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The Space Group of Sodalite and its Structure Collapse

By

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Abstract

The space group of sodalite was examined by taking Weissenberg photographs, and it has been revealed that the space group is neither $P\bar{4}3n$ nor $P\bar{4}3m$ but $I\bar{4}3m$. A rotation photograph with a cleavage splinter gave a rotation pattern together with a powder pattern, showing that the splinter is divided into powdered crystals, a greater part of them still holding the [113] axis in parallel. The structure collapse of the mineral may begin with the rotation of $(Al, Si)O_4$ tetrahedra about [113] axis.

Introduction

The space group and crystal structure of sodalite were first analyzed, more or less in a complete fashion, by L. PAULING (1930). Using data from rotation and Laue photographs he showed that the unit of structure of sodalite contained $2[Na_4Al_3Si_3O_{12}Cl]$ and the lattice was a primitive cubic one being in close approximation to a body-centered cubic one. The point group of the mineral was determined by etch figures and he obtained $\bar{4}3m$. Taking the point group $\bar{4}3m$ and the data from the X-ray photographs as well into account, he determined the space group and crystal structure of the mineral, the former being $P\bar{4}3n$. T. F. W. BARTH (1932) examined the structure of sodalite by means of the powder method and says that almost the same structure as that proposed by L. PAULING can be derived from the space group $P\bar{4}3m$, and that the space group $P\bar{4}3m$ is more plausible than the space group $P\bar{4}3n$ to explain the isomorphous relationship among sodalite, noselite and hauyne. M. KALACZKOWSKA (1935) also examined the space group and structure of sodalite by means of the rotation method and says that the space group of the mineral is $I\bar{4}3m$. A. W. DEER, R. A. HOWIE and J. ZUSSMAN (1963) chose the space group $P\bar{4}3m$ for sodalite and say that when *Al*, *Si* distribution is random the cell may be body-centered, it may, however, be primitive when it is in order.

Recently the authors have examined sodalite from Fukushinzan, Kogen-do, Korea; Auvergne, France; Ditro, Siebenbürgen, Rumania and Bancroft, Ontario, Canada, and

they have come to the conclusion that the space group of the mineral is neither $P\bar{4}3n$ nor $P\bar{4}3m$ but $I\bar{4}3m$, and also have found that the structure collapse of the mineral may result from the rotation of $(Al, Si)O_4$ tetrahedra about [113] axis. In the following details will be given.

Experimental

Sodalite from Fukushinzan, Kogen-do, Korea was used for taking rotation and Weissenberg photographs. The specimen is massive and light blue in colour. The chemical composition and some of the physical properties of the mineral were reported by K. HARAGUCHI (1928). They are as follows:

Constituent	Weight Percentage	Molecular ratio	
SiO_2	37.42	6.240	
Al_2O_3	31.14	3.053	
Fe_2O_3	trace		
CaO	0.93	0.166	
MgO	0.39	0.098	3.798
Na_2O	21.68	3.514	
K_2O	0.13	0.020	
Cl	7.12	1.014	
SO_4	none		
$H_2O^{(+)}$	2.46		
$H_2O^{(-)}$	0.45		
	101.72		
$O=Cl$	−1.60		
	100.12		

Specific gravity: 2.30
Refractive index: 1.483
Hardness: 5.5

Hence the chemical formula: $Na_4Al_3Si_3O_{12}Cl$

Rotation and Weissenberg photographs were taken about [111] axis, using a slender cleavage splinter. The rotation and Weissenberg photographs are shown in Fig. 1∼Fig. 4. As will be seen in Fig. 2, Fig. 3 and Fig. 4 the plane lattice types of the zero, lst and 2nd levels are C_{61}, C_{31} and C_{31} respectively. The 3rd level pattern was exactly the same as the zero level pattern. From the rotation photograph the translation period in the direction of [111] was obtained as follows:

$$t_{[111]} = 7.722 \pm 0.005\,\text{Å}$$

Prior to going on, some considerations will be given. In a case when the lattice is primitive $t_{[111]}$=7.722 Å corresponds to the length of the cube diagonal. In such

