The hydrothermal mobility of the rare earth elements

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Extended Abstract

Although magmatic processes commonly control the formation of REE ores, in many deposits the REE have been remobilized by hydrothermal fluids, and some are almost exclusively hydrothermal in origin. Genetic models for the hydrothermal transport and deposition of the REE generally assume that the REE are transported mainly as fluoride complexes. This is partly because of a common association of hydrothermal REE mineralization with fluorite and partly because aqueous REE-fluoride complexes are more stable than REE species involving most other plausible ligands. As a result, the potential role of these other ligands in transporting the REE to sites of ore formation has largely been ignored. This contribution evaluates the nature of hydrothermal REE transport, and the processes of REE mineral deposition in chlorine-, fluorine-, and sulphate-bearing hydrothermal fluids.

Hydrothermal fluids appear to have concentrated the REE in numerous deposits. For example, the Gallinas Mountains deposit, New Mexico, USA, is an exclusively hydrothermal light REE deposit of marginal economic interest in which a fluorite-bastnäsite-(Ce)-barite assemblage cemented quartz-syenite, rhyolite porphyry and sandstone breccias (Fig. 1). Based on a detailed study of fluid inclusions, the deposit is interpreted to have formed between 300 and 400ºC from brines containing 12 to 18 wt.% NaCl equivalent (Williams-Jones et al., 2000). Although the source of the mineralizing fluids is uncertain, it is inferred to be the magma that crystallized the quartz syenite or rhyolite porphyry. However, some researchers (e.g., Schreiner, 1993) have speculated that the fluids may have originated from a hidden carbonatite. In contrast, the Browns Range deposit, Australia, is a predominantly heavy REE hydrothermal deposit that hosts a potentially economic resource containing 8.98 million tonnes of ore grading 0.63 wt.% total REE oxide, of which the heavy REE make up 85%. The REE mineralization is hosted by hematite-altered meta-sandstones in veins and breccias or as disseminations, and takes the form of xenotime-(Y) and minor florencite-(Ce). The geological context is poorly known because of poor outcrop, but the presently accepted interpretation is that the mineralizing system was emplaced along a failed continental rift, and that the source of the fluids was a granitic magma (Cook et al., 2013). The Wicheeda deposit, British Columbia, Canada, is an example of a carbonatite-hosted light REE deposit (LREE) containing 11.3 million tons, grading 1.95 wt.% total REE oxide (Trofanenko et al., in press). The REE mineralization, mainly bastnäsite-(Ce), occurs with dolomite mostly in vugs and veins in dolomite-carbonatite that forms the core of a small intrusion with a marginal calcite carbonatite facies. Proximal potassic and distal sodic fenites surround the intrusion; the potassic fenites host very minor REE mineralization in the form of monazite-(Ce). On the basis of its mode of occurrence, the REE mineralization is interpreted to be hydrothermal or carbo-hydrothermal, an interpretation that is supported by carbon and oxygen isotopic data (Trofanenko et al., in press). The latter suggest that the fluids originated from a carbonatite magma, which ‘stewed in its own juices’ and deposited the ores at a temperature between 300 and 400°C.

Fig. 1. Bastnäsite (beige rectangular crystals) cemented by fluorite in a sample of sandstone-hosted breccia (numerous small irregularly shaped fragments) from the Gallinas Mountains deposit, New Mexico.

