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The Critical West: raw materials and rare earths

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Abstract

Critical raw materials are defined as raw materials that are economically important but vulnerable to supply disruption. They are important now because we mine and use a wider range of elements than ever before. Digital and medical technologies, clean energy and electric vehicles are examples of applications that use the properties of particular materials. These high-technology applications often only need small amounts of raw material that can come from just a few mines in one or two countrie,s and hence the supply risk. The UK South West has the world's fourth largest deposit of the critical metal, tungsten, being mined at the Drakelands mine in Devon. The South West may also have potential for indium, as well as lithium and tin, which although not defined as 'critical' at the moment are also important high-technology raw materials. The UK Natural Environment Research Council funds a research programme called 'SoS Minerals' that is helping to find secure and environmentally-friendly solutions to critical metals supply for environmental technologies. Rare earth elements (REE) are perhaps the most famous critical metals. They have many use,s but supply is dominated by China. The geochemistry of REE is controlled by the lanthanide contraction, which results in the 15 REE almost always being associated with each other, but undergoing a smooth fractionation of light from heavy members of the series. The SoS RARE project is researching how light and heavy REE are transported and concentrated, including working on carbonatites in Malawi and Namibia, in order to help exploration companies target the REE that are needed the most. There are many different types of REE deposit to choose from and besides working to help make exploration and processing of carbonatites and alkaline rocks more efficient, SoS RARE is working to understand how REE are concentrated in ion-adsorption clay deposits and how they may be extracted in an environmentally friendly way. If this can be achieved, they could provide a low-impact way to produce REE in the future.

Introduction

This article considers the need for raw materials and the relatively new concept of 'critical raw materials', using the rare earth elements (REE) as particular examples. It takes a worldwide view, but will show that there is particular interest in this topic area in south-west England, both in leading research and in critical raw materials of our own in the region.

New technologies use an increasingly wider range of elements in their manufacture. A century ago the main metals used were iron, copper, gold and silver; now it takes 60 different elements to manufacture a modern computer chip (Graedel *et al.* 2015). In the Periodic Table of the elements (Fig. 1) there are some that are easy to recognise as commodities that are mined. For example the first row of the transition metals includes iron, zinc and copper. Aluminium will be familiar and tin is a famous metal in the south-west of England. Most of the other elements also have commercial uses. Some of these are small volume and specialist

uses, but nevertheless, particular elements do the job better than any of the others. For example, a coating of indium tin oxide makes all of our touch screens on digital devices work, tantalum is an ingredient of small capacitors in electronics, including mobile phones, and platinum is an essential ingredient of catalytic converters in cars. Geologists now have an opportunity to work on a much more diverse range of these more unusual elements and this has signalled a change for people who are interested in ore deposits.

Critical raw materials — rare earth elements

A prime example of the use of specialist metals in digital and green technologies is that of the rare earth elements (REE). These consist, according to the International Union of Pure and Applied Chemistry (IUPAC), of 17 elements: lanthanum (La) to lutetium (Lu) (the lanthanoids) plus yttrium (Y) and also scandium (Sc) (Fig. 1). Scandium actually behaves geologically rather differently to the other REE, so is not considered further here. Promethium (Pm) has no long-lived isotopes and does not exist to any appreciable extent in nature, so this gives a group of 15 elements.

There are many applications of REE (Hatch 2012), including many in close proximity to us all the time. Examples include: direct drive motors in large wind turbines and electric cars, nickel metal hydride batteries in hybrid cars, catalytic converters, catalysts used in petroleum refining, lasers, MRI medical imaging, fluorescence is medicine, cancer therapies, anti-forgery marks on bank notes, self-cleaning ovens, low-energy lighting, and computer hard disk drives, phosphors in computer and TV screens and voice coil motors (speakers) in mobile phones. Most of these uses rely on just one element of the rare earth series and many rely on neodymium (Nd) in the form of neodymium iron boron permanent magnets, which are the strongest permanent magnets made. Most of the applications do not use very much of any of the REE, usually only a few pence worth. The main exception to

Figure 1 Periodic Table: brown = Scandium, yttrium and the lanthanides (lanthanoids), which together comprise the rare earth elements (REE); blue = critical metals, tungsten and indium, that occur in Cornwall and Devon; purple = other elements that occur in Cornwall and Devon and are discussed in this article: lithium, tin and copper.

Figure 2 Location of the world's main REE mines. The largest mine, which provides the majority of the light REE, is Bayan Obo, Inner Mongolia, China. Almost all of the world's heavy REE come from ion-adsorption deposits in southern China. There are smaller mines for light REE at Weishan and Maoniuping/Dalucao China. The main REE source outside of China is the carbonatite mine at Mt Weld, Western Australia, which refines its monazite ore in Malaysia. The mineral, loparite, is mined from nepheline syenite rock at Lovozero, Kola Peninsula, Russia as a source of niobium with REE as a by-product. India produces REE from monazite recovered from mineral sands along its coasts.

these very low levels of REE is the amount of REE needed for large, offshore wind turbines. A Siemens D6 wind turbine has blades the size of an A380 airplane and can use half a ton per megawatt of wind turbine power. In most cases, it is not that REE are valuable in terms of money, but that they are essential for functionality. In almost every application, the REE are the only thing that will do the job. Without them, that application — the car motor, the catalyst, the medical application, the smartphone — will not work. They cannot be easily substituted by other materials and that is why they have become so important in our everyday lives. Despite all of their uses, only 126,000 tons of REE where mined worldwide in 2016 (U.S. Geological Survey 2017). For comparison, this figure is over one hundred times *lower* than the 19.4 million tons of copper produced in 2016 (U.S. Geological Survey 2017).

