

## Solubility of CePO<sub>4</sub> and YPO<sub>4</sub> in H<sub>2</sub>O, H<sub>2</sub>O-NaCl and H<sub>2</sub>O-NaF at 800°C and 1 GPa: Implications for REE transport during high-grade metamorphism

P. TROPPEL<sup>1,2\*</sup>, C.E. MANNING<sup>1</sup> AND D. HARLOV<sup>3</sup>

<sup>1</sup>Dept. of Earth and Space Sciences, Univ. California, Los Angeles, CA 90095, USA

(\*correspondence: Peter.Tropper@uibk.ac.at)

<sup>2</sup>Institute of Mineralogy and Petrography, University of Innsbruck, Innrain 52, A-6020 Innsbruck, Austria

<sup>3</sup>GeoForschungsZentrum Potsdam, Telegrafenberg, D-14473 Potsdam, Germany

Monazite (CePO<sub>4</sub>) and xenotime (YPO<sub>4</sub>) are important accessory minerals because they host REE and Y and are useful for geochronology. It is therefore essential to understand their behavior during high-grade metasomatic processes. To constrain solubilities at high *P* and *T*, we carried out weight-loss experiments on synthetic single crystals of each phosphate at 800°C, 1 GPa, with H<sub>2</sub>O, H<sub>2</sub>O-NaCl or H<sub>2</sub>O-NaF (methods of [1-3]). Results indicate that the molality (*m*, mol/kg H<sub>2</sub>O) of CePO<sub>4</sub> and YPO<sub>4</sub> dissolved in pure H<sub>2</sub>O is very low (CePO<sub>4</sub>: 0.0006 *m*, YPO<sub>4</sub>: 0.0002 *m*) but that CePO<sub>4</sub> solubility increases strongly with increasing NaCl to 0.021 *m* at 40 mol% NaCl, similar to fluorite [3] and calcite [4]. Solubility of YPO<sub>4</sub> increases only moderately, to 0.0037 *m* at the same NaCl content. Thus CePO<sub>4</sub> shows a stronger solubility enhancement by NaCl than YPO<sub>4</sub>. Data from the NaF-H<sub>2</sub>O system show an enormous increase in solubility of both phosphates: CePO<sub>4</sub> and YPO<sub>4</sub> solubility increase to 0.22 and 0.49 *m* in only 10 mol% NaF; YPO<sub>4</sub> thus shows stronger solubility enhancement. These data support previous indications that REE and Y mobility are strongly promoted by complexing with Cl and especially F in the aqueous phase. Because F is readily partitioned into high-grade fluids, even small amounts of this element in metasediments will yield at least local REE metasomatism during devolatilization reactions associated with high-grade metamorphism.

[1] Manning & Boettcher (1994) *American Mineralogist* **79**, 1153-1158. [2] Tropper & Manning (2005) *American Mineralogist* **90**, 502-505. [3] Tropper & Manning (2007) *Chemical Geology* **242**, 299-306. [4] Newton & Manning (2002) *American Mineralogist* **87**, 1401-1409.

## Redox reactions induced by hydrogen in nuclear waste repository: An experimental study

L. TRUCHE<sup>1,2\*</sup>, G. BERGER<sup>3</sup>, C. DESTRIGNEVILLE<sup>2</sup>, D. GUILLAUME<sup>2</sup> AND E. GIFFAUT<sup>1</sup>

<sup>1</sup>ANDRA, 1/7 rue Jean Monnet, 92290 Châtenay-Malabry, France (\*correspondence: truche@lmtg.obs-mip.fr)

<sup>2</sup>Université Toulouse, LMTG, 14 av. E. Belin, 31400 Toulouse, France

<sup>3</sup>CNRS, LMTG, 14 av. E Belin, 31400 Toulouse, France

Corrosion of steel canisters stored in deep geological nuclear waste repository leads to the generation and accumulation of H<sub>2</sub> gas in the surrounding environment. This study focussed on the mechanism and rate of redox reactions induced by the accumulation of H<sub>2</sub> in an argillite host-rock.

Preliminary batch experiments carried out with Callovo-Oxfordian argillite [1], synthetic porewater and H<sub>2</sub> gas led to an important H<sub>2</sub>S production in only few hours at 250°C to few months at 90°C. In order to explore whether H<sub>2</sub>S can originate from sulphate or pyrite reduction we performed dedicated experiments.

Sulphate reduction experimented in diphasic systems (water+gas) at 250-300°C and under 4 to 16 bar H<sub>2</sub> partial pressure exhibits a high activation energy (131kJ/mol) and requires H<sub>2</sub>S initiation and low pH condition as already observed in other published TSR experiments [2, 3]. The corresponding half-life is 210,000 yr at 90°C (thermal peak of waste repository). These features can be modelled by three chemical steps between H<sub>2</sub> and non symmetric sulphate species. Heterogeneous reactions were explored by using magnetite, an usual steel corrosion by-product and a well known catalyst for redox reduction [4, 5]. First results showed enhanced reduction rates.

Beside TSR, pyrite reduction into pyrrhotite is another possible H<sub>2</sub> sinks. Rates measured under slightly alkaline buffered pH conditions (calcite) in the 90-180°C interval showed a fast reaction proportional to the hydrogen pressure.

In addition to the contribution for the nuclear waste storage assessment, this study may also provide relevant conclusions in the understanding of redox processes governing hydrothermal systems.

[1] Andra, Dossier (2005) Public report. [2] Cross *et al.* (2004) *Org Geochem.* **35**, 393-404. [3] Zhang *et al.* (2008) *GCA* **72** (14), 3518-3530. [4] Peterson *et al.* (1996) *Colloids and Surfaces* **107**, 77-88. [5] Shevdov & Tremaine (2000) *Journal of Solution Chemistry* **29**, 889-904.