

Mechanisms for the generation of HREE mineralization in carbonatites: Evidence from Huanglongpu, China.

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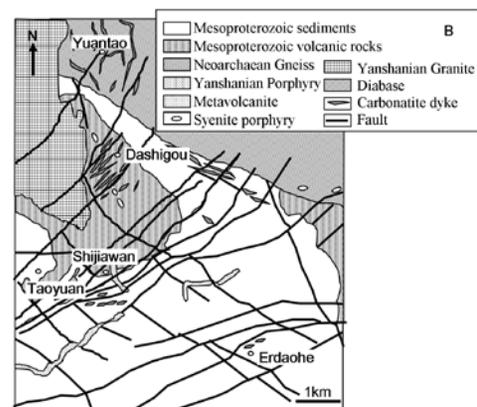


Figure 1: (A) Geological map of the eastern Qinling Mountains showing the location of the Huanglongpu area. Inset shows the overall location within China in relation to major crustal blocks. (B) Geological map of the Huanglongpu Mo-district (highlighted in bold in A). Maps adapted from Xu et al. (2010).

Abstract. The Huanglongpu carbonatites, Qinling Mountains, China, are exceptional as they form both an economic Mo resource, and are enriched in the HREE compared to typical carbonatites, giving a metal profile that may closely match projected future demand. The carbonatites at the level currently exposed appear to be transitional between magmatic and hydrothermal processes. The multistage dykes and veins are cored by quartz which hosts a fluid inclusion assemblage with a high proportion of sulphate daughter or trapped minerals, and later stage, cross-cutting veins are rich in barite-celestine. The REE mineral paragenesis evolves from monazite, through apatite and bastnäsite to Ca-REE fluorocarbonates, with an increase in HREE enrichment at every stage. Radio-isotope ratios are typical of enriched mantle sources and sulphur stable isotopes are consistent with magmatic S sources. However, Mg stable isotopes are consistent with a component of recycled subducted marine carbonate in the source region. The HREE enrichment is a function of both unusual mantle source for the primary magmas and REE mobility and concentration during post-magmatic modification in a sulphate-rich hydrothermal

system. Aqueous sulphate is a non-specific ligand for the REE, and this coupled with crystal fractionation lead to HREE enrichment during subsolidus alteration.

1 Introduction

The rare earth elements have become a focus of intense economic interest because of the restriction in supply caused by a focus of production in China, coupled with increasing use in renewable energy and high technology applications. Rare earth element resources are dominated by concentrations associated with alkaline igneous rocks, notably carbonatites. Elements enrichments in carbonatite tend to be in the light REE (La to Nd). Middle to HREE enriched carbonatites do occur however, and may have REE distributions which are a closer match to project future REE demand than typical carbonatites (Goodenough et al., 2017). Here we present data on the geochemical and mineralogical evolution of the Huanglongpu carbonatites, China (Fig. 1), which show overall REE patterns that bridge a gap between typical and HREE mineralised carbonatites (Smith et al., 2018).

Figure 2: Comparison of ratios characterising the REE pattern for the Huanglongpu carbonatites with typical carbonatites (Hornig-Kjarsgaard, 1998), and those with reported high HREE contents (Bodeving et al., 2017; Moore et al., 2017; Ngwenya, 1993; Swinden and Hall, 2012).

2 Geology

Figure 3: Example of field relationships in the Huanglongpu carbonatites, with a calcite-quartz-molybdenite dyke cross-cut by a conjugate barite-rich dyke.

The Huanglongpu district is composed of four carbonatite-related orefields (Fig. 1) with a total ore reserve of N180 Kt of Mo. Re-Os dates indicate the dykes are 50-90Ma older than porphyry mineralisation in the district and hence not related to overprinting sulphide mineralisation (Song et al., 2016; Stein et al., 1997). The ore bodies occur discontinuously over a total distance of 6 km and an area of 23 km². The carbonatite dykes are highly parallel, predominantly dipping N to NNW, at steep angles (strike/dip ~260/50–88°N) and consist of calcite, kutnahorite, quartz, potassium feldspar, barite, pyrite, galena, sphalerite, molybdenite, monazite, Ca-REE-fluorcarbonates, apatite, britholite, pyrochlore, uraninite, REE fluorides, burbankite, celestine, strontianite and brannerite. Minor fluorite is found at Shijiawan and Yuantao. The dykes range in thickness from ~10m to ~0.1m (Fig. 3) with lateral extents ranging from 10m to N1 km. Rarer dykes occur in orientations conjugate to the main set (strike/dip ~350/50–80°E). Minor offsets suggest this set may be

