

## INCLUSIONS SYNTHESIZED FROM NaF-(NaCl) -CONTAINING FLUIDS

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Increased content of F in magmatic fluid is frequently related with concentration of REE, Mo, W, Sn, Ta, Nb, U, Th, Be, Li, Rb, Cs and other elements. There is very few data on fluorine-containing fluids, their phase state under high temperature and pressure corresponding to fluid separation from magma. The concentration of fluorine in solutions trapped in natural fluid inclusions ranges from tenths to a few weight percent.

In order to obtain experimental evidence on fluorine-containing fluids, we synthesized fluid inclusions in natural quartz under  $T = 500\text{-}800^\circ\text{C}$  and  $P=0.5\text{-}2$  kbar in solutions containing NaF or NaF+NaCl by the crack healing method. Fluid components were introduced as 0.5M (2.1 wt %) NaF solution or dry solid NaF and water (NaF solubility is 4.1 wt % at room temperature). NaCl was put as 1M or 2M solution. The measurement accuracy was  $\pm 50$  bar for pressure and  $\pm 5^\circ$  for temperature. Experiments were carried out in hydrothermal high-pressure cold-seal vessels and autoclaves. Samples were brought to experimental conditions within 1.5-2 h, quenching took 5-8 min in cold-seal vessels and 20-30 min in autoclaves. The experimental duration was 23-35 days.

NaF solubility depends inversely on temperature: it is 4.1 wt % at  $25^\circ\text{C}$ , and close to zero at  $374^\circ\text{C}$ . The behavior of solubility at higher temperatures is unknown. The  $\text{H}_2\text{O}$ -NaF phase diagram is of the P-Q (II) type, i.e. critical phenomena are observed in saturated solutions. The three-phase equilibria solid (S)+liquid (L)+vapor (V) or  $\text{S}+\text{L}_1+\text{L}_2$  exist under temperatures less than lower critical point P or greater than upper critical point Q. There are no critical phenomena and three-phase equilibria in the P-Q interval, where above-critical fluid or fluid+solid is present. In such systems salt solubility increases drastically near critical point Q. Moreover, under high parameters, the interaction between NaF and  $\text{SiO}_2$  becomes possible, which leads to incongruent quartz solubility.

### Results

#### *500°C isotherm*

The inclusions trapped under 500 bar from 2.1 wt % NaF solution homogenized into either liquid or vapor phases at  $356\text{-}380^\circ\text{C}$  under conditions close to the critical isochor. Sometimes boiling within inclusions was observed at the homogenization temperature. The character of inclusions trapped under different pressures suggests that NaF solubility under a constant temperature of  $500^\circ\text{C}$  increases up to 5 wt % as pressure rises from 500 to 1000 bar.

In the samples obtained at 2 kbar, we found four-(three)-phase inclusions containing a “glassy” phase (G) in addition to vapor, solid and liquid. The “glassy” phase-liquid boundary had a form of a regular meniscus, and these inclusions were visually similar to natural melt inclusions with high fluid contents. But the synthetic inclusions were trapped under a temperature about  $1000^\circ$  lower than the quartz melting temperature. Sometimes, a crystalline phase was also present. The number of inclusions containing the “glassy” phase was not high, 2 to 10 over the whole sample. Upon heating, the vapor+liquid portion homogenized, while the “glassy” phase showed no visible changes up to  $400^\circ\text{C}$ . Further heating was not conducted to avoid inclusion opening.

In addition, we met two-phase vapor-liquid (V+L) inclusions, which homogenized into liquid within the interval of the homogenization temperatures of fluid phase from the multi-phase inclusions with “glassy” phase. The scatter of homogenization temperatures was quite high, up to  $20\text{-}30^\circ$ . These inclusions were situated not only along partially healed cracks, but also in the newly grown part of the sample. In several cases, a crystal appeared in the gas-liquid inclusions upon heating above  $160^\circ\text{C}$ . This crystal grew with rising temperature and shrank back to full invisibility when temperature decreased.

Our results show that under  $t=500^\circ\text{C}$  and  $P=2$  kbar fluid interacted with quartz producing sodium fluorine silicates and hydrosilicates. This process could occur under lower temperatures, but the experimental technique employed did not allow us to observe it. Thus, the system under study cannot be regarded as binary  $\text{H}_2\text{O}$ -NaF at high pressure and temperature, but rather as the ternary  $\text{H}_2\text{O}$ -NaF- $\text{SiO}_2$  system, because quartz is no more inert.

