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Synthetic Hydrogen-containing Ultramarine Phases

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Hydrogen was analyzed on synthetic sulfur-containing sodalite-type sodium aluminosilicates. Specimens synthesized from the $NaAlSiO_4$-Na_2S system in a H_2 or N_2 atomsphere or in a N_2-S_2 atmosphere contained hydrogens which were introduced by ion-exchange during water-washing. Specimens synthesized from the same system in H_2S-containing atmospheres also contained hydrogens introduced from the synthetic atmosphere. The latter specimens had the formula: $Na_8Al_6Si_6O_{24}S\cdot xH_2S\cdot yS$, which was characterized by a constant number of sodium ions (eight per unit cell), whereas the former contained variable numbers of sodium ions according to the duration of water-washing. A difference in correlation between the sulfur content and the lattice constant was observed between these two series of specimens, indicating different manners of existence of the hydrogen.

In previous papers,[1,2] two sorts of sulfur-containing sodalite-type sodium aluminosilicates, designated sulfosodalite and leuco-ultramarine, were reported on. The former was synthesized by heating a $NaAlSiO_4$-Na_2S mixture at temperatures of from 850 to 950°C in a H_2 or N_2 atmosphere with no sulfur vapor pressure, while the latter was synthesized in a N_2 atmosphere with a sulfur partial pressure of from 0.75 to 1.0 atm. Almost all of the sulfur was contained in a sodalite-type aluminosilicic framework as the monosulfidic ion S^{2-} in the former compound, and in the latter, as the disulfidic ion S_2^{2-}. The nomenclature was based on this fact. According to the results of these papers, the formulae for these compounds were $6NaAlSiO_4\cdot xNa_2S$ and $6NaAlSiO_4\cdot xNa_2S_2$ respectively, and solid solutions were formed continuously between these phases.

The present paper has two objects. First, a fact overlooked in the previous papers[1,2] is reported —that the specimens previously analysed contained some hydrogen. Second, the syntheses of new sorts of sulfur-containing sodalite-type sodium aluminosilicates which also contain hydrogens but which are different from the compounds mentioned above will be reported. These new compounds will be reported. These new compounds will be synthesized by heating the $NaAlSiO_4$-Na_2S system in atmospheres containing H_2S. The composition and lattice constant will be determined, and a comparison made between these two series of synthetic hydrogen containing ultramarine phases.

Experimental

Specimens. The sulfosodalite and leuco-ultramarine specimens to be examined here are those which have been prepared in the previous investigations.[1,2] They were synthesized from the starting mixture of

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[1] G. Yamaguchi and Y. Kubo, This Bulletin, **41**, 2641 (1968).

[2] G. Yamaguchi and Y. Kubo, *ibid.*, **41**, 2645 (1968).

the $NaAlSiO_4$-Na_2S system. The details of the method of preparation were given in those papers. The former specimens were obtained by heating the mixture in a H_2 or N_2 atomosphere at temperatures of from 850 to 950°C. The latter specimens were prepared by heating the mixture in a N_2-S_2 atmosphere at various sulfur partial pressures, from 0.25 to 1.00 atm. To indicate these specimens, the system of specimen symbols used in the previous papers will be employed in this paper.

It was found that, when the starting mixture was heated in a H_2-H_2S or H_2S-S_2 atmosphere, sodalite-type phases were also obtained. Specimens of these new phases were prepared by almost the same method as that used for the above-described specimens, except that the atmosphere system was changed. Details of these specimens will be given in a subsequent paper, which will also treat the relationship between the synthetic conditions and the compositions of these phases.

Analyses. After they had been synthesized, all the specimens were immersed in water as soon as they had cooled and were taken out of the furnace of the synthetic apparatus. They were fully washed with water until no alkali could be detected by a phenolphthalein indicator, and then dried at 110°C. Subsequently, a carbon disulfide extraction was made in order to remove completely the free sulfur condensed on the specimen.

