Common problems - and progress towards solutions - in the process mineralogy of rare earths

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Abstract

The geochemistry and mineralogy of rare earth element (REE) deposits is diverse and ranges from carbonatite-related deposits and alkaline rocks to mineral sands, ion adsorption clays, marine crusts, nodules and clays, by-products of phosphate and bauxite, and re-use of waste materials. Despite the large number of recent exploration projects, very little additional REE production has started. An in-depth understanding of the mineralogy is essential for process design and all of the deposit types have mineralogical advantages and challenges, which will be reviewed and explained. For example, the deposits with the best established processing routes are monazite-bearing mineral sands but monazite radioactivity renders most unusable. Ion adsorption clays are easily leachable but deposits are low grade and shallow so new environmentally-friendly leaching techniques are needed. The diverse mineralogy of alkaline rocks has required development of processing routes for rare minerals such as steenstrupine and eudialyte. Carbonatites tend to have high proportions of the least valuable, lightest REE in REE fluorcarbonates or monazite. A deposit with two ore minerals, REE fluorcarbonate and apatite, that combine to give a REE profile close to that required by industry has an advantage if the ore minerals can be recovered efficiently.

Keywords : rare earth ore deposits, process mineralogy

1.   Introduction

1.1. Aim of review
Economic and environmentally-friendly methods to concentrate rare earth minerals, and then to extract and separate their rare earth elements (REE) are essential to production of a diversified and secure supply of REE. Recent reviews of minerals processing and extractive metallurgy of REE are given in Jordens et al. (2013) and Krishnamurthy and Gupta (2016). The aim of this contribution is to discuss the mineralogy and geology of rare earth ore deposits in terms of their process mineralogy. These deposits range from igneous, metamorphic and hydrothermal rocks to placers and clays. There is a saying that 'mineralogy is king and grade is queen' for the REE. Mineralogy is important not only in designing processing routes but also in predicting and mitigating potential environmental problems.

Despite the large number of recent exploration projects, very little additional REE production has started. However the large number of exploration projects have resulted in advances in

the understanding of geology, mineralogy and processing properties and so it is timely to review progress.

1.2 Nomenclature and behaviour of the rare earths
The term rare earth element(s) (REE) is used here according to the definition of the International Union of Pure and Applied Chemistry to include Sc, Y and the 15 lanthanoids (lanthanides). The REE can be subdivided depending on their atomic number into light rare earth elements (LREE - La, Ce, Pr, Nd, Sm, and Eu), and heavy rare earth elements (HREE - Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu). Pm has no naturally occurring long-lived isotope and so does not occur in nature. The similar physical and chemical properties of the individual REE means that they are often found together as elemental constituents of their host minerals but the variation in cation radius (Figure 1) means that minerals are usually enriched in either the light *or* the heavy REE. See section 3 and Chakhmouradian and Wall (2012) and Wall (2014) for further discussion. The REE form their own minerals (section 3) which are usually the main point of interest in potential ore deposits but they also substitute in ppm quantities into many rock-forming minerals (e.g. plagioclase, clinopyroxene, calcite) and this must also be considered when determining REE deportment.

Behaviour is also controlled by the absolute crustal abundances of the REE in that light REE are up to 200 times more abundant in the Earth's crust than heavy REE. At 64 ppm, Ce for example is similar to copper. Light REE deposits must usually contain weight per cents of REE whereas the heavy REE with their lower absolute abundances may be economic at lower concentrations. Odd atomic number REE are more abundant than their even atomic number neighbours (the Oddo-Harkins effect) giving a 'zig-zag' pattern to REE concentrations in most minerals. Geologists almost always even out this effect by normalising the data to a standard chondrite meteorite or shale composition, producing 'chondrite-normalised' or 'shale-normalised' graphs with smooth variations in REE that are more useful in helping to interpret geological processes.

The process mineralogy of Sc is rather different to the other REE because of its smaller cation size (Figure 1). It tends not to partition with the other REE and is more usually found in clinopyroxene, aeschynite and zirconosilicates and associated with iron oxides in laterites (Williams-Jones and Vasyukova, 2018; Siegfried et al., 2018; Chassé et al., 2016).

1.3 Rare earth supply and demand and the 'balance problem'
Rare earth demand is predicted to increase, especially in response to the need for neodymium iron boron permanent magnets for direct drive motors in electric vehicles and wind turbines and although there are plenty of deposits that could be mined to meet this demand, each has variable proportions of the REE, particularly of proportions of light and heavy REE (Figure 2) and matching supply with demand is not only about enough REE but enough of the right REE (Goodenough et al., 2017). The most 'in-demand' deposit just now is a Nd deposit – to produce the Nd needed for permanent magnets. Unfortunately there is no such thing! Owing to the geochemical constraints described in section 1.2, all deposits with substantial Nd will also contain higher amount of La and Ce and lower Pr, with lower concentrations of the other REE. Likewise, deposits with Dy and Tb, will contain much higher

levels of Y. This means that some of the REE, such as Ce, are in oversupply if others such as Nd are produced in the quantities needed and this is called the 'balance problem'. The best answer to this would be to find more uses for La and Ce, but a hydrometallurgy solution being considered in several deposits under development is to precipitate out Ce as Ce^{4+} (because this is easy) and leave it on the mine site. The concentrations of individual REE and their distribution in the ore and gangue minerals is, therefore, an important consideration during process mineralogy.

2. Analytical approaches and protocols

The analytical techniques used in the process mineralogy of REE are similar to those used for most minerals but achieving accurate analyses takes time and care because of the similarity of the REE to each other and because of the importance of major and trace element quantities of REE in many minerals.

Scanning electron microscopy with energy-dispersive X-ray microanalysis (SEM/EDS) works well as a technique for initial reconnaissance. The high atomic number of the REE means that most REE minerals are bright on a backscattered electron image (BSE). Minerals that are too small to see easily in hand specimen and often occur in turbid altered patches that are poorly defined under an optical microscope 'stand out' easily on a BSE image. With careful calibration and quality control, quantitative analysis can be done by SEM/EDS but better X-ray spectral resolution and thus ability to distinguish individual REE from each other, as well as its lower detection limits make wavelength-dispersive analysis, usually on a dedicated electron microprobe, the technique of choice for REE minerals. Levels of heavy REE in LREE minerals and vice versa are important in the valuation of a deposit but usually below detection limits of both wavelength-dispersive and energy-dispersive electron microprobe analysis. The technique most usually used to follow up and determine trace components is laser-ablation ICP-MS, which lowers detection limits to ppm concentrations but has less good spatial resolution, of about 25 μm upwards, than the ca. 1 μm resolution of electron beam analysis. Ion probe and SIMS are also possible but more expensive techniques.

