

PHASE CHANGES AT WATER-SILICATE-FLUORIDE SYSTEMS

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We synthesized fluid inclusions in natural quartz by cracks healing method. Water-sodium fluoride phase diagram is of the P-Q type: the critical phenomena are observed in saturated solutions. Three-phase equilibria solid (S) + liquid (L) + vapor (V) or S+L 1+L2 exist under temperatures less than lower critical point P or greater than higher Q. In P-Q interval above-critical fluid or fluid plus solid are present.

500 °C isotherm.

Under pressures in the range of five hundreds – one thousand bar, the inclusions contain liquid and vapor bubble. Sometimes small crystals stick to this bubbles, depending on the salt concentration in the fluid generating mixture.

Under pressure of two kbar we found four- or three- phase inclusions, containing conventionally named “glassy” phase besides vapor, solid and liquid. This phase boundary with liquid had a form of regular meniscus. These inclusions were similar to natural melt inclusions. But it was trapped under temperature five hundred degrees at hydrothermal conditions. The amount of inclusions containing “glassy” phase was not high, from two to ten over the whole sample. Under heating, the fluid phase homogenized with liquid, while “glassy” phase didn't show observable changes up to four hundred degrees. The further heating was not conducted, to avoid inclusions' opening.

Besides that, we met two-phase V+L inclusions, homogenizing with liquid in the interval covering the homogenization temperatures fluid phase of multi-phase inclusions with “glassy” phase. Homogenization temperatures spread was quite high - up to twenty-thirty degrees.

These inclusions were placed not only along partially healed cracks, but also in the neogenic part of the sample.

1 kbar isobar.

In all the experiments up to seven hundred degrees we found V+L inclusions. It was trapped at homogeneous conditions. Under 725 and 800°C there were coexisting V+L and V+L+S inclusions. It was trapped from immiscible fluid. As far as the temperature in Q point minimal for upper three-phase domain, this temperature for water solutions of sodium fluoride can be taken as seven hundred ten degrees.

Under pressure of 1 kbar “glassy” phase was found in the samples of experiments conducted under temperature of 725°C and higher.

2 kbar isobar.

In all the samples we met V+L inclusions. Besides that, in all the samples we met inclusions with “glassy” phase. As a rule, we didn't observe solution of crystalline phase up to 500-550°C. “Glassy” phase from run in homogenous conditions didn't change. However, in inclusions trapped under temperature greater than point Q temperatures in the presence of heterogeneous fluid, “glassy” phase showed different behavior. Some solids melt. With temperature increase, vapor phase volume grows. This allows for suggestion that “glass” composition includes crystalline hydrates of sodium hydrosilicates, chipping water off under heating. In some V+L+S+Gl (glass) inclusions, liquid “list” appears around the vapor bubble.

Under temperature about 300-350°C in “glass” occur phenomena, similar to eutectic melting: instantaneous melting of one of the phases is accompanied by appearing of multiple solids in the liquid. During further heating, a part of them melts, but, about from 400-450 °C many inclusions open.

When we added NaCl solution to NaF solution at 500°C and pressure 500 bar, the heterogenization of fluid into L and V phases occurred. Phase L of the pure H₂O- sodium chloride system contains about 32 weight % of NaCl. Solid disappears under heating at 210°C. In our case solids were dissolved at 240-300°C and total homogenization was at 533-554°C. Vapor-liquid inclusions homogenized both in G and L at the same temperature intervals.

Similar results were obtained at another parameters.

In the case of presence of NaCl in the solution, the pressure required for appearance of “glassy” phase decreased to 500 bar.

The obtained results show that under 500°C and pressure 2 kbar the active interaction of fluid with quartz began. If it took place under lower temperatures, the used experimental technique did not allow for finding it. So, with temperature and pressure increase, it is impossible to speak about the system under study as binary H₂O- NaF, but only as ternary system H₂O- NaF -SiO₂, because quartz is no more inert.

It is important to understand the basics of the phase diagram structure of this system.

With temperature rise the chemical interactions take place. Sodium silicates and malladrite (Na₂SiF₆) are the products of this interaction. It takes three times much fluorine as sodium for formation of the malladrite molecule. Thus, as the atomic quantities of fluorine and sodium in the fluid are the same, excess of sodium in the form of Na(OH) can interact with quartz and generate sodium silicates or hydrosilicates.

So, we are dealing with the ternary system with the intermediate compounds. It is necessary to choose possible variants of phase diagrams. In our case, if the dynamics of the chemical interaction would be confirmed, the problem would be considerably simplified, as the water-sodium oxide-quartz system is quite well studied. Let's consider the results of our experiments in the terms of this system.

The existence of two liquids in our system is possible under very low temperatures, theoretically even lower than water critical point. One of these liquids is a water solution, and the other is silica-rich water saturated phase with the content of silica up to fifty weight percent and higher. For mixtures considerably different from eutonic, the immiscibility of liquids (saturated with solid phase or not) is wide spread. The equilibrium of immiscible liquids exists in the whole domain above the three-phase curve. This system has some features. Above-critical fluid heterogenizes when pressure decreases. But this heterogenous state can be preserved to low temperatures with cooling. The end of heterogenous condition is critical state contrary three-phase curve.

Conclusion:

1. Quartz-water-sodium fluorite system has alkaline character under high temperatures.
2. Apparently, in water-sodium fluorite-quartz ternary system, equilibria V+L₁+L₂+SNaF or V+L₁+L₂+SSiO₂ are possible. This equilibria absent in boundary binary systems.
3. Quartz solubility in this system is quite high in the wide range of temperatures and pressures. Practically, the "heavy fluid" was trapped in the inclusions, which is a low-temperature silicate melt containing much water.

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