The procedure for the determination of the chemical composition of the sodalite-type phase involves two processes; chemical analysis for every component and the determination of the yield of the sodalite-type phase by the X-ray diffraction method. The details of these processes were given in a previous paper.1)

The amount of hydrogen present in the specimen was determined by measuring the amount of water which was liberated when the specimen was heated in an O_2 gas stream at about 800°C. For this purpose, an element-analysis apparatus, Shimadzu UM-3, was employed. About an 80-mg portion of the specimen was placed in the combusting system of the apparatus. Prior to oxidation, the specimen was heated at about 170°C in a N_2 gas stream for 1 hr in order to fully remove the water absorbed on the surface of the specimen. The gas stream was then changed to that of O_2 gas, and the temperature was raised to about 800°C. Any SO_3 gas which may have been produced by this treatment was trapped by Ag meshes, and the water was absorbed with magnesium perchlorate. The results obtained were found to be sufficiently reproducible.

X-Ray Diffraction Measurements. The lattice constant was determined by a diffractometer measurement using Cu-$K\alpha$ radiation. MgO powder was added as an internal standard. The diffraction (444), (710, 550, 543), or (721, 633, 552) of the sodalite-type phase, at 2θ values of about 73°, 74° and 77.5° respectively, was measured at the scanning speed of 0.25°/min; calibration was made using the diffraction, (311) or (222), of MgO, at 2θ values of 74°41.52′ and 78°38.52′ respectively on the same diffractometer trace.

Results and Discussion

Specimens Synthesized in a H_2 or N_2 Atmosphere. The results of the analyses of several typical specimens are given in Table 1. The content of every component is represented by the number per unit cell. Lattice constants are also given in the last column of the same table.

Although there must not have been any water in the reaction system, $NaAlSiO_4$-Na_2S, in either the H_2 or N_2 atmosphere, the sulfosodalite specimens liberated considerable amounts of water (about 1 to 1.3%) when heated in O_2 gas. In a previous paper,1) it was remarked that, in these specimens, the sodium content determined from the residual Na_2SO_4 was always less than that expected from the charge balance with anions. Thus, in that paper, the content given by the latter method, *i. e.*, that determined indirectly from the ionic charge balance, was adopted as more reliable. The liberation of water as revealed in the present experiment strongly indicates that hydrogen is another constituent of the cations in these specimens. It may be seen that, by taking the hydrogen content into account, the balance of ionic charges between the cations, $Na^+ + H^+$, and the S^{2-} anion is greatly improved. (The sign of the "Charge Balance," + or −, in Table 1 indicates an overbalance of cations or anions respectively). Thus, the inconsistency observed in the sodium analysis can be attributed to the presence of hydrogen. Here the values given as the Na^+ content and the total Na content in Table 2 of a previous paper1) are cor-

Table 1. Molar compositions of sodalite-type specimens synthesized in H_2, N_2 and (N_2, S_2) atmospheres

Sample	Yield (%)	SiO_2	$AlO_{1.5}$	$NaO_{1.5}$	Ionic S	Non-ionic S	Na^+	H^+	Charge balance	Total Na	a (Å)
H-C	95.5	6.23	5.77	5.77	1.47	0.01	1.56	1.42	+0.04	7.33	8.948
H-F	94	6.11	5.89	5.89	1.60	0.08	2.54	0.85	+0.20	8.43	8.959
H-M	91	6.21	5.79	5.79	1.49	0	2.19	1.29	+0.53	7.99	8.951
H-T	98	5.96	6.04	6.04	1.65	0.08	2.50	1.36	+0.56	8.54	8.906
N-E	81	6.11	5.89	5.89	1.76	0.22	2.70	1.61	+0.79	8.59	8.976
N-I	84	6.11	5.89	5.89	1.80	0.14	2.88	1.21	+0.48	8.78	8.972
U-H	100	6.12	5.88	5.88	1.50	0.61	2.11	0.87	−0.02	7.99	9.058
U-O	97	6.19	5.81	5.81	1.51	1.58	2.34	0.49	−0.19	8.15	9.064

