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13.21 Geochemistry of the Rare-Earth Element, Nb, Ta, Hf, and Zr Deposits

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13.21.1 Introduction

Rare-element mineral deposits, also called rare-metal deposits, contain economic concentrations of lithophile elements. There is no strict definition on what elements constitute these deposits. Some publications include alkaline and alkaline earth elements such as Li, Rb, Cs, and Be, and the metals Sc, Sn, and W as rare elements, but this chapter is restricted to Y, the rare-earth elements (REE, La to Lu), Zr, Hf, Nb, and Ta. The rare

elements are not particularly rare, but one feature that they share is that they can be difficult to separate (i.e., separate individual REE, Hf from Zr and Ta from Nb). The estimated abundances of Zr, Hf, Nb, and Ta in the upper continental crust are 193, 5.3, 12, and 0.9 ppm, respectively, which is slightly higher than in the bulk continental crust, 132, 3.7, 8, and 0.7 ppm, respectively (See [Chapter 4.1](#)). These concentrations are much higher than those estimated for the primitive mantle, 10.8 ppm Zr, 0.300 ppm Hf, 0.588 ppm Nb, and

0.040 ppm Ta (see Chapter 3.1). For comparison, the concentration of Cu in the upper continental crust and in primitive mantle is 28 and 20 ppm, respectively (See Chapter 3.1). The distribution of REE is similar. In the upper continental crust, the concentrations of Y and two of the light REE (LREE), La and Ce, are 21, 31, and 63 ppm, respectively, whereas their concentrations in the bulk continental crust are 19, 20, and 43 ppm, respectively, and in the primitive mantle are 4.37, 0.686, and 1.786 ppm, respectively (See Chapter 3.1). The abundance of REE decreases with increasing atomic number (following the saw-toothed Oddo–Harkins rule, see below) and the heavy REE (HREE), for example Yb and Lu, have concentrations of 1.96 and 0.31 ppm, respectively, in the upper continental crust, 1.9 and 0.3 ppm, respectively, in the bulk crust, and 0.462 and 0.071 ppm, respectively, in primitive mantle (See Chapter 3.1). Typical ore grades for these elements range from several hundred parts per million in the case of Ta to a few weight percent in the case of Zr, Nb, and REE (commonly reported as total rare-earth oxide, TREO). Thus, the enrichment factors from primitive mantle to ore deposit range from ~1000 for Zr to 50 000 for Nb.

All of the rare elements considered here share several characteristics. In igneous environments, they are generally incompatible (partition to the melt over minerals) and are typically concentrated in accessory phases. Consequently, these elements are enriched in melts that result either from very low degrees of partial melting or from extreme fractionation. This includes carbonatites, peralkaline granites and silica-undersaturated rocks, and peraluminous granites and pegmatites. The above behavior also explains why these elements are enriched in the crust. Figure 1 shows the abundance of the REE in primitive mantle, bulk continental crust, and upper continental crust normalized to CI chondrite. Primitive mantle shows a flat profile, with values of approximately two. The strong incompatible behavior of the LREE (La to Eu) compared to HREE (Gd to Lu) is clearly visible for the continental crust, as is the enrichment of Zr–Hf and Nb–Ta.

As a group, the rare elements are relatively insoluble in most aqueous fluids and are commonly used as immobile elements in calculations designed to estimate mass changes of

elements in hydrothermally altered rocks. However, there is also abundant evidence that the rare elements are mobile in fluids with specific ‘hard’ ligands and one of the challenges in understanding rare-element deposits is being able to identify magmatic and metasomatic processes and evaluate their relative importance as ore-forming processes.

13.21.1.1 Uses of Rare Elements

Rare elements are becoming increasingly important to society. LREE are used in the petroleum refining industry as cracking catalysts, to transform heavy molecules into refined diesel fuel and gasoline. They are also essential in the catalytic converters of automobiles; Ce carbonate and Ce oxide are used to convert pollutants in exhaust gases. Neodymium is used in high-strength permanent magnets that have applications in ‘green technologies’ such as hybrid cars and wind turbines. Because of their high strength at small size, they are used in electronic goods such as high performance speakers, hard disks, and DVD-drives. Combined, these uses account for roughly 20% of REE consumption by volume. The next 40% is in metal alloys, polishing, and glass. The metal alloys generally use Nd and Pr for ignition devices, but LREE and Y are also components in superalloys used in applications at high temperature, oxidizing environments such as gas turbine engines. Europium, Y, Tb, and Ce are used as phosphors in televisions and computer screens, and Nd, Er, and other REE are used in various laser and fiber-optic applications. The glass and ceramic industries use Ce to oxidize Fe and Nd, Pr, Ho, and Er to color glass. Other uses of REE are to absorb UV light, as a polishing agent, and in ceramic capacitors. There are a variety of other specialty applications and new uses of REE are continually being developed.

Niobium is dominantly used to produce the ferroniobium that is used in high-strength low alloy (HSLA) steel (89% of the use in 2010). The light weight and high strength of HSLA steel make it suitable for use in vehicle bodies, ship hulls, railway tracks, and oil and gas pipelines. Niobium-bearing chemicals are used for surface acoustic wave filters, camera lenses, coating on glass for computer screens, and ceramic capacitors. Niobium carbide is used for cutting tools, and Nb metal and alloys have various specialty applications.

The primary use of Ta is in capacitors, particularly for wireless devices and touch screen technologies. It is also added to superalloys, because of its resistance to high temperature and corrosion, and is used in high-temperature turbines. Tantalum is biocompatible with human tissue and thus is used in prosthetic joints and pacemakers. Other applications are similar to those of Nb, for example, in surface acoustic wave filters and in carbides for cutting tools.

There is less information on the end-uses of Zr and Hf than for the other rare elements. In 2010, zircon was used for ceramics, zirconia and chemicals, refractory and foundry, and casting (*USGS 2010 Minerals Yearbook*). Yttria-stabilized zirconia is also used in oxygen sensors, which are employed to control combustion in automobile engines and furnaces. Both Zr and Hf have important applications in nuclear reactors. Zirconium has a very low thermal neutron capture cross section and is used as cladding for nuclear fuel rod tubes, whereas Hf has a very high neutron capture cross section and is therefore used in nuclear control rods.

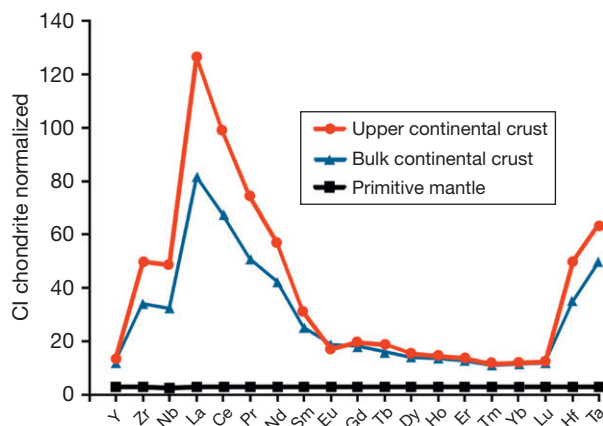


Figure 1 Distribution of rare elements in the continental crust and mantle, normalized to CI chondrite using the data of.

13.21.1.2 Rare-Element Mineralogy

Despite the generally low abundances of rare elements in crustal and mantle rocks, minerals that contain these elements as essential components make up approximately 12% of the total number of mineral species known to date, although only a small fraction has been used, or may potentially be used, for the extraction of rare elements (Table 1). The bulk of global LREE (La to Eu) production (70–80%) comes from bastnäsite-(Ce); monazite-(Ce) is another important LREE mineral, whereas xenotime-(Y) and ion-adsorption clays (see below) are the primary source of HREE (Gd to Lu). Pyrochlore and zircon account for over 90% of the Nb and Zr production, respectively. Intermediate members of the complex ferrocolumbite–manganotantalite series (colloquially known as ‘coltan’) are the major source of Ta, although it is difficult to estimate their exact share of the market because they are typically accompanied by a variety of other Ta ore minerals, the most common of which are wodginite, microlite, and tapiolite (Table 1). Altogether, rare elements are produced from fewer than 30 minerals, whereas the amenability of other potential ore types to extraction of these elements on a commercial scale remains to be demonstrated. For example, igneous apatite from peralkaline rocks, carbonatites, phoscorites, Kiruna-type, and other Fe-REE-rich ores commonly contain in the order of $n \times 10^3$ – 10^4 ppm REE substituting for Ca (values in excess of 18 wt% TREO have been reported; Roeder et al., 1987). Although extraction of REE from apatite is technologically feasible, particularly where large quantities of this mineral are mined and processed for phosphate using nitric digestion (e.g., at Khibiny in Russia: Samonov, 2008), none of these extraction technologies have been implemented industrially thus far. In addition to processing problems, the industrial value of some ore minerals listed in Table 1 is compromised by their rare occurrence in tonnages amenable to mechanized mining, or by the appreciable levels of radioactive or toxic elements in their composition (e.g., Th and U in monazite, Th in loparite, and Sb in stibiotantalite).

Of great importance to mineral exploration is the relative abundance of individual REE in the ore. Depending on such structural constraints as cation coordination and the relative availability of specific REE in the crystallization environment, different minerals and even samples of the same mineral from different deposits may vary significantly in their REE distribution patterns (Figure 2). Given that the price of individual REE per kilogram varies by two orders of magnitude, these geochemical variations affect the potential commercial value of a rare-earth resource.

In addition to the minerals listed in Table 1, REE, Nb, and Ta can be extracted from other minerals containing minor concentrations of these elements either substituting in the crystal lattice (e.g., $2\text{Ca}^{2+} \rightleftharpoons \text{REE}^{3+} + \text{Na}^+$, $3\text{Sn}^{4+} \rightleftharpoons 2\text{Ta}^{5+} + \text{Fe}^{2+}$, etc.) or bound to these phases in some other form. For example, a portion of the global Ta and Nb production comes from placer and bedrock deposits of Ta–Nb-bearing cassiterite (up to 8 wt% Ta_2O_5 and 3 wt% Nb_2O_5 ; Belkasmı et al., 2000) associated with rare-metal granites, pegmatites, and greisens (e.g., in the southeast Asian tin belt). Niobium and Ta in these deposits are also derived from oxide inclusions in cassiterite, for example, columbite–tantalite, ilmenorutile, and struverite.

Hafnium substitutes for Zr to a variable degree in all Zr minerals. The highest levels are in zircon from rare-element-enriched peraluminous leucogranites and LCT-type pegmatites (spanning almost the entire ZrSiO_4 – HfSiO_4 series), but because of their negligible modal abundances, neither Hf-rich zircon nor hafnon (HfSiO_4) in granitic rocks has any commercial value. Both Hf and Zr are extracted primarily from placer zircon, containing, on average, 1.3 wt% HfO_2 ($\text{Zr}/\text{Hf} = 44$). One notable exception is zircon from beach deposits in India, which is relatively depleted in Hf ($\leq 0.8 \text{ HfO}_2$ at $\text{Zr}/\text{Hf} > 70$; Angusamy et al., 2004). Baddeleyite is a minor source of ZrO_2 , and currently is extracted only from phoscorites at Kovdor, although the Phalaborwa in South Africa has produced baddeleyite in the past (Gambogi, 2010). Other notable occurrences of this mineral of potential economic interest are laterite at Poços de Caldas, metasomatized dolomite in the exocontact of the Ingili ijolite–melteigite intrusion, and phoscorites at Vuorijärvi. Regardless of origin, the proportion of Hf and other substituent elements in baddeleyite is typically low ($< 3 \text{ wt}\% \text{ HfO}_2$); the highest Hf, Nb, and Ta contents (Table 1) have been reported in samples from carbonatites.

Owing to their structural flexibility, most minerals concentrating rare elements exhibit wide compositional variations (Table 1), ranging in scale from submicroscopic zones in individual crystals to rock units in a series of genetically related intrusions. Figure 3 shows examples of compositional variation in columbite–tantalite and Figure 4, in pyrochlore. Relationships among the chemical evolutionary trends exhibited by rare-element minerals and various petrogenetic processes have been explored in a large number of studies (e.g., Chakhmouradian and Williams, 2004; Selway et al., 2005; Smith et al., 2000; Van Lichtenvelde et al., 2007), but there have been relatively few attempts to link the data to economically significant parameters (such as ore grade and distribution, recovery efficiency, and radioactivity).

13.21.2 Geochemistry of Rare Elements

With the exception of Ce and Eu, the REE (i.e., the lanthanides and the group 3b elements, Sc, and Y) have a 3+ valence in most environments. Cerium can also be in the 4+ state and Eu in the 2+ state. Zirconium and Hf are tetravalent (4+), and Nb and Ta are pentavalent (5+). Such high valences combined with moderate ionic radii of between 64 and 125 pm ($100 \text{ pm} = 1 \text{ Å}$) in six- or eightfold coordination (Shannon, 1976) result in these elements having high ionic potentials (field strengths) and therefore they are referred to as high field strength elements (HFSE). The differences in charge and size between these elements and the more abundant elements (Si, Al, K, Na, Fe, Mg, etc.) mean that they do not readily substitute into the structures of the common rock-forming silicates and thus behave incompatibly. They are also regarded as being ‘hard’ cations (high charge/radius ratio) in hydrothermal fluids and therefore complex with ‘hard’ anions.

Zirconium and Hf have the same valence (4+), and to all intents and purposes, the same ionic radii (86 vs. 85 pm, respectively, in sixfold coordination), and therefore behave in a very similar manner. Similarly Nb^{5+} and Ta^{5+} both have an ionic radius of 78 pm in sixfold coordination. By contrast, the