At several important deposits, hydrothermal fluids remobilized magmatically concentrated REE. An example is the Nechalacho deposit in the Northwest Territories, which is hosted by a layered, silica-undersaturated alkaline complex (varieties of nepheline syenite), and contains a resource of 62 million tonnes grading 1.65 wt.% total REE oxide (22% HREE) and 0.4 wt.% Nb oxide (Sheard et al., 2012; Ciuculescu et al., 2013). There, the primary magmatic REE mineralization formed as a result of gravity settling of eudialyte (a complex zirconosilicate containing ~7 wt.% REE_2O_3) and zircon (containing ~3 wt.% REE_2O_3) in the upper parts of the layered suite during the end stages of crystallization (Sheard et al., 2012). This crystallization culminated with the exsolution of orthomagmatic hydrothermal fluids that altered the mineralized horizon and overlying rocks to a biotite-magnetite assemblage. These fluids dissolved the primary ore minerals and re-precipitated the REE as fergusonite-(Y), secondary zircon, allanite-(Ce), bastnäsite-(Ce) and monazite-(Ce) together with fluorite. The HREE were deposited proximal to the precursor minerals, whereas the LREE were mobilized upwards on a scales of metres and perhaps 10s of metres.

Experimental studies have shown that the REE form very stable fluoride complexes in hydrothermal fluids, that REE-sulphate complexes have lower stability, and that REE complexes with chloride ions are less stable than with the other two ligands (Migdisov and Williams-Jones, 2008; Migdisov et al., 2009). Experimental data on the stability of other potentially important REE complexes, such as those involving carbonate, are lacking. However, theoretical calculations suggest that the stability of REE-carbonate complexes is comparable to that of REE-fluoride complexes. The experimental studies have shown that the stability of the REE fluoride and chloride complexes decreases with increasing atomic number of the lanthanides, implying that the light REE are likely to be more mobile than the heavy REE (Fig. 2). This effect, however, is not observed with sulphate complexes.

In some cases, such as the Gallinas Mountains deposit, the fluids were chloride-bearing brines which, from the association of the ores with fluorite and in some cases barite, also may have contained significant fluorine and sulphate ions. Unfortunately, the only reliable measurements of the fluorine and sulphate concentrations of fluids known to have precipitated REE minerals are those of Banks et al. (1994). These fluids contained ~500 ppm F and ~2 wt.% $SO4^{2-}$. We have modelled the transport of the REE for a fluid containing these concentrations of fluoride and sulphate and a concentration of chloride equivalent to 10 wt.% NaCl, and temperatures up to 400°C. From this modelling, it is evident that significant concentrations of REE (>10 ppm) can only be transported as chloride complexes and at low pH, or as sulphate complexes at mildly acidic pH and high temperature (Fig. 3). There are no conditions at which fluoride complexes can transport significant REE, and the reason for this is that at low pH, fluoride activity is low because HF is a weak acid and at higher pH, saturation of the fluid with fluocerite buffers fluoride activity to very low values. The modelling also showed that REE ore deposition is promoted by a decrease in temperature (Fig. 4) and an increase in pH. Although the REE form very stable complexes with carbonate ions, we do not consider that carbonate complexes are significant in REE transport. On the contrary, because of the very low solubility of bastnäsite-(Ce) (Williams-Jones, et al., 2012; Migdisov and Williams-Jones, 2014; Gysi and Williams-Jones, 2015), the main role of carbonate ions is to promote REE ore deposition. The same is also true of fluoride ions as inferred above. In principle, the REE should form strong complexes with phosphate ions because the REE are hard cations and phosphate is a hard anionic species (Williams-Jones and Migdisov, 2014). However, both monazite-(Ce) and xenotime-(Y), the main REE phosphate ore minerals, are extremely insoluble (Migdisov and Williams-Jones, 2014; Gysi et al., 2015). It therefore follows that the main role of phosphate ions in hydrothermal ore formation, like that of fluoride and carbonate ions, is not to transport the REE but rather to facilitate their deposition.

