The importance of post-collisional magmatism for global rare earth element resources

Kathryn M Goodenough, Éimear Deady and Charles Beard
British Geological Survey, Edinburgh, UK

Abstract. The rare earth elements are critical metals for modern technology, and are most commonly found in deposits associated with alkaline igneous and carbonatite complexes. Although much research has focused on alkaline-carbonatite magmatism in intraplate settings, in reality many REE deposits occur in post-collisional settings. This review of post-collisional REE deposits demonstrates that they typically show evidence for liquid immiscibility between potassic alkaline magmas and F-, Ba- and REE-rich carbonatitic melts or carbo-hydrothermal fluids. The carbonate-rich melts/fluids rise through the magmatic system and are emplaced at shallow levels, forming the main REE deposits in such complexes. A detailed understanding of the processes operating in these systems can be used to generate geomodels that will be useful for exploration targeting in post-collisional complexes.

1 Introduction

The rare earth elements (REE) are critical metals for which demand is growing as they are used in a wide range of technologies. Neodymium (Nd), praseodymium (Pr) and dysprosium (Dy) are considered to be the most critical of the REE, due to their use in high strength magnets that are needed for the motors of electric cars and wind turbines (Goodenough et al. 2018).

Primary resources of the REE are found in a range of settings, but all known large and giant-sized deposits are associated with alkaline igneous rocks and carbonatites (Smith et al. 2016). Alkaline-carbonatite igneous complexes are most commonly associated with continental intraplate magmatism, but can also occur at plate boundaries, typically as part of post-collisional magmatic suites. Post-collisional magmatism is often voluminous, and occurs in a period of 'relaxation' generally post-dating continental collision by 25-75 Ma; emplacement of magmas is commonly linked to movement along major transcurrent shear zones (Sylvester 1989; Bonin 2004). Post-collisional alkaline magmatic rocks are typically potassic to ultrapotassic, with rarer sodic compositions (Bonin 2004).

Much research relating to alkaline igneous rocks and carbonatites, and their associated mineralization, has focused on continental intraplate settings (Dostal 2017). However, many significant REE deposits worldwide are associated with post-collisional alkaline-carbonatite magmatic complexes. This contribution reviews some of the key characteristics of post-collisional REE deposits, and builds up a preliminary model for these magmatic-mineralised systems.

2 REE deposits associated with post-collisional magmatism

The majority of well-known REE deposits formed in post-collisional settings are Mesozoic to Cenozoic in age, and relatively shallow levels of the alkaline-carbonatite magmatic suite are exposed at the surface. Common rock-types include shallow-level syenitic, phonolitic and trachytic intrusions and carbonatite dykes, with the REE mineralization hosted in breccias, carbonatite dykes and carbo-hydrothermal veins. Alkaline rocks are typically potassic to ultrapotassic in composition, whilst the REE deposits are carbonate-dominated and enriched in F, Ba, and the REE.

The most economically important REE deposits associated with post-collisional magmatism lie in the Mianning-Dechang REE belt of southwestern China, which includes the Maoniuping and Dalucao REE deposits. These deposits occur as veins, lenses and breccias of barite-fluorite-bastnäsite-calcite ore with a range of alkaline silicate minerals (Guo and Liu 2019). They are associated with post-collisional syenite-carbonatite complexes of Cenozoic age, which were emplaced into the Himalayan collision zone during shearing on regional strike-slip faults (Liu et al. 2015; Hou et al. 2009). REE deposits in post-collisional alkaline-carbonatite complexes are also known from elsewhere in China, for example at Miaoya (Xu et al. 2015).

In Turkey, Cenozoic post-collisional alkaline-carbonatite suites are associated with a number of fluorite deposits. One of these, the Kizilcaören deposit, comprises lenses and veins of fluorite-barite-bastnäsite ore which represent a REE deposit (Öztürk et al. 2019). Igneous rocks in the area are represented by shallow-level phonolitic to carbonatitic intrusions.

