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Ultramarines Synthesized under Controlled Sulfur Vapor Pressures

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Ultramarine was synthesized in the systems $NaAlSiO_4$-Na_2S and $NaAlSiO_4 \cdot aNa_2O$-Carbon under a sulfur vapor pressure controlled between 0 and 1 atm. The average valence of sulfur contained in ultramarine changed from 2.0 to 1.0 with increase in sulfur vapor pressure. This was due to the formation of a sulfide containing monosufidic sulfur ion at 0 atm and of a polysulfide containing disulfidic ion at elevated sulfur vapor pressures. Sigmoidal characteristics were observed in the relationships between the sulfur content of ultramarine and the sulfur vapor pressure.

It is well known that ultramarine, a blue sodium aluminosilicate containing sulfur, is a non-stoichiometric compound with its composition varying to a large extent in ionic and non-ionic sulfur contents and in sodium content, as well as in alumina-silica ratio. The various chemical and physical properties of ultramarine as revealed by previous investigators[1-3] are related to its non-stoichiometric characteristics. However, the most fundamental problem, by what factor and in what range the composition of ultramarine is varied, has not yet been elucidated. The greatest reason for this is that the composition of ultramarine is so complicated that the preparation of well-characterized specimens under well-controlled conditions is

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1) F. M. Jaeger, *Trans. Faraday Soc.*, **25**, 320 (1929).
2) J. Hoffmann, *Z. anorg. u. allgem. Chem.*, **183**, 37 (1929).
3) K. Leschewski, *Angew. Chem.*, **48**, 533 (1935).

Table 1. Chemical composition of zettlitz kaolinite (%)

Ig-loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Total
14.05	45.13	37.17	0.55	0.83	0.49	98.22

quite difficult. The circumstances may be common to almost all sulfide minerals, the study of which has progressed much less.

It may help to understand this situation to overlook the manufacturing process of ultramarine. In principle, the manufacture of ultramarine consists of heating a mixture of kaolin or aluminosilicic gel, sulfur or sodium sulfate and carbonaceous reducing agents to about 800°C in the absence of air. A yellow-green mass containing pale-colored ultramarine is thereby obtained, and successive reheating in air causes a deepening of the blue color; finally a dark blue product is obtained. Soluble sodium salts are then leached out, leaving blue ultramarine. It must be stressed here that, though a product excellent for practical use can be thus obtained, the meaning of these processes is not always understood. The system and the reactions are too complicated to permit a scientific approach.

In this study, an attempt was made to reduce the complicated synthetic conditions of ultramarine to its essential factors. Thus, synthesis was carried out by controlling the components necessary to produce ultramarine, $NaAlSiO_4$ and Na_2S, the sulfur vapor pressure and temperature. The relationships between the product composition and the synthetic conditions thus simplified, were investigated.

Experimental

Reaction Systems and Raw Materials. In order to strictly control reaction conditions in the production of ultramarine, as simple a reaction as possible is desired. The choice of reaction system, however, is conditioned by the reaction rate; too low a reaction rate makes synthesis practically impossible.

Through preliminary experiments, the following systems were found adoptable. In these systems, the ultramarine phase was formed in tolerable or high yields at the indicated temperatures in the reaction time of 1 hr.

(1) $NaAlSiO_4$ - Na_2S - S_2 (in an S_2+N_2 atmosphere) 950°C

(2) $NaAlSiO_4 \cdot aNa_2O$ ($a \geqq 0.5$) - C(carbon) - S_2 (in an S_2+N_2 atmosphere) 850°C

The oxides $NaAlSiO_4$ and $NaAlSiO_4 \cdot aNa_2O$ ($a=0.50$ and 0.75) were prepared by heating a mixture of Zettlitz kaolinite (chemical composition given in Table 1) and Na_2CO_3 reagent (E. P. grade) at about 700°C. The actual composition of these oxides were $Na_{0.98}Al_{0.98}Si_{1.02}O_4$ and so on, because of the composition of the original kaolinite. These oxides are composed mainly of high-carnegieite (L) phase,[4] and are favorable for use as starting material in respect to homogeneity and activity. As other raw materials, Na_2S reagent (E. P. grade), charcoal for carbon and sulfur reagent (G. R. grade) were used.