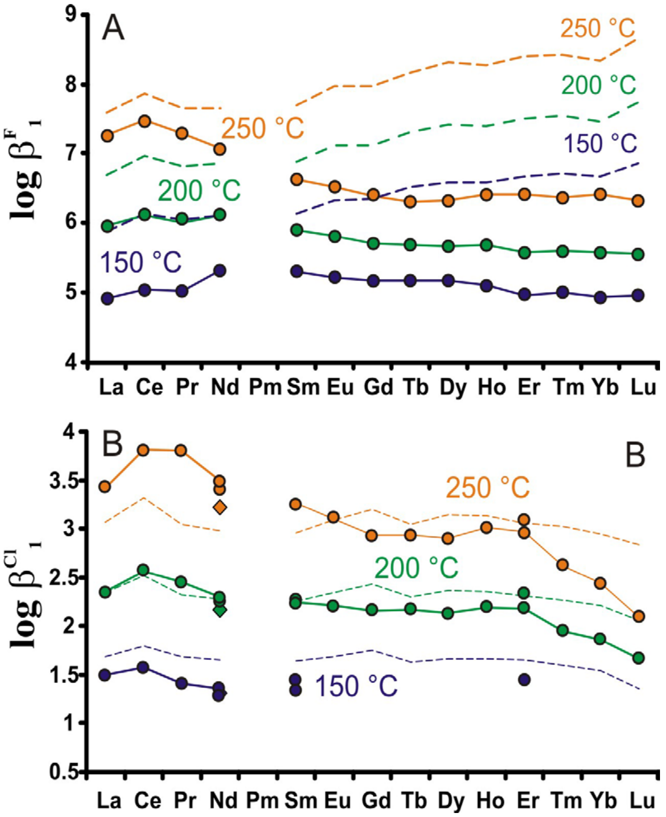

Fig. 2. Stability constants for **a)** $REEF^{2+}$ and **b)** $REECl^{2+}$ at elevated temperature. The solid lines represent experimentally derived values from Migdisov et al., (2009) and the dashed lines, theoretical estimates from Haas et al. (1995). The experimental data show that the REE are more stable as REE-fluoride complexes than REE chloride complexes, and that overall their stability decreases with increasing atomic number, i.e., from light REE to heavy REE. The comparison with the theoretical estimates emphasizes the danger inherent in extrapolating to higher temperature based on experimental determinations made at ambient temperature.

Because the light REE form much more stable complexes in chloride-bearing solutions, they will be more mobile than the heavy REE, as shown for the Nechalacho REE deposit. Modelling of the solubility of various end-members of monazite in an environment of decreasing temperature and increasing fluid-rock interaction confirms this observation. The modelling shows that the heavier REE-bearing monazite end members will be deposited at high temperature close to the point of fluid input, whereas monazite-(La) will deposit at locations