In Southern Mongolia, the Lugiin Gol, Mushghai Khudag and Bayan Khushu alkaline complexes show a suite of syenitic to trachytic intrusions associated with carbonatite and phonolite dykes, magnetite-apatite rocks, and fluorite-barite-carbonate veins (Baatar et al. 2013; Nikolenko et al. 2018). At Mushghai Khudag, the magnetite-apatite rocks represent the most important REE mineralization, but the carbonatitic dykes and veins in all complexes are also significantly REE-enriched (Kynicky et al. 2019). These complexes are not well-dated, but are thought to be late Jurassic in age, part of an alkaline magmatic province that formed in association with a tectonic transition from contractional to extensional deformation during the late Jurassic (Meng 2003).

In the USA, Cenozoic post-collisional alkaline

magmatic complexes were emplaced towards the end of the Laramide Orogeny, and include several REE deposits (McLemore 2018). These include the Gallinas Mountains of central New Mexico, which host Cenozoic, syn- to post-collisional alkaline intrusives with associated REE deposits in breccia pipes and fault-hosted breccias. The REE deposits comprise the fluorite-bastnäsite-barite-calcite-quartz breccia matrices (Olivo et al. 2000). The Bear Lodge REE deposit in Wyoming is also hosted in an alkaline-carbonatite complex within this belt. The most heavily-explored part of the deposit is in the Bull Hill diatreme, comprising a breccia pipe with a stockwork of carbonatite veins and dykes; REE mineralization is related to multiple phases of carbo-hydrothermal activity within this diatreme (Moore et al. 2015). Carbonatite dykes and veins extend throughout much of the alkaline complex, and some peripheral zones are HREE-enriched (Andersen et al. 2016).

It is evident that in most deposits in post-collisional settings, the REE mineralization occurs in carbonate- and fluorite-dominated ore bodies, which are associated with potassic alkaline igneous rocks. These REE deposits are likely to have formed by liquid immiscibility of a carbonatitic melt (or carbothermal fluid) from the alkaline silicate magma at deeper levels in the system (Kynicky et al. 2019). The REE, F, and Ba were all preferentially partitioned into the carbonatitic phase, as indicated by experimental data (Song et al. 2015). These volatile-rich carbonatitic melts/carbothermal fluids were subsequently emplaced at shallow levels as dykes, sheets, and in the matrix of breccia pipes. Such immiscible melts/ fluids may have also formed REE mineralization at deeper levels in the igneous complexes; to understand this it is necessary to investigate older and more deeply eroded examples.

3 Understanding the deeper levels of post-collisional REE deposits

Few REE deposits associated with deeper levels of alkaline-carbonatite complexes have been positively recognized as post-collisional. However, the Proterozoic Mountain Pass REE deposit is associated with ultrapotassic alkaline igneous rocks and was likely formed in a post-collisional setting. These ultrapotassic rocks are relatively enriched in Ba and the LREE, and have allanite, apatite, monazite, fluorite and magnetite as accessory minerals (Castor 2008). The REE deposit is in a tabular carbonatite body that is enriched in barite, bastnäsite and monazite.

Similar features are recognized in the post-collisional Silurian alkaline intrusions of the NW Highlands of Scotland, which were emplaced at the end of the Caledonian orogeny, and are characterized by ultrapotassic, high Ba-Sr compositions (Fowler et al. 2008; Goodenough et al. 2011). The complexes largely comprise under- to oversaturated syenites with minor carbonatites. The main REE enrichment has been recognized in the form of biotite-magnetite-allanite-apatite veins in syenites at the Cnoc nan Cuilean locality

(Walters et al. 2013). These veins represent pathways exploited by late-stage, fluorine- and carbonate-rich fluids or melts rising through the magma chamber. Late allanite-monazite-fluorcarbonate veins also form the REE mineralization at the Ditrău Alkaline Complex in Romania, which was emplaced after the Variscan orogeny (Honour et al. 2018).

Such examples are consistent with immiscibility of a F-Ba-REE-rich carbonatitic melt within the alkaline magma chamber and subsequent migration upwards through the magmatic system.