So what is the problem; this all seems like good news, with interesting elements doing wonderful things, and still only needed in small amounts? The problem is that practically all the REE that are mined in the world are coming out just one country, and that country is China. China has the largest mine producing REE and it is no coincidence that they dominate the REE market. There is a plaque in Baotou, Inner Mongolia, China with words by the former Chinese premier, Deng Xiaoping, in 1992, "There is oil in the Middle East, there is rare earth in China". As China produced REE from the world's largest mine at Bayan Obo in Inner Mongolia, the rest of world was content to buy the resulting REE products at conveniently low prices. China established dominance over the whole REE manufacturing supply chain. Life went on as normal elsewhere, until in 2010 China reduced export quotas of REE by 40% and prices rose dramatically. In 2011 there was a diplomatic incident in the South China Sea when a Japanese patrol boat collided with a Chinese trawler (Hatch 2012) and this story made news headlines. Prices of REE

went 'sky high' as users tried to secure their supply and governments started inquiries about how they had become so reliant on China. Exploration companies raced to find new and alternative supplies, and manufacturing companies tried to find raw materials to substitute for REE. Two REE mines have opened up since 2010: one, at Mountain Pass , USA, had been the world's main supplier of REE before Chinese dominance and re-opened, but went bankrupt and was forced to close again in 2015; and Mt Weld in Western Australia finally came into production, some 20 years after first exploration and development work. It can often take 10 years from first exploration of any type of ore deposit to opening a mine, so raw materials production is not very flexible in coping with changing demand. By 2014 the World Trade Organisation ruled that China had to remove quotas, which was done in 2015, and by 2017 prices are back to where they were in 2010; and, many exploration projects have come to an end. China still dominates REE supply (Fig. 2) and we will see what happens next.

The story of REE illustrates the problem of what are now called 'critical' raw materials. These are defined as raw materials that are economically important but at potential risk of supply disruption. There has been a variety of studies and measures of criticality. One of the best known was done by the European Commission and first published in 2010, updated in 2014 (European Commission 2014). In Figure 3 the economic importance goes on the x-axis and supply risk on the y-axis. The units are arbitrary and the values are calculated by a methodology to calculate the benefit these raw materials have for the European manufacturing economy and supply risk from concentration of supply from countries with poor governance, less the potential for recycling and substitution. So copper, for example, is economically important, but with many suppliers around the world in lots of different countries (Fig. 4, *opposite*), it is not critical. If one country stopped supplying copper, there are plenty of other options. The amount of recycling is also higher than for other

Figure 3 A schematic graph of criticality based on the European Commission (2014) criticality assessment and showing the current positions of rare earth elements, plus copper for comparison, and four metals associated with South West England: tungsten, indium, lithium and tin. There are no units for the axes and the exact position of the threshold between critical and non-critical raw materials does not have a fixed value; each study decides where to make the divide.
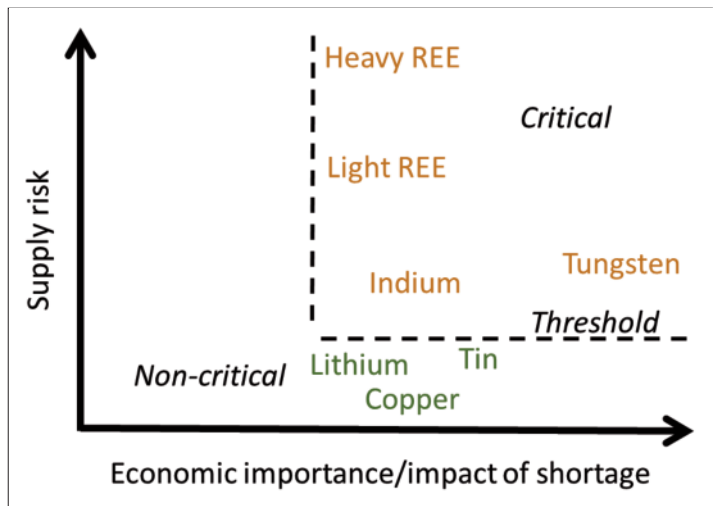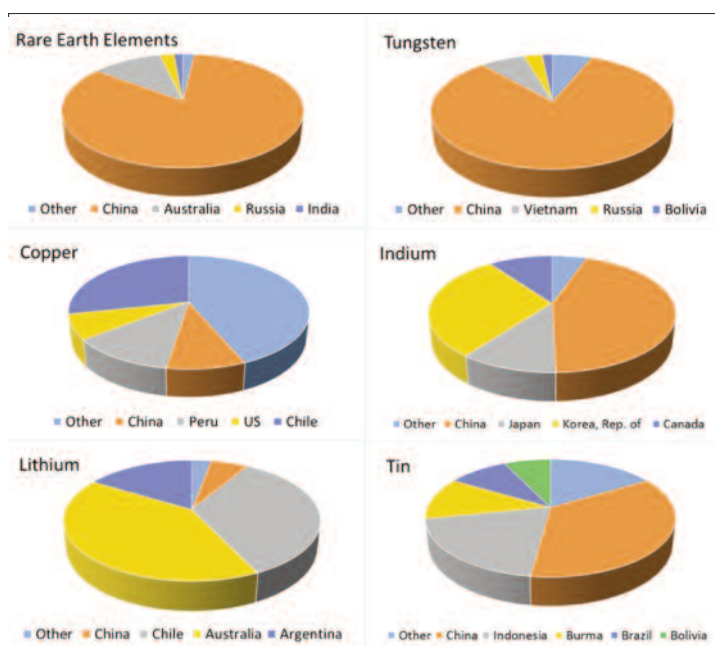
Figure 4 Countries that supply a selection of raw materials, including copper and REE for comparison of a major and critical commodity; three commodities required for high-technology applications, for which there is potential in Devon and Cornwall: tungsten, indium and lithium; and a plot of the volume of copper mined compared to the four minor metals. Mineral statistics are from U.S. Geological Survey (2017).

more specialist metals. At the moment, 20 raw materials are defined as critical raw materials for Europe. Other studies of criticality might relate to different countries or more specific uses, or have different methodologies and thus produce different lists of critical raw materials. The grouping will also change over time. In 2010, the EC listed 14 critical raw materials; in its new study in 2014, it increased this number to 20.

The British Geological Survey has taken a slightly different view to that of the EC, and published a 'risk list' (British Geological Survey 2015; *see* Table 1) that considers seven criteria: production concentration, reserve distribution, recycling rate, substitutability, governance in the countries that are the main producer and main reserve holder, and companion metal fraction (a measure of whether the material is a by-product and thus supply controlled by another commodity). Again, REE top the list because of the dominance of China, and the next four elements are also specialist and minor raw materials for which supply is dominated by China. Gold,is at the bottom of the table because it has many sources and no supply risk is perceived; likewise, for other major commodities such as copper, titanium, zinc and aluminium. In general, it is the specialist raw materials produced in small amounts that are most vulnerable to being critical.