The mixtures $NaAlSiO_4+aNa_2S$($a=0.50$, 0.75 and 1.00) and $NaAlSiO_4 \cdot aNa_2O+aC$ ($a=0.50$ and 0.75) were prepared by mixing these raw materials with a motor-driven mortar. For the former mixture containing Na_2S, the mixing was done in liquid hexane to prevent Na_2S from being oxidized, and the mixture was heated at 550°C in an H_2 gas stream for 1 hr prior to use in order to reduce completely the partially oxidized Na_2S.

Apparatus. The vapor pressure of sulfur was controlled by making use of the temperature dependence of the vapor liquid equilibrium of sulfur. The main apparatus is shown in Fig. 1. This apparatus made of transparent silica glass, consists of two regions; the sulfur reservoir (lower part of the apparatus)and the reactor (upper part of the apparatus). Two electric furnaces were used to heat the two regions separately. The temperatures at the surface of the liquid sulfur and at the sample holder were detected with a three-forked Pt-PtRh

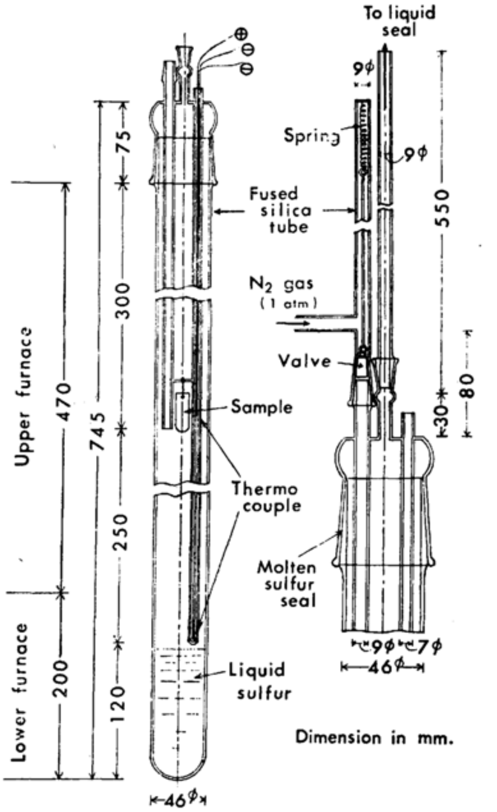

Fig. 1. Apparatus for synthesis under controlled sulfur vapor pressure.

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[4] Y. Kubo, G. Yamaguchi and K. Kasahara, *Mineral. J.*, **5**, 213 (1967).

thermocouple and were kept by a temperature controller at predetermined values between 380 and 440°C for the sulfur reservoir and between 850 and 950°C for the reactor.

At about 200mm above the ground glass joints, the temperature was held above the melting point of sulfur. Therefore, the condensation of sulfur took place in the perpendicular long thin tube connected to a gas outlet sealed with liquid paraffine. The condensed sulfur was melted away with a hand burner from time to time. The ground glass joints were sealed by molten sulfur.

The apparatus was also connected to an N_2 gas tank of a constant pressure of 1 atm through a valve, in order to remove the contained air before the experiment, as well as to prevent outside air from leaking in during a temporary fall in the inner gas pressure in such an instance as during the cooling process of the sample.

The temperature of the sulfur reservoir could be controlled by a derivative control within ± 3°C, which corresponds to a variation in the sulfur vapor pressure of ± 0.02 atm around 0.25 atm, and of ± 0.04 atm around 0.75 atm. For data on the equilibrium vapor pressure of sulfur, those given by West⁵⁾ were used. Except for visual observation at the head of the apparatus, the actual sulfur vapor pressure at the sample holder was not measured. Therefore, agreement between this pressure and that at the surface of the liquid sulfur was not verified. However, since the temperature above the sulfur reservoir was so distributed as to increase towards the sample holder, the stagnation of the sulfur vapor in the lower part of the apparatus could not have occurred.

