

## Experimental Study of the Na<sub>2</sub>CO<sub>3</sub>-Bearing Fluids Using Synthetic Fluid Inclusions in Quartz

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Fluid inclusions in quartz were synthesized from Na<sub>2</sub>CO<sub>3</sub> solution. It was shown that at the experiments conditions the fluid was heterogeneous and was not inert with respect to quartz and albite. The liquid separation occurred in some inclusions during heating. This indicates on the possibility of multi-stage heterogenization of the fluid.

*Key words: synthetic fluid inclusions, heterogenization, liquid separation*

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Experimental studies of phase equilibria in fluid systems are necessary for reconstruction of natural mineral formation conditions and further progress in theoretical and experimental research. The heterogeneous fluid equilibria in the second type H<sub>2</sub>O–Na<sub>2</sub>CO<sub>3</sub> system in the presence of SiO<sub>2</sub> or SiO<sub>2</sub> + NaAlSi<sub>3</sub>O<sub>8</sub> are considered in this paper.

The both boundary binary H<sub>2</sub>O–Na<sub>2</sub>CO<sub>3</sub> and H<sub>2</sub>O–SiO<sub>2</sub> systems belong to the second type with metastable liquid immiscibility. In the H<sub>2</sub>O–SiO<sub>2</sub> system coordinates of point Q correspond to 1050°C, 9.8 kbar, and 40–50 wt % SiO<sub>2</sub> according to Kennedy [Kennedy *et al.*, 1962]. The location of the upper critical point Q of binary H<sub>2</sub>O–Na<sub>2</sub>CO<sub>3</sub> system corresponds to 480°C, 1600 bar, and 30–40 wt % Na<sub>2</sub>CO<sub>3</sub> according to Ravich [1974] or 500 ± 10°C, 1505 ± 0.01 bar, and 12 ± 2 wt % Na<sub>2</sub>CO<sub>3</sub> according to Koster van Groose [Koster van Groose, 1962]. Butuzov and Bryatov [1957] investigated a fragment of the H<sub>2</sub>O–Na<sub>2</sub>CO<sub>3</sub>–SiO<sub>2</sub> system enriched in H<sub>2</sub>O at 300–400°C and under a pressure exceeding the pressure of saturated vapor. They noticed that solubility of quartz in the homogeneous region directly depends on salt concentration in water, but when the fluid became heterogeneous with appearance of two liquids differing in density, called heavy and light phases, the loss of quartz in weight increases abruptly. The heavy phase contained 30–50 wt % SiO<sub>2</sub> and concentrated Na<sub>2</sub>O.

Method of synthetic fluid inclusions used. The runs were conducted under 1–3 kbar and at 700°C. Special runs with addition of albite were carried out. It is suggested that the effect of aluminosilicate on experimental results can be regarded as indirect evidence for interaction of quartz with fluid.

Run at  $P = 1$  kbar. Fluid inclusions studying implies that the inclusions entrapped a heterogeneous fluid: two immiscible vapor- and liquid-like phases contrasting in density coexisted under the run conditions. Heating of synthesized inclusions resulted in appearance of one more immiscible liquid phase in some inclusions at a temperature of ~ 250°C. These data are completely consistent with the results obtained by Ravich [1974], who described equilibrium of two liquids rather than liquid and vapor in the upper two-phase region. The results of freezing experiments on inclusions with liquid immiscibility show that salt is the last phase melted at a positive temperature. The salt concentration of the solution filling such inclusions is sufficiently high (13.5–13.8 wt %). A light denser liquid that arose between the inclusion's wall and residual liquid phase slightly increased in volume with further rise of the temperature and existed up to 550°C. Two aqueous salt-bearing solutions and vapor coexisted within a temperature range of 250–382°C.