X-ray diffraction is particularly useful to identify major minerals in the early stages of a study (Thompson et al. 2011) but is limited because of the potential for complex mineral assemblages, requiring spatially-resolved information, the importance of accessory minerals that may be below XRD detection limits, and variation in the proportions of individual REE that are important in determining the value of a deposit.

Automated mineralogy is an essential part of process mineralogy and is used, with varying challenges, on all of the types of REE deposits (e.g. Smythe et al., 2011; Grammatikopoulos et al., 2013; Edahbi et al. 2018). One of the problems encountered is the difficulty in distinguishing Ca REE fluorcarbonates (Table 1) from each other owing to their chemical similarity and occurrence either as bladed crystals or syntaxial intergrowths. A recent QEMSCAN® study optimised conditions to distinguish parisite and synchysite based on the Ca content and resolved syntaxial intergrowths on a scale of about > 20 μm (Al-Ali, 2016). Alkaline rocks with their complex mineral assemblages will also require individual development work in order to achieve good results. Another problem is that individual REE cannot usually be distinguished, and are often below detection limits. Linking automated mineralogy results to trace element analysis e.g. by LA-ICP-MS is the next step in good

process mineralogy for REE, and some protocols are available in LA-ICP-MS software for doing this although the author is not aware that this is offered routinely.

Cathodoluminescence (CL) is useful in determining trace element (<0.1 wt%) distribution of REE in non-REE minerals such as apatite and may be carried out using optical microscope-mounted cold CL equipment or a CL detector mounted in an SEM or electron microprobe. The review of apatite in carbonatitic rocks by Chakhmouradian et al. (2016) contains examples of zoning and alteration imaged using CL and BSE images. None of this detail would be visible on an optical image. REE minerals, with major amounts of REE, do not usually give a cathodoluminescence signal.

Portable XRF (pXRF) analysis is useful for fieldwork (Simandl et al., 2014) and rapid analysis in the laboratory. A suitable specification of instrument needs to be available, not all models can detect the higher energy REE lines.

For bulk chemical analysis, a challenge with REE-bearing minerals is ensuring that they are properly dissolved. Highly insoluble phases such as zircon, crandallite and monazite can all be important REE hosts. Sodium peroxide fusion and lithium metaborate/tetraborate fusion are the preferred methods of preparation for ICP-MS analysis.

3. The Minerals

There are over 200 rare earth minerals in the mineral kingdom of ca. 5000 species (www.ima-mineralogy.org) i.e. about one in 25 mineral species contains predominant REE in an essential crystallographic site. Luckily (for mineral processing purposes) most of these minerals are rare and the list of minerals important in ore deposits is shorter (Table 1) (British Geological Survey, 2011; Chakhmouradian and Wall, 2012, Wall, 2014 and Krishnamurthy and Gupta, 2016). It will not be comprehensive because of the range of minerals that occur in alkaline rock deposits of potential commercial interest (see section 4). Minerals processing properties are known well for only a few of these minerals.

REE mineral species are named using suffixes to denote the individual REE that is predominant (Bayliss and Levinson, 1988). A mineral such as monazite has several official mineral species: monazite-(Ce), monazite-(La), monazite-(Nd). All must have been observed in nature in order to be valid. The –(Ce) varieties are by far the most common for LREE-enriched minerals, such as monazite and bastnäsite and the –(Y) varieties are practically always the species of the heavy-REE minerals because of the much greater crustal abundance of Y compared to the heavy lanthanides (Eu- Lu). Although Nd is in demand at the moment, there are few –(Nd) mineral species and none of which the author is aware that occur in large enough quantities to be of commercial interest.

In practice almost all REE minerals contain mixtures of REE. The LREE minerals, e.g. monazite, bastnäsite etc. (Table 1) contain La, Ce (usually in the largest quantity) with lesser Nd, smaller amounts of Pr, Gd, Sm and traces of the other heavier REE. HREE minerals usually contain predominant Y plus weight per cent levels of Eu – Dy and lower levels of the heavier REE that have lower absolute crustal abundances and of the LREE. The LREE /HREE fractionation is controlled by the 'lanthanide contraction' (section 1.2). The exceptions to this rule are Ce, which can oxidise to Ce^{4+}, especially in weathering environments and form minerals that only contain Ce, and Eu^{2+} that forms in more reducing conditions.

Unfortunately, Eu^{2+} substitutes in trace quantities into bulk, i.e. rock-forming, minerals such as plagioclase and this means that it does not form Eu minerals of its own. The main minerals that are mined currently: bastnäsite-(Ce), monazite-(Ce), xenotime-(Y) have over 60 wt% REE. Loparite-(Ce), at just about 30 wt% REE is an exception but was mined originally its niobium, with REE extracted as a by-product.

Recent studies have shown that it is important to identify REE fluorcarbonate minerals accurately. Bastnäsite-(Ce) is the best known member of the family and as a starting point it is assumed that other REE fluorcarbonates, such as parisite-(Ce) and synchysite-(Ce) and various other less common related minerals, will behave in a similar way during minerals processing. This assumption does indeed seem a reasonable starting point for flotation (e.g. Owens et al. 2018) but has proved wrong for the magnetic properties. The magnetic susceptibility of REE fluorcarbonates varies according to the amount of Ca present, so that bastnäsite -(Ce) and parisite-(Ce) are paramagnetic but synchysite-(Ce) is diamagnetic (Al-Ali et al, submitted).