4 Genesis and evolution of REE-enriched magmas in post-collisional settings

Parental magmas in post-collisional settings are commonly potassic to ultrapotassic, and enriched in Ba, Sr, and the LREE. These compositional features are considered to be derived from an enriched mantle source that has interacted with subducted continental material (or melts/fluids derived from the subducting material) and subsequently been melted (Couzinié et al. 2016). This enriched mantle source must typically also have been rich in carbonate; carbonate is stable in the shallower parts of modern subduction zones, but is eventually extracted through formation of carbonatitic melts, which metasomatise the overlying lithospheric mantle (Dasgupta and Hirschmann 2010). Compilations of Sr, Nd and Hf data for post-collisional alkaline complexes are consistent with addition of continentally-derived material into the mantle source.

An overarching model for the formation of REE deposits associated with post-collisional alkaline magmatism can be summarized as follows. Small-degree partial melting of the enriched mantle source, triggered by 'relaxation' and extension of the orogenic belt, produces a parental magma that is relatively rich in F, CO_2, K, Ba, Sr and the LREE. Such magmas are emplaced along major crustal structures, reactivated in an extensional manner, into magma chambers at medium levels in the crust. Evolution by fractional crystallization produces trachytic/syenitic magma compositions which are volatile-rich, and thus eventually a fluorine-rich carbonatitic melt is formed by liquid immiscibility. These carbonatitic melts rise through the magma chamber and into the overlying country rocks, to be emplaced as REE-enriched dykes and veins with associated metasomatic alteration.

The HiTech AlkCarb project is developing new geomodels for REE mineralization in alkaline igneous rocks and carbonatites, which will incorporate information about complexes in post-collisional settings. A schematic diagram illustrating some of the features of this type of mineralized system is shown in Figure 1.
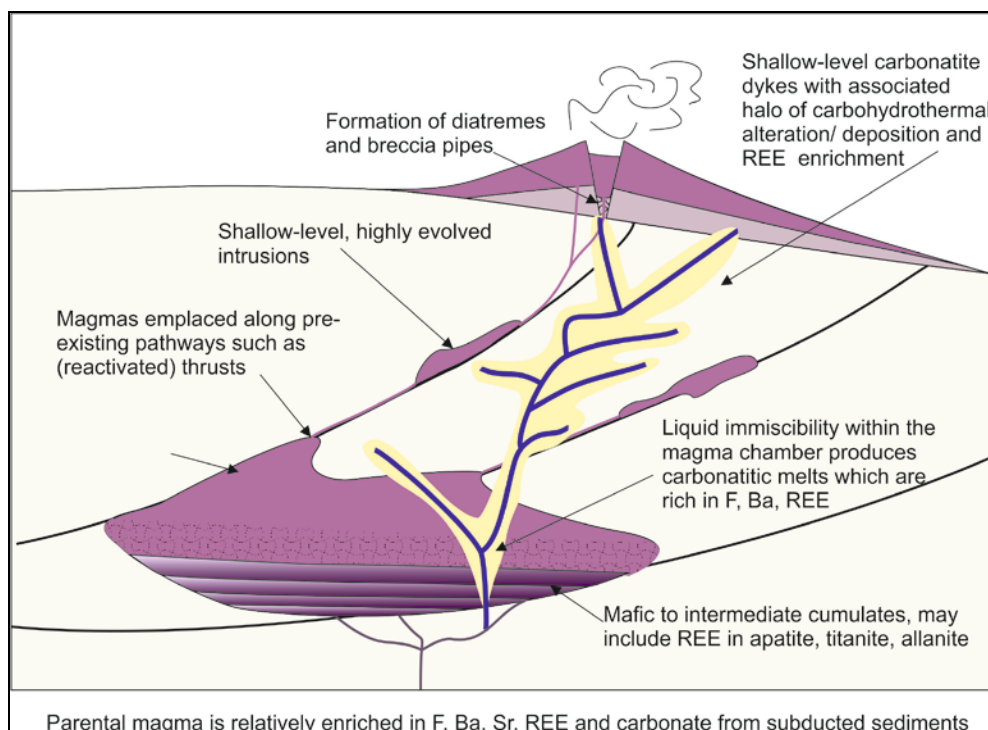
5 Conclusions

REE deposits in post-collisional alkaline-carbonatite complexes represent a discrete sub-type, which should be distinguished in exploration geomodels. They can be identified by regional tectonic setting and by the K-, Ba- and LREE-rich nature of the associated alkaline igneous rocks. The REE deposits at the upper levels of these complexes will typically take the form of carbonatitic dykes and veins or carbo-hydrothermal ore bodies, which are enriched in fluorite, barite and fluorcarbonates. At deeper levels, carbonatites and alteration zones within the alkaline complexes may be enriched in monazite, allanite and apatite which have the potential to represent significant REE mineralization.