slightly later than the main set, although the conjugate orientation and presence of conjugate veins merging with the main set suggest they were very nearly contemporaneous. Barite-celestine bearing dykes and veins cut the earlier carbonate-quartz-sulphide bearing dykes (Fig. 3). Quartz is dominantly restricted to cores of dykes and may be mainly hydrothermal in origin. This suggests the primary dykes may have been calico-carbonatite in composition although the bulk dyke composition is silico-carbonatite. In the carbonatites, molybdenite occurs mainly as disseminated grains and intergranular and fracture-hosted films, sometimes associated with pyrite, galena and sphalerite suggesting a subsolidus, hydrothermal origin for at least some of the sulphide assemblage. Disseminated molybdenite is also found along fractures in fenitized gneiss near its contact with the dykes. The overall HREE enrichment of the Huanglongpu carbonatites has been previously related to a recycled ocean crust component in the lithospheric mantle indicated by Nd-Sr radioisotope studies and Mg stable isotope analyses of calcite (Song et al., 2016). This primary source control has been proposed to be enhanced by fractional crystallisation of calcite, with the dykes at the current level of exposure representing relatively HREE-enriched carbonate residuum (Xu et al., 2007).

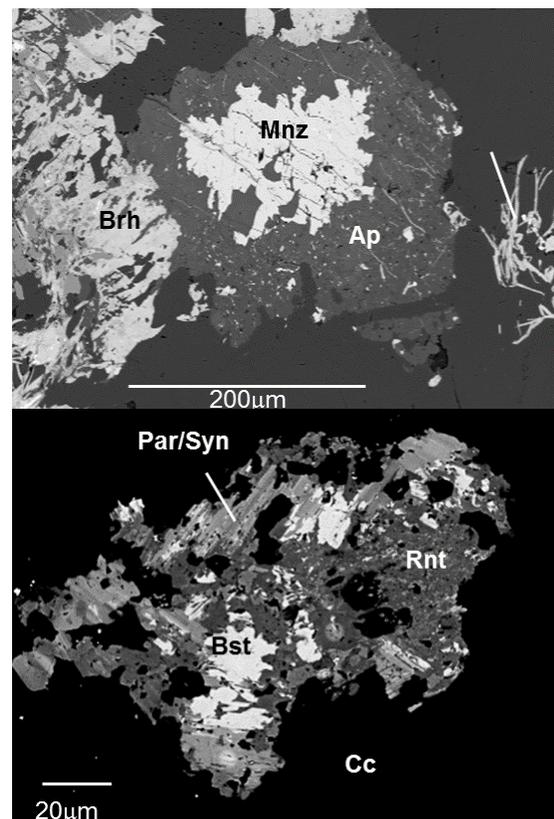


Figure 4: Examples of mineral textures at Huanglongpu as backscattered electron images. (A) Monazite replaced by apatite, which is in turn replaced and overgrown by britholite. (B) Bastnäsite overgrown by syntaxially intergrown paristite and synchysite, and all these replaced by röntgenite.

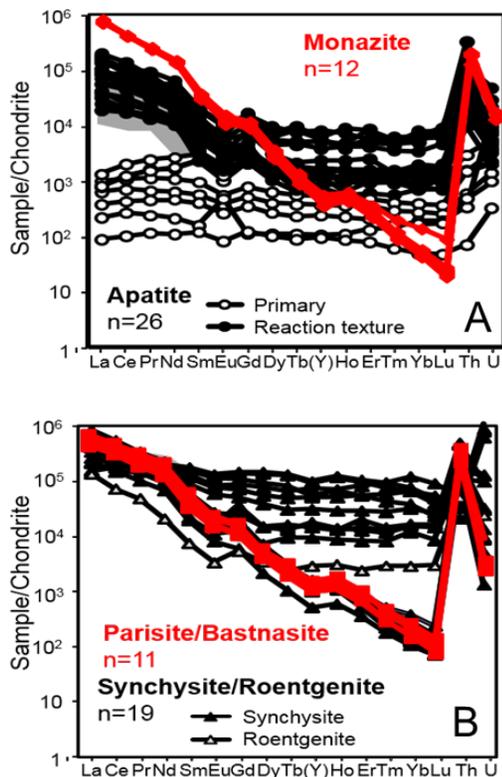


Figure 5: Chondrite normalized REE patterns for phosphates and fluorcarbonates from Huanglongpu. Determined by LA-ICPMS. Th and U are included to illustrate actinide behavior.

