Thermodynamic analysis of geofluids

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Although recent Equations Of State (EOS) for geological fluids of the H2O-NaCl-CO2 (-CH4-N2-...) system can give P-V-T properties and free energy functions of the fluids almost accurately, enthalpy and other functions derived from differentiation of the energy functions are not enough precise at temperatures around 300-400C.   This may be due to inaccurate interaction parameter(s) between H2O and NaCl of the EOS.   Since major species of dissolved NaCl may change from NaCl(aq) (high-T) to Na+ + Cl- (low-T) at around the temperatures, the parameter(s) can not exactly follow an effect of the changing species on thermodynamic properties of the fluids.

A change in dielectric constant of geothermal fluids with varying temperatures and/or fluid compositions may play an important roll in mineral precipitation/dissolution.   However, there may be no exact equation for the constant of the H2O-NaCl fluids at geological temperatures up to now.

Since we cannot accurately calculate water-rock interaction with high-NaCl solutions because of the above reasons, the author preliminarily simulates the interactions with boiling H2O-CO2 fluids.   Taking into consideration enthalpies and change of dielectric constants during boiling, it has been clarified that a decrease of CO2 in the liquid phase results in an increase of the dielectric constant of the solvent, which in turn increases solubilities of minerals.   It follows that boiling of the H2O-CO2 fluids is unlikely to be a general trigger for mineral deposition.   However, the results are not consistent with observations of many natural hydrothermal ore deposits in which boiling of the fluids has been thought as a direct trigger of ore formation.   Therefore, it can be concluded that although a decrease of CO2 during boiling in ore formation processes does not directly affect ore deposition, a resultant increase in concentration of dissolved NaCl species may cause dielectric constants to change suitable for ore deposition.

SUPCRT92 (Johnson et al., 1992) has been widely used for thermodynamic calculations of geochemical processes.   Unfortunately, however, the code cannot give exact thermodynamic functions of solutes in supercritical conditions.   This is due to uncertainty of P/T-dependent difference function of solvent (f-function of pure water) in the conditions on which Born coefficients of the solutes depend.   Thus, we cannot simulate water-rock interaction even with pure water in the conditions.

It should be emphasized again that we can not exactly estimate thermodynamic properties of solutes and solvents in the geothermal fluids at the temperatures 300-400C around which most interesting water-rock interaction occurs.   Detailed and accurate experimental data, theoretical formulation and analytical procedures of the geofluids at the temperatures should be needed in quite near future.