Critical and high technology raw materials in South West England

South West England does not have REE deposits, but hosts potential deposits of some other elements that are on the critical lists. The Drakelands mine at Hemerdon near Plymouth (Wolf Minerals 2017) is the World's fourth largest deposit of the critical metal, tungsten, needed for hard materials in many cutting tools in manufacturing (Brown and Pitfield 2014). Like the REE, supply is dominated by China (Fig. 4), and so although it has received significantly less press coverage, it is still extremely important (Fig. 3). The tungsten occurs as wolframite associated with greisen mineralisation in a large granite dyke, just south of but separate from the Dartmoor granite (British Geological Survey 2011a).

Indium (In) is also classed as a critical raw material for Europe (Fig. 3; European Commission 2014). Nearly half of all production goes into making indium tin oxide for computers, phones and other touch screen applications. Although the production looks more diverse than REE and tungsten (Fig. 4), the problem is that In rarely forms its own minerals and there are no indium mines (Schwarz-Schampera,2014). Instead, In substitutes into other sulphide minerals, especially the zinc sulphide, sphalerite. It is only produced as a by-product when the sphalerite, and more rarely copper and tin, ore is refined by smelting, and this increases the supply risk. Significant levels of In have been found around the granites in Cornwall and Devon., located in the sulphide portions of granite-related skarn and vein systems, following highest concentrations of tin but hosted by chalcopyrite and sphalerite (Andersen *et al.* 2016). Although there are no active exploration projects at the moment, this could be of interest in the future.

Lithium (Li) is another specialist metal that may have potential deposits in Cornwall and Devon. It is just outside the critical category at the moment because there are Li mines in several countries, with notable sources from continental brines (salars) in South America and pegmatites such as Greenbushes in Western Australia (Evans *et al.* 2014; Figs 3 and 4). However, if Li continues to be used as the material of choice for lithium ion batteries in electric vehicles, much larger amounts will need to be mined. Potential sources in the South West UK are the reprocessing of Li-bearing micas from china clay processing waste (e.g. Siame and Pascoe 2011; British Geological Survey 2016), and extracting Li from underground brines in granite and related areas (Beer *et al.* 1978; *TheGuardian* 2017).

Tin is perhaps the most famous metal associated with South West England, and this has been calculated as important, but just outside the critical category for Europe (Fig. 3), with a reasonable diversity of sources, including China and Indonesia as the major providers (Fig. 4); and higher levels of recycling than the very specialist metals.

Table 1 A sample of the British Geological Survey Risk List 2015, showing the top five highest-risk elements (1–5, red) and bottom five lowest risk elements (36–40, green)

No.	name		risk	Country	No.	name		risk	country
1	Rare earths	REE	9.5	China	36	Titanium	Ti	4.8	Canada
2	Antimony	Sb	9.0	China	37	Copper	Cu	4.8	Chile
3	Bismuth	Bi	8.8	China	38	Zinc	Zn	4.8	China
4	Germanium	Ge	8.6	China	39	Aluminium	Al	4.8	Australia
5	Vanadium	V	8.6	China	40	Gold	Au	4.5	China

UK research on security of supply of critical raw materials

There are various strategies to overcome the problem of criticality. One solution is to try to substitute another material for the critical raw material. The problem is that by definition, critical raw materials are difficult to substitute. Manufacturers who can use alternatives will do so as soon as the price rises, and if others are encouraged to substitute, this can actually increase the problem of criticality for the remaining users. A second idea, is the obvious point that once a material has been mined, it should be kept in circulation by re-use and then by recycling. Not only is this resource efficient, it is also a good way to diversify supply. Unfortunately, it is also very difficult for many materials. In many applications, the components using the critical raw materials are complex and too expensive to recycle to recover the small amounts involved, and are thus low-value critical raw materials. A third solution is the geological one of providing additional, diverse and secure new deposits for primary raw materials supply. In the UK, the Natural Environment Research Council, and the Engineering and Physical Sciences and Research Council have sponsored a research programme called 'Security of Supply of Minerals' (www.bgs.ac.uk/sosminerals/). There are four large projects in the programme and each consortium has *c.* £2.5 million of research council support, plus additional resources from industry partners and international collaborators. Each consortium in the programme is tackling two goals. The first is to understand how the critical raw materials are concentrated in order to improve exploration targeting, and the second is to make mining and processing more efficient and environmentally friendly.

One of the research projects is called 'SoS RARE' and concentrates on the REE. The others centre on cobalt (CoG3), tellurium and selenium (TEaSE) and deep-sea minerals (MarineE-tech). Research is done in large collaborative teams, divided into work packages to make manageable units (Fig. 5). Most large projects also have international participants, for example, colleagues from Germany, Canada, South Africa, Japan, Czech Republic and even China are involved in SoS RARE, as these countries are also

Figure 5 Structure of the SoS RARE project on 'Multidisciplinary research towards a secure and environmentally sustainable supply of critical rare earth elements (Nd and HREE)'. The project consortium has 17 academic investigators at 6 UK research organisations, plus 7 post-doctoral scientists, 6 PhD students, 8 overseas collaborators and 10 industry partners (www.sosrare.org).
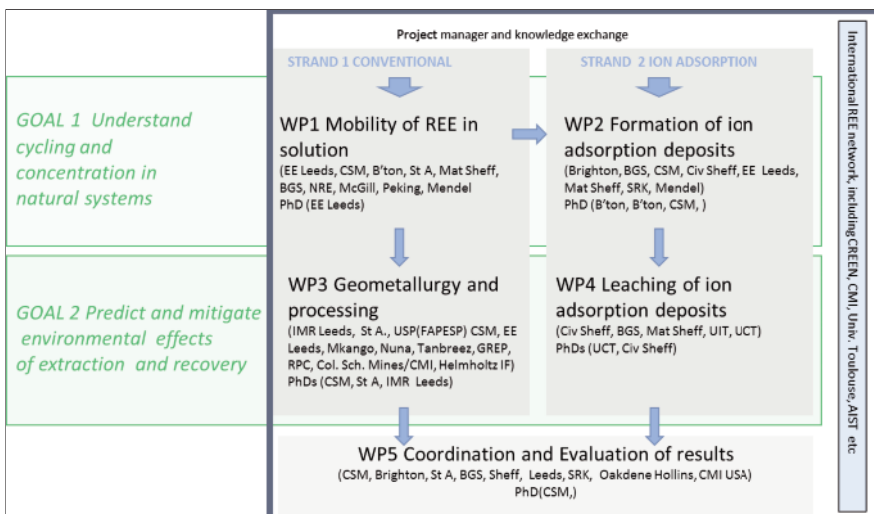
industry partners who support the research and will benefit directly from it.