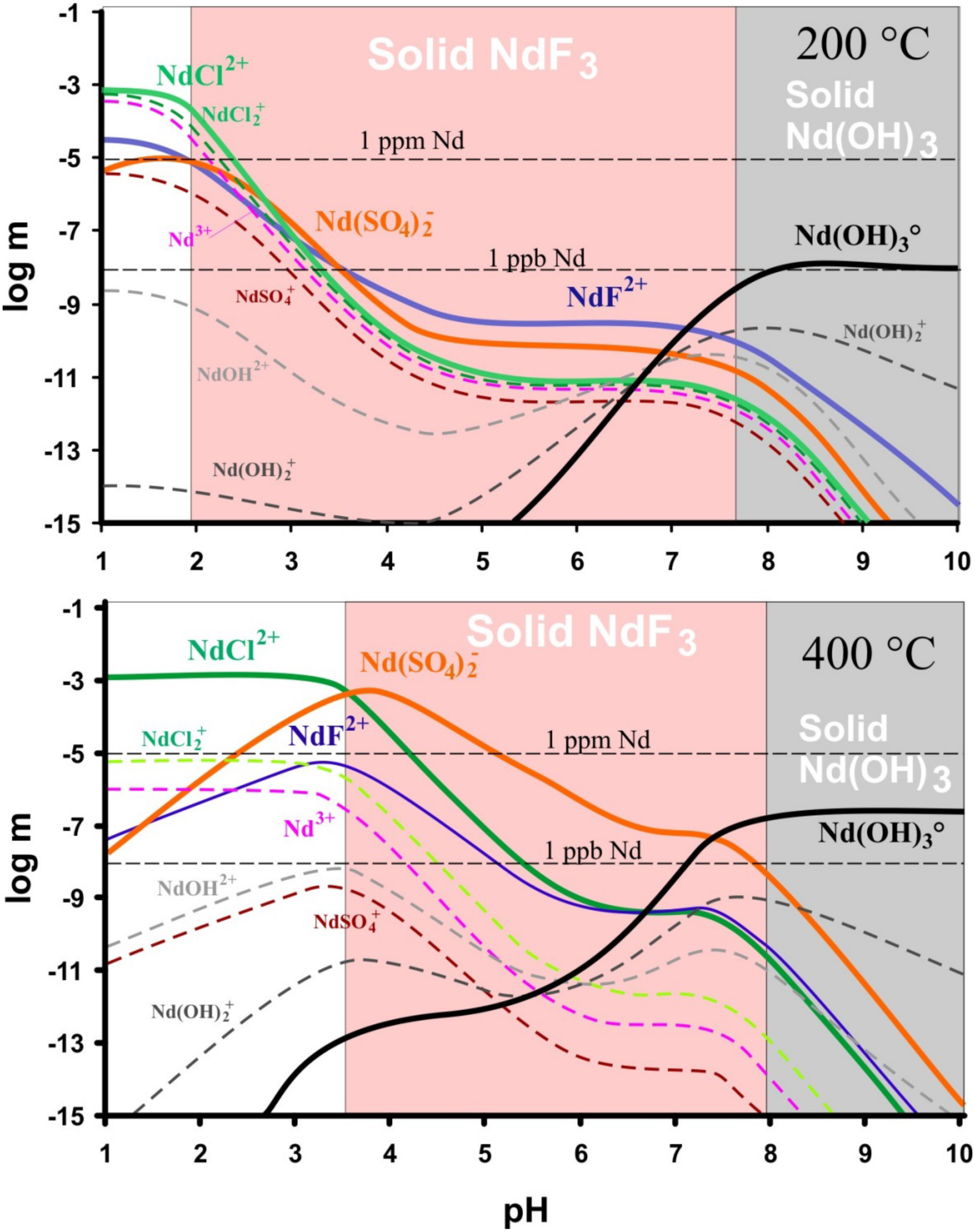

Fig. 3. The speciation of Nd as a function of pH, assuming that the fluid contains 10 wt.% NaCl, 2 wt.% Na_2SO_4, 500 ppm F, 200 ppm Nd (See Banks et al., 1994). The pink region shows conditions for which Nd-solubility is buffered by the precipitation of NdF_3 and the blue region for which it is buffered by precipitation of $Nd(OH)_3$.

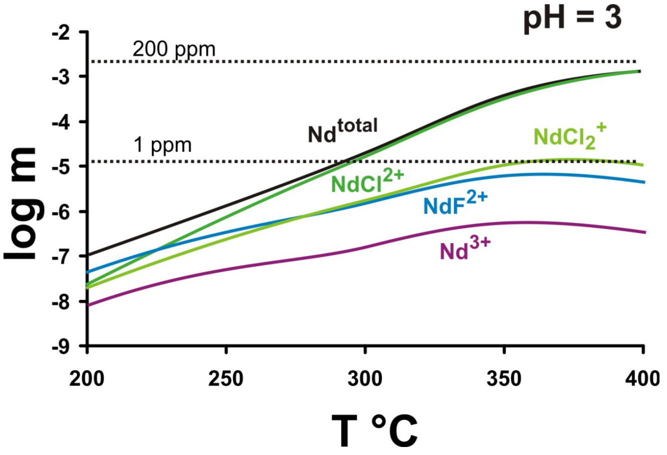

Fig. 4. The solubility of Nd as a function of temperature, assuming that the fluid contains 10 wt.% NaCl, 500 ppm F, 200 ppm Nd (See Banks et al., 1994).

