



Review Rare Earth Element Deposits of Alkaline Igneous Rocks

Jaroslav Dostal 问

Department of Geology, Saint Mary's University, 923 Robie Street, Halifax, NS B3H 3C3, Canada; jdostal@smu.ca; Tel.: +1-902-420-5747

Received: 9 May 2017; Accepted: 21 July 2017; Published: 25 July 2017

Abstract: Alkaline igneous complexes host deposits of rare earth elements (REE), which represent one of the most economically important resources of heavy REE and Yttrium (Y). The hosts are differentiated rocks ranging from nepheline syenites and trachytes to peralkaline granites. These complexes usually occur in continental within-plate tectonic settings associated with rifts, faults, or hotspot magmatism. The REE mineralization is found in layered alkaline complexes, granitic stocks, and late-stages dikes and rarely trachytic volcanic and volcaniclastic deposits. The bulk of REE is present in accessory minerals, which can reach percentage levels in mineralized zones. The mineralization contains various REE-bearing minerals that can display complex replacement textures. Main REE minerals present in these deposits are bastnäsite, eudialyte, loparite, gittinsite, xenotime, monazite, zircon, and fergusonite. The parent magmas of alkaline igneous complexes are derived from partial melts of mantle sources. Protracted fractional crystallization of the magma led to an enrichment in REE, particularly in the late stages of magma evolution. The primary magmatic mineralization is commonly overprinted (remobilized and enriched) by late magmatic to hydrothermal fluids. Elevated abundances of U and Th in the deposits make a gamma-ray (radiometric) survey an important exploration tool, but also represent a significant environmental challenge for exploitation.

Keywords: rare earth elements; alkaline igneous rocks; deposits; REE-bearing minerals; ore genesis; petrogenesis; exploration

1. Introduction

Alkaline igneous rocks host deposits of a variety of rare metals and industrial rocks and minerals. The commodities of special economic importance in these rocks are rare earth elements (REE). In the past 25 years, REE have become essential components of modern technologies. Their demand has increased significantly because of their use in high-technology applications. Among others, they play a vital role in high-strength magnets, mobile phones, flat-screen TVs, lasers, energy-efficient lighting, and superconductors. REE are important in "green technology" where they are used in wind turbines and hybrid gas-electric vehicles (particularly light-weight magnets). In addition, due to the critical role and wide and diverse use of the REE in electronic, military, and environmental applications, there is concern over the security of the supply of these critical elements [1].

The rare earth elements are a group of 16 chemically similar elements including 15 lanthanides and yttrium. The lanthanides are elements with atomic numbers ranging from 57 (Lanthanum) to 71 (Lutetium). They are frequently subdivided into light rare earth elements (LREE) with lower atomic weight i.e., spanning from lanthanum through to europium and the heavy rare earth elements (HREE) ranging from gadolinium (or europium) through to lutetium. Yttrium (atomic number 39) is considered a REE as it has similar chemical and physical properties. Its ionic radius is nearly identical to that of holmium (Ho) and thus is commonly included with HREE. REE exhibit "lanthanide-contraction", the steady decrease in the size of the atoms and ions with increase of atomic number from lanthanum to lutetium. Thus, the LREE have larger ionic radii than the HREE and, hence, they behave differently

during petrogenetic processes. For example, the HREE generally behave more mantle-compatible than the LREE during partial melting.

The rare earth elements are not as rare in nature as their name implies, in fact, they are relatively abundant in the earth's crust. The crustal abundance of their most abundant element—cerium (Ce) is ~43 ppm compared to copper ~27 ppm and lead ~11 ppm [2]. However, the abundances of individual REE can vary widely, e.g., the crustal abundance of thulium (Tm) is only ~0.28 ppm. Compared to LREE, heavy REE are relatively rare in nature but are economically more valuable. The prices of individual REE vary by one or two orders of magnitude.

As the demand for REE has dramatically increased in recent years so have the prices of individual REE, leading to an exploration boom and an increased visibility of REE. They have even become the basis for a bestselling video game. However, economic deposits of REE are rare. Presently, the global production of REE comes from only from a few deposits such as Bayan Obo (China). The REE deposits exist primarily in four geologic environments: carbonatites, alkaline igneous systems, ion-absorption clay deposits, and monazite-bearing placer deposits. This paper focuses on REE deposits associated with alkaline igneous rocks. It reviews and discusses their characteristics and classification, describes examples of the major types of the deposits and comments on their origin and exploration methods. These REE deposits have attracted a great deal of interest in the exploration industry as well as in the geological literature (e.g., [3–6]). They represent one of the most economically important resources of HREE and Y. However, their genesis is still under debate (e.g., [3,6,7]).

2. Mineralogy

In nature, REE do not exist individually, as gold often does, but instead they are present together in numerous ore/accessory minerals as either minor or major constituents. REE occur in a wide range of mineral species. There are over 250 minerals which contain REE as important constituents in their chemical formula and crystal structure (Table 1). They are mainly silicates, fluorocarbonates, oxides, and phosphates. These minerals typically comprise the bulk of the REE in a rock. REE are also hosted in minor amounts in the mafic rock-forming minerals such as amphiboles and biotite, where they substitute for major cations of comparable radius and charge.

