The MINES thermodynamic database for simulating the hydrothermal mobilization of REE in critical mineral deposits

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Abstract. The rare earth elements (REE) are essential for the high-tech and green technology industries, and used, for example, in computers, smartphones, and wind turbines. The REE are considered critical minerals and can be highly enriched in certain magmatic-hydrothermal systems including alkaline complexes and carbonatites. Almost all of the critical mineral deposits show a complex overprint by hydrothermal processes during their genesis. However, our understanding of the mobility in these ore-forming systems and our knowledge about the stability of REE minerals is still very limited. The MINES thermodynamic database is an open-access database and continuously updated with the most up to date thermodynamic data for REE aqueous species and minerals. This database also includes rock-forming minerals and permits simulating the mineralogy and alteration geochemistry that relates to the formation of these critical mineral deposits. This study gives a short overview of the MINES thermodynamic database and the GEMS code package for simulating the formation of hydrothermal calcite, fluorite and bastnäsite-(Ce) veins relevant to interpreting critical mineral deposits.

1 Introduction

Critical mineral deposits evolve through a complex sequence of magmatic-hydrothermal processes, and most of them, are overprinted by late auto-metasomatic processes (e.g. Gysi et al. 2016; Elliott et al. 2018). The mobilization, fractionation and/or enrichment of critical elements, such as the rare earth elements (REE), can be predicted using thermodynamic modeling (Migdisov et al. 2016; Perry and Gysi 2018). These geochemical models yield insights about the controls and distribution of REE in these deposits and can potentially be used together with field geochemical data to predict alteration vectors for mineral exploration. However, our current ability to predict the behavior of REE in high temperature aqueous fluids and interpret these natural systems depends on the availability of thermodynamic data for the REE minerals and aqueous species.

The hydrothermal solubility of the REE phosphates, monazite and xenotime, has only recently been determined experimentally (Gysi et al. 2015, 2018; Van Hoozen et al. 2020; Gysi and Harlov 2021). The same applies to the thermodynamic properties of bastnäsite-(Ce) (e.g. Gysi and Williams-Jones 2015; Shivaramaiah et al. 2016; Goncharov et al. 2022). Furthermore, new models are developed based on experimental work, which aid in simulating the mechanisms of REE incorporation into gangue vein minerals such as apatite, calcite, and fluorite (Perry and Gysi 2020; Payne et al. 2023).

Thermodynamic data are available to predict the mobility of REE in acidic aqueous fluids to ~350-400ºC, whereas more experimental work is needed to simulate the mobility of REE in alkaline and supercritical fluids >350-400ºC. The properties of many aqueous REE species have been determined experimentally, including fluoride, sulfate, and chlorite complexes that control REE transport in acidic fluids (Migdisov et al. 2016). Previous modeling studies further indicate the potential importance of REE hydroxyl and carbonate complexes in alkaline fluids (Perry and Gysi 2018). The thermodynamic properties of these aqueous species are, however, still poorly known at elevated temperature, and the properties of a few of the REE carbonate complexes were determined only recently in hydrothermal solutions (Louvel et al. 2022; Nisbet et al. 2022).

Here, I present the MINES thermodynamic database and a modeling study using the GEMS code package (Kulik et al. 2013) to show an application of geochemical modeling in economic geology. This study gives an example of the replacement of a calcite vein by hydrothermal fluorite and bastnäsite-(Ce), and related compositional changes in fluorite to highlight advances and capabilities for modeling critical mineral deposits.

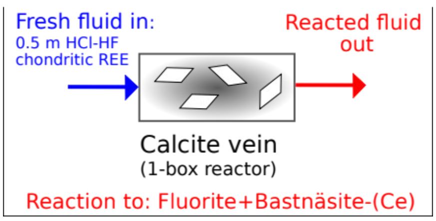

Figure 1. Conceptual model of a multipass leaching model (or 1-box flow-through reactor model), showing the input/output of fresh/reacted aliquots of acidic REE-F-bearing fluids passing through a calcite vein.

2 Methods

The MINES thermodynamic database (https://geoinfo.nmt.edu/mines-tdb) is an open-access database updated on a rolling release model (i.e., as new data become available, and have been implemented and tested). The current database comprises >700 aqueous species and minerals relevant to modeling hydrothermal ore-forming processes and fluid-rock interaction. The database includes aqueous REE species (Migdisov et al. 2009, 2016), REE phosphate minerals, and REE fluorocarbonates (Gysi and Williams-Jones 2015; Gysi et al. 2015, 2018; Van Hoozen et al. 2020; Gysi and Harlov 2021). The database also includes rock-forming minerals (Robie and Hemingway 1995; Holland and Powell 1998), zeolites, and clay minerals (Gysi and Stefánsson 2011).