Table 1 contains eudialyte, apatite, fluorite and zircon, that are not technically REE minerals but they are important hosts for REE, forming ore minerals in some deposits. Eudialyte is a complex silicate that occurs in peralkaline igneous rocks (section 4). Schilling et al. (2011) reviewed the composition of the eudialyte group minerals. Both light and heavy REE can substitute into its cation sites and it is important in giving alkaline rock deposits higher proportions of heavy REE than, for example, carbonatite deposits. Eudialyte is paramagnetic and usually concentrated by magnetic separation. The more problematic step is to dissolve eudialyte without creating a silica gel that impedes the reaction. Some progress has been made on this recently (Davris et al., 2017).

In apatite, REE substitute for Ca and can be dominantly LREE, HREE or mid-REE depending on the geological environment. Substitution of REE is coupled with either Na or Si and it is the Si coupled substitution that facilitates the highest levels of REE in apatite, reaching 10 wt% and more, in a solid solution series through to britholite-(Ce). Fluorite usually only contains trace levels of REE but can be of interest in some deposits. Zircon contains HREE, again usually in trace levels and is not of interest in its own right as a REE ore but occurs in polymetallic ores in alkaline rocks (Section 4).

Radioactivity is the single most important environmental issues for REE ore deposits. The REE themselves are not radioactive (except for Pm that has such a short half-life that it does not occur in nature) but thorium and uranium often substitute into REE minerals. Amounts of Th and U can vary in many minerals but there are some general rules and controls in particular geological environments (Table 1). Firstly, the higher the wt% content of REE, the higher the Th and U are likely to be (Figure 3). Apatite and eudialyte with <1 to about 10 wt% REE usually have very low actinide contents. Conversely, in monazite-(Ce) formed in granites, levels of ThO_2 can reach 10 wt% (in the substitutions towards other members of the monazite group, Table 1) and concentrates of such ores require special arrangements to process and ship. Monazite-(Ce) in carbonatites and especially in weathered carbonatite usually contains much lower Th and U, e.g. < 0.5 wt% and is much easier to handle. A solution, at least in part, to the radioactivity problem comes if there is a market for the actinides. Steenstrupine at Kvanefjeld, Illimaussaq, Greenland contains U and required a change of legislation in Greenland to permit U mining and allow the REE exploration project

to go ahead. Uranium is a possible marketable by-product. Thorium is less marketable, except in India, which has an interest in developing Th reactors.

4. The Deposits

The geology of REE deposits is diverse (Orris and Grauch, 2002; Verplanck and Van Gosen, 2011; Wall, 2014; Haque et al. 2014; Voncken, 2016; Wall et al., 2017) ranging from carbonatite-related deposits including fresh rocks and laterites, alkaline syenites and granites, weathered silicate rocks with REE adsorbed to clay surfaces (ion adsorption clays) (Figure 4), to a whole variety of other hydrothermal deposits, marine deposits, by-products of placers, bauxite production and waste, and phosphate production for fertiliser. Although processing flow sheets have to be designed carefully for each deposit, it is possible to make some generalisations (Figure 5).

4.1 Mineral Sands
Together with some very small production from granite pegmatites, mineral sands are the oldest type of REE deposit, mined in the 1950s and 60s, and until Mountain Pass carbonatite started production, the main source of REE. Monazite-(Ce) and to a much lesser extent xenotime-(Y) are the by-products of the titanium and zirconium minerals more usually associated with mineral sands. These are the REE deposits most likely to have the simplest processing routes. Mineral grains are usually separate and well-liberated, amenable to well-established physical methods of processing mineral sands to give high quality concentrates, usually of monazite-(Ce). However, as mentioned in section 3, the environmental issue that most concerns the public is radioactivity. Mineral sands usually contain monazite mainly derived from granite and metamorphic rocks in which levels of ThO_2 tend to be high, up to about 10 wt% ThO_2 (see radioactivity comparison in Figure 3). This is enough to make the monazite, and also xenotime, difficult to handle in concentrated.

4.2 Carbonatite-related deposits (including weathered deposits)
Carbonatites are igneous rocks composed of at least 50% carbonate minerals. Carbonatite-related deposits are the World's main source of light REE, including Nd. Mountain Pass, California, USA and the World's largest REE mine, at Bayan Obo, Inner Mongolia, China, are both carbonatite-related deposits that contain bastnäsite-(Ce) as the main ore mineral. Both use flotation to produce bastnäsite concentrates and both have potential subsidiary monazite-(Ce) products but their geological features are rather different, and they are both rather atypical of all the other carbonatites currently or recently under exploration. Mountain Pass contains coarse-grained bastnäsite-(Ce) and also some more complex textures of syntaxial intergrowths of REE fluorcarbonates as well as sub-solidus alteration, and the rare mineral, sahamalite-(Ce). It was probably formed by precipitation from calcite carbonatite magma and the high degree of magma fractionation has produced an extreme light REE-enriched composition (Figure 2). The intrusion consists of tabular, dipping bodies in a 10 km long belt, associated with ultrapotassic rocks and smaller carbonatite dykes (Castor, 2008). There are many hypotheses the Bayan Obo bastnäsite deposit for may have formed. The most favoured idea at the moment is that the deposit is a dolomite marble (H8 unit) intruded by of carbonatites and metamorphosed and metasomatically altered in multiple stages (Smith et al., 2016). The deposit is rich in hematite and magnetite and until recently was mined for iron ore, with banded textures and also aegirine, fluorite, a whole suite of REE minerals in addition to the main ores and suite of niobium minerals including pyrochlore. The

ore bodies are 'stratabound' within the H8 dolomite, with no resemblance to igneous intrusions.

Elsewhere, in general REE minerals in carbonatites are less diverse than in alkaline rocks and the most common minerals are REE fluorcarbonates (bastnäsite-(Ce), parisite-(Ce), synchysite-(Ce)), plus ancylite-(Ce) and monazite-(Ce). The problem is that Mountain Pass-style large bastnäsite crystals of are rare. REE minerals in carbonatites have usually formed in the transition between magma and hydrothermal fluid, often in pegmatite-type environments, or by reworking of the original magmatic carbonatite by later fluids. These environments often result in final fine-grained intricate textures, often with thin plates of REE fluorcarbonates that look like needles in two dimensions, syntaxial intergrowths and pseudomorphs. Minerals closely associated with REE minerals including strontianite, barite and also quartz.

