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SHORT COMMUNICATIONS

Isotopic Thermometry of Sodalite-Bearing Mineral Associations

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This publication is a logical continuation of our earlier isotopic studies of sodalite as a promising tool for the evaluation of temperatures and fluid regimes of mineral-forming processes [1]. The first data on the intrastructural oxygen isotopic distribution in synthetic sulfate-sodalite (nosean) $Na_8Al_6Si_6O_{24}SO_4$ have demonstrated the possibility of using this mineral as a monomineralic isotopic geothermometer.

Further exploring this avenue, we conducted a study of the infrastructural oxygen isotopic effects in Cl-sodalite and minerals coexisting with it in sodalite-bearing mineral assemblages. The first task of our research was to determine the temperature dependence of the fractionation factor $\Delta^{18}O$ in the Cl-sodalite–H_2O system with the aim of evaluating the temperatures and nature of aqueous fluids.

For this purpose, we synthesized samples of Cl-sodalite within the temperature range of 300–700°C according to the reaction

$$6NaAlSiO_4(Ne) + 2(NaCl_{(aq)}) = 6Na_8Al_6Si_6O_{24}Cl_2(Cl\text{–}Sod). \quad (1)$$

The starting materials were natural nepheline, which was preparatorily purified in a NaCl melt at 900°C, and nepheline gels (*Ne*); the seed material was a small amount of fine-grained natural sodalite. The composition of the solution was determined by a mixture of NaCl and distilled water. The synthesis was conducted in high-pressure hydrothermal apparatuses with external heaters and cold seals (the temperature and pressure were controlled accurate to ±5°C and ±50 bar, respectively). All experiments were conducted in Pt ampoules. The oxygen potential was specified by the Ni–NiO buffer.

In order to maintain a constant NaCl concentration in the fluid, we applied the so-called large ampoule technique, in which the sample/fluid ratio was varied from 1 : 5 to 1 : 20.

The experimental products were analyzed by immersion and X-ray powder diffraction techniques and on a Camebax microprobe equipped with a Link EDS detector. Selected samples were additionally used to refine the unit-cell parameters of the mineral. The X-ray powder diffraction study of sodalite was conducted on a HZG-4 diffractometer in the continuous scanning mode. The internal standard was Si of spectral-grade purity (a = 5.4307 [A]). The unit-cell parameters were refined using 10–17 reflections at angles of 7–39.

It is most convenient methodically to conduct the equilibrium reaction in the mineral–water hydrothermal system with an excess of water to eliminate the necessity of the additional analysis of the oxygen isotopic composition of water after the experiments. The experiments on Cl-sodalite synthesis were carried out in the field of fairly high NaCl concentrations. The limited volumes of the Pt ampoules did not allow us to use an excess of the aqueous phase, and thus, the factor of the oxygen isotopic fractionation $\Delta^{18}O$ was determined on the basis of isotopic balance:

$$\Delta^{18}O_{Cl\text{-}sod.\text{-}w} = (1 + 1/r)\delta^{18}O_{sod} - 1/r\delta^{18}O_{gel} - \delta^{18}O_w, \quad (2)$$

where $\delta^{18}O_{sod}$ is the oxygen isotopic composition of the synthesized Cl-sodalite measured in each experiment; $\delta^{18}O_{gel}$ and $\delta^{18}O_w$ are the oxygen isotopic compositions of the starting materials [gel and distilled water, respectively; synthesis reaction (1)], these values were equal to 11.2 and –12.0‰, respectively, and remained unchanged in all of the experiments; and r is the water/gel oxygen proportion in each experiment.

The oxygen isotopic composition of sodalite and silicate minerals was analyzed by the fluorination of the sample by ClF_3 with oxygen release in the form of O_2 and the successive mass spectrometric recording of the isotopic composition of the molecular oxygen. The reference standard was the oxygen of the GIN-1 standard [2]. The values of $\delta^{18}O$ were determined on a MI 1201 mass spectrometer precise to $\delta^{18}O \pm 0.2‰$. To extract SO_2 from sulfates for isotopic analysis of the sulfur, a