Mineral	Formula	Approx. TREO (wt %)	
Allanite	$(Y,Ln,Ca)_2(Al,Fe^{3+})_3(SiO_4)_3(OH)$	39	
Apatite	$(Ca,Ln)_5(PO_4)_3(F,Cl,OH)$	19	
Bastnäsite	(Ln,Y)(CO ₃)F	75	
Eudialyte	$Na_4(Ca,Ln)_2(Fe^{2+},Mn^{2+},Y)ZrSi_8O_{22}(OH,Cl)_2$	9	
Fergusonite	(Ln,Y)NbO ₄	53	
Gittinsite	CaZrSi ₂ O ₇		
Iimoriite	$Y_2(SiO_4)(CO_3)$	68	
Kainosite	$Ca_2(Y,Ln)_2Si_4O_{12}(CO_3)\cdot H_2O$	38	
Loparite	(Ln,Na,Ca)(Ti,Nb)O ₃	30	
Monazite	(Ln,Th)PO ₄	65	
Mosandrite	(Na,Ca) ₃ Ca ₃ Ln (Ti,Nb,Zr)(Si ₂ O ₇) ₂ (O,OH,F) ₄	33	
Parisite	$Ca(Ln)_2(CO_3)_3F_2$	61	
Pyrochlore	(Ca,Na,Ln) ₂ Nb ₂ O ₆ (OH,F)		
Rinkite (rinkolite)	$(Ca,Ln)_4Na(Na,Ca)_2Ti(Si_2O_7)_2(O,F)_2$	20	
Steenstrupine	Na ₁₄ Ln ₆ Mn ₂ Fe ₂ (Zr,Th)(Si ₆ O ₁₈) ₂ (PO ₄) ₇ ·3H ₂ O	31	
Synchysite	$Ca(Ln)(CO_3)_2F$	51	
Xenotime	YPO ₄	61	
Zircon	(Zr,Ln)SiO ₄	4	

Table 1. Names and formulae of important rare earth elements (REE)-bearing minerals associated with REE mineralization.

Ln-lanthanides; TREO—oxides of lanthanides and Yttrium (Y); Estimates of TREO content are based on Webmineral composition (www.webmineral.com).

REE-bearing minerals tend to be dominated by either LREE or HREE, although each REE can be present. In some mineralized zones, the abundances of REE-bearing accessory (ore) minerals can reach >10 vol %. In alkaline igneous complexes, mineralization is commonly composed of a variety of REE-bearing minerals, which can exhibit complex replacement textures in part due to late magmatic to hydrothermal overprinting of the primary mineralogy, commonly producing pseudomorphs of pre-existing phases. However, there are only a relatively small number of REE minerals, which can be economically exploited. They include bastnäsite, monazite, xenotime, synchysite, loparite, eudialyte and parasite (Table 1). Overall, the bulk of resources is mostly associated with three REE-rich minerals: bastnäsite, monazite and xenotime (e.g., [3,4]). Bastnäsite and monazite are dominated by LREE whereas xenotime is the main source of HREE and Y (Figure 1). Many other accessory/ore minerals are either sparse or it is difficult to extract REE from them on a commercial scale. In alkaline igneous rocks, the grain size of the ore minerals in REE mineralization varies from coarse grained (commonly cumulate phases in the nepheline syenitic complexes) to fine grained in volcanic rocks and replacement textures.

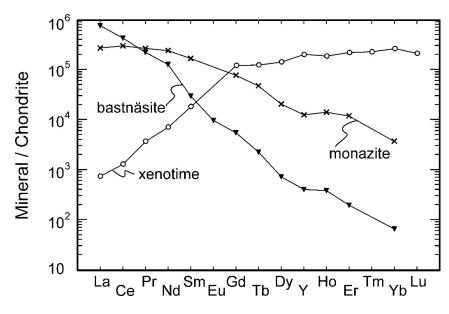


Figure 1. Chondrite-normalized REE (lanthanides and Y) patterns of minerals that are the major components of REE ores: monazite, xenotime [8] and bastnäsite [9]. Note that Yttrium is plotted as a pseudo-lanthanide between Dy and Ho. Normalizing values are after Sun and McDonough [10].

3. Alkaline Igneous Rocks

The generally accepted definition of the "alkaline rocks" means a primary enrichment of Na_2O and K_2O in a rock of a given SiO_2 content. Alkaline igneous rocks are so enriched in alkalis that they contain abundant Na- and K-bearing minerals (such as feldspathoids, alkali pyroxenes and alkali amphiboles) which are not commonly present in other rock types. Na-rich amphiboles (e.g., arfvedsonite and riebeckite) and Na-rich pyroxenes (e.g., aegirine) are dominant mafic minerals in these rocks rather than common Fe-Mg silicates. Likewise, feldspars may be replaced or accompanied by feldspathoids such as nepheline, sodalite, leucite, or cancrinite. However, there are some ambiguities when using the term alkaline for the felsic rocks. To resolve this problem, petrologists revived the name "peralkaline" to specify important chemical characteristics of the alkaline rocks even for the felsic types. The peralkaline rocks have a higher molecular proportion of combined sodium and potassium than aluminum (Figure 2) and their CIPW norms typically contain acmite and Na-metasilicate.