The highly light REE-enriched nature of REE minerals in carbonatites (Figure 2) leaves them depleted in the (more expensive) heavier REE. Ironically, the same geological processes in carbonatites that create complex, inter grown minerals can also upgrade the proportions of the heavier and more valuable REE and help to produce REE proportions closer to industry needs. The flowsheet for Songwe Hill carbonatite recovers both synchysite-(Ce) and mid-REE-enriched apatite (Croll et al., 2014; Broom-Fendley et al., 2017). The apatite and synchysite are not directly associated with each other and have formed at different stages in the emplacement of the carbonatite.

Understanding the rock-forming carbonates is also important. The clean-looking white calcite of 'sovite' is rare in REE-rich carbonatites, which are much more likely to be dark, rust brown in appearance, and contain ferroan dolomite, ankerite or occasionally ferroan calcite. Ferrocarbonatite and siderite are used as field terms but siderite-magnesite series carbonates are rare. The theoretical properties of pure calcite, dolomite or ankerite may well not be applicable to processing studies because the carbonates often contain fine-grained Fe (hydr)oxide, released from the original carbonate by hydrothermal alteration or weathering. Apatite is an important rock-forming mineral in many carbonatites and an important REE host because of its abundance (Chakhmouradian et al., 2017).

Gravity, magnetic, and particularly flotation methods are used on various carbonatite deposits. Owing to the difficulty in liberating the minerals, some flowsheets go quickly to acid leaching. For example, at Bear Lodge (Wyoming, USA), the proposal for the bastnäsite-(Ce), synchysite-(Ce), monazite-(Ce), cerianite-(Ce) and ancylite-(Ce) bearing carbonatite to acid leach the highest grade ore 4.7 wt% total REE oxide after just crushing and screening during the first nine years of mine life (Dahlberg, 2014). An alternative method of magnetic separation and flotation has also been proposed (Cui and Anderson, 2017). At Songwe Hill, the concentration of REE is upgraded by 2 -3 times from an average grade of 1.62 wt% total REE oxides by flotation and then subject to a sequence of acid leach (Croll et al., 2014).

The carbonatites that contain REE have often intruded as a sequence of dykes, which may range from many metres diameter to just a few cm and often follow earlier (calcite) carbonatite. There are often associated metasomatic fenites, especially K-feldspar resulting from country rock alteration and brecciation. Geological studies will separate these phases of activity into a paragenetic sequence and discuss their mineral assemblages individually but minerals from multiple events are likely to be mixed together in a process mineralogy

sample. The form of the Intrusions means that most fresh rock carbonatite deposits are open to depth.

Weathering of carbonatite, removes the rock-forming carbonates (and also apatite in more intense weathering) and upgrades the concentration of REE which if released from original minerals, re-precipitate in weathering products, such as monazite, crandallite group minerals (including florencite) and cerianite. Concentrations of actinides are usually low in monazite formed during weathering. The Mt Weld mine in weathered carbonatite, Western Australia supplies 20 % of the World's REE. Other examples of deposits are Zandkopsdrift (South Africa), the niobium mine at Araxá (Brazil) and Tomtor (Russia). Although weathering is useful in creating higher grade ores, it produces problematic highly intergrown, minerals, with ubiquitous fine grained, poorly crystalline Fe (hydr)oxides coating grains. Liberation is difficult and high grade concentrates are difficult to achieve. Flotation is usually the best beneficiation process. One solution to this is that high grade concentrates are not always needed. Lynas Corporation Ltd ships a 38 wt% REE oxide monazite-(Ce) concentrate from Mt Weld (cf 70 wt% REE oxide in pure monazite, Table 1). This is also helpful in keeping the radioactivity as low as possible for shipping.

4.3 Alkaline rocks
The challenge of alkaline rocks is that the REE-rich varieties contain the most diverse and complex mineralogy in the World. The nepheline syenite at Khibiny (Khibina) on the Kola Peninsula Russia, for example, has 522 valid minerals (about 10% of the whole mineral kingdom), of which 121 were described for the first time at this locality (https://www.mindat.org/loc-2680.html). The Ilimaussaq complex, South Greenland, which has two REE projects at Kvanefjeld and Tanbreez, contains about 200 species (Sørensen, 1996).

By definition an alkaline rock is igneous and has high enough Na and K that to have formed foid minerals such as nepheline or leucite and/or alkaline amphiboles or pyroxenes (e.g. arvfedsonite, riebeckite, aegirine). The most extreme compositions are agpaitic, peralkaline nepheline syenites characterized by complex Zr and Ti minerals, such as eudialyte (Figure 4) and mosandrite (rinkite), rather than simple minerals such as zircon and ilmenite (Le Maitre, 2002; Sørensen, 1996). They have high contents of rare elements such as Li, Be, Nb, Ta, REE, Zr, Th, etc. and of volatiles, F and Cl, and this produces the wide ranges of mineral species. Major REE minerals that are new to science have been described in potential ore deposits (Atencio et al., 2015). Development of the Kvanefjeld deposit, Ilímaussaq, Greenland has required a new processing flowsheet for the rare mineral steenstrupine-(Ce) which is the major ore mineral.

The alkaline complexes that have been of main interest so far are large, igneous bodies, formed through multiple pulses of magma injection and a complex series of cooling, crystallisation and settling processes. Vertical zonation of mineralogy and mineral compositions is likely. For example, in the loparite-bearing nepheline syenite intrusion at Lovozero Kola Peninsula, Russia (Figure 4), the composition of the loparite (Table 1) changes systematically through a 1.6 km vertical section of the intrusion (Kogarko et al., 2002).

Although minerals precipitated from the magma tend to have clean, coarse-grained textures, sub-solidus alteration of the original minerals by magma-derived fluids can remobilise REE,

causing enrichments in some cases but also producing fine-grown alteration products, such as those described in Sheard et al. (2012) and Borst et al. (2016).

4.4 Other hard rock deposits - metamorphic rocks and hydrothermal veins
There are a variety of other significant REE deposits that do not fall easily into the main classifications. Notable is Gakara, Burundi, which consists of veins rich in coarse-grained bastnäsite-(Ce) and monazite-(Ce), with in-situ grades in the range of 47-67% total rare earth oxide (TREO). It is currently being mined on a small scale by Rainbow Rare Earths. They use manual mining of a free-digging ore and the REE minerals are large enough and high enough concentrations to be processed by minimal physical upgrade before the concentrate is shipped from the mine site (http://rainbowrareearths.com).

