Composition, Structure, and Conditions of Formation of Fluorine-Bearing Sodalite: Experimental Evidence

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Abstract—Fluoro-sodalite was synthesized for the first time at temperatures of 400–800°C and H₂O pressures of 1–2 kbar in the Si–Al–Na–H–O–F system. X-ray diffraction and infrared spectroscopic investigations showed that fluorine is incorporated in the sodalite structure as anionic octahedral groups, $[AlF_6]^{3-}$, the number of which can vary from 0 to 1. Correspondingly, the end-members of the F-sodalite series are Na₇(H₂O)₈[Si₅Al₇O₂₄] and Na₈(AlF₆)(H₂O)₄[Si₇Al₅O₂₄]. Depending on the composition of the system, F-sodalite associates at 500–650°C with nepheline, albite, cryolite, and villiaumite, which are joined by analcime below 500°C and aluminosilicate melt above 650°C. Fluorine-bearing sulfate—chlorine-sodalite was found for the first time in a pegmatite sample from the Lovozero massif. The highest fraction of the fluorine end-member in natural sodalite is 0.2. The incorporation of F into the sodalite structure requires much more

energy compared with Cl^- and SO_4^{2-} , because it is accompanied by a structural rearrangement and a transition from tetrahedral Al to octahedral Al.

Keywords: fluoro-sodalite, hydroxyl-, chlorine-, and sulfate-sodalite, aluminofluoride complex, melt, fluid, anionic group, phase

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INTRODUCTION

A fluorine-rich phase similar to sodalite in major component composition and X-ray diffraction patterns was first obtained in our experiments at 800°C and 1000 bar (Gramenitskii et al., 2005). Subsequently, its crystals were purposely synthesized using the hydrothermal technique by Kotel'nikov et al. (2011).

Sodalite is a common major mineral of intrusive and extrusive alkaline rocks and products of their metasomatic alteration. It is represented by hydroxyl-, chlorine-, and sulfate-bearing varieties. In contrast to most other minerals containing a similar group of additional anions, the presence of fluorine has not been previously reported in natural sodalite, although this mineral often associates with fluorides: villiaumite, cryolite, or fluorite (Gerasimovsky et al., 1966; Shchekina et al., 2013; Markl et al., 2001; Krumerei et al., 2007).

The synthesis and formation conditions of chlorineand sulfate-bearing sodalite similar in composition to the natural mineral were addressed by Sharp et al. (1989) and Kotel'nikov et al. (1994, 2004, 2009). A number of papers reported the results of synthesis and investigation of the structure and properties of sodalite with substitution of Be, Ge, and P for Si; Ga and Be for Al; etc. (e.g., Depmeier, 2005). Most of such substitutions do not occur in nature, but these studies have practical applications related to the use of sodalite as a catalyst for the production of halogenbearing ceramics and photo- and cathodochromic materials. The use of synthetic sodalite as a matrix for the immobilization of radioactive waste is promising. Sodalite containing the rare earth elements was synthesized by Pentinghaus et al. (1990).

To our knowledge, F-sodalite was first mentioned by Denisov et al. (1977), who studied the luminescence of cathodochromic sodalites with different anionic compositions (F, Cl, Br, and I). The synthesis conditions, composition, and properties of F-sodalite, as well as the methods of its identification were not reported. Subsequently, Denks (1989) discovered an important property of F-bearing sodalite, its very high radiation resistance. Feron et al. (1994) reported the hydrothermal synthesis of fluorosodalite at 100-200°C and claimed that their study filled a gap in the series of halogen-bearing sodalites. They obtained X-ray powder diffraction data and determined the cubic unit-cell parameter a = 8.99 Å. According to chemical analysis, the maximum F content of sodalite was 3 wt %. The presence of F and molecular H₂O in the synthesized phase was confirmed by NMR spectroscopy. The proposed formula of F-sodalite, $Na_6[Al_6Si_6O_{24}] \cdot 2NaF \cdot$ H₂O, was based on the supposed similarity of the synthetic phase to hydrosodalite, and this phase was assigned by the authors to zeolites, the framework of which is looser and more favorable for isomorphic substitutions compared with sodalites. Based on these results, the X-ray diffraction patterns of zeolite with the formula $Na_6[Al_6Si_6O_{24}] \cdot 2NaF \cdot xH_2O$ were included in the PDF-2 database (Card no. 490937). Yakubovich et al. (2011) synthesized F-sodalite at 650°C and 2000 bar and investigated it by single-crystal X-ray diffraction. The crystal structure of the new member of the sodalite structural type with extraframework anions was determined for the first time. It was found that the new compound has cubic symmetry with a = 9.045(1) Å, space group P43m. It is based on an unordered Si-Al tetrahedral framework topologically identical to that of the mineral sodalite. Fluorine is incorporated into the sodalite structure as octahedral aluminofluoride complexes, [AlF₆]³⁻, which occur in framework cavities similar to Na⁺ and H₂O. The proposed chemical formula $Na_{7.38}(AlF_6)_{0.70}(H_2O)_{4.88}[(Si_{6.74}Al_{5.26})O_{24}]$ refers to a particular monocrystal composition and does not explain the compositional variations that were established subsequently in experiments differing in synthesis conditions, starting mixtures, and phases associating with F-sodalite.

This study aims at determining more comprehensively the characteristics of the new phase, reasons for its compositional variations, conditions of formation, and possibility of its occurrence in nature.