The addition of NaCl solution to NaF solution resulted in the heterogenization of fluid into phases L and V. Phase L of the pure  $\text{H}_2\text{O}$ -NaCl system contains 32.2 wt % NaCl (solid NaCl disappears in the V+L+S inclusions at  $210^\circ\text{C}$ ). In our case solids were dissolved at  $241\text{-}301^\circ\text{C}$ , and total homogenization was attained at  $533\text{-}554^\circ\text{C}$ . The V+L inclusions homogenized both into gas ( $392\text{-}454^\circ\text{C}$ ) and liquid ( $428\text{-}449^\circ\text{C}$ ). The anomalous character of inclusions could be related to the capture of the products of interaction between fluid and quartz. In the case of NaCl-bearing solution, the pressure required for appearance of the “glassy” phase decreased to 500 bar.

#### *1000 bar isobar*

In all the experiments up to  $700^\circ\text{C}$  we found V+L inclusions (homogeneous fluid), and under  $725^\circ\text{C}$ , coexisting V+L and V+L+S (immiscible fluid). Since the temperature of point Q is minimal for the upper three-phase domain,  $T_Q$  for NaF water solutions can be taken as  $710^\circ\text{C}$ .

A distinct crystalline phase appeared in some of the V+L inclusions synthesized under 750-800 °C upon heating up to 360°C. Cooling to 244°C resulted in the dissolution of this phase, which was evidently NaF crystals. The concentration of NaF in V+L inclusions synthesized under 750 °C is about 2 wt %, as determined by criometry. The estimation of V+L+S inclusions composition showed 60-70 wt % NaF.

V+L inclusions trapped at 700° homogenized into liquid at 376-378°C and into vapor at 378-382°C, i.e. under near-critical parameters. Under a pressure of 1 kbar the "glassy" phase was found in samples from experiments conducted under a temperature of 750°C and higher.

When we added NaCl to the solution, the homogenization temperatures of V+L inclusions increased compared to the pure fluorine inclusions, synthesized under similar conditions. For example, inclusions of NaF solutions trapped under 600°C homogenized at 366-373°C, while those of NaF+NaCl solutions, at 394-412°C (both into liquid). Similar to the pure NaCl system, heterogenization took place at 700°C. Solid phase was represented by two types of crystals, but the dissolution temperature was reliably estimated only for NaCl. In three experiments with different Cl/F ratios, it corresponded to 44-53 wt% NaCl (in the pure H<sub>2</sub>O- NaCl system, liquid contains 49wt % of salt).

### 2 kbar isobar

In all the samples we observed V+L inclusions. Their homogenization occurred at 290-315°C (into liquid) in 500°C run; at 352-364°C (into liquid) in 700°C run; at 378-382°C (both into liquid and gas) in 750°C run; at 376-390°C (into liquid), 385°C (into gas), and boiling was observed at 365-379°C in 800°C run. Besides that, all the samples contained inclusions with the "glassy" phase: V+L+G and/or V+L+G+S, and in the 800°C run, also V+G. Heating of such inclusions synthesized under 500 and 700°C lead to the homogenization of their vapor-liquid portions (into liquid) at 306-313°C and 339-345°C respectively (i.e. within the homogenization interval of coexisting V+L inclusions); no changes in phase G were detected. As a rule, we did not observe dissolution of crystal phases up to 500-550°C.

The "glassy" phase showed a different behavior in inclusions trapped under temperatures greater than T<sub>Q</sub> in the presence of heterogeneous fluid. Under 140-160°C a grainy pattern appeared on its surface, and in certain cases it was clearly seen that bubbling occurred in the "glass". When temperature increased, the liquid-"glass" interface boundary became rough, toothed in places, and liquid phase volume grew at the expense of "glass" and gas. This allows us to suggest that the "glass" composition includes crystal hydrates of sodium hydrosilicates, which liberated water upon heating. In V+G+S inclusions, a liquid film appeared around the vapor bubble. Under a temperature of about 350°C phenomena similar to eutectic melting occurred in glass: instantaneous melting of one of the phases was accompanied by the appearance of numerous tiny crystals in the liquid. During further heating, part of them melted, but many inclusions leaked at about 400°C.

It is evident that V+L<sub>1</sub>+L<sub>2</sub>+S<sub>NaF</sub> or V+L<sub>1</sub>+L<sub>2</sub>+S<sub>SiO2</sub> equilibria are possible in the ternary H<sub>2</sub>O-NaF-SiO<sub>2</sub> system, in contrast to boundary binary systems. In the critical points of the ternary system, the minimum temperature and pressure of critical equilibria correspond to L<sub>1</sub>=L<sub>2</sub>+V+S<sub>NaF</sub> and L<sub>1</sub>=L<sub>2</sub>+V+S<sub>SiO2</sub>, rather than to point Q with the L<sub>1</sub>=L<sub>2</sub>+S<sub>NaF</sub>+S<sub>SiO2</sub> equilibrium. SiO<sub>2</sub> solubility in this system is quite high in a wide range of temperatures and pressures. In fact, the "heavy fluid" was trapped in the inclusions, which is a low-temperature silicate melt containing much water.