of mineralogical and chemical variations in lateritic profiles at REE deposits can be found in Mariano (1989a,b), Lottermoser (1990), Wu and others (1990), Morteani and Preinfalk (1996), and Bao and Zhao (2008).

Laterization is driven by the interaction between infiltrating groundwater and the bedrock it contacts. Physical properties, such as cleavage and porosity, are important because they control the amount of mineral surfaces available for interaction. Aqueous properties, such as temperature, acidity, redox potential, and dissolved constituents affect the type of chemical reactions that will occur and their rate. The primary mineralogy of the rock being weathered not only plays a role in the rate of weathering, but also influences the composition of the aqueous phase, which in turn can control the formation of secondary phases. In general, Ca, Mg, K, and Na partition to the aqueous phase and are then leached from the system. In contrast, Fe is quite reactive, as can be Al, and these elements end up in secondary phases, including goethite, hematite, gibbsite, and various clay minerals. Bao and Zhao (2008) showed that as the degree of weathering increases, the concentration of

Ca, Mg, K, and Na in the solid phase decreases, whereas Al becomes enriched.

In carbonatites, the REEs can be hosted in calcite, dolomite, and apatite, and these minerals are quite susceptible to dissolution in the lateritic weathering environment. Oxygenated groundwater in the near-surface environment can be slightly acidic and, if it interacts with sulfide minerals, the waters can become more acidic. Minor sulfides are reported in some carbonatites, such as galena at Mountain Pass. This acidic water interacts with primary minerals, such as calcite, dolomite, and apatite, to mobilize Ca and Mg and liberate REEs. Other elements, such as Al, Fe, P, K, and Na, are also released from other phases. Mobility of the REEs in this environment is quite complex due to variations in solution chemistries and properties. Whether the REEs sorb to clays or form secondary phases depends on the pH (acidity) and Eh (redox potential) of the solution, the availability of ligands for complexation, and mineral saturation state. In this environment, dissolved ligands likely available to complex REEs include phosphate, carbonate, fluoride, and chloride. Because of these complexities, it is difficult to make general statements concerning the mineralogy of lateritic REE deposits.

Detailed mineralogical analyses at Mount Weld led Lottermoser (1990) to conclude that the LREEs primarily sequester into the secondary minerals rhabdophane, monazite, and the plumbogummite-group. The HREEs were mobilized further down the weathering profile and became adsorbed onto non-crystalline phases and incorporated into churchite. Work by Mariano (1989a) also highlighted the importance of secondary monazite, as well as cerianite and crandallite subgroup minerals, as host phases for REEs at Mount Weld. At Araxá and Catalão, secondary phases which include apatite, monazite, rhabdophane, florencite, and gorceixite, host the REEs (Mariano, 1989a; Morteani and Preinfalk, 1996). Leaching experiments by Morteani and Preinfalk (1996) document that only 2–30 percent of the REEs are bound to iron hydroxides.

## Effects of Micro and Macro Climates

The laterite deposits in Araxá are at approximately latitude 19°S in a sub-tropical climate of Brazil that is warm, humid, and receives 1,700 millimeters (mm) of annual precipitation. Similarly, the known localities in China of the lateritic REE deposits (not associated with carbonatites or peralkaline intrusions) mainly occur in areas south of latitude 28°N in a sub-tropical climate that is warm, humid, and receives more than 1,500 mm of annual precipitation (Bao and Zhao, 2008). Optimal conditions for the formation of substantial lateritic zones are where the topography allows the entrapment of newly formed residual minerals and where formation occurs within a tectonically stable region, which ensures that denudation rates are low and the weathering profiles are preserved from erosion.

# Geochemical Characteristics

## Trace Elements and Element Associations

Trace elements have been classified into groups based on charge and ionic radius, for example HFSEs and large ion lithophile elements (LILEs). Large ion lithophile elements include Cs, Rb, K, Ba, and Sr. Many of the elements in these two groups tend to occur in carbonatites and alkaline intrusions at concentrations much greater than trace levels, in part because of the unusual mineralogy and chemistry of these rock types. Other elements associated with some carbonatite and alkaline intrusion-related REE deposits include Cl, Fl, Mn, and P. The geochemistry of rare earth elements will be discussed in this section, along with that of other elements associated with the REE deposits.

On average, carbonatites contain the highest concentration of REEs of any rock type (Cullers and Graf, 1984). Their REE patterns typically display LREE enrichment and negative slopes (figs. 4, 15–19). One measure of the steepness of the pattern is the  $La_{cn}/Yb_{cn}$  ratio (the ratio of the chondrite-normalized value (cn) of La divided by the chondrite-normalized value of Yb). This ratio commonly ranges from 20 to 11,050, with a median of 1,380 (fig. 20). Most REE patterns for carbonatite-hosted REE deposits have similar slopes for La through Nd, such that the variation in the  $La_{cn}/Yb_{cn}$  ratio generally reflects the shape of the pattern for the HREEs. For example, the HREE concentrations for some of the Bear Lodge oxide ore samples are substantially greater than for Mountain Pass and Bayan Obo carbonatite-hosted ore samples (figs. 4, 15, 16, and 18). Carbonatite REE patterns do not contain appreciable negative Eu anomalies ( $Eu/Eu^*$ ; figs. 15–19). The europium anomaly is calculated as follows:

$$Eu/Eu^* = [Eu]_{cn} / ([Sm]_{cn} \times [Gd]_{cn})^{0.5}$$

Where,

$Eu/Eu^*$  represents the ratio of the actual concentration of europium in the sample to the ideal concentration, assuming an REE distribution profile matching that of a reference material, in this case chondrites (dimensionless),

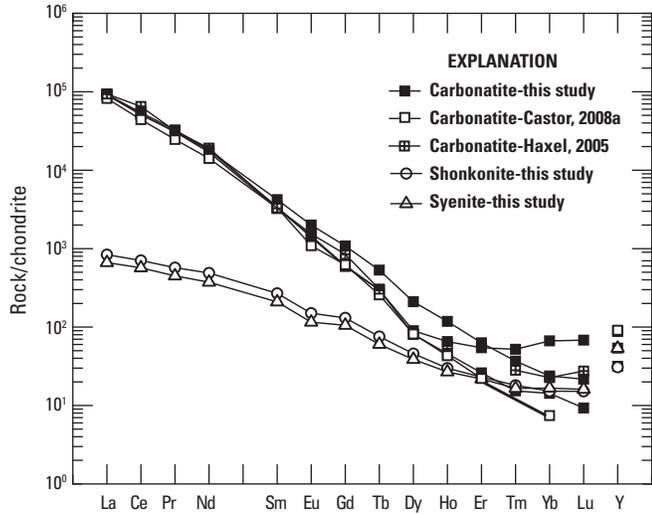
$[Eu]_{cn}$  is the chondrite-normalized concentration of Eu (dimensionless),

$[Sm]_{cn}$  is the chondrite-normalized concentration of Sm (dimensionless), and

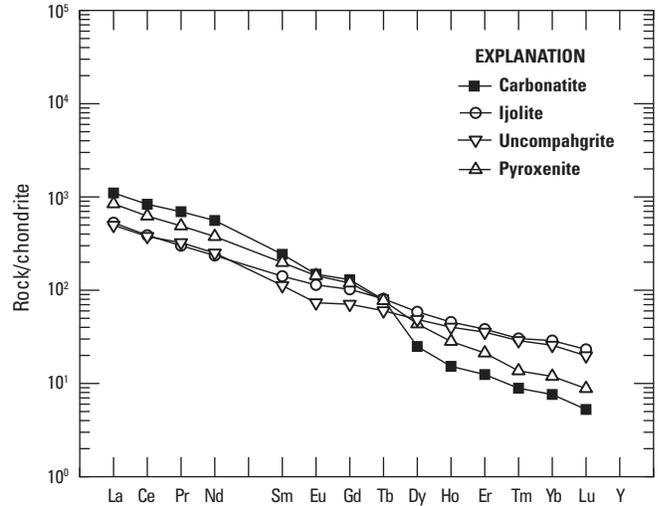
$[Gd]_{cn}$  is the chondrite-normalized concentration of Gd (dimensionless).

Values of  $Eu/Eu^*$  less than one are called negative anomalies, whereas values greater than one are considered positive.

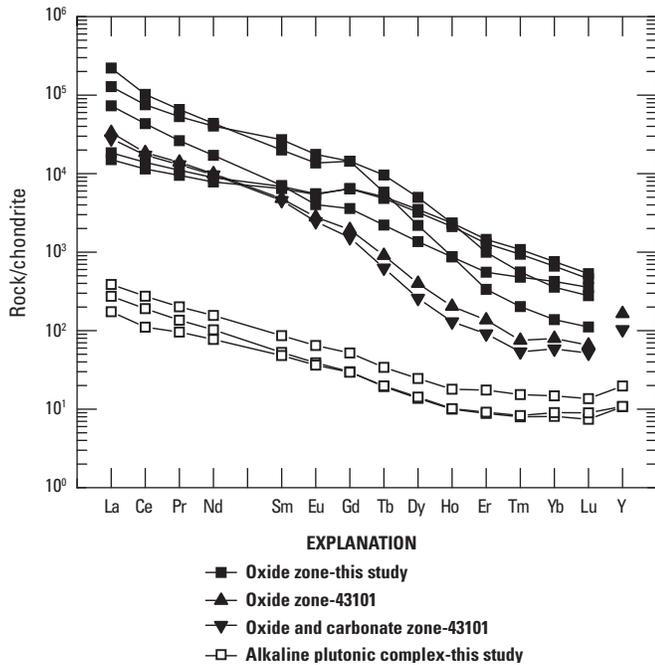
In contrast, REE patterns of peralkaline intrusion-hosted REE deposits are relatively less enriched in LREEs and more enriched in HREEs compared to carbonatite-related deposits (figs. 4 and 21). The  $La_{cn}/Yb_{cn}$  ratio for peralkaline



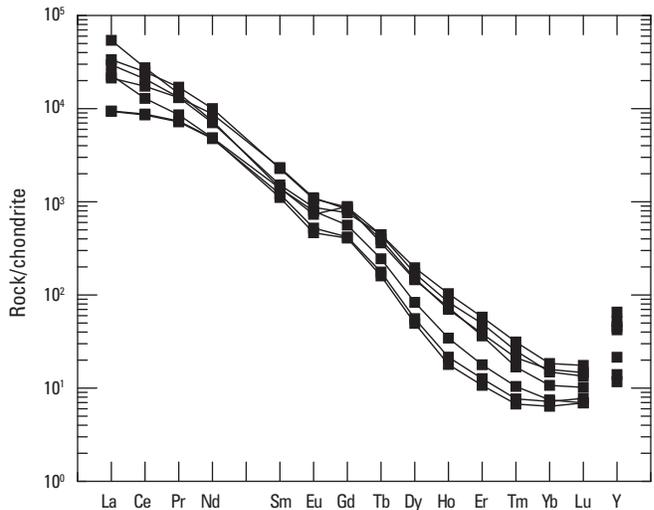
**Figure 15.** Rare earth elements in Mountain Pass deposit lithologies. Concentrations normalized to C1 chondrite values from Anders and Ebihara (1982).



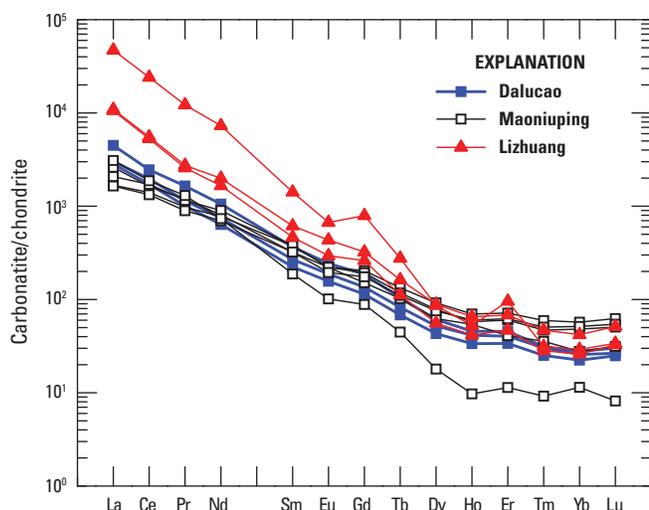
**Figure 17.** Rare earth elements in Iron Hill complex lithologies. Concentrations normalized to C1 chondrite values from Anders and Ebihara (1982).



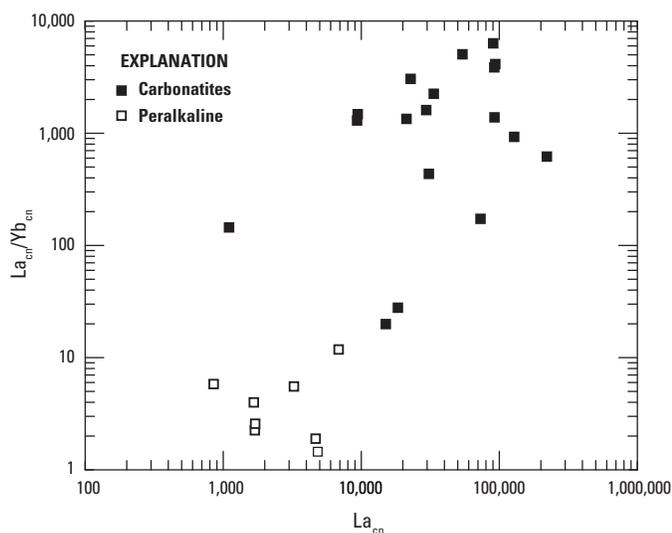
**Figure 16.** Rare earth elements in Bear Lodge lithologies. Concentrations normalized to C1 chondrite values from Anders and Ebihara (1982).



**Figure 18.** Rare earth elements in carbonatite samples from Bayan Obo deposit. Carbonatite sample data from Yang and others (2011). Concentrations normalized to C1 chondrite values from Anders and Ebihara (1982).



**Figure 19.** Rare earth elements in Dalucao, Maoniuping, and Lizhuang carbonatite deposits, China. Dalucao, and Lizhuang are deposits within the Maoniuping district. Concentrations normalized to C1 chondrite values from Anders and Ebihara (1982). Data from Hou and others, 2006.