The SoS RARE project is helping the search for new supplies of REE by working on how fluids concentrate heavy and light REE so that it is possible to predict better when to search for neodymium and the heavy REE, which are the most in demand at the moment. Geological and mineralogical work is combined closely with work on minerals processing to concentrate the REE minerals and to dissolve and separate REE. This is a crucial energy-intensive stage where there is great potential for making the extraction process more environmentally friendly. As part of the quest for environmentally-friendly ores, the project is examining, in its Strand 2, the formation and processing of a group of REE deposits called 'ion adsorption' deposits (*see below)*, to try to understand where else besides China these deposits form and to establish if there is potential for more environmentally-friendly ways to extract the REE.

REE geochemistry

The geochemistry of the REE is controlled by the smooth variation in size of the REE^{3+} cations found in nature, which is largest for the low atomic number REE, lanthanum (La), and then becomes progressively smaller as the atomic number increased to lutetium (Lu). This is counter intuitive and called the 'lanthanide contraction' (Fig. 6, *opposite*). Yttrium is the same cation charge and size as holmium. This close relationship in size and charge means that the REE are always found together in nature; but given the change in size from La to Lu, there is a gentle fractionation between the light (lowest atomic number) and heavy (highest atomic number) REE. Nature makes its division between light and heavy REE at gadolinium (Gd), where the structure of REE phosphate minerals changes from monazite $(LREE)PO_4$ to xenotime $(HREE)PO_4$. There are two exceptions to this rule of gentle fractionation: in oxidising environments, cerium forms Ce^{4+} and in reducing environments, Europium can be most stable as Eu^{2+}. The change in oxidation state and cation size means that these two cations can be fractionated from the rest of the REE series. For economic geologists, the challenge is that apart from Ce and Eu, the REE never occur alone in nature. Neodymium is particularly sought after at the moment for use in neodymium iron boron permanent magnets, but there are no deposits of just Nd. A Nd deposit is always likely to contain much higher quantities of La and Ce than of Nd.

The diversity of REE deposits

REE in nature are a bit like REE in manufactured goods in that they are all around us but almost always in low quantities. This wide distribution at trace-element levels makes REE useful for many geological studies, for example, in modelling of fractionation of melts in igneous petrology.

Finding REE in quantities that are economic to mine is more difficult. However, REE are not particularly rare. Cerium, one of the light REE, is as abundant in the crust as copper, and even though the heavy REE have much lower abundances, they are still more abundant than silver (U.S. Geological Survey 2002). There is more good news in that there are many different geological environments that can potentially concentrate REE

Project manager and knowledge exchange

STRAND 1 CONVENTIONAL   STRAND 2 ION ADSORPTION

GOAL 1 Understand cycling and concentration in natural systems

WP1 Mobility of REE in solution
(EE Leeds, CSM, B'ton, St A, Mat Sheff, BGS, NRE, McGill, Peking, Mendel PhD (EE Leeds)

WP2 Formation of ion adsorption deposits
(Brighton, BGS, CSM, Civ Sheff, EE Leeds, Mat Sheff, SRK, Mendel PhD (B'ton, B'ton, CSM,)

GOAL 2 Predict and mitigate environmental effects of extraction and recovery

WP3 Geometallurgy and processing
(IMR Leeds, St A., USP(FAPESP) CSM, EE Leeds, Mkango, Nuna, Tanbreez, GREP, RPC, Col. Sch. Mines/CMI, Helmholtz IF) PhDs (CSM, St A, IMR Leeds)

WP4 Leaching of ion adsorption deposits
(Civ Sheff, BGS, Mat Sheff, UIT, UCT) PhDs (UCT, Civ Sheff)

WP5 Coordination and Evaluation of results
(CSM, Brighton, St A, BGS, Sheff, Leeds, SRK, Oakdene Hollins, CMI USA) PhD(CSM,)

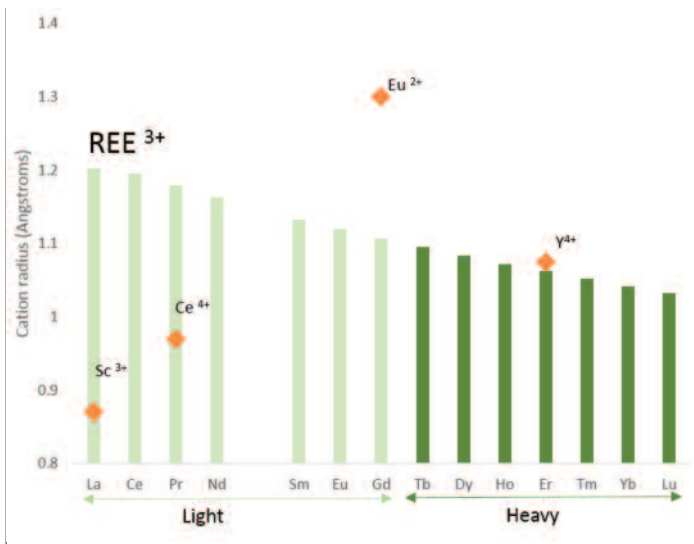International REE network, including CREEN, CMI, Univ. Toulouse, AIST etc

Figure 6 The lanthanide contraction, which controls the geochemical behaviour of REE. In nature the divide between light and heavy REE is between gadolinium (Gd) and terbium (Tb) where the REE phosphate mineral structure changes from monazite to xenotime. Chemists tend to put the divide between samarium (Sm) and Europium (Eu). Values for ionic radii are from Shannon (1976).

to create economic deposits (Fig. 7, *overleaf*). Reviews of REE ore deposits are given in British Geological Survey (2011a), Chakhmouradian and Wall (2012), Wall (2014), Goodenough *et al.* (2016), and Verplanck and Hitzman (2016).