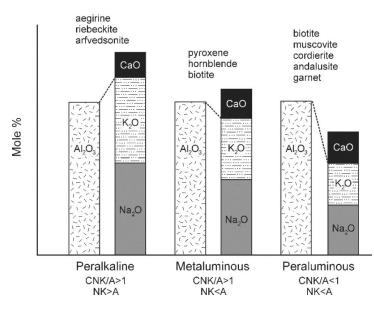


Figure 2. Classification of felsic rocks based upon molecular proportions of Al_2O_3 , CaO, Na_2O and K_2O . Common non-quartz-feldspathic minerals for each type are shown. Vertical axis is schematic. CNK = CaO + Na₂O + K₂O; NK= Na₂O + K₂O; A = Al₂O₃.

The peralkalinity reflects not only the mineralogy and major element composition of the rocks but it has an effect on the distribution of several rare metals. The peralkaline rocks are very high in REE, uranium, thorium and high-field strength elements (HFSE) such as zirconium, niobium and tantalum as well as halogens (Cl and F). In fact, these rocks, particularly of nepheline syenitic and granitic composition, can host REE deposits, which are commonly enriched in yttrium and HREE (Figure 3). The Nb-Y-F type of pegmatites [11], which may host Be, REE, Th, U and Zr mineralization, has also been correlated with the peralkaline granites. Alkaline rocks including peralkaline ones, are commonly found in anorogenic and within-plate tectonic settings, mostly in continental rift and/or crustal extension zones [3].

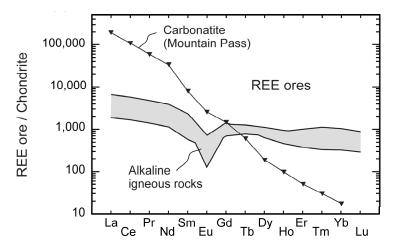


Figure 3. Chondrite-normalized REE patterns of an average ore of Mountain Pass (California, USA), a major carbonatite-hosted REE deposit [1,9] and the range of the average ores of the REE deposits associated with alkaline igneous rocks (Thor Lake, Strange Lake, Kipawa, Norra Kärr, and Bokan). The data are from Hatch [12,13]. Normalizing values are after Sun and McDonough [10].

4. Rare Earth Element Deposits

Economically, the REE mineralization and deposits include two separate types: LREE and HREE deposits. Most LREE are produced from carbonatite deposits (Figure 4) including Bayan Obo in China and Mountain Pass in California (currently shut down). It is likely that these large deposits will satisfy, for the medium-term future, the needs for LREE, including neodymium. Monazite-bearing placer deposits were important REE sources in the past. In fact, several decades ago, placer deposits met most of the world's REE needs. From beach/placer deposits, LREE-rich monazite can still be recovered as a by-product during the exploitation of the Ti-rich minerals. However, monazite contains significant amounts of uranium and thorium and thus these deposits are presently out of favour due to environmental concerns (high radioactivity). Additionally, carbonatite and monazite-rich placer deposits contain only trace amounts of the HREE. Thus, these deposits do not provide a sufficient supply of HREE. Ion-adsorption clay deposits in southern China (referred to as "south China clays") are currently the world's main source of HREE. These deposits have low contents in REE but they are economic because the REE can be easily extracted from them. The second significant HREE sources are alkaline rock-hosted deposits containing HREE and Y as their primary product or coproduct (Figures 3 and 4). The deposits containing HREE generally tend to be lower grade than the LREE deposits. However, the HREE, based on unit value, can be more valuable and their low grade deposits may still be economically exploitable.

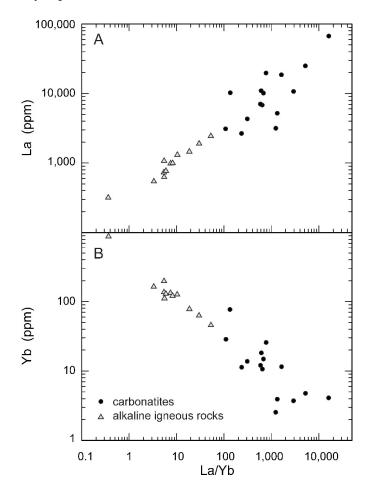


Figure 4. The variations of La and Yb (ppm) relative to La/Yb ratios in REE ores of carbonatites and alkaline igneous rocks. Most data reflect the average grades of the REE ores in the deposits and exploration projects reported by Hatch [12,13].

There is no shortage of prospective REE deposits, many of which have been discovered and explored before the recent collapse of REE prices. The factors to determine whether prospects and discoveries are viable include not only the grade (REE concentrations) and tonnage (size) of REE ore in a deposit but also other essential technical and economic criteria including amendable mining and refining. The REE are chemically very similar to each other, occur together, and thus it is difficult to separate individual elements from each other. The separation and purification of individual REE require complex processing, which can be rather expensive. There are also numerous social and

solved as well as a market issue (i.e., to find an off-taker that will buy the product). One of the principal environmental challenges of these deposits is the presence of radioactive elements (Th and U) that are usually associated with them. On the other hand, the acid-drainage hazards of these deposits are low due to the very small contents of potentially acid-generating sulfides as well as the presence of feldspars and even subordinate amounts of carbonates (buffer).

environmental issues (e.g., energy, water, land use, potential pollution and socioeconomic issues) to be