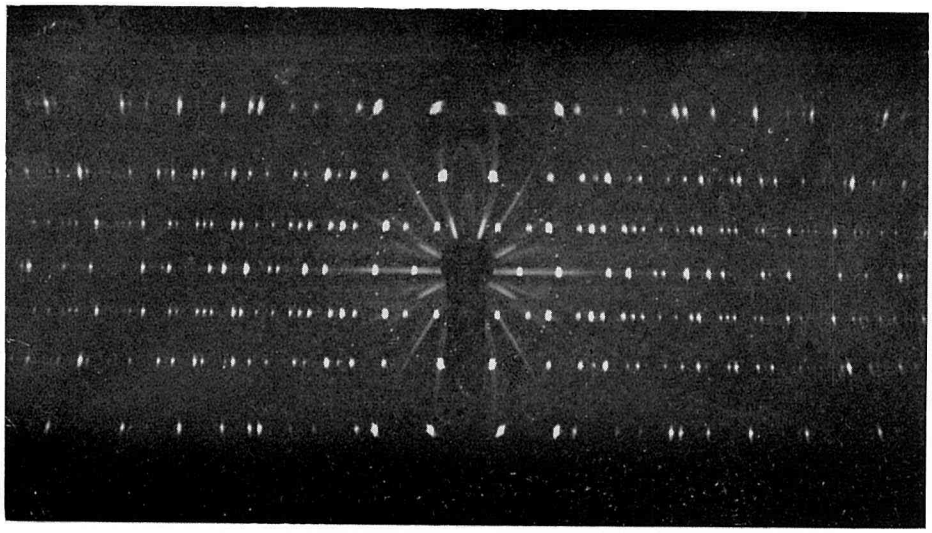

Fig. 1. Rotation photograph about [111] axis.

a case the cell edge is 4.458$\mathring{A}$ in length and since the reciprocal cell is also primitive, the reciprocal cell edge is, therefore, 0.2243 in length. (Fig. 5-A, A') On the other hand, when the lattice is body-centered $t_{[111]}=7.722\,\mathring{A}$ corresponds to the half length of the cube diagonal. In such a case

$$a = 8.917 \pm 0.005\,\mathring{A}$$

and since the reciprocal cell is face-centered, viz., reflexions disappear when $h+k+l=2n+1$, the reciprocal cell edge is, therefore, 0.2243 in length. (Fig. 5-B, B') In a case when the lattice is face-centered $t_{[111]}=7.722\,\mathring{A}$ corresponds to the length of the cube diagonal as it does when the lattice is primitive. In such a case the cell edge is, therefore, 4.458$\,\mathring{A}$ in length, and since the reciprocal cell is

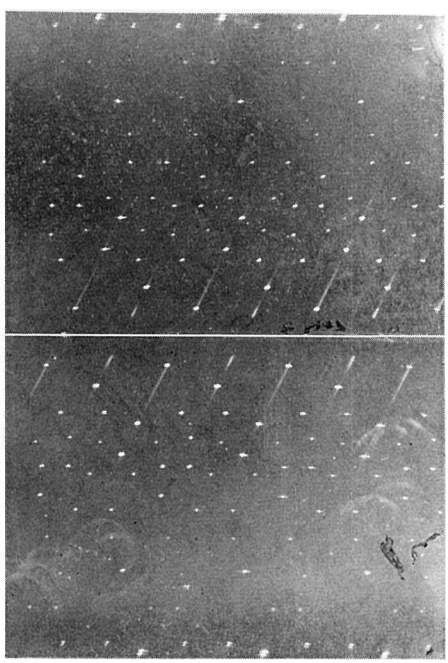

Fig. 2. The zero layer Weissenberg photograph about [111] axis.

