Fractionation of the *REE* in a carbonate hosted hydrothermal system: Bayan Obo, China

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The rare earth element (*REE*) distribution in hydrothermal fluids may provide constraints on fluid source and chemistry. The compositions of hydrothermal *REE* minerals have, in turn, the potential to record variations in the fluid composition. Bayan Obo, China, is a hydrothermal Fe-*REE*-Nb deposit hosted in Proterozoic dolomites, and is the worlds largest *REE* deposit (Chao *et al.*, 1997). This makes it an ideal setting for investigating the hydrothermal fractionation of the *REE*. In this study we report the results of electron microprobe analyses of *REE* minerals from Bayan Obo carried out using the method of Williams (1996), which, coupled with fluid inclusion studies, provide new insights into hydrothermal fractionation of the *REE* and further constraints on the genesis of the deposit.

Paragenetic setting

At Bayan Obo the *REE* are mainly hosted in monazite ($LnPO_4$) and bastnäsite ($LnCO_3F$), with minor amounts of Ca- and Ba-*REE* fluorocarbonates. The *REE* mineralisation is accompanied by replacement of the host dolomite marble by magnetite, aegirine, apatite, fluorite, alkali amphibole and baryte. The main stages of *REE* mineralisation can be summarised as: (1) Disseminated monazite in relatively unaltered dolomite. (2) Banded ores - bastnäsite and monazite associated with magnetite, apatite, aegirine and fluorite. (3) Post-aegirine - bastnäsite and minor monazite filling the interstices between euhedral aegirine in veins and vugs. (4) Syn-fluorite - bastnäsite and Ca-*REE* fluorocarbonates associated with fluorite alteration and veining. (5) Baryte stage - bastnäsite and Ca-*REE* fluorocarbonates from stages 2-4 replaced by baryte and huanghoite ($BaLn(CO_3)_2F$).

Variations in the rare earth distribution

All the *REE* minerals analysed are dominated by Ce (i.e. monazite-Ce; bastnäsite-Ce etc. sensu stricto). The main observed variation in *REE* distribution is in the range La to Sm and correlates with paragenetic setting (Fig. 1). *REE* heavier than Gd were below the detection limits for the method used. La_2O_3 and Nd_2O_3 vary by up to 10 wt.% in monazite and bastnäsite and Pr_2O_3 varies by up to 2 wt.%. Disseminated monazites show La/Nd ratios in the range $\approx 2-3$, but from one sample they are strongly La enriched (La/Nd $\approx$ 6−7). Monazite and bastnäsite from the banded ores show a wide range in *REE* distribution, from samples with La/Nd ratios comparable to the majority of the disseminated monazite, to La-rich examples (La/Nd $\approx$ 5−5.6). Bastnäsite and Ca-*REE* fluorocarbonates associated with fluoritisation are La-depleted and Nd-enriched relative to bastnäsite from the banded ores (La/Nd $\approx$ 0.7−2.4), whilst bastnäsite, and associated monazite, forming post-aegirine in veins and vugs, are La-enriched (La/Nd $\approx$ 5−5.8). At the baryte stage huanghoite is always depleted in La relative to the minerals it is replacing. Despite the correlation with paragenetic setting, the *REE* distribution does not evolve in a continuous manner with relative time as indicated by the paragenetic sequence.

Discussion

All the minerals studied have similar Ln sites and no evidence was found for crystallographically controlled variations within individual minerals. *REE* mineral alteration during several stages of metasomatism also could not have led to the main variation in composition, as no change in the *REE* distribution occurs between the precursor and secondary phases during replacement reactions (except for at the baryte stage). The variations in mineral chemistry must therefore reflect variations in the relative concentrations of the *REE* in the metasomatic fluid. The initial control on the *REE* distribution in the fluid is the fluid source, which at Bayan Obo has been suggested to be either carbonatite magmatism or lower crustal rocks. Although the fluid source at Bayan Obo must have been strongly *LREE* enriched neither of these possibilities is likely to have given rise to the discontinuous variation in *REE* distribution.
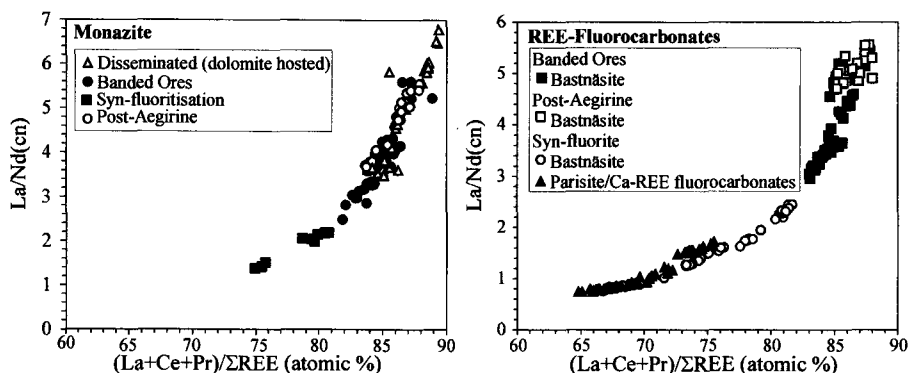
FIG. 1. Variation of the chondrite normalised La/Nd ratio with the overall *LREE* enrichment for *REE* minerals from Bayan Obo.

Variations in the bulk fluid chemistry are, however, indicated by fluid inclusions. Fluid inclusions in aegirine, apatite and bastnäsite from the banded ores are moderately saline (c. 5–15 wt.% NaCl eq.) with estimated mole fractions of CO_2 varying from below microthermometric detection to c.15%. In contrast apatite and bastnäsite from aegirine veins contain CO_2-rich, low salinity fluid inclusions (0–5 wt.% NaCl eq; c. 20 to >55 mole % CO_2). Fluorite contains both low salinity, CO_2-rich inclusions, and CO_2-free, halite saturated, aqueous inclusions, possibly indicating periods of fluid immiscibility. Both experimental data and theoretical predictions indicate that the association constant increases with atomic number across the *REE* series for first aqueous complexes with fluoride and carbonate (both likely ligands at Bayan Obo), which would lead to greater H*REE* solubilities in aqueous fluids at hydrothermal temperatures. However, Haas *et al*. (1995) predicted an increase in aqueous complex stability for La and Ce relative to Pr, Nd and Sm at high T and high ligand numbers (e.g. LnF_3^0). High ligand number, neutral complexes would be expected to form preferentially in CO_2-rich fluids relative to charged complexes, because of the reduction in the fluid dielectric constant relative to aqueous solutions at high X_{CO_2}. This suggests that La and Ce could be concentrated in CO_2-rich fluids, probably as neutral,

high co-ordination number complexes, relative to Pr, Nd, and Sm. This concept is supported by the work of Wendlandt and Harrison (1979) who demonstrated high solubilities of La and Ce in CO_2 relative to Sm and Tb, albeit at very high T and P. Such a model could explain the fractionation from intermediate to high La/Nd ratios seen in minerals from Bayan Obo. Variations in the speciation of the *REE* in aqueous and carbonic fluids could have important consequences for their use as tracers of hydrothermal processes. Similar La-Nd fractionations have been reported in late stage carbonatites, where they have been attributed to increased relative solubilities of La and other *LREE* in CO_2-rich, 'carbothermal' fluids compared to later stage aqueous fluids.

References

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