

SHORT
COMMUNICATIONS

Temperature Range for the Formation of Sodalite-Bearing Assemblages

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Sodalites are framework aluminosilicates with the general formula $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24} \cdot (\text{X})_{(1-2)}$, where X represents Cl^- , Br^- , I^- , SO_4^{2-} , CO_3^{2-} , OH^- , and other anions. Sodalites usually crystallize in a cubic structure with space group *P43n* for chlorine-sodalite and *P43m* for sulfate-sodalite (nosean) [1]. Sodalite occurs in alkaline igneous rocks and, occasionally, in pegmatites. The greatest diversity of sodalite-group minerals was observed in the Lovozero alkaline massif, where hydroxyl-, chlorine-, and sulfate-bearing sodalites were found.

The extensive isomorphous substitutions in sodalites and the relatively wide occurrence of sodalite-bearing assemblages allow us to regard the sodalite solid solution as promising for the estimation of the temperature and fluid regime of mineral formation [2].

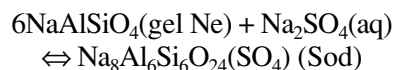
Owing to its composition, sodalite is a very important indicator of fluid behavior during mineral formation. The framework aluminosilicates sodalites are rock-forming minerals of alkaline igneous rocks, which are relatively common in the Earth's crust. Sodalite-group minerals are characterized by anionic isomorphous substitutions, and their anionic composition records the geochemical features of petrogenesis and can be used for the estimation of the composition of mineral-forming fluids.

The attractiveness of sodalite as a target for geochemical studies emphasizes the importance of isotopic methods for the elucidation of the formation conditions of sodalite-bearing assemblages. The most promising for isotopic geochemical investigations is sulfate-sodalite ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{SO}_4$), which has two oxygen-bearing functional groups providing an opportunity to study intracrystalline isotopic effects for the construction of a monomineralic geothermometer and determination of the mechanisms of mineral reactions [3]. The choice of sulfate-sodalite as a target for our

study extends the list of minerals used for intracrystalline studies; moreover, information on oxygen isotope shift between the silicate and sulfate functional groups is used for the first time in this case.

In order to evaluate isotopic effects, samples of sulfate-bearing sodalite were synthesized at various temperatures.

The initial materials were represented by gels of nepheline (500 mg) and natural Cl-bearing sodalite (5 mg as a seed). The starting solution was prepared by mixing high-purity Na_2SO_4 with distilled water. Experiments were carried out using hydrothermal pressure vessels with external heating and a cold seal (the accuracy of temperature and pressure control was $\pm 5^\circ\text{C}$ and ± 50 bar, respectively). Platinum ampoules were used in all experiments. Oxygen fugacity was maintained by the Ni–NiO buffer. The conditions of sulfate-sodalite synthesis via the reaction



are given in Table 1.

The experimental products were examined by the immersion and X-ray diffraction methods. The compositions of synthetic sulfate-sodalites were determined

Table 1. Conditions and results of experiments on the synthesis of sulfate-sodalite

Run no.	Temperature, °C	Solution, mg	C, wt % Na_2SO_4	Duration, day
5615 ¹	400	700	30	29
5616 ²	400	700	30	34
5708 ³	450	630	30	34
5717 ⁴	550	630	30	29
5715 ⁵	700	630	30	29

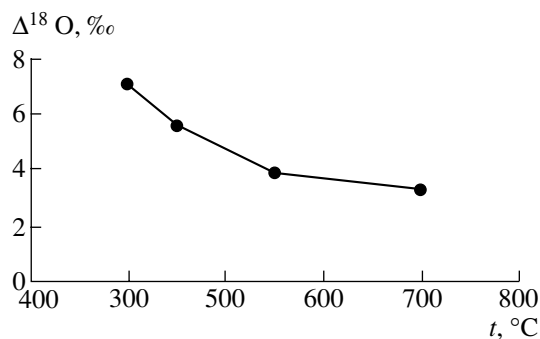
Table 2. Isotopic compositions of oxygen and sulfur in sodalite

