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Synthesis of Sulfosodalite, an Ultramarine-Relating Phase

Goro YAMAGUCHI and Yasushi KUBO[*1]

Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Tokyo

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A sulfur-containing sodalite-type aluminosilicate, $6NaAlSiO_4 \cdot Na_2S$ (designated sulfosodalite in this paper), was synthesized in the system $NaAlSiO_4$-Na_2S at temperatures 850 to 950°C in an H_2 or N_2 atmosphere. All of the sulfur in this substance was contained as sulfide ion S^{2-}, and its equilibrium content in a unit cell increases with temperature from 1.5 S at 850°C to 1.8 S at 950°C. This substance was only pale colored, yellowish or pinkish, but the partial substitution of Si for Al produced a deep vermilion red color.

By heating the system $NaAlSiO_4$-Na_2S in an H_2 or N_2 atmosphere at temperatures 850 to 950°C, a sulfur-containing aluminosilicate phase of sodalite-type was obtained. This phase was found to contain sulfur only in the form of monosulfidic sulfur ion S^{2-}, and thus gave an X-ray diffraction pattern closely resembling that of sodalite, $6NaAlSiO_4 \cdot 2NaCl$. Differing from ultramarine, which contains disulfidic sulfur ion,[1] this substance is only very lightly colored, yellowish or pinkish.

Kirk has already synthesized a sodalite solid-solution of the composition $6NaAlSiO_4 \cdot xNaCl \cdot yNa_2S$ in his study of the luminescence of sodalite.[2,3] The phase synthesized in the present study corresponds to the Na_2S-end member, and thus the name of sulfosodalite may be given. The essential difference between this substance and sodalite, however, is that its composition is not constant as with sodalite but varies considerably with synthetic conditions; also this phase contains usually more than eight Na ions. The synthetic conditions and the composition will be reported in this papaer.

Experimental

Starting Materials. The starting material $NaAlSiO_4$ was prepared by heating a mixture of kaolinite and Na_2CO_3 at about 700°C. The actual composition of this material was $Na_{0.98}Al_{0.98}Si_{1.02}O_4$ because of the composition of the kaolinite employed as raw material. To examine the effect of substitution of Si for Al, SiO_2 (Merck's silica gel for chromatographic use, ignition loss 3.68%) was added to the kaolinite - Na_2CO_3 mixture and the same heat-treatment made. The starting materials $Na_uAl_uSi_{2-u}O_4$ (u=0.90, 0.80 and 0.66) were thus prepared.

The starting mixtures $NaAlSiO_4+aNa_2S$ (a=0.50, 0.75, 1.00, 1.25 and 1.50) and $Na_uAl_uSi_{2-u}O_4+Na_2S$ were made with sufficient caution against the oxidation of Na_2S.

Details on these raw materials and on the mixing method are described in another paper.[1]

Apparatus. A silica glass tube set perpendicularly in a cylindrical electric furnace was used as the heating apparatus. H_2 or N_2 gas, which was purified by passage through active copper and water absorbent, was passed through this pipe. The starting mixture, which was put in a silica crucible, was hung from a molybdenum wire into the heating zone kept at the predetermined temperatures between 850 and 950°C. After heating for 1 hr, the crucible was removed rapidly to a cool zone for quenching.

Method of Analysis. *a) Treatment of the Synthesized Specimen.* The synthesized specimen was fully washed with water until no alkali was detected by phenolphthalein indicator, and was dried at 110°C. Then carbon disulfide extraction was carried out to completely remove any free sulfur which condensed on the specimen.

b) Chemical Analysis. The specimen was decomposed by dilute sulfuric acid and the analyses of SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO and alkalis were carried out following the usual procedure of silicate analysis. Fe_2O_3 was determined colorimetrically using sulfosalicylic acid. CaO+MgO, the total content of which was about 1%, was removed on the way and was not determined. The alkalis were determined as residual sulfates where the ratio of K_2SO_4/Na_2SO_4 was determined to be less than 0.005 by flame photometry. The alkali content can also be determined indirectly by the charge balance to the ionic sulfur content. Since the former residual sulfate method always gave a lower result, the latter more reliable method was actually adopted.

Total sulfur content was determined through $BaSO_4$ precipitation. In this case, the specimen was decomposed by a Br_2+HCl solution.

For the analysis of ionic sulfur, the specimen was suspended in a solution of $AgNO_3$ and decomposed with dilute sulfuric acid. To decompose the specimen completely, warming in a hot-water bath was necessary. After the Ag_2S precipitate formed was filtered off, the residual $AgNO_3$ was back-titrated with a KCNS solution.

c) Determination of the Sodalite-type Phase Content. Usually the complete formation of the sodalite-type phase

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[*1] Present address: Institute of Industrial Science, The University of Tokyo, Roppongi, Tokyo.