Table 1 Major rare-element minerals^a

<i>Mineral^b</i>	<i>Formula^c</i>	<i>Rare element (wt% range or max. content)</i>	<i>Major deposit type(s)^d</i>	<i>Localities: key examples (past, present, and potential producers)</i>
Bastnäsite	LREECO ₃ (F,OH)	53–79 ΣREE ₂ O ₃	Carbonatites and associate metasomatic rocks, altered peralkaline feldspathoid rocks	Mountain Pass ^U , Bayan Obo ^{Ch} , Weishan ^{Ch} , Maoniuping ^{Ch} , Nechalacho ^{Ca}
Parisite	CaLREE ₂ (CO ₃) ₃ (F,OH) ₂	58–63 ΣREE ₂ O ₃	Carbonatites and associate metasomatic rocks, hydrothermal deposits	Mountain Pass ^U , Bayan Obo ^{Ch} , Weishan ^{Ch} , Snowbird ^U
Synchysite	CaREE(CO ₃) ₂ (F,OH)	48–52 ΣREE ₂ O ₃	Carbonatites and associate metasomatic rocks, altered peralkaline feldspathoid and granites	Barra do Itapirapua ^B , Lugiin Gol ^M , Ak-Tyuz ^K , Nechalacho ^{Ca}
Monazite	(LREE,Th,Ca)(P,Si)O ₄	38–71 wt% ΣREE ₂ O ₃	Carbonatites and associate metasomatic rocks P-rich nelsonite, weathering crusts; placers	Mountain Pass ^U , Bayan Obo ^{Ch} , Eneabba ^A , Mt Mount Weld and WIM 150 ^A , Kangankunde ^{Ma} , Tomtor ^R , Steenkampskraal ^{SA} , Manavalakurichi ^I
Xenotime	(HREE,Zr,U)(P,Si)O ₄	43–65 ΣREE ₂ O ₃	Carbonatites and associate metasomatic rocks, weathering crusts, placers	Lofdal ^N , Ak-Tyuz ^K , Pitinga ^B , Tomtor ^R , Mt Weld and WIM 150 ^A , Kinta and Selangor ^{Ms}
Churchite	HREEPO ₄ ·2H ₂ O	43–56 ΣREE ₂ O ₃	Weathering crusts	Chuktukon ^R , Mt Weld ^A
Gadolinite	REE ₂ FeBe ₂ Si ₂ O ₁₀	45–54 ΣREE ₂ O ₃	Granitic pegmatites	Ytterby ^S , Strange Lake ^{Ca} , Barringer Hill ^U
Rutile	(Ti,Nb,Ta,Fe,Sn)O ₂	≤56 Ta ₂ O ₅ , ≤34 Nb ₂ O ₅ , ≤7 SnO ₂	Carbonate metasomatic rocks, granitic pegmatites, placers, weathering crusts	Bayan Obo ^{Ch} , Greenbushes ^A , Kinta Valley ^{Ms} , Morro dos Seis Lagos, and Borborema ^B
Loparite	(Na,REE,Ca,Sr,Th) (Ti,Nb,Ta)O ₃	28–38 ΣREE ₂ O ₃ , ≤20 Nb ₂ O ₅ , ≤1 Ta ₂ O ₅	Peralkaline feldspathoidal rocks	Karnasurt and Umbozero ^R
Fergusonite	REENbO ₄	43–57 ΣREE ₂ O ₃ , 40–55 Nb ₂ O ₅ , ≤0.8 Ta ₂ O ₅	Metasomatic carbonate and peralkaline feldspathoid rocks, granitic pegmatites	Bayan Obo ^{Ch} , Barringer Hill ^U , Nechalacho ^C
Columbite–tantalite	(Fe,Mn,Mg)(Nb,Ta,Ti) ₂ O ₆	≤72 Nb ₂ O ₅ , ≤85 Ta ₂ O ₅	Carbonatites and associate metasomatic rocks, granites, and granitic pegmatites, placers	Blue River ^{Ca} , Bayan Obo ^{Ch} , Greenbushes and Wodgina ^A , Koktokay and Yichun ^{Ch} , Pitinga and Mibra ^B , Kenticha ^E , Marropino ^{Mz} , Nord-Kivu and Sud-Kivu ^{DRC}
Tapiolite	(Fe,Mn)(Ta,Nb) ₂ O ₆	72–86 Ta ₂ O ₅ , ≤9 Nb ₂ O ₅	Granitic pegmatites	Tanco ^{Ca} , Greenbushes ^A
Wodginite	(Mn,Fe)(Sn,Ti)(Ta,Nb) ₂ O ₈	56–85 Ta ₂ O ₅ , ≤15 Nb ₂ O ₅ , 3–18 SnO ₂	Granitic pegmatites	Tanco ^{Ca} , Greenbushes, and Wodgina ^A
Ixiolite	(Ta,Nb,Mn,Fe,Sn,Ti) ₄ O ₈	70 Ta ₂ O ₅ , ≤72 Nb ₂ O ₅ , ≤20 SnO ₂	Granitic pegmatites	Tanco ^{Ca} , Borborema ^B

(Continued)

Table 1 (Continued)

<i>Mineral^b</i>	<i>Formula^c</i>	<i>Rare element (wt% range or max. content)</i>	<i>Major deposit type(s)^d</i>	<i>Localities: key examples (past, present, and potential producers)</i>
Pyrochlore	(Ca,Na,Sr,Ba,Pb,K,U) _{2-x} (Nb,Ti,Ta,Zr,Fe) ₂ O ₆ (F,OH) _{1-y} · nH ₂ O	29–77 Nb ₂ O ₅ , ≤16 Ta ₂ O ₅ , ≤22 wt% REE ₂ O ₃	Carbonatites and associated phoscorites Peralkaline granites and associated Pegmatites, fenites, weathering crusts	Barreiro and Catalão I and II ^B , Oka, Niobec and Strange Lake ^{Ca} , Tomtor, Chuktukon, Tatarskoye, Bol'shetagninskoye and Belaya Zima ^R , Lueshe and Nord-Kivu ^{DRC} , Pitinga ^B Tanco ^{Ca} , Greenbushes ^A , Koktokay and Yichun ^{Ch}
Microlite	(Ca,Na,Pb,U,Sb,Bi) _{2-x} (Nb,Ta,Ti) ₂ O ₆ (OH,F) _{1-y}	46–81 Ta ₂ O ₅ , ≤20 Nb ₂ O ₅ , ≤9 SnO ₂	Granites and granitic pegmatites	
Baddeleyite	(Zr,Hf,Nb,Fe)O ₂	88–99 ZrO ₂ , ≤4.8 HfO ₂ , ≤6.5 Nb ₂ O ₅	Phoscorites, altered peralkaline feldspathoid syenites, carbonate metasomatic rocks, placers	Kovdor and Algama ^R , Palabora ^{SA} , Poços de Caldas ^B
Zircon	(Zr,Hf,HREE,Th,U) (Si,P)O ₄	64–67 ZrO ₂ , ≤1.5 HfO ₂ , ≤19 ΣREE ₂ O ₃	Placers; peralkaline, feldspathoid syenites (including altered varieties)	Jacinth-Ambrosia and Eneabba ^A , Richards Bay ^{SA} , Manavalakurichi and Chavara ^I , Poços de Caldas ^B , Nechalacho ^{Ca}

^aThis table does not include minerals that may contain appreciable levels of rare elements, but their presence is not essential (e.g., REE in apatite, or Ta in cassiterite). Also omitted are minerals, whose industrial potential as a rare-element resource is yet to be demonstrated. These include (in alphabetical order): allanite (REE), britholite (REE), eudialyte (Zr, REE, Nb), gagarinite (REE), gerenite (REE), gittinsite (Zr), kainosite (REE), mosandrite (REE), steenstrupine (REE, Zr, U), vlasovite (Zr).

^bThe majority of minerals listed in this table are members of multicomponent solid solutions; for example, the columbite–tantalite series incorporates columbite-(Fe), columbite-(Mn), tantalite-(Mn) and a few other, less common end-members. For simplicity, their names are given here as these minerals have been historically referred to in the geological literature and exploration reports. For recent modifications to the mineralogical terminology and nomenclature, interested readers are referred to online publications of the International Commission on New Minerals, Nomenclature, and Classification.

^cREE = lanthanides + Y; LREE = light lanthanides; HREE = heavy lanthanides. The general symbol REE is used for minerals that can incorporate appreciable levels of both LREE and HREE, and are known to occur in industrially viable concentrations. Only element concentrations relevant to commercially exploitable resources are listed; the actual compositional variation of some of these minerals is more extensive than shown.

^dListed here are only those types of mineral deposits that do or may potentially represent some economic interest. Country abbreviations are ^AAustralia, ^BBrazil, ^{Ca}Canada, ^{Ch}China, ^{DRC}Democratic Republic of the Congo, ^EEthiopia, ^IIndia, ^KKyrgyzstan,

^MMongolia, ^{Ma}Malawi, ^{Ms}Malaysia, ^{Mz}Mozambique, ^NNamibia, ^RRussia, ^SSweden, ^UUSA.

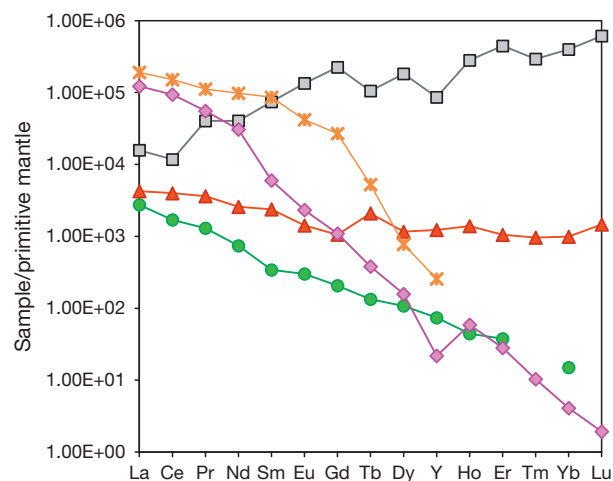


Figure 2 Chondrite-normalized REE distribution patterns for selected minerals, including monazite from Lofdal (brown asterisks; Wall et al., 2008), xenotime from Tomtor (gray squares; Tolstov and Tyan, 1999), eudialyte from Lovozero (red triangles; Samonov, 2008), fluorapatite from Khibiny (green circles; Samonov, 2008), and loparite from Lovozero (purple diamonds, unpublished data).

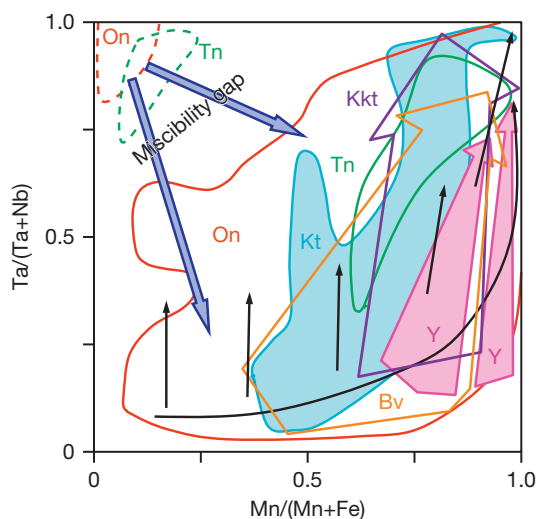


Figure 3 Variations in columbite-tantalite compositions from Beauvoir (Bv) and Yichun (Y) (Belkamsi et al., 2000), Kenticha (Kt) (Tadesse and Zerihun, 1996), Koktokay (Kkt) (Zhang et al., 2004), Ontario (On) (Selway et al., 2005), and Tanco (Tn) (Van Lichtervelde et al., 2006). The evolutionary trends for individual pegmatites are shown as thin black arrows (Ontario) or block arrows (other deposits), and compositional changes owing to wall-rock contamination are indicated by blue arrows.

REE show systematic changes in their behavior (e.g., in their partitioning and complexation), dominantly due to a systematic decrease in ionic radius with increasing atomic number. In sixfold coordination, their ionic radii range from 117 pm (La) to 100 pm (Lu); Y has the same ionic radius as Ho (104 pm). Thus, the LREE are generally less compatible than the HREE in common rock-forming minerals.

Elements with even atomic numbers have higher cosmic (and terrestrial) abundances than elements with odd atomic

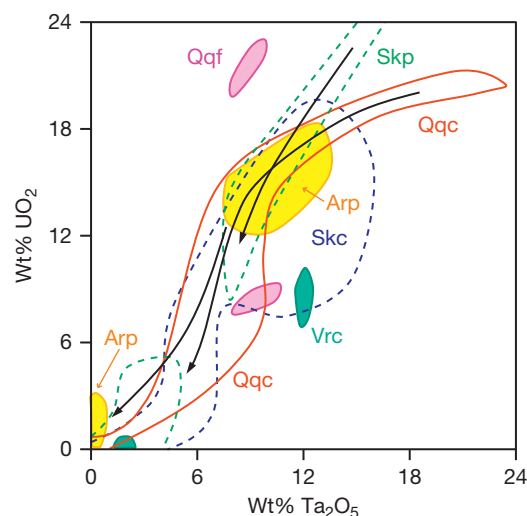


Figure 4 Variations in pyrochlore compositions from Arbarastakh (Arp) (Tolstov et al., 1995), Qaqarsuk (Qqc-carbonatite and Qqf-fenite) (Knudsen, 1989), Sokli (Skc-carbonatite and Skp-phoscorite) (Lee et al., 2006), and Verity (Vrc) (Simandl et al., 2001).

numbers. This is due to the greater stability of nuclei with an even number of protons, referred to as the Oddo-Harkins effect. A consequence of this is that a saw-tooth pattern is evident in graphical representations of the natural abundances of any sequence of elements ordered by atomic number. In order to eliminate this effect, the abundance of each element is generally normalized to its concentration in a well-characterized reservoir. The choice of reservoir depends on the processes that are of interest. Commonly employed normalization reservoirs include chondritic meteorites, primitive mantle, and continental crust (See Chapters 3.1 and 4.1).

In some geological environments, Ce and Eu can have valences of 4+ and 2+, respectively, which may lead to anomalous behavior for these two elements relative to the other REE. These differences can cause the development of Ce and Eu anomalies, which are defined as the difference between the actual normalized concentration of these elements and their concentration estimated by interpolation between La and Pr, or between Sm and Gd, respectively. Such anomalies tend to develop where Eu^{2+} or Ce^{4+} represents a significant proportion of the total Eu or Ce in a fluid or magma, and, due to their valence and size, these elements are incorporated into fractionating minerals that cannot accommodate significant amounts of the trivalent REE. A good example of this is the incorporation of divalent Eu into Ca-rich minerals, like calcic plagioclase. As Eu^{2+} has the same charge as Ca (2+) and a similar radius (121 vs. 126 pm), it can readily substitute for Ca^{2+} . Consequently, if conditions in a magma favor the presence of a significant proportion of Eu^{2+} (low $f\text{O}_2$), fractional crystallization of calcic plagioclase will leave the residual magma depleted in Eu, and produce a negative Eu anomaly. Conversely, dissolution of primary Eu-enriched minerals may lead to enrichment of Eu (positive anomalies) in a fluid. The $\text{Eu}^{2+}/\text{Eu}^{3+}$ and $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratios in a fluid or magma are a function of redox conditions and/or temperature (cf. Sverjensky, 1984; Wood, 1990b).

13.21.2.1 Magmatic Behavior and Processes

13.21.2.1.1 Concentrations of rare elements in magmatic rocks

An explanation of the distribution of REE and HFSE in all magmatic systems is beyond the scope of this chapter, but their concentrations in normal mid-ocean ridge basalt (N-MORB) are low, <10 ppm except for Y and Zr (<100 ppm). One of the characteristics of ocean island basalt (OIB) is that the concentrations of rare elements are elevated relative to N-MORB. For example, a typical OIB contains 280 ppm Zr, 48 ppm Nb, and REE abundances that range from 80 to 0.3 ppm (Hollings and Wyman, 2005). However, ore deposits are not directly associated with these rocks, but rather are associated with carbonatites, peralkaline granites and feldspathoid-bearing rocks, or peraluminous granites and pegmatites. Rare-element pegmatites have long been recognized as having two characteristic suites of rare elements. The classification by Černý and Ercit (2005) recognizes LCT (Li–Cs–Ta), NYF (Nb–Y–F), and mixed families of pegmatites. The former are also enriched in Rb, Be, Sn, B, P, and F and the latter are characterized by elevated concentrations of Be, REE, Sc, Ti, Zr, Th, and U. Linnen and Cuney (2005) correlated these pegmatite families broadly with different suites of granites. Peralkaline rare-element granites have an NYF affinity, whereas peraluminous rare-element granites have an LCT affinity. One feature of note is that both suites are enriched in fluxing elements, particularly F.

Carbonatites are well known for LREE enrichment. A typical carbonatite can have La and Ce concentrations of >1000 × chondrite (i.e., >1000 ppm), whereas Yb can be as low as 2 × chondrite in this rock type (<1 ppm, Barker, 1996). Niobium and Zr contents are typically several hundred parts per million, whereas Ta and Hf are generally <10 ppm (Chakhmouradian, 2006). A more enriched trace-element signature is observed for the peralkaline granites. The REE concentrations range from several hundred to 1000 ppm La to 50–100 ppm Yb, ~1000 ppm Nb, several thousand ppm Zr (locally >1 wt%), and <100 ppm Ta and Hf (although both can be >300 ppm; Linnen and Cuney, 2005). This is in strong contrast to the trace-element compositions of peraluminous granites, and in particular high phosphorus granites, which have very low REE contents (e.g., many high-phosphorus Hercynian granites in Western Europe have Ce contents at or below 1 ppm; Linnen and Cuney, 2005). Niobium and Zr concentrations are also much lower in peraluminous granites, ~100 ppm and <50 ppm, respectively. By contrast, Ta is enriched in peraluminous granites, locally with values of >100 ppm, and Hf is typically present in concentrations of a few parts per million (Linnen and Cuney, 2005).