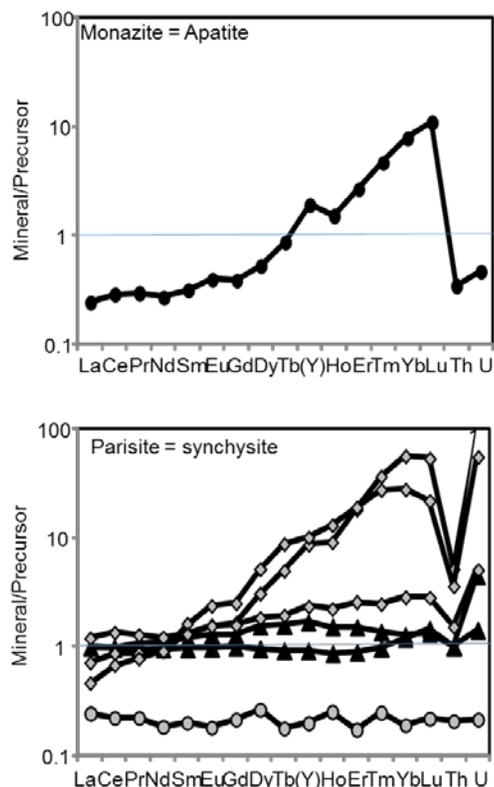


Figure 6: Composition of minerals in reaction textures normalised to the precursor phase for phosphates and fluorcarbonates.

3 Results

3.1 REE mineral Paragenesis

The earliest stage of REE mineralization is the formation of monazite-(Ce) as eu- to subhedral crystals within calico carbonatite. Monazite is a potentially magmatic phase as it is fractured, and the fractures subsequently filled by the sulphide mineral assemblage, specifically molybdenite. Additional potentially early REE-bearing phases include pyrochlore, apatite, zircon and parisite which occurs intergrown with galena and molybdenite. Monazite is overgrown and replaced by apatite, which is in turn overgrown and replaced by britholite-(Ce) ($\text{REE}_3\text{Ca}_2\text{SiO}_4\text{F}$) (Fig. 4). The formation of britholite is accompanied by the formation of allanite-(Ce) in the surrounding rock. Both are common in the quartz-rich cores to the dykes. Within the fluorcarbonate assemblage early bastnäsite-(Ce) and parisite-(Ce) are replaced by parisite-synchysite-(Ce) syntaxial intergrowths, and by röntgenite-(Ce). At the same time as the development of the REE mineral paragenesis the early niobium phases undergo alteration. Early aeschynite-(Ce) is altered to urano-pyrochlore, which is then altered to pyrochlore with uraninite inclusions.

3.2 Mineral Chemistry

Analyses of REE and niobate mineral chemistry were carried out by LA-ICPMS at the Natural History Museum, London.

Figure 5 shows typical chondrite normalized REE patterns for phosphates and fluorcarbonates. In all cases the mineral chemistry is dominated by the LREE, and all REE minerals are the Ce-dominant variety. However, there is a clear distinction in HREE contents between monazite and apatite and britholite, with the latter being significantly more HREE-rich. The same is also true of the fluorcarbonates, and aeschynite, uranopyrochlore and pyrochlore, with the level of HREE enrichment increasing in later paragenetic stages (Fig. 5). When minerals are normalized to their precursor phase identified from textural studies, it becomes apparent that at every stage of alteration the REE minerals become more HREE-rich (Fig. 6).