Experimental Procedures. The starting mixture was put in the sample holder and heated at temperatures of 850 to 950°C for 1 hr. Rapid cooling was carried out by opening the upper electric furnace. The specimen thus obtained was fully washed with water until no alkali was detected by phenolphthalein indicator, and was then dried at 110°C. The free sulfur condensed on the specimen was removed completely by carbon disulfide extraction.

Determination of product composition was made on the specimen by chemical and X-ray diffraction analyses. The methods were described in detail in a previous paper.⁶⁾

Results and Discussion

Product Composition. Analytical data for the specimens which were synthesized under conditions given in columns 2 and 3 of Table 2, are given in columns 4 to 7 of the same table.

Figure 2 shows the variation in the average was valence of sulfur (in column 7) with sulfur vapor pressure, P_{S_2}. As can be seen in the figure, the average valence is 2.0 at no sulfur vapor pressure, and decreases toward 1.0 as the sulfur vapor pressure is increased. This indicates the change from sulfide to polysulfide, and the chemical composition can be expressed conventionally by the formula $6NaAlSiO_4 \cdot xNa_2S \cdot yS$ per unit cell. Based on this formula, the numbers of ionic sulfur, non-ionic sulfur and total sulfur per unit cell, x, y and $x+y$, respectively, were calculated in columns 8 to 10 of Table 2.

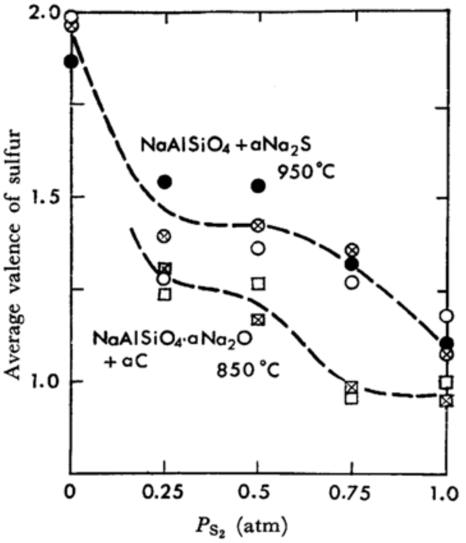

Fig. 2. Variation of average valence of sulfur with sulfur vapor pressure in atmosphere.

Relationships between Synthetic Condition and Product Composition. These values, x, y and $x+y$, change not only with sulfur vapor pressure, P_{S_2}, but also with the amount of Na_2S mixed in the reaction system, a. Changes with the former factor, P_{S_2}, are shown in Figs. 3 and 4; Fig. 3 for the system $NaAlSiO_4 + aNa_2S$ at 950°C and Fig. 4 for the system $NaAlSiO_4 \cdot aNa_2O + aC$ at

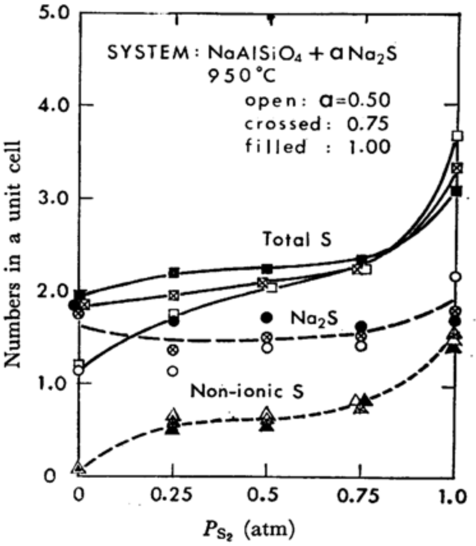

Fig. 3. Variation of numbers of total S, Na_2S, and non-ionic S in a unit cell with sulfur vapor pressure, for specimens synthesized in the system $NaAlSiO_4 + aNa_2S$ in (S_2, N_2) atmosphere at 950°C.