13.21.2.1.2 Partial melting and fractional crystallization

The concentrations of rare elements in magmatic systems are a function of both partial melting and fractional crystallization. In large part the trace-element signatures reflect the source and tectonic setting. Exploitable or potentially exploitable deposits of the REE, Nb, and Zr are spatially and genetically associated with alkaline to peralkaline or ultra-alkaline intrusive igneous rocks and carbonatites, and occur in regions of subcontinental epeirogenic mantle uplift. In many cases, the uplift leads to

rifting. However, the onset of magmatism is commonly earlier, and in some cases, there is no clear evidence of rifting (Le Bas, 1987). Thus, although many rare-element deposits occur in continental rifts, this is not true for all of them, as shown by the deposits of the Kola peninsula, for example, Lovozero and Khibiny, which occur in a region of epeirogenic uplift marked by cross-cutting lineaments, but do not occupy an identifiable rift or rifts. Alkaline to peralkaline or ultra-alkaline igneous rocks can also form in oceanic crust, for example, the Cape Verde province, but to the best of our knowledge there are no examples of exploitable or potentially exploitable rare-element deposits in oceanic crust.

Martin and De Vito (2005) proposed that metasomatism in rift environments, if H₂O-rich, will generate A-type granites (NYF affinity), whereas, if metasomatism involves CO₂-rich fluids, carbonatitic and nephelinitic melts will result. For mantle sources, garnet and perovskite, where stable, likely control the Zr and Hf contents of the partial melts (Dalou et al., 2009). The main reservoirs of the REE are also garnet and perovskite, but it is important to note that, as pressure increases, garnet composition changes, and consequently the partitioning also changes. There is less agreement on the behavior of Nb and Ta. It is well known that Nb and Ta partition into rutile; however, rutile solubility in basaltic melts is several weight percent, making it unlikely that residual rutile controls Nb/Ta in melts (Ryerson and Watson, 1987). Amphiboles and perovskite are also likely to be the most important reservoirs of Nb and Ta in the mantle (Dalou et al., 2009; Tiepolo et al., 2000), although, if titanite is present, it will strongly affect the Nb and Ta, as well as the REE, Zr, and Hf content of the melt (Prowatke and Klemme, 2005). Many authors have proposed that carbonatite magmas are the result of low degrees of partial melting of a metasomatized mantle, but that these magmas undergo fractional crystallization and possible silicate–carbonatite melt immiscibility (e.g., Chakhmouradian, 2006). During fractional crystallization of carbonatites, REE are primarily concentrated in three groups of minerals: oxides (pyrochlore and perovskite), phosphates (apatite and monazite), and fluorocarbonates (Jones and Wyllie, 1986), but relative partitioning of LREE and HREE among these groups is poorly understood (e.g., Xu et al., 2010). Zirconium, Hf, Nb, and Ta are controlled by the crystallization of Ti, Nb, and Zr minerals, notably perovskite, pyrochlore, ilmenite, baddeleyite, zirconolite, and zircon (Chakhmouradian, 2006).

In contrast to peralkaline and carbonatite melts, peraluminous melts are generated in orogenic settings (syn- to late tectonic), and their trace-element signature is controlled by the composition of the protolith. For example, cordierite in the source will sequester Be, and mica will control the Rb, Cs, and Li content of the melt (London, 2005). The muscovite + quartz and muscovite + albite + quartz dehydration reactions are particularly important in controlling the concentrations of the alkali and alkaline earth elements. London (2005) noted that for A-type magmas with NYF affinities, high concentrations of Li and Rb distinguish crustal from mantle sources, and London (2008) further suggested that melting on different sides of a garnet–orthopyroxene thermal divide could lead to compositionally distinct ultramafic to carbonatite trends relative to A-type granite trends. For magmas with crustal sources, the nature of the accessory phases

in the source rock and the solubilities of these phases in melts play a critical role in controlling the rare-element content of the melt. Zircon, apatite, monazite, allanite, and titanite are important REE accessory phases and the very low contents of REE in highly evolved (LCT) peraluminous melts are consistent with a model in which these phases buffer REE contents. Zirconium and Hf concentrations are controlled primarily by zircon, and Nb and Ta are generally controlled by Ti phases, primarily rutile, titanite, magnetite, and ilmenite (Linnen and Cuney, 2005). It is important to note that the Zr–Hf–Nb–Ta suite is moderately incompatible to moderately compatible in silicate phases that can accommodate Ti, for example, garnet, pyroxene, amphibole, and biotite.

13.21.2.1.3 Solubility of rare elements in carbonatite melts

There have been relatively few studies of the solubility of rare elements in carbonatite melts. Jones and Wyllie (1986) investigated La solubility in the system $\text{CaCO}_3\text{--Ca(OH)}_2\text{--La(OH)}_3$. The solubility of La, and probably other REE, is very high with a 100 MPa ternary eutectic at $\sim 610^\circ\text{C}$ and 20 wt% La(OH)_3 . Apatite is also, as noted above, an important REE-bearing phase in carbonatites, and early crystallization of apatite may prevent carbonatite melts from attaining economic concentrations of REE. Hammouda et al. (2010) studied apatite solubility and partitioning in calcic carbonatite liquids and found that weight percent levels of P_2O_5 in the melt are required for apatite saturation, but there is an inverse correlation between the CaO and P_2O_5 content of the melt because saturation depends on the apatite solubility product: $(a_{\text{CaO}}^{\text{melt}})(a_{\text{P}_2\text{O}_5}^{\text{melt}})(a_{\text{F}}^{\text{melt}})$, where a represents the activity of the components in the melt.

Pyrochlore solubility in carbonatite melts has been investigated by Mitchell and Kjarsgaard (2004), who determined that 20–40 wt% NaNbO_3 in the melt is needed for pyrochlore to occur as a solidus phase with CaF_2 and CaCO_3 . Other important observations are that pyrochlore is the stable phase in F-bearing systems, but perovskite-structure minerals are stable in H_2O -rich systems. Thus, F is important for stabilizing pyrochlore. A similarly high solubility is observed for the Ta pyrochlore-group mineral, microlite (Kjarsgaard and Mitchell, 2008). An important difference, however, is that microlite is stable in F-poor melts, in contrast to Nb-bearing systems, in which the perovskite-group mineral lueshite is stable. Consequently, in F-poor melts, early-crystallized pyrochlore crystals are Ta rich, such that pyrochlore crystallization can lead to an increase in the Nb/Ta ratio of the residual melt (opposite to the behavior observed in peraluminous systems; see below). Experimental investigations of Zr-phase solubility in carbonatite melts are lacking.

13.21.2.1.4 Solubility of rare elements in silicate melts

Melt structure plays a key role in controlling the solubility of the HFSE in silicate melts. The ‘peralkaline effect’ is where the solubility of a HFSE is directly related to the alkali, or nonbridging oxygen content, of the melt. For example, Watson (1979) observed that for every 4 mol of excess alkalis ($\text{Na} + \text{K} - \text{Al}$) in metaluminous to peralkaline granitic melts, the molar solubility of zircon increased by 1, that is, a slope of 0.25, which suggests an $\text{M}_4\text{Zr(SiO}_4)_2$ stoichiometry, where M is an alkali cation. Niobium and Ta are pentavalent, and

consequently the increase of columbite–tantalite solubility with the alkali content of the melt has a slope of 0.2 (Linnen and Keppler, 1997).

Monazite solubility, like the solubility of other rare-element minerals, is much higher in peralkaline melts than in metaluminous to peraluminous melts (Montel, 1993). Figure 5 shows how the solubility of monazite-(Ce) increases as the melt composition varies from an alumina saturation index ($\text{ASI} = \text{molar Al}/(\text{Na} + \text{K})$) of 1.0–0.64, using the equation of Montel (1993). Figure 5 also shows that the solubilities of monazite and other rare-element minerals are strongly temperature dependent. The solubility of monazite decreases from ~ 2100 ppm TREO at 1000°C to 50 ppm at 700°C for a granitic melt with an ASI of 1.0. Keppler (1993) showed for similar melts at 700°C that the solubility of $\text{LaPO}_4 < \text{GdPO}_4 < \text{YbPO}_4$, but their solubilities are apparently independent of the F content of the melt.

Zircon solubility has been investigated by several authors, including Watson (1979), who showed that zircon saturation in granitic melts at 800°C and 200 MPa occurs at a concentration of 3.9 wt% ZrO_2 for a melt with an ASI value of 0.5. As the melt becomes progressively less alkaline, zircon solubility decreases sharply, to a value of ~ 100 ppm ZrO_2 at an ASI composition of 1.0. For melts with high SiO_2 contents, zircon solubility is nearly independent of silica content, but at lower SiO_2 content zircon is not stable, and phases such as baddeleyite (ZrO_2) or wadeite ($\text{K}_2\text{ZrSi}_3\text{O}_9$) are the saturated Zr

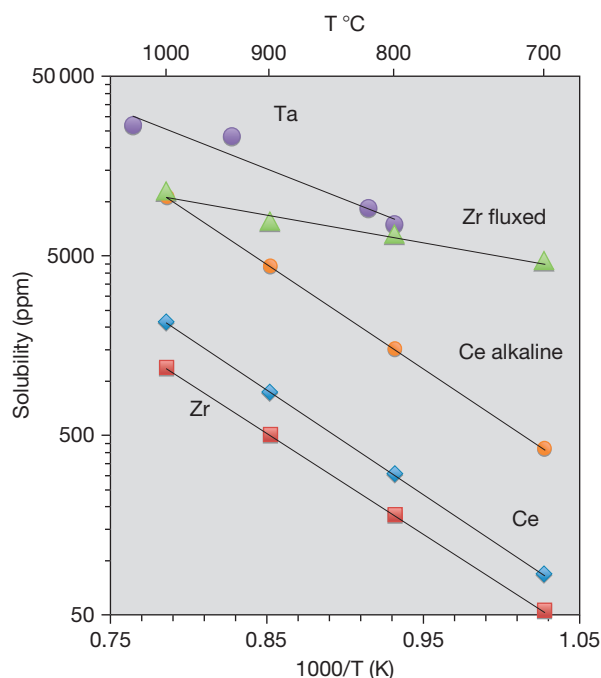


Figure 5 Temperature dependence of rare-element mineral solubility in 200 MPa H_2O saturated granitic melts in terms of ppm by weight of the ore metal. Ce and Ce alkaline are monazite-(Ce) solubilities for melts with ASI of 1.0 and 0.64, respectively, from Montel (1993), Ta is tantalite-(Mn) from Linnen and Keppler (1997) for a melt with ASI of 1.0, Zr is zircon solubility from Harrison and Watson (1983) for a melt with an ASI of 1.0, Zr fluxed is zircon solubility from Van Lichtenvelde et al. (2010) for a melt with ASI as $\text{Al}/(\text{Na} + \text{K}) = 1.15$ and $\text{Al}/(\text{Na} + \text{K} + \text{Li}) = 0.83$.

phases (e.g., Marr et al., 1998). A very important Zr-REE phase in natural feldspathoid-bearing rocks is eudialyte, but there have been no reports of experiments investigating the stability of this phase.

The fluorine content of the melt is an important parameter controlling Zr-phase solubility in ore systems. Keppler (1993) showed that zircon solubility increases strongly with increasing F content in haplogranite (ASI=1) melts at 800 °C and 200 MPa, from 100 ppm at 0 wt% F to 2500 ppm at 6 wt% F. It is not clear whether Zr-F complexes exist in the melt, as proposed by Keppler (1993), or whether F indirectly increases zircon solubility by depolymerizing the melt and creating non-bridging oxygens (Farges, 1996). In peralkaline melts, Marr et al. (1998) observed the opposite effect, that is, that F decreased zircon solubility. This is explained by (Na, K)-F bonding in peralkaline melts, as opposed to the Al-F bonding in subaluminous and peraluminous melts. Linnen and Keppler (2002) demonstrated that the molar solubilities of zircon and hafnon are similar in strongly peralkaline melts, but that hafnon is more soluble in subaluminous to peraluminous melts. Consequently, the Zr/Hf ratio of peralkaline melts will remain nearly constant during zircon fractionation, but will decrease in subaluminous to peraluminous melts.

The solubility of columbite-tantalite has also been the subject of several experimental studies. Linnen and Keppler (1997) showed that the solubility of both columbite and tantalite increases with alkali content in peralkaline melts; similar to Zr, it is at a minimum at ASI=1.0, and increases with Al in peraluminous melts. The behavior of Nb and Ta in peraluminous melts differs from that of Zr and Hf, and may be a consequence of the formation of bonds with Al, which does not occur with Zr and Hf (Van Lichtervelde et al., 2010). In peralkaline granitic melts, Nb/Ta will not change with columbite crystallization, but in sub- and peraluminous melts tantalite solubility is greater than that of columbite resulting in a systematic decrease of Nb/Ta during the crystallization of these melts (Figure 3). Linnen and Coney (2005) showed that the Fe end-members are more soluble than the Mn end-members. This should lead to Fe enrichment during columbite-tantalite crystallization, when in fact the opposite occurs; that is, Mn enrichment. Such Mn enrichment trends can be explained by tourmaline and muscovite crystallization controlling the Fe/Mn ratio of the melt (Linnen and Coney, 2005).

The effect of fluxing compounds is somewhat controversial. Li increases the solubility of columbite and tantalite, but decreases zircon and hafnon solubility in haplogranite melts (Linnen, 1998). Keppler (1993) proposed that F increases columbite-tantalite solubility, but the experiments of Fiege et al. (2011) show that F does not increase columbite-tantalite solubility. The work of Bartels et al. (2011) demonstrates that flux-rich granitic melts can dissolve weight percent levels of Nb and Ta; however, if Li is considered as an alkali, then it is not clear whether or not the increased solubility is simply a consequence of the lower effective ASI of the highly fluxed melts. Lastly, as with other rare elements, the solubility of columbite and tantalite is strongly temperature dependent, although both Linnen and Keppler (1997) and Van Lichtervelde et al. (2010) observed that the temperature dependence is greatest for peraluminous melt compositions and is less important for peralkaline melt compositions.

13.21.2.1.5 Fluid-melt partitioning of rare elements

There are very few experimental investigations of carbonatite melt-fluid partitioning and to date there are no studies that have determined the distribution of rare elements between carbonatite melts and aqueous fluids. However, there have been several fluid inclusion studies, as summarized by Rankin (2005). Of note, some fluid inclusions are estimated to have contained up to 3 wt% TREO, e.g., at the Kalkeld carbonatite. Niobium is interpreted to have partitioned into the melt, Y and REE weakly in favor of the fluid, and Zr, U, and Th, strongly to the fluids (Rankin, 2005). Mass balance of fenite alteration also provides evidence of fluid transport of REE, Nb, and Zr (e.g., Amba Dongar; Palmer and Williams-Jones, 1996). Two other processes that may be relevant to ore formation are carbonatite melt-chloride melt (salt melt) and carbonatite melt-silicate melt immiscibility. Carbonate-salt melt immiscibility has been recognized in some natural systems (e.g., Panina, 2005). However, the partitioning behavior of rare elements during this immiscibility is poorly understood. There is considerable debate in the literature on silicate melt-carbonatite melt immiscibility, although the importance of this process as an ore-forming mechanism has received much less attention. Veksler et al. (1998) investigated immiscibility in anhydrous and F-free, five to eight component systems and observed that REE, Zr, Hf, Nb, and Ta all partition in favor of the silicate melt. This contrasts with the earlier results of Wendlandt and Harrison (1979), who found that Ce, Sm, and Tm partitioned in favor of the carbonatite melt. However, it should be noted that the melt compositions and physical conditions of the two sets of experiments are different, and thus are not directly comparable.

In silicate-melt fluid systems, most of the experimental and natural data for rare-element partitioning are for granitic systems, and to a lesser extent for melts with intermediate SiO₂ content. Borchert et al. (2010) observed that the fluid-melt partition coefficients for Y and Yb range from 0.003 to 0.13, and vary weakly with the ASI composition of the melt, but are independent of the Cl molality of the fluids, P and T. This is in contrast to previous studies (Reed et al., 2000; Webster et al., 1989), in which REE partition values were observed to increase with Cl concentration. Reed et al. (2000) also observed that fluid-melt partition coefficients of LREE are greater than those of HREE. There is consensus that, at moderate salinity, REE partitioning favors the melt. This is in broad agreement with analyses of coexisting natural fluid and melt inclusions. For example, Zajacz et al. (2008) measured the composition of coexisting fluid and melt inclusions from the Mt. Malosa alkaline granite, Malawi, and observed values for La and Ce between 0.1 and 1.