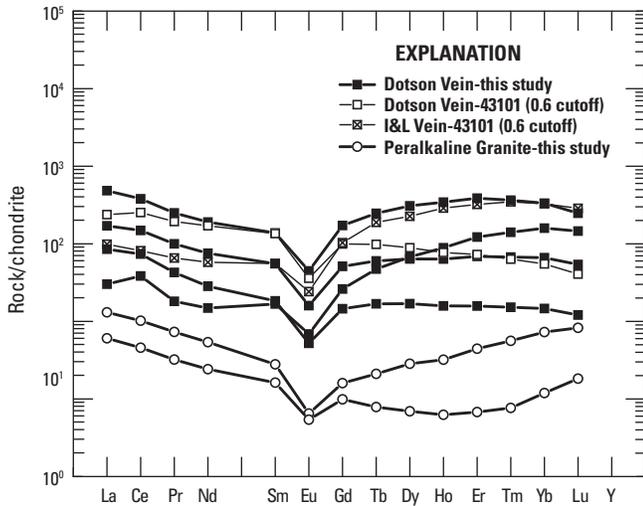


**Figure 20.** Variation in chondrite normalized lanthanum concentration in relation to chondrite normalized ratio of lanthanum over ytterbium for carbonatite and peralkaline intrusion-related REE deposits.  $La_{cn}$ ; lanthanum concentration of sample divided by lanthanum concentration in chondrite.  $Yb_{cn}$ ; ytterbium concentration of sample divided by ytterbium concentration in chondrite.

intrusion-related REE deposits compiled here varies from 0.2 to 12, with a median value of 2.4. In figure 20, the carbonatite samples plot in the upper right corner, which is the field with greater LREE concentrations and steeper slopes, compared to the peralkaline-related REE deposits. These REE patterns for the peralkaline-REE deposits exhibit negative Eu anomalies, with  $Eu^*/Eu$  ranging from 0.21 to 0.43, and the median value of 0.32 (figs. 4 and 21).

Although many petrologic studies of carbonatites include elemental data, only a few studies of REE deposits associated with carbonatites include elemental data. Also, most studies of REE deposits associated with carbonatites have incomplete suites of elements, making generalized statements difficult. World-wide compilations of carbonatite occurrences and chemistry can be found in Woolley and Kempe (1989) and Woolley and Kjarsgaard (2008). In carbonatites, the concentration of Ba, Mn, and Sr (LILEs) can be in excess of one percent (Pell and Høy, 1989). These elements are at such high concentrations in carbonatites that they can be reported as oxides. Woolley and Kempe (1989) reported that carbonatites can contain as much as 20 percent BaO, 5.47 percent MnO, and 5.95 percent SrO. Castor and Nason (2004) published major oxide data for carbonatite samples at Mountain Pass and reported BaO ranging from 1.70 to 33.10 percent and SrO ranging from 0.14 to 14.15 percent. The highest BaO concentrations occur in the barite-rich units; the SrO concentrations are quite variable, with the highest and lowest concentrations occurring in the same unit. Yang and others (2011) reported Ba and Sr data for Bayan Obo, with ore-bearing dolomite samples ranging from 0.026 to 2.2 weight percent BaO and 0.092 to 0.27 weight percent SrO.

Similarly, REE deposits associated with peralkaline intrusions can be enriched in a variety of elements. In contrast to carbonatites, they do not tend to be enriched in LILE, such as Ba and Sr. Long and others (2010) compiled chemical data on various prospect locations at Bokan. Ranges of various constituents, all in weight percent, include BeO (0.025 to 0.16),  $Nb_2O_5$  (0.083 to 0.300),  $Ta_2O_5$  (0.01 to 0.026),  $ThO_2$  (0.009 to 3.64),  $U_3O_8$  (0.008 to 0.59),  $Y_2O_3$  (0.132 to 0.458), and  $ZrO_2$  (0.320 to 3.34). Indicated resources at the eudialyte exploration target at Ilimaussaq (Kringlerne) include grades of 2 weight percent  $ZrO_2$ , 0.25 weight percent  $Nb_2O_5$ , 0.2 weight percent  $Y_2O_3$ , and 0.025 weight percent  $Ta_2O_5$  (Geological Survey of Denmark and Greenland, 2011). Indicated reserves at Strange Lake, with a 1.2 weight percent REE oxide cutoff, include 2.77 weight percent  $ZrO_2$ , 0.37 weight percent  $Nb_2O_5$ , 0.06 weight percent  $HfO_2$ , 0.19 weight percent BeO, 0.01 weight percent  $U_3O_8$ , and 0.07 weight percent  $ThO_2$  (Daigle and others, 2011). Indicated reserves at Thor Lake lower zone



**Figure 21.** Rare earth elements in Bokan Mountain lithologies. Concentrations normalized to C1 chondrite values from Anders and Ebihara (1982). Values for Dotson vein and I&L vein 43101 (0.6 cutoff) from Robinson and others (2011).

are reported as 2.99 weight percent  $ZrO_2$ , 0.40 weight percent  $Nb_2O_5$ , 0.06 weight percent  $HfO_2$ , 0.004 weight percent  $Ta_2O_5$ , and 0.18 weight percent  $Y_2O_3$ , and the upper zone are reported as 2.41 weight percent  $ZrO_2$ , 0.34 weight percent  $Nb_2O_5$ , 0.04 weight percent  $HfO_2$ , 0.002 weight percent  $Ta_2O_5$ , and 0.05 weight percent  $Y_2O_3$  (Daigle and others, 2011).

Studies of two peralkaline granitoids with disseminated REE mineralization document enrichments in many of the elements presented above. Niobium, Ta, Sn, Th, U, and Zr are associated with the REE mineralization at Ghurayyah (Drysdall and others, 1984), and Zr, Nb, Be, Sn, Rb and locally Li, Pb, Zn, Hf, and Ta are associated with the REE mineralization at Khaldzan-Buregtey (Kovalenko and others, 1995).

## Zoning Patterns

Little detailed work has been published describing the zoning patterns of elements associated with these deposits. As described above, hydrothermal alteration can produce a fenitization halo surrounding the deposit, but the extent of this alkali metasomatism can be quite limited, as is the case at the Mountain Pass deposit. The fluids that produced the aureole introduced Ca, Na, K, carbon dioxide, and locally fluorine and chlorine. A review of fenites associated with carbonatites by Le Bas (2008) concluded that potassium fenites are commonly located in the upper levels of the carbonatite intrusive bodies and sodium fenites are more commonly formed at deeper levels.

## Fluid Inclusion Geochemistry

Fluid inclusion studies of carbonatites and peralkaline intrusion-related REE deposits are less common than studies performed on many ore deposits because the major deposits occur in carbonatites, which lack silicate minerals. Silicate minerals are generally chosen for fluid inclusion studies because they are less likely to undergo fluid leakage or exchange. In carbonatites and alkaline intrusives, apatite appears to be the least susceptible mineral to post-entrapment modification (Andersen, 1986). Gittens and others (1990), Rankin (2005), and Veksler and Lentz (2006) summarized the state of the knowledge gleaned from fluid inclusion studies. Most of the fluid inclusion studies attempted to constrain the magmatic evolution and were not focused on fluids responsible for ore genesis.

Xie and others (2009) undertook a fluid inclusion study of the Maoniuping deposit, documenting a complex melt-fluid history. Using melt and fluid inclusions in quartz and fluorite, they concluded that the initial ore-forming fluid was high temperature (600–850°C), high pressure (greater than 350 MPa), sulfate-rich, and contained K, Na, Ca, Ba, Sr, and REEs. The initial fluid evolved to a moderate temperature (227–453°C),  $CO_2$ -rich fluid, and then to a lower temperature (less than 200°C), aqueous-rich fluid. The REE mineralization was shown to be related to precipitation from the moderate temperature,  $CO_2$ -rich fluid (Xie and others, 2009).

At the Thor Lake peralkaline REE deposit, Taylor and Pollard (1996) analyzed fluid inclusions in quartz and fluorite from the upper Intermediate zone of the T-zone REE-Y-Be deposit, which is composed of aegerine, potassium feldspar, albite, REE-fluocarboxates, quartz, polyolithionite, biotite, chlorite, magnetite, fluorite, thorite, and phenakite. They concluded that the temperature range of the fluid responsible for the quartz deposition and the REE-fluocarboxate mineralization was between 350 and 400°C. The fluid trapped in hydrothermal quartz intergrown with REE-fluocarboxate mineralization is aqueous-carbonic with a salinity of 2 to 20 weight percent NaCl (Taylor and Pollard, 1996).

Determining the composition of fluids expelled from carbonatites and alkaline magmas is key to understanding the mobilization and transport of REEs. Roedder (1973) and Rankin (1975) identified saline aqueous-carbonic fluid inclusions in apatite from the Amba Dongar carbonatite, India, and the Wasaki carbonatite, Kenya. Andersen (1986) undertook a fluid inclusion study of apatite crystals within the Fen complex, Norway. He documented the progressive evolution of alkali chloride fluids from an early stage of magmatic evolution with 88–90 percent  $H_2O$ , 5–7 percent  $CO_2$ , and 5 percent NaCl, to a later meteoric fluid with 1–24 percent NaCl and no  $CO_2$ . Anderson (1986) concluded that the fluid evolution at Fen evolved from a  $CO_2$  and  $H_2O$  magmatic stage to a groundwater-derived aqueous fluid that was devoid of  $CO_2$ .

To determine the composition of fluids responsible for mineralization of country rock surrounding carbonatites and alkaline intrusions, Böhn and Rankin (1999) looked in detail

at fluid inclusions trapped in the quartzite country rock of the Kalkfield carbonatite complex, Namibia. Fluid types included (1) a low-density CO<sub>2</sub> fluid; and (2) a Na-, K-, Ca-, Cl-, and bicarbonate-bearing aqueous brine (Bühn and Rankin, 1999). The REE patterns of the trapped fluids display LREE enrichment. Bühn and Rankin (1999) concluded that virtually all the alkali metals and chloride, as well as significant F, Th, Ti, and U, preferentially partitioned into a mixed alkali-carbonic fluid.

## Stable Isotope Geochemistry

Although stable isotopic studies of carbonatite and alkaline intrusion REE deposits are lacking, petrologists have studied a variety of stable isotopic systems (H, C, O, and S) of non-mineralized carbonatite and alkaline intrusions to gain insight into their genesis. One application of stable isotope geochemistry has been to differentiate between carbonate sedimentary rocks and carbonatites of igneous origin by utilizing carbon isotopes. Carbonate sedimentary rocks have a carbon isotopic composition similar to sea water ( $\delta^{13}\text{C}$  -2 to 2 ‰) and carbonatites generally have lower values ( $\delta^{13}\text{C}$  -8 to -2 ‰; Deines, 1989).

Most of the stable isotope studies of carbonatite and alkaline intrusions have used various isotopic systems to determine the origin of the parental magmas and to constrain the magmatic evolution, and more specifically to evaluate the roles of fractional crystallization, crustal contamination, degassing, and hydrothermal alteration. The most thorough review of stable isotope geochemistry of carbonatite and alkaline intrusions is provided by Deines (1989).

Andersen (1987), Pearce and others (1997), Demény and others (2004), and Drüppel and others (2005) determined the carbon and oxygen isotopic composition of samples from the Fen complex, Norway; the Grønneidal-Ika complex, Greenland; the Kola Alkaline Province Russia; and Swartbooisdrift, Namibia, respectively; all concluded that the parental magmas were derived from the mantle. Demény and others (2004) compiled isotopic results from many sites within the Kola province and attributed the isotopic variability to mantle heterogeneity. Although the parental magmas at Fen were derived from mantle sources, Andersen (1986, 1987) documented post-magmatic oxygen and carbon isotopic reequilibration resulting from groundwater-derived hydrothermal solutions.

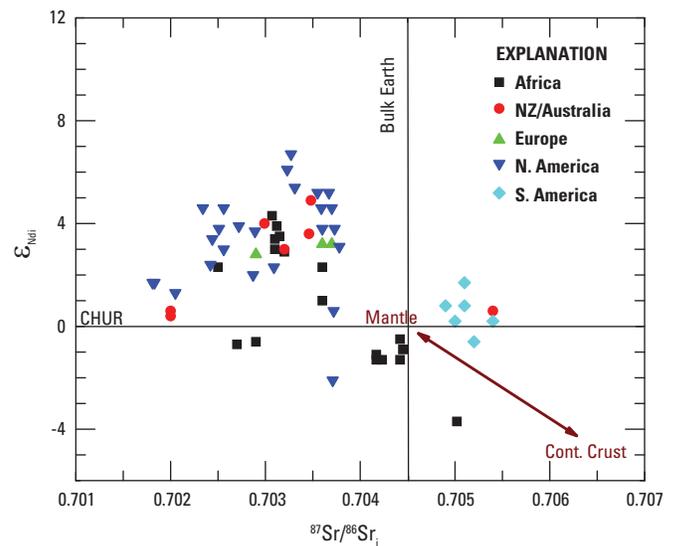
At the Thor Lake peralkaline REE deposit, Taylor and Pollard (1996) compared the oxygen and hydrogen isotopic compositions of fluid inclusion waters. The isotopic data are consistent with the fluids responsible for the REE mineralization and hydrothermal alteration as being of magmatic origin.

## Radiogenic Isotope Geochemistry

Similar to most of the stable isotope studies of carbonatite and alkaline intrusives, most of the studies of radiogenic isotope geochemistry focus on the origin of the parental magmas and the evolution of the magmatic system. 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 (fig. 22). The radiogenic isotopic data (Nd, Sr, and Pb) document that the carbonatites are of mantle origin, but the range in isotopic data suggests that the subcontinental upper mantle is heterogeneous (Bell and Blenkinsop, 1989). Because the discussion of isotopic systematics in the upper mantle is beyond the scope of this report, the reader is referred to the discussions in Bell and Blenkinsop (1989) and Bell (1998).