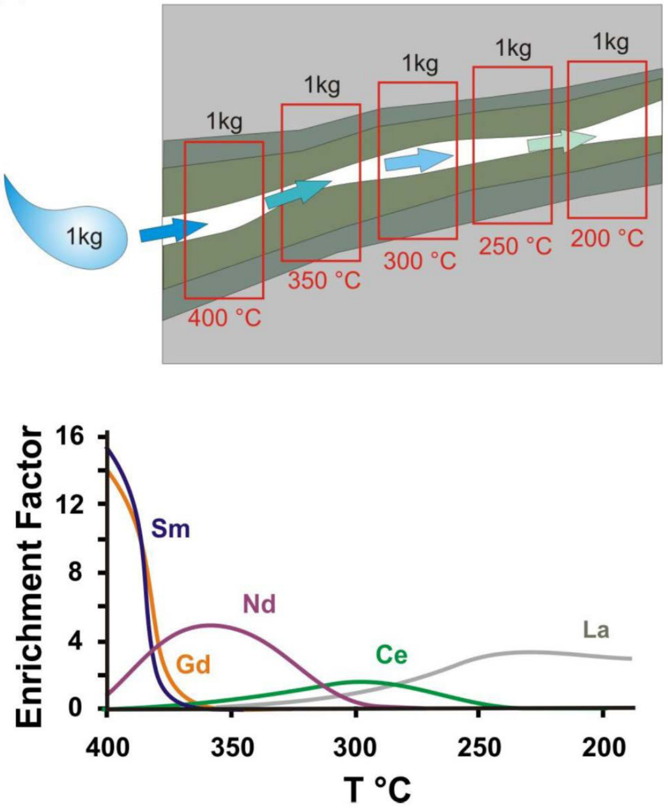

Fig. 5. A model of the fractionation of the REE as a result of fluid-rock interaction. Consecutive 1 Kg aliquots of a fluid containing 10 wt.% NaCl, 500 ppm F, and 50 ppm are introduced along a thermal gradient into 1 Kg of nepheline syenite containing 100 ppm P (illustrated by the cartoon). This results in the deposition of monazite in decreasing proportions away from the fracture due to the increasing pH (bands coloured by shades of green). Each red box defines a region at constant temperature. The binary diagram illustrates the enrichment of the rock in each of the REE after the introduction of five aliquots of fluid. As is evident, La is most enriched at low temperature, i.e., distal from the source, whereas Sm and Gd are most enriched at the source. Thus the light REE are more mobile than the heavy REE. The enrichment factor is $(REE/\Sigma REE)_{Rock}/(REE/\Sigma REE)_{Initial\ solution}$.

distal from the point of fluid input and at lower temperature (Fig. 5). An important question concerning the Browns Range REE deposit is why its mineralization is so rich in heavy REE, particularly given that almost any conceivable ore fluid will be enriched in the light REE relative to the heavy REE; the light REE have much greater crustal abundance than the heavy REE. A possible answer to this question is that the deposit formed relatively close to the source of fluid input and that the host-rocks (sandstones) had limited capacity to buffer the pH of the fluid to higher pH. In such a scenario, the light REE would have been transported to crustal levels above the current level of erosion, whereas the heavy REE would have been deposited in the rocks immediately above the granite, which is inferred to have been the source of the fluids.

To conclude, in many environments where hydrothermal processes play a role in ore formation, the REE are transported predominantly as REE-chloride complexes. In these cases, ore deposition will be promoted by processes that increase pH and decrease temperature such as interaction with cold rocks having high pH buffering capacity (e.g., marbles and limestones), boiling (which decreases temperature and increases the pH of the ore fluid) and fluid mixing (e.g., with a lower temperature external fluid of higher pH). Finally, fluids transporting the REE as chloride complexes will fractionate the REE to varying degrees depending on the pH buffering capacity of the host rocks. This could explain why deposits such as Browns Range (hosted by rocks with low pH buffering capacity) are enriched in the heavy REE, whereas others are light REE-enriched (hosted by rocks with higher pH buffering capacity).

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