



Phase equilibria in water-silicate-salt (fluoride-sulfate) systems

Z.A. Kotelnikova (1), A.R. Kotelnikov (2)

(1) Institute of ore geology, petrography, mineralogy and geochemistry RAS, (2) Institute of Experimental Mineralogy RAS (kotelnik@igem.ru)

Fluorine and sulfur are essential components of alkaline complexes. They affect mineral formation processes and occur in various mineral phases, including villiamate, nozeane, cancrinite, etc.

Experimental investigations were conducted in the $\text{SiO}_2\text{-H}_2\text{O-NaF-Na}_2\text{SO}_4$ (-NaCl) systems at 400-800°C and $P=1\text{-}2$ kb. Similar to other silicates, the aqueous systems of such salts, show critical phenomena in saturated solutions. SiO_2 is incongruently dissolved with increasing temperature producing several transitional compounds: millardite and Na (hydro)silicates.

Visual observation revealed unmixing in a liquid phase in the vapor-saturated $\text{SiO}_2\text{-H}_2\text{O-NaF}$ and $\text{SiO}_2\text{-H}_2\text{O-NaF-Na}_2\text{SO}_4$ systems at temperatures of 250-400°C. The concentration of one of the liquid phases may be higher than that of the initial solution. In this case an increase in the number of components in the fluid stabilizes the metastable immiscibility field. Three or four noncrystalline phases could be in equilibrium in such systems.

The heating of the unmixed solutions resulted in critical phenomena between vapor and solution in presence of the second liquid: $L_1=L_2+V$ at $\sim 400^\circ\text{C}$. Further heating did not result in the disappearance of either liquid. This implies that there is a pressure region at supercritical temperatures for saturated solutions where a homogeneous fluid can unmix to two phases with different densities. Immiscible water-rich and silicate—salt noncrystalline phases coexist under parameters between the solidus and liquidus curves. Up to the attainment of the solidus, silicates and water fluid must be formed

form the former and silicates, salts, and melt, from the latter. The equilibrium between the two phases is retained. The water-silicate-salt phase contains about 60 wt % SiO_2 and 2 wt % F. When temperature increases up to the upper three-phase field (above 700°N), the fraction of water in it increases at the expense of silica. During changes in P-T parameters, the fluid phase may gradually transform into a gas or liquid within the whole temperature range.

According to our results, the fluid systems studied are extremely inhomogenous in a wide range of temperature. Heterogenisation processes occur at temperatures from 800°C up to $250\text{-}350^\circ\text{N}$.

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