What is relevant to this model is the use of radiogenic isotopes to evaluate the timing of light REE enrichment and the extent of open system behavior. If the magmatic evolution is controlled primarily by closed system processes, then the ultimate source of the REEs is from the primary magma, shown to be derived from the upper mantle. Bell and Blenkinsop (1989) documented that, at least for Canadian carbonatites, the relationship between  $^{143}\text{Nd}/^{144}\text{Nd}_i$  and time is nearly linear, which suggests that the LREE enrichment must have occurred early in the magmatic evolution. The isotopic data do not, however, constrain the process or processes responsible for the LREE enrichment (see below sections on “Petrology of Associated Igneous Rocks” and “Theory of Deposit Formation”). Various studies (see Grünenfelder and others, 1986; Bell and Blenkinsop, 1989; Bell, 1998) have used radiogenic isotopes to determine the nature and extent of crustal interaction in the evolution of carbonatite melts and the association of carbonatites and alkaline intrusions. Although the degree



**Figure 22.** Variation in neodymium isotopic composition in relation to strontium isotopic composition. Data from Bell and Blenkinsop (1989).  $\epsilon_{\text{Nd}}$  = common notation for the neodymium isotopic composition relative to of the silicate portion of the earth's mantle (DePaolo and Wasserburg, 1976).  $^{87}\text{Sr}/^{86}\text{Sr}_i$  = initial strontium isotopic ratio (measured ratio corrected for isotopic decay of rubidium). (CHUR; chondrite uniform reservoir, NZ = New Zealand).

of crustal interaction is variable, studies clearly showed that crustal contamination can be minimal. The nearly closed system evolution of some carbonatites documents that the ultimate source of the REEs is most likely the upper mantle.

One example of a detailed petrogenetic study of carbonatites and alkaline intrusions is by Harmer (1999) on the Spitskop complex, South Africa. The radiogenic isotopic results for Nd, Sr, and Pb, clearly demonstrate that the carbonatites, which all display LREE enrichments, are derived from mantle sources and evolved with little, if any, crustal assimilation. In this complex, the carbonatites, as with most carbonatites, are younger than the spatially associated alkaline intrusions. Harmer (1999) concluded that the carbonatites could not have evolved directly from the magmas that formed the spatially associated alkaline plutons. This conclusion was based on contrasting radiogenic isotopic compositions, as well as trace element geochemical evidence.

## **Petrology of Associated Igneous Rocks**

### **Importance of Igneous Rocks to Deposit Genesis**

By definition, igneous rocks play an essential role in the formation of carbonatite and peralkaline intrusion-related REE deposits. Because of the relatively unusual and complex chemistry of these magmas, the crystallization history of these magmas is less well understood than other magmatic systems. Discerning primary magmatic compositions is difficult because: (1) extrusive equivalent rocks are quite rare; (2) many of the rock units associated with REE deposits are cumulates and hence do not represent the composition of the magma that they crystallized from; and (3) late-stage hydrothermal alteration is common.

Most carbonatites are spatially associated with an alkaline intrusive complex and tend to form near the end of the magmatic activity. Because of the common spatial association, many researchers have called upon a genetic association, but Gittens and Harmer (2003) concluded that a genetic link is not necessary. A detailed evaluation of this topic is beyond the scope of this report. However, a brief summary of the nature of associated igneous rocks and the origin of carbonatites and alkaline intrusive rocks is necessary because it is generally believed the REEs and Y in the deposits are of magmatic origin and magmatic processes play a key role in concentrating these elements into potentially ore-grade deposits

### **Rock Names and Mineralogy of Associated Igneous Rocks**

Within the United States, two examples of carbonatite intrusions associated with alkaline igneous complexes are the Mountain Pass district (Castor, 2008b) and the Iron Hill (Powderhorn) carbonatite complex of southwestern Colorado (Olson and Hedlund, 1981). Olson and Hedlund (1981, p. 5)

described the Iron Hill carbonatite complex as "...the best example of the carbonatite-alkalic rock association in the United States and is one of the outstanding occurrences in the world, comparable to many of the classic areas in Africa and other continents." Various rock units at Iron Hill have been explored for Fe, Ti, Nb, Th, and REEs. Unlike most carbonatite complexes, the carbonatites at Mountain Pass are associated with ultrapotassic alkaline intrusions.

At Iron Hill, the primary rock types of the igneous complex are, from oldest to youngest, pyroxenite, uncomphagrite, ijolite, nepheline syenite, and carbonatite (Olson, 1974; Hedlund and Olson, 1975; Olson and Hedlund, 1981; Armbrustmacher, 1983). The medium-grained, equigranular pyroxenite is composed of diopside, with biotite, phlogopite, perovskite, fluorapatite, ilmenite, magnetite, titanite, and melanite (Olson and Hedlund, 1981). This unit has been an exploration target for titanium. The medium- to coarse-grained uncomphagrite consists of melilite and diopside with minor amounts of magnetite, apatite, phlogopite, melanite, biotite, calcite, and perovskite. The ijolite consists of nepheline, aegerine-augite, and melanite and accessory calcite, apatite, magnetite, ilmenite, and titanite (Olson and Hedlund, 1981). The nepheline syenite is medium to coarse grained and consists of mainly orthoclase microperthite (as much as 75 percent) with aegerine-augite, melanite, and nepheline and accessory magnetite, titanite, apatite, muscovite, calcite, and zeolites (Olson and Hedlund, 1981). The carbonatite stock at Iron Hill is the largest exposed carbonatite in the United States and is a dolomitic carbonatite, primarily consisting of ankeritic dolomite, with minor amounts of apatite, phlogopite, biotite, barite, pyrite, calcite, magnetite, ilmenite, pyrochlore, and sodic amphiboles (Olson and Hedlund, 1981). The carbonatite displays enrichment in LREEs, Nb, Ba, and Th. In addition, Van Gosen (2009) documented the presence of REE minerals, which are bastnäsite, synchysite, and rhabdophane; lesser amounts of REE occur in fluorapatite and monazite.

At Mountain Pass, Calif., the associated ultrapotassic igneous rocks have been described by Olson and others (1954), Castor and Nason (2004), Haxel (2005), and Castor (2008b). The ultrapotassic igneous rocks at Mountain Pass predated the Sulphide Queen carbonatite ore body and formed several stocks and hundreds of dikes (Olson and others, 1954; DeWitt and others, 1987; Castor, 2008b). Olson and others (1954) grouped the alkaline intrusive rocks into shonkinite, syenite, quartz syenite, and granite. Le Maître (2002) defined a shonkinite as dark syenite with more than 60 percent mafic minerals. The shonkinite at Mountain Pass is composed of phlogopite and pyroxene, primarily diopside, with minor amounts of potassium feldspar, amphibole, and olivine and accessory phases of apatite, magnetite, ilmenite, rutile, zircon, fluorite, barite, monazite, baddeleyite, thorite, ancylite, and allanite. The syenite is fine to coarse grained, grades into quartz syenite, and contains potassium feldspar and quartz, with minor sodic amphibole, phlogopite, biotite, and aegerine; trace minerals include apatite, rutile, magnetite, ilmenite, pyrite, zircon, thorite, allanite, and monazite (Olson and others, 1954; Castor,

2008b). The granite consists of perthitic microcline, quartz, and albite, with accessory aegirine, sodic amphibole and ilmenite, and with traces of biotite, fluorite, rutile, thorite, and zircon (Olson and others, 1954; Castor, 2008b).

Salvi and Williams-Jones (2005) provided an overview of REE deposits associated with peralkaline igneous complexes. The Thor Lake area deposits provide a good example of REE mineralization associated with alkaline igneous rocks. The Thor Lake complex is the youngest known intrusive phase of the Blatchford Lake complex, a suite of alkaline to peralkaline rocks (Davidson, 1978). Units within the Blatchford complex include from oldest to youngest: Caribou Lake gabbro, White-man Lake quartz syenite, Hearne Channel and Mad Lake granites, and the Thor Lake syenite (Taylor and Pollard, 1996). The Thor Lake syenite, also referred to as the Nechalacho layered alkaline complex, is a layered complex primarily consisting of sodic syenite and aegirine nepheline syenite. The medium-grained sodalite syenite is a highly altered and believed to have been a eudialyte cumulate lithology (Sheard and others, 2012).

## Petrogenesis of Carbonatites and Alkaline Intrusions

### Carbonatite Intrusions

Carbonatites and alkaline intrusions are clearly igneous, and radiogenic and stable isotopic studies have shown that the parental magmas are derived from mantle melts. However, a question that is still debated is: what is the nature of the initial melts and how do the magmas evolve to form the observed rock types. As summarized by Winter (2001), petrogenetic discussion focuses on: (1) Are carbonatite and alkali magmas developed separately by partial melting within the mantle or do carbonatites evolve from parental alkali magmas?; (2) if carbonatites evolve from parental alkali magmas, then is it by fractional crystallization or liquid immiscibility and at what depths does this occur?; and (3) if carbonatites are derived directly from a carbonatite magma, what is the nature of the parental carbonatite magma? Field data, experimental petrology, stable and radiogenic isotopic systematics, trace element geochemistry, and evaluation of mantle xenoliths provide insight into the nature of the initial melts and their possible evolutionary paths. Mitchell (2005) stressed that not all carbonatites are alike and suggested that the chemical variations of carbonatites could be the result of different mantle-source characteristics. Current models for the generation of carbonatites have been summarized in recent reviews by Le Bas (1987), Gittins (1989), Bailey (1993), and Winter (2001). These models may be divided into those in which carbonatite magmas are produced as a derivative magma from a silicate parent, through direct differentiation or through liquid immiscibility, and those in which carbonatites are produced directly as primary melts from carbonated mantle peridotite.

The generation of primary carbonatite melts or alkali-rich melts in the mantle cannot occur by melting of ordinary

mantle, but rather requires a mantle source that has been enriched in lithophile elements, as well as H<sub>2</sub>O and CO<sub>2</sub> (Bailey, 1987; Winter, 2001). Bailey (1987) provided an excellent review of insight gained from studying mantle xenoliths and experimental petrology to constrain the nature of metasomatized mantle as the source of alkaline magmas. He called upon the introduction of elements such as H, C, F, Na, Al, P, S, Cl, K, Ca, Ti, Fe, Rb, Y, Zr, Nb, Ba, and the REEs, to preexisting garnet or spinel peridotite (ordinary mantle material). This influx of constituents can lead to changes in mantle mineralogy, including the formation of minerals such as biotite, amphibole, clinopyroxene, and carbonate. Experimental studies (see Wyllie and Huang, 1975; Wyllie, 1989; Wyllie and Lee, 1999) demonstrated that carbonatite melts can be created directly from a metasomatized mantle source, depending on pressure and temperature conditions. Furthermore, the formation of different types of carbonatites may reflect melting of somewhat different types of mantle source material.

Because of the very common spatial association of alkaline intrusions with carbonatites, it has been proposed that carbonatites are the product of alkaline silicate magmas (see Kjarsgaard and Hamilton, 1989; Castor, 2008b). In these intrusive complexes, the carbonatites tend to form late and are volumetrically minor relative to the alkaline intrusions, suggesting that the carbonatites may be an end-product of alkaline magma evolution. However, this genetic association has been questioned (Gittens, 1989; Harmer, 1999). Gittens and Harmer (2003) argued that a spatial link between alkaline intrusions and carbonatites need not imply a genetic link. Fractional crystallization of an alkaline magma has been proposed as a mechanism to produce carbonatites. However, work by Gittens (1989) concluded that this is unlikely because parental magmas would not contain enough CO<sub>2</sub> to crystallize abundant carbonate and fractionation could not generate the high concentrations of Nb and REEs that are found in many carbonatites.

Work by Koster van Groos and Wyllie (1968) and Lee and Wyllie (1996) focused on the processes of liquid immiscibility, the separation of magmas into two or more immiscible liquid phases, as a mechanism to derive a carbonatite melt from an evolving alkaline silicate melt. Brooker and Kjarsgaard (2010) concluded that silicate-carbonatite liquid immiscibility is possible at crustal pressures; however, the high CO<sub>2</sub> requirement at high pressures indicated that liquid immiscibility is not likely within the mantle. This suggested that the parental magma needs to reach crustal depths for the processes to be a viable mechanism. Furthermore, moderate amounts of alkali elements, of 5 weight percent, and elevated CO<sub>2</sub> partial pressures are also required. Once again, this points to the need for an alkaline-silicate magma as a parental melt.

Each of the proposed mechanisms for the generation of carbonatite melts has its strengths and weaknesses, such that a universally accepted theory is still lacking. It may be that each mechanism is possible and carbonate intrusions are formed by a variety of processes.

## Alkaline Intrusions

The generation of REE-rich alkaline intrusive complexes is less controversial than for carbonatites, but the processes ultimately responsible for producing REE-rich lithologies is debated. These alkaline complexes generally fall in the peralkaline subclass and, as stated above, radiogenic isotopic studies clearly showed that parental magmas were derived from the mantle, and partial melting of metasomatized mantle was called upon to account for the observed enrichment in lithophile elements. How and where these magmas evolve is not well understood. Some REE-rich alkaline complexes are associated with large layered complexes, such as Thor Lake, Ilímaussaq, and Lovozero. Their magmatic evolution via fractional crystallization and magma-chamber processes is clearly evident. At Bokan Mountain, Thompson and others (1982) and Thompson (1988) called upon fractional crystallization of an already evolved magma at shallow crustal levels to produce the observed magmatic suite of lithologies.

Although different processes are suggested for the generation of the observed rock types at various REE-rich sites, all of the proposed mechanisms for the generation of carbonatites and alkaline intrusive rocks associated with REE deposits call upon a mantle source for the constituents of economic interest: REEs, Y, Nb, Zr, Ba, P, and F. The evolution of the parental magma and the generation of fluid phases that ultimately produce ore-grade material is an area ripe for study.

## Petrology of Associated Sedimentary Rocks

Sedimentary rocks are not genetically associated with carbonatite and alkaline intrusive REE deposits, but may comprise the country rocks that host the intrusive-related deposits.

## Petrology of Associated Metamorphic Rocks

Metamorphic rocks are not genetically associated with carbonatite and alkaline intrusive REE deposits, but can form the country rocks that host the intrusive-related deposits.

## Theory of Deposit Formation

### Ore Deposit Types

Carbonatite and peralkaline-related REE deposits have been discussed together in this report because of the spatial, and potentially genetic, association between carbonatite and alkaline rocks. Major carbonatite-REE occurrences in the

United States, including Mountain Pass, Bear Lodge, Elk Creek, and Iron Hill, are spatially associated with alkaline intrusive units. In contrast, peralkaline intrusion-related REE deposits occur within alkaline complexes, but they are not generally associated with carbonatites. Example deposits include Bokan Mountain, Strange Lake, Nechalacho (Thor Lake), Kipawa, and Norra Kärr. Thus, although carbonatites and peralkaline rocks may be genetically linked, REE deposits associated with these rock types do not generally occur together within an intrusive complex.