1) G. Yamaguchi and Y. Kubo, This Bulletin, **41**, 2645 (1968).

2) R. D. Kirk, *J. Electrochem. Soc.*, **101**, 461 (1954).

3) R. D. Kirk, *Am. Mineral.*, **40**, 22 (1955).

TABLE 1. DETERMINATION OF THE COMPOSITION OF SODALITE-TYPE PHASE

Sample	Phase content, %	SiO_2	Al_2O_3	Fe_2O_3	Ionic S	Non-ionic S	Na
		37.6	30.4	0.4	4.88	0.26	19.5
H-F	Neph. 6	2.6	2.1		—	—	1.0
	Sod. 94	35.0	28.7		4.88	0.26	18.5

was not achieved and unreacted nepheline phase coexisted in the specimen. Quantitative analyses of both phases were made by powder X-ray diffraction. As internal standard, 1 part (by weight) of MgO powder was added to 2 parts of the specimen. The diffraction intensity of the peak (20·2) of nepheline at $2\theta=29°38'$ ($CuK\alpha$), I_N, that of the peak (211) of the sodalite-type phase at $2\theta=$about 24°, I_S, and that of the peak (220) of magnesia at $2\theta=62°18.5'$, I_{MgO}, was measured using a diffractometer. A calibration curve between the nepheline content in the mixture and the value I_N/I_{MgO} was made. Another calibration curve between the sodalite-type phase content and the value I_S/I_{MgO} was also made. Strictly speaking, however, the diffraction intensity of the sodalite-type phase may vary in every specimen differeing in composition. Therefore, the calibration was made using the former calibration curve for the nepheline content as far as possible. Thus the sodalite-type phase content was determined from 100(%)−Nepheline(%). In the specimens where SiO_2 was added, an amorphous phase coexisted in addition to nepheline. In this case, calibration had to be made based on the latter calibration curve.

d) Determination of the Composition of Sodalite-type Phase. Components present due to unreacted nepheline were calculated using the nepheline content determined from X-ray diffraction analysis. Then, these values were subtracted from those obtained from the total chemical analysis and the rest was considered to be in the sodalite-type phase. Impurities such as Fe_2O_3, CaO and MgO were neglected.

e) An Example. An Example of this analytical procedure is given for one of the specimens. The results obtained from the total chemical analysis are given in the first line of Table 1. From an X-ray diffraction analysis, the coexisting nepheline and sodalite-type phase components of this specimen were determined as 6% and 94%, respectively. The components due to coexisting nepheline, as given in the second line, were subtracted from values obtained from the total chemical analysis given in the first line, and components in the sodalite-type phase were obtained as given in the third line. The chemical formula for a unit cell of the sodalite-type phase is calculated from this result as $Na_{8.43}Al_{5.89}Si_{6.11}O_{24}\cdot 1.60\ S^{2-}\cdot 0.08\ S$ (the Na ion content required from charge balance with the S^{2-} ion content is 9.08.).

Results and Discussion

Product Composition. The molar compositions which were determined, based on an analysis of total components are shown in Table 2 for several specimens. The values for a unit cell of sodalite-type structure are given. The analytical data for all specimens which were synthesized under conditions given in columns 2 to 4 of Table 3, are shown in columns 5 to 8 of the same table; Al number in the product, sodalite-type phase content and total and ionic sulfur contents are given.

Now, the average valences of sulfur ions (defined as 2×Ionic S/Total S) were calculated as given in column 9 of Table 3, and were also plotted in Fig. 1.

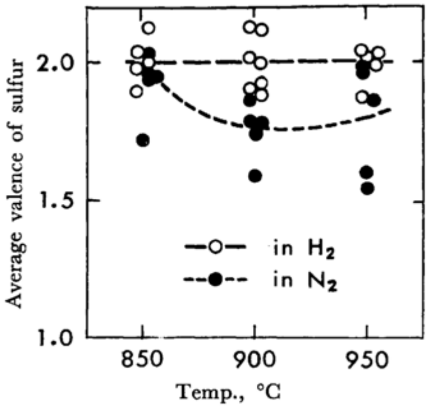

Fig. 1. Average valence of sulfur for specimens synthesized in H_2 and N_2 atmospheres.