The following abbreviations were used in the paper: *Ab*, albite; *Anc*, analcime; *Cns*, cancrisilite; *Crl*, cryolite; *Flu*, fluorite; Fl, fluid; L, aluminosilicate glass; *Nsi*, sodium silicate, Na₂SiO₃; *Ne*, nepheline; *Sdl*, sodalite (Cl-*Sdl*, F-*Sdl*, and SO₄-*Sdl* are chlorine, fluorine, and sulfate varieties, respectively); *Vil*, villiaumite; Al^{tot}, total aluminum content in the mineral formula; and apfu, the number of atoms per formula unit.

METHODS

Experimental Equipment Used for F-Sodalite Synthesis

Experiments were conducted at temperatures of $400-800^{\circ}$ C and fluid pressures ($P_{\rm Fl}$) of 1 and 2 kbar using externally heated cold-seal pressure vessels and 20 mL autoclaves at the petrology department of the

Moscow State University and Institute of Experimental Mineralogy of the Russian Academy of Sciences. The accuracy of temperature and pressure control and monitoring was $\pm 5^{\circ}$ C and ± 50 bar. The pressure within the autoclaves depended on the degree of filling and was maintained within ± 100 bar. The oxygen fugacity was imposed by the material of the high-pressure vessels at the level of the Ni–NiO buffer. Starting materials were loaded into platinum capsules 3–7 mm in diameter and sealed hermetically by arc welding. The experimental conditions were reached within 2-4 h, and the run duration was 5–7 days at 750–800°C and 21-49 days at 400-650°C. The pressure vessels were quenched by compressed air and simultaneous water dispersion, and the autoclaves were quenched in flowing water. The quenching time to 200°C was estimated as 2-5 min for the high-pressure vessels, several seconds for similar rapid-quench vessels, and 3-5 min for the autoclaves.

Starting Materials

The following materials were used for the preparation of starting mixtures: high-purity NaF, AlF₃, and NaAlO₂ reagents; stoichiometric dried gels of SiO₂, NaAlSiO₄, and Al₂SiO₅; natural nepheline purified from K in NaCl melt at 900°C; and distilled water. Natural Cl-bearing sodalite was used as a seed for monocrystal growth. The proportions of major components (Table 1, Fig. 1) in the 400–650°C experiments corresponded to a series of mixtures of Na₃AlSiO₄F₂ (hypothetical sodalite composition) and NaF with 27–72 wt % H₂O. In the experiments at 750 and 800°C, the starting mixtures contained 6.54 wt % H₂O, and the F content was mostly ~40 at % of the total of Si, Al, Na, and F.

Criteria for Equilibrium

The equilibration of experimental products was demonstrated by the constant compositions of experimental phases and independence of phase relations on run duration and the phase composition and state of reactants (reversal experiments approaching equilibrium compositions from two sides). Quench phases were distinguished from equilibrium ones mainly on the basis of the morphology of crystals (grains). In some cases, the phase compositions of experimental products obtained on different apparatuses under identical conditions, loading, and duration, but at sharply different quenching rates.

Phase Composition of Fluids during Experiments

It is known that aqueous NaF solutions are described by a type II phase diagram with critical phenomena in saturated solutions (Kotel'nikova and Kotel'nikov, 2002, 2008). The solubility of such salts decreases with increasing temperature and show different signs of pressure dependence. To evaluate the phase state of the fluid, special experiments were performed by the method of synthetic fluid inclusions. This experimental approach (Kotel'nikova and Kotel'nikov, 2008, 2011) is based on the assumption that synthetic fluid inclusions trapped in healed fractures in quartz crystals in hydrothermal experiments can be used as microscopic fluid samplers allowing observation of phase transformations in fluid under varying temperature.

The analysis of data on NaF solubility in fluid at high T and P suggested that sodalite is synthesized in aqueous solutions with an initial concentration of 0.5 mol/L (2.1 wt %). At a pressure of 1 kbar and temperatures from 450 to 600°C, only two-phase inclusions were found in quartz. They contained liquid (L) and a gas bubble (G) at room temperature (Table 2) and were homogenized into a liquid phase at 364-370°C, independent of the synthesis temperature. The results of cryometric measurements provide compelling evidence that the solution composition changed owing to reactions between the water-salt fluid and silicates. An increase in homogenization temperature, both into liquid and gas, at a temperature of inclusion synthesis of 700°C and finding of a few multiphase inclusions with a solid phase indicate that the experimental conditions approached the critical point. The appearance of inclusions with crystals and a glassy phase forming a meniscus-like phase boundary with liquid as a temperature increased up to 750°C suggests that the fluid was heterogeneous under experimental conditions. A pressure increase up to 2 kbar at the same temperature (750°C) prevented unmixing. Thus, the investigation of synthetic fluid inclusions showed that all experiments on sodalite synthesis at 450-650°C were conducted in the presence of a homogeneous fluid.

Analysis of Experimental Products

Solid experimental products were explored by the methods of optical microscopy, electron microscopy, X-ray diffraction, infrared (IR) spectroscopy, and electron microprobe analysis.

The X-ray diffraction patterns of sodalites were obtained using an HZG-4 diffractometer in a continuous scanning mode. Spec-pure silicon (a = 5.4307 Å) was used as an internal standard. The unit-cell parameters were refined from 10–17 reflections in the θ range 7°–39°. The calculations were made using the programs LCC, PUDI (Burnham, 1991), and REFLAT (Chichagov, 1994), accepting the hypothesis of a cubic cell and space group *P*43*n*.

