

Origin of heavy REE mineralisation in carbonatites: Constraints from the Huanglongpu Mo-HREE deposit, Qinling, China.

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The carbonatite dykes of the Huanglongpu area, Lesser Qinling, China, are unusual in that they are quartz-bearing, Mo-mineralised and enriched in the heavy rare earth elements (HREE) relative to typical carbonatites. Carbonatite monazite (208.9 ± 4.6 Ma to 213.6 ± 4.0 ; Song et al., 2016) gives a comparable U-Pb radiometric age to molybdenite (220Ma; Stein et al., 1997), confirming interpretations that Mo is derived from the carbonatite, and not a subsequent overprint from regional porphyry-style mineralisation (~ 141 Ma). The sulphides in the carbonatites have mantle-like $[U+Th]/^{34}S$ ($\sim 1\%$) and low $\delta^{26}Mg$ values (-1.89 to -1.07%), similar to sedimentary carbonates, suggesting a recycled sediment contribution in their mantle sources that may be responsible for the Mo and HREE enrichment (Song et al., 2016). The textures of REE minerals indicate crystallisation of monazite-(Ce), bastnäsite-(Ce), parisite-(Ce) and aeschynite-(Ce) as magmatic phases. Monazite-(Ce) was subsequently altered to produce apatite, which was in turn replaced by britholite-(Ce), accompanied by the formation of allanite-(Ce). The REE-fluorcarbonates were replaced by synchysite-(Ce) and röntgenite-(Ce). Aeschynite-(Ce) was altered initially to uranopyrochlore and then pyrochlore with uraninite inclusions. The mineralogical evolution reflects the evolution from magmatic carbonatite, through to more silica-rich conditions during the magmatic-hydrothermal transition, to fully hydrothermal conditions accompanied by the formation of sulphate minerals. Each alteration stage resulted in the preferential leaching of the LREE and enrichment in the HREE. Mass balance considerations indicate that the HREE enrichment could not be a passive process, and that hydrothermal fluids must have contributed HREE to the system. The evolution of the fluorcarbonate mineral assemblage requires an increase in aCa^{2+} and aCO_3^{2-} in the metasomatic fluid, and so breakdown of HREE-enriched calcite may have been the HREE source. Solubility products are lower for LREE minerals compared to HREE minerals, so leaching in the presence of strong, LREE-selective ligands (Cl^- , CO_3^{2-}) may account for the depletion in late stage minerals in the LREE, but cannot account for subsequent preferential HREE addition. Fluid inclusion data indicate the presence of sulphate-rich brines during late stage alteration, and hence sulphate complexation may have been important for preferential HREE transport, as sulphate has been shown to be non-LREE selective during the formation of complex ions. The combination of mantle source with a recycled oceanic sediment component, and REE enrichment during magmatic processes, and late stage alteration with non-LREE selective ligands such as sulphate may be critical in forming HREE-enriched carbonatites.

Song et al., (2016) Origin of unusual HREE-Mo-rich carbonatites in the Qinling orogen, China. *Scientific Reports*, 6:37377 | DOI: 10.1038/srep37377.

Stein et al. (1997) Highly precise and accurate Re-Os ages for molybdenite from the East Qinling-Dabie molybdenum belt, Shaanxi province, China. *Econ. Geol.* 92, 827–835 (1997)