A new method for solubility measurement: application to $NdPO_4$ system in H_2O-NaCl-HCl hydrothermal fluids

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Monazite has been shown to be the principal host for the light *REE* and Th in the continental crust, is a mineral widely used for geochronology and has been also proposed as a possible host for nuclear wastes. Therefore, there is a strong need for accurate thermodynamic data on this mineral. In order to determine the monazite behaviour relative to hydrothermal fluids, we performed an experimental study of monazite solubility in hydrothermal conditions; we restricted the study to the neodymium end-member phase: $NdPO_4$.

Material and experimental methods

The experiments were carried out with synthetic monazite crystals (less than 1mm in size) grown by the flux method. The solubility was measured at 200 Mpa and at temperature between 450 and 800°C in gold capsules using either the weight-loss method or an isotopic dilution method. With the loss-weight method, quenching is obtained by a violent decompression of the system at the experimental temperature which lead to the explosion of the capsule and the loss of the solution. That way prevent any precipitation of monazite on the crystal during cooling. With the second method, monazite is allowed to react with a ^{145}Nd- rich solution until equilibrium is reached. During experiments, the dissolution of the monazite with natural $^{145}Nd/^{146}Nd$ modifies the composition of the starting solution. As the solution cooled to room temperature, monazite precipitation may occur but did not affect the $^{145}Nd/^{146}Nd$ ratio in the fluid. At the end of the runs, the samples were filtered through a 0.2 μm Nucleopore™ membrane, acidified and analysed with a mass spectrometer (CAMECA TSN 206). The solubility of $NdPO_4$ is then derived from the final isotopic composition of the solution using mass-balance equation.

Results and discussion

Results of solubility experiments performed in H_2O between 450 and 800°C are depicted in Fig. 1. The solubility of $NdPO_4$ increases with temperature. The good agreement between data generated by isotopic dilution and loss-weight methods indicates that isotopic dilution is a reliable technique for mineral solubility investigation in so far as isotopically-rich solutions are available for the element involved in the solid phase. This highly sensitive method can be used at any P-T conditions, does not require large crystals and is not sensitive to precipitation during quenching. Note that our results are several orders of magnitude higher than solubilities predicted using available thermodynamic data (Wood and Williams-Jones, 1998; Hass *et al.*, 1995).

The pH-dependence of monazite solubility was determined at 650°C in H_2O-NaCl-HCl solution by the weight-loss method. NaCl concentration was held constant while pH were adjusted to the target value with various HCl amounts. Results are shown and compared to calculation in Fig. 2. Monazite solubility is constant with increasing pH from 3.5 to 6. These results indicate that in a large pH range, i.e. from near acidic to neutral pH conditions, uncharged Nd aqueous complexes dominate in solution. We interpret this as resulting from the low dielectric constant value of water at this temperature. Considering the composition of the starting solution, three neutral species could be expected in our experiments: $NdCl_3^0$, $NdPO_4^0$ and $Nd(OH)_3^0$. However, similar solubilities are measured in H_2O-NaCl-HCl solution and in pure water that clearly indicates the negligible role played by chloride complexes on *REE* mobility at high temperature and pressure. This result is in good agreement with recent spectroscopic study on yttrium speciation in hydrothermal solution reported by Ragnarsdottir *et*

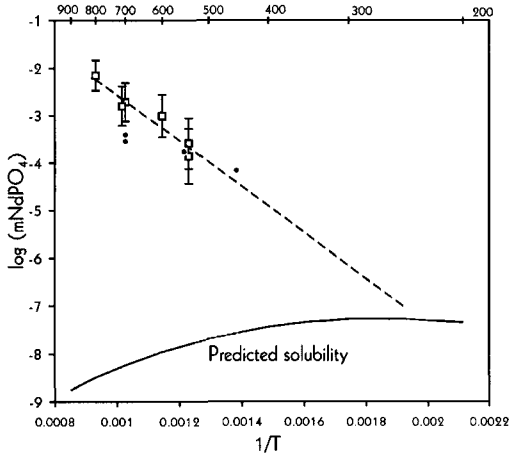

FIG. 1. Solubilities of $NdPO_4$ in H_2O as a function of 1/T, from weight-loss measurements and isotopic dilution (black circles).

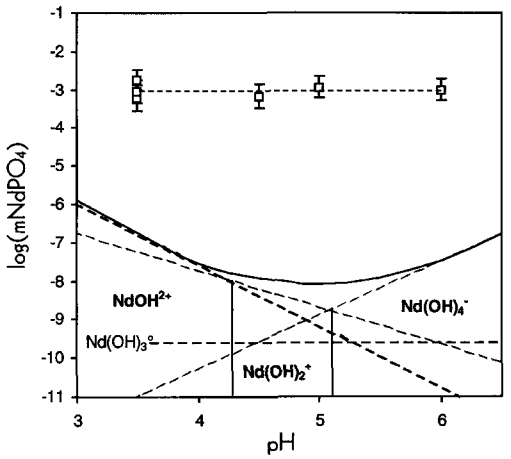

FIG. 2. Observed solubility as a function of pH at 650°C and 200 MPa in H_2O-NaCl-HCl (squares) compared with predicted speciation (see text).

al. (1997) but differs from the conclusions of Gammons *et al.* (1996). Based on the common ion effect technique, these authors have derived new equilibrium constants for Nd (III) chloride complexes and have estimated that Nd chloride complexes could be strong enough to account for important transport of this element.

Finally, this study emphasises that available models failed to predict *REE* behaviour in hydrothermal fluids at high P-T conditions. Thus new experimental data are needed to understand *REE* speciation at high P-T.

References

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