Fluorine-bearing sodalite from the same run (no. 6202) from which grown crystals (Fig. 2a) were taken for the determination of the crystal structure and unit-cell parameters (Yakubovich et al., 2011) was investigated by IR spectroscopy using a FSM-1201

Fable 1.	Compositions	of starting	mixtures	for experi	ments
on F-soc	lalite synthesis	, wt %			

Run no.	SiO ₂	Al ₂ O ₃	Na ₂ O	F	Cl	H ₂ O	Total*
		40	00°C, 1	kbar			
6191	17.88	15.20	11.46	1.28	0.15	54.60	100.57
6192	17.79	15.12	13.49	2.55	0.15	52.00	101.11
6193	17.73	15.07	15.52	3.82	0.15	49.37	101.64
6194	17.68	15.02	17.54	5.08	0.15	46.71	102.17
	1	50	00°C, 1	kbar	1		
6195	17.79	15.12	13.49	2.55	0.15	52.00	101.11
6196	17.73	15.07	15.52	3.82	0.15	49.37	101.64
6197	17.68	15.02	17.54	5.08	0.15	46.71	102.17
6798	17.62	14.97	21.61	7.59	0.15	41.29	103.23
6199	17.60	14.96	25.72	10.11	0.15	35.76	104.29
		6	50°C, 1	kbar			
6200	17.62	14.98	29.87	12.65	0.15	30.10	105.36
579	19.82	16.85	14.06	2.25	0.17	47.84	100.99
580	17.49	14.86	17.17	4.91	0.15	47.52	102.10
	•	6	50°C, 2	kbar			
582	13.13	11.16	35.74	17.68	0.11	29.64	107.47
6104	17.88	15.20	11.46	1.28	0.15	54.60	100.57
6105	14.63	12.44	12.81	3.15	0.12	58.21	101.35
6106	14.55	12.37	17.85	6.27	0.12	51.50	102.67
6107	14.30	12.15	24.24	10.26	0.12	43.28	104.35
6201	18.71	15.91	25.59	9.67	0.16	34.07	104.11
6202	18.73	15.92	29.55	12.10	0.16	28.67	105.13
	•	7:	50°C, 1	kbar	-		
540	28.04	10.50	39.88	25.96	**	6.54	110.93
544	17.96	15.27	46.89	23.04	—	6.54	109.70
516, 524	34.61	20.94	21.58	28.20	—	6.54	111.87
517	33.66	22.55	20.87	28.28	—	6.54	111.91
518	27.65	26.30	23.56	27.56	—	6.54	111.61
523	21.28	19.72	40.99	19.80	—	6.54	108.34
800°C, 1 kbar							
5 20	31.56	28.69	27.51	9.82	—	6.54	104.13
7 15	39.69	28.81	20.51	7.68	_	6.54	103.24
o 1	27.87	9.76	47.72	14.02	—	6.54	105.91
о9	12.87	11.20	57.31	20.86	-	6.54	108.78
1 1ch	11.41	25.64	47.59	15.23	-	6.54	106.41
1 1nf	14.20	12.07	58.83	14.44	-	6.54	106.08
4 60	13.35	8.60	51.26	34.99	_	6.54	114.74

^{*}Totals of components in starting mixtures are higher than 100%, because the contents of cations are given in the form of oxides ignoring the contributions of halogens present in the mixtures to charge balancing. Accounting for this substitution results in lower totals.

**Element was not introduced into the system.



Fig. 1. Major-component compositions of (1) synthetic F-sodalite, (2) associating melt, (5) other phases, and starting mixtures used in experiments at (3) $400-650^{\circ}$ C and (4) $750-800^{\circ}$ C.

Fourier spectrometer in the wavenumber range 400–4000 cm⁻¹. The sample was prepared as powdered mineral suspended in Vaseline petroleum jelly.

The compositions of synthetic solid phases and quenched glasses were determined by electron microprobe analysis using the following instruments: Came-

Dun no	Temperature °C	Characteristics of inclusions					
Kull IIO.	Temperature, C	G + L	G + L $G + L + Cr$				
		1 kbar					
4913	450	367-369, L* (26)**	—	—			
5036	500	364–370, L (23)	—	—			
5035	500	366, L (7)	-	-			
5150	600	367–373, L (60)	—	—			
5152	600	364–368, L (5)	—	—			
5240	700	376–380, L and G (15)	-	-			
6045	700	376–381, L and G (28)	-	-			
4988	750	387, L and G (4)	385 p.h.***, L (2)	385–397 p.h., L, G (3)			
2 kb	ar						
5890	700	354–361, L (50)	_	_			
5185	750	382, L (3)	378, 380 p.h.***, L (2)	_			

Table 2. Conditions and results of experiments on the synthesis of NaF-bearing fluid inclusions

*Homogenization to liquid (L) or gas (G); appearance of a crystalline (Cr) or glassy (Gl) phase.

