

STUDY OF NaF-H₂O SYSTEM BY THE SYNTHETIC FLUID INCLUSIONS METHOD

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This study was supported by the Russian Fundamental Research Foundation (Project No. 99-05-65225)

Herald DGGGMS RAS № 5 (15) 2000 v.2

URL: http://www.scgis.ru/russian/cp1251/h_dgggms/5-2000/hydroterm20.eng

Introduction

The system NaF-H₂O was not investigated at high temperatures and pressures before. The solubility of NaF has been studied up to 100°C; it equals 3.7% for 20°C and increases up to about 4.9% for 100°C. Sole definition of solubility at temperature near 300°C (Ravitch, 1974 [1]) has shown that it is close to zero. So phase diagram of this system is of the P-Q type, which means that critical and solubility curves have two crossing points, named P and Q.

This is the first experience of studying the P-Q type system by the synthetic fluid inclusions method, so analysis of opportunities of this method is necessary. The coordinates of point P lay close to critical parameters of pure water for the water-salt systems with low salt solubility, as the case with NaF. Biphasic area (vapor + solution) should exist at vapor pressures below saturation pressure. If fluid inclusions were synthesized, it would be possible to study the vapor composition by measurements of cryometric temperatures. To analyze the composition of equilibrium liquid phase, one should know the solubility of NaF at high temperatures, but such data is absent.

It is important to consider area between P and Q points. Neither critical phenomena, nor three-phase balance (vapor+solution+solid salt), cannot occur in interval P-Q. Critical phenomena should take place in supersaturated solutions, which cannot be obtained. On the other hand, since vapor and liquid do not exist simultaneously under supercritical conditions, three-phase equilibrium is impossible too. Only pure supercritical fluid or supercritical fluid+solid salt can exist in this area. Corresponding types of synthetic fluid inclusions should exist (vapor+ liquid or vapor+ liquid+solid).

The second critical point Q is low temperature limit of upper biphasic area. It is possible to find the border of biphasic area position by condensing a grid of runs. The analysis of the immiscible phases has the same features as for lower biphasic area. The accurate definition of coordinates of point Q is improbable.

From the above said, it is clear that for investigation of synthetic inclusions, it is necessary to provide measurements under both negative and positive temperatures. Temperature and composition of eutectic mixture are known. Unfortunately, the eutectic temperature of the system NaF-H₂O is very high (-3.5°C). That inevitably increases a mistake of definition of salt concentration in a vapor. The curve of solubility of NaF is unknown at temperatures above 100°C. Using the method of synthetic fluid inclusions one can estimate the solubility of NaF under homogeneous conditions. Ampoules should be loaded in accordance with given weights of

NaF and H₂O. If solubility of NaF decreased or is constant with growth of temperature, the concentration of salt may be estimated by cryometry. If solubility grows, condensing of grids of runs should be useful to determine the first solid NaF in inclusions.

Experimental part

Synthesis of fluid inclusions have been realized at 400-800°C and 500-2000 bars in 0.5M solution of NaF. As was expected, the pressure of 500 bar appeared above critical for point P. All inclusions contained a solution corresponding to initial one for each run. The heterogenization of solution occurred only at pressures of 1000 bar at temperature close to 700°C, so we can say that the point Q lays between 1000 and 2000 bar and 650-700°C.

Inclusions of liquid phase contain large quantity of small crystals of NaF. The equilibrium vapor phase contains about 0.02 % NaF. So villiaumite can be crystallized as an mineral phase from rather low concentration, undersaturated NaF solution by heterogenization.

All inclusions at run examples in interval 400-700°C have not solid phase: it means that supercritical fluid without salt crystal occurs at temperatures between points P-Q.

The attempt was made to estimate solubility of NaF at 400-700°C in homogeneous fluid. The 5, 10 and 15 weight % of solid NaF and pure water was loaded in capsules. After run no solid phase were in inclusions. It means that solubility was not more than of saturated solution at room temperature.

The study of the system with NaF is complicated because of the opportunity of interaction of NaF and quartz at high parameters. The formation is possible of compound similar to Na₂SiF₆. At 700°C, 2 kbar the samples of quartz after run have on their surfaces thick layer of quenched phase and appear to be covered by glass. Below this «glass» layer the belt of the spherical gas inclusions with tiny solid occur. This inclusions are quite different from ones in healed cracks and were trapped at the time of quench. Such phenomena is connected with high solubility of quartz in NaF fluid. Rough estimate of solubility of quartz by measurements of thickness of quenched layer gives about 70 kg/m³.

1. Ravitch M.I. Water-salt system under high temperatures and pressures. (in Russian). M.: Nauka, 1974, 150 p.