The Zajacz et al. (2008) study also reported $D_{\text{melt}}^{\text{fluid}}$ values for Zr and Nb of <0.1. This is consistent with experimental studies of Zr, Hf, Nb, and Ta partitioning, in which $D_{\text{melt}}^{\text{fluid}}$ values are <1 (e.g., Borodulin et al., 2009; London et al., 1988). It should be noted that salt melts are interpreted to be important in natural systems (e.g., Badanina et al., 2010), but the partitioning behavior of rare elements in salt melts is poorly understood.

13.21.2.2 Hydrothermal Behavior and Processes

13.21.2.2.1 Concentrations of rare metals in natural fluids

There is a considerable body of data for the concentration of REE in fluids, particularly for modern hydrothermal systems

(see reviews by Wood (2003) and Samson and Wood (2005)). In mid-ocean ridge (MOR) systems most hydrothermal liquids have REE concentrations in the parts per trillion to parts per billion range (10^{-5} to 10^{-2} times chondrite for individual REE). These liquids have consistent chondrite-normalized patterns, being LREE enriched with a strong positive Eu anomaly. Concentrations of REE in continental geothermal systems are considerably lower, generally $< 10^{-3}$ times chondrite. Concentrations of REE generally increase with decreasing pH and can achieve values as high as 10^{-1} times chondrite in acid-sulfate fluids with pH < 4 .

The only comprehensive analysis of REE concentration in fluid inclusions is that of Banks et al. (1994) from REE-enriched veins in Capitan pluton, New Mexico. They showed, from crush-leach analyses, that total REE concentration in the bulk liquid varied from 200 to 1300 ppm, that the bulk liquid was highly enriched in LREE relative to chondrite, and that it had a negative Eu anomaly. Concentrations of individual REE ranged from ~ 0.2 ppm for HREE such as Tm or Lu, to several 100 ppm for LREE such as La and Ce. Audetat et al. (2008) measured similar Ce concentrations (300–390 ppm) in individual fluid inclusions from the same pluton using LA-ICP-MS analysis. They also reported La and Ce concentrations for a single vapor-rich inclusion of 70 and 13 ppm, respectively. Cerium has been analyzed in fluid inclusions in a variety of other felsic intrusive environments (e.g., Audetat et al., 2008). Zajacz et al. (2008) also reported data for La (~ 1 –10 ppm), Sm (0.7–3.2 ppm), and Yb (1–5.3 ppm). The results of these analyses show that concentrations of Ce and the other REE are lower than in the Capitan pluton, generally < 10 ppm, but can be as high as ~ 200 ppm. Elsewhere, Zajacz et al. (2008) reported fluid inclusion data for Zr (1–45 ppm), Nb (3–79 ppm), and Hf (4–7 ppm).

Although most of the data on the behavior of the REE in hydrothermal fluids is for the liquid phase, there is evidence from the high concentration of REE in fumarole encrustations at Ol Doinyo Lengai volcano in Tanzania (Gilbert and Williams-Jones, 2008), and from moderate concentrations of REE in geothermal fluids (e.g., Möller et al., 2009) and vapor-rich fluid inclusions (2–13 ppm Ce) in intrusion-related hydrothermal systems (e.g., Audetat et al., 2008), that hydrothermal vapors are also capable of transporting significant concentrations of REE.

13.21.2.2.2 Aqueous complexation and mineral solubility

The valence and size characteristics that make the rare elements incompatible also make them hard acids in the Pearson classification. As such, they will prefer to bond electrostatically to form aqueous complexes with hard bases (ligands), for example, F^- and OH^- (cf. Wood, 1990a; Wood and Samson, 1998) and should also form strong complexes with moderately hard ligands such as SO_4^{2-} , CO_3^{2-} , and PO_4^{3-} , but should be less likely, in a competitive situation, to bond with the borderline ligand Cl^- (Wood, 1990a, 2005).

13.21.2.2.2.1 Aqueous complexation of the REE

A significant amount of data has now accumulated on the stability of many REE complexes at low temperature. Depending on the environment in question and on pH, the REE may

exist dominantly as the free ion (REE^{3+}) or as F^- , OH^- , SO_4^{2-} , CO_3^{2-} , or PO_4^{3-} complexes, with the free ion being more prevalent at low pH and low temperature (Lee and Byrne, 1992; Wood, 1990a). Organic ligands may also be important in low-temperature environments, including seawater (Byrne and Li, 1995). In addition, differences in the nature and stability of complexes across the REE series may lead to fractionation (Byrne and Li, 1995; Lee and Byrne, 1992).

Wood (1990b) and Haas et al. (1995) estimated stability constants for REE species under hydrothermal conditions, based on extrapolations from room temperature data. Both sets of calculations, as expected, bear out the predictions from hard-soft acid-base principles that F^- and OH^- form the strongest complexes, that SO_4^{2-} , CO_3^{2-} , HCO_3^- , and PO_4^{2-} complexes are somewhat weaker, although they are still very stable, and that Cl^- complexes are the weakest. These calculations also show that most REE complexes increase in stability with increasing temperature, but generally decrease in stability with increasing pressure. The magnitude of these effects depends on the ligand in question, and the stoichiometry of the complex. In theory, the chloride ion should become harder with increasing temperature and indeed the calculations of Haas et al. (1995) show that REE-chloride complexes become increasingly more stable relative to fluoride complexes with increasing temperature. As noted earlier, Eu^{2+} may constitute a significant proportion of the Eu in a fluid. This proportion will increase with increasing temperature due to a shift in the redox equilibria between Eu^{2+} and Eu^{3+} , such that at temperatures above 250 °C, Eu^{2+} will predominate (Sverjensky, 1984; Wood, 1990b). The calculations of Wood (1990b) further indicate that other REE may also have significant proportions of divalent ions at 'magmatic' temperatures (> 500 °C).

More recently, a variety of techniques have been employed to experimentally determine stability constants for REE chloride, fluoride, and sulfate species at elevated temperatures (e.g., Gammons et al., 2002; Migdisov and Williams-Jones, 2008; Migdisov et al., 2009). In general, the data from these experiments bear out the theoretical prediction that chloride and fluoride complexes become increasingly stable with increasing temperature. In some cases, the calculated stability constants are similar to those predicted by Haas et al. (1995) but in other cases differ. For example, $NdCl_2^{2+}$ and $NdCl_2^+$ have been shown by Migdisov and Williams-Jones (2002) to be more stable at > 150 °C and less stable at < 150 °C than predicted by Haas et al. (1995). Most importantly, it has been shown (Migdisov et al., 2009) that the theoretical extrapolations described above significantly overestimated the stability constants of REE-fluoride complexes and significantly underestimated the stability of REE-chloride complexes, particularly those of the HREE. In addition, whereas stability constants for the REE-fluoride complexes change little with atomic number at low temperature, at temperatures above 150 °C the LREE species are significantly more stable than the HREE species. The same is true for the REE-chloride complexes (Migdisov et al., 2009). This contrasts with the theoretical extrapolations of Haas et al. (1995), who predicted that at low temperature and pressure, stability increases slightly from La to Lu, but at higher temperatures, the stability constants do not vary monotonically as a function of atomic number, with a minimum at

Nd and Sm. As with low-temperature complexation, such effects could lead to fractionation of the REE from one another.

13.21.2.2.2 Speciation calculations and REE transport in hydrothermal environments

Although knowledge of the stability constants of REE complexes is very important for determining the concentration of the REE that can be transported hydrothermally, the amount of REE actually transported will depend on the availability (activity) of ligands in solution that can form stable REE complexes (it will also depend on the solubility of the REE minerals; see the next section). This, in turn, will be determined by the total concentration of the elements in question, pH, fO_2 , T, P, and ionic strength. For example, the contribution of F^- and Cl^- species will be enhanced by high concentrations of these ligands, and of OH^- complexes by high pH. To understand the roles of the various complexes in the mass transfer of REE, it is necessary to calculate the activities of the different REE complexes.

The only speciation calculations for an REE-rich mineralizing system are those of Migdisov and Williams-Jones (2007), who assessed the system in the Capitan pluton using the fluid inclusion chemistry data from Banks et al. (1994) and published experimental stability constants. For purposes of comparison, they also calculated the REE speciation using the extrapolated data of Haas et al. (1995). The calculations based on their experimental data resulted in a speciation model in which $NdCl_2^{2+}$ and $NdCl_2^+$ were by far the dominant species in solution (Figure 6). This contrasts with the predictions based on the theoretical data of Haas et al. (1995), which showed that NdF_2^{2+} dominated the fluid, with important although subordinate contributions from $NdCl_2^{2+}$, $NdCl_2^+$, and Nd^{3+} (Figure 6).

A number of studies have reported speciation calculations for geothermal fluids. The calculations of Haas et al. (1995) for the continental geothermal system at Valles, New Mexico, showed that sulfate complexes dominate in low pH (acid-sulfate) fluids, carbonate complexes predominate in moderate pH fluids, and hydroxide complexes at high pH. The absence of Cl and F complexes is consistent with the low concentrations of these ligands in the fluids. Similarly, OH complexes dominate in the high pH (7.52) fluid from Reykjafol, Iceland. The calculations of Lewis et al. (1998) for Yellowstone acid-sulfate ($\pm$ chloride) waters are generally consistent with the calculations of Haas et al. (1995), showing that sulfate species dominate where Cl or F concentrations are low, but are subordinate to species involving these ligands where Cl or F concentrations are higher relative to SO_4^{2-} . However, their calculations differ from those of Haas et al. (1995) in that the free ion (REE^{3+}) dominates in the most acidic (~ 2), dilute waters. In contrast to geothermal waters, calculated species for an oceanic (East Pacific Rise) fluid (Haas et al., 1995) mainly involve Cl^- and F^- for the LREE and F^- species for the HREE, although it should be pointed out that F concentrations were poorly constrained and these calculations utilized the older, extrapolated values for F and Cl complexes, rather than the more recently determined experimental values. Subsequent analysis of MOR vent fluids illustrated that the F concentrations used by Haas et al. (1995) were too high and that at 300 °C, REE complexation in such fluids should be dominated by chloride species

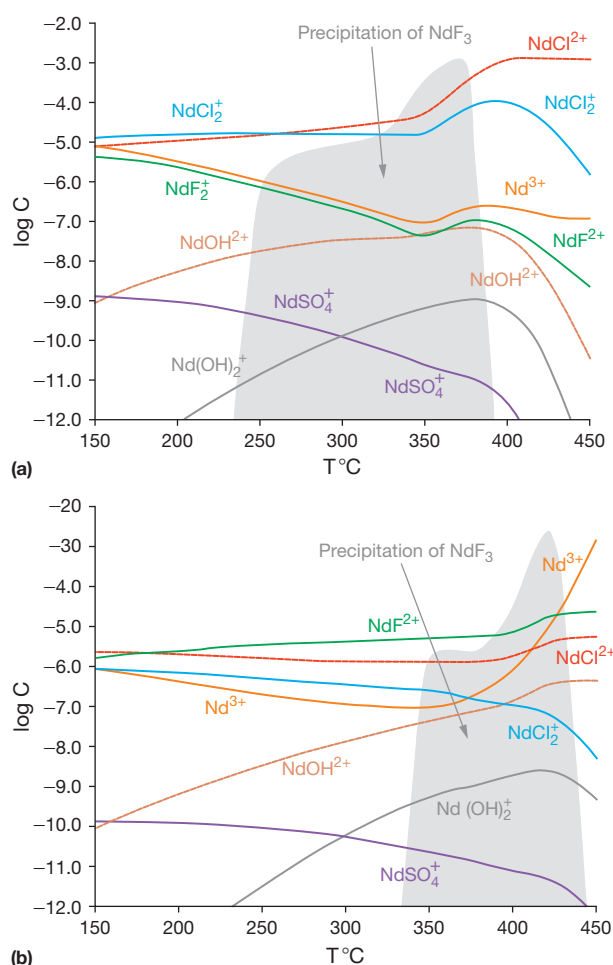


Figure 6 Comparison of concentrations (log C) of Nd species for fluids from the Capitan pluton (Banks et al., 1994) using the stability constants of (a) Migdisov and Williams-Jones (2002, 2007) and (b) Haas et al. (1995).

(Douville et al., 1999). This differs from the earlier calculations of Wood and Williams-Jones (1994), who concluded that hydroxide complexes should dominate in such fluids at 300 °C, although Cl^- and the free ion would be increasingly important at lower pH and temperatures.

From the above summary, it is evident that the speciation of REE in natural fluids will be highly dependent on the environment in question, and that generalizations can be made only with great caution. In particular, the commonly held view (e.g., Samson et al., 2001; Williams-Jones et al., 2000) that fluoride complexes invariably dominate aqueous transport of REE may be erroneous (Migdisov and Williams-Jones, 2007), and has important implications for depositional models for REE mineralization (see below).

13.21.2.2.3 REE mineral solubility

The only important REE mineral for which there is a sizeable body of solubility data for conditions relevant to the formation of REE mineral deposits is monazite. Wood and Williams-Jones (1994) estimated the solubility of monazite by extrapolating its stability constant at 25 °C and combining these data

with stability constants for aqueous species estimated by Wood (1990b). They concluded that the solubility of monazite in a typical MOR vent fluid at 200–300 °C is low (~ 0.2 –15 ppb) and comparable to measured values for such fluids. They also concluded that monazite has retrograde solubility up to 300 °C. More recently, the solubility of NdPO_4 has been measured experimentally by Poitrasson et al. (2004) and Cetiner et al. (2005) under acidic conditions. Both studies confirmed that monazite has retrograde solubility up to 300 °C under acidic conditions. Calculations carried out by Poitrasson et al. (2004) indicate, however, that monazite solubility becomes prograde at higher pH. At any given temperature, monazite solubility is pH dependent, although the exact dependence is a function of fluid composition and the attendant speciation; in general, the solubility of monazite is lower under alkaline than under acidic or neutral conditions. The estimate of the solubility of monazite in vent fluids by Poitrasson et al. (2004) was similar to that of Wood and Williams-Jones (1994). Pourtier et al. (2010) measured monazite solubility at higher temperatures (300–800 °C, 2 kbar) and pH. Under these conditions, monazite solubility is prograde. Overall, the solubility of monazite varies as a function of solution composition, pH, and temperature, such that precipitation mechanisms will vary depending on these parameters.

The only study of which we are aware dealing with the solubility of a bastnäsite-group mineral is that of Aja et al. (1993) who reported measurements for hydroxylbastnäsite-(Nd) at 25 and 200 °C in alkaline fluids. The measured solubility was relatively high, and it is unknown how applicable these data are to natural bastnäsite, which contains a high proportion of fluorine in the hydroxyl site, or to the low pH conditions that exist in many hydrothermal systems.

13.21.2.2.4 Zirconium

Our knowledge of the complexation of Zr in hydrothermal fluids is considerably poorer than for the REE. A thorough review of the complexation and solubility of these elements, particularly at low temperatures, was provided by Wood (2005). Available experimental data indicate that hydroxy, chloride, fluoride, and sulfate complexes are all stable (e.g., Aja et al., 1995; Ryzhenko et al., 2008). The calculations of Aja et al. (1995) indicate that F^- and OH^- and then SO_4^{2-} are the strongest, and that they are significantly stronger than Cl^- at 200 °C. Hydroxide complexes were predicted by them to dominate over fluoride complexes at 200 °C except at very low pH ($\sim < 3$) or high F activity. A number of studies have proposed the existence of mixed OH–Cl and OH–F complexes (e.g., Ryzhenko et al., 2008) and, recently, Migdisov et al. (2011) have confirmed their existence experimentally. The experimental data of Migdisov et al. (2011) show that $\text{ZrF}(\text{OH})_3^0$ and $\text{ZrF}_2(\text{OH})_2^0$ are the principal mixed OH–F species and, most importantly, that at temperatures up to 400 °C and pressures up to 700 bar (the conditions of the experiments) they are considerably more stable than simple fluoride complexes. This study also confirmed that baddeleyite has retrograde solubility in HF-bearing aqueous solutions. Limited experimental solubility data for the zirconium-bearing minerals vlasovite, catapleiite, and weloganite show that they all have very low solubility at 50 °C and for elpidite at 50 and 150 °C (e.g., Aja et al., 1995). Although the solubility of zircon (the mineral

that controls zirconium mobility in many hydrothermal systems) has not been measured directly, it can be calculated reliably using the thermodynamic data for the aqueous hydroxyl–fluoride species determined by Migdisov et al. (2011). Application of these solubility data to fluids with the composition of fluid inclusions from the Capitan pluton (Banks et al., 1994) suggests that Zr concentrations can reach concentrations of several hundred parts per billion in some hydrothermal systems, at temperatures between 100 and 300 °C (Migdisov et al., 2011).