The program GEM-Selektor (https://gems.web.psi.ch) was used with the MINES thermodynamic database to simulate the replacement reaction of calcite vein by secondary fluorite and REE fluorocarbonates (Fig. 1); a typical reaction texture observed in many critical mineral deposits. The simulations were carried out in the Ca-REE-F-Cl-C-H-O system at 400ºC and 500 bar with an acidic REE-F-Cl-bearing starting fluid (0.5 m HCl/HF) interacted with a calcite vein. The REE concentrations used are the chondrite values listed in McDonough and Sun (1995).

The first model is a multipass leaching model (Figs. 1-3) where at each step a fresh aliquot of acidic REE-F-Cl-bearing fluid interacts with the calcite vein while the alteration mineralogy, fluid chemistry, and the compositions of both calcite and fluorite can be monitored. The second model is a 1-D reactive transport model (Fig. 4), which permits simulating fluid-flow using the GEM2MT module implemented in the GEMS code package. In this model, 50 sequential rock nodes containing calcite were interacted simultaneously with the acidic fluid, which is flushed as sequential “waves” through each of the rock nodes. The resulting mineral distribution is then recorded after 200 and 2000 steps or waves.

3 Modeling examples

3.1 Multipass leaching model

Figure 2 shows the progressive replacement of the calcite vein by fluorite and bastnäsite-(Ce) upon increased fluid-rock interaction (i.e., aliquots of fluid added). The pH is initially buffered by calcite to a value slightly below ~6.5. Interaction of the acidic REE-F-bearing fluid with calcite leads to the formation of bastnäsite-(Ce) and fluorite according to:

$CaCO_3$ (calcite) + $3F^-$ + REE^{3+} = CaF_2 (fluorite) + $REEFCO_3$ (bastnäsite) **(Eq. 1)**

Once all calcite is consumed (~140 aliquots of fluid in Fig. 2), bastnäsite-(Ce) becomes unstable and all the remaining REE (i.e., not flushed out through the reactor box) are retained in fluorite. Figure 3 shows the compositional evolution of the simulated REE-bearing fluorite. These preliminary simulations indicate that fluid-rock reaction can lead to significant REE variations in fluorite including the light (L) and heavy (H) REE. Furthermore, the simulations show a REE enrichment in fluorite of up to ~100 times chondrite.

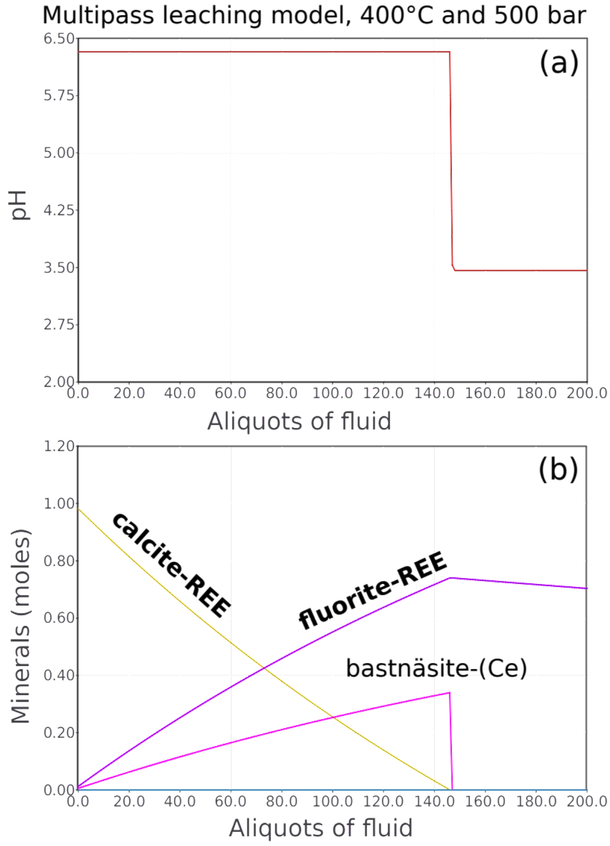

Figure 2. Multipass leaching model (or 1-box reactor flow-through) showing (a) the simulated pH and (b) the simulated mineralogy as a function of aliquots of fluids flushed through the calcite vein. Calcite-REE and fluorite-REE both indicate that the REE concentrations were simulated for these minerals.