As seen in Fig. 1, the average valence of sulfur ions for specimens synthesized in an H_2 atmosphere is equal to 2 within an error of ±5%, while that for specimens synthesized in an N_2 atmosphere ranges from 1.8 to 2. Thus, the former specimens which completely form sulfide may be expressed by the formula $6NaAlSiO_4\cdot xNa_2S$, while the latter, containing some polysulfidic ions, may be expressed by the formula $6NaAlSiO_4\cdot xNa_2S\cdot yS$. When variation in the Si/Al ratio or Al number is taken into consideration, the general formula is given by $6Na_uAl_uSi_{2-u}O_4\cdot xNa_2S\cdot yS$ for a unit cell of a sodalite-type structure.

Based on the general formula, the numbers of ionic sulfurs and non-ionic sulfurs per unit cell (x and y, respectively) were calculated using analytical data on the Al number in the product, u_P, and the total and ionic sulfur contents given in Table 3. The results are shown in columns 10 and 11 of the same table, respectively. When comparison is made between the values (x and y) of Tables 2 and 3, those of Table 2, which were calculated based on an analysis of total components, are in good agreement with those of Table 3, which were calculated based on only the total and ionic sulfur contents according to the general formula. This justifies the general formula, and

TABLE 2. MOLAR COMPOSITION OF SULFOSODALITE FOR A UNIT CELL

Sample	SiO_2	$AlO_{1.5}$	$NaO_{1.5}$	Ionic S	Non-ionic S	Na^+	Total Na
H-C	6.23	5.77	5.77	1.47	0.01	2.94	8.71
H-F	6.11	5.89	5.89	1.60	0.08	3.20	9.08
H-M	6.21	5.79	5.79	1.49	0	2.97	8.76
H-N	6.52	5.48	5.48	1.32	0	2.64	8.12
H-O	7.5	4.5	4.5	0.8	0.15	1.7	6.2
H-T	5.96	6.04	6.04	1.65	0.08	3.30	9.34
N-E	6.1	5.9	5.9	1.8	0.2	3.5	9.4
N-I	6.1	5.9	5.9	1.8	0.1	3.6	9.5
N-J	6.2	5.8	5.8	1.7	0.3	3.4	9.2
N-M	6.1	5.9	5.9	1.7	0.1	3.4	9.3
N-N	6.5	5.5	5.5	1.3	0.3	3.7	9.2
N-O	7.4	4.6	4.6	0.9	0.2	1.9	6.5

the values x and y can be used as characteristic values of the specimen.

Relationships between Synthetic Conditions and Product Composition. Figure 2 shows the variation in the number of ionic sulfurs (or total sulfurs) per unit cell (x), with the amount of Na_2S mixed in the reaction system (a) for specimens synthesized in an H_2 atmosphere at 900°C. The value x increases with increase in a for a less than 1.0, and reaches a constant value for a greater than 1.0. This indicates that the system has not reached equilibrium in a reaction time of 1 hr, until the amount of Na_2S mixed in the reaction system, a, was increased to greater than 1.0 which corresponds to about three times the Na_2S content of the product phase. A similar tendency was observed in specimens synthesized at other temperatures.

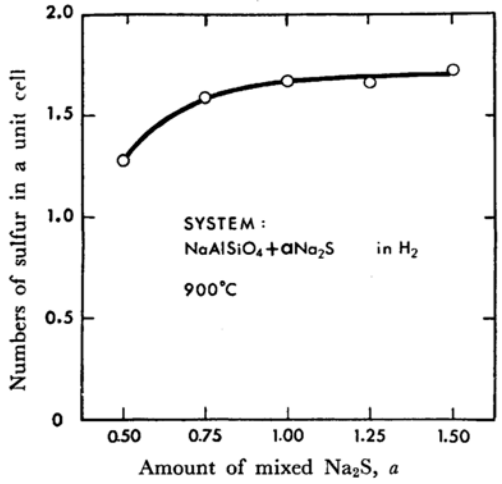

Fig. 2. Variation of sulfur content expressed by numbers in a unit cell with the amount of Na_2S mixed in the reaction system.

Figure 3 shows the change in the value x for a equal to 1.0 with reaction temperature. The value x increases with temperature; the higher the temperature, the more sulfur ions are pressed into the sodalite-type structure. This means that the increase in chemical potential of the Na_2S component with temperature is larger in the Na_2S phase than in the sodalite-type phase.