5. Rare Earth Element Deposits of Alkaline Igneous Rocks

The locations of several prominent REE deposits and advanced exploration targets which are hosted in alkaline (peralkaline) igneous rocks are shown in Figure 5. In addition to REE, some of these deposits contain economically important amounts of other rare metals, including HFSE such as Zr, Nb, Ta and Hf as well as U and Th. The calculated ore reserves as well as the average grades of the deposits are given in Table 2 and a brief description of the most important deposits is given below. The age of the mineralized alkaline complexes ranges from Neoarchean/Paleoproterozoic to Mesozoic (e.g., [3]) with a significant peak during the Mesoproterozoic (1000–1460 Ma). Similarly, large carbonatite-hosted REE deposits are also of Proterozoic age including the Mountain Pass (~1400 Ma), Bayan Obo (~1300 Ma) and Palabora (South Africa; ~2050 Ma).

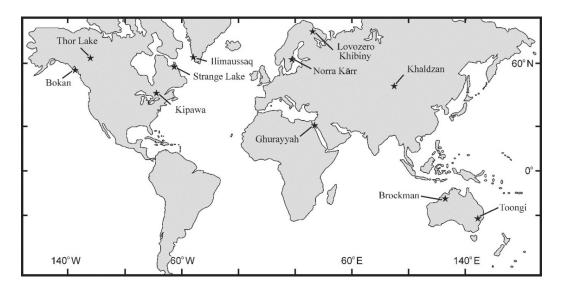


Figure 5. World map showing the locations of major REE deposits hosted in alkaline/peralkaline igneous rocks.

The REE deposits of alkaline complexes are typically hosted by nepheline syenites, peralkaline granites (including pegmatites) and, less commonly, peralkaline felsic volcanic rocks. In all these deposits, the mineralization is closely related to the crystallization of magma, particularly to its late fractions.

Deposit	Ore Reserves (Mt)	TREO Ore Grade (wt %)	TREO Reserves (Mt)	HREO/TREO (%)
Thor Lake (Nechalacho), Canada				
Basal zone	125.7	1.43	1.799	20.9
Upper zone	177.7	1.32	2.353	10.0
Ilimaussaq, Greenland				
Kvanefjeld deposit	619.0	1.06	6.547	11.8
Sørensen deposit	242.0	1.10	2.667	11.7
Zone 3 deposit	95.3	1.16	1.106	12.1
Kipawa, Canada	27.1	0.40	0.107	36.2
Norra Kärr, Sweden	58.1	0.59	0.343	50.3
Strange Lake, Canada				
Enriched zone	20.0	1.44	0.288	49.7
Granite zone	472.5	0.87	4.118	36.5
Bokan, Alaska, USA	4.9	0.61	0.030	40.1
Toongi, Australia	73.2	0.89	0.651	23.3
Brockman, Australia	36.2	0.21	0.076	85.8

Table 2. Tonnage and ore grade of selected rare earth elements (REE) deposits hosted by alkaline igneous rocks.

Data from Hatch (2014). Abbreviations: Mt—million metric tons. TREO—oxides of lanthanides and Y; HREO—oxides of heavy REE and Y. Recent data are not available for some deposits discussed in the text including Lovozero, Khibiny, Khaldzan-Buregtey, and Ghurayyah.

The REE deposits comprise three distinct groups, based on their host rocks. The *first* deposit type is hosted by nepheline syenitic rocks of the large layered alkaline intrusions. The host rocks show textures suggestive of crystal accumulation where the REE mineralization occurs in layers containing mineral cumulates that are rich in REE-bearing minerals. Cumulate textures indicate that the initial REE enrichment was due to magmatic processes and the ore-bearing layers represent cumulate layers within a magma chamber. The thickness of the ore horizons is variable ranging from ~0.5 m to more than 100 m. The REE minerals accumulated at the highly fractionated parts of the intrusions. These deposits (Figure 5) include Ilimaussaq (Greenland), Lovozero and Khibiny (Kola Peninsula, Russia), Thor Lake/Nechalacho (NWT, Canada), Kipawa (Canada), and Norra Kärr (Sweden).

The *second* group encompasses the deposits associated with peralkaline granites such as mineralization in pegmatites (e.g., Strange Lake, Quebec-Labrador, Canada), felsic dikes (e.g., Bokan Mountain, southeastern Alaska, USA) and minor highly fractionated intrusions where the REE-bearing minerals occur mostly disseminated and do not show any features of crystal accumulation (e.g., Khaldzan-Buregtey, western Mongolia; Ghurayyah, Saudi Arabia). The *third* type is associated with peralkaline felsic volcanic rocks, mainly trachytes containing disseminations of very fine-grained REE-bearing minerals. An example of these relatively rare deposits is Toongi (Dubbo Zirconia) and Brockman/Hastings, both in Australia (Figure 5). Although a number of alkaline rock-hosted REE deposits are in advanced stages of exploration, the only REE deposits that are actively mined at present are those on the Kola Peninsula in Russia.