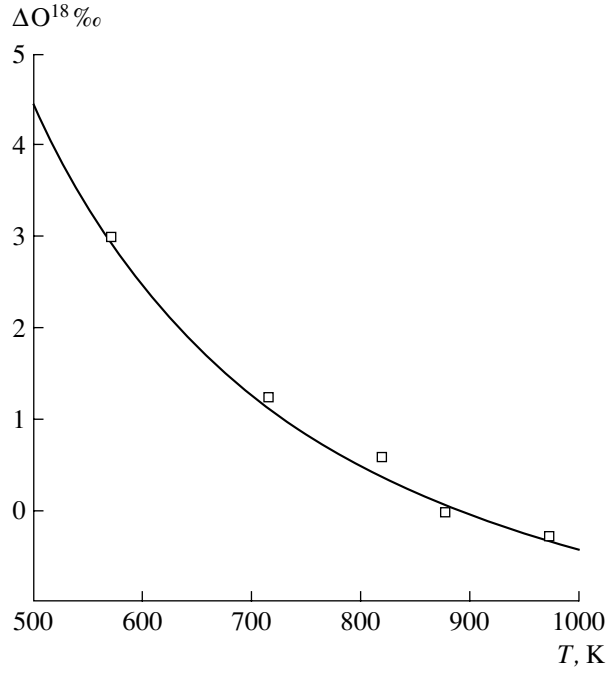
Table 1. Experimental conditions and the results of experiments on the synthesis of Cl-sodalite

Experiment no.	T, °C	Time, days	Parameter r	$\delta^{18}O$, ‰	$\Delta^{18}O_{sod.-H_2O}$, ‰
5763	300	45	1.75	–1.7	+3.0
5798	450	31	1.92	–3.2	+1.3
5718	550	33	2.34	–4.6	+0.6
5794	600	30	2.52	–5.5	–0.1
5716	700	20	1.72	–3.8	–0.3

mixture of $BaSO_4$, V_2O_5, and SiO_2 taken in the proportion 1 : 3 : 3 was heated in a vacuum vessel to 1000°C for 15 min [3, 4]. In order to reduce the possibility of formation of SO_3, Cu wire was placed in the glass pipe. The mixture of the released $SO_2 + H_2O + CO_2$ was separated by means of low-temperature distillation: SO_2 and CO_2 were separated from H_2O at –78°C (alcohol with dry ice), and SO_2 was then separated from CO_2 at –131°C (melting *n*-pentane). Sulfides were oxidized in a vacuum vessel by CuO at 800°C [5]. The precision of the $\delta^{34}S$ measured on the MI 1201 mass spectrometer was ±0.5‰. The experimental conditions of Cl-sodalite synthesis and the results of these experiments are listed in Table 1.

Based on the data of Table 1, we obtained the following analytical expression and plotted (figure) the temperature dependence:

$$\Delta^{18}O_{Cl\text{-}sod.\text{-}H_2O} = 1.69\ (10^6/T^2, K) - 2.1. \quad (3)$$



Dependence of $\Delta^{18}O_{Cl\text{-}sod.\text{-}H_2O}$ on temperature.

Equation (3) can be applied to the development of a new isotopic geothermometer for the system Cl-sodalite—the other mineral for studying the temperature regimes at which sodalite-bearing assemblages are formed.

Isotopic thermometry is underlain by the assumption that the minerals are in equilibrium, i.e., crystallized under the same conditions (temperature and the composition of the mineral-forming fluid), and isotopic equilibrium was reached between the minerals. If a mineral pair for this study is selected based on the results of its mineralogical examination alone, the aforementioned criteria can sometimes be violated because some minerals could not crystallize simultaneously, and this resulted in a distortion of the results owing to changes in the temperature and fluid composition in the course of the successive crystallization of the minerals. To rule out this uncertainty, three minerals are selected, and the coincidence of the temperatures calculated for the two pairs from experimental isotopic data is considered to be an accuracy criterion of the results.

An important methodological approach to the evaluation of temperature regimes that form associations with silicates, carbonates, sulfates, and sulfides is the comparison of data obtained by oxygen and sulfur isotopic thermometers. The coincidence of the formation temperatures of silicate (carbonate) and sulfur-bearing minerals testifies to the existence of equilibrium between them.

Our geochemical thermometric studies were conducted on samples from rocks of the Lovozero (S-61, S-3, and 904/908) and Tiksheozero (158-200 and 158-203) alkaline massifs.

In this research, the temperatures at which the sodalite-bearing assemblages were formed were evaluated with the use of a complex approach, combining the monomineralic oxygen isotopic (sulfate–sodalite) and two infrastructural (oxygen and sulfur isotopic) geothermometers.