Carbonatites can be enriched in a variety of elements, including REEs (Mountain Pass, Bear Lodge, Elk Creek, Bayan Obo, Maoniuping, Daluxiang, Weishen, and Mount Weld), Fe (Bayan Obo), Nb (Araxá, Catalão, and Elk Creek), and copper (Palabora in South Africa). Because this is a model for the REEs, the discussion will center on this suite of elements. As discussed above, peralkaline intrusion-related REE deposits can be divided into layered magmatic occurrences (Kringlerne, Ilímaussaq complex, Lovozero, Strange Lake, and Nechalacho) and as veins and dikes (Bokan Mountain) and disseminated mineralization (Ghurayyah and Khaldzan-Buregtey). Processes responsible for ore-grade enrichment in REEs in carbonatites and both styles of peralkaline intrusion-related deposit types can overlap, but each deposit type has somewhat different features and genesis.

For REE-enriched carbonatites and peralkaline complexes to be economical for mining, a number of geological factors need to be considered which include grade and tonnage, mineralogy, REE distribution, and presence of other commodities, as well as other factors including depth to ore, transportation costs, power cost, environmental considerations, and workforce availability. Although grade and tonnage have to be significant, there is more to consider. The market price of individual REEs can vary by a factor of 100. For example, Eu oxides sell for approximately 100 times that of La and Ce oxides (Lynas Corporation, 2012); thus, the REE distribution within a deposit is important. The REEs can be hosted in a variety of minerals (table 1), and these minerals may or may not be easily processed to extract the REEs. Furthermore, at some deposits, the REE mineral phases are extremely fine grained, which can complicate the extraction processes. Mountain Pass is an example of a deposit with favorable mineralogy. The deposit is fairly coarse grained and the dominant REE mineral, bastnäsite, is relatively easy to separate and extract the REEs from. If other commodities can be mined at a deposit, then this can enhance the potential for REE production. For example, at Bayan Obo, the primary commodity is iron ore, and the REEs are mined as a byproduct commodity.

Magma genesis and evolution are instrumental in the formation of carbonatite- and peralkaline-related REE deposits. Initial magma is generated from small degrees of partial melt of metasomatized mantle. Debate still occurs over whether carbonatite magmas are generated as primary mantle melts or result from the evolution of alkaline-rich magma; regardless, at some point primary carbonatite magmas are generated (Winter, 2001). The initial magmas are not only enriched in

REEs, but also HFSEs, and likely halogens (F and Cl). Evolution of these magmas leads to extreme enrichment in these elements. With decreases in pressure and temperature, these alkaline and carbonatitic magmas evolve by fractional crystallization. In most magma, the REEs are not incorporated into rock-forming minerals. As a result, the REEs become enriched in the residual magma as crystallization progresses. Similarly, other HFSEs elements and volatiles tend to reside in the residual magma and the residual magma can become enriched in HFSEs. Both carbonatite and peralkaline intrusion-related REE deposits are characterized by wallrock alteration (fentitization), brecciation, and late-stage pegmatites and (or) dikes. These features attest to the release of fluids and volatiles from the evolving magma.

Mountain Pass is thought to be the only carbonatite REE deposit where the REE-bearing ore minerals are primary magmatic phases (Mariano 1989a,b). Thus, at some point during magmatic evolution of the carbonatite at Mountain Pass, the REE phases of bastnäsite, parisite, and monazite became saturated in the magma and crystallized. In most other carbonatite-hosted REE deposits, the residual magma became enriched in REEs and evolved to an orthomagmatic fluid with extreme REE enrichments.

Both basic types of peralkaline intrusion-related REE deposits—layered complexes or dike/vein/disseminated deposits—are associated with evolving peralkaline systems, but they have somewhat different evolutionary paths. The REE deposits associated with layered complexes clearly display primary magmatic, REE-rich phases forming distinct layers. In the Ilímaussaq complex, 29 distinct eudialyte-bearing layers have been identified, which are interpreted to be formed by the differential settling of minerals and the repeated injection of magma (Sørensen, 1992). The magma evolved to the appropriate composition and pressure-temperature conditions for eudialyte to crystallize, and these crystals became concentrated in individual layers by magma-chamber processes. Another example of REE mineral enrichment in a layered complex is the Lovozero complex, where repeated sequences of gravitationally derived units occur. Oriented crystals of eudialyte occur within the laminations of some units. In other units, loparite is concentrated in distinct layers (Arzamastsev and others, 2008). Similarly, the two ore zones at the Nechalacho deposit display characteristics associated with primary magmatic concentration of minerals rich in REEs and HFSEs.

In contrast, mineralization at Bokan Mountain does not show these features; there the REEs likely resided in the residual magma as crystallization progressed. Thompson (1988) and Philpotts and others (1998) concluded that elevated REE and HFSE concentrations in late-stage veins, such as the Dotson system at Bokan Mountain, occurred by protracted fractional crystallization and the separation of volatile-rich fluids, with REEs and HFSEs. These fluids escaped and followed faults and fractures to form the vein-dike systems.

Details of the formation of carbonatite and peralkaline intrusion-related REE deposits can be quite different. Hence,

for clarity of presentation the remainder of this section of the model will be divided, with peralkaline intrusion-related REE deposits described first and carbonatite-related REE deposits to follow.

## Ore Deposit System Affiliation(s)—Peralkaline REE deposits

As the name implies, peralkaline intrusion-related REE deposits are associated with peralkaline intrusive complexes. Other constituents that can be enriched in these systems include Be, F, Nb, Sr, Ta, Th, Ti, V, and Zr.

## Sources of Metals and Other Ore Components—Peralkaline REE Deposits

The source of the REEs, including yttrium, in peralkaline intrusion-related REE deposits is widely accepted to be from the initial magma that was generated as a mantle partial melt. Stable and radiogenic isotopic studies point to a mantle source for these magmas (Bell and Blenkinsop, 1989). Neodymium isotopic data from Bokan Mountain (Philpotts and others, 1998; J. Dostal, Saint Mary's University, written communication, 2011) and the Mont Saint-Hilaire complex, Canada (Schilling and others, 2011) demonstrated that the REEs came from the mantle. In many systems, evidence for crustal contamination is lacking; how these initial magmas evolve to create the extreme enrichments in the REEs is still debated. Magmatic evolution is driven by changes in pressure and temperature, but various processes have been called upon to account for the evolution of the magma and accompanying fluid and crystal phases.

## Sources of Ligands Involved in Ore Component Transport—Peralkaline REE Deposits

The mineralogy of REE-rich phases in peralkaline intrusion-related REE deposits primarily consists of silicate minerals, but carbonates, fluorides, phosphates, and oxides are also present. This suggests that important ligands include carbonate, fluoride, and phosphate species; experimental work has shown that chloride species can also be important (Migdisov and others, 2009). Boily and Williams-Jones (1994) evaluated the role of magmatic and hydrothermal processes in the genesis of the Strange Lake deposit and concluded that F-rich parental magma allowed for the high concentrations of REEs and HFSEs as fluorocomplexes and that these complexes were concentrated in late-stage residual magma. Further work by Salvi and Williams-Jones (1996) showed that multiple hydrothermal events occurred at Strange Lake, with an initial transport in an orthomagmatic fluid consisting of Zr, Y, and HREEs as fluorine complexes. These studies suggest that the parental magma was the source of F.

Salvi and others (2000) evaluated the transport and deposition of REEs and HFSEs in the Tamazeght Complex (Morocco), a peralkaline complex with elevated concentrations of Zr, Nb, and REEs. Similar to what was recognized at Strange Lake, they concluded that orthomagmatic, F-rich fluids played an important role in concentration of the REEs.

Few fluid inclusion studies have been conducted that evaluated fluid compositions of peralkaline intrusion-related REE deposits, so attempts to directly determine ligands are limited. Williams-Jones and others (2000) did note the presence of sulfate in inclusions at the Gallinas Mountains, New Mexico, REE occurrence. Thus, sulfate may need to be considered as a ligand in some deposits.

### **Sources of Fluids Involved in Ore Component Transport—Peralkaline REE Deposits**

Studies of fluids involved in the transport of REEs in peralkaline intrusion-related deposits are few. Magmatic and hydrothermal processes are called upon to transport and concentrate these elements. Layered complexes clearly document the role of magmatic transport and deposition of REEs. For example, at Lovozero, REEs are concentrated in primary magmatic phases that crystallized and then formed discrete layers by gravitational separation within a magma chamber. Other deposits have a more complex fluid evolution. With protracted fractional crystallization, peralkaline magmas become saturated with aqueous fluids and enriched in REEs and HFSEs. These fluids are derived from the parental magma, but the processes that control the complexation of ore components and the separation of these fluids from the magma are poorly understood.

One characteristic of many peralkaline intrusion-related REE deposits is the complex mineralogy and the overprinting of hydrothermal mineralization upon primary REE-rich minerals. This is a recurring theme of studies at Strange Lake (Boily and Williams-Jones, 1994; Salvi and Williams-Jones, 1990, 1992, 1996) and at the Nechalacho deposit (Sheard and others, 2012). At Strange Lake, primary ore minerals are clearly magmatic, but the origin of the hydrothermal fluid that reacted with these phases is controversial. Birkett and Miller (1991) argued for a magmatic origin for the mineralization, and Salvi and Williams-Jones (2005) presented data showing that fluids responsible for the Ca-metasomatism were meteoric. Salvi and Williams-Jones (2005) proposed that mixing of magmatic and meteoric fluids could have caused the precipitation of the ore components. At Nechalacho, Sheard and others (2012) proposed that the hydrothermal fluids that altered the primary REE phases (eudialyte and zircon) were likely orthomagmatic fluids that exsolved from the parental syenite magma.

### **Chemical Transport and Transfer Processes—Peralkaline REE Deposits**

Compared to many ore deposit types, there has been little study of the nature of chemical transport and transfer processes for peralkaline intrusion-related REE deposits. Because of the recent interest in these HREE deposits, many studies are underway, but few have been published. The source of the REEs is the peralkaline magma, and with protracted fractional crystallization, the REEs become enriched in the residual magma. Petrogenetic studies of layered alkaline complexes documented the extreme enrichments of HFSEs and REEs in residual liquids (Larsen and Sørensen, 1987; Kovalenko and others, 1995). Kogarko (1990) evaluated the role that alkali elements play on the retention of volatiles in alkaline magmas. He concluded that high concentrations of these elements prevent the separation of volatiles (F, Cl, and S) from the magma and increase the potential for REEs and HFSEs to accumulate in the residual magma.

At some point late in magmatic evolution, REEs can become saturated in the residual magma, causing REE-bearing phases to crystallize. These phases are relatively dense and can accumulate and form as individual layers, such as at Ilímaussaq and the Nechalacho deposit. Once crystallized, these phases can be affected by secondary processes, leading to increased enrichment of REEs. Fluorine and chlorine are important ligands for the transport of REEs in hydrothermal solutions (Wood, 1990; Haas and others, 1995; Gammons and others, 1996; Migdisov and Williams-Jones, 2007; Migdisov and others, 2009).

Extensive experimental, theoretical, and field investigations on the aqueous complexation of REEs at surface temperature have led to a strong understanding of the REE behavior in springs, rivers, mine drainage, and oceans. In contrast, little work has been undertaken to evaluate REEs in hydrothermal solutions at moderate temperatures of 250–400°C. Wood (1990) modeled the behavior of REEs to 350°C in a theoretical study by extrapolating available low temperature stability constant data. Migdisov and others (2009) presented experimental results for the solubility and speciation of REEs in F and Cl solutions up to 300°C. Their speciation results for the REEs documented that at higher temperatures, LREE-fluoride and -chloride species are more stable than HREE-fluoride and -chloride species. This suggests that REEs may become fractionated during hydrothermal transport in which the LREE are more easily transported than the HREEs.

Building on these experimental results, Sheard and others (2012) evaluated the REE mineralization at the Nechalacho deposit and constructed a genetic model for the enrichment in HREEs. Primary magmatic cumulate minerals, eudialyte and zircon, were altered by orthomagmatic fluids, which were likely F- and Cl-rich. This hydrothermal activity mobilized the REEs, with the HREE being mobilized on the scale of a few micrometers to tens of micrometers, whereas the LREEs were transported to distal parts of the deposit (Sheard and others, 2012).

To explain the observed mineralogy and textures in the vein-type mineralization at Bokan Mountain, Thompson and others (1982), Thompson (1988), and Philpotts and others (1998) called upon protracted fractionation crystallization and enrichment of the REEs in residual, water- and volatile-rich, upper parts of the magma chamber. The negative Eu anomaly in the REE patterns (fig. 21) attests to the crystallization and removal of feldspar (Philpotts and others, 1998). Thompson (1988) called upon caldera collapse and the release of the residual magma into faults and cracks to form the REE-rich vein system. Philpotts and others (1998) suggested that separation of an immiscible fluid occurred and the REEs were partitioned into it. These fluids were, in part, responsible for ore transport and deposition. The lack of intermediate composition rocks and the evidence for widespread hydrothermal activity are consistent with this interpretation.

### **Fluid Drive, Including Thermal, Pressure, and Geodynamic Mechanisms—Peralkaline REE Deposits**

Fractional crystallization of an alkaline magma is the process at least partially responsible for the formation of peralkaline intrusion-related REE deposits. Decreases in pressure and temperature are the driving forces for fractional crystallization (Winter, 2001). As REE-bearing minerals crystallize, magma-chamber dynamics can lead to the concentration of these phases into individual layers through gravitational settling to the base of the chamber or accumulation at the roof zone. Fractional crystallization without the formation of REE-rich phases drives the residual magma to extreme enrichments in REEs, HFSEs, alkali elements, and volatiles. Orthomagmatic fluids can be generated, which either hydrothermally alter existing phases or are released into adjacent lithologies. These fluids migrate from higher to lower pressure regimes.