13.21.2.2.5 Tantalum and niobium

There are even fewer data available on the hydrothermal complexation of Nb and Ta or for the solubility of key Nb and Ta minerals. Zarsky et al. (2010) determined the solubility of Ta_2O_5 and Ta-bearing columbite in F^- , Cl^- , HCO_3^- , and CO_3^{2-} -bearing solutions at 300–550 °C. The presence of F^- increased the solubility of both phases by several orders of magnitude, indicating formation of F- or OH–F-bearing aqueous complexes. The maximum columbite solubility was $\sim 10^{-2}$ m Ta and Nb in 1 m HF solutions at 300 °C. Chloride, carbonate, and bicarbonate had negligible effect on columbite solubility, but the stoichiometry of the complexes was not determined and hence no thermodynamic parameters were derived. Research has been conducted in the field of hydrometallurgy, where Ta–Nb ores are commonly treated with mixtures of concentrated HF and H_2SO_4 , although strongly alkaline KOH solutions are also used (e.g., Wang et al., 2009).

13.21.3 Deposit Characteristics

13.21.3.1 Introduction

Rare-element mineralization occurs in primary or secondary deposits. Primary deposits are dominantly associated with igneous rocks, where the mineralization is either magmatic or hydrothermal in origin, have remained in place after the cessation of the magmatic-hydrothermal system, and can be subdivided based on their igneous association: (1) Carbonatites: these rocks host the bulk of the world's Nb resources and historically have produced most of the world's REE; (2) peralkaline granitic and silica-undersaturated rocks: mineralization in these rocks is characterized by high concentrations of REE–Y–Nb–Zr, and, in some cases, high concentrations of Ta are also present; and (iii) Metaluminous and peraluminous granitic rocks: these rocks are host to the world's most important Ta deposits. Where the mineralization is granite-hosted, Nb and Sn mineralization are also present, and there is a gradation between Ta–Nb granites with accessory Sn phases to Sn granites with accessory Ta–Nb phases. Pegmatite-hosted Ta deposits are also commonly exploited for Li and/or Cs. Secondary deposits contain rare-element mineralization that has been concentrated either mechanically or chemically. Placers are very important sources of Ta, Zr, and Hf and supergene laterites clays are host to REE.

13.21.3.2 Deposits in Alkaline Igneous Provinces

13.21.3.2.1 Carbonatites and genetically related rocks

The term 'carbonatite' is reserved for igneous rocks containing 50% or more of modal carbonate (typically, calcite, dolomite,

ankerite, or siderite). Igneous, metasomatic, and hydrothermal rocks with less than 50 modal percent carbonate, but related to carbonatitic magmas, are termed rocks genetically related to carbonatites. A number of important mineral deposits (e.g., Bayan Obo in China and Nolans Bore in Australia) having an unascertained origin, but proposed to be linked to a carbonatitic source (e.g., magma or fluid), are termed metasomatic and hydrothermal deposits possibly related to carbonatites.

Rare-metal deposits of carbonatitic affinity can be grouped into several distinct categories:

1. Nb ($\pm$ Ta) and REE deposits in carbonatites, *sensu stricto*;
2. Zr and Nb ($\pm$ Ta) deposits in phoscorites;
3. Nb deposits in metasomatic rocks associated with carbonatites;
4. Complex rare-element deposits in metasomatic and hydrothermal rocks possibly related to carbonatites; and
5. Weathering crusts developed at the expense of carbonatites (discussed in the [Section 13.21.3.5](#)).

Most carbonatite intrusions that carry significant Nb ($\pm$ Ta) mineralization occur as stocks within, or in the vicinity of, complex multiphase intrusions emplaced in continental rift settings (such as the East African Rift or St. Lawrence graben) and comprise a variety of silica-undersaturated, ultramafic, and alkaline rocks. The most common rock types found in this association are clinopyroxenites, melteigite-urtite series rocks, and nepheline syenites (e.g., Beloziminskiy and Tomtor complexes), although more Mg- and Ca-rich ultramafic and exotic feldspathoid-bearing rocks also occur at some localities (e.g., olivinite at Kovdor, plutonic melilitic rocks at Kovdor and Oka, and sodalite syenites at Blue River). Some mineralized carbonatites are not accompanied by any alkaline or ultramafic igneous rocks (e.g., Tatarskiy); however, because broadly coeval intrusions of such rocks are known elsewhere within the same structural domain in most of these cases, it remains to be determined whether these isolated occurrences represent primary carbonatitic magmas or are simply apical parts of a poorly exposed multiphase intrusion. Carbonatites emplaced in rift settings are commonly enriched in Nb (on average, 340 ppm in calciocarbonatites, and $\sim$ 250 ppm in magnesio- and ferrocarnatites), which is typically not accompanied by concomitant enrichment in Ta. The average Nb/Ta value in carbonatites is 35, which is significantly higher than in other mantle-derived magmas, including alkali-ultramafic rocks spatially associated with carbonatites ([Chakhmouradian, 2006](#)). Relatively few of these occurrences contain economically viable concentrations of Nb in fresh carbonatite; a typical mean grade ranges from 0.5 to 0.7 wt% Nb₂O₅, but may be as high as 1.6 wt% Nb₂O₅ (e.g., Araxá; [Biondi, 2005](#)). Both calcite and dolomite carbonatites (e.g., Lueshe and Niobec mines, respectively) host Nb mineralization, usually as pyrochlore, ferrocolumbite, and their replacement products. The Ta content of primary carbonatite ores is typically low, although some localities contain Ta-rich niobates (up to 14 wt% Ta₂O₅ in ferrocolumbite and 34 wt% Ta₂O₅ in pyrochlore; [Chakhmouradian and Williams, 2004](#); [McCrea, 2001](#)), which are largely confined to early carbonatitic facies. Some of these carbonatites show near-economic levels of Ta coupled with subchondritic Nb/Ta values (up to 500 ppm Ta at an average grade of $\sim$ 200 ppm and Nb/Ta = 1–11 in the Blue

River area; [McCrea, 2001](#)). The Ta enrichment in early pyrochlore is commonly accompanied by high levels of U (up to 29 wt% UO₂; [Tolstov et al., 1995](#)), which could be an environmental impediment to the commercial development of these resources.

Niobium mineralization in multiphase intrusions is almost invariably confined to carbonatites (see below). In the associated igneous silicate lithologies, the Nb content rarely exceeds 300 ppm, although values up to 1700 ppm have been reported in ultramafic and ijolitic rocks from a few localities ([Treiman and Essene, 1985](#)). The bulk of the Nb budget in these rocks is accounted for by perovskite (in feldspar-free parageneses) or titanite, neither of which is readily amenable to processing.

Carbonatites and their consanguineous hydrothermal assemblages exhibit some of the highest levels of REE enrichment observed in igneous systems; for example, values of up to 25 wt% TREO in bastnäsite-barite dolomitic sövite have been reported from the Mountain Pass mine ([Castor, 2008](#)). The lowest reported mineable grade is 1.6 wt% TREO (Weishan; [Wu et al., 1996](#)). Although the whole-rock REE content has been reported to increase from calciocarbonatites to magnesio-carbonatites ([Woolley and Kempe, 1989](#)), there are many localities where the reverse is true (e.g., Kovdor and Lueshe; [Verhulst et al., 2000](#)), or where variations in REE content do not follow a consistent pattern (e.g., Sokli; [Lee et al., 2004](#)). Hydrothermally modified carbonatites commonly exhibit enrichment in REE relative to fresh rocks, yielding fluorocarbonate-, ancylite-, or monazite-bearing assemblages of potential economic value ([Ruberti et al., 2008](#); [Wall and Mariano, 1996](#); [Zaitsev et al., 2004](#)). However, the majority of carbonatites currently exploited for REE are bastnäsite-rich igneous bodies associated with silica-saturated syenitic to granitic rocks (e.g., Maoniuping) and, less commonly, leucite syenites ([Castor, 2008](#)). These types of intrusions lack any temporal relation to rifting or mantle-plume activity, but appear to be confined to the zones of continental collision (e.g., [Hou et al., 2009](#)). Carbonatites in postorogenic settings are characteristically poor in Nb and Ta.

Carbonatites and associated ore deposits are almost invariably enriched in LREE. In the majority of cases, (La/Yb)_{CN} ranges from 20 to 300, although values as high as 9600 and as low as 1 have been reported ([Zaitsev et al., 2004](#) and [Xu et al., 2007](#), respectively). The relative enrichment in HREE is observed in both igneous rocks and rocks overprinted by hydrothermal processes (e.g., [Wall et al., 2008](#)). For example, xenotime mineralization at Lofdal in Namibia, yielding locally economic Y + HREE grades (up to 2 wt% Y, 550 ppm Eu, and 300 ppm Tm), is interpreted to have spanned from the magmatic to hydrothermal stage of carbonatite evolution ([Wall et al., 2008](#)). The commercial potential of these carbonatites remains to be determined.

Phoscorite, *sensu stricto*, is an apatite-forsterite-magnetite intrusive rock containing subordinate phlogopite and calcite, and almost invariably is associated with carbonatites. It was first recognized at Phalaborwa and subsequently identified at some 25 other localities worldwide; the term has now been extended to incorporate apatite-magnetite-rich rocks where the major ferromagnesian silicate is phlogopite, tetraferriphlogopite, diopside, or aegirine, and the carbonate constituent is either calcite or dolomite. Baddeleyite is a common

accessory mineral in forsterite- and phlogopite-dominant phoscorites associated with calcite carbonatites, where Zr contents of up to 2600 ppm have been reported (Lee et al., 2004). At both Phalaborwa and Kovdor baddeleyite is, or has been, extracted from phoscorite ore, at an average grade of ~0.2 wt% ZrO₂. This level of enrichment is insufficient to support an independent mining operation, but the relative ease of extraction and processing makes baddeleyite an attractive by-product of large-scale operations, the primary target of which is apatite, magnetite, or phlogopite in the phoscorite (Ivanyuk et al., 2002). The HfO₂ content of baddeleyite from phoscorites rarely exceeds 2 wt%, averaging 1.7 wt% at Zr/Hf = 54. Some phoscorites (in particular, tetra-ferriphlogopite and apatite-rich varieties) contain potentially economic Nb–Ta mineralization (up to 2 wt% Nb₂O₅ and 280 ppm Ta; Lee et al., 2004) represented predominantly by pyrochlore. In common with carbonatites (see above), the high U and, in some cases, Th contents of this pyrochlore (Lee et al., 2006; Tolstov et al., 1995) may be a significant environmental deterrent to commercial development of these resources.

Pyrochlore mineralization has been reported in several occurrences of alkali-rich metasomatic rocks associated with carbonatites. These occurrences include both fenites, developed after various silicate country rocks, and where the nature of a precursor rock cannot be established with certainty, and the parageneses are named simply on the basis of their modal composition (e.g., glimmerite and microclinite). High average Nb₂O₅ grades (0.8–1.0 wt%) have been reported at a few localities (e.g., Knudsen, 1989), but none of these deposits have been exploited commercially thus far.

Rare-element deposits hosted by metasomatic or hydrothermal rocks that have been tentatively linked to a hypothetical carbonatitic source exhibit significant diversity in geological setting, structure, petrography, geochemistry, and style of mineralization. Evidence that has been commonly presented to support such a link includes enrichment of the host rock in elements and minerals ‘characteristic’ of carbonatites (e.g., Sr-rich calcite or REE-rich apatite), radiogenic and C–O isotope compositions consistent with a mantle source, inclusions indicating crystallization from a CO₂-rich melt or fluid, and the existence of coeval carbonatites in relative spatial proximity to the deposit. Of the many rare-element deposits that can be included in this category, by far the most economically significant and hence, best-studied, is the Bayan Obo (Bayunebo) deposit in China, which is the world’s largest known REE deposit and has been the world’s leading REE producer since the mid-1990s. This deposit is largely confined to dolomite marbles (unit H8), forming the core of a syncline composed of Proterozoic metasedimentary clastic and carbonate rocks deposited on a rifted passive margin of the Sino–Korean craton. The rifting was manifested also in the emplacement of carbonatites and alkali-mafic rocks in the Late Paleoproterozoic or Mesoproterozoic, possibly controlled by an earlier extensional structure (Yang et al., 2011). The deposit is situated some 100 km south of a Paleozoic plate-collision zone separating the craton from the Central Asian orogenic belt. Intermittent activity in this zone throughout the Paleozoic, culminating in the closure of the Paleo-Pacific Ocean, was responsible for deformation, metamorphic overprint, and subduction related to postcollisional magmatism in the Bayan Obo area. The deposit

comprises two large (located in the thickest exposed section of H8) and 16 smaller orebodies that exhibit significant variations in mineralogy, texture, and grade, from 2 to 6 wt% TREO in marble with disseminated monazite and bastnäsite mineralization, to 6–12 wt% and, locally, over 48 wt% TREO, in banded ores enriched in fluorite, alkali clinopyroxene, and amphibole. In addition to iron ore (a primary commodity) Bayan Obo contains 750 million tonnes at 4.1% TREO, the mine is a source of Nb, with an average grade of 0.19 wt% Nb₂O₅, and Sc (grades are not published, but whole-rock values up to 240 ppm Sc have been reported). The major REE ore minerals, in approximate order of decreasing importance, are bastnäsite and monazite (both strongly enriched in LREE with (La/Nd)_{CN} = 1–7), as well as exotic REE–Ba carbonates (e.g., cebaite REE₂Ba₃(CO₃)₅F₂). Niobium is concentrated in columbite, aeschynite, fergusonite, fersmite, and Nb-rich rutile; in contrast to carbonatites, pyrochlore is rare.

The genesis of the Bayan Obo deposit is debatable, primarily because neither the age nor the source of the mineralization has been established with certainty. The primary textures, mineralogy, and geochemical characteristics of the mineralized carbonate rock(s) have been modified by collision-related deformation, metamorphism, and fluid infiltration throughout the Paleozoic (see above). The available radiometric age determinations for REE minerals range from Mesoproterozoic (~1.3–1.0 Ga), and broadly coeval with the rifting and emplacement of carbonatites, to Early Paleozoic (~550–400 Ma), correlated with the subduction beneath the Sino–Korean craton and Caledonian orogeny (Chao et al., 1997; Liu et al., 2005). Isotopic evidence indicates the involvement of both mantle and crustal sources, but their exact nature remains problematic. A number of petrogenetic models have been proposed for the rare-element mineralization at Bayan Obo, including: (1) metasomatic postdepositional reworking of Mesoproterozoic marbles by fluids derived from a carbonatitic source, subduction zone, or an anorogenic silicate magma; (2) metasomatic postdepositional reworking of Mesoproterozoic marbles by fluids reequilibrated with a Precambrian REE-enriched crustal source (e.g., allanite-bearing gneiss or monazite-bearing slate) mobilized during the Caledonian collision; (3) metamorphism of a large intrusion of fractionated REE-rich carbonatite; (4) a syngenetic sedimentary-exhalative or volcano-sedimentary origin; and (5) multistage evolutionary models involving fluids from a variety of sources or a single long-lived source (reviewed in Campbell and Henderson, 1997; Chao et al., 1997; Wu, 2008; Yang et al., 2009; Yuan et al., 1992). The presence of abundant sedimentary structures and fossils in the H8 unit, ubiquitous replacement textures, and a strong crustal isotopic signature characteristic of the mineralized marble, as well as the age constraints and fluid-inclusion record, are most consistent with epigenetic models. A protracted (>150 Ma) metasomatism of a metasedimentary host rock was by initially halide-rich ore-bearing fluids whose chemistry, and the ability to retain specific REE, changed in response to wall rock–fluid interaction, decreasing temperature (~450–200 °C), and the onset of fluid immiscibility (Fan et al., 2005; Smith et al., 2000). Although the provenance of these fluids remains to be ascertained, a carbonatitic source is advocated in a number of studies (Campbell and Henderson, 1997; Yang et al., 2009).

