The thermodynamic stability of monazite for vectoring the hydrothermal mobility of REE in ore deposits

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The growing applications of the rare earth elements (REE) to the high-tech and green technology industry has led to an increased interest in the thermodynamic behavior of REE minerals and their aqueous complexes within the geochemical community. The REE minerology and rock chemistry of REE deposits can display significant variations during hydrothermal overprint[1,2]. Monazite ($CePO_4$) is a common mineral in these deposits and, in several cases, can be attributed to hydrothermal mineralization processes. The giant REE deposit in the Bayan Obo carbonatite[3] and the IOA deposit in Pea Ridge[4,5] contain monazite displaying significant compositional and textural variations that may provide useful vectors of fluid-rock interaction and ore deposition processes. To quantify the meaning of these variations using thermodynamic modelling will require a robust thermodynamic dataset for REE minerals and their aqueous complexes[6].

In this study, a series of hydrothermal batch solubility experiments have been conducted using $LaPO_4$, $PrPO_4$, $NdPO_4$ and $EuPO_4$ to assess the compatibility of available calorimetric data of these minerals and the thermodynamic data of the aqueous REE species. Additional calorimetric and XRD measurements were carried out to determine the thermodynamic properties of a series of monazite solid solutions. Solubility experiments were carried out in aqueous $HClO_4$-H_3PO_4-bearing solutions at temperatures between 100 and 250 °C at saturated water vapor pressure. The equilibrium constants (K_{s0}) determined for each endmember was then evaluated as a function of temperature and extrapolated to standard conditions of 25 °C and 1 bar. The results indicate significant differences in retrieved solubilities in comparison to the available literature data. We will demonstrate the impact of this new thermodynamic data by analyzing the results of several batch system equilibrium simulations using the GEMS code package (http://gems.web.psi.ch) and the MINES thermodynamic database (http://tdb.mines.edu). Our current and future thermodynamic data will be implemented in this thermodynamic framework and allow for the more accurate prediction of the hydrothermal behavior of REE in mineral deposits.

[1] Gysi and Williams-Jones (2013), *GCA* 122, 324-352; [2] Gysi et al. (2016), *Econ. Geol.* 111, 1241-1276; [3] Smith et al. (2000), GCA 64, 3141-3160; [4] Harlov et al. (2016), *Econ. Geol.* 111, 1963-1984;[5] Hofstra et al. (2016*), Econ. Geol.* 111, 1985-2016; [6] Gysi et al. (2015), *Chem. Geol.* 401, 83-95.