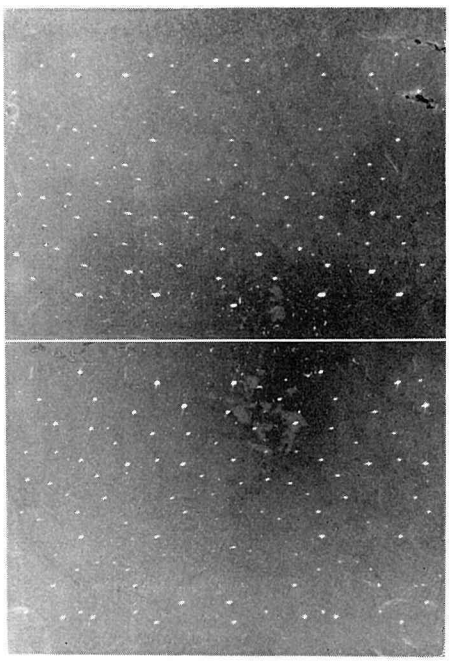

Fig. 3. The 1st layer equi-inclination Weissenberg photograph about [111] axis.

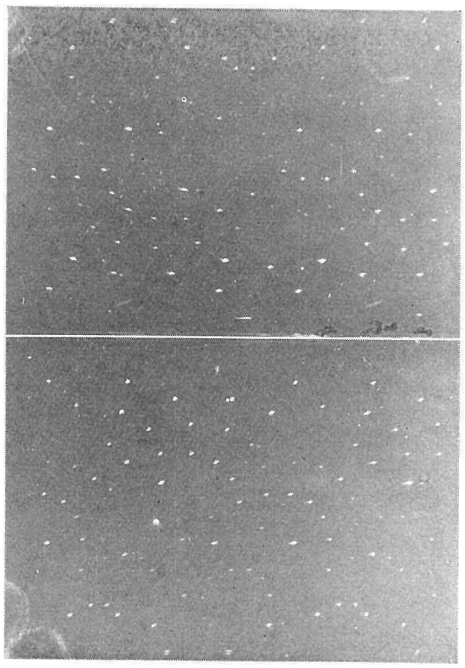

Fig. 4. The 2nd layer equi-inclination Weissenberg photograph about [111] axis.

body-centered, viz., reflexions disappear when $h+k=2n+1$ and $k+1=2n+1$, the reciprocal cell edge is 0.4486 in length. (Fig. 5-C, C')

Stacking the reciprocal plane lattices obtained from the Weissenberg and equi-inclination Weissenberg photographs in a level order, the authors obtained the reciprocal face-centered cubic cell the edge of which is 0.2243 in length. It follows immediately that the direct lattice is body-centered with a cell edge of 8.917 $\mathring{A}$ in length.

The edge length of the reciprocal face-centered cubic cell can be evaluated in several other ways by finding the ξ value between the two adjacent reciprocal lattice points lying, for instance, on the $[0\bar{1}1]$ lattice line in the zero layer Weissenberg photograph or on the [101] lattice line in the 1st layer equi-inclination Weissenberg photograph. Measuring the ξ value on the $[0\bar{1}1]$ lattice line, the authors obtained 0.244 in average. Then, a^* equals 0.224. The edge length of the direct cell obtained through the above way is 8.93 $\mathring{A}$, which is in accordance with the length evaluated from the translation period in the direction of [111].