**Number of measurements.

***p.h. is partial homogenization of the fluid part.



Fig. 2. Morphology of F-sodalite in the system Si–Al–Na–H–O–F. (a) Sodalite monocrystals and intergrowths obtained in run 6202 at 650°C and 2 kbar (dots numbered *1*–9 indicate analysis spots); (b) polygonal section of a sodalite crystal from run 523 at 750°C and 1 kbar; (c) faceted and rounded sodalite grains in a villiaumite matrix from run 540 at 750°C and 1 kbar; (d) sodalite and villiaumite in aluminosilicate glass from run 4-60 at 800°C and 1 kbar. (a) Secondary electron image and (b)–(d) back-scattered electron images.

bax electron microprobe with a LINK AN-10000 energy-dispersive system, Camscan MV2300 (VEGA TS 5130MM) digital scanning electron microscope equipped with a Link INCA Energy energy-dispersive analytical system with a Si(Li) semiconductor detector (both at the Institute of Experimental Mineralogy, Russian Academy of Sciences), and Jeol JSM-6480LV scanning electron microscope with an INCA Energy 350 energy-dispersive system at the department of petrology of the Moscow State University. The analytical conditions were the following: 15 kV accelerating voltage, 2 nA beam current, and 70 s counting time per spot for the Camebax instrument; 20 kV accelerating voltage and 1 nA beam current of Co-absorbed electrons for the CamScan MV2300; and 10 kV accelerating voltage and 0.7 nA beam current for the Jeol JSM-6480LV. A program package developed at the Institute of Experimental Mineralogy of the Russian Academy of Sciences and a program for the analysis of fluorine-rich glasses and other fluoride phases developed at the laboratory of local analytical methods of the petrology department of the Moscow State University were used. The analytical precision for major elements in the synthesized phases was no higher than 2-5% relative. The detection limit for F was 0.05 wt %.

RESULTS AND DISCUSSION

Phase Composition of Experimental Products

Fluorine-bearing sodalite was obtained instead of expected nepheline in experiments on the determination of liquidus phase relations in the ultraagpaitic Na-rich and Si-poor part of the Si–Al–Na–H–O–F system (Gramenitskii et al., 2005), first at 800°C and then at 400–750°C and pressures of 1 and 2 kbar.

Since the proportions of major components in the starting mixtures did not correspond to the composition of synthetic sodalite, other phases coexisted with it in different runs (Tables 3, 4): villiaumite, cryolite, melt (quenched to glass), nepheline, albite, analcime, cancrisilite, fluorite, and sodium silicate and hydrosilicate. Except for the latter three phases, most of these minerals were at equilibrium during the experiments, which extended our knowledge of subsolidus phase relations.

Nepheline occurs as short columnar crystals 20– 50 μ m in size. Its composition includes up to 0.03 mol % of the potassium component, which was formed at the expense of seed crystals of natural nepheline and sodalite. The content of excess SiO_2 is up to 6.5 mol %. Albite forms well developed subtabular crystals up to 15 µm in size. The fraction of the potassium endmember is insignificant. The presence of quench albite was demonstrated in run 516, in contrast to run 524, which was conducted with the same starting mixture and under the same conditions, but on the rapidquench apparatus. Cryolite forms ellipsoid grains 30-40 um in size at 750–800°C and shows sometimes fragments of crystal faces. Villiaumite grains are similar in shape but much larger in size, up to 200 µm. In the 400-650°C experiments, cryolite forms short columnar crystals up to 100 µm across, and subcubic villiaumite crystals are up to 200 µm in size. At low NaF concentrations in the initial solution, villiaumite occurs as small and obviously quench crystals. The proportions of major components in these phases closely match the theoretical formulas (Table 4).

The assemblages of F-sodalite at $500-650^{\circ}$ C are shown in a tentative diagram in Fig. 1. The proportions of Si and Al are not reflected in this diagram, and the associations of nepheline and albite with both villiaumite and cryolite are therefore not forbidden.

The equilibrium character of sodium silicate and hydrosilicate phases obtained at 800° C in experiments in the poorly studied extremely agpaitic part of the system is questionable. Cancrisilite was observed in the products of two experiments at 650°C and 2 kbar as acicular crystals up to 10 µm long, which are probably of a quench origin (Olysych, 2010).

Analcime was observed in the experimental products only at 400°C, although the investigation of its synthesis conditions (Kotel'nikov et al., 2007) suggests that the reaction $Anc = Ne + Ab + H_2O$ occurs at higher temperatures. Its subisometric resorbed crystals are up to 20 μ m in size and have cubic habits and, sometimes, atoll-like shapes.

Glass (quenched melt) appears in experimental products above 650°C in the compositional region between albite and cryolite.

Morphology of F-Sodalite Crystals

The synthetic F-sodalites are usually subisometric colorless transparent crystals of cubic or rhombododecahedral habits, sometimes with truncated faces and edges. Their sections are usually hexagons or rectangles (Figs. 2a-2d), which correspond to transverse or lengthwise sections of a prism. The grain size is from 5 to 50-100 µm, although in some experiments the sections of sodalite crystals are up to 500 µm across, and their intergrowths may be up to 2.5 mm in size (Fig. 2a). The largest F-sodalite crystals were obtained in a long (41 days) experiment at 650°C and 2 kbar. There is no distinct dependence of crystal morphology on synthesis conditions, composition, and associating phases. It can only be noted that the sodalite crystals are idiomorphic in contact with villiaumite (Fig. 2c). Cryolite is less abundant than sodalite in the experimental products. It forms small $(5-10 \ \mu m)$ rounded transparent crystals with fragments of crystal faces and sometimes occurs as inclusions in larger sodalite crystals.

In the presence of aluminosilicate melt (glass), sodalite forms individual crystals or aggregates with villiaumite, in which sodalite crystals are faceted, and villiaumite grains are rounded or oval-shaped (Fig. 2d). Perhaps, these phases crystallized simultaneously from the melt, but the crystallization ability of sodalite was higher than that of cryolite.