Run at  $P = 1$  kbar in the presence of albite. In contrast to the run without albite, liquid immiscibility was not observed in the presence of albite. Low-density inclusions were not detected, so that fluid remained homogeneous under the accepted run conditions. At the same time, a wide dispersion of the measured thermometric characteristics indicates that the run conditions were close to the phase boundary of heterogenization. Comparison of experimental results obtained for the inclusions synthesized in the presence of albite and without this phase shows that albite exerts effect on equilibria in fluid, which shift markedly. Thus, solubility of albite in carbonate-bearing solutions is rather high.

Run at  $P = 2$  kbar. The increase in pressure led to the absence of the vapor phase: inclusions homogenized only into liquid at 352–365°C. The salt concentration determined from freezing experiments ranged from 8 to 17 wt %. Sporadic inclusions revealed liquid immiscibility. The run conditions were close to the phase boundary. The low-density phase was likely formed in insignificant amounts and entrapped only together with high-density liquid. As a result, the thermometric characteristics of inclusions are widely scattered. Because quartz interacted with aqueous salt-bearing fluid, the established temperature range of homogenization and melting of salt reflects kinetics of such interaction: inclusions varying in composition and density were captured at different stages of proceeding reaction.

Run at  $P = 2$  kbar in the presence of albite. In two- and three-phase inclusions with a glasslike phase (Gl+V+S), when temperature rises up to 250°C, numerous small liquid bubbles arise, gradually increasing in volume and merging. While heating, they accumulate around a gas bubble, which dissolved in liquid at 351–361°C. Thus, the phase entrapped in the inclusions at  $T = 700^\circ\text{C}$  and  $P = 2$  kbar, being cooled, enables to bind a significant amount of water. If it is assumed that fluid is composed of pure water and glass is sodium silicate, the volumetric proportions make it possible to estimate an amount of  $\text{H}_2\text{O}$  dissolved in glasslike phase at room temperature at 9–13 wt %.

Run at  $P = 3$  kbar. The occurrence of low- and high-concentrated inclusions and the inclusions containing glasslike phase of heavy fluid implies that three immiscible phases coexisted under the run conditions. This is additional evidence for interaction of quartz with fluid and existence of tricritical point in the ternary  $\text{H}_2\text{O}$ – $\text{Na}_2\text{CO}_3$ – $\text{SiO}_2$  system. Thus, the interaction of silicate phase with aqueous salt-bearing fluid is supported by all experimental results obtained at various pressures and in the presence of albite.

The experimental results for the  $\text{H}_2\text{O}$ – $\text{Na}_2\text{CO}_3$ – $\text{SiO}_2$ – $\text{NaAlSi}_3\text{O}_8$  systems confirm liquid immiscibility in the lower two-phase region. Because of this, heterogeneous fluid equilibria are reached in much wider temperature range than in the first type systems. The immiscible phase of heterogeneous fluid entrapped under experimental conditions in the upper two-phase region, in turn, can separate into two noncrystalline phases when temperature and pressure drop.

Heterogenization in the upper two- or three-phase-region is accompanied by radical redistribution of dissolved components between immiscible phases. According to Ravich (1974), the  $\text{Na}_2\text{CO}_3$  concentrations in immiscible liquids are distinguished by no less than an order of magnitude. Immiscible liquids are also enriched or depleted in ore components. Thus, fluid immiscibility is an efficient mechanism of partitioning of ore components. If heterogenization proceeds during several stages, partitioning will be even more efficient.

The available experimental data allow us to suggest that fluid immiscibility is widespread in nature within a range of temperature and pressure beginning from the magmatic fluid release and up to the following hydrothermal process; multistage heterogenization of fluid is possible. The hydrolysis resulted in contrasting pH of immiscible phases is noted in many aqueous salt-bearing systems under high temperature heterogeneous conditions. A relatively dense and concentrated heavy fluid acquires alkaline reaction and interacts with quartz and other silicates with formation of intermediate compounds. The apparent solubility of silicates under heterogeneous conditions markedly increases with formation of intermediate compounds. Solubility of other poorly soluble compounds, for example, some ore minerals having the second type phase diagrams, can increase in the same manner. Such a fluid phase is able to transfer components of both gangue and ore minerals. Pressure release can be more important for the discharge of that fluid than a drop in temperature.

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