6. Exploration

The REE deposits are spatially and genetically associated with alkaline igneous suites and thus exploration is targeting these rock types, which occur in continental anorogenic and within-plate tectonic settings and typically are along zones of rifting and/or faulting. In layered intrusions, the mineralization mostly appears in the more evolved parts of the complex. The elevated concentrations of the elements: REE, HFSE, U, Th, and F compared to regional background abundances are useful reconnaissance indicators for geochemical exploration (e.g., [3,7]). Other geologic exploration indicators are alteration halos and heavy minerals. The presence of abundant resistate REE-rich minerals in heavy mineral concentrates of stream sediments or soils is a useful exploration tool (e.g., [3,7]). These indicator minerals include zircon, monazite, and xenotime. Some alkaline igneous intrusions are surrounded by alteration halos due to the escape alkali-rich magmatic fluids into surrounding country rocks producing alkali metasomatism. This process converts the host rock minerals to an assemblage dominated by alkali-rich minerals, particularly albite.

Ground and airborne geophysical exploration methods are "standard" exploration tools for the REE deposits hosted in alkaline rocks. An enrichment of the deposits in U and Th, and hence their radioactivity, makes radiometric surveys very effective exploration methods. Many known REE deposits such as Bokan, Thor Lake, Kipawa, and Greenland were discovered during exploration for uranium deposits. In addition, magnetic and gravity surveys are also used to locate alkaline igneous complexes and their deposits.

7. Origin of Alkaline Rocks and REE Mineralization

Host nepheline syenites, syenites, and peralkaline granites are commonly considered to be generated by extensive fractional crystallization of alkaline basaltic magmas. In turn, these melts are usually assumed to be derived by a small degree of partial melting of lithospheric mantle metasomatically enriched in HFSE, REE, Th, U, and halogens rather than a primitive mantle source [14]. The high abundances of halogens indicate the presence of amphibole or phlogopite in the mantle source. Chakhmouradin and Zaitsev [4] infer that the bulk of the REE in the source was either in amphibole or in accessory minerals.

High concentrations of REE and associated metals in alkaline felsic rocks are partially due to prolonged fractional crystallization. These elements are strongly mantle-incompatible and thus are distinctly enriched in the residual melts during crystallization. Furthermore, the presence of volatiles, particularly fluorine, extends the range of crystallization to low temperatures [15] and suppresses crystallization of HFSE- and REE-bearing minerals until the last stages of crystallization when the magma becomes fluid-saturated and enriched in rare metals [16]. The rare metal mineralization in both nepheline syenites and peralkaline granites typically occurs in the highly evolved parts of the respective intrusions.

The origin of the REE mineralization in the alkaline rocks is still debated, in particular whether the mineralization is magmatic, hydrothermal, or a combination of both (e.g., [3,7]. However, more recent studies (e.g., [6,17,18]) imply that both magmatic and hydrothermal processes contributed to the origin of the REE deposits. The primary magmatic mineralization was overprinted by late magmatic to hydrothermal fluids rich in REE, HFSE, Th, and U that remobilized and enriched the original mineralization during multiple metasomatic events and re-deposited them as secondary phases (e.g., [6,7,19]). Large layered intrusions, such as Lovozero, which do not show any sign of crustal input, are also hydrothermally altered. This suggests that fluids are of an orthomagmatic origin and released during the last stages of magma evolution i.e., derived from the magma itself. Crustal-derived fluids could have played a role in some of the smaller layered intrusions. However, the relative contributions of both processes are variable. In some cases, where REE minerals-rich layers form part of cumulate sequences, magmatic processes might have been predominant, while in other examples, hydrothermal processes have played a more dominant role in the upgrading of initial magmatic concentrations.

8. Examples of REE Deposits in Alkaline Rocks

Several prominent deposits associated with alkaline rocks (Table 2; Figure 5) are briefly described below. They include deposits hosted by (a) nepheline syenites: Ilimaussaq (Greenland), Lovozero and Khibiny (Russia) and Thor Lake (Nechalacho; Northwest Territories, Canada), (b) peralkaline granites: Strange Lake (Quebec-Labrador, Canada) and Bokan Mountain (Alaska, USA), and (c) trachytic volcanic rocks: Toongi (Dubbo Zirconia) and Brockman (Hastings) both from Australia.

8.1. Ilimaussaq, Southern Greenland

The 1.13 Ga-old Ilimaussaq complex, which contains several economically exploitable deposits (Table 2) of REE, zirconium, niobium, and uranium, is one of the best-known alkaline intrusions in the world. It is the famous mineralogical locality of several minerals, which are unique to this intrusion. In addition, the complex is the type locality for 33 minerals including eudialyte, sodalite,

9 of 12

and arfvedsonite [20,21]. The ellipsoid-shaped layered complex is ~17 km in length and 8 km in width with an exposed vertical thickness of about 1700 m [20,21]. It is composed of nepheline syenites, syenites, and peralkaline granites that contain eudialyte-rich cumulate layers. The magmatic evolution of the complex ended with the emplacement of hydrothermal veins rich in Zr, U, and REE minerals. The main REE-bearing minerals of the complex are eudialyte, rinkite, and steenstrupine (Table 1). The complex was already explored for uranium in the 1950's to 1970's.

8.2. Lovozero and Khibiny, Russia

The ~370 Ma old Lovozero complex of the Kola Peninsula of Russia (Figure 5), which intruded into Precambrian rocks, is one of the largest alkaline layered intrusions in the world. It is an oval-shaped layered sheet-like lopolith, which extends over an area of about 650 km² and continues to a depth of several kilometers [22,23]. This complex, composed of various nepheline syenitic cumulates, is rich in REE, yttrium, zirconium, niobium, tantalum, and phosphorus, which occur in eudialyte, loparite, and apatite. Loparite has been mined for about 50 years with an annual production of ~30,000 tons of loparite concentrate containing about 34% REE [17].