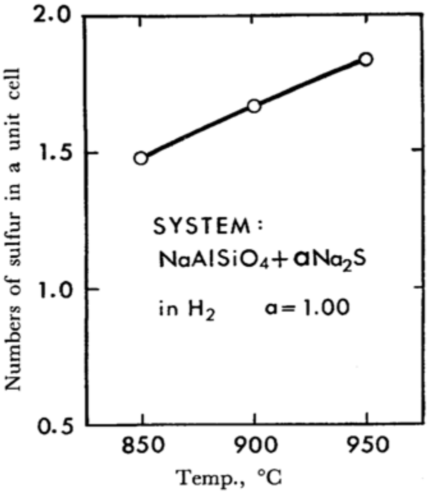

Fig. 3. Variation of sulfur content expressed by numbers in a unit cell with reaction temperature.

For specimens synthesized in an N_2 atmosphere, the composition is similar to that of specimens synthesized in an H_2 atmosphere, but the data do not show a constant tendency. Some oxidation of sulfur ion has occurred, giving rise to a small amount of non-ionic sulfur. This may be due to an error caused by residual O_2 in the N_2 gas stream.

Effect of Si Substitution for Al. It must be noted that in this experiment only a small portion of the added SiO_2 has been taken up in the product phase. As shown in columns 4 and 5 of Table 3, the Al number in the reaction system (u_R) and that in the product (u_P) differ considerably; 0.90 *vs.* 0.97, 0.80 *vs.* 0.92 and 0.66 *vs.* 0.76, respectively. Thus, the substitution of Si for Al has taken place only to a small extent compared with the amount of SiO_2 added to the reaction system. This may

TABLE 3. SYNTHETIC CONDITIONS AND ANALYTICAL DATA OF SULFOSODALITE SPECIMENS SYNTHESIZED FROM $Na_uAl_uSi_{2-u}O_4+aNa_2S$ SYSTEMS

1) In H_2 atmosphere

$6Na_uAl_uSi_{2-u}O_4\cdot xNa_2S\cdot yS$

(1) Sample	(2) Temp. °C	(3) a	(4) u_R	(5) u_P	(6) S. C.	(7) Total S	(8) Ionic S	(9) A. V.	(10) Na_2S x	(11) S y	(12) Total S, $x+y$
H-A	850	0.50	0.98	0.98	66	3.6	3.4	1.9	1.0	0	1.0
H-B	850	0.75	0.98	0.98	70	4.2	4.2	2.0	1.2	0	1.2
H-C	850	1.00	0.98	0.98	96	4.9	4.9	2.0	1.5	0	1.5
H-D	900	0.50	0.98	0.98	68	4.3	4.6	2.1	1.3	0	1.3
H-E	900	0.75	0.98	0.98	88	5.2	5.3	2.0	1.6	0	1.6
H-F	900	1.00	0.98	0.98	94	5.5	5.2	1.9	1.7	0	1.7
H-S	900	1.25	0.98	0.98	81	5.5	5.2	1.9	1.7	0	1.7
H-T	900	1.50	0.98	0.98	98	5.6	5.4	1.9	1.7	0	1.7
H-G	950	0.50	0.98	0.98	80	4.9	4.9	2.0	1.5	0	1.5
H-H	950	0.75	0.98	0.98	83	4.9	5.0	2.0	1.5	0	1.5
H-I	950	1.00	0.98	0.98	88	5.9	5.6	1.9	1.8	0	1.8
H-J	850	1.00	0.90	0.97	93	4.9	4.9	2.0	1.5	0	1.5
H-K	850	1.00	0.80	0.92	81	4.5	4.8	2.2	1.3	0	1.3
H-L	850	1.00	0.66	0.76	96	3.4	3.0	1.8	0.95	0	0.95
H-M	900	1.00	0.90	0.97	91	5.0	5.0	2.0	1.5	0	1.5
H-N	900	1.00	0.80	0.92	92	4.4	4.7	2.1	1.3	0	1.3
H-O	900	1.00	0.66	0.76	82	3.5	2.9	1.7	0.97	0	0.97
H-P	950	1.00	0.90	0.97	68	5.9	6.0	2.0	1.8	0	1.8
H-Q	950	1.00	0.80	0.92	78	5.5	5.0	1.8	1.7	0	1.7
H-R	950	1.00	0.66	0.76	41	4.7	4.6	2.0	1.4	0	1.4