F-Sodalite Composition

On account of the structure (Yakubovich et al., 2011), the chemical composition of F-sodalite should be normalized to $(Si + Al)^{IV} = 12$. The calculation procedure is the following: (1) the AlF_6 group is subtracted from the atomic amounts of elements obtained from the analysis ($Al^{VI} = F/6$ and $Al^{IV} = Al^{tot} - Al^{VI}$); (2) the common factor $K = 12/(\text{Si} + \text{Al}^{\text{IV}})$ is calculated; (3) formula coefficients are obtained by multiplying the atomic amounts of Na, Al^{VI}, Al^{IV}, Si, F, and O by K. The consistency of F-sodalite formulas in any particular experiment was comparable with the analytical uncertainty (standard deviations were no higher than 6% relative for Si and Al^{IV}, 10% for Na, and reached occasionally 30% only for AlF_6), but the difference between the experiments was much more significant (Table 3). Thus, F-sodalite is a mineral of variable composition.

Given the established structure, the most probable reason for the compositional variations is the different filling of sodalite cages with anionic octahedral groups $[AIF_6]^{3-}$. Theoretically, their number can be from 0 to 1.

COMPOSITION, STRUCTURE, AND CONDITIONS OF FORMATION

Na	Dhaca-*	***		Analyt	tical data	, wt %		Formula***				
	Phases*	n***	SiO ₂	Al ₂ O ₃	Na ₂ O	F	Total	Si	Al	Na	AlF ₆	0
				4	00°C, 1	kbar						<u> </u>
6191	Ne + Anc	3	37.85	34.28	23.58	7.41	103.12	6.115	5.885	7.375	0.630	23.800
6192	Anc	3	38.79	32.43	24.26	7.81	103.29	6.391	5.609	7.741	0.678	24.049
6193	Crl	6	38.68	32.99	23.99	7.52	103.18	6.357	5.643	7.642	0.646	24.030
6194	Crl + Anc?	6	40.61	32.01	24.72	4.59	101.93	6.424	5.576	7.567	0.382	24.422
500°C, 1 kbar												
6195	Ne	8	38.91	33.98	22.52	7.93	103.34	6.252	5.748	7.011	0.671	23.624
6196	Ne + Crl	9	40.55	32.04	22.48	8.52	103.59	6.590	5.410	7.565	0.660	24.088
6197	Crl	8	40.65	31.74	23.72	6.73	102.84	6.488	5.512	7.298	0.628	23.951
6198	Crl + Flu	5	39.70	31.92	23.55	8.33	103.5	6.540	5.460	7.508	0.723	23.939
6199	-	8	40.68	31.93	22.89	7.77	103.27	6.582	5.418	7.172	0.662	23.883
			•	6	50°C, 1	kbar	•		•	•		
6200	Crl	5	39.28	32.23	23.70	8.26	103.47	6.472	5.528	7.559	0.717	23.940
579	Ne + Flu	6	39.63	34.23	23.06	5.32	102.24	6.174	5.826	6.973	0.438	23.916
580	Ne + Crl	2	40.09	34.66	22.31	5.09	102.15	6.147	5.853	6.634	0.411	23.774
				6	50°C, 2	kbar						
582	Ne + Vil	3	40.44	34.58	21.60	5.84	102.46	6.239	5.761	6.326	0.491	23.546
6104–6106	Ne	17	39.62	33.48	23.81	5.35	102.26	6.241	5.759	7.260	0.445	24.083
6107	—	5	39.20	33.30	24.36	5.42	102.28	6.228	5.772	7.493	0.454	24.180
6201	Crl + CnS	4	39.21	31.88	23.87	8.70	103.66	6.522	5.478	7.686	0.762	23.961
6202	Ab + Crl + CnS	16	42.49	31.71	21.81	6.89	102.9	6.700	5.300	6.667	0.577	23.818
				7	50°C, 11	kbar						
540	Vil	12	38.39	35.64	23.46	4.24	101.73	5.900	6.100	6.979	0.343	23.925
544	Vil	5	40.98	37.78	18.49	4.73	101.98	5.930	6.070	5.236	0.359	23.044
516, 517	Ab + Crl	4	41.35	29.94	23.20	9.53	104.02	6.934	5.066	7.530	0.841	23.971
518	Vil	3	40.08	29.79	23.76	10.99	104.62	6.936	5.064	7.959	1.001	23.947
524	Crl + L	3	41.93	29.74	22.86	9.45	103.98	6.993	5.007	7.380	0.829	23.943
523	Crl + Vil	8	36.06	34.07	24.49	9.28	103.9	6.074	5.926	8.001	0.832	23.789
800°C, 1 kbar												
7 15	L	2	42.47	30.83	21.94	8.22	101.73	6.848	5.152	6.848	0.697	23.802
5 20	L	4	39.09	27.14	28.36	9.35	101.98	6.848	5.152	6.848	0.697	23.802
o1	<i>Vil</i> + Nsi	2	40.77	31.81	27.04	0.67	104.02	7.097	4.903	9.968	0.894	25.192
09	<i>Vil</i> + NaOH	5	33.11	28.64	30.31	13.70	104.62	6.285	5.715	8.068	0.055	25.094
1 1ch	<i>Crl</i> + NaOH	8	39.05	35.86	23.42	2.89	103.98	5.878	6.122	6.822	0.229	24.007
1 1nf	<i>Vil</i> + NaOH	5	39.65	33.46	26.47	0.73	103.9	6.052	5.948	7.818	0.059	24.847
4 60	Vil	11	33.35	35.35	24.79	6.51	101.73	5.691	6.309	7.876	0.559	23.946

Table 3. Mean compositions of synthesized F-sodalite

* Phases identified in experimental products together with F-sodalite.