Since the ξ value obtained above is the one between the two adjacent reciprocal

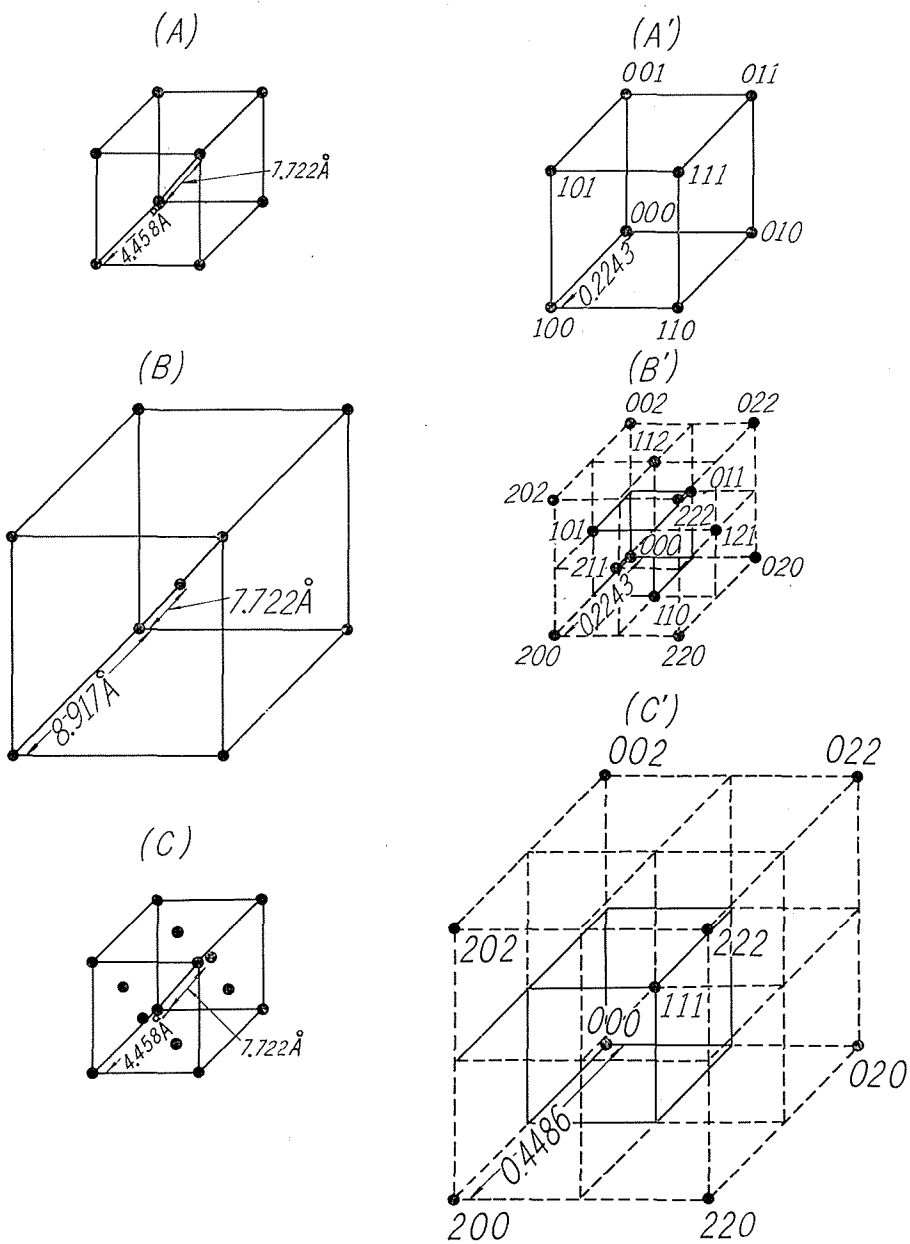

Fig. 5. Direct primitive (A), body-centered (B) and face-centered (C) cubic cells, and their reciprocals (A', B', C') respectively.

lattice points on the lateral axes when the reciprocal hexagonal lattice is chosen, using the ξ value, the reciprocal lattice points on the zero layer Weissenberg photograph, and the 1st and 2nd layer equi-inclination Weissenberg photographs were indexed in hexagonal and the indices were transformed into isometric. Then *hkl* reflexions were observed to appear when $h+k+l=0$ in the zero layer, when $h+k+l=2$ in the 1st layer and when $h+k+l=4$ in the 2nd layer, and *hhl* reflexions were when $l=2n$. Evidently, the space group of sodalite is $I\bar{4}3m$.

Taking powder photographs, the authors examined the specimens not only from Korea but also from Auvergne, France; (Fig. 6-A) Ditro, Siebenbürgen, Rumania; and Bancroft, Ontario, Canada. (Fig. 6-B) The diffraction lines were indexed graphically and the lattice constant was determined by the method of least squares. General reflexions were observed to appear when $h+k+l=2n$ and *hhl* reflexions were when $l=2n$. The lattice constant obtained is as follows:

$$a = 8.920 \pm 0.005 \, \mathring{A}$$

Any variations were not observed among the specimens which differ in locality.

Using the lattice constant and the density described above, the authors calculated the number of chemical units ($Na_4Al_3Si_3O_{12}Cl$) per unit cell as follows:

$$Z = \frac{709.0 \times 2.30 \times 10^{-24}}{484.8 \times 1.66 \times 10^{-24}} = \frac{1630.7}{804.8} = 2.03$$

Then, $Z=2$.