Table 2. Molar compositions of sodalite-type specimens synthesized in (H_2S, H_2) and (H_2S, S_2) atmospheres

Sample	Temp. (°C)	Mixing Ratio of Gases			Yield (%)	SiO_2	$AlO_{1.5}$	$NaO_{1.5}$	Ionic S	Non-ionic S	Na^+	H^+	Charge balance	Total Na	a (Å)
		H_2S	H_2	S_2											
HS1-A3	855	0.33	0.66		96.5	6.14	5.86	5.86	1.80	0.09	2.11	1.87	+0.37	7.97	8.940
HS2-A3	860	0.66	0.33		94	6.16	5.84	5.84	1.88	0.22	2.22	1.98	+0.44	8.06	8.950
HS3-A3	850	1.00	0		90	6.19	5.81	5.81	1.84	0.27	2.21	2.06	+0.59	8.01	8.960
HS1.5-B3	900	0.50	0.50		100	6.08	5.92	5.92	2.03	0.15	2.09	2.00	+0.04	8.01	8.939
HS3-B3	935	1.00	0		97	6.22	5.78	5.78	2.04	0.56	2.12	2.01	+0.04	7.90	8.964
SH4-A3	863	0.75		0.25	91	6.19	5.81	5.81	1.86	1.14	2.13	1.57	−0.03	7.94	8.998
SH5-A2	860	0.50		0.50	71	6.25	5.75	5.75	1.66	1.45	2.46	1.23	+0.37	8.21	9.001
SH6-A3	857	0.25		0.75	73	6.20	5.80	5.80	1.67	1.28	2.35	1.41	+0.42	8.15	8.996

rected to those given in Table 1 of the present paper.

The hydrogen seems to have originated from the process of washing with water after synthesis. Just after having been synthesized and cooled, the sulfosodalite phase may have contained more than eight Na^+ ions per unit cell. It is rather natural that the excess sodium ions should be easily ion-exchanged in water. This may have occurred to various extents according to the duration of water-washing; the sodium content, which apparently varies at random in Table 1, seems to indicate such conditions. As can also be seen in the table, the content of the cations, $Na^+ + H^+$, usually over-balances that of the anion, S^{2-}. This may indicate that some hydration has also occurred in these specimens.

Specimens Synthesized in a (N_2, S_2) Atmosphere. The results of analyses for two other specimens, U-H (950°C, $P_{S_2}=0.50$ atm) and U-O (950°C, $P_{S_2}=1.00$ atm), are also given in Table 1. These specimens are characterized by a low hydrogen content, indicating that these specimens are more stable than sulfosodalite when washed in water.

Specimens Synthesized in a (H_2S, H_2) or (H_2S, S_2) Atmosphere. For specimens synthesized in atmospheres of various gas compositions, the analytical results are given in Table 2 in the same manner of representation as in Table 1. The second and the third columns of the table give, respectively, the synthetic temperature and the mixing ratio of two gases in atmosphere. The relation between the synthetic conditions and the composition is not treated here, but will be discussed in a separate paper. Lattice constants are also given in the last column.

The hydrogen content in these specimens is much larger than in the sulfosodalite and leuco-ultramarine of the preceding section. Furthermore, it must be pointed out that the number of Na^+ ions per unit cell is almost constant at eight, corresponding to the ideal number of cation sites per unit cell of the sodalite-type structure. The rather large deviations from eight in the SH5-A2 and SH6-A3 specimens may be attributed to an enlarged experimental error due to lower yields of the sodalite-type phase in these specimens. The same phenomenon as in sulfosodalite, that the content of cations, $Na^+ + H^+$, exceeds that of the anion, S^{2-}, is also observed in these specimens, indicating the possibility of some hydration in the water-washing process. However, if the secondary effect by water-washing is elim-