** Number of F-sodalite analyses.

*** Calculated crystal chemical formulas.

Runs 524 and 6104–6107 were conducted on the rapid-quench apparatus.

Microprobe analyses, wt %							
Run no., phase	T, °C; P, kbar	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	F	total
6191 Ne	400; 1	45.51	33.98	19.62	0.81	_	99.62
6195 Ne	500; 1	44.29	34.06	20.84	0.78	—	99.97
581 Ne	650; 1	44.41	34.20	20.56	0.89	—	100.06
6102 Ne	650; 2	47.31	33.15	19.02	0.20	—	99.68
6102 <i>Ab</i>	650; 2	68.59	19.51	11.71	0.10	—	99.91
6102 Cns	650; 2	54.69	22.57	18.30	—	0.43	95.99
6191 Anc	400; 1	51.33	26.57	14.61	—	—	92.51
5 20 L	800; 1	58.38	20.72	12.10	—	16.20	107.40
7 15 L	800; 1	51.06	21.85	22.08	—	12.80	107.79
			Crystal chemi	ical formulas*			
Run no., phase	<i>T</i> , °C; <i>P</i> , kbar	Si	Al	Na	K	F	Q**
6191 Ne	400; 1	1.067	0.939	0.892	0.024	_	4.3
6195 Ne	500; 1	1.045	0.947	0.954	0.023	—	3.2
581 Ne	650; 1	1.046	0.950	0.939	0.027	—	3.3
6102 Ne	650; 2	1.102	0.910	0.857	0.006	—	6.5
6102 Ab	650; 2	2.997	1.005	0.992	0.006	—	_
6102 Cns	650; 2	8.073	3.927	5.237	—	0.200	_
6191 Anc	400; 1	1.880	1.147	1.037	—	—	—
5 20 L	800; 1	16.396	6.847	6.571	—	15.405	—
7 15 L	800; 1	15.767	7.920	13.172	—	13.800	—

Table 4. Compositions of phases coexisting with synthesized F-sodalite

*Crystal chemical formulas were normalized to 8 cation charges for nepheline, 16 cation charges for albite, 12 cation charges for analcime, 12 (Si + Al) atoms for cancrisilite, and 100 cation charges for melt.

**Q is the excess silica in calculated nepheline formulas.

Charge balance and other structural requirements suggest that the number of other atoms should change correspondingly: Si increases linearly from 5 to 7 (Fig. 3, dash-dot line 1), Na increases from 7 to 8, Al^{IV} decreases from 7 to 5, and the number of H₂O molecules decreases from 8 to 4. The theoretical endmembers are $Na_7(H_2O)_8[Si_5Al_7O_{24}]$ and $Na_8(AlF_6)(H_2O)_4[Si_7Al_5O_{24}]$. Indeed, the whole set of analyses (180) exhibits significant positive correlations of Si and Na with AlF_6 , although there is a considerable scatter relative to the calculated linear approximation. The linear correlation between Si and AIF_6 is indicated in Fig. 3 by dashed line 2. The significance of such a correlation increases considerably if all the F-sodalite analyses are divided into two sets corresponding to synthesis from SiO₂-poor staring mixtures (coexisting with nepheline, line 3) and SiO₂rich starting mixtures (coexisting with albite, line 4). Moreover, the slopes of these trends are closer to the theoretical value. The structure is compatible with an increase in the number of Si atoms coupled with the incorporation of [Al(OH)₆]³⁻ groups independent of F content. Such a substitution could be responsible for the shift of trends depending on SiO_2 content in the starting mixture. Independent methods are needed to test this hypothesis. There is no clear dependence of F-sodalite composition on synthesis conditions, except for an increase in the scatter of contents of all components with increasing temperature.

F-Sodalite Properties

The refractive index of F-bearing sodalite from samples 540 and 544 was determined by A.M. Batanova as 1.417 ± 0.003 , and the density is D = 2.370 g/cm³.

The IR absorption spectrum of F-sodalite containing extraframework anions $[AlF_6]^{3-}$ (Fig. 4a) was obtained for the first time. Five absorption regions were distinguished in the spectrum. Within the range 3200-3700 cm⁻¹ corresponding to the stretching vibrations of OH groups, there is a complex broad absorption band consisting of several components centered at 3265, 3434, 3594, and 3647 cm⁻¹. The highest frequency weak narrow component is considered as an indicator of the presence of hydroxyl groups bonded to framework cations. The broader lower fre-



Fig. 3. Correlation of the contents of Si and $[AlF_6]$ groups (per formula unit, pfu) in synthetic F-sodalite: (1) theoretical line obtained by the interpolation of end-member compositions; (2) approximation of all data; (3) from silica-poor (+nepheline) compositions; and (4) from silica-poor (+albite) compositions.

quency components are related to the stretching vibrations of hydroxyl groups in water molecules. The presence of molecular water is supported by the two intense absorption bands at 1640 and 1691 cm⁻¹ corresponding to bending vibrations of H₂O molecules in two independent structural sites. The different intensity of these bands is due to the different occupancy probabilities of these sites (approximately 1 : 4).

