THE EXPERIMENTAL STUDY OF SODALITE - NOSEAN SOLID SOLUTIONS

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Introduction

Sodalites are the framework aluminosilicates, which are widespread minerals of alkaline intrusive rocks, sometimes they occur in pegmatites. The general formula of sodalites is $Na_8Al_6Si_6O_{24}\cdot(X)$, where X – such anions as Cl^-, Br^-, I^-, SO_4^{2-}; CO_3^{2-}; OH^- and other. Sulphur and chlorine play an important part in mineral forming fluid. Sodalites are the minerals which formation closely connected with the fluid conditions and may indicate the composition of mineral-forming fluids.

Run and analytical procedures

The runs on sodalite study were carried out by the capsule method in cold-seal hydrothermal vessels with external heating (accuracy of temperature control was ±5°C; pressure ±50 bar). Starting material for the sodalites and their solid solution synthesis was gel of $NaAlSiO_4$ composition, solutions were presented by a mixtion of NaCl, Na_2SO_4 and H_2O. The composition of the synthesized sodalite solid solutions was set by a ratio) ($NaCl/Na_2SO_4$ in an initial solution. Phase analyses of the run products were carried out by the immersion and X-ray methods. Chemical compositions of sodalite solid solutions were determined by X-ray powder diffraction and microprobe methods. X-ray powder diffraction measurements for sodalite solid solutions were carried out on HZG-4/PC and DRON-1.5 automatic diffractometers. Silicon (spectral purity grade, a=5.4305A) was used as the internal standard. Cell parameters were calculated using the LCC and PUDI programs [1] and the MINCRYST information-calculating system of crystal structure data of minerals [2].

Nosean stability

For synthesis of (Cl, SO_4)- sodalite solid solutions it was necessary to determine the concentration of salt solutions, at which the sodalite will be formed from nepheline. The stability of chlorine sodalite under the hydrothermal conditions was studied earlier [3]. The runs on nosean stability were carried out at 600-800°C and P=2 kbar. The run duration was 4-21 days. The following reaction was studied:

$$6NaAlSiO_4\ (Ne) + Na_2SO_4\ (aq) = Na_8Al_6Si_6O_{24}\cdot(SO_4)\ (Sod)$$

It was shown, that SO_4- sodalite is stable relatively nepheline at concentration Na_2SO_4 (≥2 wt. % at 600°C; ≥1 wt. % at 700°C; and ≥5 wt. % at 800°C). Sulphate sodalite in comparison with Cl- sodalite is stable relatively nepheline at considerably smaller concentrations of salt (Na_2SO_4) in fluid. On the data of the end members of (Cl, SO_4)- sodalite solid solutions stability, the following equation for an estimation of the minimal concentration of mineral forming fluid was derived:

$$C\ (wt.\ \%) = (255\text{-}214.3 \cdot X_S^{Sod}) + (-330 + 270 \cdot X_S^{Sod}) \cdot (1000/T) + (107.4\text{-}85 \cdot X_S^{Sod}) \cdot (1000/T)^2,$$

where X_S^{Sod} – mole fraction of sulphur in sodalite, X_S^{Sod} =S/(Cl+S); T - absolute temperature, K.

T-X diagram of (Cl, SO_4)- sodalites

The runs on synthesis of (Cl, SO_4)- sodalite solid solutions (for T-X diagram construction) were carried out under hydrothermal conditions at temperatures 300, 400, 500, 600, 700, 750, 800°C and pressure of fluid 1-3 kbar. Run duration was 12-35 days. On the X-ray data the dependences of unit cell parameters on composition of these sodalite solid solutions were expressed by the following equations:

$$a = 8.8730 + 0.273998 \cdot X_S^{Sod} + 0.0837151 \cdot (X_S^{Sod})^2 - 0.160896 \cdot (X_S^{Sod})^3\ (\pm 0.003\ A)$$

$$V = 698.58 + 64.9000 \cdot X_S^{Sod} + 22.88935 \cdot (X_S^{Sod})^2 - 40.24799 \cdot (X_S^{Sod})^3\ (\pm 0.1\ A^3)$$

On the data of X-ray and microprobe investigation of (Cl, SO_4)- containing sodalites, synthesized at the different temperatures (300-800°C) and pressures 1 – 3 kbar, phase (T-X) diagram of Cl-

sodalite – nosean was constructed. The existing of wide immiscibility gap at the temperature 300-750° C for solid solutions of the (Cl, SO_4)- bearing sodalites is shown. The solvus of this solid solution is nonsymmetrical: at 700°C the sulphate minal contains up to 24 mol. % of the Cl- sodalite, the chloride minal of sodalite contains only 7 mol. % of sulphate one. Basing on the coexisting sodalite compositions, the dependence for an estimation of mineral-forming temperature was derived:

$$T, °C = \{1000/ [0.122 + 1.8324 \cdot (\ln K) - 1.2157 \cdot (\ln K)^2 + 0.253646 \cdot (\ln K)^3]\} - 273 (\pm 40°C),$$

where $K = [X_S^{Sod\ II}/X_S^{Sod\ I}]$; Sod I – phase of Cl- sodalite; Sod I – phase of SO_4- sodalite.

The distribution of sulphur between sodalite and fluid

The sulphur distribution between sodalite and fluid was studied at temperatures 300-800°C and pressures 1-3 kbar. The salt concentration of solutions depending on temperature of experiences varied from 10 to 45-50 wt. %. Run duration was 12 - 30 days. The following reaction was studied:

$$Na_8Al_6Si_6O_{24}\cdot(Cl_2)\ (Sod) + Na_2SO_4\ (aq) = Na_8Al_6Si_6O_{24}\cdot(SO_4)\ (Sod) + NaCl\ (aq)$$

On the results of the experiences was shown, that sulphur enriches sodalite relatively fluid. The sulphur distribution between sodalite and fluid at all temperatures (except 800°C) strongly depends on the sodalite composition. On the basis of the experimental data the analytical dependence for calculation of the sulphur mole fraction in mineral-forming solutions using the compositions of the coexisting sodalite phases and temperature was derived:

$$X_S^{fl} = 1/\{\exp [(-4.19+0.0067\cdot T+(-3.12+0.0296\cdot T-0.0000243\cdot T^2\cdot X_S^{Sod})] \cdot [(1-X_S^{Sod}) / X_S^{Sod})]+ 1\}$$

where X_S^{Sod} – mole fraction of sulphur in sodalite, T - absolute temperature, K.

An estimation of the mineral-forming conditions of Lovozersky alkaline massif

The estimation of temperatures and regime of fluids for the sodalite nepheline syenites of Lovozersky alkaline massif were conducted. Temperatures of formation of nepheline syenites were estimated on various mineral geothermometers (Fsp-Ne, Fsp1-Fsp2, Sod-Ne, Sod-S - Sod-Cl, Sod-Fsp, Bi-Cpx). Temperatures of mineral-forming processes vary in a range from 930 up to 400°C. These temperatures reflect different stages of mineral crystallization and cover the whole temperature interval of the mineral paragenesis formation. On the basis of sodalite compositions and temperatures of their formation a mole fraction of sulphur in mineral-forming fluids was estimated as 0.05-0.12. Received data characterize temperature and fluid mode of formation sodalite- bearing nepheline syenites of Lovozersky alkaline massif**.**

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