Steenkampskraal, South Africa is also an extremely high grade deposit, with an average of 14.36 % TREO in monazite-(Ce), apatite veins in metamorphic rock. The monazite-(Ce) was mined previously for Th, and its high Th content is problematic from the REE production point of view because of the high radioactivity that it conveys. The processing route proposed uses gravity separation followed by flotation to give a 90% concentrate, which will be dissolved on site to form a mixed REE product. A by-product containing copper, gold and silver will also be produced (https://www.steenkampskraal.com/).

4.5 Ion adsorption clays
Ion adsorption clays are easy to process and low in Th and U. Their low (> 500 ppm) concentrations of easily leachable REE can be exchanged direct from the clay minerals using ammonium sulphate solution without the need for crushing, grinding or physical upgrade. Leaching is considered in Moldoveanu and Papangelakis (2012, 2013 and 2016), Chi and Tian (2008) and Burcher-Jones et al. (2018). The leaching may be done in situ or by removing material to leaching tanks. Some 200 ion adsorption clay deposits in southern China supply almost all of the World's heavy REE; these deposits are described in Chi and Tian (2008). There are similar deposits elsewhere, although none are used commercially, and studies, including work by the SoS RARE project in the UK, are characterising the residual minerals, adsorbed components and working on the potential for new leaching reagents, including bioleaching. Some Chinese ion adsorption clays are spectacularly enriched in heavy REE (Figure 2) but most are essentially light REE-enriched but with higher proportions of heavy REE than most other deposit types (e.g. Bao and Zhao, 2008) and discoveries outside of China are also light REE enriched but with higher proportions of heavy REE than most carbonatites.

Ion adsorption clays form by weathering of an original igneous silicate rock, most usually granite. The key ingredients are the formation of kaolinite or halloysite and dissolution of original REE or REE-bearing minerals to release REE that can then be adsorbed onto the clay surfaces. Insoluble REE minerals, such as monazite or xenotime are much more common as REE hosts but will remain as residual minerals in the weathered profile (Santana et al. (2015), even in intense weathering. The implications for process mineralogy are firstly that only part of the bulk REE content will be adsorbed onto clays and exchangeable, so leaching tests are needed, with mineralogical studies to determine the nature of the other REE host minerals. The next is to determine if possible what the weathering reactions are, i.e which minerals are releasing the REE. Hydrothermal alteration in granite is responsible for forming the Chinese soluble REE minerals, such as REE fluorcarbonates (Bao and Zhao, 2008) and this alteration may not be related to the original emplacement of the granite (Xu et al., 2017). It is likely to

be heterogeneous and will affect the lateral composition and leachability of the profile. There is also strong vertical zonation in ion adsorption clays and only one horizon, will contain substantial exchangeable REE (e.g. Chi and Tian; 2008, Bao and Zhao, 2008; Sanematsu et al., 2013). The depth of the weathered profile can vary; deposits occur in shallow (<10m) saprolite profiles (Figure 4) and deeper laterite.

There are environmental challenges with these deposits (Wall et al., 2017) The extremely low grade, at about 500 ppm, requires high amounts of chemical reagents and a substantial amount of land. Considerable environmental damage has been caused in China by removal of clays without suitable remediation. In-situ leaching results in less visible impact but leaves the ground rich in sulphate from the use of the ammonium sulphate exchange reagent.

4.6 Other by-product sources – bauxite and phosphate

Bauxite and apatite deposits are also of interest as sources of REE because even though their concentrations of REE are low (usually ppm levels), such large amounts of material are processed that useful quantities of REE may be produced at the same time. Historically, much of REE production has been a by-product of other ores. Monazite from mineral sands is a by-product of titanium and zirconium minerals. Even at Bayan Obo, China, the bastnäsite-(Ce) has always been a by-product of iron ore mining. This has now finished but and it is the bastnäsite-(Ce)-rich waste piles that are being reworked. There has been much research on producing REE from red mud waste. It may also be possible to extract REE partway through the first bauxite treatment in aluminium production (Figure 5). Likewise, small amounts of REE in the huge amounts of apatite mined for fertiliser production each year, if extracted could amount to a significant proportion of the ca. 140 000 tonnes per year needed. Processing routes are rather different from conventional deposits (Figure 5) but most of the usual process mineralogy challenges apply, and are joined by a need to follow the through production plants. In phosphate production for example, the REE split into different fractions. REE concentrations and host mineralogy will vary through bauxite deposits. As described in section 3, apatite REE contents are variable. Sedimentary phosphorites have only ppm concentrations of REE but alkaline igneous rocks, such as the World's largest igneous apatite producer at Khibiny, Kola Peninsula, Russia can have over a wt% REE in its apatite. Production using a nitric acid process rather than the much more common sulphuric acid route is for extracting REE. Using sulphuric acid means that the REE mostly report to the phosphogypsum waste.

5.   Comparison of deposits

The diversity of REE minerals and rocks gives a wide range of characteristics for processing that lead to various advantages and disadvantages for each deposit (Wall et al., 2017 and Table 2). Comparisons may be made more quantitative by using a life cycle assessment approach (Weng et al., 2016; Pell et al., 2017) and this can be used during deposit development in combination with process mineralogy to ensure that the economic and environmental performance is optimised (Wall et al., 2017).

6.   **Conclusions**

Mineralogical and geological controls on the process mineralogy of REE vary such that there is no 'perfect' deposit. Mineral sands have the simplest processing routes but their monazite

is too radioactive. Alkaline rocks have the most diverse and complex mineralogy but this is compensated by their proportions of heavy REE and potential for physical beneficiation. Carbonatites are less complex and tend to have higher grades but REE fluorcarbonates and carbonates can have fine-grained textures that make liberation impossible. Ion adsorption clay deposits do not require beneficiation steps before leaching. Their disadvantage is the low grade and often shallow depth that requires significant land use or a new, environmentally-friendly in-situ leaching protocol.

