

THE MODELING OF MINERALIZATORY COMPONENTS-CONTAINING FLUID SYSTEMS

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Phase ratios in $\text{Na}_2\text{CO}_3\text{--H}_2\text{O}$ system are especially interesting for geochemistry in connection with carbonatite genesis problems. Solubility of anhydrous Na_2CO_3 at 25°C is 8.13 mass%. It goes down to almost zero at the critical temperature of water. Critical phenomena in these solutions occur both in saturated and unsaturated solutions. Peculiarities of Na_2CO_3 solutions had been studied up to 550°C and 1900 bar by Ravich [1] and up to 925°C and 400-3700 bar by Koster van Groos [2]. Lower critical point's coordinates are slightly higher than the critical point of water. The upper critical point Q, according to Ravich [1] is 480°C , 1600 bar and 30-40 mass% Na_2CO_3 . Koster van Groos [2] gives $500\pm 10^\circ\text{C}$, 1505 ± 0.01 bar and 12 ± 2 mass% Na_2CO_3 for point Q. It was not mentioned in both papers whether liquid separation under temperatures lower than the critical point Q took place or not. However in [1] it was observed the equilibrium of two liquids, in two-phase area, in contrast to liquid and vapor in [2]. This indicates that the upper part of critical curve connecting Q with salt critical point does not continue to the lower part, connecting critical point of water with P. Hence, both parts of the critical curve can have metastable continuation. In this case, the phase diagram will contain a region of metastable separation of liquid. Intersection of this region with the two-phase region of vapor+liquid lead to a liquid1+liquid2+vapor equilibrium. The data on such equilibrium are not published so far.

This paper describes experiments on $\text{H}_2\text{O--Na}_2\text{CO}_3\text{--SiO}_2$ system by synthetic fluid inclusions method under 700°C and 1-3 kbar. The fluid inclusions have been synthesized from 1M Na_2CO_3 solution (9.58 mass%).

Inclusions: vapor(V)+liquid(L), glass(Gl)+V and Gl+V+L has been synthesized at 1 kbar. The vapor volume percentage in Gl+V inclusions is around 15 to 20%. The vapor

bubble shrinks insignificantly during heating up to 565°C . Heating was stopped at this temperature because of the danger of decrepitation. V+L inclusions homogenized both into vapor and into liquid at temperatures between 363 and 393°C . The Na_2CO_3 concentration in these inclusions is around 2–8 mass%. In some inclusions, with a maximum salt content, separation of liquid and vapor has been observed under heating up to 240°C . A second liquid phase appeared close to the inclusion rim. Vapor expanded gradually and, at temperature of $381\text{--}383^\circ\text{C}$, the lower density liquid phase was absorbed. The phase changes of this experiment fall into the P-Q interval, in which neither critical phenomena nor three-phase equilibria are possible, but only pure fluid or fluid in equilibrium with crystal salt phase is present. However the presence of different types of inclusions is in contradiction with this phenomenon. It is assumed that fluid has been actively interacting with quartz resulting in intermediate compounds.

V+L and V+L+S inclusions have been synthesized at 2 kbar. The fluid is immiscible at experimental conditions. The concentration of V+L fluids is 7.5–14 mass% Na_2CO_3 . Homogenization into the liquid phase takes place at $352\text{--}365^\circ\text{C}$. This fact proves the co-existence of two liquids under experiment's conditions. In some fluid inclusions, liquid separation took place during heating: a second liquid appeared around the vapor bubble. Vapor gradually dissolved in this liquid at $367\text{--}368^\circ\text{C}$. V+L and V+L+S inclusions obtained at 3 kbar. The Na_2CO_3 concentration is 3–4.5 mass%. Homogenization into liquid occurred at $335\text{--}339^\circ\text{C}$. In none of the inclusions liquid separation has been observed. Crystals have not dissolved up to decrepitation temperatures.

Described phenomena evidently prove that non-variant equilibrium does not appear at the cross-section of two critical curves with vapor=liquid and liquid=liquid. Transition of one critical equilibrium into the other, in this case, occurs gradually. Therefore the term phase boundary is not applicable. Eventually this phenomenon is the peculiarity of phase diagram of the studied system. The existence area of heterogeneous fluid expands to lower temperatures, up to 220°C .

It is known that meta-stable equilibria of separated liquids might become stable if the number of components increases. Heating and cooling of the inclusions at different speeds have not influenced the phase transition temperature. Therefore one can conclude that in this case liquid separation is a stable process. This, in turn, is the evidence of the fact that quartz playing an active role in phase equilibrium, meaning that the system has ternary $\text{H}_2\text{O--Na}_2\text{CO}_3\text{--SiO}_2$ rather than binary character. Partici-

pation of silica in heterogeneous fluid equilibriums assumes the occurrence of high temperature Na_2CO_3 hydrolyses.

Different characteristics of binary water-saline systems are commonly used in the modeling of natural fluids. In the multi-component fluid-silica systems the fluid heterogenization possibility increases significantly and, as a result of this heterogenization, equilibrium of more than two fluid phases is also possible.

Heterogeneous equilibria, eventually, are unavoidable processes of natural fluids. They are usually accomplished by redistribution of substances between the phases. Under the further decrease of the temperature and pressure fluid phases, separated during magmatic stage, are also separating up to low temperatures around 200 °C. In high-concentrated and high-dense phases, different components (ore as well) can be concentrated. It is important that this phase is enriched by both silica and ore substances. If such a phase could separate spatially and evolve further separately, than, under the decrease of P-T parameters, it could also experience heterogenization. As a result the appearance of low temperature high-productive phase, which can explain joint transition of ore and vein staff minerals, is possible.

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References

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