The Khibina complex (Figure 5) is another nepheline syenitic cumulate intrusion that may be genetically related to the nearby Lovozero massif. It has a similar age and forms an elliptical-shaped ring complex, which is about 40 km long and covers an area of >1300 km². The complex hosts several nepheline-apatite deposits containing ~15 wt % P₂O₅ and 0.4 wt % oxides of rare earth elements [19]. The ore is typically made up of ~60–90% apatite and has been mined for phosphate over 80 years. The apatite was formed by accumulation during fractional crystallization of the magma.

8.3. Thor Lake (Nechalacho), Northwest Territories, Canada

This Early Proterozoic deposit, located ~100 km south of Yellowknife, along the southern margin of the Slave Province of the Canadian Shield, is hosted in a layered alkaline complex dated at ~ 2100 Ma, and it contains a variety of nepheline syenites. Many rocks have cumulate textures. The intrusion, which is only locally exposed on surface, was drilled over an area of ~5 km². The mineralization occurs primarily within two tabular cumulate zones about 15–60 m thick (Table 2). The primary ore minerals are zircon and eudialyte, which were subsequently pseudomorphed by orthomagmatic hydrothermal fluids. At present, the major ore minerals are zircon, fergusonite, allanite, synchysite, and bastnäsite [24].

8.4. Strange Lake, Eastern Canada

The Strange Lake deposit is hosted by a circular ring complex composed of peralkaline granites dated at 1240 Ma [25], and straddles the boundary between the Canadian Provinces of Quebec and Newfoundland and Labrador (Figure 5). The complex intrudes the Rae Province of the Canadian Shield. It is about 8 km in diameter and consists of three intrusive phases. There are two types (Table 2) of mineralization: (1) low-grade disseminated in granites of the intermediate intrusive phase and (2) high-grade mineralization hosted by pegmatites (the youngest phase). The dominant REE-bearing mineral is gittinsite, but other important minerals include bastnäsite, monazite, kainosite, thorite, pyrochlore, and gadolinite. Some of these minerals are of secondary origin as hydrothermal overprinting played a significant role during the formation of the ore [17].

8.5. Bokan Mountain, Alaska, USA

The Jurassic (177 Ma) Bokan Mountain complex, located at the southern part of the Prince of Wales Island (southeastern Alaska), is a circular intrusion of about 3 km in diameter. This concentrically zoned body consists of a core made up of arfvedsonite granite and an outer zone composed predominantly of aegirine granite. The major REE mineralization occur in clusters of subparallel mineralized dikes and metasomatically enriched alteration halos (albite rich) associated with shear zones [18,26]. The mineralized dikes occur both within the complex as well as in the surrounding Paleozoic granites.

The largest cluster is in a zone which is about 50 m wide and >2 km long. The REE-bearing minerals are xenotime, fergusonite, monazoite, bastnäsite, synchysite, zircon, immoriite, and kainosite and many of them are secondary occurring as replacements of pre-existing REE-bearing minerals by late-magmatic to post-magmatic fluids. The complex also hosts a U-Th deposit, which was intermittently mined between 1957 and 1971. The mine produced about 85,000 t of ore with a grade of ~1 wt % U₃O₈ and 3 wt % ThO₂. The main ore minerals are thorite and uraninite. The Th-U deposit is a mineralized pipe-shaped alteration zone which measures about 24 m in width. Both thorium-uranium and REE deposits are of magmato-hydrothermal origin where the primary magmatic mineralization was overprinted and upgraded by late-stage orthomagmatic hydrothermal fluids.

8.6. Toongi (Dubbo Zirconia), Australia

This deposit is located about 400 km NW of Sydney in New South Wales and is hosted by a nearly vertical trachyte plug ~900 m long and 600 m wide. The plug is a part of the Mesozoic alkaline intraplate volcanic complex ~15–20 km in diameter. It is composed of Jurassic (184 Ma) peralkaline trachyte with microphenocrysts of K-feldspar, plagioclase, and aegirine enclosed in a fine-grained matrix containing accessory ore minerals. The ore minerals are very fine grained (typically < 20 μ m) and include eudialyte (Zr, Y, HREE), niobite (Nb and Ta), and bastnäsite (REE), which are relatively uniformly dispersed throughout the plug [27,28]. Ore minerals are considered to represent primary interstitial phases which were subsequently enriched by late magmatic to hydrothermal fluids.

8.7. Brockman (Hastings), Australia

The Brockman (or Hastings) deposit is located ~18 km southeast of Hall Creek, Western Australia. The mineralization is hosted by fluorite-bearing felsic volcaniclastic rocks known as the "Niobium tuff" [29,30]. It is the lowermost unit of the early Proterozoic Brockman volcanic suite, a sequence composed of trachytic and rhyolitic lavas, volcaniclastic units, and subvolcanic intrusions. The "Niobium tuff" is 5 to 35 m thick and over 3.5 km long with volcanic detritus dated at ~1870 Ma [29,30]. The rock unit, which is distinctly enriched in HFSE and HREE, contains very fine grained (<20 μ m) and disseminated ore minerals including zircon, bastnäsite, parasite, and synchysite. Like in other REE deposits, the mineralization is considered to be the result of extensive fractional crystallization, where late-stage fluorine-rich fluids that enriched the rare metal concentrations have overprinted the primary ore minerals.