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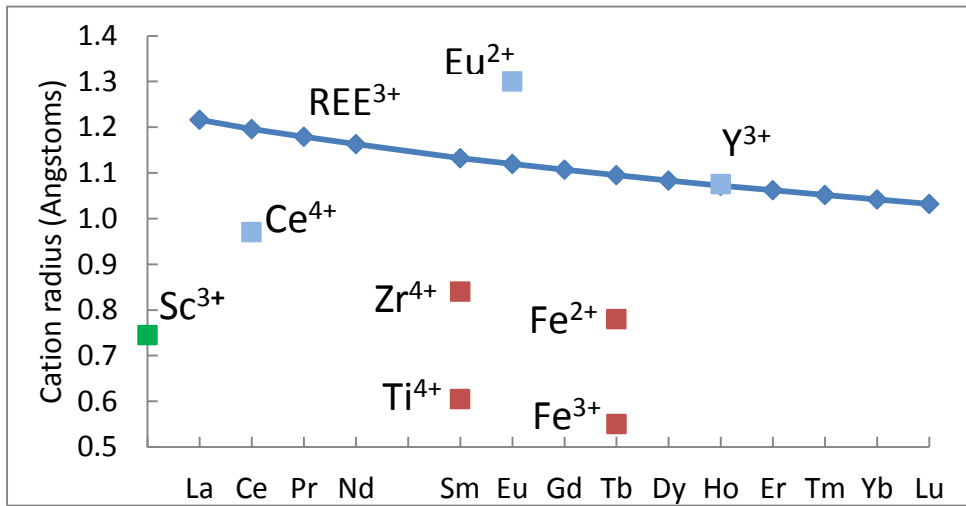   monazite geochronology. *Contributions to Mineral Petrology 137, 351-363.*

Figure 1 The lanthanide contraction - smooth variation in cation radii of the +3 REE cations, La through to Lu and Y, compared with the larger and smaller Eu^{2+} and Ce^{4+} cations and the much smaller Sc^{3+} cation is key to understanding REE distribution in minerals. Sc is more likely to substitute into minerals containing Zr, Ti, Fe than to partition with the other REE. Zr, Ti and Fe are plotted at arbitrary positions on the x axis. Graph from Siegfried et al. (2018).
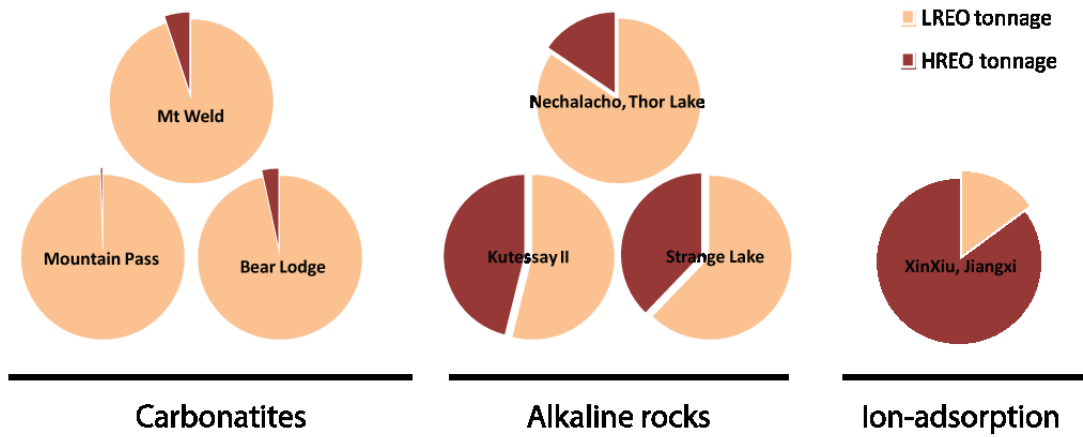
Figure 2 Proportions of light and heavy REE in a selection of carbonatite and alkaline rock deposits and one ion adsorption clay deposit. In general, carbonatites tend to be most rich in the light REE (La, Ce, Nd, Pr), whereas alkaline rocks have higher proportions of the beavy REE. Some of the Chinese ion adsorption clays have very high proportions of heavy REE although most ion adsorption clay deposits are not as extreme as the one shown here.
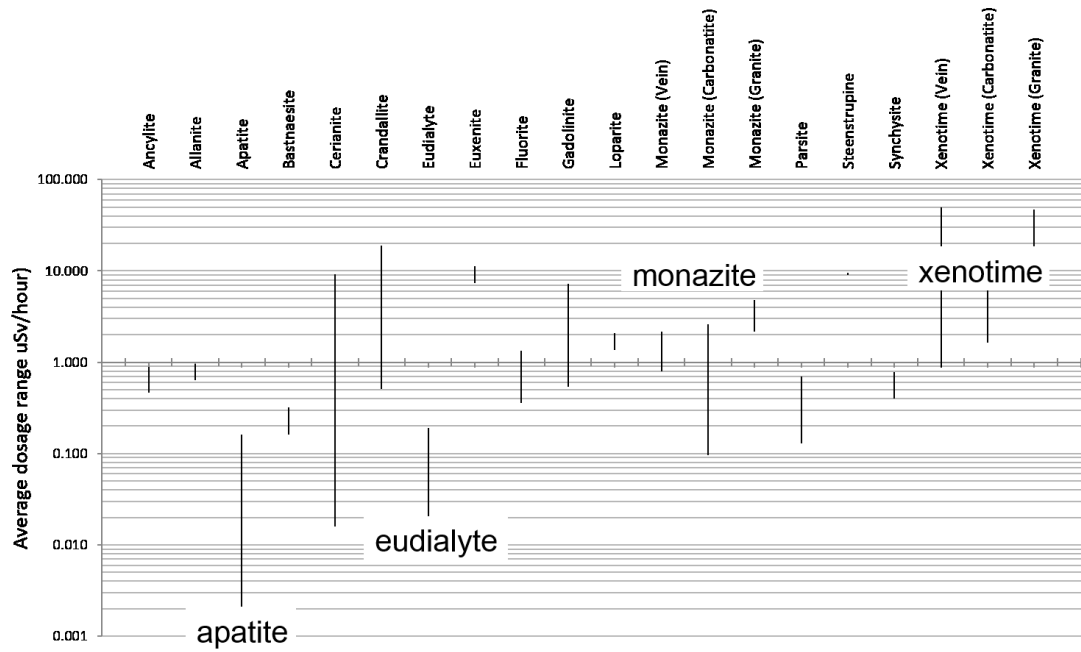
Figure 3 Radioactivity of rare earth minerals (1 kg concentrate). Calculated by Jon O'Callaghan using calculations from Rad-Pro Calculator© software. Data from Zacek et al. 2009; Fujino et al. 2000; Mariano 1989; Sal'nikova et al. 2010; Graham 1955; Wall 2000; Jerden & Sinha 2006; Steenfelt & Bohse 1975 Melnik et al. 2003; Skoda & Novak 1978; Smellie et al. 1978; Raslan 2009; Demartin 1993; Segalstad & Larsen 1978; Kogarko 2002 Zhu & O'Nions 1999; Wall et al. 2008; Ekambaram et al. 1986; Makovicky 1980; Sorensen & Lundgaard 1966; Forster 2000; Wark & Millar 1993; Wall & Zaitzev 2008;Forster 1998