Other notable deposits of possible carbonatitic affinity include Nolans Bore (REE–U resource in apatite-rich veins containing cheralite, monazite, and bastnäsite), Lemhi Pass in Idaho–Montana (Th–REE resource in thorite-rich veins with monazite, xenotime, and allanite), and Karonge in Burundi (bastnäsite and REE phosphates).

13.21.3.2.2 Silicate-hosted deposits

Deposits of REE, Nb, and Zr hosted by silicate intrusions are found in rocks ranging in composition from alkaline to peralkaline (silica-saturated) or ultra-alkaline (silica-undersaturated). However, the most important and only economic, or potentially economic, deposits are in peralkaline and ultra-alkaline rocks, with the latter predominating. The best examples of deposits hosted by ultra-alkaline intrusive rocks are provided by the Khibiny and Lovozero intrusions in Russia (Kola Peninsula), the Ilímaussaq intrusion in Greenland, and the Nechalacho layered suite at Thor Lake in the Northwest Territories of Canada. All comprise multiple intrusions and all display evidence of extensive in situ magmatic differentiation. However, whereas the Lovozero, Ilímaussaq, and Nechalacho intrusions are layered igneous complexes in the sense of the Skaergaard or Bushveld igneous complexes, Khibiny is better described as a ring complex. The Strange Lake deposit in northern Québec, Canada, is an example of a peralkaline intrusion (granite) hosting a potentially economic REE–Nb–Zr deposit. Significant Ta mineralization is also associated with peralkaline granites. The Ghurayyah (Saudi Arabia), Khaldzan-Buregtey (Mongolia), and Motzfeld (Greenland) deposits are three of the largest reserves of Ta in the world (Fetherston, 2004). However, these are essentially Zr–Nb–REE deposits that contain Ta as a potential by-product and are hosted by alkalic, rather than peraluminous granites. The dominant Ta mineral is pyrochlore, which is dominantly magmatic in origin.

13.21.3.2.2.1 Khibiny and Lovozero

The Khibiny and Lovozero intrusions are among the largest ultra-alkaline igneous bodies in the world, outcropping over areas of 1327 and 650 km², respectively, and are host to large resources of the REE. They form two horseshoe-shaped ring complexes only a few kilometers apart, which nevertheless have separate roots (Kramm and Kogarko, 1994; Zubarev, 1980). The intrusions were emplaced into an Archean granite-gneiss basement and Paleoproterozoic metavolcanics of the Iandra-Varzuga belt and are part of the Kola Alkaline Igneous Province, in which nearly 25 ultra-alkaline complexes were emplaced between 380 and 360 Ma. The Khibiny and Lovozero complexes are the largest and the most evolved of these Palaeozoic centers, consisting mostly of agpaitic and, to a lesser extent, alkali-ultramafic alkali rocks with minor melilitolites and carbonatites reported only at the former locality.

The Khibiny intrusion consists of a variety of nepheline syenites arranged in eight concentric rings of inwardly decreasing ages (Kramm and Kogarko, 1994). The oldest unit is fine-grained nepheline syenite, which is followed inward by massive and trachytoid khibinites (coarse-grained nepheline syenites), which make up most of the western parts of the intrusion. Further inward, there is an arcuate, complexly stratified urtite–ijolite zone, followed in the southern part of the complex by rischorrite (K-rich poikilitic nepheline syenite).

The structural relations between the foidolitic rocks and rischorrites are more complex in the western and northern parts of the pluton. Apatite ores forming the large Rasvumchorr, Yukspor, Kukisvumchorr, and Koashva deposits occur at the contact between these last two zones (Zubarev, 1980). These rocks comprise layers up to 200 m thick containing >40 vol% apatite, >40 vol% nepheline, and small proportions of aegirine, titanite, titaniferous magnetite, albite, and K-feldspar, and represent a combined resource of 8×10^9 metric tons of ore grading ~15% P₂O₅ (Arzamastsev et al., 2001). Although the deposits are not being exploited for their REE, the apatite contains ~1 wt% TREO and thus they also represent a potentially enormous low-grade REE (mainly LREE) resource grading ~0.4 wt% TREO. The center of the intrusion is composed almost exclusively of foyaite (leucocratic nepheline syenite displaying a massive or trachytic texture), except for a small body of mineralogically diverse carbonatites, which represent the youngest intrusive phase.

The Lovozero complex is formed in six intrusive phases (Bussen and Sakharov, 1972). The bulk of the pluton (~95% of the exposed area) consists of three intrusive series, including (in order of emplacement): (1) nepheline and nosean syenites, (2) a differentiated series of urtites and feldspathoid syenites, and (3) eudialyte lujavrites (trachytic meso- to melanocratic nepheline syenites). The differentiated series consists of layered sequences of lujavrites, urtites (containing up to 10 vol% loparite), and foyaite. The last of these phases, which was volumetrically the most important (its maximum thickness is estimated at 800 m; Bussen and Sakharov, 1972), forms the upper part of the pluton and is represented by layered eudialyte lujavrites and associated feldspathoid rocks (foyaite, ijolite, etc.), some of which contain up to 80 vol% of euhedral eudialyte. Typically, the eudialyte content ranges from <1 vol% in some varieties of ijolite to 20 vol% in coarse-grained eudialyte lujavrite (Bussen and Sakharov, 1972). Locally, the eudialyte lujavrite is a potential source of rare metals, including REE, Zr and Nb. However, as the TREO, ZrO₂, and Nb₂O₅ contents of the eudialyte are low (2.3, ~14, and 0.8 wt%, respectively), and the extraction of REE from this mineral is technologically problematic, this unit has not been commercially exploited thus far. The main source of REE, Nb, and Ta at Lovozero is the mineral loparite (see Table 1). This mineral forms a cumulate phase in the urtites of the differentiated series, where it is currently being exploited from orebodies reported to contain >1 × 10⁹ tons of ore grading between 0.8 and 1.5 wt% TREO.

13.21.3.2.2.2 Ilímaussaq

The 1.13 Ga Ilímaussaq intrusion, measuring 180 km² in plan, is one of the nine major alkaline igneous bodies located in the Gardar Igneous Province of South Greenland, and is associated with a failed rift of the same name (Sørensen, 2001). Most Gardar complexes evolved along silica-undersaturated (syenite, foyaite, and peralkaline to agpaitic nepheline syenite) or silica-saturated (augite syenite to peralkaline granite) trends. The Ilímaussaq intrusion, however, which was one of the last Gardar complexes to form, contains both agpaitic nepheline syenites and peralkaline granites. Emplacement of the intrusion is believed to have taken place in four distinct pulses from a deep-seated magma chamber fed by a single, mantle-derived, nephelinitic basaltic magma (cf. Markl et al., 2001). The first

pulse produced silica-undersaturated augite syenite and was followed by injection of crustally contaminated quartz syenite and alkali granite sheets, enriched in silica through crustal contamination (e.g., Marks et al., 2003). The third pulse comprised phonolitic magma, which fractionated in situ to form pulaskite, foyaite, and sodalite foyaite roof cumulates, and was followed by a fourth phase in which a similar magma produced floor cumulates represented by spectacularly layered eudialyte-rich nepheline syenites (lujavrites and kakortokites; Markl et al., 2001). The crystallization history terminated with intrusion of numerous pegmatites, formation of hydrothermal veins rich in Zr and REE minerals (e.g., steenstrupine, pyrochlore; Sørensen, 2001), and fenitization of the country rock. The potentially economic mineralization is concentrated in the lujavrites, particularly near the northwestern margin of the intrusion where the Kvanefeld deposit is currently being evaluated, and which is reported to contain indicated reserves of 365×10^6 tons grading 1.07 wt% TREO and 0.028 wt% U_3O_8 . Although the original source of the REE is likely to have been primary magmatic eudialyte, which contain ~ 3 wt% TREO (Karup-Møller et al., 2010), the bulk of the REE and uranium is hosted by the U-Th-REE silicophosphate steenstrupine ($Na_{14}Mn_2(Fe,Mn)_2Ce_6(Zr,U,Th)(Si_6O_{18})_2(PO_4)_7 \cdot 3H_2O$), which replaced eudialyte (Sørensen and Larsen, 2001).

13.21.3.2.2.3 Thor Lake (the Nechalacho deposit)

In many respects, the Thor Lake intrusive system, located in the Northwest Territories of Canada, is very similar to the Ilímaussaq intrusion. Rocks hosting the Nechalacho deposit form a silica-undersaturated, layered, ultra-alkaline suite exposed by drilling over a plan area of ~ 5 km² within the larger Blachford Lake complex (Sheard et al., 2012). The suite was emplaced in a failed rift (Athapuscaw aulacogen) at ~ 2.0 Ga and comprises a sodalite nepheline syenite roof cumulate, lujavrites, and a variety of other nepheline syenites, all of which show evidence of cumulate textures. In contrast to Ilímaussaq, however, the layered sequence was intensely altered, particularly in its upper parts. The potentially economic mineralization occurs in two subhorizontal layers, a miaskitic upper zone comprising cumulates dominated by zircon (Figure 7(a)) and an agpaitic lower zone consisting dominantly of pseudomorphs after a cumulate phase that is interpreted to be eudialyte. These rocks were intensely altered, mainly to biotite and magnetite,

which replaced precursor ferromagnesian minerals, including aegirine. The upper zone contains 31×10^6 tons of indicated reserves grading 1.48 wt% TREO and the basal zone 58×10^6 tons of indicated reserves grading 1.58 wt% TREO. The HREO proportions of TREO in the two zones are 10.3 and 20.7%, respectively. In addition, the upper and basal zones contain appreciable concentrations of Zr (average of 2.10 and 2.99 wt% ZrO_2 , respectively) and Nb (average of 0.31 and 0.40 wt% Nb_2O_5 , respectively). The HREE are concentrated mainly in zircon and fergusonite, and the LREE in monazite, allanite, bastnäsite, and synchysite. Except for zircon in the upper zone, the REE minerals are all secondary, and obtained their REE content from the breakdown of zircon in the upper zone and inferred eudialyte in the lower zone. All are disseminated among the major rock-forming minerals.

13.21.3.2.2.4 Strange Lake

The Strange Lake intrusive is a small, Mesoproterozoic (1.24 Ga; Miller et al., 1997) peralkaline granite, which outcrops over an area of about 36 km² on the border between the provinces of Québec and Newfoundland in northern Canada, and is considered to represent an extension of the Gardar peralkaline province of Greenland into Canada. Three intrusive facies have been recognized based on the nature of the alkali feldspar (Nassif and Martin, 1991): a hypersolvus granite, which crops out in the core, a transolvus granite, and a subsolvus granite that makes up the bulk of the intrusion (60% by area; Salvi and Williams-Jones, 1990). The subsolvus granite also hosts numerous flat-lying or gently dipping pegmatites, commonly >10 m in thickness, and small numbers of thinner subvertical pegmatites. The main ferromagnesian mineral is arfvedsonite and there are significant proportions of sodic titanosilicates and zirconosilicates. Rocks of the subsolvus facies, particularly the pegmatites, show widespread evidence of hydrothermal alteration. Two stages of alteration have been recognized, an early high-temperature alteration, represented mainly by the replacement of arfvedsonite by aegirine (an oxidation event), and a later low-temperature alteration marked by the occurrence of fine-grained hematite and quartz, which accompanied replacement of aegirine and primary HFSE minerals by Ca-bearing HFSE minerals and zircon (Figure 7(b); Salvi and Williams-Jones, 1990). The potentially

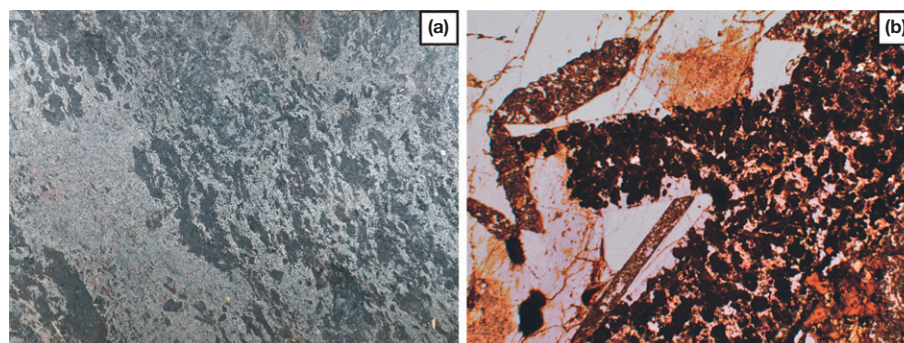


Figure 7 (a) Drill core from Thor Lake (approximately 6×12 cm) showing wispy zircon (light gray) and a mixture of altered silicate minerals and magnetite. (b) Replacement textures at the Strange Lake deposit. A dipyrarnid of gittinsite + quartz after elpidite and rectangular crystals of gittinsite + quartz + hematite after aegirine. Field of view approximately 2 mm across.

economic REE mineralization identified to date occurs in two zones: the Main zone located in the center-north of the intrusion and the B-zone near its northwestern margin. In both cases the highest REE grades occur in pegmatites. The main zone contains 30×10^6 tons grading 1.96 wt% TREO and the B-Zone has an indicated resource estimate of 140×10^6 tonnes grading 0.93 wt% TREO (Daigle et al., 2011; Zajac et al., 1984). The bulk of the REE mineralization occurs as disseminated secondary calcic minerals, for example, allanite, kinosite, and gerinite, and appears to have been derived from the breakdown of primary magmatic minerals like zircon and pyrochlore.

13.21.3.3 Peraluminous Granite- and Pegmatite-Hosted Deposits

13.21.3.3.1 Peraluminous granite-hosted deposits

Peraluminous granites host significant reserves of Ta, either as a primary commodity (e.g., Yichun, China; Huang et al., 2002) or as a by-product (e.g., Pitinga, Brazil; Basto Neto et al., 2009). There are several other occurrences that are either undeveloped or have had limited production, for example, Orlovka in Russia (Reyf et al., 2000). It has long been debated whether the mineralization is metasomatic or magmatic in origin (see the discussion of metasomatic 'apogranites' vs. magmatic sodic rare-metal granites in Linnen and Cuney, 2005). These granites are rich in Li and F as well as Rb and Cs, with variable P and B. The mineralization is dominated by disseminated Ta–Nb–Sn oxide minerals with W±Sn (wolframite–cassiterite) commonly hosted by peripheral quartz veins. The granites are highly evolved, late to postorogenic intrusions that are interpreted to have evolved from low-phosphorus metaluminous to peraluminous I- or crustal A-type granites, or high-phosphorus S-type peraluminous parent intrusions. Several deposits are zoned with depth. For example, the Yichun deposit is a topaz–lepidolite granite that, based on a 300 m vertical drill hole, is K-feldspar rich at depth, has a middle zone that is albite-rich and an upper mixed albite–K-feldspar granite. Mica compositions also change with depth; the deepest intrusion intersected is a biotite–muscovite granite (the biotite is intermediate between annite and zinnwaldite, termed protolithionite) and with decreasing depth grades into a Li-muscovite granite to a topaz–lepidolite granite at the top. The lower to middle zones are interpreted to have been dominated by magmatic processes: snowball-texture albite in K-feldspar, the mineralization (dominantly columbite–tantalite and cassiterite) is disseminated, the Ta/(Ta + Nb) of columbite–tantalite and cassiterite, and the Hf content of zircon both increase upward. However, in the upper zone, columbite is enriched in Fe and W and there is an increase in the Fe content of lepidolite, which is interpreted to reflect the involvement of hydrothermal fluids (Huang et al., 2002).