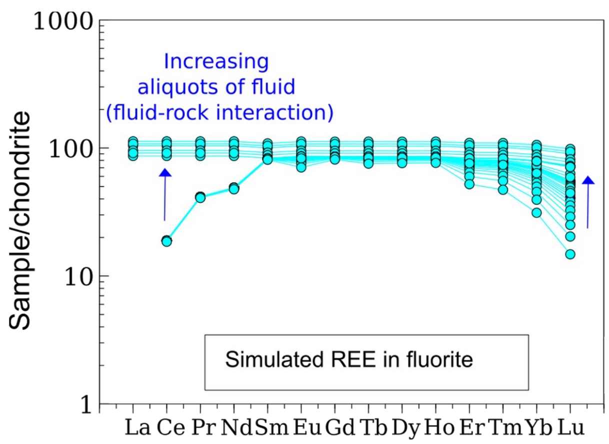

Figure 3. Simulated REE variations in fluorite normalized to chondrite. The stability of fluorite is shown in Figure 2 and variations correspond to various degrees of fluid-rock interaction or aliquots of fluid flushed through the rock.

3.2 1-D reactive transport model

Figure 4a shows the evolution of a calcite vein after 200 steps, with the development of a large zone of REE mineralization (i.e., fluorocarbonate veins) and a smaller zone of fluorite plus bastnäsite-(Ce). Upon increased fluid-rock interaction (Fig. 4B; after 2000 simulations steps), a large zone of fluorite develops at the input side of the acidic REE-F-bearing fluid, and a large zone of calcite plus bastnäsite-(Ce) forms on the output side of the reactive fluid flow path. A smaller zone comprising fluorite plus bastnäsite-(Ce) forms at the interface between the calcite and fluorite rich zones.

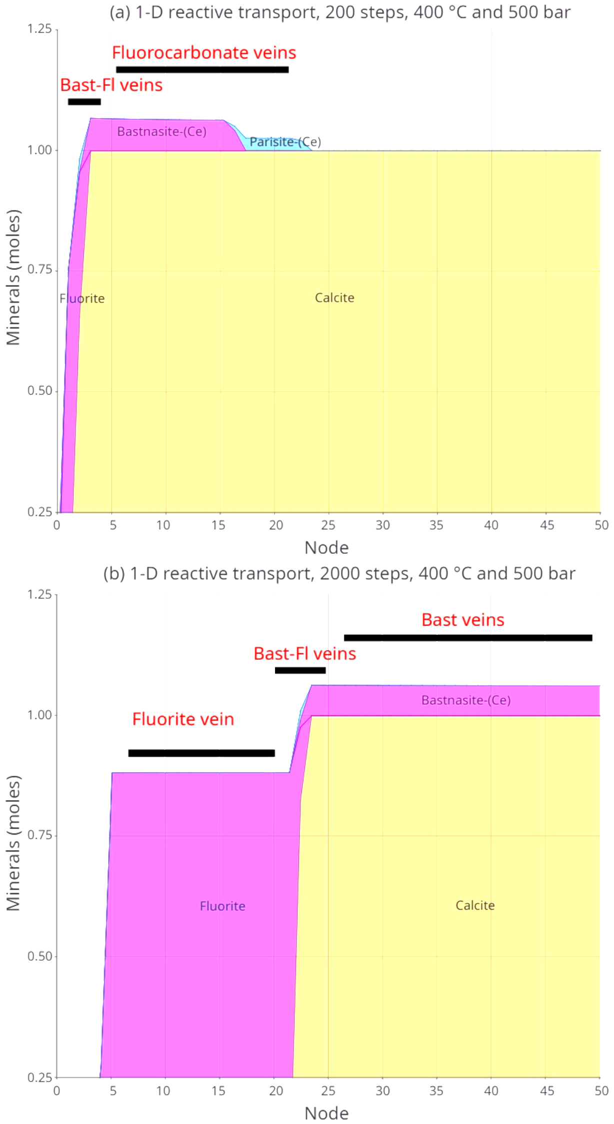

Figure 4. 1-D reactive transport simulations showing the mineralogy in 50 nodes or boxes of rock after (a) 200 steps and (b) 2000 steps, representing the number of fluid “waves” flushed through all the calcite boxes.

4 Conclusions

Numerical modeling provides a powerful tool to interpret the mineralogy, geochemistry, and alteration zones developed in natural critical mineral deposits. The MINES thermodynamic database was used here to show an example application to fluid-rock interaction processes that control REE mobilization. This can be extended to different mineral systems (Gysi and Williams-Jones 2013; Perry and Gysi 2018; Payne et al. 2023). Many of the REE mineral deposits associated with carbonatites and alkaline deposits contain hydrothermal barite,calcite, fluorite, and/or bastnäsite-(Ce) bearing veins. Hence the simulations presented in Figures 2-4 provide a first step in quantifying the processes that affect the stability of these minerals and concurrent change in fluorite REE chemistry. Prominent examples where this type of reactions could be of importance include the hydrothermal fluorite-REE-bearing breccia/vein deposit in Gallinas Mountains in New Mexico (McLemore et al. 2021), Bear Lodge in Wyoming (Andersen et al. 2019), the giant Bayan Obo carbonatite deposit in China (Gao et al. 2021), and the Mianning-Dechang REE belt in China (Guo and Liu 2019).

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