### **Character of Conduits/Pathways that Focus Ore Forming Fluids—Peralkaline REE Deposits**

A discussion of this topic is not applicable for most peralkaline intrusion-related REE deposits because they are associated with layered complexes and not related to conduits or pathways. An exception is the vein mineralization at Bokan Mountain, which extends outward from the main pluton and follows pre-existing fractures and shears (Thompson, 1988; Warner and Barker, 1989). The Dotson vein system consists of a series of subparallel veins that can be traced for 2 km along strike (Thompson, 1988). The main Dotson vein is as wide as 3 m and can be traced along strike for 1,900 m (Robinson and others, 2011).

### **Nature of Traps and Wallrock Interaction that Trigger Ore Precipitation—Peralkaline REE Deposits**

A discussion of this topic is not applicable for most peralkaline intrusion-related REE deposits because this deposit type is generally associated with layered complexes. Also, very little information on this topic is available. Two studies that discuss a mechanism for the precipitation of REEs from evolved, magmatic fluids are Salvi and Williams-Jones (1996) for the Strange Lake deposit and Sheard and others (2012) for the Nechalacho deposit. Both studies called upon the late-stage transport of REEs as fluoride complexes in an orthomagmatic fluid, and REE precipitation as this fluid mixed with a Ca-rich fluid. The mixing resulted in fluorite crystallization, which dramatically decreased the F activity and thereby destabilized the REE fluoride complexes. Salvi and Williams-Jones (1996) presented isotopic evidence that the Ca-rich fluid at Strange Lake was meteoric in origin.

### **Ore Deposit System Affiliation(s)—Carbonatite REE Deposits**

As the name implies, carbonatite-related REE deposits are associated with carbonatites, which can form part of an alkaline intrusive complex. Other constituents that can be enriched in these systems include Ba, Fe, Cu, Nb, P, Sr, Th, Ta, Ti, U, and Zr.

### **Sources of Metals and Other Ore Components—Carbonatite REE Deposits**

The source of the REEs and yttrium in carbonatites is from the initial magma that was generated as a mantle partial melt, either directly or as a product of an alkaline magma. Stable and radiogenic isotopic studies, including Nd isotopic data, clearly pointed to a mantle source for carbonatite magmas (Bell and Blenkinsop, 1989). In many systems, evidence for crustal contamination is lacking. How these initial magmas evolve to create the extreme enrichments in the REEs is still debated. Magmatic evolution is driven by changes in pressure and temperature, but various processes have been called upon to account for the evolution of the magma and accompanying fluid and crystal phases.

### **Sources of Ligands Involved in Ore Component Transport—Carbonatite REE Deposits**

Unlike peralkaline intrusion-related REE deposits, extensive work has been undertaken to evaluate the source of ligands in REE transport in carbonatites. Rankin (2005) summarized information gleaned from fluid inclusion studies of carbonatites. He concluded that orthomagmatic fluids derived

from carbonatite magmas are dominantly Na-K-Cl-carbonate/bicarbonate brines and that sulfate and fluoride contents may also be elevated. The composition of these fluids suggests that important ligands include chloride, carbonate/bicarbonate, fluoride, sulfate, and possibly phosphate. Because these fluids evolve from the parental carbonatite magma, which was derived from the mantle, the ligands were likely derived from a mantle source. As discussed below, other studies called upon orthomagmatic fluids, containing various ligands, which are derived from the carbonatite magma.

### **Sources of Fluids Involved in Ore Component Transport—Carbonatite REE Deposits**

The generation of orthomagmatic fluids is an important topic in the understanding of carbonatite REE deposit formation. A possible exception is the Mountain Pass deposit, a unique example of dominantly primary magmatic mineralization. Rare earth element mineralization tends to occur late in the magmatic evolution of these carbonatite systems (Wall and Mariano, 1996), so understanding the evolution of carbonatite magmas is germane to the understanding of REE deposit genesis.

There is general agreement that in carbonatite magmas, calcite and dolomite are early to crystallize, and crystallization of these phases can continue throughout carbonatite formation (Gittens, 1989; Kjarsgaard and Hamilton, 1989; Wall and Mariano, 1996). Crystallization of these phases will enrich the residual magma in H<sub>2</sub>O and deplete the magma in Mg. Apatite may crystallize with these phases, and depending on the amount crystallized, this apatite can be an economic source of REEs. In general though, the residual magma will become enriched in REEs, H<sub>2</sub>O, and ligands. Wall and Mariano (1996) noted that REE mineralization tends to be greatest in units emplaced late in the magmatic sequence. These are typically ferrocarbonates.

As crystallization continues, dominated by calcite and dolomite, the residual magma becomes enriched in H<sub>2</sub>O, until it becomes saturated and a fluid is exolved. Keppler (2003) undertook a series of experiments to evaluate water solubility in carbonatite magmas at 900°C and 0.25–2.25 kb. At 1 kb and an approximate depth of 3 km, the water solubility of the carbonatite magma is approximately 10 percent, which is two to three times greater than for silicate magmas at similar pressures. The point where saturation is reached depends on pressure, temperature, H<sub>2</sub>O content, and magma composition (Gittens, 1989). The extent to which this fluid removes alkali elements and REEs from the magma is due to the partitioning of ligands, such as Cl and F, from the magma to the fluid phase. Fluid inclusion studies are consistent with this scenario (for example, Morogan and Lindblom, 1995). The common presence of fenitized wallrock supports the concept of the separation of alkali-rich fluids from the evolving carbonatite magma. At the Daluxiang and Maoniuping carbonatite REE deposits in China, petrogenetic work by Xu and others (2008)

revealed that the calcite is likely cumulate in origin in these deposits. With crystallization and accumulation, the residual magma became enriched in REEs, which then partitioned into a fluid phase with F.

### **Chemical Transport and Transfer Processes—Carbonatite REE Deposits**

With the exception of the Mountain Pass deposit, most carbonatite-hosted REE ore zones are formed from a fluid phase that separated from the evolving carbonatite magma. Although F is commonly called upon as the important ligand (for example, Williams-Jones and others, 2000; Xu and others, 2008), fluid inclusion studies documented the presence of significant chloride, sulfate, and carbonate/bicarbonate. Phosphate is another potentially important ligand. The REEs likely form stable aqueous complexes with the ligands and are transported in the orthomagmatic fluid. Changes in chemistry or physical properties, such as temperature, pressure, or oxygen fugacity, destabilize the complexes.

### **Fluid Drive, Including Thermal, Pressure, and Geodynamic Mechanisms—Carbonatite REE Deposits**

The mechanism(s) that control the migration of the carbonatite-related fluid have not been studied. Fenitized wallrock surrounding carbonatite bodies document that fluids can travel into the surrounding wallrock (Le Bas, 1981, 2008; Woolley, 1982; Morogan, 1994). Thermal and pressure gradients likely drive the fluid from the magma into the wallrock.

### **Character of Conduits/Pathways that Focus Ore Forming Fluids—Carbonatite REE Deposits**

A detailed discussion of this topic is not possible because very little information exists on this subject.

### **Nature of Traps and Wallrock Interaction that Trigger Ore Precipitation—Carbonatite REE Deposits**

Parameters of carbonatite-related fluids that control REE deposition include changes in pressure, temperature, oxygen fugacity, and composition, any of which could result in the destabilization of aqueous REE complexes. Xu and others (2008) proposed that REE precipitation at the Maoniuping deposit resulted from the interaction of orthomagmatic fluids with the country rock leading to fluorite precipitation. If the REE were carried in the orthomagmatic fluid as fluoride complexes, then the rapid removal of F would prompt the precipitation of the REEs. This mechanism is similar to the

model that Williams-Jones and others (2000) proposed for the genesis of hydrothermal fluorite-REE deposits in the Gallinas Mountains, New Mexico. They proposed that the REEs were traveling as REE-fluoride complexes in an orthomagmatic fluid. Mixing with a Ca-rich fluid (likely formation water) caused fluorite to precipitate and in turn decreased the activity of F in the fluid, which led to a destabilization of the REE-fluoride complexes. In this case, bastnäsite crystallized and the REEs were deposited (Williams-Jones and others, 2000).

## Exploration/Resource Assessment Guides

### Geological

As has been described throughout this descriptive model, REE concentrations are spatially and genetically associated with a wide variety of alkaline igneous rocks and carbonatite types. Economic deposits of REE are particularly linked to intrusive complexes composed of peralkaline rocks and, where they exist, carbonatites. Thus, the search for REE deposits begins with identifying, exploring, and evaluating provinces composed of alkaline igneous rocks and (or) known carbonatites.

A century ago, alkaline rocks and carbonatites were generally thought to be rare, sparsely occurring rock types. Woolley (1987, p. 1) noted, “At the beginning of the century [early 1900s] the known and described occurrences of alkaline rocks were probably fewer than 100, while only three carbonatites were known.” Aided by the pursuit of economic mineral deposits, an explosion of geological exploration and petrologic research during the 20<sup>th</sup> century led to discoveries of carbonatites and alkaline rocks on every continent. Now, 527 carbonatites are known in the world according to Woolley and Kjarsgaard (2008). About 40 percent of the world’s known occurrences of carbonatite are in Africa (Woolley, 2001). China, currently the world’s leading supplier of REE (as of 2012), has 27 known occurrences of carbonatite (Yang and Woolley, 2006). Brief descriptions of alkaline provinces and individual alkaline complexes are available for North and South America (Woolley, 1987), the former U.S.S.R. (Kogarko and others, 1995), and Africa (Woolley, 2001); these volumes are useful sources of information for the initial stages of REE exploration.

*Plate tectonic settings:* The majority of the known carbonatites are located in relatively stable crustal regions, commonly on deep-seated extensional fault zones (intra-continent rift zones). Active and recent alkaline and carbonatite magmatism along the southern end of the East Africa rift reinforces the model that alkaline-carbonatite melts ascend from the upper mantle into the crust along continental zones of rifting and extension. Thus, ancient, deep-seated rift zones within continental plates are favorable areas for REE mineralization,

particularly where they coincide with alkaline igneous rocks. Lithospheric doming, as much as several kilometers or more in diameter, can occur where alkaline complexes and carbonatites were intruded. Less commonly, some carbonatites are found near plate margins, possibly linked to processes of crustal-plate separation or orogeny.

*Lithologic associations:* Within an alkaline igneous complex, the alkaline rock types generally progress from oldest to youngest as ultramafic–mafic lithologies (pyroxenite, biotite shonkinite, peridotite, and jacupirangite) to felsic compositions (syenite, alkaline granites, ijolite, trachyte, and phonolite) to carbonatite. Locating coincidences of these alkaline rock types is a useful exploration guide. A complex, evolved intrusive complex may indicate an alkaline system that evolved and differentiated over time, perhaps leading to higher concentrations of REE and other incompatible elements in the late phases. The carbonatite mass is a late, typically final, phase of the alkaline complex and is generally centrally located in the complex. Carbonatite dikes, if present, are also late phases, which may extend for kilometers outward from the complex into surrounding country rocks. Due to doming combined with steep intrusive contacts, many alkaline complexes will erode into roughly circular topographic patterns.

*Mineralogy:* Most of the mineralogy of carbonatites is generally subdued in outcrop. That is, the principal REE ore minerals are typically not colorful, coarse grained, or euhedral. The gangue carbonate minerals, such as calcite and dolomite, can be identified with weak acid (as can be done with any carbonate rock).

In peralkaline intrusions, Richardson and Birkett (1996b) noted that REE deposits can contain some relatively rare but useful indicator REE and alkali minerals, such as sodalite (dark blue), eudialyte (pink/red), acmite (brown/green), alkali-amphiboles (blue/black), rinkolite (red brown/yellow brown), and gadolinite (green/brown-black). Most fluorite in REE deposits is purple due to internal U-Th irradiation. In field surveys, radioactivity is the most distinct and useful characteristic of identifying REE mineralization, due to associated Th-U-bearing minerals.

*Buried Deposits:* As in most mineral resource exploration, one must consider that the ore-bearing zone may not outcrop. Therefore, one must recognize that some or many of the alkaline rock types that typically form an ultramafic to felsic suite in an alkaline intrusive complex may not be visible, yet may still exist at depth. The most altered, REE-enriched parts of the complex may be buried, and thus will need to be detected and mapped by geophysical techniques followed by exploratory drilling. Dikes or veins of carbonatite can indicate that a larger carbonatite mass lies below or in the area. Ground and airborne geophysical techniques have been used to identify and define the size of buried carbonatites and mineralized alkaline masses.

## Geochemical

Fenitization caused by alkali metasomatism during the emplacement of an alkaline intrusion or carbonatite can form alteration aureoles of variable widths and intensity. This fenitization halo can occur in the intrusion and the surrounding country rock. Although fenitization is not always obvious or well developed, the presence of a fenite halo indicates that alkali-rich hydrothermal fluids were present, which is generally a favorable indication of REE enrichment.

The most diagnostic geochemical elements for carbonatites and peralkaline-hosted REE deposits are the HFSEs and some LILE. Associated elements can include Cl, F, Mn, and P. Many of these elements occur in heavy, dense minerals that are resistant to weathering (resistates); thus, heavy mineral concentrates from stream sediments are a useful sampling technique in the exploration for these deposit types. In Canada, geochemical surveys of lake waters, using F, U, and Pb as pathfinders, and glacial deposits led to discoveries of REE deposits (summarized in Richardson and Birkett, 1996b). In regions with deep, intense weathering, such as laterite weathering of the upper parts of carbonatites in Brazil and Australia, the laterites contain resistate ore minerals, such as pyrochlore and monazite (Lottermoser, 1990; Morteani and Preinfalk, 1996).

Carbonatites highly enriched in REE, whether from primary magmatic processes or as a result of orthomagmatic fluids, are low in P, Ti, Zr, and Nb relative to earlier formed units, according to Richardson and Birkett (1996a).

Thus, favorable reconnaissance geochemical indicators of REE mineralization in an alkaline igneous setting are:

- Anomalous radioactivity found for an intrusion, sets of veins, fracture zone(s), and (or) areas that contain concentrations of alkali minerals.
- Anomalous concentrations of the HFSEs in stream sediments, residual soils, or rocks.
- Resistate HFSE-rich minerals in heavy mineral concentrates of stream sediments or soils, such as monazite, pyrochlore, xenotime, allanite, zircon, kainosite, thorite and uranothorianite, and euxenite (Barker and Van Gosen, 2012).

