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Synthesis of fluorine-bearing sodalite and its properties study

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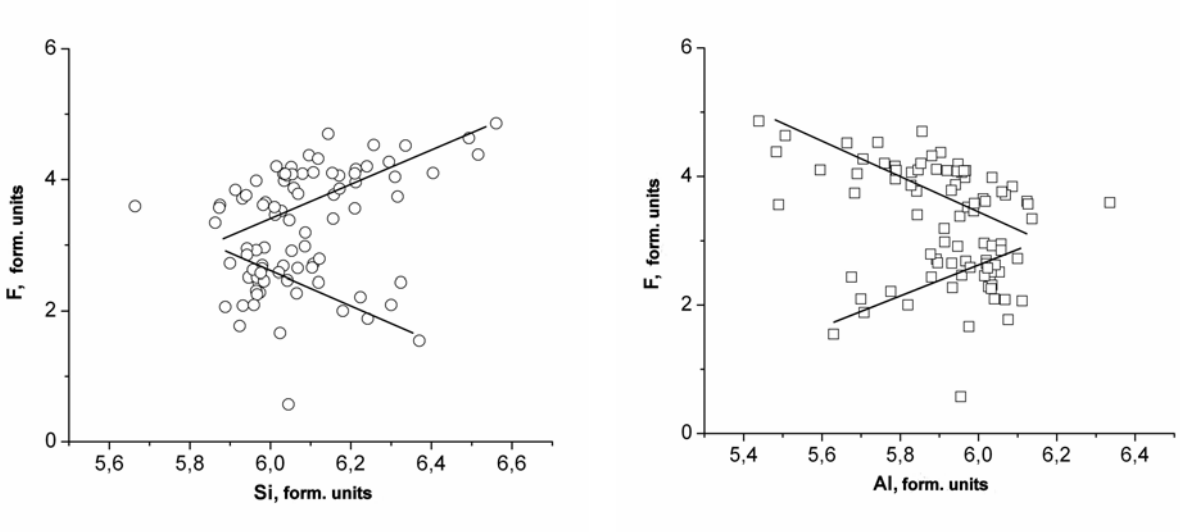
Synthesis of fluorine-beating sodalite was carried out in temperature interval 400÷750°C and pressure 1.0÷2.0 kbar in presence of NaF solutions of different concentrations. It is shown that sodalite is stable when sodium fluoride concentration is more than 5 wt % (at 400°C), 10 wt % (at 500 and 650°C). Compositions of synthetic F-sodalites have been studied by microprobe analysis. Earlier [*Yakubovich, et al.*,2010] it has been shown that fluorine incorporates into the structure as "cryolite" anion – AlF_6^3 group. Based on a lot of microprobe analyses of fluorine-bearing sodalites (recalculation of sodalite analyses to crystal-chemical formula was produced using the sum Al+Si=12) it has been indicated that when fluorine concentrations are up to 3 formula units (f. un.) his content in sodalite linearly correlates with Al amount (f. un.); and when F content is 3.5 ÷ 5 (f. un.) it linearly correlates with Si amount (f. un.) (fig. 1). This fact gives evidence of possibility of fluoride incorporation to sodalite as malladrite anion (SiF_6^{2-}). Based on the x-ray data the specification of cell parameters of synthetic fluorine-bearing sodalites has been produced. The average cell parameters are shown to be following: a=9.045(±0.006) [A]; V=740.0(±1.5) $[A]^3$. Based on the data [*Epelbaum, et al.*, 1970] the correlation dependence of parameter "a" of synthetic sodalites on anion radius has been obtained: a, [A] = 8.6795 + 0.13187*(R) [A] ± 0.025 [A] (calculation for n=8; S_x = 0.29); where (R) – anion radius, [A]. This dependence is shown at fig. 2. Based on these data the size of anion group AlF_6^{3-} is estimated, it is 2.7± 0.2 [A] approximately. AlF_6^{3-} radius is comparable with the size of SO_4^{2-} (2.98 A) anion group. So, it is possible to wait for good miscibility in the fluorine- and sulphate-bearing sodalites sequence.



a b

Fig. 1. Dependence of fluorine content on the amount of silicon (a) and aluminum (b)