While the authors were trying to get a rotation photograph about [111] axis with sodalite from Korea, they accidentally obtained interesting photographs. One is a rotation pattern accompanied by a powder pattern; (Fig. 7-A) the other is a powder pattern. (Fig. 7-B) In either case the specimen used was a slender cleavage splinter. In the former, the rotation pattern is completely overlapped on the powder pattern and the lattice constant obtained from the powder pattern is as follows:

$$a = 8.920 \pm 0.005 \, \mathring{A} \, ,$$

which is in agreement with that obtained from the rotation photograph about [111] axis. On the other hand, the lattice constant obtained from the photograph which gave a powder pattern only is as follows:

$$a = 8.945 \pm 0.005 \, \mathring{A} \, ,$$

showing a little longer than that obtained from the rotation photograph about [111] axis. The sodalite from Korea may be composed of three portions, viz., a portion

Fig. 6-A

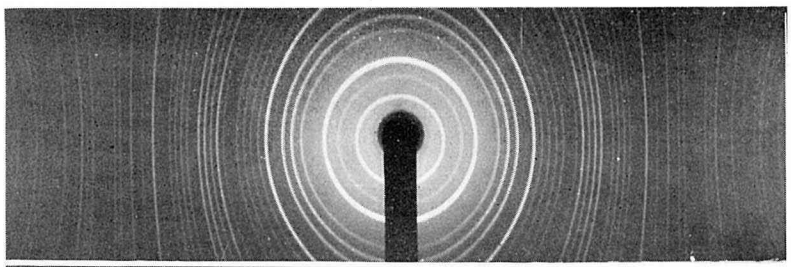

Fig. 6-B

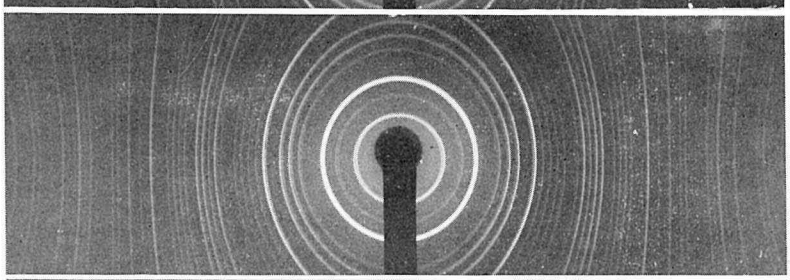

Fig. 7-A

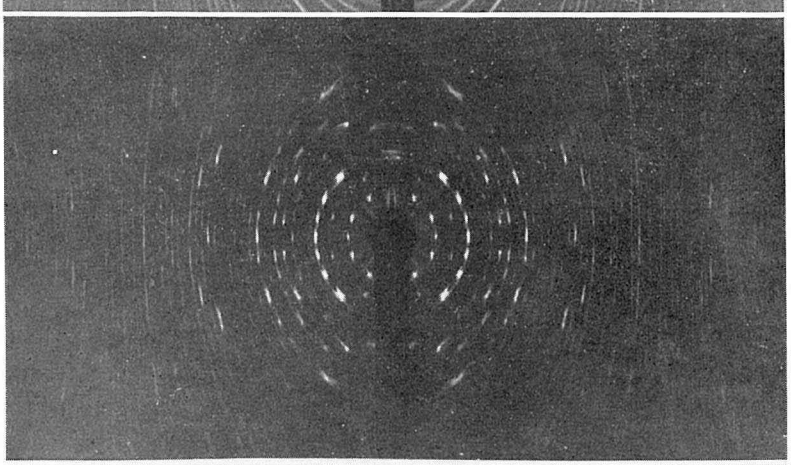

Fig. 7-B

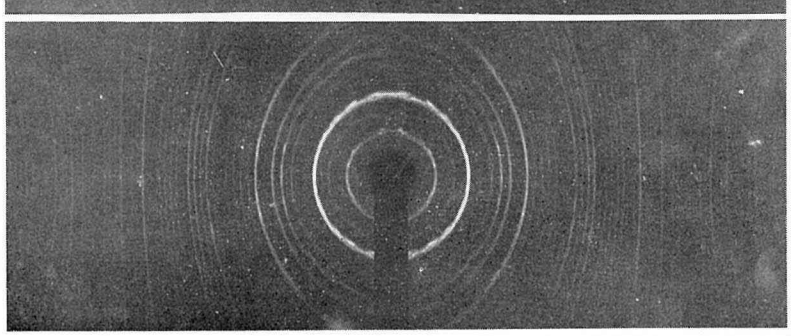

Fig. 6-A Powder photograph of a specimen from France.
Fig. 6-B Powder photograph of a specimen from Canada.
Fig. 7-A Rotation photograph of a specimen from Korea, obtained by using a slender cleavage splinter.
Fig. 7-B Powder photograph of a specimen from Korea, obtained by rotating a slender cleavage splinter.

showing a single crystalline state, that showing a preferred orientation and that showing a random orientation. From the rotation photograph which gave a rotation pattern together with a powder pattern, the authors obtained the translation period in the direction of the rotation axis as follows:

$$t = 14.90 \pm 0.05 \, \mathring{A}$$

The direction of the rotation axis is, therefore, [113].

Giving an index to each of the reflexions on the layer lines of the rotation photograph, the authors observed that the reflexions on the zero layer appeared when $h+k+l=2n$, where $h=0$, 1, 2, 3 and 4 when $l=0$, 1, 2, 3 and 4 respectively; the reflexions on the 1st layer when $h+k+l=2n$, where $n=1$, 2, 3, 4 and 5 when $l=0$, 1, 2, 3 and 4 respectively; the reflexions on the 2nd layer when $h+k+l=2n$, where $n=2$, 3, 4, 5 and 6 when $l=0$, 1, 2, 3 and 4 respectively, and so on. Such a regularity verifies that the rotation axis is parallel to [113] axis. It is plausible that the portion giving a rotation and a powder pattern is divided into powdered crystals, a greater part of them still holding the [113] axis in parallel.