Acknowledgements

Figure 1. Schematic figure indicating the components of a post-collisional alkaline-carbonatite REE deposit.

References

Andersen AK, Clark JG, Larson PB, Neill OK (2016) Mineral chemistry and petrogenesis of a HFSE(+HREE) occurrence, peripheral to carbonatites of the Bear Lodge alkaline complex, Wyoming. American Mineralogist 101:1604-1623. doi: 10.2138/am-2016-5532.

Baatar M, Ochir G, Kynicky J, Iizumi S, Comin-Chiaramonti P (2013) Some Notes on the Lugiin Gol, Mushgai Khudag and Bayan Khoshuu Alkaline Complexes, Southern Mongolia. International Journal of Geosciences 4:1200.

Bonin B (2004) Do coeval mafic and felsic magmas in post-collisional to within-plate regimes necessarily imply two contrasting, mantle and crustal, sources? A review. Lithos 78:1-24. doi: https://doi.org/10.1016/j.lithos.2004.04.042.

Castor SB (2008) THE MOUNTAIN PASS RARE-EARTH CARBONATITE AND ASSOCIATED ULTRAPOTASSIC ROCKS, CALIFORNIA. The Canadian Mineralogist 46:779-806. doi: 10.3749/canmin.46.4.779.

Couzinié S, Laurent O, Moyen J-F, Zeh A, Bouilhol P, Villaros A (2016) Post-collisional magmatism: Crustal growth not identified by zircon Hf–O isotopes. Earth and Planetary Science Letters 456:182-195. doi: https://doi.org/10.1016/j.epsl.2016.09.033.

Dasgupta R, Hirschmann MM (2010) The deep carbon cycle and melting in Earth's interior. Earth and Planetary Science Letters 298:1-13. doi: https://doi.org/10.1016/j.epsl.2010.06.039.

Dostal J (2017) Rare Earth Element Deposits of Alkaline Igneous Rocks. Resources 6. doi: https://doi.org/10.3390/resources6030034.

Fowler MB, Kocks H, Darbyshire DPF, Greenwood PB (2008) Petrogenesis of high Ba–Sr plutons from the Northern Highlands Terrane of the British Caledonian Province. Lithos 105:129-148. doi: https://doi.org/10.1016/j.lithos.2008.03.003.

Goodenough KM, Millar I, Strachan RA, Krabbendam M, Evans JA (2011) Timing of regional deformation and development of the Moine Thrust Zone in the Scottish Caledonides: constraints from the U–Pb geochronology of alkaline intrusions. Journal of the Geological Society 168:99-114. doi: 10.1144/0016-76492010-020.

Goodenough KM, Wall F, Merriman D (2018) The Rare Earth Elements: Demand, Global Resources, and Challenges for Resourcing Future Generations. Natural Resources Research 27:201-216. doi: 10.1007/s11053-017-9336-5.

Guo D, Liu Y (2019) Occurrence and geochemistry of bastnäsite in carbonatite-related REE deposits, Mianning–Dechang REE belt, Sichuan Province, SW China. Ore Geology Reviews 107:266-282. doi: https://doi.org/10.1016/j.oregeorev.2019.02.028.

Honour VC, Goodenough KM, Shaw RA, Gabudianu I, Hirtopanu P (2018) REE mineralisation within the Ditrău Alkaline Complex, Romania: Interplay of magmatic and hydrothermal processes. Lithos 314-315:360-381. doi: https://doi.org/10.1016/j.lithos.2018.05.029.

Hou Z, Tian S, Xie Y, Yang Z, Yuan Z, Yin S, Yi L, Fei H, Zou T, Bai G, Li X (2009) The Himalayan Mianning–Dechang REE belt associated with carbonatite–alkaline complexes, eastern Indo-Asian collision zone, SW China. Ore Geology Reviews 36:65-89. doi: https://doi.org/10.1016/j.oregeorev.2009.03.001.