13.21.3.3.2 Peraluminous pegmatite-hosted deposits

Pegmatite-hosted Ta mineralization has been mined from peraluminous pegmatites in Canada (Tanco) and Australia (Greenbushes and Wodgina) in the past, but recently production has shifted to Brazil (Mibra) and Africa (notably Kenticha, Ethiopia, and pegmatite-derived placer deposits in the Democratic Republic of the Congo). Using the pegmatite

classification system of Černý and Ercit (2005), the major Ta pegmatites are rare-element–Li subclasses, complex type pegmatites that belong to the LCT (Li–Cs–Ta) family. The Tanco pegmatite has been the subject of most scientific researches and has recently been summarized by Černý (2005). Tanco is a complex pegmatite with nine distinct zones that are crudely distributed in a concentric pattern that is interpreted to reflect inward crystallization. The most important units for Ta mineralization are the aplitic albite zone and the central intermediate zone, although other units also contain Ta mineralization, in particular the lepidolite zone. More detailed work on Tanco has focused on magmatic and metasomatic styles of mineralization at Tanco. Van Lichtenvelde et al. (2006) studied one particular area of mineralization (the '26 H area') where the bulk of the mineralization was hosted by albite aplite and lower intermediate zones. Based on textural relationships, they concluded that the mineralization was primarily magmatic, a conclusion that is supported by an increase of the Ta/Nb ratio of columbite group minerals from the margin to the core of this pegmatite cell. They also concluded that the variation of Mn/Fe values in columbite was controlled by silicate phases, notably tourmaline. An association between metasomatic albite is observed elsewhere in the Tanco pegmatite and is described in other pegmatites (e.g., Kontak, 2006). A second metasomatic style of mineralization is an association with muscovite replacement, termed 'MQM' (muscovite–quartz after microcline) at Tanco. Van Lichtenvelde et al. (2007) completed a detailed study of this style of mineralization from the lower pegmatite zone at Tanco. Key textural observations were the complexity of the intergrowths several Ta oxide phases within single grain aggregates and an association of these aggregates with other HFSE minerals, for example, zircon and apatite. These features led the authors to propose a magmatic–metasomatic origin for the mineralization, that is, replacement by a melt rather than a fluid phase. The largest Ta pegmatites in Australia, Greenbushes, and Wodgina, also belong to the LCT family, but lack the classic zonation seen elsewhere. Greenbushes is a spodumene pegmatite that consists of four layers. The Ta mineralization is associated with a massive albite–quartz-rich unit, and, like Tanco, the Li is mined from a different unit (Fetherston, 2004; Partington et al., 1995). In the Wodgina area, Ta has been mined from two areas. The Mount Tinstone–Mount Cassiterite area consists of a swarm of albite–spodumene pegmatites (Fetherston, 2004), whereas, in the Wodgina area, Ta occurs in albite pegmatites that are interpreted to having been derived from the albite–spodumene pegmatites (Sweetapple and Collins, 2002). Less information has been published in international journals on African and Brazilian pegmatites, but mineral chemistry data are available for a number of African pegmatites because of the problem of 'blood coltan' (Melcher et al., 2008). One of the most important Ta pegmatites in Africa is Kenticha in Ethiopia. This is a complexly zoned spodumene subtype LCT pegmatite that Küster et al. (2009) grouped the zones into three units. Most of the Ta mineralization occurs in the upper zone, which also contains most of the spodumene mineralization, and is thought to represent the most evolved unit (bottom-to-top crystallization; Küster et al., 2009). Other pegmatites in Africa include Morrua and Marrapino in Mozambique, which are deeply weathered, and the Democratic

Republic of the Congo contains many eluvial and alluvial placer deposits that are pegmatite-derived (Fetherston, 2004).

13.21.3.4 Supergene Deposits

The extreme susceptibility of carbonatites to weathering and erosion in humid climates, coupled with relatively low mobility of Nb and REE in the weathering profile, are conducive to the development of high-grade (>1 wt% Nb_2O_5), large-tonnage ($n \times 10^7$ – 10^8 tonnes) residual deposits that are amenable to low-cost open-pit mining. Indeed, some 85% of the current global Nb production comes from a single residual deposit, at Barreiro, Brazil (Araxá). This deposit developed on pyrochlore-bearing dolomite carbonatites and contains 450 Mt of laterite ore, with an average grade of 2.5 wt% Nb_2O_5 and an additional (as yet unexploited) REE resource averaging 4.4 wt% TREO (Biondi, 2005). The Catalão I deposit is located approximately 200 km north-northwest of Araxá. It is also a lateritic deposit and contains 32 million tonnes of 1.17% Nb_2O_5 . The geology of this deposit is broadly similar to Araxá; pyrochlore mineralization is associated with dolomitic carbonatite and phosphorite (Cordeiro et al., 2010). Another giant deposit, which is geologically similar to Araxá, is Morro dos Seis Lagos (not currently exploited) that has comparable grades (2.8 wt% Nb_2O_5 and 3.7 wt% TREO), but much greater combined reserves of ~ 2.9 billion tonnes. However, this deposit lies within the boundaries of a national park of virgin rain forest and it is unlikely that it will be exploited. Three major types of residual deposits can be distinguished (Lapin and Tolstov, 1995; Morteani and Preinfalk, 1996; Tolstov and Tyan, 1999).

13.21.3.4.1 Saprolite deposits

Saprolites (also referred to as hydromicaceous crusts) are characterized by ochreous and leached, commonly unconsolidated carbonatite regolith in the lower horizons grading into progressively finer grained material composed of Fe ($\pm$ Mn) oxyhydroxides, vermiculite ('hydromica') and apatite, as well as magnetite, pyrochlore, and other weathering-resistant minerals derived from the precursor carbonatite. Saprolitic crusts developed on silicate-rich lithologies associated with carbonatites (e.g., fenites) may contain up to 60% kaolinite. The most notable mineralogical characteristics of these deposits are the predominance of igneous apatite and pyrochlore in the weathering profile, accompanied by the incipient deposition of REE- CO_3 -enriched secondary apatite (up to 5 wt% TREO) and replacement of the relict pyrochlore by ion-deficient hydrated varieties enriched in Sr and Ba. The most notable examples include the Belaya Zima and Tatarskoye I deposits in Russia.

13.21.3.4.2 Laterite deposits

Laterite-hosted deposits are a product of more advanced chemical weathering under oxidizing and more acidic conditions relative to saprolites. This deposit type is characterized by complete breakdown of primary mineral assemblages, largely to a mixture of Fe–Mn oxyhydroxides (hematite, goethite, ramsdellite, etc.), barite and various phosphate minerals. Secondary apatite, stable in the underlying saprolite and lower horizons of the laterite profile, is replaced in more acidic upper horizons by a variety of crandallite-group phases ($(\text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}, \text{REE})\text{Al}_3(\text{PO}_4)_2(\text{OH})_{5-6}$) and secondary monazite is

accompanied in some deposits by churchite, xenotime, and rhabdophane ($\text{REEPO}_4 \cdot \text{H}_2\text{O}$). LREE may be preferentially concentrated in monazite, apatite, or a crandallite-group mineral (e.g., at Araxá and Seis Lagos), whereas a significant proportion of HREE may be bound in Y phosphates (e.g., Mount Weld and Chukotukon). Bastnäsite and cerianite ($(\text{Ce}, \text{Th})\text{O}_2$) are common accessory minerals in the lower and upper parts of the laterite profile, respectively. Niobium mineralization is typically represented by cation-deficient hydrated pyrochlore that is enriched in Sr, Ba, Pb, LREE, or K (e.g., Araxá, Catalão, Lueshe, and Mount Weld); Nb-rich TiO_2 phases are much less abundant, but may constitute an economic resource (Seis Lagos).

13.21.3.4.3 Reworked laterite deposits

Epigenetically reworked laterites are typically mature crusts showing evidence of epigenetic mobilization of Fe and Mn under reducing conditions (e.g., Tomtor). These deposits form where the laterite profile is buried under organic-rich clastic sediments and 'flushed' by groundwater draining the organic-rich carapace (Figure 8). The defining characteristics of this type of deposit are bleaching of the upper laterite horizons owing to the removal of Fe+Mn and enrichment in kaolinite. Ferrous iron and Mn^{2+} are immobilized in the underlying laterite as siderite and other secondary carbonates, and chlorite (chamosite; locally up to 60 vol%). These processes lead to extreme enrichment of the bleached horizon in rare elements (e.g., up to 7.7 wt% Nb_2O_5 , 18.5 wt% TREO in the Buranniy area of the Tomtor deposit) concentrated in monazite, pyrochlore, xenotime, and crandallite-group minerals.

The thickness of a weathering profile and its ability to retain specific rare elements depend not only on climatic conditions and bedrock geology, but also on the local paleotopography and drainage pattern, groundwater chemistry, and tectonic regime. Uplifted areas tend to develop thin crusts owing to continuous erosion of weathering products, leading, for example, to exhumation of saprolite in lateritic deposits (e.g., Tatarskoye), and lateral variations in composition and thickness of individual horizons (Figure 8). Deposits in saprolitic profiles develop subaerially under near-neutral conditions, whereas pH values below six facilitate the development of laterite. Removal of Fe+Mn from the laterite and the subsequent precipitation of Fe and Mn as carbonates and chlorite requires reducing conditions at pH values gradually increasing from <6 to neutral (Lapin and Tolstov, 1995). Secondary rare-element enrichment factors relative to unweathered precursor carbonatite increase from 2 to 4 (Nb and REE) in saprolites to 10–20 (Nb and LREE) and ~ 30 (Y) in epigenetically reworked laterites. In all of the above, supergene rare-element mineralization is typically accompanied by economically viable enrichment in phosphate.

13.21.3.4.4 Ion-adsorbed clay deposits

Perhaps, the most remarkable example of rare-element production from ore types containing low levels of these elements is the so-called ion-adsorption (or ion-adsorbed) clays derived by lateritic weathering of granitoids, coupled with a threefold to fivefold enrichment of the laterite in REE relative to the precursor rock. In this type of ore, up to 70% of the total REE content is believed to be in the form of cations adsorbed to the surface of clay minerals (predominantly, kaolinite, and

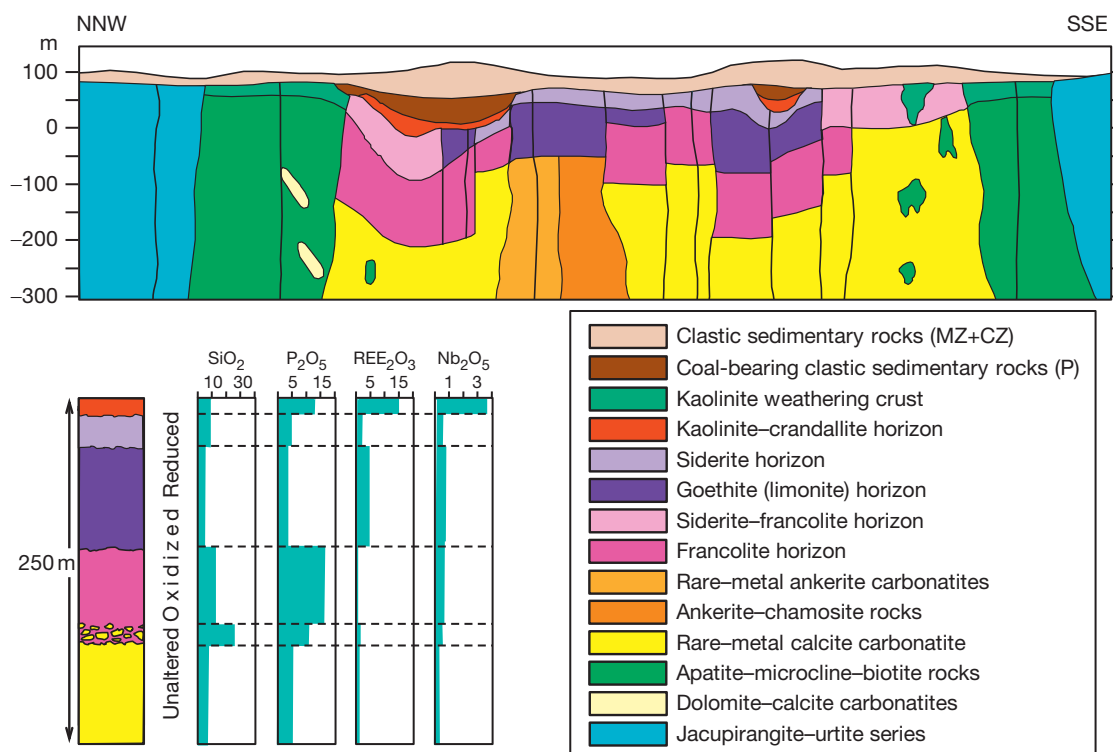


Figure 8 Cross section through the Tomtar deposit. Modified from Tolstov AV and Tyan OA (1999) *Geology and Ore Potential of the Tomtar Massif*. Yakutsk: Siberian Branch Russian Academy of Science (in Russian).

halloysite), but the exact mechanisms of ion-clay interaction are unknown. Although ion-adsorption deposits have very low grades (<2000 ppm TREO: Wu et al., 1996), the high proportion of valuable HREE and low levels of radioactive elements in their composition, as well as their amenability to open-cast mining and easy processing, make this type of deposit a very attractive exploration target.

13.21.3.5 Placer Deposits

Placer deposits of Ta and Nb are close to the original source and in most cases the source(s) is readily identifiable (see Sections 13.21.3.2 and 13.21.3.4). By contrast, zircon occurs in true placer deposits, concentrated in beach sands. These are primarily Ti deposits (rutile and ilmenite), in which zircon is a by-product, along with minor monazite. The leading producers of zircon in 2009 were Australia and South Africa (Gambogi, 2010). In both Australia (Roy, 1999) and South Africa (MacDonald and Rozendaal, 1995), the heavy minerals were concentrated during numerous stages of reworking. Zircon is also produced from heavy mineral beach sands in the United States, India (Gambogi, 2010), China, Indonesia (Central Kalimantan), and Russia (Ptyk-Kara, 2005).

13.21.4 Genesis of HFSE Deposits

13.21.4.1 Magmatic Controls of Carbonatite Deposits

In many carbonatites and related rocks, rare-element mineralization is part of the primary igneous paragenesis. Even in cases

where the concentration of rare elements was enhanced through hydrothermal activity (e.g., Ruberti et al., 2008; Wall and Mariano, 1996), or intense chemical weathering (e.g., Morteani and Preinfalk, 1996; Tolstov and Tyan, 1999), enrichment of the precursor rock in these elements (either in the form of disseminated accessory minerals, or incorporated into rock-forming minerals) appears to be essential for the formation of a viable mineral deposit. It is, hence, important to examine those petrogenetic factors that contribute to the unusual trace-element signature of carbonatites. It has been increasingly recognized that these rocks have a multiplicity of origins. Carbonatitic magmas can be generated by very low degrees ($F < 1\%$) of partial melting of carbonated (i.e., metasomatized) peridotite in the upper mantle, or derived from a mixed carbonate-silicate melt of mantle provenance by either crystal fractionation or liquid immiscibility (Brooker and Kjarsgaard, 2011; Dalton and Wood, 1993; Lee and Wyllie, 1998; Wallace and Green, 1988). Although all three mechanisms are supported by experimental evidence, and may feasibly operate together or separately even on a local scale (Bell and Rukhlov, 2004; Downes et al., 2005), only one of them is typically invoked to explain the petrographic and geochemical characteristics of individual carbonatites (cf. Mitchell, 2009; Verhulst et al., 2000). It is also possible that some rocks previously identified as carbonatites may, in fact, have a hydrothermal (carbothermal) or metasomatic origin (e.g., Nielsen and Veksler, 2002).