9. Conclusions

Alkaline igneous rocks are distinctly enriched in sodium and potassium and contain Na- and/or K-rich minerals such as feldspathoids, alkali pyroxenes, and alkali amphiboles. Some of these rocks are peralkaline, which have a higher molecular proportion of combined K and Na than Al, and can contain economically important mineralization of REE. These rocks occur in continental anorogenic or within-plate tectonic settings where they are related to rifting and/or extensional tectonics.

The mineralization is commonly related to the late stages of the magma evolution. The bulk of the REE occurs in ore minerals which locally show complex replacement textures. REE-bearing ore minerals include fluorocarbonates, phosphates, silicates, and oxides. The REE mineralization is typically accompanied by elevated concentrations of U and Th, which make gamma-ray (radiometric) surveys important exploration tools, but also represent a significant environmental challenge during exploitation of the deposits.

The host nepheline syenitic and peralkaline granitic rocks are typically formed by fractional crystallization from parent magmas that were in turn derived from a lithospheric mantle source metasomatically enriched in REE. The deposits typically represent two periods of mineralization. The first, primary magmatic period is associated with crystallization of highly fractionated magma rich in REE. The minerals of this period are commonly overprinted during the second period by late magmatic to hydrothermal fluids that remobilized and enriched the primary ore during multiple

metasomatic events. These deposits represent one of the most economically important resources of HREE and Y.

Acknowledgments: The research was supported by U.S. Geological Survey Mineral Resources External Research Program and the Natural Sciences and Engineering Research Council of Canada. Thanks are due to Daniel Müller and an anonymous referee for constructive reviews which improved the manuscript.

Conflicts of Interest: The author declares no conflict of interest.

References

- Long, K.R.; Van Gosen, B.S.; Foley, N.K.; Cordier, D. *The Principal Rare Earth Elements Deposits of the United States—A Summary of Domestic Deposits and A Global Perspective*; U.S. Geological Survey, Scientific Investigations Report 2010–5220; 2010; 96p. Available online: http://pubs.usgs.gov/sir/2010/5220/ (accessed on 24 July 2017).
- 2. Rudnick, R.L.; Gao, S. Composition of the continental crust. In *The Crust Treatise on Geochemistry*; Rudnick, R.L., Ed.; Elsevier: Amsterdam, The Netherlands, 2003; Volume 3, pp. 1–64.
- Richardson, D.G.; Birkett, T.C. Peralkaline rock-associated rare metals. In *The Geology of North America*; Eckstrand, O.R., Sinclair, W.D., Thorpe, R.I., Eds.; Geological Society of America: Boulder, CO, USA, 1996; Volume P-1, pp. 523–540.
- 4. Chakhmouradian, A.R.; Zaitsev, A.N. Rare earth mineralization in igneous rocks: Sources and processes. *Elements* **2012**, *8*, 347–353. [CrossRef]
- 5. Mariano, A.N.; Mariano, A., Jr. Rare earth elements: Rare earth mining and exploration in North America. *Elements* **2012**, *8*, 369–376. [CrossRef]
- 6. Dostal, J. Rare metal deposits associated with alkaline/peralkaline igneous rocks. *Rev. Econ. Geol.* **2016**, *18*, 33–54.
- Verplanck, P.L.; Van Gosen, B.S.; Seal, R.R.; McCafferty, A.E. A Deposit Model for Carbonatite and Alkaline Intrusion-Related Rare Earth Element Deposits; Scientific Investigations Report 2010-5070-J; U.S. Geological Survey: Reston, VA, USA, 2014; p. 58.
- 8. Förster, H.J.; Tischendorf, G.; Trumbull, R.B.; Gottesmann, B. Late-collisional granites in the Variscan Erzgebirge, Germany. J. Petrol. **1999**, 40, 1613–1645. [CrossRef]
- 9. Castor, S.B. The Mountain Pass rare-earth carbonatite and associated ultrapotassic rocks, California. *Can. Mineral.* **2008**, *46*, 779–806. [CrossRef]
- 10. Sun, S.S.; McDonough, W.F. Chemical and isotopic systematics of oceanic basalts: Implications for mantle composition and processes. *Geol. Soc. Lond. Spec. Publ.* **1989**, *42*, 313–345. [CrossRef]
- 11. Černy, P.; Ercit, T.S. Classification of granitic pegmatites revisited. *Can. Mineral.* **2005**, *43*, 2005–2026. [CrossRef]
- 12. Hatch, G.P. TMR Advanced Rare-Earth Projects Index. Technology Metal Research. October 2012. Available online: http://www.techmetalsresearch.com/metrics-indices/tmr-advanced-rare-earth-projects-index/ (accessed on 24 July 2017).
- 13. Hatch, G.P. TMR Advanced Rare-Earth Projects Index. Technology Metal Research. March 2014. Available online: http://www.techmetalsresearch.com/metrics-indices/tmr-advanced-rare-earth-projects-index/ (accessed on 24 July 2017).
- 14. Pilet, S.; Baker, M.B.; Stolper, E.M. Metasomatized lithosphere and the origin of alkaline lavas. *Science* **2008**, 320, 916–919. [CrossRef] [PubMed]
- 15. Markl, G.; Marks, M.; Schwinn, G.; Sommer, H. Phase equilibrium constraints on intensive crystallization parameters of the Ilmaussaq Complex, South Greenland. *J. Petrol.* **2001**, *42*, 2231–2258. [CrossRef]
- 16. Halter, W.; Webster, J.D. The magmatic to hydrothermal transition and its bearing on ore-forming systems. *Chem. Geol.* **2004**, *210*, 1–6. [CrossRef]
- Salvi, S.; Williams-Jones, A.E. Alkaline granite-syenite deposits. In *Rare-Element Geochemistry and Mineral Deposits*; Linnen, R.L., Samson, I.M., Eds.; Short Course Notes; Geological Association of Canada: St. John's, NL, Canada, 2005; Volume 17, pp. 315–341.