The majority of deposits that are mined or under exploration are associated with carbonatites and alkaline rocks. These igneous rocks have some of the most unusual and diverse compositions of any rocks on Earth. Carbonatites are made of at least 50% carbonate, but nevertheless formed by crystallisation from molten magma and alkaline rocks, and silicate igneous rocks with higher sodium and potassium to silica ratios than most other igneous rock types. Both start off as small degree partial melts from the mantle, which is a first step in enriching them in REE. Further magma fractionation, and often hydrothermal processes — even lateritic weathering that removes soluble minerals and concentrates REE in residual minerals — serve to concentrate REE up to weight percent levels, at which point they may be economic to mine.

The oldest mined type of REE deposits are mineral sands, literally beach sands, in which the REE minerals, monazite-(Ce) and (in lesser quantities) xenotime-(Y) are concentrated along with other tough and heavy minerals such as rutile, ilmenite, magnetite and zircon in bands among quartz-rich beach sands. The deposits mined in India are formed by this process. Similar types of deposits that occur along rivers (alluvial) and have been preserved in the geological record (palaeoplacers) may also be of interest.

The deposits in China that provide the world's heavy REE are rather unusual in that they are weathered granitic rocks, in which the REE have been released from the original igneous and hydrothermal minerals and are now adsorbed onto the surface of clays, such as kaolinite, that formed during the weathering process. Adsorbed cations are not part of the mineral structure but are simply attracted to the surface of the mineral. This means that they can easily be leached out of the clays by ion exchange reagents. This can even be done by *in situ* mining. Given the higher prices paid for heavy REE, these kinds of deposits can contain REE grades as low as 500ppm.

There are also many other types of rocks that are being considered as potential REE resources, including several where there is no obvious connection to alkaline rocks or to carbonatites, but where hydrothermal fluids appear to have concentrated REE and deposits where REE concentrations are low but might be produced as by-products alongside the main commodity. These include phosphate deposits, mined as raw materials for fertiliser, and bauxite, the ore of aluminium.
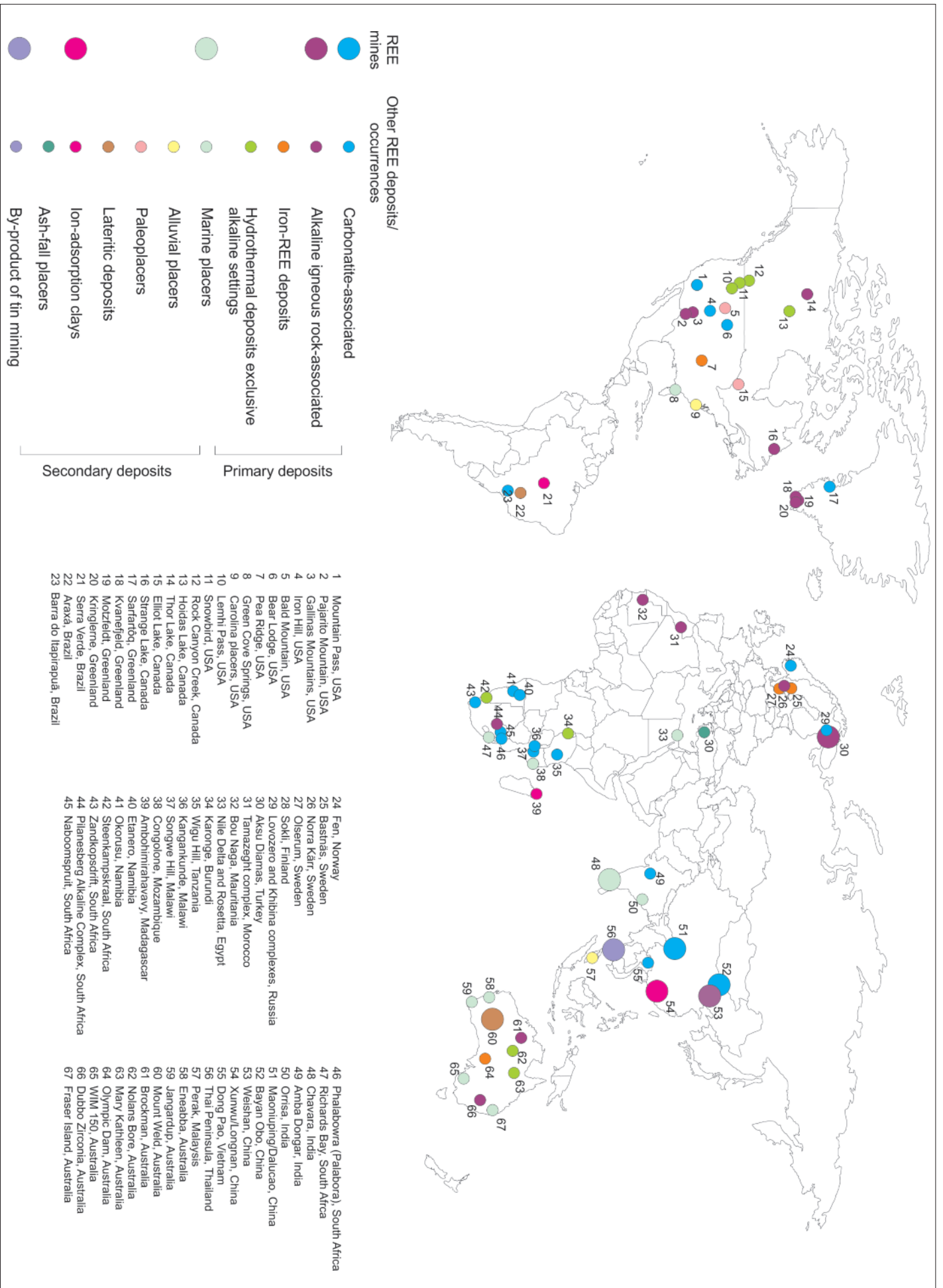
REE in carbonatites