The study was carried out according to the following three combinations of various geothermometers:

(1) intrastructural (sulfate–sodalite) + infrastructural (sulfate group of sodalite—sulfide FeS);

(2) infrastructural for the triad Cl-sodalite (Cl-sod)—biotite (Bi)—amphibole (*Amf*); and

(3) infrastructural feldspar (*Fsp*)–pyroxene (*Cpx*) + infrastructural (sulfate group of sodalite—sulfide FeS).

The results of the isotopic research are presented in Table 2.

In sample S-61, the value of $\delta^{18}O_{silicate}$ = +3.3‰, $\delta^{18}O_{sulfate}$ = +6.7‰, and the difference $\Delta^{18}O$, which is equal to +3.4‰, corresponds, according to the monomineralic isotopic geothermometer of sulfate–sodalite, to 700°C [1]. The data of the sulfur isotopic geothermometer for the sulfate component of sodalite ($\delta^{34}S$ = 5.9‰)—equilibrium sulfide ($\delta^{34}S$ = –0.3‰)

Table 2. Isotopic characteristics of sodalite-bearing associations

Sample no.	$\delta^{18}O$, ‰								$\delta^{34}S$, ‰			
	Cl-sod	*Fsp*	*Ne*	*Cpx*	*Bi*	*Am*	$\Delta^{18}O$	*T*, °C	SO_4 sod	FeS	$\Delta^{34}S$	*T*,***
S-61	–	–	–	–	–	–	–	700	5.9	–0.3	6.2	780
S-3	–	–	9.0	6.5	–	–	2.5	480*	–	–	–	–
904/98	–	8.7	–	5.8	–	–	2.9	520	7.6	–3.1	10.7	570
158-200	–	–	–	–	2.1	3.7	1.6	100**	14.4	+1.1	13.3	440
158-203	8.7	–	–	–	5.5	5.8	3.2	520	–	–	–	–

Note: The temperatures were calculated base don data from: * [6], ** [7], *** [4].

indicate that this mineral pair was produced at a temperature of 780°C. The results obtained by two independent isotopic geothermometers testify that the silicate and sulfide minerals crystallized at a high temperature simultaneously.

In sample 158-203, the oxygen isotopic composition of the Cl-sod + Bi + *Amf* three-mineral association yielded similar temperature for the mineral pairs of Cl-sod + Bi ($\Delta^{18}O$ = 3.2‰), which corresponds to 510°C, and Cl-sod + *Amf* ($\Delta^{18}O$ = 2.9‰), 540°C. Thus, the crystallization temperature of this association can be assumed to be equal to $T_{ave.}$ = 520°C.

In sample 904/98, the difference in the oxygen isotopic composition for the pairs of feldspar (*Fsp*) + pyroxene (*Cpx*) ($\Delta^{18}O$ = 2.9‰) corresponds to *T* = 520°C according to the *Fsp–Cpx* isotopic geothermometer. The sulfur isotopic geothermometer for this sample yielded a temperature of 570°C. The temperature values obtained by two isotopic geothermometers (accurate to ±25°C) are in good agreement.

In sample S-3, we managed to evaluate the temperature regime only for the pair of nepheline (Ne)–pyroxene (*Cpx*): *T* = 480°C.

Sample 158-200 displays a significant difference between the temperature values given by the oxygen and sulfur isotopic geothermometers. The value of $\Delta^{18}O$ (1.6‰) for the *Bi–Amf* pair corresponds to a temperature of approximately 100°C, and the values of $\delta^{18}O$ (H_2O) of the fluid is equal to –1.7‰, whereas the values of $\Delta^{34}S$ between the sulfate group of sodalite and sulfide is equal to 14‰ and testifies to a much higher temperature: 440°C. These discrepancies between the temperature values for this association can be explained by the effect of secondary processes on the silicate minerals, which finds further support in the low $\delta^{18}O$ values of the fluid water and, in turn, testifies to the possible involvement of meteoric waters in the hydrothermal activity.

A remarkable fact is the high temperatures at which the sodalite-bearing mineral assemblages were formed and the broad variations of the temperatures: from 440 to 780°C.

CONCLUSIONS

1. In order to determine the conditions under which sodalite-bearing associations were formed, the isotopic fractionation factor $\Delta^{18}O$ was experimentally measured for the synthetic Cl-sodalite–water system at 300–700°C.

2. The study of the infra- and intrastructural distribution of oxygen isotopes in sodalite-bearing associations and equilibrium minerals and sulfur isotopes in the sulfate group of sodalite and equilibrium sulfides were used to develop a complex approach to the evaluation of the temperatures and fluid regimes of mineral-forming processes.

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