Mineral precipitation/dissolution from water and brine with decreasing temperatures along hydrostatic pressures

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Mineral-fluid interactions with decreasing temperatures along hydrostatic pressures, from 15.84 MPa - 500°C to 6.64 MPa - 200°C, have been simulated for 0.01 molal and 1 molal NaCl solutions. The dielectric constants of the former were taken from SUPCRT92 (Johnson et al., 1992), while those of the latter has been proposed from quartz solubility data in brine as:

$$\varepsilon_b / \varepsilon_w = a / (2\pi b)^{0.5} \exp(-(T - c)^2 / (2 b)) + d,$$

where, ε_b is the constant of the 1 molal NaCl solution, ε_w is that of water derived by SUPCRT92, π represents the ratio of the circumference of a circle to its diameter, T is a temperature in Celsius, the parameter a depends on a pressure (P in MPa) as $a = -0.9 * P + 420$, and b, c and d are the constants as 13000, 300 and 0.8, respectively.

On the other hand, a difference in chemical potentials of a jth solute ($\Delta\mu^{\circ}_j$) in the solution and water may be expressed as:

$$\Delta\mu^{\circ}_j = \omega_j (1/\varepsilon_b - 1/\varepsilon_w),$$

where, ω_j is the Born coefficient of the solute. Since the coefficients of the most charged species as well as $SiO_{2(aq)}$ are positive and ε_b is larger than ε_w in the simulated conditions, the chemical potentials of the above solutes in brine are smaller than those in water. This causes great differences between mineral solubilities in water (0.01M NaCl) and in brine (1M NaCl) as below.

Quartz

Since quartz solubility decreases with decreasing temperatures in water and brine, quartz precipitates from the both solvents with decreasing temperatures. However, because a decreasing rate of solubility in brine is smaller at higher temperatures and larger at lower temperatures, the precipitation amount shows a maximum at around 350 - 400°C. On the other hand, the amount decreases monotonically with decreasing temperatures in water.

Feldspar

Aluminum is dissolved mostly as AlO_2^- (= $Al(OH)_4^-$) in the both solvents. Equilibrium constants of dissolution reactions of K-feldspar, albite and anorthite with the above Al species decrease with decreasing temperatures. Therefore, the precipitation amounts of those feldspar from water solvent decrease monotonically with decreasing temperatures. On the other hand, it is quite interesting that they dissolve in brine at higher temperatures, while precipitate at lower.

Pyroxene and Al-free amphibole

Most pyroxene and amphibole show similar tendencies as feldspar. They gradually precipitate or dissolve small amounts with decreasing temperatures in water, while they dissolve in brine at higher temperatures and precipitate at lower.

One of the conceivable causes of the above temperature dependencies of the silicate precipitation/dissolution in brine is a great difference in activity coefficients of charged species. For

example, the activity coefficients (Debye-Hückel terms) for a divalent element in 0.01M NaCl solutions at 450°C and 300°C are 0.34 and 0.47, respectively, while they differ largely in 1M solutions as 0.023 and 0.20, respectively.

Carbonate

$CO_{2(aq)}$ is the major dissolved species above 250°C in the both solvents. Since the equilibrium constants of dissolution reactions of calcite, dolomite and magnesite with $CO_{2(aq)}$ decrease with decreasing temperatures, they precipitate from water gradually with decreasing temperatures, while they dissolve in brine at higher temperatures and precipitate at lower as feldspar, pyroxene and amphibole.

It should be emphasized that the temperatures of brine at which the above all silicate and carbonate minerals change their modes from dissolution to precipitation are around 400°C - 300°C.

Precipitation/dissolution of solid solutions of the above minerals and alteration (hydration) of some of the above minerals will also be discussed in the presentation.

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