The majority of working mines are connected in some way with the igneous rocks called carbonatites (Fig. 8). Carbonatites are intracontinental rocks, usually intruded into Precambrian crust and often formed associated with rift valleys (Woolley and Bailey 2012). Volcanic carbonatites, such as the natrocarbonatite lavas and ashes erupted form the only active carbonatite volcano at Oldoinyo Lengai, Tanzania rarely contain high concentrations of REE. The highest levels of REE are found in subvolcanic carbonatites, where the magma seems to have been most fractionated to cause the highest degree of enrichment. The concentration of REE can reach over 10 wt% in places as in some of the bastnäsite-bearing carbonatite at Mountain Pass, California (Castor 2008). In a number of cases, the REE are interpreted as having become concentrated in a fractionating

Figure 8 Carbonatite dyke at Lofdal, Namibia. Another carbonatite environment where heavy REE have been concentrated, forming xenotime-(Y), which is being studied as part of the SoS RARE project (Sam Broom-Fendley for scale).

Figure 7 Mines and deposits of rare earths. Contains British Geological Survey materials (© NERC [2011], see British Geological Survey 2011b). The lateritic deposits listed here are in weathered carbonatite.

REE mines

Other REE deposits/ occurrences

REE deposits/ occurrences

Carbonatite-associated

Alkaline igneous rock-associated

Iron-REE deposits

Hydrothermal deposits exclusive alkaline settings

Marine placers

Alluvial placers

Paleoplacers

Lateritic deposits

Ion-adsorption clays

Ash-fall placers

By-product of tin mining

Primary deposits

Secondary deposits

1 Mountain Pass, USA
2 Pajarito Mountain, USA
3 Gallinas Mountains, USA
4 Iron Hill, USA
5 Bald Mountain, USA
6 Bear Lodge, USA
7 Pea Ridge, USA
8 Green Cove Springs, USA
9 Carolina placers, USA
10 Lemhi Pass, USA
11 Snowbird, USA
12 Rock Canyon Creek, Canada
13 Hoidas Lake, Canada
14 Thor Lake, Canada
15 Elliot Lake, Canada
16 Strange Lake, Canada
17 Sarfartôq, Greenland
18 Kvanefjeld, Greenland
19 Motzfeldt, Greenland
20 Kringlerne, Greenland
21 Serra Verde, Brazil
22 Araxá, Brazil
23 Barra do Itapirapuã, Brazil

24 Fen, Norway
25 Bastnäs, Sweden
26 Norra Kärr, Sweden
27 Olserum, Sweden
28 Sokli, Finland
29 Lovozero and Khibina complexes, Russia
30 Aksu Diamas, Turkey
31 Tamazeght complex, Morocco
32 Bou Naga, Mauritania
33 Nile Delta and Rosetta, Egypt
34 Karonge, Burundi
35 Wigu Hill, Tanzania
36 Kangankunde, Malawi
37 Songwe Hill, Malawi
38 Congolone, Mozambique
39 Ambohimirahavavy, Madagascar
40 Etanero, Namibia
41 Okorusu, Namibia
42 Steenkampskraal, South Africa
43 Zandkopsdrift, South Africa
44 Pilanesberg Alkaline Complex, South Africa
45 Naboomspruit, South Africa

46 Phalabowra (Palabora), South Africa
47 Richards Bay, South Africa
48 Chavara, India
49 Amba Dongar, India
50 Orrisa, India
51 Maoniuping/Dalucao, China
52 Bayan Obo, China
53 Weishan, China
54 Xunwu/Longnan, China
55 Dong Pao, Vietnam
56 Thai Peninsula, Thailand
57 Perak, Malaysis
58 Eneabba, Australia
59 Jangardup, Australia
60 Mount Weld, Australia
61 Brockman, Australia
62 Nolans Bore, Australia
63 Mary Kathleen, Australia
64 Olympic Dam, Australia
65 WIM 150, Australia
66 Dubbo Zirconia, Australia
67 Fraser Island, Australia

36

magma, but then precipitated right at the final stages of crystallisation, in transition environments between magma and hydrothermal fluid, where unidirectional textures suggest a pegmatite-like environment of formation (Fig. 9). Although at first glance the crystals look big, they have usually been altered by hydrothermal fluids derived from the magma and are now pseudomorphed by a fine-grained, mixed assemblage of minerals such as monazite-(Ce), strontianite and baryte.

In the SoS RARE project, we are particularly interested in learning about environments in which the heavy REE can be concentrated. Such environments are rare in carbonatites because the processes of partial melting and igneous fractionation all tend to preferentially concentrate the light REE. However, it has been found that where hydrothermal alteration has been pervasive, such that it has changed the nature of original minerals, such as apatite, as in the Songwe Hill carbonatite, Malawi, with the right fluids, temperatures and mineral components it is possible to produce higher concentrations of the sought after heavy REE (Broom-Fendley *et al.* 2017).

The challenge of processing REE deposits

Finding rocks with high enough concentrations to make them economical to mine is just the start of the story. A particular challenge is finding efficient and environmentally-friendly ways to extract the REE minerals from the ore and the individual REE from the minerals. The crystallisation textures of REE minerals can be complex, with small crystals and fine intergrowths (Fig. 10; Wall 2014). Little research on minerals processing of REE deposits was done until the surge in exploration interest from 2010, and many minerals that now form potential ore deposits have never been commercially mined and processed (Table 2; Jordens *et al.* 2013; Krishnamurthy and Gupta 2016; Cui and Anderson 2016). Even where processing routes are well established, it is necessary to do detailed mineralogical and geometallurgical work (connecting geology to minerals processing behaviour) before it is possible to design an efficient processing method. Processes for bastnäsite and monazite have been well

