The structure of Yb³⁺ and Y³⁺ aquo ion and chloro complexes in hydrothermal solutions

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There is a distinct need for structure and speciation determinations of rare earth ions in hydrothermal fluids. Such data are necessary in order to improve our knowledge about the association of rare earth ions and ligands such as H₂O, Cl⁻, OH⁻, CO_3^{2-} , SO_4^{2-} and transport of these elements in hydrothermal environments within Earth's lithosphere. X-ray absorption fine structure (XAFS) spectra were measured separately for 0.006m YbCl₃/0.017m HCl and for 0.1m YCl₃ aqueous solution samples at the Yb L₃ and Y K edge, respectively, at up to 500 °C and 270 MPa. The measurements were made in the fluorescence mode on the PNC-CAT beam line at the Advanced Photon Source. The solution samples were loaded in the sample volume of a hydrothermal diamond anvil cell. One diamond of the cell has been laser milled to include two grooves oriented at 90° towards a 300 _mdiameter sample cavity centered in the anvil face. The grooves extend to within 80 _m of the sample cavity greatly reducing attenuation of both incident-beam and fluorescence-signal xrays. Spectral analysis shows no evidence of ytterbium chloro complexes and the predominance of Yb³⁺ as an aquo ion species in the ytterbium chloride aqueous solution in the 25 to 150 °C range. From 300 to 500 °C, chloro complexes most likely of the type Yb(H₂O) $_{n}Cl_{n}^{+3-n}$ (_ ~ 7) occur in the solution. The number of chlorine ligands (n) increases steadily from 0.5 ± 0.3 to 1.8 ± 0.2 whereas the Yb-Cl bond length decreases with temperature at a rate of about 0.02 Å/100 °C in this same temperature range. Y^{3+} and Cl^{-} ion association is found to occur at significantly lower temperatures. The number of chlorine ligands of the Y(H₂O)_mCl_n⁺³⁻ⁿ step-wise complexes increases steadily with temperature from 1.4 ± 0.6 at 150 °C to 3.9 ± 0.2 at 500 °C. The total number of ligands (m + n) in this temperature range undergoes a gradual transition from eight-fold to four-fold coordination so that the predominant complex at 500 °C is YCl₄-. The Y-Cl bond length decreases with temperature at a rate of about 0.01 Å/100 °C. Our results suggest that the Y³⁺-Cl⁻ion association is more like that of a 3d transition metal ion rather than a heavy rare earth ion in hydrothermal fluids.

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Constraining reactive transport models using mineralogical data

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The Role of Reactive Transport Modelling

Reactive transport modelling can be a useful tool when investigating complex groundwater systems. However, model results often remain highly non-unique. When matching model results to observed aqueous concentrations, it has to be kept in mind that these concentration profiles only provide a snapshot in time, and by themselves cannot provide a sufficient constraint on model results.

Using Mineralogical Data as a Model Constraint

On the other hand, the depletion of primary minerals and the formation of secondary minerals offer an additional constraint. The advantage of mineralogical data is that these data encompass the integrated effect of past geochemical reactions.

Example applications

Two demonstration examples are presented. The first example investigates the generation, and attenuation of acid mine drainage from mine tailings. The simulation results are compared to aqueous and mineralogical data (Johnson et al., 2000) 47 years after the tailings deposition ceased. Model results compare favourably to aqueous concentrations, but the model can be constrained better using secondary mineralogical accumulations. The second example investigates geochemical changes in a permeable reactive barrier designed for the treatment of contaminated groundwater (Mayer et al., 2000). The simulated results agree well with measured aqueous concentrations and predict the formation of a secondary mineral assemblage focussing on the entry area of the barrier. These results are supported by solid phase data (e.g. Wilkin et al., 2001).

Conclusions

Using mineralogical data as a constraint can improve model reliability, and increases the usefulness of reactive transport models for hypothesis testing. In particular secondary mineral accumulations can be used to minimize model non-uniqueness.

References

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