Consideration

A. W. DEER, R. A. HOWIE and J. ZUSSMAN (1963) chose the space group $P\bar{4}3m$ for sodalite, saying that when *Al*, *Si* distribution is random the cell may be body-centered and it may be primitive when it is in order. However, little is known about the ordering of *Al*, *Si* atoms. The authors are of the opinion that the random distribution of *Al*, *Si* atoms should be taken as an essential property of the mineral.

L. PAULING (1930) reported that he observed 432 reflexion on a Laue photograph and 210 reflexion on a oscillation photograph, and therefore he chose the space group $P\bar{4}3n$ for sodalite. In the present investigation the authors have not observed even a trace of such reflexions.

It is well known that sodalite is markedly brittle, and in this respect L. PAULING (1930) says that the framework consisting of $(Al, Si)O_4$ tetrahedra are not rigid on account of the rotation of the tetrahedra about their two-fold rotation axes (strictly speaking, four-fold rotatory inversion axes). However, he did not show any evidence. In the present investigation the authors have observed that sodalite from Korea consists of three portions; among them one portion may be thought to be divided into powdered crystals being oriented in the direction of [113] axis. It may be plausible that the $(Al, Si)O_4$ tetrahedra have taken place a rotation about [113] axis. The direction of [113] axis is that which joins the sodium ions in the sodalite structure. The authors are of the opinion that the collapse of the framework of sodalite may begin with the rotation

of $(Al, Si)O_4$ tetrahedra about [113] axis.

L. PAULING (1930) says that partial collapse of the framework reduces the length of the cell edge from its maximum value, about 9.4 Å to 8.87 Å. If so, it is reasonable that the constant, 8.945 Å, obtained from the powder photographs is greater than that obtained from the rotation photograph, 8.917 Å.

Summary

The space group of sodalite is $I\bar{4}3m$. The lattice constant obtained from a rotation photograph about [111] axis is 8.917 ± 0.005 Å and that obtained from powder photographs is 8.945 ± 0.005 Å. The structure collapse of sodalite may begin with the rotation of $(Al, Si)O_4$ tetrahedra about [113] axis.

Acknowledgment

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