Figure 9 Unidirectional crystallisation textures (nucleation centre top-left and centre towards lower-left) shown by pseudomorphs of green monazite-(Ce), strontianite, baryte (both white) in ferroan dolomite carbonatite, Kangankunde, Malawi (width of picture c. *60mm).*
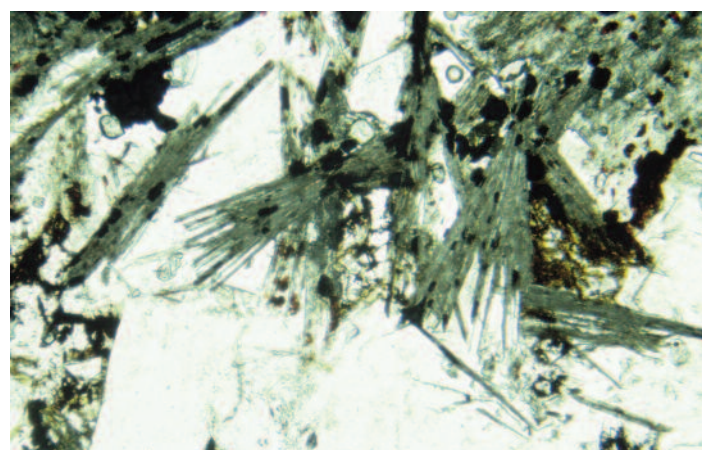

Figure 10 Photomicrograph of sheaves of bastnäsite-(Ce) needles in quartz-bearing carbonatite, Kangankunde, Malawi (Wall 2000), in plane polarised light (width of image c. *0.6mm).*

Table 2 Minerals in REE ore deposits and established processing techniques

mineral	*formula*	*processing techniques used*
processing techniques well-established		
bastnäsite-(Ce)	$CeCO_3F$	flotation
monazite-(Ce)	$CePO_4$	flotation or gravity/electrostatic/magnetitc
xenotime-(Y)	YPO_4	gravity/electrostatic/magnetic (flotation)
loparite-(Ce)	$(Na,Ce,Sr)(Ce,Th)(Ti,Nb)_2O_6$	gravity / magnetic[1]
apatite	$Ca_5(PO_4)_3F$	flotation
minerals similar to bastnäsite so processing likely to be similar		
parisite-(Ce)	$CaCe_2(CO_3)_3F_2$	flotation
synchysite-(Ce)	$CaCe(CO_3)_2F$	flotation
minerals not yet concentrated in commercial operations		
ancylite-(Ce)	$SrCe(CO_3)_2(OH) H_2O$	scrubbing, acid dissolutio
eudialyte	$Na_{15}Ca_6Fe_3Zr_3Si(Si_{25}O_{73})(O,OH,H_2O)_3(Cl,OH)_2$	flotation[2]
steenstrupine-Ce)	$Na_{14}Ce_6Mn_2Fe_2Zr(PO_4)_7Si_{12}O_{36}(OH)_2 3H_2O$	flotation[3]

Formulae are taken from www.ima-mineralogy.org. Ce represents the light REE, which are Ce-dominant; Y represents the HREE, which are Y-dominant. Based on Wall (2014), with additional information from [1]Hedrick et al. *(1997), Jordens* et al. *(2013) [2]Stark* et al. *(2016), and [3]Greenland Minerals and Energy (2015).*

established, but will still vary depending on the deposit characteristics (Krishnamurthy and Gupta 2016). For example, in mineral sands, the monazite grains are usually free from other minerals and can be separated by cheap and chemical-free physical separation methods such as gravity separation, whereas in lateritic deposits, monazite is likely to be intergrown with minerals such as iron oxides and must be ground to a finer grain size and separated by flotation, requiring additional energy and chemicals. Minerals such as ancylite, parisite, synchysite in carbonatites and eudialyte, steenstrupine and allanite in alkaline rocks were poorly understood until a flurry of recent research, which is still yet to be put into practice at an industrial scale. However, many more investigations are needed before any of these minerals are as well understood as bastnäsite and monazite.

Once the mineral is concentrated, it is then necessary to dissolve it up to release the REE, and this is a chemical-intensive process. Then comes an even more chemical-intensive process to separate the individual REE from each other and produce the single REE intermediate products that manufacturers need (Krishnamurthy and Gupta 2016).

SoS RARE is working on improvements to conventional techniques for separating REE minerals, such as flotation, and also working on potential new methods for ion-adsorption deposits, and using a type of ionic liquids for separating REE from each other.

Conclusions

A wider range of raw materials is needed now than ever before as we exploit the specialist properties of the chemical elements in our high-technology communication, clean energy generation, transportation and computing systems. Some of these elements are only needed in small quantities, which means that in many cases the amounts mined per year are more than one hundred times lower than a major metal such as copper. These specialist raw materials can therefore be very important economically, but vulnerable to supply disruption and are given the term 'critical raw materials'.

Mining is a global industry and the research and innovation skills developed in South West England can be applied for worldwide problems such as the search for secure and environmentally-friendly sources of REE. The Natural Environment Research Council is funding a programme called SoS Minerals to help secure several critical raw materials needed for environmental technologies.

There are some critical raw materials in the South West UK. Most notably, the world's fourth largest deposit of tungsten is being mined at Drakelands Mine, near Hemerdon, Devon. There is also some potential for indium. Lithium is of interest, even though not defined as 'critical' at the moment, it is likely to be in high demand for batteries in electric vehicles; and tin should not be forgotten, as it is also a key ingredient of many electronic devices.

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References

Andersen, J. C. Ø., Stickland, R. J., Rollinson, G. K., and Shail, R. K., 2016 'Indium mineralisation in SW England: host parageneses and mineralogical relations'. *Ore Geol Rev* **78**, 213–38 **http://dx.doi.org/10.1016/j.oregeorev.2016.02.019**

Beer, K. E., Edmonds, W. M., and Hawkes, J. R. 1978 'A preliminary look at lithium in the United Kingdom', *in* Penner, S. S. (ed) 'Lithium needs and resources (Corning, N.J., 1977)'. *Energy* **3**, 281–92. Oxford: Pergamon Press

British Geological Survey 2011a 'Tungsten mineral profile, British Geological Survey, Nottingham, U.K'. **http://www.bgs.ac.uk/mineralsUK/statistics/mineralProfiles.html** (accessed 5.2.2017)

British Geological Survey 2011b 'Rare earths mineral profile, British Geological Survey, Nottingham, U.K'. **http://www.bgs.ac.uk/mineralsUK/statistics/mineralProfiles.html** (accessed 1.3.2017)

British Geological Survey 2015 'Risk list 2015'. **http://www.bgs.ac.uk/mineralsuk/statistics/riskList.html** (accessed 4.2.2017)