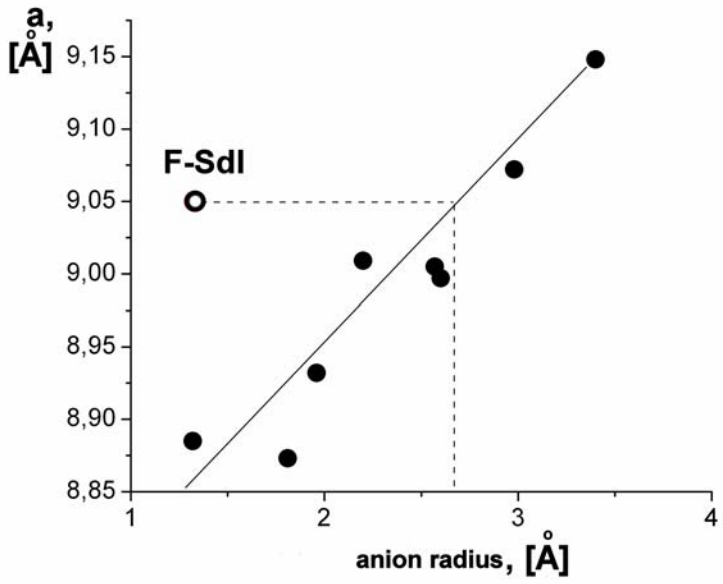


Fig. 2. Dependence of sodalite cell parameter on the anion radius

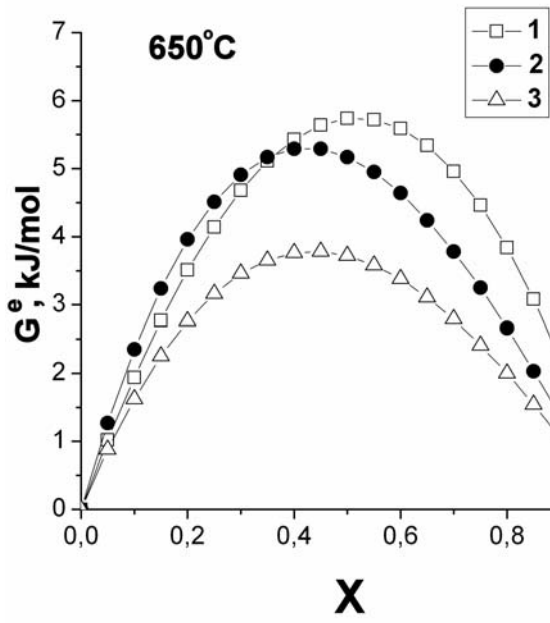


Fig. 3. The excess mixing energies of solid sol
(Cl, AlF_6)–Sdl; 2 – (Cl, SO_4)–Sdl; 3 – (Na, K

The isomorphism between chlorine- and fluorine-bearing sodalites has been studied at 650°C and 2 kbars. It is shown that the disintegration field of sodalites solid solution exists, the boundary lines are following: X_F^{Sod}=0.09 and X_F^{Sod}=0.945. Based on the immiscible borderlines the parameters of Margules model for solid solutions of chlorine- and fluorine-bearing sodalites are estimated, they are W1=24.7(±4.2) and W2=21.3(±3.8) kJ/mol. By these parameters the excess mixing energies of chlorine- and fluorine-bearing sodalites solid solutions have been calculated (fig. 3). The excess mixing energies of (Na, K)-Fsp are presented at fig. 3 too.

Table 1. Mineral paragenesis of pegmatites of Lovozerskii massif containing F-sodalite

Paragenesis: (Cl,S,F)-*Sdl* + Williomite + K- feldspar + Amf1 + Amf2 + Ussingite + Natrolite + Lomonosovite + Eudialite + Stenstrupine + (Na,Ce)-Apatite	
Mineral	Formula
(Cl,S,F)-sodalite	$Na_{8.28}Al_{6.03}Si_{5.96}O_{23.57}(Cl)_{1.41}(SO_4)_{0.61}(F)_{0.48}$
Williomite	NaF
K-feldspar	$KAlSi_3O_8$
Amf(1)	$(Na_{2.35}K_{0.75})_{3.10}(Mg_{0.70}Fe^{2+}_{1.92}Mn_{0.70})_{3.32}(Al_{0.20}Fe^{3+}_{0.78})_{0.98}[Si_{8.00}Ti_{0.33}]\ O_{22}(OH)_2$
Amf(2)	$Na_{3.80}(Mg_{0.16}Mn_{0.08}Fe^{2+}_{1.63})_{1.87}Ti_{0.34}(Al_{0.23}Fe^{3+}_{1.47})_{1.70}Si_8O_{22}(OH)_2$
Ussingite	$Na_{1.97}Al_{0.99}Si_{3.04}O_8[OH]_{1.10}$
Natrolite	$Na_{1.95}Al_{2.00}Si_{3.05}O_{10.07}*2H_2O$
Lomonosovite	$Na_{8.47}(Mg_{0.11}Fe_{0.25}Mn_{0.27})_{0.63}Si_{3.89}P_{1.96}Ti_{2.19}Nb_{0.84}O_{24}$
Eudialite	$Na_{6.56}Ca_{0.73}K_{0.14}Mn_{0.53}Fe_{0.2}Zr_{0.95}Ti_{0.19}Si_{9.05}Nb_{0.08}O_{24}[SO_4]_{0.11}Cl_{0.15}(OH)_{2.4}$
Stenstrupine	$Na_{6.49}Mn_{0.48}Ca_{1.14}(La_{0.15}Ce_{0.50}Nd_{0.23})_{0.88}Th_{0.05}Si_{5.47}P_{2.70}O_{24}$
(Na,Ce)-Apatite	$Na_{8.15}(Ca_{0.31}Sr_{0.46}Ba_{0.05})_{0.82}(La_{0.46}Ce_{1.31}Pr_{0.15}Nd_{0.73})_{2.65}P_{6.45}O_{24}(OH)_2$

The paragenetic associations of minerals from Lovozerskii alkaline massif containing sodalite and williomite have been studied. The minerals from this paragenesis are presented in the table 1. It has been shown the fluorine intromission to the sodalite represented by the solid solution of nozeane and chlorine-sodalite. Mole fraction of fluorine-sodalite is 0.15 approximately.

References

Epelbaum, M. B., Yu. E. Gorbaty, V. F. Gusynin, I P. Ivanov (1970), The study of sodium sodalites with different frame anions, *Sketch-book of physics-chemistry petrolog,.v. II*, pp. 269–280.

Yakubovich, O. V., A. R. Kotelnikov, T. I. Tschekina, E. N. Gramenitskiy, E. S. Zubkov (2011), New agent in structural type of sodalite with $[AlF_6]^{3-}$ anions in micropores of tetrahedral frame, *Crystallography. v. 56*, N 2, pp. 217–224.