2) In N_2 atmosphere

$6Na_uAl_uSi_{2-u}O_4\cdot xNa_2S\cdot yS$

(1) Sample	(2) Temp. °C	(3) a	(4) u_R	(5) u_P	(6) S. C.	(7) Total S	(8) Ionic S	(9) A. V.	(10) Na_2S x	(11) S y	(12) Total S $x+y$
N-A	850	0.50	0.98	0.98	66	4.4	4.3	2.0	1.3	0.0	1.3
N-B	850	0.75	0.98	0.98	62	5.2	5.0	1.9	1.5	0.1	1.6
N-C	850	1.00	0.98	0.98	55	4.3	4.2	2.0	1.3	0.0	1.3
N-D	900	0.50	0.98	0.98	68	4.6	4.1	1.8	1.2	0.1	1.4
N-E	900	0.75	0.98	0.98	81	6.3	5.6	1.8	1.7	0.2	1.9
N-F	900	1.00	0.98	0.98	83	5.4	5.0	1.9	1.5	0.1	1.6
N-G	950	0.50	0.98	0.98	70	4.1	4.0	2.0	1.2	0.0	1.2
N-H	950	0.75	0.98	0.98	81	6.0	5.9	2.0	1.8	0.0	1.9
N-I	950	1.00	0.98	0.98	84	6.2	5.8	1.9	1.8	0.1	1.9
N-J	850	1.00	0.90	0.97	86	6.5	5.6	1.7	1.7	0.3	2.0
N-K	850	1.00	0.80	0.92	86	5.5	5.6	2.0	1.7	0	1.7
N-L	850	1.00	0.66	0.76	58	4.8	4.4	1.8	1.3	0.1	1.4
N-M	900	1.00	0.90	0.97	84	6.2	5.8	1.9	1.8	0.1	1.9
N-N	900	1.00	0.80	0.92	85	5.7	4.5	1.6	1.4	0.3	1.7
N-O	900	1.00	0.66	0.76	55	4.2	3.6	1.7	1.0	0.2	1.2
N-P	950	1.00	0.90	0.97	100	6.0	4.6	1.5	1.4	0.4	1.8
N-Q	950	1.00	0.80	0.92	92	5.3	4.2	1.6	1.2	0.3	1.5
N-R	950	1.00	5.66	0.76	58	3.9	3.0	1.5	0.8	0.3	1.1

(3) a: Amount of Na_2S mixed in the reaction system.
(4) u_R: Al number in the reaction system.
(5) u_P: Al number in the product.
(6) S. C.: Sulfosodalite content determined by X-ray diffraction.
(7) Total S and (8) Ionic S: Total and Ionic sulfur contents corrected by sulfosodalite content.
(9) A. V.: Average valence of sulfur defined by Ionic S/Total S.
(11) For the specimens in H_2 atmosphere y is taken as 0 according to Fig. 1.

be due to the method of preparation of the starting material, and more well-prepared starting material would result in a more complete substitution of Si for Al.

With increase in the Si substitution for Al, an amorphous phase as a coexisting phase in the specimen increased. This increases the error in the determination of the sodalite-type phase content by X-ray diffraction, since the detarmination is based on only the diffraction peak of the sodalite-type phase. Therefore, a detailed discussion can not be made only these data. As a general tendency, the sulfur content increased or did not change up to an Si fraction, Si/(Si+Al), of 0.52 (u_P of 0.97), and decreased with further increase in the Si fraction. However, it is not clear whether equilibrium had been reached in this system.

It is a noteworthy fact that, as the Si fraction increases, specimens synthesized in both H_2 and N_2 atmospheres turned vermilion red. This color faded gradually upon washing with water for a long time.

Crystal Structure. As regards the ionic valence of the anion which is contained in the sodalite-type aluminosilicic framework, the present substance is similar to noselite which contains SO_4^{2-} ion. Since the number of anions per unit cell of noselite ($Na_8Al_6Si_6O_{24}SO_4$) is half that of sodalite ($Na_8Al_6Si_6O_{24}Cl_2$), the crystal structures are not completely homo-structural.[4] In the X-ray diffraction pattern of noselite, diffractions with $h+k+l=$odd appeare, while in that of sodalite the diffractions vanish due to the extinction rule.

The present substance usually contains more than one but less than two S^{2-} ions per unit cell, and the diffraction pattern is identical with that of sodalite. It is noteworthy that the same characteristics of the diffraction pattern are maintained even in specimens which contain almost one or less than one S^{2-} ion per unit cell, though a noselite-like structure is expected in this case. This means that the anion vacancy distributes at random on the anion sites in the structure. The ionic radius of S^{2-} ion being smaller than that of SO_4^{2-} may account for the difference in the structure. Based on the characteristics of its diffraction pattern, the present substance may be named sulfosodalite.

It is a well-known fact that ultramarine abounds in varieties which have various sulfur contents and various colors. Sulfosodalite may perhaps be a phase corresponding to an end-member of a variety of ultramarine.

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[4] Y. Kubo and G. Yamaguchi, *J. Mineral. Soc. Japan*, **8**, 235 (1967).