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5) J. R. West, *Ind. Eng. Chem.*, **42**, 713 (1950).

6) G. Yamaguchi and Y. Kudo, This Bulletin, **41**, 2641 (1968).

TABLE 2. SYNTHETIC CONDITIONS AND ANALYTICAL DATA OF ULTRAMARINE SPECIMENS SYNTHESIZED IN (S_2, N_2) ATMOSPHERE

1) From $Na_{0.98}Al_{0.98}Si_{1.02}O_4+aNa_2S$ systems at 950°C

$6Na_{0.98}Al_{0.98}Si_{1.02}O_4\ xNa_2S\cdot yS$									
(1) Sample	(2) P_{S_2} atm	(3) a	(4) U. C.	(5) Total S	(6) Ionic S	(7) A. V.	(8) Na_2S x	(9) S y	(10) Total S $x+y$
A*1	0	0.50	70	4.1	4.0	2.0	1.2	0.0	1.2
B*2	0	0.75	81	6.0	5.9	2.0	1.8	0.0	1.9
C*3	0	1.00	84	6.2	5.8	1.9	1.8	0.1	1.9
D	0.25	0.50	92	5.9	3.8	1.3	1.1	0.6	1.8
E	0.25	0.75	100	6.5	4.5	1.4	1.4	0.6	2.0
F	0.25	1.00	100	7.0	5.4	1.5	1.7	0.5	2.2
G	0.50	0.50	95	6.7	4.6	1.4	1.4	0.7	2.1
H	0.50	0.75	100	6.8	4.9	1.4	1.5	0.6	2.1
I	0.50	1.00	94	7.2	5.5	1.5	1.7	0.5	2.2
J	0.75	0.50	97	7.3	4.7	1.3	1.4	0.8	2.3
K	0.75	0.75	100	7.3	4.9	1.4	1.5	0.7	2.3
L	0.75	1.00	94	7.6	5.1	1.3	1.6	0.8	2.4
M	1.00	0.50	85	11.0	6.5	1.2	2.2	1.5	3.7
N	1.00	0.75	90	10.4	5.5	1.1	1.8	1.6	3.4
O	1.00	1.00	97	10.0	4.9	0.98	1.6	1.6	3.2

2) From $Na_{0.98}Al_{0.98}Si_{1.02}O_4\cdot aNa_2O+aC$ systems at 850°C

$6Na_{0.95}Al_{0.98}Si_{1.02}O_4\cdot xNa_2S\cdot yS$									
(1) Sample	(2) P_{S_2} atm	(3) a	(4) U. C.	(5) Total S	(6) Ionic S	(7) A. V.	(8) Na_2S x	(9) S y	(10) Total S $x+y$
P*4	0	0.50	66	4.4	4.3	2.0	1.3	0.0	1.3
Q*5	0	0.75	62	5.2	5.0	1.9	1.5	0.1	1.6
R	0.25	0.50	51	9.7	6.0	1.2	1.9	1.2	3.1
S	0.25	0.75	43	9.1	5.9	1.3	1.9	1.0	3.0
T	0.50	0.50	64	9.4	6.0	1.3	1.9	1.1	3.0
U	0.50	0.75	54	9.3	5.4	1.2	1.7	1.2	3.0
V	0.75	0.50	84	12.8	6.1	0.96	2.0	2.2	4.2
W	0.75	0.75	70	11.4	5.6	0.99	1.9	1.9	3.8
X	1.00	0.50	79	13.7	6.8	1.0	2.3	2.4	4.7
Y	1.00	0.75	76	12.8	6.1	0.95	2.1	2.3	4.3

1*—*5: These data are of sulfosodalite in N_2 atmosphere.[6]

(3) a: Amount of Na_2S mixed in the reaction system.