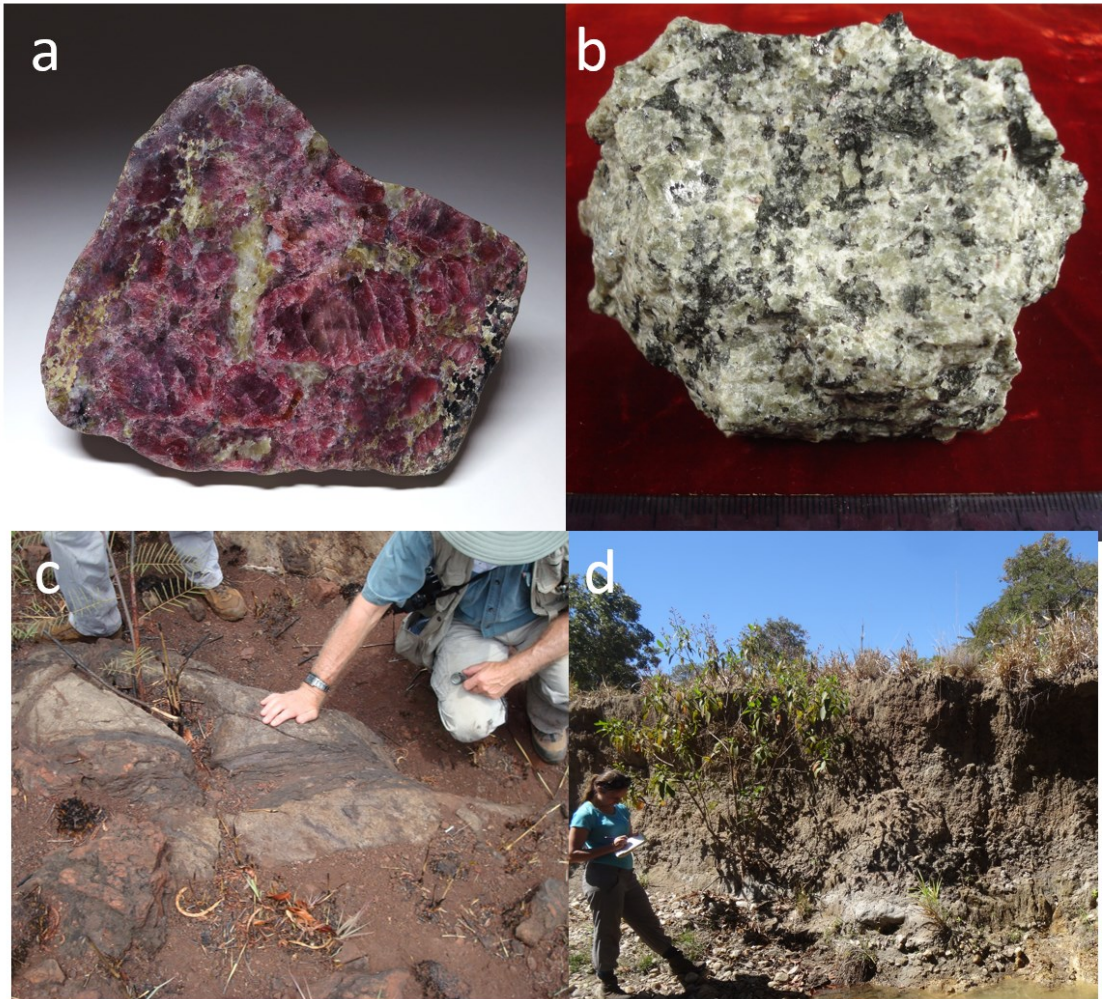Figure 4 Images of rare earth deposits. (a) Red eudialyte in nepheline syenite pegmatite, Canada (specimen is ca. 10 cm wide) (b) loparite-bearing nepheline syenite, Lovozero, Kola Peninsula, Russia (c) cross-cutting dykes and veins of synchysite-(Ce) and apatite-bearing carbonatite, Songwe Hill, Malawi (d) saprolitic weathered granite containing a horizon with REE adsorbed onto kaolinite, Serra Dourada, Brazil.

	MINING	PHYSICAL PROCESSING e.g. density, magnetic	FLOTATION	DISSOLUTION (CRACKING)	SEPARATION OF INDIVIDUAL REE	WASTE
CARBONATITE-RELATED DEPOSITS (FRESH ROCK)	Open pit	Rarely applicable on its own, might be first stage or used for monazite.	Usually required (REE fluorcarbonates).	Well established techniques of acid dissolution	Multistage Solvent Exchange	Th – lower than mineral sands
WEATHERED/ALTERED CARBONATITE	Open pit	Rarely applicable on its own, might be first stage	Usually required for fine, intergrown minerals (monazite)	Well established techniques of acid dissolution		Th usually lower than in fresh rock deposits
ALKALINE ROCKS	Open pit (Lovozero underground)	Variable used for some deposits	Variable used for some deposits	Unproven on operating mines for many of the minerals		U, Th variable, low in eudialyte
MINERAL SANDS	Open pit/dredge	Routine methods, compatible with production Ti, Zr minerals	Not needed	Well established processes for monazite		Highest Th
ION ADSORPTION CLAYS	Open pit or in situ leaching			Cation exchange with ammonium sulphate		Ammonium cations in clay after in situ leach
PHOSPHATE	Usually open pit, with main commodity			Needs in-line chemical process to remove REE		Phosphogypsum
BAUXITE						Red mud
RED MUD	Remining waste			REE removed directly by dissolution		Red mud
		Mineral concentrate		Mixed REE oxide/ carbonate/ oxalate	Separate REE oxide or metals e.g. La$_2$O$_3$	Th,U-bearing processing waste

Figure 5 Summary of mining and processing of the main types of rare earth deposits.