Kynicky J, Smith MP, Song W, Chakhmouradian AR, Xu C, Kopriva A, Galiova MV, Brtnicky M (2019) The role of carbonate-fluoride melt immiscibility in shallow REE deposit evolution. Geoscience Frontiers 10:527-537. doi: https://doi.org/10.1016/j.gsf.2018.02.005.

Liu Y, Hou Z, Tian S, Zhang Q, Zhu Z, Liu J (2015) Zircon U–Pb ages of the Mianning–Dechang syenites, Sichuan Province, southwestern China: Constraints on the giant REE mineralization belt and its regional geological setting. Ore Geology Reviews 64:554-568. doi: https://doi.org/10.1016/j.oregeorev.2014.03.017.

McLemore VT (2018) Rare Earth Elements (REE) Deposits Associated with Great Plain Margin Deposits (Alkaline-Related), Southwestern United States and Eastern Mexico. Resources 7. doi: http://dx.doi.org/10.3390/resources7010008.

Meng Q-R (2003) What drove late Mesozoic extension of the northern China–Mongolia tract? Tectonophysics 369:155-174. doi: https://doi.org/10.1016/S0040-1951(03)00195-1.

Moore M, Chakhmouradian AR, Mariano AN, Sidhu R (2015) Evolution of rare-earth mineralization in the Bear Lodge carbonatite, Wyoming: Mineralogical and isotopic evidence. Ore Geology Reviews 64:499-521. doi: https://doi.org/10.1016/j.oregeorev.2014.03.015.

Nikolenko AM, Redina AA, Doroshkevich AG, Prokopyev IR, Ragozin AL, Vladykin NV (2018) The origin of magnetite-apatite rocks of Mushgai-Khudag Complex, South Mongolia: mineral chemistry and studies of melt and fluid inclusions. Lithos 320-321:567-582. doi: https://doi.org/10.1016/j.lithos.2018.08.030.

Olivo GR, Williams-Jones AE, Samson IM (2000) The Genesis of Hydrothermal Fluorite-REE Deposits in the Gallinas Mountains, New Mexico. Economic Geology 95:327-341. doi: 10.2113/gsecongeo.95.2.327.

Öztürk H, Altuncu S, Hanilçi N, Kasapçı C, Goodenough KM (2019) Rare earth element-bearing fluorite deposits of Turkey: An overview. Ore Geology Reviews 105:423-444. doi: https://doi.org/10.1016/j.oregeorev.2018.12.021.

Smith MP, Moore K, Kavecsánszki D, Finch AA, Kynicky J, Wall F (2016) From mantle to critical zone: A review of large and giant sized deposits of the rare earth elements. Geoscience Frontiers 7:315-334. doi: http://dx.doi.org/10.1016/j.gsf.2015.12.006.

Song W, Xu C, Veksler IV, Kynicky J (2015) Experimental study of REE, Ba, Sr, Mo and W partitioning between carbonatitic melt and aqueous fluid with implications for rare metal mineralization. Contributions to Mineralogy and Petrology 171:1. doi: 10.1007/s00410-015-1217-5.

Sylvester PJ (1989) Post-Collisional Alkaline Granites. The Journal of Geology 97:261-280. doi: 10.1086/629302.

Walters AS, Goodenough KM, Hughes HSR, Roberts NMW, Gunn AG, Rushton J, Lacinska A (2013) Enrichment of Rare Earth Elements during magmatic and post-magmatic processes: a case study from the Loch Loyal Syenite Complex, northern Scotland. Contributions to Mineralogy and Petrology 166:1177-1202. doi: 10.1007/s00410-013-0916-z.

Xu C, Kynicky J, Chakhmouradian AR, Li X, Song W (2015) A case example of the importance of multi-analytical approach in deciphering carbonatite petrogenesis in South Qinling orogen: Miaoya rare-metal deposit, central China. Lithos 227:107-121. doi: https://doi.org/10.1016/j.lithos.2015.03.024.