Sample no.	$\delta^{18}\text{O}_{\text{silicate}}$, ‰	$\delta^{18}\text{O}_{\text{sulfate}}$, ‰	$\Delta^{18}\text{O}_{\text{sulfate-silicate}}$, ‰	t , °C	$\delta^{34}\text{S}$, ‰
C-61	+3.3	+6.7	+3.4	700	+10.3
C-82	+0.2	+4.3	+4.1	540	+8.4
904-14	+1.6	+4.3	+2.7	770	+6.7
904-22	-3.7	+0.8	+4.5	530	+5.8
56-15	-3.2	+4.0	+7.2	400	+8.1*
56-16	-3.5	+3.5	+7.0	400	+8.1*
57-08	-3.1	+2.5	+5.6	450	+8.3*
57-17	-2.2	+1.7	+3.9	550	
57-15	-2.1	+1.2	+3.3	700	

* $\delta^{34}\text{S}$ of residual solution is +8.7‰.

by X-ray spectral microanalysis. Unit-cell refinement was performed for some samples. The X-ray diffraction patterns of sodalites were obtained on an HRZ-4 diffractometer in a continuous scanning mode. Spec-pure silicon ($a = 5.43307 \text{ \AA}$) was used as an internal standard. The refinement of unit-cell dimensions was performed on the basis of 10–17 reflections in the range 7–39 (Θ). The parameters were calculated by the LCC, PUDI, and REFLAT programs. The electron microprobe analysis of synthetic sodalites showed that they correspond to the theoretical formula $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{SO}_4)$.

The oxygen isotope analysis of sodalites included sulfate component extraction by sample decomposing with fluoric acid at 50°C for 12 h and subsequent precipitation of BaSO_4 from the solution. It was difficult to separate the barium sulfate from aluminum fluoride. However, using ClF_3 for mixture fluorination, we managed to extract the oxygen of BaSO_4 as O_2 for the mass spectrometer isotope analysis of oxygen. Oxygen



Temperature dependence of the intracrystalline isotopic effect, $\Delta^{18}\text{O}$.

extracted from oceanic sulfate ($\delta^{18}\text{O} = +9.5\text{‰}$ SMOW) [4] by the same fluorination procedure was used as a standard. The isotopic composition of oxygen was measured on a MI-1201 mass spectrometer with a $\delta^{18}\text{O}$ precision of $\pm 0.2\text{‰}$. The same fluorination procedure was used for the analysis of the oxygen isotope composition of the bulk mineral, and the $\delta^{18}\text{O}$ value of the silicate group was calculated from mass balance.

In order to extract SO_2 from sulfates for sulfur isotope analysis, the mixture of BaSO_4 , V_2O_5 , and SiO_2 in the proportion 1 : 3 : 3 was heated in a vacuum furnace at 1000°C for 15 min [5]. A copper wire was placed into the quartz tube in order to inhibit SO_3 formation. The mixture of released components, $\text{SO}_2 + \text{H}_2\text{O} + \text{CO}_2$, was separated by low-temperature distillation: SO_2 and CO_2 were separated from water at -78°C (alcohol and dry ice), and SO_2 was separated from CO_2 at -131°C (*n*-pentane melting). The precision of $\delta^{34}\text{S}$ measurement on the MI-1201 mass spectrometer was $\pm 0.5\text{‰}$ [6].

It is important to note that the conditions of sodalite synthesis and sulfate group extraction were chosen taking into account the kinetic parameters of oxygen isotope exchange in the $\text{SO}_4^{2-} - \text{H}_2\text{O}$ system [7].

This paper reports the first reconnaissance results on oxygen isotope exchange between the silicate and sulfate constituents of natural and synthetic sodalites (Table 2).