(4) U. C.: Ultramarine content determined by X-ray diffraction.

(5) Total S, and (6) Ionic S: Total and ionic sulfur contents corrected by ultramarine content.

(7) A. V.: Average valence of sulfur defined by 2 Ionic S/Total S.

850°C, respectively. Sigmoidal changes are characteristic of these curves.

Changes with the latter factor, a, are shown in Figs. 5, 6 and 7 for the system $NaAlSiO_4+aNa_2S$ at 950°C. The amount of Na_2S taken up in the product phase correspodns to a value of a of about 0.3. The fact that the product composition expressed by these values varies with the amount of excess Na_2S in the reaction system, indicates that the system has not yet attained equilibrium in a reaction time of 1 hr in the range of a less than 1.0. An increased amount of Na_2S in the reaction system would result in the approach of these values to constant values at equilibrium, as was observed in the sulfosodalite synthesis of the previous paper.[6] However, the tendency of the values at equilibrium can be seen by extrapolating the curves of Figs. 5 to 7; the value x which changes greatly with a, appears to decrease with P_{S_2} at the larger value of a, while the other values, y and $x+y$, increase. The sigmoidal characteristics at equilibrium are strongly seen in Figs. 6 and 7. It is reasonable to conclude that the plateau in the sigmoidal curve corresponds to a stable composition.

Sulfur Ion Species. Now, the sulfur ion species which exist in these specimens and which give the above sulfur composition expressed

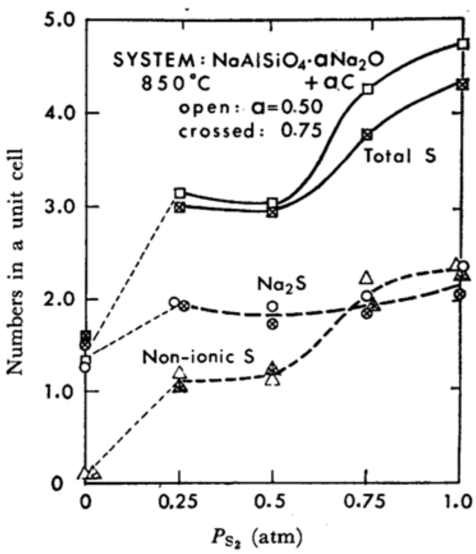

Fig. 4. Variation of numbers of total S, Na_2S, and non-ionic S in a unit cell with sulfur vapor pressure, for specimens synthesized in the system $NaAlSiO_4 \cdot aNa_2O+aC$ in (S_2, N_2) atmosphere at 850°C.

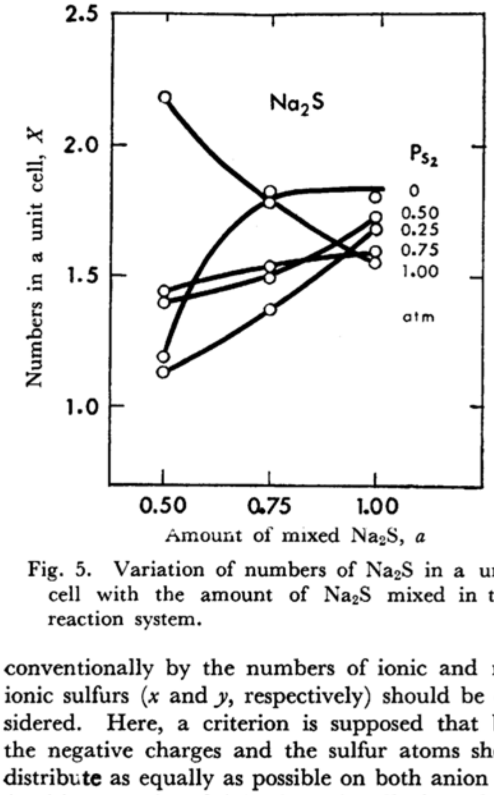

Fig. 5. Variation of numbers of Na_2S in a unit cell with the amount of Na_2S mixed in the reaction system.