British Geological Survey 2016 'Lithium mineral profile, British Geological Survey, Nottingham, U.K' **http://www.bgs.ac.uk/mineralsUK/statistics/mineralProfiles.html** (accessed 5.2.2017)

Broom-Fendley, S., Brady, A. E., Wall, F., Gunn, G., and Dawes, W. 2017 'REE minerals at the Songwe Hill carbonatite, Malawi: HREE-enrichment in late-stage apatite'. *Ore Geol Rev* **81**, 23–41 **http://dx.doi.org/10.1016/j.oregeorev.2016.10.019**

Brown, T., and Pitfield, P. 2014 'Tungsten', *in* Gunn, G. (ed) *Critical Metals Handbook*. Chichester: John Wiley & Sons, 385–413

Castor, S. B. 2008 'The Mountain Pass rare-earth carbonatite and associated ultrapotassic rocks, California'. *Canadian Mineralogist* **46**, 779–806. **DOI : 10.3749/canmin.46.4.779**

Chakhmouradian, A. R., and Wall, F. 2012 'Rare earth elements: minerals, mines, magnets (and more)'. *Elements* **8**, 333–40. **DOI:10.2113/gselements.8.5.333**

Cui, H., and Anderson, C. G. 2016 'Fundamental studies on the surface chemistry of ancylite, calcite, and strontianite'. *J Sustainable Metal* **3**, 1–14. **DOI: 10.1007/s40831-016-0097-x**

European Commission, 2014 'Report on critical raw materials for the EU'. Report of the Ad Hoc Working Group on defining critical raw materials, May 2014

Evans, T., Piper, D. M., Kim, S. C., Han, S. S., Bhat, V., Oh, K. H., and Lee, S. H. 2014 'Ionic liquid enabled FeS2 for high-energy-density lithium-ion batteries'. *Advanced Materials* **26**, 7386–92

Goodenough, K. M., Schilling, J., Jonsson, E., Kalvig, P., Charles, N., Tuduri, J., Deady, E. A., Sadeghi, M., Schiellerup, H., Müller, A., Bertrand, G., Arvanitidis, N., Eliopoulos, D. G., Shaw, R. A., Thrane, K., and Keulen, N. 2016 'Europe's rare earth element resource potential: an overview of REE metallogenetic provinces and their geodynamic setting'. *Ore Geol Rev* **72**, 838–56

Graedel, T. E., Harper, E. M., Nassar, N. T., and Reck, B. K. 2015 'On the materials basis of modern society'. *PNAS* **112**, 6295–6300. **DOI: 10.1073/pnas.1312752110**

Greenland Minerals and Energy Ltd 2015 **http://www.ggg.gl/docs/ASX-announcements/Refinery-Update-ContinuousLeachTestwork.pdf** (accessed 9.2.2017)

Hatch, G. P. 2012 'Dynamics in the global market for rare earths'. *Elements* **8**, 341–6. **DOI: 10.2113/gselements.8.5.341**

Hedrick, J. B., Sinha, S. P., and Kosynkin, V. D. 1997 'Loparite, a rare-earth ore (Ce, Na, Sr, Ca)(Ti, Nb, Ta, Fe^{+3})O$_3$'. *J Alloys and Compounds* **250**, 467–70

Jordens, A., Cheng, Y. P., and Waters, K. E. 2013 'A review of the beneficiation of rare earth element bearing minerals'. *Minerals Engineering* **41**, 97–114

Kishnamurthy, N., and Gupta, C. K. 2016 *Extractive Metallurgy of Rare Earths* (2nd edn). Boca Raton, USA: CRC Press

Schwarz-Schampera, U. 2014 'Indium', *in* Gunn, G. (ed) *Critical Metals Handbook*. Chichester: John Wiley & Sons, 204–29

Shannon, R. D. 1976 'Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides'. *Acta Crystallographica Section A* **32**, 751–67
DOI: 10.1107/S0567739476001551 (accessed via **http://www.knowledgedoor.com/2/elements_handbook/shannon-prewitt_effective_ionic_radius.html#sthash.uv4DSn27.dpuf** (accessed 9.2.2017)

Siame, E., and Pascoe, R. D. 2011 'Extraction of lithium from micaceous waste from china clay production'. *Minerals Engineering* **24**, 1595–1602

Stark, T., Silin, I., and Wotruba, H. 2016 'Mineral processing of eudialyte ore from Norra Kärr'. *J Sustainable Metal* **3**, 1–7.
DOI: 10.1007/s40831-016-0073-5

TheGuardian 2017 'Mining firm hopes to extract lithium from Cornwall's hot springs'. Thursday 19 January 2017 11.00 GMT. **https://www.theguardian.com/uk-news/2017/jan/19/cornwall-mining-firm-extract-lithium** (accessed 5.2.2017)

U.S. Geological Survey 2002 'Rare Earth Elements—Critical Resources for High Technology, Fact Sheet 087-02' (modified 2005). **https://pubs.usgs.gov/fs/2002/fs087-02** (accessed 5.2.2017)

U.S. Geological Survey 2017 'Mineral commodity summaries 2017: U.S. Geological Survey'. **http://dx.doi.org/10.3133/70180197** (accessed 4.2.2017)

Verplanck, P. L., and Hitzman, M. 2016 *Rare Earth and Critical Elements in Ore Deposits*. Littleton, Colorado: Soc Econ Geologists

Wall, F. 2000 'Mineral chemistry and petrogenesis of rare earth-rich carbonaites with particular reference to the Kangankunde carbonatite, Malawi'. Unpubl PhD thesis, University of London

Wall, F. 2014 'Rare earth elements', *in* Gunn, G. (ed) *Critical Metals Handbook*. Chichester: John Wiley & Sons, 312–39

Wolf Minerals 2017 'Drakelands Mine'. **http://www.wolfminerals.com.au/irm/content/drakelands-mine.aspx?RID=324** (accessed 5.2.2-17)

Woolley, A. R., and Bailey, D. K. 2012 'The crucial role of lithospheric structure in the generation and release of carbonatites: geological evidence'. *Mineralogical Mag* **76**, 259–70.
https://doi.org/10.1180/minmag.2012.076.2.02