

## 3.6.12

### Lanthanide behaviour in hydrothermal fluids

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Previous solubility studies of pure Nd monazite (NdPO<sub>4</sub>) at high temperature and pressure [1,2] have shown that experimentally derived standard thermodynamic properties (STP), obtained at low temperature and pressure [3,4] fail to predict lanthanide (Ln) behaviour in hydrothermal systems.

#### STP determination (V°, Cp°) of La, Nd, Gd and Yb.

In order to obtain more realistic values of STP at high temperatures, we determined apparent molar volumes and heat capacities of Ln triflates solutions up to 300°C and 300 bars, using a vibrating tube flow densimeter [5] and a differential flow calorimeter [6]. The triflate anion of a large size is stable at high temperature and prevents a lanthanide from forming complexes. Properties of triflic acid and sodium triflate are also measured in order to obtain the properties of triflate anion. Our new data will be used to readjust the Ln<sup>3+</sup> parameters in the revised HKF model [4].

#### Solubility measurements of synthetic pure Nd monazite and speciation of lanthanides.

We used isotope dilution to study the effect of chloride and phosphate as complexing agents. Previous studies indicate chloride complexes have no influence on Ln mobility at 650°C-2 kbars [2]. Our work with H<sub>2</sub>O-H<sub>3</sub>PO<sub>4</sub>-NaCl-HCl solutions suggest Nd(OH)<sub>3</sub> is the major species at high temperature and pressure. At 300°C, under acidic conditions, solutions with Cl-rich solutions increase Ln solubility. The nature of the charged species remains to be determined.

Combining our new STP and solubility data will allow us to model Ln behaviour in hydrothermal systems. The results from this study could potentially be applied to nuclear waste storage problems, as the behaviour of lanthanides is similar to the behaviour of actinides and monazite is considered as a potential confining matrix.

#### References

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## 3.6.13

### REE partitioning between Fe oxyhydroxide and NaCl solutions under hydrothermal conditions

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To examine various REE patterns in terms of quantum-chemical energetics [1, 2] certainly provides us fundamental understandings of their behavior in natural systems. REE partitioning in hydrothermal systems has been hardly studied from this point of view although normal temperature results have been reported [3, 4]. In this study, REE partitioning between Fe oxyhydroxide and NaCl solutions were performed at 100 to 170°C.

The experiments without NaHCO<sub>3</sub>, which were run at 100, 150 and 170°C, made the characteristics of series variation of logarithmic REE partitioning coefficients further clear: the tetrad effect variation becomes smaller with increasing temperature. This is because the tetrad effect of entropy term tends to cancel the one of enthalpy term in higher temperatures since  $\Delta G_f = \Delta H_f - T\Delta S_f$ .

Also based on the results of REE partitioning experiments with NaHCO<sub>3</sub>, stability constants for REE(CO<sub>3</sub>)<sup>+</sup> and REE(CO<sub>3</sub>)<sub>2</sub><sup>-</sup> were determined. REE(CO<sub>3</sub>)<sup>+</sup> indicates almost constant stability constant values across REE series, whereas REE(CO<sub>3</sub>)<sub>2</sub><sup>-</sup> increase their stability constants in heavy lanthanides and Sc. Compared with the results in 25°C [5], the logarithmic stability constants for REE(CO<sub>3</sub>)<sup>+</sup> and REE(CO<sub>3</sub>)<sub>2</sub><sup>-</sup> at 100°C show smaller convex tetrad effect variations in an analogous way as the partitioning coefficients in the system without NaHCO<sub>3</sub>. The structural change of light REE in REE(CO<sub>3</sub>)<sub>2</sub><sup>-</sup> seems to become larger than in 25°C.

By fitting the partitioning coefficients and stability constants to the Refined Spin-Pairing Energy Theory equation [1, 2], it appears that the octad-effect term relating to the total spin quantum number of S more easily decreases with increasing temperature than the tetrad-effect term relating to the total orbital one of L. Therefore, the octad-like variation is apt to diminish overall tetrad effects with increasing temperature as a result of tetrad effects in entropy.

#### References

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