## Geophysical

Geophysical data are collected and available at a wide range of scales and, as such, can contribute to defining regional areas of permissive tracts down to characterization of detailed information at an individual deposit. Modern airborne geophysical technologies offer the capability to collect gamma-ray, magnetic, and gravity data concurrently. Electromagnetic data can also be acquired this way. The combination and integration of these methods provide significant insight into a number of physical properties, which, in combination,

can substantially enhance an exploration program for intrusion-hosted REE deposits.

*Plate Tectonic Settings:* On a regional scale, magnetic and gravity data, such as that available for the United States (U.S. Geological Survey, 1993) can identify large geologic structures, such as deep-seated extensional fault zones (intra-continent rift zones), known to be associated with carbonatite/alkaline magmatism. Major intra-continent rifts are often expressed on magnetic and gravity maps as parallel to subparallel, elongate lineaments that extend for tens to hundreds of kilometers.

*Lithologic Associations:* Once prospective terranes are identified, high-quality airborne geophysical surveys are typically flown to enhance prospectivity, primarily because the host intrusions are excellent geophysical targets. Carbonatites and alkaline intrusions are normally radioactive and can have distinct magnetic and density properties. Many exploration companies developing REE deposits in the United States have included high-resolution geophysical surveying as part of their exploration program. Airborne geophysical surveys that are flown over prospective deposits include magnetic, gamma-ray, and, most recently, gravity and gravity gradiometry data. The choice of airborne geophysical tool(s) and platform (helicopter or fixed-wing) used to explore for an intrusion-hosted REE deposit will depend on a number of factors including accessibility to the deposit, ruggedness of terrain, and whether the deposit is entirely or partly exposed or is concealed by rock, glacial deposits, vegetation, or water/ice.

*Buried Deposits:* Gravity and magnetic surveys can be particularly useful to map partially or entirely concealed carbonatites and alkaline intrusions. Some REE deposits were initially discovered based on magnetic and gravity surveys. Although these methods do not provide direct detection of REE mineralization, they can provide necessary geologic controls on the depth, geometry, and extent of the intrusion-hosting REE mineralization. The success of these methods, as with all geophysical mapping tools, depends on there being a physical property contrast, such as density or magnetization, between the intrusion and the surrounding rocks.

## Attributes Required for Inclusion in Permissive Tract at Various Scales

Regional-scale attributes:

- Alkaline igneous provinces and known alkaline intrusive complexes.
- Major crustal rift zones.
- Known carbonatites (Woolley and Kjarsgaard, 2008).
- Known REE deposits and occurrences (Orris and Grauch, 2002).

Local-scale attributes:

- Known alkaline intrusive complexes, and (or) known carbonatites.

- Known REE deposits and occurrences in the area.
- Anomalous concentrations of HFSEs and LILEs in sample media, such as in the heavy mineral fraction of stream sediments, residual soils, and (or) rock.
- Fenite alteration zones.
- Concentrations of HFSE-bearing minerals.
- Anomalous radioactivity, particularly where U occurrences are unrecognized.
- Distinct magnetic and gravity anomalies that suggest favorable lineaments and (or) igneous bodies.

### Knowledge that Enables Favorability Zonation of Permissive Tracts

- Spatial trends in radioactivity, magnetism, and gravity as delineated by geophysical surveys.
- Spatial trends in HFSEs and LILEs anomalies in residual soils, rock, and (or) stream sediments.
- Zoning in the distribution of HFSE-rich minerals across the intrusive complexes.
- Structures and linear alkaline intrusive bodies, such as dikes, which indicate possible pathways and locations for late-stage hydrothermal activity.
- Known REE deposits and occurrences in the area.
- Known carbonatites.
- Results of previous exploration activities or mineral development within the tract, such as past results of exploratory drilling and sampling.

### Factors Influencing Undiscovered Deposit Estimates (Deposit Size and Density)

- Results of previous exploration or mineral development within the tract, such as past results of exploratory drilling and sampling.
- Geophysical signatures relative to geophysical signatures at known deposits in the area.
- Size, spatial distribution, and characteristics of known REE deposits and occurrences in the area

## Geoenvironmental Features

### Introduction

The features of mineral deposits that are typically of environmental concern are those that affect the acid-generating or acid-neutralizing potential of mine waste, and the source, transport, and fate of trace elements of environmental concern. For many deposit types, useful insights can be found commonly in published case studies of abandoned mines and existing mines and in unpublished reports associated with permit applications for advanced exploration projects that companies are trying to develop into mines. In the case of REEs, Mountain Pass has been the only significant primary REE producer in the United States. It began operation in the 1950s prior to the period of modern regulatory oversight that required extensive environmental monitoring. Thus, limited environmental data are available from the sole primary REE source in the United States. Global REE production has been dominated by the Bayan Obo deposit in China, and environmental data are limited from the world's largest source of REEs as well. The most significant information related to the environmental geochemistry of REE deposits comes from the mineralogical and geologic characteristics of representative deposits, unpublished reports associated with some advanced exploration projects, and published studies on the aqueous geochemistry and toxicology of REEs and associated elements.

For many mineral deposit types, the presence of sulfide minerals, particularly pyrite, influences the mobility of potentially toxic trace elements in the weathering environment due to the formation of acid-mine drainage (Nordstrom, 2011). The oxidative weathering of pyrite produces sulfuric acid, which can attack associated ore and gangue minerals and liberate these trace elements of potential concern. In the case of carbonatite-hosted REE deposits and alkaline-intrusion-related REE deposits, the abundance of sulfide minerals, including pyrite, is generally low relative to the abundance of carbonate minerals, such that the likelihood of the formation of acid mine drainage is minimal. In fact, tailings from metallurgical testing at the Nechalacho alkaline intrusion-related deposit near Thor Lake contain less than 0.1 weight percent total sulfur (Avalon Rare Metals, Inc., 2011).

### Pre-Mining Baseline Signatures in Sediment and Water

Baseline geochemical data for surface water, groundwater, and sediment are only available for the Nechalacho alkaline intrusion-related deposit, which is currently an advanced exploration project (Avalon Rare Metals, Inc., 2011). The deposit is located in the Canadian Shield on the northern shore of Great Slave Lake, approximately 90 km southeast of Yellowknife. The area is dominated by numerous lakes. The surface water and sediment sample sites encompass an area that extends for as much as 6 km from the deposit, but

the groundwater samples are solely from within the deposit as reported by Avalon Rare Metals, Inc. (2011). The pH of surface water and groundwater is neutral to slightly alkaline, ranging between 6.9 and 8.6 (fig. 23). The cationic species in groundwater and surface water surrounding the deposit are dominated by Mg, followed by Ca and Na. Water hardness values range between 71 and 470 mg/L CaCO<sub>3</sub>, with surface water and groundwater spanning a similar range (fig. 23A). Bicarbonate, as reflected by the alkalinity values ranging between 74 and 442 mg/L CaCO<sub>3</sub> (fig. 23B), is the most important anionic species, followed by sulfate (fig. 23C), chloride, and fluoride (fig. 23D). Groundwater tends to have higher concentrations of anions than surface water.

Trace elements are generally low in the vicinity of the Nechalacho deposit, but tend to be slightly higher in groundwater compared to surface water. Baseline dissolved iron concentrations in surface water and groundwater are noteworthy and range from less than 30 to over 10,000 µg/L (fig. 23E). Pyrite has been identified as a locally significant accessory mineral in the hydrothermal assemblage associated with the deposit (Sheard and others, 2012), which may explain some of the elevated iron concentrations. Baseline dissolved copper concentrations range from 0.2 to 48 µg/L (fig. 23F). Chalcopyrite has been identified in the hydrothermal assemblage of the deposit (Sheard and others, 2012), and may serve as a source for the copper. Dissolved aluminum concentrations generally range 0.5 to 108 µg/L, with one sample of groundwater reaching 15,300 µg/L. Dissolved manganese ranges from 0.2 to 544 µg/L. Baseline dissolved nickel and molybdenum concentrations range from 0.25 to 6.6 µg/L (fig. 23G), and from 0.2 to 63 µg/L, respectively. Dissolved concentrations of uranium range from less than 0.05 to 20 µg/L (fig. 23H). Dissolved concentrations of arsenic and antimony are less than 5 and 0.3 µg/L, respectively.

The geochemistry of selected elements in sediments in the vicinity of Thor Lake has been reported by Avalon Rare Metals, Inc. (2011) and is summarized in table 4. This table compares the geochemical ranges of sediments in the vicinity of Thor Lake to average crustal abundances for these elements (Taylor, 1964), to threshold effects concentration (TEC), and to probable effects concentration (PEC) values for sediment toxicity from MacDonald and others (2000). The entire baseline geochemical range documented surrounding Thor Lake is greater than the average crustal abundance for Sb, As, and Se, and the high end of the range is greater than the average crustal abundance for Ba, Hg, Mo, U, and Zn. Relative to sediment toxicity guidelines, the high end of the baseline geochemical range exceeds both the TEC and PEC for As, but only the TEC for Cu, Hg, Ni, and Zn. An explanation for the elevated background concentrations is not given in the report.

## Past and Future Mining Methods and Ore Treatment

It is difficult to make general statements about mining and ore treatment methods for REE mining because of

the limited number of deposits being mined, their geologic diversity, and the diversity of REE ore minerals that are commonly encountered. Nevertheless, REE deposits can be mined by either open pit or underground mining methods depending upon the geometry of the ore body. Open pit mining requires greater removal of waste rock to access the ore compared to underground mining. For example, production at the Mountain Pass mine had a stripping ratio (waste:ore) of 5:1 (Castor and Hedrick, 2006). Once mined, ore is crushed to a grain size that allows the ore mineral(s) to be separated from other minerals in the rock. Ore mineral separation is done with either froth flotation, gravity, or electromagnetic methods, depending on the mineralogy and physical character of the ore and associated gangue minerals (Castor and Hedrick, 2006). Ore grades for recently active carbonatite and peralkaline intrusion-related REE deposits generally range between 0.8 and 12 weight percent rare earth oxide. Thus, the bulk of the material that is mined is waste.

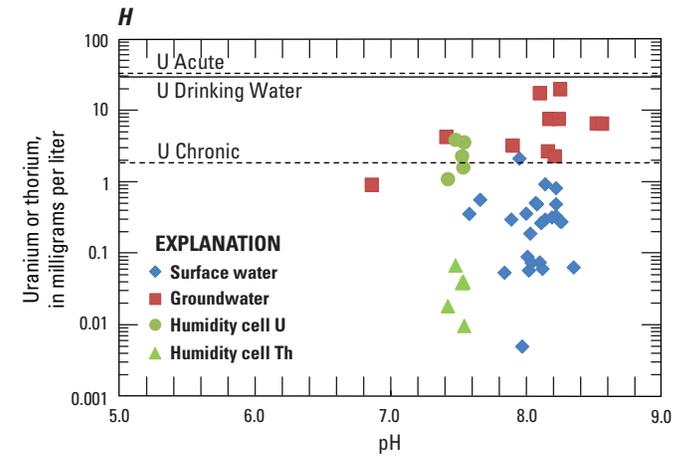
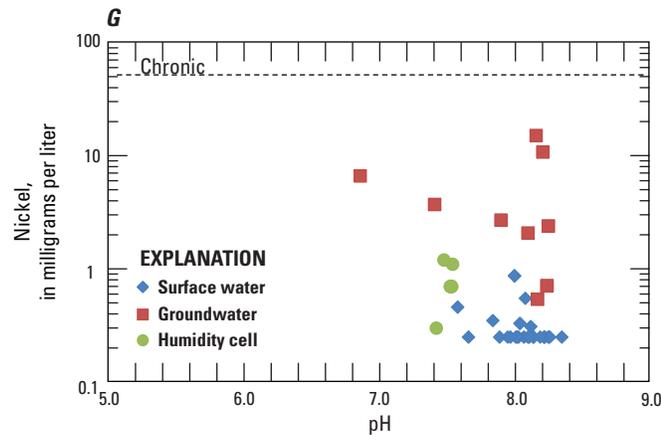
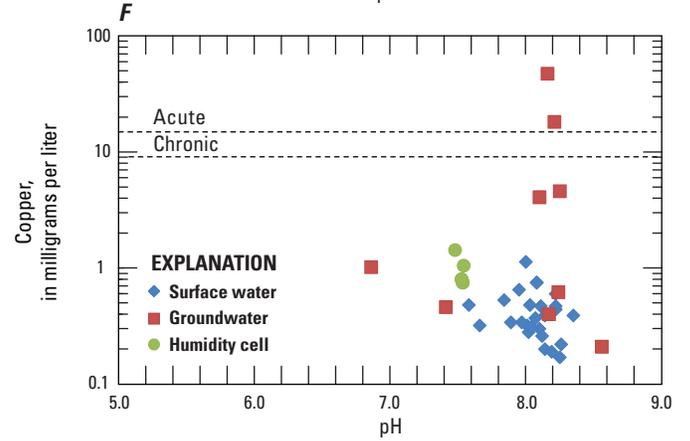
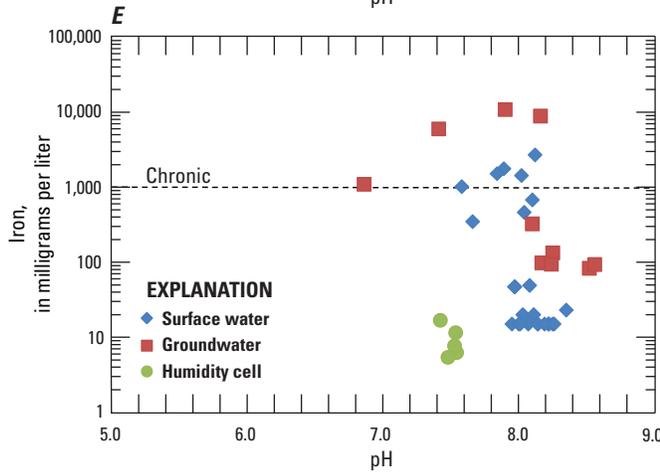
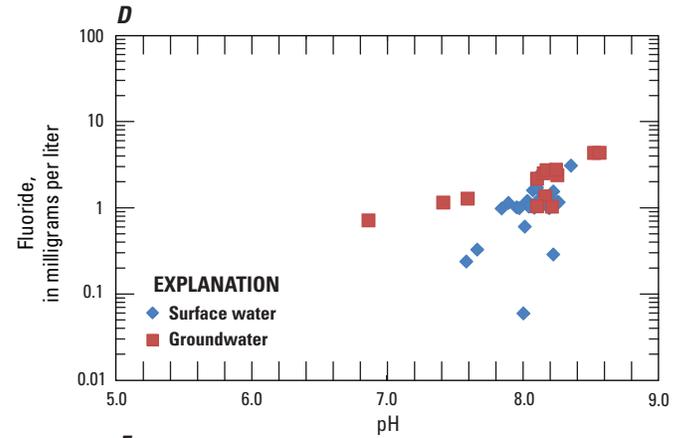
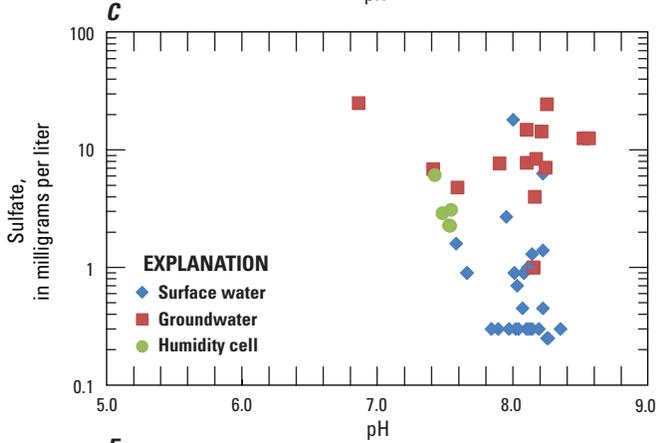
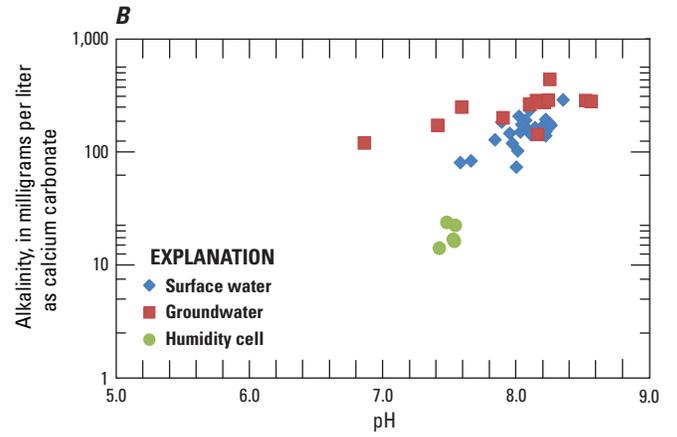
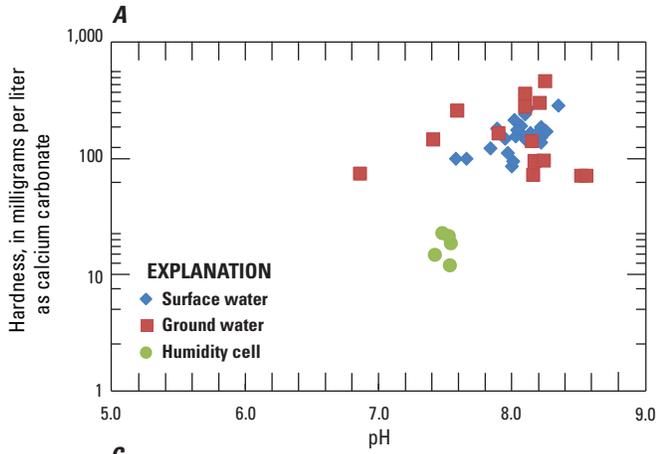
The treatment of ore mineral concentrates to extract REEs will vary depending upon the nature of the ore and the specific ore mineral. For example at Mountain Pass, several different approaches were taken with bastnäsite concentrate (Haxel, 2005). It was either shipped directly, leached with dilute hydrochloric acid to remove carbonate gangue, or roasted and leached with hydrochloric acid to decompose bastnäsite and liberate the REEs. The REE-rich solution then undergoes a series of wet chemical, solvent extraction separation steps to separate individual REEs (Castor and Hedrick, 2006).