Available experimental data indicate that most incompatible elements (with the exception of Ti and in garnet, Zr, Hf, and HREE) partition into a carbonate (dolomitic)-melt relative

to silicate minerals in metasomatized peridotite in the P–T range of subcontinental lithosphere (e.g., [Sweeney et al., 1995](#)). Clearly, the extent of enrichment of primary carbonatitic magmas in REE, Nb, Ta, and Zr will depend, to a large extent, on the concentration of these elements in the mantle source. It is uncertain whether the presence of ‘typical’ metasomatic silicate minerals (e.g., pargasite and phlogopite) in the mantle source is sufficient to provide the level of enrichment observed in carbonatites, or if a significant proportion of incompatible elements are actually derived from accessory titanate and phosphate phases in metasomatized peridotites ([Arzamastsev et al., 2001](#)). Protracted fractionation of alkali-rich carbonate–silicate magma, for example, of melilititic, nephelinitic, or basanitic bulk composition, can yield evolved carbonate melts with elevated levels of REE, Sr, and Ba ([Cooper and Reid, 1998](#); [Lee and Wyllie, 1998](#); [Verhulst et al., 2000](#)), but it is difficult to reconcile this with the HFSE budget of many carbonatites, including those hosting Nb or Zr deposits ([Chakhmouradian, 2006](#)). Liquid immiscibility is a viable mechanism for generating alkali-rich carbonate melts at crustal pressures, particularly from CO₂-saturated peralkaline magmas ([Brooker and Kjarsgaard, 2011](#); [Suk, 2001](#)). Although this process is capable of generating extrusive natrocarbonatites (such as those at Oldoinyo Lengai; [Mitchell, 2009](#)), experimentally determined carbonate–silicate element partitioning data clearly indicate that the immiscible carbonate liquid does not exhibit the level of Nb, Zr, and REE enrichment (particularly relative to the conjugate silicate liquid) observed in economically mineralized carbonatites ([Jones et al., 1995](#); [Suk, 2001](#); [Veksler et al., 1998](#)).

In synthetic systems, hydrous haplocarbonatitic melts can incorporate extremely high levels of Nb and Ta (on the order of $n \times 10^5$ ppm), the solubility of which is further enhanced in F-bearing melts (e.g., [Kjarsgaard and Mitchell, 2008](#); [Mitchell and Kjarsgaard, 2002](#)). The solubility of lanthanides in alkali-free experimental systems is also sufficiently high to produce magmatic REE mineralization on the scale observed at Mountain Pass, Maoniuping, and other similar deposits ([Wyllie et al., 1996](#)). According to some experimental data (e.g., [Suk, 2001](#)), partitioning of REE into a carbonate liquid is enhanced in immiscible carbonate–silicate systems that are enriched in P₂O₅ and F, although the REE partition coefficients are still close to or below unity in melt compositions relevant to natural systems. It is noteworthy in this regard that high levels of P₂O₅ and F in carbonatitic magmas will lead to early, and commonly voluminous, crystallization of apatite that will have a profound effect on the REE budget of an evolved melt ([Bühn et al., 2001](#); [Wyllie et al., 1996](#); [Xu et al., 2010](#)).

13.21.4.2 Hydrothermal Controls of Carbonatite Deposits

Subsolidus processes involving interaction of carbonatites with fluids of different provenance undoubtedly play an important role in the redistribution and concentration of rare elements, but these processes have not been studied experimentally in adequate detail. Pyrochlore tends to form at lower temperature than perovskite-type phases and in systems enriched in U, Ba, and other elements not readily incorporated into perovskite (*ibid.*). Experimental evidence also indicates greater stability of ferrocolumbite relative to pyrochlore in carbonate fluids and

the replacement of the latter by a variety of secondary niobate phases ([Korzhinskaya and Kotova, 2011](#)). These data are in agreement with mineralogical observations (e.g., [Chakhmouradian and Williams, 2004](#)).

The behavior of REE in carbonate-bearing fluids is not well constrained, and the available empirical evidence is contradictory (cf. [Bühn and Rankin, 1999](#); [Michard and Albarède, 1986](#)). Bastnäsite (the principal ore mineral of many magmatic deposits) is stable over a wide range of F activities up to at least 800 °C, but its stability in hydrothermal systems is reduced at high activities of Ca and CO₂ ([Hsu, 1992](#)). The hydrothermal controls of REE mineralization is discussed in more detail, in alkaline silicate environments, below.

13.21.4.3 Magmatic Controls of Alkaline Silicate Environments

As has already been noted, the HFSE in silica-saturated alkaline rocks are largely concentrated in highly evolved pegmatitic facies, whereas in silica-undersaturated alkaline rocks, they are in units that are petrologically equivalent to other units in the intrusion, except that the HFSE phases are major rock-forming minerals. In both cases, potentially fertile intrusions can be distinguished from barren intrusions by their high alkalinity. Another feature of alkaline magmas that enables them to concentrate the HFSE is their high content of fluorine, which promotes HFSE dissolution through fluoride complexation with Al, thereby making nonbridging oxygen available for complexation with the HFSE, or by direct F complexation ([Keppler, 1993](#)). Finally, the HFSE are highly incompatible as are the elements that promote their solubility in magmas, that is, the alkalis and fluorine. Consequently, fractional crystallization can produce residual magmas that are strongly enriched in the HFSE. The above notwithstanding, early crystallization of accessory phases, such as apatite or titanite, which sequester the HFSE, can severely limit the ability of alkaline magmas to concentrate HFSE. Such early crystallization will tend to occur if concentrations of P, Ti, and Ca are high, and in the case of titanite, if temperature is low and pressure is high; temperature has little effect on apatite solubility, but low pressure will promote its saturation ([Green and Adam, 2002](#)). These effects are exemplified by the Khibiny intrusion, Russia, which contains an enormous low-grade REE resource hosted by apatite; the apatite crystallized early owing to the very high P content of the magma (2 wt% P₂O₅; [Kogarko, 1990](#)), thereby precluding later, higher grade concentration of potentially exploitable REE minerals.

Deposition of HFSE in concentrations sufficient to form ore deposits requires a reduction in the solubility of the HFSE minerals and in turn a change in one or more of the physico-chemical parameters that control HFSE mineral solubility. This reduction is precipitous because of the need to crystallize the HFSE phase as a major rock-forming mineral. Although the magmatic processes that lead to HFSE ore formation have received comparatively little attention, we can speculate that in the case of pegmatites, HFSE mineral deposition may be facilitated by saturation of the magma in a volatile phase (which could be related to a pressure decrease). This is because of: (1) a drop in temperature that will accompany the exsolution of a volatile phase and (2) a possible reduction in the

activity of fluorine, which, as discussed earlier, plays an important role in controlling the solubility of some of the HFSE in silicate melts. In the case of silica-undersaturated magmas, prediction of the likely cause of HFSE mineral deposition is more difficult. However, it is reasonable to expect that a sharp decrease in the peralkalinity (and fluorine content), such as might occur due to mixing of the host magma with a more aluminous magma or through assimilation of argillaceous sediments, could lead to a large decrease in HFSE mineral solubility. As HFSE minerals are generally denser than the common rock-forming minerals, they could be efficiently segregated by processes like gravity settling, leading to their accumulation in concentrations sufficient for economic exploitation. Examples of such gravitational segregation of HFSE minerals are the eudialyte-rich layers in the Ilímaussaq intrusion, the loparite layers at Lovozero, and the zircon layers at Nechalacho.

13.21.4.4 Hydrothermal Controls of Alkaline Silicate Environments

In some alkaline intrusions, there is evidence of extensive hydrothermal alteration and mobilization of HFSE. There are even cases where the HFSE minerals have been concentrated beyond the confines of the intrusion (e.g., Gallinas Mountains; Williams-Jones et al., 2000). Most importantly, there is compelling evidence that hydrothermal remobilization, at least for the REE, is a prerequisite for the formation of economically exploitable deposits, for example, Strange Lake and Thor Lake, both with respect to grade and beneficiation (replacement of refractory minerals like zircon by less refractory, secondary minerals). Commonly, the secondary HFSE phases are Ca-bearing. For example, in the pegmatite-hosted deposits at Strange Lake, Zr is concentrated mainly as gittinsite (which partly replaced zircon), and the REE as kainosite (significant REE were initially hosted by zircon). In these deposits, pegmatite formation was accompanied by exsolution of an alkali-rich brine that is interpreted to have mobilized the HFSE and later mixed with a low temperature, Ca-rich brine, which brought about their deposition (Salvi and Williams-Jones, 1990). According to this interpretation, the HFSE were transported as fluoride or hydroxy-fluoride complexes in the magmatic-hydrothermal fluid and deposited when the increased Ca activity caused precipitation of fluorite (a common gangue to the HFSE minerals) and destabilized the fluoride complexes. This model has also been applied to other HFSE deposits, notably the Gallinas Mountains REE deposit (Williams-Jones et al., 2000) and the Nechalacho HFSE deposit (Sheard et al., 2012). In settings where the HFSE are mobilized beyond the confines of the intrusion, fluorite precipitation and in turn HFSE mineral deposition may be the result of interaction of the fluids with calcic lithologies such as limestones or marbles (e.g., Samson et al., 2001) to explain the occurrence of HFSE mineralization in carbonate rocks.

Migdisov and Williams-Jones (2007) have shown that the REE may, in some cases, be transported primarily as chloride complexes. In such cases, alternative depositional mechanisms must be considered. Chloride activity, pH, and temperature will all affect the stability of the aqueous REE complexes and, in turn, REE mineral solubility. Unfortunately, the only mineral for which REE mineral solubility can be reliably evaluated

is monazite. We can predict that a one log unit decrease in chloride activity will decrease monazite solubility by one log unit, and a one log unit increase in pH will decrease its solubility by two log units. A decrease in temperature will either increase or decrease its solubility depending on the pH (at low pH and temperature, the solubility of monazite is retrograde; see Section 13.21.2.2.3). Therefore, processes that could lead to the deposition of monazite are mixing of a magmatic ore fluid with meteoric water, which would reduce temperature and chloride activity and increase pH, and interaction of the ore fluid with host rocks, which would increase pH (acid neutralization via wall-rock alteration).

13.21.4.5 Magmatic Controls of Peraluminous Environments

There is abundant evidence that crystallization plays a major role in the concentration of rare elements in peraluminous settings. This is best illustrated by mineralization in zoned pegmatite fields, where mineral chemistry indicates fractionation from a source granite, through beryl-bearing pegmatites to highly evolved Ta-bearing, complex LCT pegmatites (e.g., Selway et al., 2005). Within a single pegmatite body, changes in mineral chemistry are also consistent with crystallization from a silicate melt (Figure 3). The decrease of Nb/Ta in columbite-tantalite and of Zr/Hf in zircon is consistent with fractionation of a silicate melt (Linnen and Keppler, 1997, 2002). The most contentious question concerning the magmatic controls of mineralization is how the ore minerals, primarily columbite-tantalite, become saturated. Analyses of natural glasses and melt inclusions indicate that the most highly evolved granitic melts rarely achieve Ta concentrations greater than a few hundred parts per million, yet experiments indicate that at magmatic conditions (800 °C, 200 MPa and H₂O saturated) an order of magnitude more Ta is required for tantalite-(Mn) saturation (Linnen and Cuney, 2005). These calculations are based on an MnO melt concentration of 500 ppm. Given that tantalite-(Mn) solubility can be described by a molar solubility product ($[MnO] \times [Ta_2O_5]$), higher MnO should result in correspondingly less Ta₂O₅ required for saturation. There are a number of phases that control the Fe/Mn ratio of LCT pegmatite melts, including micas and tourmaline (Van Lichtervelde et al., 2006), but for peraluminous systems, garnet stability, in particular, will influence the Mn content of the melt. Based on spessartine stability in their experiments with peraluminous melt compositions, Linnen and Keppler (1997) used a value of 500 ppm MnO to extrapolate solubility product values to 600 °C (a reasonable crystallization temperature for pegmatites). Using this MnO content, they calculated that on the order of 500–1400 ppm Ta is needed for tantalite-(Mn) saturation at these conditions. There is no evidence that even the most highly evolved melts contain more than a few hundred parts per million Ta, thus the Ta values for magmatic saturation are unreasonably high and a mechanism is needed to explain magmatic tantalite. Two potential explanations are discussed here: First, MnO concentrations in the melt could be higher than 500 ppm. Garnet, micas, tourmaline, and columbite-tantalite all contain Fe–Mn solid solutions and the FeO+MnO content of peraluminous melts are probably much greater than 500 ppm. Nevertheless, near end-member spessartine and tantalite-(Mn) do occur in nature, so the

addition of Fe does not resolve this problem. It should be noted that garnet stability was not the focus of the Linnen and Keppler (1997) investigation and no experiments were conducted to evaluate garnet stability in low-temperature melts (at 600 °C or lower), or whether F or other fluxing compounds affect garnet stability. Thus, an alternative explanation is that there is enough Mn in natural melts at 600 °C at Ta concentrations in the melt in the order of a few hundred parts per million, but this is yet to be demonstrated experimentally.

The second possible explanation is that rare-element mineralization in peraluminous melts is controlled by temperature. Pegmatites contain abundant textural evidence of rapid growth (disequilibrium crystallization) from oversaturated melts. These textures are either the result of chemical quenching or undercooling, and, in the latter case, magmatic temperatures as low as 450 °C have been proposed (London, 2008). At these temperatures, tantalite and other rare-element minerals will be oversaturated in peraluminous melts, but it remains to be demonstrated that temperature was the controlling mechanism in the formation of world-class Ta deposits in granites or pegmatites, such as Yichun, Tanco, or Greenbushes.

13.21.4.6 Hydrothermal Controls of Peraluminous Environments

Linnen and Cuney (2005) argued that hydrothermal processes are not important to the formation of Ta deposits, based on the lack of Ta metasomatism in the wall rocks that surround granite- or pegmatite-hosted mineralization. This is also true, to a lesser extent, for Nb and REE mineralization in peraluminous environments. However, it is also clear that metasomatic (MQM) Ta mineralization is important at Tanco and other Ta deposits. Van Lichtevelde et al. (2007) tried to reconcile these observations by proposing that the metasomatizing agent was a highly fluxed silicate melt, rather than an aqueous fluid. Rare elements are highly soluble in such melts (e.g., Fiege et al., 2011), although it is unclear what the relative contributions of effective ASI versus fluxing compounds are to the solubility of the rare elements. Melts with high concentrations of fluxing compounds will have very low viscosity (Bartels et al., 2011), and thus be highly mobile. They will also have a very low solidus temperature. By contrast, a different school of thought proposes that high concentrations of rare elements, Ta in particular, are the result of salt-melt or silicate-melt immiscibility (Badanina et al., 2010; Thomas et al., 2011). At Orlovka, the uppermost Ta-rich granite was interpreted by Reyf et al. (2000) to have been caused by a late melt, and Badanina et al. (2010) further suggested that this may have involved an immiscible F-rich salt melt. Thomas et al. (2011) concluded that daughter crystals of lithiotantite (LiTaO₃) are present in alkaline and carbonate-rich melt inclusions in tantalite at the Alto do Giz pegmatite, Brazil, and that immiscible peralkaline melts are therefore generated in peraluminous magmatic systems. These melts will transport high concentrations of rare elements and mineralization may result from metasomatic back-reactions involving these melts.

13.21.5 Commonalities of Rare-Element Mineralization

Rare-element mineralization is observed in three, geochemically very different environments: carbonatites, peralkaline (Si-undersaturated and granitic), and peraluminous granitic environments. The solubility of rare element (HFSE) minerals is very high in all three environments and magmatic processes are critical for at least the initial stages of metal concentration. It is currently challenging to explain the controls of primary magmatic mineralization, and the role of fluxing compounds, fluorine in particular, remains controversial. The main importance of these elements may be to lower solidus temperatures, which both enables extreme fractionation and allows melts to become saturated with HFSE minerals at the lower temperatures. Fluxing compounds also decrease viscosity, which can enhance extreme fractional crystallization and promote crystal settling, but other potential roles are to increase or decrease rare-element solubility in melts, to promote immiscibility, or to be a source for ligands that will complex and transport rare elements in aqueous fluids. With the latter, there are clearly important, metasomatic styles of mineralization in all three environments and future research will unravel the interplay and relative importance of magmatic and hydrothermal processes in concentrating these elements.

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