

A numerical simulation of brine-rock interaction

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The thermodynamic database, SUPCRT92 (Johnson et al., 1992) has been widely used for analyses of water-rock interactions. However, since it gives thermodynamic data of solutes in pure water solvents, they cannot be applied to solutes in mixed solvents as common geological fluids.

According to Hoshino et al. (2009), the dielectric constant is a key parameter characterizing chemical properties of solvents. Within the framework of electrostatic approach to predict thermodynamic properties of aqueous fluids taken in SUPCRT92, a chemical potential of a certain solute can be divided to the structural non solvation and solvation terms (Akinfiev and Zotov, 1999). The latter is expressed by the Born equation with the Born parameter of the solute and the dielectric constant of the solvent. Hence, if we can estimate the dielectric constants of brines, we may calculate the chemical potentials of solutes in the brines from those in pure water solvents given by SUPCRT92. They also tried to estimate the constants of 1 molal NaCl solutions from quartz solubilities in brines measured in previous experiments. The estimated constants are higher than those of water below 400 C at 100 MPa and abruptly increase with decreasing temperatures at around 400 C. However, they estimated the constants from quite rough inter- and/or extrapolations of solubility data of experiments under various temperature and pressure conditions with different salinities.

Therefore, we carried out solubility measurements for the assemblage of quartz and wollastonite in 1 molal NaCl solutions at 400 and 300 C at 100 MPa by using Dr. HIP (internally heated pressure vessel) of the Institute for Study of the Earth's Interior, Okayama University. Small amounts of quartz and wollastonite crystals were sealed with 1 molal NaCl solutions in gold capsules. Each capsule was hung by Mo wire in the hot spot of a Mo furnace within the pressure vessel, and held for 91 and 64 hours at 300 and 400 C, respectively. At the end of the run, the hanging wire was broken with a surging current, thereby letting the capsule fall into the cold bottom of the vessel, resulting in quenching the capsule.

Since Si is dissolved in the brines mainly as SiO₂(aq), while Ca is CaCl⁺ in the experimental conditions, the solubilities of the both minerals, i.e., concentrations of Si and Ca saturated with the minerals, are used for the consistency check of estimated dielectric constants and thermodynamic data for neutral and charged species.

The dielectric constants of the brines estimated from concentrations of Si, 15.83 for 400 C and 27.84 for 300 C, were, however, different from those estimated from Ca concentrations, 19.32 for 400 C and 34.38 for 300 C, probably due to analytical errors during concentration measurements. Another possibility is that the solutions continued to react with the minerals slightly after the ends of runs. Then, we estimated the quench temperatures where unique dielectric constants could be obtained for the both Si and Ca concentrations. The resultant temperatures are 385 C with the constant of 20.14 and 290 C with 34.51 for the 400 and 300 C runs, respectively. The constants are almost consistent with those estimated from Ca concentrations at 400 and 300 C. It should be emphasized that the born parameter of Ca²⁺ is about one order of magnitude larger than that of SiO₂(aq), resulting in the larger effect of a difference in the dielectric constant on Ca concentrations than the effect on Si concentrations, and that a dilution rate of the solutions for concentration measurements of Si is 10 times larger than the rate for Ca measurements. Therefore, the dielectric constants estimated from Ca concentrations may be much reliable than those from Si concentrations.

Results of numerical simulations of brine-rock interactions using the above estimated dielectric constants will be shown in the presentation.

Keywords: dielectric constant, H₂O-NaCl solution, solubility, SUPCRT92, geological fluid