## Mine Waste Characteristics

### Mineralogy

The mineralogy of mine waste (waste rock and tailing) determines its potential environmental impact. Iron sulfide minerals, such as pyrite and pyrrhotite, control the acid-generating potential of mine waste and the presence of carbonate minerals, and to a lesser extent silicate minerals dictate the acid-neutralizing potential of mine waste. The ore and gangue mineralogy also reflects the suite of trace elements of potential environmental concern associated with these deposits. Table 5 summarizes the formula and REEs, Th, and U content of REE-bearing minerals found in carbonatite and peralkaline intrusion-related deposits.

Insights into ore and mine waste mineralogy are largely restricted to the Mountain Pass carbonatite deposit (Castor, 2008a,b) and the Nechalacho (Thor Lake) alkaline intrusion related deposit (Avalon Rare Metals, Inc., 2011; Sheard and others, 2012). The mineralogy of the Mountain Pass carbonatite, in terms of ranges and means, is summarized in table 6. At Mountain Pass, the dominant gangue minerals are calcite and dolomite, followed by barite. Sulfide minerals are only present in trace amounts. The primary ore mineral is bastnäsite. The mineralogy of mill feed, tailing, and concentrate from metallurgical testing on material from the Nechalacho



**Figure 23.** (Previous page.) Dissolved concentrations of various constituents associated with the Nechalacho deposit, Thor Lake, Northwest Territories, Canada. Data include results from surface water and groundwater from pre-mining environmental baselines studies and from humidity cell tests on pilot tailing samples. Data are from Avalon Rare Metals, Inc. (2011). Environmental guidelines shown on various plots are from U.S. Environmental Protection Agency (2006; 2009) and Suter (1996). “Acute” and “Chronic” refer to acute and chronic toxicity guidelines for the protection of aquatic organisms. The guidelines shown for copper and nickel vary as a function of water hardness and were calculated assuming a water hardness of 100 milligrams per liter (mg/L) CaCO<sub>3</sub>. (µg/L; micrograms per liter).

**Table 4.** Ranges of selected elements in sediments in the vicinity of the Thor Lake deposit, Northwest Territories, Canada, compared to average crustal abundances and threshold effects concentration and probable effects concentration values.

[mg/kg, milligrams per kilogram]						
Element		Low	High	Average crustal abundance <sup>1</sup>	TEC <sup>2</sup>	PEC <sup>2</sup>
Antimony	mg/kg	0.21	0.68	0.2		
Arsenic	mg/kg	2.92	33.9	1.8	9.79	33
Barium	mg/kg	82.6	665	425		
Beryllium	mg/kg	<1	2	2.8		
Cadmium	mg/kg		<0.5	0.2	0.99	4.98
Chromium	mg/kg	2.5	33.4	100	43.4	111
Cobalt	mg/kg	<2	12.4	25		
Copper	mg/kg	8.4	53.1	55	31.6	149
Lead	mg/kg	<5	11.1	12.5		
Mercury	mg/kg	<0.05	0.111	0.08	0.18	1.06
Molybdenum	mg/kg	<1	14.3	1.5		
Nickel	mg/kg	4.3	39.9	75	22.7	48.6
Selenium	mg/kg	0.21	1.7	0.05		
Uranium	mg/kg	<2	23.6	2.7		
Vanadium	mg/kg	4.6	43.2	135		
Zinc	mg/kg	23	374	70	121	459

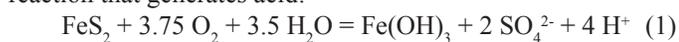
<sup>1</sup>Average crustal abundance values are from Taylor (1964).

<sup>2</sup>Threshold effects concentration (TEC) and Probable Effects Concentration (PEC) values are from MacDonald and others (2000).

deposit, Thor Lake, Northwest Territories (NWT), Canada are summarized in table 7. At Nechalacho, the dominant gangue minerals are quartz, feldspars (plagioclase and potassium feldspar), and micas (biotite and muscovite). Carbonate minerals constitute up to 5 percent of the ore and sulfide minerals constitute less than 0.1 percent.

## Acid-Base Accounting

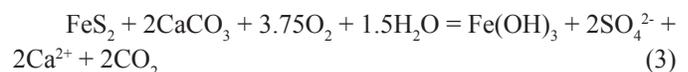
Acid-base accounting considers the acid-generating potential and acid-neutralizing potential of mine waste in terms of the balance between a generalized pyrite-oxidation reaction that generates acid:



and a generalized calcite-dissolution reaction that neutralizes acid:



which, when combined to eliminate the hydrogen ion (H<sup>+</sup>) from the equation, yields a “net neutral” reaction in which the acid and base are balanced:



From a practical perspective, the acid-generating potential (AP) is estimated on the basis of the amount of sulfide sulfur present in the sample as reflected by pyrite in reaction 1 and the acid-neutralizing potential (NP) is estimated on the basis of the amount of calcite present in the sample as reflected in reaction 2 (Sobek and others, 1978). Both AP and NP values are expressed in units of kilograms of calcium carbonate per metric ton of waste material (kg CaCO<sub>3</sub>/t). AP and NP data are typically interpreted in terms of a net neutralization potential

**Table 5.** Formula and rare earth element, thorium, and uranium contents of rare element minerals found in carbonatite and alkaline intrusion-related rare earth element deposits. Modified from Long and others (2010).

[REO, rare earth oxide; Wt%, weight percent]

Group-mineral	Formula*	REO Wt%	ThO <sub>2</sub> Wt%	UO <sub>2</sub> Wt%
Oxides				
Aeschnynite	(Ln,Ca,Fe)(Ti,Nb) <sub>2</sub> (O,OH) <sub>6</sub>			
Euxenite	(Y,Ln,Ca)(Nb,Ta,Ti) <sub>2</sub> (O,OH) <sub>6</sub>			
Fergusonite	YNbO <sub>4</sub>			
Carbonates				
Bastnäsitate	(Ln,Y)CO <sub>3</sub> F	70–74	0–0.3	0.09
Parisite	Ca(Ln) <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> F <sub>2</sub>	59	0–0.5	0–0.3
Synchisite	Ca(Ln,Y)(CO <sub>3</sub> ) <sub>2</sub> F	49–52	1.6	
Tengerite	Y <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> •n(H <sub>2</sub> O)			
Phosphates				
Apatite	(Ca,Ln) <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (OH,F,Cl)	0–20		
Monazite	(Ln,Th)PO <sub>4</sub>	35–71	0–20	0–16
Xenotime	YPO <sub>4</sub>	52–67	0–3	0–5
Silicates				
Allanite	(Ln,Y,Ca) <sub>2</sub> (Al,Fe <sup>3+</sup> ) <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub> (OH)	3–51	0–3	
Eudialyte	Na <sub>4</sub> (Ca,Ce) <sub>2</sub> (Fe <sup>2+</sup> ,Mn <sup>2+</sup> ,Y)ZrSi <sub>8</sub> O <sub>22</sub> (OH,Cl) <sub>2</sub>	1–10		
Thalenite	Y <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>			
Zircon	(Zr,Ln)SiO <sub>4</sub>	0–0.7	0.1–0.8	

\*Ln: lanthanide (rare earth) element.

(NNP) value, which is the difference between the NP and AP values:

$$NNP = NP - AP \tag{4}$$

where negative values reflect excess acid-generating potential and these samples are designated as being “net acid”; positive values reflect excess acid-neutralizing potential and these samples are designated as being “net alkaline.” Alternatively, these data may be interpreted in terms of a neutralizing potential ratio (NPR), which is the ratio of NP to AP:

$$NPR = NP/AP \tag{5}$$

A NPR value of zero represents “net neutral” material (NNP = 0 kgCaCO<sub>3</sub>/t) where the theoretical acid-generating potential is balanced by the theoretical acid-neutralizing potential. In practice, samples with NPR values less than 1 are designated as being “potentially acidic drainage generating,” those with NPR values greater than 2 are designated as being “non-potentially acidic drainage generating,” and those with

**Table 6.** Modal mineralogy, in percent, of mineralized rock from the Mountain Pass deposit, California. Data from Castor (2008b).

Mineral	Low	High	Average
Calcite	trace	80	28.4
Dolomite	trace	97	23.7
Strontianite	trace	46	8.1
Barite	trace	33	16.9
Celestite	trace	11	1.4
Bastnäsitate	trace	25	9.5
Monazite	trace	4	0.7
Quartz	trace	55	4.5
Talc	trace	50	4.3
Iron oxide	trace	10	2.5

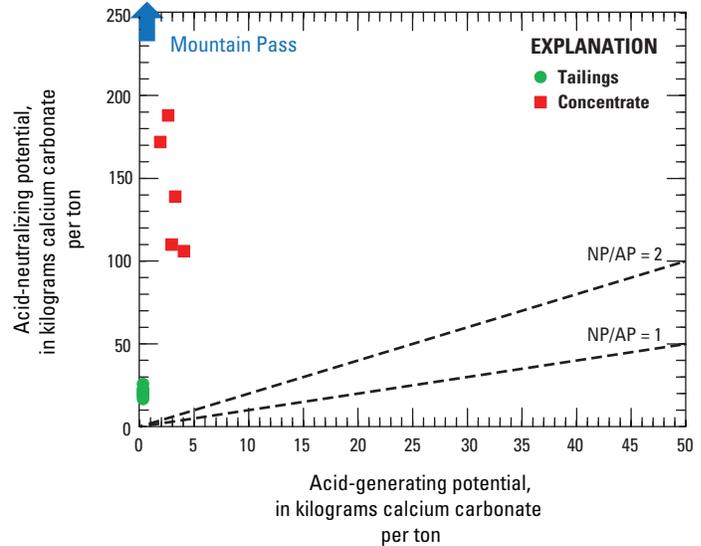
NPR values between 1 and 2 are designated as having uncertain potential for generating acid (Price, 2009). Note that a NPR value greater than 2 represents twice the amount of alkalinity needed for net neutrality under equilibrium conditions.