- Dostal, J.; Kontak, D.J.; Karl, S.M. The Early Jurassic Bokan Mountain peralkaline granitic complex (southeastern Alaska): Geochemistry, petrogenesis and rare-metal mineralization. *Lithos* 2014, 202–203, 395–412. [CrossRef]
- 19. Linnen, R.L.; Samson, I.M.; Williams-Jones, A.E.; Chakhmouradian, A.R. Geochemistry of the rare-earth element, Nb, Ta, Hf and Zr deposits. *Treatise on Geochem.* **2014**, *13*, 543–568.
- Sørensen, H. Brief introduction to the geology of the Ilímaussaq alkaline complex, South Greenland, and its exploration history. In *The Ilímaussaq Alkaline Complex, South Greenland: Status of Mineralogical Research with New Results*; Sørensen, H., Ed.; Geology of Greenland Survey Bulletin (190); GEUS: Copenhagen, Denmark, 2001; pp. 7–23.
- 21. Sørenson, H. *The Ilimaussaq alkaline Complex, South Greenland—An Overview of 200 Years of Research and an Outlook;* Museum Tusculanum Press: Copenhagen, Denmark, 2006.
- 22. Kogarko, L.N.; Lahaye, Y.; Brey, G.P. Plume-related mantle source of super-large rare metal deposits from the Lovozero and Khibina massifs on the Kola Peninsula, Eastern part of Baltic Shield: Sr, Nd and Hf isotopic systematics. *Mineral. Petrol.* **2010**, *98*, 197–208. [CrossRef]
- 23. Kogarko, L.N.; Williams, C.T.; Woolley, A.R. Chemical evolution and petrogenetic implications of loparite in layered, agpaitic Lovozero complex, Kola Peninsula, Russia. *Mineral. Petrol.* **2002**, *74*, 1–24.
- 24. Sheard, E.R.; Williams-Jones, A.E.; Heoligmann, M.; Pederson, C.; Trueman, D.L. Controls on the concentration of zirconium, niobium, and the rare earth elements in the Thor Lake Rare metal deposit, Northwest Territories, Canada. *Econ. Geol.* **2012**, *107*, 81–104. [CrossRef]
- 25. Miller, R.R.; Heaman, L.M.; Birkett, T.C. U-Pb zircon age of the Strange Lake peralkaline complex: Implications for Mesoproterozoic peralkaline magmatism in north-central Labrador. *Precambr. Res.* **1997**, *81*, 67–82. [CrossRef]
- 26. Dostal, J.; Karl, S.M.; Keppie, J.D.; Kontak, D.J.; Shellnutt, J.G. Bokan Mountain peralkaline granitic complex, Alexander terrane (southeastern Alaska): Evidence for Early Jurassic rifting prior to accretion with North America. *Can. J. Earth Sci.* **2013**, *50*, 678–691. [CrossRef]
- Chalmers, I. The Toongi Rare Metal and Rare Earth Deposit-Dubbo Zirconia Project. In Proceedings of 34th International Geological Congress, Brisbane, Australia, 5–10 August 2012; Available online: http://alkaneresources.com.au/pdf/presentations/20120808.pdf (accessed on 24 July 2017).
- Spandler, C.; Morris, C. Geology and genesis of the Toongi rare metal (Zr, Hf, Ta, Y, and REE) deposit, NSW Australia and implication for rare metal mineralization in peralkaline igneous rocks. *Contrib. Mineral. Petrol.* 2016, 171, 104–128. [CrossRef]
- Taylor, W.R.; Esslemont, G.; Sun, S.S. Geology of the volcanic-hosted Brockman rare-metals deposit, Halls Cree Mobile Zone, northwest Australia. II. Geochemistry and petrogenesis of the Brockman volcanics. *Mineral. Petrol.* 1995, 52, 231–255. [CrossRef]
- Taylor, W.R.; Page, R.W.; Esslemont, G.; Rock, N.M.S.; Chalmers, D.I. Geology of the volcanic-hosted Brockman rare-metals deposit, Halls Cree Mobile Zone, northwest Australia. I. Volcanic environment, geochronology and petrography the Brockman volcanics. *Mineral. Petrol.* 1995, 52, 209–230. [CrossRef]



© 2017 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).