3.3 Fluid evolution

Fluid inclusions in quartz have been studied by Song et al, (2016) and as part of this study. Early aqueous-carbonic fluid inclusions containing sulphate minerals contain nearly pure CO_2 , and have salinities in the aqueous phase determined from clathrate melting of 5–19 wt% NaCl equivalent. These inclusions decrepitate on heating, and so homogenisation temperatures cannot be determined. They occur in assemblages with liquid CO_2 inclusions. Laser Raman spectroscopic data from quartz cores to the carbonatite dykes indicate arcanite (K_2SO_4), anhydrite (CaSO_4), glauberite ($\text{Na}_2\text{Ca}(\text{SO}_4)_2$), apthitalite ($(\text{K},\text{Na})_3\text{Na}(\text{SO}_4)_2$) and gorgeyite ($\text{K}_2\text{Ca}_5(\text{SO}_4)_6 \cdot \text{H}_2\text{O}$) within fluid inclusions (Fig. 7). The wide range in solids suggests heterogeneous trapping

following sulphate saturation triggered by mixing with a CO₂-rich fluid. Fluid inclusions in fracture-fill quartz and calcite are typically 2 phase aqueous liquid plus vapour inclusions. These homogenise between 265 and 120 °C, and have salinities from 6 to 15wt% NaCl eq. Quartz and calcite from Huanglongpu analysed by SIMS mostly give δ¹⁸O values close to 10 ‰. The very small fractionation between the two minerals is indicative of near-magmatic temperatures. Thin crack-fills of secondary quartz, identified by CL imaging, are of very similar composition to the primary quartz, but a secondary crack-fill calcite is around 3 ‰ heavier, indicative of a temperature below 200°C if both crack-fills equilibrated.

Overall these data suggest that initial REE mineralisation took place at late magmatic temperatures. Early fluid inclusions were heterogeneously trapped from sulphate saturated brines which either mixed with CO₂-rich fluids, or generated CO₂ via water-rock interaction between 300 and 200 °C and 100-50 MPa. Late hydrothermal quartz deposition and the alteration of REE minerals took place down to 120°C, at pressures below 100 MPa. These fluids were present throughout REE mineral deposition.

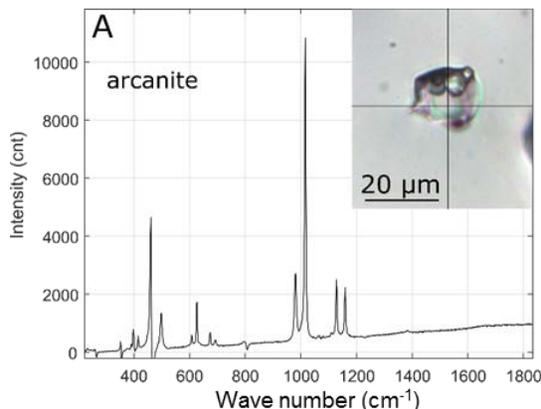


Figure 7: Example of a laser Raman spectrum of fluid inclusion hosted minerals in quartz host fluid inclusions from Huanglongpu. In this case the solid phase is identified as arcanite (K₂SO₄).

4 Discussion and conclusions.

Previous studies have demonstrated that the relative HREE enrichment of the Huanglongpu carbonatites relates to the primary magmatic source, with potential inputs from sedimentary carbonate recycled into the mantle via subduction (Song et al., 2016), followed by fractional crystallisation of LREE-rich phases resulting in further HREE enrichment of the residual carbonatite magma (Xu et al., 2007). This initial enrichment has been enhanced at the current level of exposure by hydrothermal processes involving sulphate-rich brines which operated from sub-solidus temperatures down to ~120°C.

The REE mineral paragenesis evolved throughout this process. Monazite and possibly some LREE-rich fluorocarbonates formed as magmatic phases. Subsequent depletion of the residual magma in the

REE, coupled with increasing Ca-activity resulted in the reaction of monazite to apatite. The onset of hydrothermal conditions, marked by the quartz cores to the dykes caused the reaction of apatite with REE-bearing hydrothermal fluids to form britholite. Continuous cooling and dilution of this system resulted calcite dissolution and the formation of progressively more Ca-rich REE fluorocarbonates.

The presence of sulphate as the dominant ligand in the hydrothermal fluid resulted in preferential transport and deposition of the HREE during mineral alteration. Experimental studies have shown that most common ligands (in particular Cl⁻) promote preferential solubility of the LREE (Migdisov et al., 2009; Tropper et al., 2011). However, SO₄²⁻ shows no preferential complex ion formation with the REE, and may therefore have leached the REE from HREE enriched calcite without significant fractionation (Migdisov and Williams-Jones, 2008). Sulphate enrichment in carbonatites may therefore be important in the development of HREE-rich mineral assemblages, alongside specialised magmatic source regions.

Acknowledgements

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