EXPERIMENTAL STUDY OF BERYLL AND DIOPTASE SATURATION BY C-H-O-N FLUID COMPONENTS

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Estimation of fluid composition in natural mineral-forming processes is still one of most important problem in modern petrology. Recently a new method appeared, that is direct estimation of fluid components by means of porous minerals, which have structural cavities, playing role of trap for fluid (water, CO_2, H_2S, ammonia etc.). This method seems to be the most promising [1, 2]. Having stated the problem in this form, we used the results of the research carried on cordierite. For experiments two minerals beryl and dioptase were selected. These minerals have similar frameworks and appear in various types of mineral-forming processes. Several tests were carried out to obtain experimental evidence, making possible the usage of beryl and dioptase as sensors of fluid environment in natural mineral-forming processes.

Beryl samples were of two types: natural sodium-cesium mineral and synthetic alkali-free beryl. Colorless beryl from Svetlinskoye pegmatite location (South Ural) $Na_{0.27}K_{0.01}Cs_{0.39}Be_{2.61}$ $(Al_{2.01}$ $Fe^{3+}_{0.01})$ $[Si_{6.02}O_{18}]$ $\cdot 0.82H_2O$ was heated in vacuum at 700°C**.** Synthetic alkali-free beryl Al_2Be_3 (Si_6O_{18}) was synthesized in platinum crucible from the mixture of pure oxides by fluxing. Synthesis was carried out for 14 hours at T = 1150°C. Natural dioptase crystals $Cu_6Si_6O_{18}\cdot 6H_2O$ from Altyn-Tube (Kazakhstan) were in advance dehydrated by graded heating in helium (350°C – 24 hours, 400°C – 48 hours). In experimental work mineral particles of 25-50 μm were used. Purity of initial substance was verified by IR-spectroscopy and gas chromatography. Prepared minerals were placed into annealed gold ampoule and its capsulation was made according to method [3]. All ampoules had been welded with simultaneously cooling by liquid nitrogen. Hermeticality of ampoules had been controlled by constant checking their weight before experiments and after them.

Then, beryl samples were saturated by fluid components simulated by "dry" methane, n-butane, ammonia and water-methane mixture under different pressures: 100, 150 MPa and at T=600°C. Methane molecules and binary water-methane mixture were incorporated into dioptase at 600°C and total pressure at 100 MPa. Experiments were carried out with UVD-1000 apparatus, in the Tuttle reactor with the cooled gate. The length of tests was 300 hours. Water-methane mixture in ampoule was generated the following reaction: $SiC+2H_2O \Rightarrow CH_4\uparrow+SiO_2$ at 400°C and under 25 MPa. The length of this test was 72 hours. Its parameters were chosen from the kinetics of reaction. To avoid mixing minerals with reaction products, beryl or dioptase was put into an additional 2 mm gold tube. A fluid component, such as ammonia and hydrocarbons, were standard substances, which created in the Institute of hydrocarbon and mineral materials (VNIIUMC).

X-ray analysis of beryl and dioptase after the experiments showed, that cell parameters changed only slightly. Gas chromatography of the fluid above crystals confirmed invariability of gas composition after tests in comparison with its initial state. However, some amount of hydrogen was found.

The FTIR spectra of both types of beryls treated by methane-water mixture, dry ammonia and hydrocarbons showed the presence of stretching asymmetric vibration (ν_3) of water (H_2O-I) with maxima ~3694 cm^{-1}. A weak band of symmetric vibrations of water (ν_1) H_2O-I ~3555 cm^{-1} was also found. Water (H_2O-II) hydroxyl groups vibrations in alkali-free beryl were not found. In IR spectra of sodium-cesium beryl vibrations of water (H_2O-II) are present as strong bands 3605 cm^{-1} (ν_1 H_2O-II) and 3660cm^{-1} (ν_3 H_2O-II). The presence of vibrations of hydroxyl groups connected with sodium (Na-OH 3654 cm^{-1}) and cesium (Cs-OH 3595 cm^{-1}) indicated that alkaline cations were not removed completely during annealing. Band of carbon dioxide appears in the spectra of all samples, except that of alkali-free beryl treated by of methane. Methane was undoubtedly recognized in both samples of beryl, which were treated by dry methane. C-H vibrations in chains of hydrocarbons ($-CH_4$ ~2960 cm^{-1} and 2870 cm^{-1}; $-CH_3$ ~ 2920 cm^{-1} and 2850 cm^{-1}) were found in spectra of both beryl saturated by dry n-butane and in that of sodium-cesium beryl treated by water-methane mixture. Fundamental difference of beryl spectra from cordierite one contains is the absence of the bands of vibrations of benzol ring, aromatic hydrocarbons and oligomeric saturated structures. Systematic quantitative determination of fluid component concentration in channels of beryl structure and the composition of gas above mineral upon completing the test was not made. The quantity of fluid components was determined for one sample of beryl only. Alkali-free beryl was saturated by methane and gas chromatography found that there were 113 mg/kg of methane, 164 mg/kg of carbon dioxide and 986 mg/kg of water.

IR spectra of dioptase showed the stretching vibrations of methane molecules (3014cm^{-1}). Upper limit of methane isolation was recorded by mass-spectrometry at 470 ^{o}C. Maximum concentration of methane in dioptase was treated by water-methane mixture was determined to be 548 mg/kg. For the sample of dioptase which was saturated by dry methane this concentration was 255 mg/kg other parameters being equal.

Conclusion

It is experimentally proved that ammonia and hydrocarbons can be incorporated into structural channels of beryl and dioptase. In fact, these minerals are sensors of fluid environment.

Partial conversion of hydrocarbon fluid components into water and carbon dioxide was experimentally proved to take place inside structural channels of beryl and dioptase under high temperature and pressure conditions. Conversion was proceeded at the expense of framework oxygen.

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