The absorption bands in the range $400-1300 \text{ cm}^{-1}$ (Fig. 4b) were interpreted by analogy with the calculation of the vibrational spectrum of sodalite (Creighton et al., 1994). The broad intense absorption band near 997 cm⁻¹ corresponds to the antisymmetrical stretching and bending vibrations of Si–O bonds and O–Si–O angles and, to a smaller degree, Al–O and O–Al–O in (Si, Al)O₄ tetrahedra. It is much broader than the respective band in the sodalite spectrum, which is probably related to the partial disorientation of (Si, Al)O₄ tetrahedra in 13% of cases and variations in the length of (Si, Al)–O bonds.

In the 500–750 cm⁻¹ spectral region, we observed a complex broad absorption band consisting of six components centered at 723, 703, 659, 636, 600, and 583 cm⁻¹. Three components with higher wavenumbers are related to the antisymmetrical bending and stretching vibrations of O–Al–O angles with minor contributions from O–Si–O angles and Al–O bonds. Three lower frequency components have no analogues in the spectrum of natural sodalite and were assigned to the internal vibrations of the anionic complex $[AlF_6]^{3-}$, because the IR absorption spectrum of cryolite (Fig. 4c) exhibits an absorption band at 578–604 cm⁻¹ corresponding to the triply degenerate stretching vibrations of tetrahedral bonds (Nakamoto, 1991). A slight splitting of the triply degenerate vibration into two components in the cryolite spectrum indicates some deformation of octahedra in its structure. The $[AIF_6]^{3-}$ octahedra of the F-sodalite structure have a regular shape, and, consequently, the splitting of this vibration into three components in the IR absorption spectrum (Fig. 4a) indicates a decrease in the symmetry of the octahedra owing to the incorporation of hydroxyl groups in the fluorine sites.

Two absorption bands in the low-frequency part of the spectrum at 454 and 426 cm⁻¹ were assigned by analogy with the sodalite spectrum to the stretching vibrations of the $[Al_6Si_6O_{24}]^{6-}$ framework or extra-framework vibrations of the structure.

Thus, the results of IR absorption spectroscopy confirmed the presence of $[AlF_6]^{3-}$ anionic groups and H₂O molecules in F-sodalite, which was independently established by the investigation of its structure. A new result was the discovery of the presence of $(OH)^-$ groups in its structure, possibly as constituents of the $[Al(OH)_6]^{3-}$ complexes.

The X-ray powder diffraction patterns of F-sodalite exhibit the entire spectrum of characteristic reflections of sodalite. Unit-cell parameters were calculated for 11 samples assuming the space group P43m (Table 5). As could be anticipated from the F-sodalite structure, there is a highly probable positive linear correlation between the unit-cell volume (V, Å³) or dimension (a) and the number of Na atoms in the for-



Fig. 4. Infrared absorption spectra of (a) F-bearing sodalite synthesized under hydrothermal conditions at $T = 650^{\circ}$ C and P = 2 kbar, (b) natural sodalite Na₈[AlSiO₄]₆Cl₂ (Kovdor, Kola Peninsula, Russia), and (c) synthetic cryolite Na₃AlF₆.

mula unit: V = 2.885Na + 740.41 (Fig. 5). Similar correlations with Si and AlF₆ are less pronounced.

The radius of the anionic group (*R*, Å) is explicitly dependent on *a* (Å) (Table 6). The dependence is described by the linear equation calculated for n = 8, $S_x = 0.29$, and $t_{(95\%)} = 2.4$: $R = -59.221 + 6.8493a \pm 0.2$, where *n* is the number of measurements, S_x is the mean square deviation, and $t_{(95\%)}$ is Student's *t* test at a confidence level of 95%. The *a* value of the synthesized F-sodalites ranges from 9.031 to 9.063 Å and is most similar to that of SO₄-sodalite. The mean value 9.045 \pm 0.010 Å yields a [AIF₆]³⁻ radius of 2.7 \pm 0.2 Å, which is similar to the size of the SO₄ group.

Relations of F-Sodalite with Cl- and SO₄-Sodalite and the Possibility of Its Occurrence in Nature

The established crystal structure of F-sodalite (Fig. 6) allows only limited isomorphism with

Cl-sodalite. The crystal structure of Cl-sodalite is based on an aluminosilicate framework of the $[Si_6Al_6O_{24}]$ composition and ordered occupancy of tetrahedra with equal numbers of Si and Al atoms.



Fig. 5. Linear dependence of the unit-cell volume of F-sodalite on Na content (apfu).

Run no.	Run parameters*	AlF ₆ , groups pfu	Si, apfu	Na, apfu	<i>a</i> , Å	<i>V</i> , Å ³	n**
540	750/1/7	0.343	5.900	6.979	9.044(1)	739.7(2)	8
544	750/1/7	0.359	5.930	5.236	9.031(1)	736.2(1)	10
579	650/1/21	0.438	6.174	6.973	9.037(1)	738.0(2)	12
580	650/1/21	0.411	6.174	6.634	9.041(1)	739.1(1)	11
581	650/1/21	0.372	6.166	7.109	9.046(1)	740.2(2)	15
582	650/1/21	0.491	6.239	6.326	9.037(1)	738.0(2)	10
6104	650/2/41	0.423	6.205	6.890	9.052(1)	741.7(1)	19
6105	650/2/41	0.433	6.250	7.280	9.050(1)	741.2(1)	18
6106	650/2/41	0.519	6.292	7.380	9.063(1)	744.4(2)	18
6107	650/2/41	0.454	6.228	7.493	9.053(1)	742.0(2)	20
6202	650/2/41	0.577	6.700	6.667	9.0461(1)	740.26(1)	***

 Table 5. Unit-cell parameters of F-bearing sodalite

*Run parameters: temperature (°C)/pressure (kbar)/duration (days).