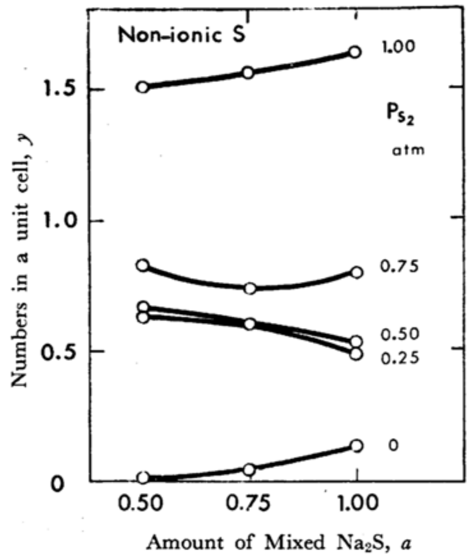

Fig. 6. Variation of numbers of non-ionic S in a unit cell with the amount of Na_2S mixed in the reaction system.

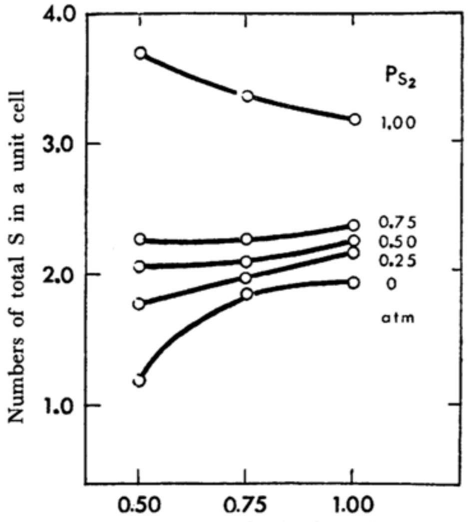

Fig. 7. Variation of numbers of total S in a unit cell with the amount of Na_2S mixed in the reaction system.

conventionally by the numbers of ionic and non-ionic sulfurs (x and y, respectively) should be considered. Here, a criterion is supposed that both the negative charges and the sulfur atoms should distribute as equally as possible on both anion sites (position notation, 2a) in the unit cell of a sodalite-type structure. This supposition is quite reasonable, since it makes anion vacancies as few as possible, as well as to make structural distortion caused by the coexistence of anions with largely different sizes as small as possible. The result of this criterion is that S^{2-} and S_2^{2-} ions coexist in most of the specimens synthesized here. In the results, this model is the same as that supposed by Podschus, Hofmann and Leschewski in their X-ray structure analysis of ultramerine.7) Thus, the ionic constitutuion at the above-mentioned plateau is given by about $1.2S^{2-}$ $0.6S_2^{2-}$ 0.2 vacancies per unit cell.

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7) E. Podshus, U. Hofmann and K. Leschewski, *Z. anorg. u. allgem. Chem.*, **228**, 305 (1936).

Some specimens, however, such as M, V, X and Y, which have either ionic sulfurs or non-ionic sulfurs, or both, more than 2 per unit cell, can not be explained by this model of ionic constitution. The formation of other sulfur ion species must be considered for these specimens. A more detailed discussion on this problem can not be made at present.

Color. In the specimen under no sulfur vapor pressure (namely sulfosodalite), the color is a very pale yellowish or pinkish. With increase in the sulfur vapor pressure, the specimens become more and more blue. This blue is particularly deep in specimens such as N, O, V, W, X and Y, the average valence of sulfur of which is near to or less than 1.0. The color, however, is much more pale than the usual ultramarine deep blue used as pigment. The heat treatment of these specimens in a SO_2 atmosphere at around 350 to 450°C caused a deepening of the blue color, with a great lowering of the average valence of sulfur. Therefore, the specimen in the present experiment is ultramarine of the leuco-form with sulfurs of a high reduction degree.