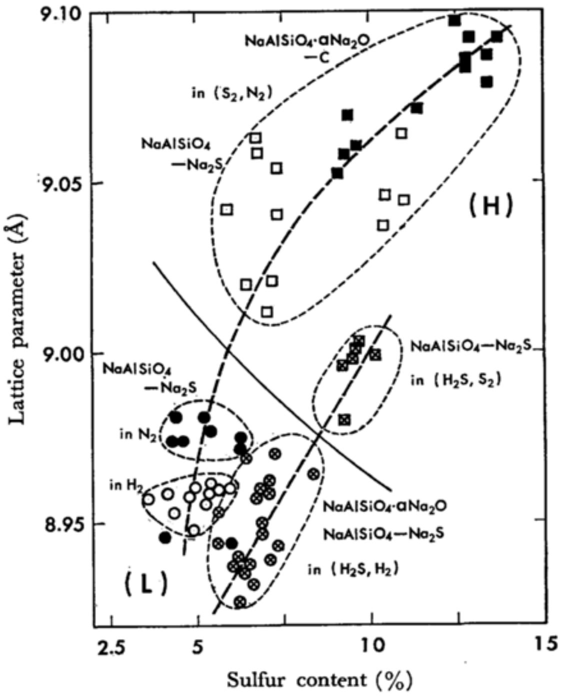

Fig. 1. Simultaneous plot of lattice parameter and sulfur content for sulfur-containing sodalite-type sodium aluminosilicates formed in every system. Two series of correlations are recognizable as shown by two broken line curves. Difference in chemical and physical characteristics are somewhat remarkable between two regions (L) and (H).

inated, the formula of the sodalite-type phase may be expressed by; $6NaAlSiO_4 \cdot Na_2S \cdot xH_2S \cdot yS$ or $Na_8Al_6Si_6O_{24}S \cdot xH_2S \cdot yS$. Thus, the composition of this compound can be represented by two characteristic values, x and y.

In the end case of $x=1$ and $y=0$, the formula becomes $Na_8Al_6Si_6O_{24}(SH)_2$, corresponding exactly to the homostructure of sodalite $Na_8Al_6Si_6O_{24}Cl_2$. In fact, in the specimen with a composition near this, the intensity distribution of the power X-ray diffraction was almost the same as that of sodalite. Thus, this compound may be named hydrosulfosodalite.

Relationship between the Total Sulfur Content and the Lattice Constant. On numbers of sulfur-containing sodalite-type phases, synthesized in various reaction systems and under various conditions by the method described above, the lattice constant (in A) was plotted against the total sulfur content (in percentages). The resulting diagram is given in Fig. 1. Since the lattice constant is not determined by the single factor of the total sulfur content, the plotted points scatter over a certain range even at the same total sulfur content. A separated region, however, proper to specimens of every atmosphere system is formed in the diagram. Furthermore, two series of correlations are clearly recognizable; they are shown by two broken lines. In these correlations, it is seen that specimens synthesized in atmospheres containing H_2S have a lattice constant smaller by about 0.8% at the same total sulfur content than that of specimens synthesized in atmospheres not containing H_2S.

Since the lattice constant was measured on specimens washed fully with water, the ion-exchange of excess Na^+ ions in the latter specimens with protons of water must have proceeded to a considerable extent; some of the specimens had almost the same Na^+ ion content as the former specimens, as can be seen in Table 1. Nevertheless, there is a difference in lattice constant between these two series of specimens. This indicates that there is some essential difference in the manner of existence between the hydrogen introduced into the former specimens from the synthetic atmospheres containing H_2S and that introduced by ion-exchange into the latter specimens, which were formed originally as alkali-rich phases in synthetic atmospheres not containing H_2S. Further details, however, have not yet been made clear.

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