**n is the number of reflections used for the calculation of unit-cell parameters of F-sodalite.

***Data for run 6202 were obtained from single-crystal X-ray diffraction.

Chlorine atoms occur in cuboctahedra in the apexes and center of the cubic unit cell in the special position $\{000\}$ of the space group P43n. The crystal chemical function of Cl atoms is the accomplishment of the coordination of Na⁺ ions, which occur in tetrahedra formed by three O atoms in six-membered windows and one halogen atom.

The presence of F in the crystallization medium results in the formation of the [AlF₆]³⁻octahedral complexes and a concomitant decrease in the number of $[AlO_4]^{5-}$ groups in the framework of aluminosilicate tetrahedra, which appear to be statistically disordered. In contrast to the identical contents of cavities in the apexes and center of the cubic cell (Fig. 6), which is typical of sodalite (space group P43n), the cage at the center of the cell does not contain an AlF_6 octahedron. 94% of the central cavities of the cells are filled with H₂O molecules, while competing H₂O molecules and $[AIF_6]^{3-}$ anionic complexes occur in the structural cavities at the apexes of the cells in a proportion of approximately 1 : 3. The space group changes to P43m. The position of Na⁺ is also modified. These structural differences are probably responsible for the limited isomorphism of F- and Cl-sodalites.

It is symptomatic therefore that there is no data in the literature on any significant F contents in natural sodalite, even in the case of its association with F-rich minerals, including fluorides: villiaumite, fluorite, and others. We searched for a natural F-bearing sodalite and observed fluorine content above the detection limit only in one sample from the pegmatite of the Lovozero massif kindly provided by I.V. Pekov. The (F, SO₄, Cl)-sodalite associates with alkali feldspar, alkali amphibole, and villiaumite. Its composition is inhomogeneous. The analysis of the F richest variety was calculated to the formula $Na_{8.28}Al_{6.03}Si_{5.96}O_{23.6}(Cl_{1.41})(SO_4)_{0.61}(F)_{0.48}$. It is possible that this sodalite contains the maximum fraction of the F-bearing end-member (0.2). Accounting for the occurrence of F in the $[AIF_6]^{3-}$ group yields an even smaller mole fraction.

The incorporation of F into sodalite requires much greater energy input compared with Cl⁻ and SO₄²⁻, because it is accompanied by a structural rearrangement and transformation of tetrahedral Al of framework aluminosilicates (nepheline and albite) or melt to octahedral coordination. Therefore, Cl⁻ and SO₄²⁻

are mainly used for the formation of sodalite, whereas F^- remains in the mineral-forming medium (melt or

 Table 6. Unit-cell parameters of synthetic sodalites with different anionic groups

Anion	<i>R</i> , Å	<i>a</i> , Å	V, Å ³
(OH) ⁻	1.32	8.885	701.4
Cl-	1.81	8.873	698.6
Br ⁻	1.96	8.932	712.6
I-	2.20	9.009	731.2
(CO ₃) ^{2–}	2.57	9.005	730.2
(NO ₃) ⁻	2.60	8.997	728.3
$(SO_4)^{2-}$	2.98	9.072	746.6
$(WO_4)^{2-}$	3.40	9.148	765.5

Unit-cell parameters are taken from the database of Chichagov (1994), and anion radii are after Smith (1963) and Perchuk and Ryabchikov (1986).



Fig. 6. Comparison of the crystal structures of F-sodalite and Cl-sodalite.



Fig. 7. Proposed scheme of correspondence of the compositions of Cl-sodalite, F-sodalite, and coexisting fluid.

aqueous solution). As a consequence, the F/(F + Cl) ratio of aqueous solution will be much higher than that of coexisting sodalite (Fig. 7). Ratios higher than 0.7 are probably not reached in natural media, and the natural analog of the synthetic F-sodalite can be found in association with F-bearing Cl- or SO₄-sodalite. Of course, these suggestions must be experimentally tested.

CONCLUSIONS

(1) Fluoro-sodalite was synthesized for the first time at temperatures of $400-800^{\circ}$ C and pressures of 1-2 kbar, and its properties were determined by physical methods.

(2) The presence of the anionic group $[AIF_6]^{3-}$ in the F-sodalite structure was established by singlecrystal X-ray diffraction and IR spectroscopy.

(3) The end-members of the synthesized F-sodalite solid solution series are $Na_7(H_2O)_8[Si_5Al_7O_{24}]$ and $Na_8(AlF_6)(H_2O)_4[Si_7Al_5O_{24}]$. It is suggested that the proportions of major components depend on the incorporation of the $Al(OH)_6^{3-}$ group.

(4) Depending on the composition of the system, F-sodalite associates at $500-650^{\circ}$ C with nepheline, albite, cryolite, and villiaumite, which are joined by analcime at temperatures below 500° C and aluminosilicate melt above 650° C.

(5) Fluorine-bearing SO_4 -Cl-sodalite was found for the first time in a pegmatite sample from the Lovozero massif. Analogues of the synthesized F-sodalites were never found in nature, which can be attributed to two circumstances. First, there is only limited miscibility between the solid solutions of F-sodalite, on the one hand, and Cl- and SO_4 sodalite, on the other hand. Second, the F/(F + Cl) ratio of mineral-forming aluminosilicate melt or aqueous solution is much higher than that of coexisting sodalite. In natural media, this ratio is probably lower than 0.7, whereas the stability of F-sodalite requires higher F/(F + Cl) values.

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