As can be seen from Table 2, the difference in $\delta^{18}\text{O}$ between the sulfate and silicate constituents is 7.1‰ at 400°C, 5.6‰ at 450°C, 3.9‰ at 550°C, and 3.2‰ at 700°C. There is a predictable decrease in $\Delta^{18}\text{O}_{\text{sulfate-silicate}}$ with increasing temperature. Based on the established temperature dependence of $\Delta^{18}\text{O}_{\text{sulfate-silicate}}$ (figure), the following analytical equation was obtained for the intracrystalline geothermometer:

$$t, \text{ }^\circ\text{C} = [0.943 \times 10^6 / (\Delta^{18}\text{O} - 1.1)]^{0.5}. \quad (1)$$

The accuracy of temperature determination for sulfate sodalite formation is $\pm 30^\circ\text{C}$ at 400–550°C and $\pm 50^\circ\text{C}$ at 550–700°C.

There was almost no sulfur isotope fractionation (within 0.5‰) during the formation of sulfate-sodalite, which allows the use of measured $\delta^{34}\text{S}$ values directly for determining the source of sulfur in fluids.

Table 2 presents the results of the isotopic analyses of sodalites from the nepheline syenites of the Lovozero alkaline massif (samples C-61, C-82, 904-14, and 904-22).

In order to reconstruct the formation conditions of the Lovozero alkaline massif, we investigated a number of sodalite-nepheline syenite samples from various levels of the section (from the eudialyte lujavrite and differentiated complexes of the massif). The sodalite-nepheline syenites are medium- and coarse-grained light gray rocks with a massive structure and a poikilitic

Table 3. Temperatures of formation of the sodalite--nepheline syenites of the Lovozero massif

Sample no.	Assemblage	Geothermometers	t , °C range*	t , °C, isotope
C-61	$Sod-S + Sod-Cl + Ne + Ab + Fsp + Aeg + Avg + Bi$	Fsp^1-Fsp^2 $Ne-Sod, Ne-Fsp$	800–420	700
C-82	$Aeg + Fsp + Sod-S + Sod-Cl$	Fsp^1-Fsp^2	500–380	540
904-14				750
904-22				530

* Obtained by the two-feldspar geothermometer at $P_s = 3$ kbar.

texture. The major minerals of the rock varieties studied are nepheline, feldspars (albite and potassium feldspar), clinopyroxenes (aegirine and aegirine–augite), alkali amphibole, and sodalite. The accessory minerals are titanite, apatite, carbonates, iron sulfides (FeS and FeS₂), titanomagnetite, and fluorite. In addition to aegirine, aegirine–augite with considerable amounts of Mg and Ca was also found. Some samples also contained biotite, which forms individual laths, intergrowths with aegirine–augite, and rims around aegirine–augite grains. Sodalite occurs mainly as euhedral grains and often forms aggregates and intergrowths. Sodalites of nosean composition were found in some samples; in addition, some assemblages contain chlorine- and sulfate-sodalites (Table 3). Estimation of the redox state of sulfur on the electron microprobe showed that sulfate sulfur is predominant in the sodalite of the Lovozero massif. Chlorine-sodalite was found as inclusions in nosean, which allowed us to suppose that there is an immiscibility field in the sodalite solid solution. The temperatures of formation of the sodalite–nepheline syenite were estimated using various mineral geothermometers ($Fsp-Ne$, Fsp^1-Fsp^2 , $Sod-Ne$, $Sod-Fsp$, and $Bi-Cpx$). In the case of the two-feldspar geothermometer, temperatures were determined for the pressure $P_s = 3$ kbar, which is probably the maximum possible volatile pressure under high-temperature conditions during the formation of intrusive complexes of such a type. The results of temperature estimation are given in Table 3.

The estimated temperatures vary from 880 to about $\approx 400^\circ\text{C}$, which reflects various stages of crystallization and embraces the whole temperature range of mineral formation. A comparison of the isotopic data for natural sodalites and the results of mineral thermometry showed that all the sodalites were formed at temperatures of $530-750^\circ\text{C}$; these values correspond to the temperature interval determined by the two-feldspar geothermometer.

Natural sodalite samples show variable $\delta^{34}\text{S}$ values (from 5.8 to 10.3‰), which indicates a crustal source. The considerable variations in the sulfur isotope composition of high-temperature sodalites suggest a pulsed character of fluid influx.

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