

## The role of fluids in the formation of REE (-Zr, Nb, Ta) deposits associated with alkaline plutons

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Mineral deposits in which a variety of rare elements, including REE, Zr, Ta, Nb, Be, and Ga, are concentrated are associated with alkaline to peralkaline plutons, typically in rift settings. Although, in general, there are common features among such deposits, the plutons can vary substantially in their internal character and structure, and their degree of Si saturation, from Si-oversaturated (e.g., Strange Lake, Quebec/Labrador) to Si-undersaturated (e.g., Thor Lake, NWT, and Illimaussaq, Greenland). The former are characterized by alkaline granites and the latter by nepheline syenites. This variable magma character is reflected in a diverse primary rare element mineralogy. For example, at Strange Lake, Zr was mainly hosted by zircon and elpidite, Nb by pyrochlore and the REE by all three minerals. In contrast, in the Nechalacho deposit at Thor Lake, Zr and REE were hosted by zircon in the upper, miaskitic, zone and by epidote in the lower, agpaitic, zone. Columbite is likely to have been the primary host for Nb. In both settings, the mineralization is characterized by higher HREE/LREE than other systems, such as those associated with carbonates.

The concentration of rare elements through fractional crystallization into pegmatites or by physical crystal accumulation was important in these deposits, however, hydrothermal fluids have played an important role in the subsequent transport and precipitation of rare elements. In particular, water-rock interaction and hydrothermal alteration have significantly modified the mineralogical character of the REE and Zr minerals, and this has increased the mineralogical diversity in such deposits, and resulted in upgrading and ease of beneficiation. The water-rock interaction history can be complex and multi-stage, leading to texturally and mineralogically complex assemblages in which pseudomorphing of early-formed minerals (both rare-element and non-rare element bearing) played a critical role in rare-element mineral precipitation.

The increasing availability of experimental data on the stability of aqueous rare element complexes is making modelling of the processes mentioned above easier, although a lack of data on mineral solubility remains a hindrance. Many models of deposit formation, both in silicic and carbonatitic environments, have employed fluoride complexes to facilitate element transport, with precipitation resulting from their destabilization as a consequence of the addition of Ca from host rocks or by fluid mixing, and the precipitation of fluorite. Although there is ample evidence for Ca metasomatism in the above-mentioned and other deposits, a true evaluation of this model is hindered by a lack of information on ligand concentrations, particularly fluoride. Furthermore, mineralogical and textural observations from these and other systems suggest that other complexation and precipitation models need to be considered.

## Zircon, zircon everywhere: What caused the zircon superfertility of Grenville magmas?

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A common assumption in many detrital zircon studies is that the abundance of zircon grains defining a particular age range directly corresponds to the area of exposed continental crust of that age. This is often not the case, however, as much modern alluvium and Paleozoic sandstone have large, sometimes exclusive, 1.3 – 1.0 Ga age peaks, a so-called Grenvillian signature. This is true even for sedimentary rocks very distal to exposed Grenville crust, such as Cambrian sandstone in California and clastic sediment in northwestern Canada. One of the reasons for the extreme abundance of ~ 1 Ga detrital zircon is that magmas associated with Grenville orogenic events contain unusually abundant, and often surprisingly large, zircon crystals. Large and abundant crystals will dominate the zircon budget of alluvium, particularly if sediment has been transported significant distances by major river systems.

A fundamental question about the Grenville Orogeny thus arises: what caused the magmas associated with the tectonic events to be so zirconium rich? One possibility is that the high Zr content, often > 500 ppm, is the result of a high abundance of zircon xenocrysts in the Grenvillian plutons. In this scenario the high Zr whole-rock contents would not be due to actual magmatic compositions but would reflect the total zircon crystal cargo of the intrusion. A second possibility is that the sources of Grenvillian magmas themselves were unusually Zr rich. A recent suggestion has been made that long-lived subduction beneath Laurentia may have significantly chemically enriched the Laurentian mantle lithosphere prior to Grenvillian magmatism. Furthermore, if Zr-enriched parent material was partially melted then the newly formed magma would be even higher in Zr content (assuming Zr distribution coefficients << 1). A third possibility is that unusually hot continental lithospheric conditions existed during the assembly of Rodinia. Very high temperature magmas can become very Zr-rich prior to reaching zircon saturation and thus can crystallize an abundant amount of zircon. These three, not necessarily mutually exclusive, hypotheses have yet to be thoroughly tested, despite their importance to an understanding of what might be one the most Zr-rich magmatic episodes in Earth history. But regardless of the cause, the role of zircon superfertility must be a primary consideration when using detrital zircon as a proxy for studies of continental crustal growth. Estimates of the amount of juvenile crust generated based on isotopic analysis of detrital zircon could be biased if variation in zircon fertility is not taken into consideration.