Acid-base accounting data are available for the Nechalacho deposit (Avalon Rare Metals, Inc., 2011) and are shown in figure 24. The higher concentration of sulfide minerals and carbonate minerals in the concentrates compared to the tailings from Nechalacho (table 7) is clearly reflected in their NP and AP values. The tailing material has NPR values ranging from 53 to 84 indicating that the risk of acid drainage associated with this mine waste is essentially non-existent. No acid-base accounting data are available for the Mountain Pass carbonatite ore. However, the modal mineralogy of the material has an average combined calcite and dolomite content of approximately 52 percent (table 6), which corresponds to a NP value of approximately 520 kg CaCO<sub>3</sub>/t. When combined with only trace amounts of sulfide minerals, this NP value indicates that the risk of acid drainage associated with carbonatite mine waste is essentially non-existent as well.

The original acid-base accounting method used the total sulfur content of the sample as a proxy for the pyrite content and the acid-generating potential of the sample. Subsequent application of this technique to porphyry copper mine wastes, where anhydrite and gypsum are important sulfur species, led to the realization that the acid-generating potential of mine waste is overestimated if non-acid-generating sulfate minerals, such as anhydrite, gypsum, and barite, are present and AP is estimated from the total-sulfur content of the sample. This fact led to the current practice of estimating AP on the basis of sulfide-sulfur contents rather than total-sulfur contents (White and others, 1999). In the case of Mountain Pass, approximately 17 percent of the ore is barite (table 6), which means that if the acid-generating potential is estimated on the basis of total sulfur rather than sulfide sulfur, it will be erroneously high.

## Geochemistry

The mineral chemistry and mine-waste chemistry exert important influences on the environmental characteristics of REE deposits. The mineral chemistry of REE ore minerals in both carbonatite and peralkaline intrusion-related deposits indicates that some of these minerals contain significant concentrations of thorium and uranium (table 5), which may represent some of the most significant environmental challenges associated with these deposits. For example, in monazite, ThO<sub>2</sub> concentrations as much as 20 weight percent and UO<sub>2</sub> concentrations as much as 16 weight percent have been documented (table 5; Long and others, 2010). Uranium has the potential for recovery as a resource, but limited current demand for thorium will likely make it an environmental liability requiring management at current and future mine sites. Since some deposits are rich in fluorine, this element may be of concern in certain circumstances, but no ecological standards have been defined. Minerals that contain F include



**Figure 24.** Acid-base accounting data for tailing and concentrate from metallurgical testing on material from the Nechalacho deposit, Thor Lake, Northwest Territories, Canada (Avalon Rare Metals, Inc., 2011). Data are not available for the Mountain Pass deposit, but geological descriptions of the ore (Castor, 2008b) suggest negligible acid-generating potential (AP) values and high acid-neutralizing potential (NP) values near 520 kilograms calcium carbonate per ton.

fluorite, fluorapatite, bastnäsite, britholite, parisite, synchysite, fluorcerite, pyrochlore, and yttriofluorite (table 5).

The geochemistry of the tailings from the metallurgical testing done at Nechalacho is anomalous for multiple selected elements compared to the average composition of crustal rocks (table 8). The elements chosen for comparison are those for which solid medium environmental guidelines in soil or sediment are available. The anomalous elements include As, Cd, Cr, Mo, Ni, Se, U, and the REEs.

## Ecosystem Issues

The primary pathways for REE mining to affect aquatic ecosystems are through water or sediment contamination. Knowledge regarding the toxicity of REEs to aquatic organisms through either pathway is limited. Environmental guidelines for REEs in surface water and sediment are lacking in the United States. However, guidelines for surface water and sediment for both fresh and salt water have been recommended in the Netherlands (table 9; Sneller and others, 2000). Several studies have documented that the toxicity and biologic uptake of REE in surface water varies as a function of water hardness and alkalinity (Barry and Meehan, 2000; Moermond and others, 2001). Furthermore, Weltje and others (2004) found that the toxicity of lutetium was proportional to the concentration of the free ion (Lu<sup>3+</sup>) in microbial bioassay studies. Therefore, REE complexation with carbonate, sulfate, or other ligands

**Table 7.** Modal mineralogy of mill feed, tailings, and concentrates from metallurgical testing at the Nechalacho deposit, Thor Lake, Northwest Territories, Canada. Data, in weight percent, from Avalon Rare Metals, Inc. (2011).

[%, percent; Std Dev, one standard deviation from the mean]

Mineral	Mill feed		Tailings		Concentrates	
	Mean %	Std dev %	Mean %	Std dev %	Mean %	Std dev %
Quartz	16.9	3.4	17.3	1.8	7.1	1.5
Plagioclase	17.4	1.7	17.0	2.5	2	0.2
K-Feldspar	13.3	2	13.8	1.6	1.2	0.6
Biotite	18.6	1.9	16.0	2.0	13.3	5
Muscovite/Clays	4.9	1.1	21.3	2.6	2	0.5
Chlorite	0.36	0.2	0.1	0.0	0.5	0.2
Amphibole	0.6	0.4	0.1	0.1	0.3	0.3
Calcite	1.3	0.3	0.2	0.1	1.9	0.4
Dolomite	0.9	0.7	0.1	0.1	1.7	0.8
Ankerite	2.6	0.9	0.7	0.3	9.1	2.6
Fe-Oxides	9.1	1.7	8.6	1.7	9.4	2.2
Sulfides	0.08	0.04	0.03	0.1	0.32	0.13
Fluorite	0.5	0.2	0.00	0.0	1.3	0.6
Columbite	0.4	0.2	0.3	0.1	2	0.7
Fergusonite	0.2	0.1	0.2	0.1	1.7	0.4
Bastnäsité	1.1	0.2	0.1	0.0	3.5	0.6
Synchysite	1.0	0.5	0.1	0.1	3.7	1.2
Allanite	1.3	0.5	0.6	0.2	2.8	0.6
Monazite	0.5	0.2	0.1	0.1	1.6	0.5
Apatite	0.02	0.04	0.00	0.0	0.3	0.2
Zircon	8.2	0.8	3.2	0.9	33.3	3.9
Total	99.3		99.8		99.0	

in natural systems may significantly influence their toxicity (Wood, 1990). In addition, Tu and others (1994) and Tai and others (2010) did not identify any synergistic or antagonistic effects in REE toxicity or bioaccumulation in experiments done with solutions with mixtures of REEs.

Insights into potential ecological risks associated with REE deposits are limited to data associated with the baseline environmental characterization of the Nechalacho deposit (Avalon Rare Metals, Inc., 2011). For pre-mining conditions, trace elements in surface water are generally low in the vicinity of the Nechalacho deposit and tend to be slightly higher in groundwater compared to surface water. Dissolved iron concentrations in surface water and groundwater are noteworthy because they reach concentrations above the chronic water-quality guideline for the protection of aquatic organisms (fig. 23E). Dissolved copper concentrations locally exceed both acute and chronic water-quality guidelines to protect aquatic organisms (fig. 23F). Dissolved nickel concentrations reach several micrograms per liter, but do not exceed environmental

guidelines for the protection of aquatic organisms (fig. 23G). Dissolved concentrations of uranium in groundwater exceed chronic guidelines for the protection of aquatic organisms (fig. 23H). The only information on potential mine drainage compositions comes from the humidity-cell tests conducted on tailings from metallurgical testing at Nechalacho (table 10; fig. 23). The leachate from these tests is characterized by slightly alkaline pH (7.4–7.5), low hardness (12–23 mg/L CaCO<sub>3</sub>), low alkalinity (14–24 mg/L CaCO<sub>3</sub>), and sulfate (2.3–6.1 mg/L). Trace element concentrations are low and below their respective water-quality guidelines, with the exception of uranium, which locally exceeds the Tier II chronic criterion for the protection of aquatic organisms (Suter, 1996; fig. 23H). Dissolved thorium concentrations are approximately one to two orders of magnitude lower than dissolved uranium concentrations (fig. 23H). Therefore, the risk of mine drainage issues associated with tailings from peralkaline intrusion-related deposits is likely minimal.

**Table 8.** Selected geochemistry of tailings from metallurgical tests on material from the Nechalacho deposit compared to various sediment and soil environmental guidelines.

[mg/kg; milligrams per kilogram]

Element	Unit	Master tailings	Average crustal <sup>1</sup> abundance	Sediment <sup>2</sup>		Soil <sup>3</sup>	
				TEC/NC	PEC/MPC	Residential	Industrial
Al	mg/kg	62,000	82,300			77,000	990,000
As	mg/kg	4.4	1.8	9.79	33	23	160
Cd	mg/kg	6	0.2	0.99	4.98	70	810
Cr	mg/kg	640	100	43.4	111	280	1,400
Cu	mg/kg	18	55	31.6	149	3,100	41,000
Mo	mg/kg	73	1.5			390	5,100
Ni	mg/kg	330	75	22.7	48.6	1,600	20,000
Pb	mg/kg	9.9	12.5	35.8	128	400	800
Se	mg/kg	3.2	0.05			390	5,100
U	mg/kg	9.9	2.7			230	3,100
Zn	mg/kg	68	70	121	459	23,000	310,000
Ce	mg/kg	1,900	60	256.2	18,800		
Dy	mg/kg	170	3.0	26.2	2,200		
Gd	mg/kg	210	5.4	23.2	1,800		
La	mg/kg	850	30	83.6	4,700		
Nd	mg/kg	970	28	43.2	7,500		
Pr	mg/kg	250	8.2	66.1	5,800		
Sm	mg/kg	210	6.0	30.9	2,500		

<sup>1</sup>Average crustal abundance values are from Taylor (1964).<sup>2</sup>NC, negligible concentration; MPC, maximum permissible concentration from Sneller and others (2000), TEC; threshold effects concentration, PEC; probable effects concentration from MacDonald and others (2000).<sup>3</sup>Residential and industrial soil guidelines are U.S. Environmental Protection Agency Regional Screening Levels (U.S. Environmental Protection Agency, 2010).

Accidental release of mill tailings, either during or after closure, can pose a risk to aquatic organisms. This risk can be assessed by the comparison of the geochemical composition of mill tailings with relevant sediment-quality guidelines (table 8). In general, most concentrations of trace elements are low. The concentrations of Cd, Cr, and Ni in the tailing sample exceed both the threshold-effects concentration and the probable-effects concentration (MacDonald and others, 2000). The REE concentrations in the sample all exceed their corresponding negligible concentration, but not their maximum permissible concentrations (Sneller and others, 2000). Therefore, only a few elements are marginally of concern in the event of accidental release of tailings.

## Human Health Issues

Human health risks associated with mining are typically associated either with contamination of potential sources of drinking water or ingestion of fine particulate mine waste (tailing). Knowledge of the human health effects of REEs is sparse. The United States lacks drinking water standards for the REEs. A review of the limited data on the toxicity of REEs

in drinking water has been done by de Boer and others (1996). None of the baseline chemistry of groundwater or surface water in the vicinity of the Nechalacho deposit nor humidity-cell leachates of mill tailings exceeds U.S. Environmental Protection Agency drinking standards, although uranium in groundwater locally approaches the limit of 30 micrograms per liter ( $\mu\text{g/L}$ ) (fig. 23H). In terms of potential ingestion risks associated with tailings, the only element in the sample of tailing from Nechalacho to exceed the residential regional screening level is chromium (table 8).

The radionuclides associated with uranium and thorium in the ore minerals and mine waste may represent some of the most important human health risks associated with REE mine waste. Radiation risks include gamma radiation (principally from radium decay), windblown radioactive tailings, and radon gas (Landa, 2004; Abdelouas, 2006). However, the concentrations of radionuclides in the Nechalacho tailings and concentrates are low. For tailing samples, the  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ , and  $^{210}\text{Pb}$  values are all less 0.2 Bq/g; for the ore concentrate, these values are all less than 2.1 Bq/g (Avalon Rare Metals, Inc., 2011). In comparison, typical  $^{226}\text{Ra}$  concentrations in uranium mill tailings range between 8.8 and 29 Bq/g (Abdelouas, 2006).

**Table 9.** Environmental guidelines for rare earth elements in fresh water and sediment. From Sneller and others (2000).

[mg/kg; milligram per kilogram; µg/L, microgram per liter]

	Sediment			Surface Water		
	Unit	NC <sup>1</sup>	MPC <sup>1</sup>	Units	NC <sup>1</sup>	MPC <sup>1</sup>
Y	mg/kg	30.7	1,400	µg/L	0.28	6.4
La	mg/kg	83.6	4,700	µg/L	0.18	10.1
Ce	mg/kg	256.2	18,800	µg/L	0.35	22.1
Pr	mg/kg	66.1	5,800	µg/L	0.17	9.1
Nd	mg/kg	43.2	7,500	µg/L	0.40	1.8
Sm	mg/kg	30.9	2,500	µg/L	0.64	8.2
Gd	mg/kg	23.2	1,800	µg/L	0.40	7.1
Dy	mg/kg	26.2	2,200	µg/L	0.31	9.3

<sup>1</sup>NC, negligible concentration; MPC, maximum permissible concentration.**Table 10.** Average humidity-cell leachate chemistry from metallurgical test tailings from the Nechalacho deposit, Northwest Territories, Canada (Avalon Rare Metals, Inc. 2011) compared to acute and chronic surface water guidelines for the protection of aquatic organisms and to drinking water standards.

[mg/L; milligram per liter; µg/L, microgram per liter]

	Chronic Surface Water	Acute Surface Water	Drinking Water <sup>1</sup>	Nechalacho Tailings Leachate
SO <sub>4</sub> mg/L			250	2.9
Y µg/L	0.28	6.4		0.18
Al µg/L	750	87	200	20
As µg/L	340	150	10	0.5
Cd µg/L	0.3	2	5	0.2
Co µg/L	3.1	195		0.1
Cr µg/L	570	74	100	1.7
Cu µg/L	13	11	1,300	1.4
Fe µg/L		1,000	300	5.8
Mo µg/L	239	10,100		12.1
Ni µg/L	470	52		1.2
Pb µg/L	65	2.5	15	0.15
Sb µg/L	104	985		52
Se µg/L		5	50	<1
Sn µg/L	73.7	2680		2.2
U µg/L	1.87	33.5	30	3.9
V µg/L	19.1	284		0.04
Zn µg/L	120	120	5,000	3
Zr µg/L	54.9	982		0.71

<sup>1</sup>Surface water criteria are from Suter (1996), U.S. Environmental Protection Agency (2006), and Sneller and others (2000). Hardness-based surface water criteria (Cd, Cr, Cu, Ni, Pb, and Zn) were calculated assuming a water hardness of 100 milligrams per liter of CaCO<sub>3</sub>.

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