Table 1 REE minerals and REE-bearing minerals important in REE ore deposits

Name	Formula	Wt% REE	Th, U	Other REE species	Usual processing method
CARBONATES AND FLUORCARBONATES					
ancylite-(Ce)	$CeSr(CO_3)_2(OH)\cdot H_2O$	43		La	GM or F
bastnäsite-(Ce)	$CeCO_3F$	75		La,Nd,Y	F
parisite-(Ce)	$CaCe_2(CO_3)_3F_2$	50		Nd	F
synchysite-(Ce)	$CaCe(CO_3)_2F$	51		Nd,Y	F
PHOSPHATES					
cheralite*	$CaTh(PO_4)_2$	s.s. mon.	H	-	-
churchite-(Y)	$Y(PO_4).2H_2O$	51	V	-	-
fluorapatite*	$Ca_5(PO_4)_3F$	v	L	-	F
florencite-(Ce)	$CeAl_3(PO_4)_2(OH)_6$	32	V	La,Nd	-
huttonite*	$ThSiO_4$	v	H	-	-
thorite*	$ThSiO_4$	v	H	-	-
monazite-(Ce)	$Ce(PO_4)$	70	V	La,Nd,Sm	GM or F
xenotime-(Y)	$Y(PO_4)$	61	V	Yb	GME or F
OXIDES					
aeschynite-(Ce)	$(Ce,Ca,Fe,Th)(Ti,Nb)_2(O,OH)_4$	32	V	Nd,Y	-
cerianite-(Ce)	CeO_2	100	V	-	-
loparite-(Ce)	$(Na,Ce,Sr)(Ce,Th)(Ti,Nb)_2O_6$	30	V	-	GM
SILICATES					
allanite-(Ce)	${CaCe}{Al_2Fe^{2+}}(Si_2O_7)(SiO_4)O(OH)$	38	V		M
britholite-(Ce)	$(Ce,Ca)_5(SiO_4)_3OH$	e.g. 23	V		-
eudialyte*	$Na_{15}Ca_6Fe_3Zr_3Si(Si_{25}O_{73})(O,OH,H_2O)_3(Cl,OH)_2$	e.g. 9	L		M
fergusonite-(Ce)	$(Ce,La,Nd)NbO_4$	53	-?	Nd,Y	-
gadolinite-(Ce)	$(Ce,La,Nd,Y)_2Fe^{2+}Be_2Si_2O_{10}$	60	V	Nd,Y	-
gerenite-(Y)	$(Ca,Na)_2(Y,REE)_3Si_6O_{18}\cdot 2H_2O$	44	-	-	-
kainosite-(Y)	$Ca_2Y_2(SiO_3)_4(CO_3).H_2O$	38	-	-	-
keiviite-(Y)	$Y_2Si_2O_7$	69	-	Yb	-
steenstrupine-(Ce)	$Na_{14}Ce_6Mn_2Fe_2Zr(PO_4)_7Si_{12}O_{36}(OH)_2\cdot 3H_2O$	31	H	-	F
zircon*	$ZrSiO_4$	<1	V	-	GME
FLUORIDES					
fluorite*	CaF_2	Y for Ca	L	-	F

| fluocerite-(Ce) | CeF$_3$ | 83 | - | - | - |

The most common minerals that are current REE ore minerals are marked in bold. Formulae are from www.mindat.org based on the International Mineralogical Association approved formulae. These use only the dominant REE in the mineral name, i.e CeCO$_3$F for bastnäsite-(Ce). In practice, a light REE mineral that contains dominant Ce in a +3 valence crystallographic site, will also contain significant La, Pr and Nd, i.e. (Ce,La,Nd,Pr)CO$_3$F for bastnäsite-(Ce). Minerals that contain Ce^{4+}, such as cerianite will not contain the other light REE.Y minerals will also contain wt% values of Gd, Dy, Er, Yb.

*indicates minerals that do not contain a REE as an essential predominant constituent in any site but commonly contain REE. Some are important REE ore minerals.

F = flotation, GME = combination of gravity, magnetic and electrostatic processes.

U, Th contents: M = usually has major (wt%) Th, V – Th and U are variable from <1wt% to major (e.g. 10wt%) amounts. Other minerals usually only have <1wt% Th, U but almost all will contain trace quantities of these elements.

Table 2 Examples of REE deposits and qualitative analysis of their mining and processing characteristics from Wall et al. (2017). Characteristics shaded green and in bold are generally advantageous to responsible sourcing, grey are less so and unshaded cells are less favourable.

Ore type	Energy for crushing and grinding	Grain size/ Difficulty of beneficiation	Chemicals (acid, flotation reagent)	Radioactivity: ore mineral and host rock	Amount of rock to be moved*	By-products
Carbonatite	Med.- High	Variable – 10 μm	Flotation - medium	Medium	**Low**	Not usually
Weathered carbonatite	Medium	10 μm and finer	Flotation - medium	**Low-med.**	**Low**	Not usually
Alkaline rock	High	Variable - 1 μm and larger	Variable	Variable	High	Co-products common
Ion adsorption clay (in-situ leaching)	**None**	**Beneficiation not needed**	Leaching, so can be high	**Low**	**Low**	None
Mineral sand (placer)	**None-Low**	**10 – 100 μm**	**Low**	High	High	**from TiO$_2$, zircon etc production**
By-product of igneous apatite	High	100 μm-mm	Medium	**Low**	High	**from fertiliser manufacture**
Red mud	Bauxite processing	**n/a REE from red mud**	Medium?	**Low**	High	**from Al production**

*i.e. low grade = large amount of rock