

Table 7. Shortest $N^+ \cdots Cl^-$ approaches and corresponding angles

The primed atoms belong to asymmetric units other than that at (x, y, z).			
$N(1) \cdots Cl(1')$	3·17 Å	$Cl(1)-N(1)-Cl(1')$	118°
$N(1) \cdots Cl(1)$	3·17	$Cl(1)-N(1)-Cl(3')$	108
$N(1) \cdots Cl(3')$	3·23	$Cl(1')-N(1)-Cl(3')$	108
$N(2) \cdots Cl(2)$	3·10	$Cl(2)-N(2)-Cl(2')$	122
$N(2) \cdots Cl(2')$	3·10		
$N(3) \cdots Cl(1')$	3·24	$Cl(1')-N(3)-Cl(3')$	107
$N(3) \cdots Cl(3')$	3·18	$Cl(3')-N(3)-Cl(3')$	117
$N(3) \cdots Cl(3)$	3·18	$Cl(1')-N(3)-Cl(3')$	107

The situation is summarized in Table 7, where only the shortest $N^+ \cdots Cl^-$ approaches are taken into account. Also the $C-NH_3^+ \cdots Cl$ angles support this conclusion since their values vary between 106° and 114° with an average value of 108°. These results seem to point to the formation of three hydrogen bonds, at variance with spermine tetrahydrochloride in which the interactions between terminal nitrogen atoms and the four chloride ions surrounding them are equal in pairs and only two chloride ions form angles near to tetrahedral value with nitrogen and carbon atoms. In addition the $-NH_3^+$ and $-NH_2^+$ groups in spermidine are surrounded respectively by another three and two chloride ions which are located at distances varying between 3·71 and 4·13 Å. Moreover, it is interesting to note that the arrangement of the chloride ions surrounding each nitrogen atom is very similar to that of the nitrogen atoms surrounding each chloride ion. The crystal packing may be explained on the basis of a layer structure formed by the spermidine molecules being held in sheets by van der Waals forces (Fig. 4). The chloride ions form rows between the sheets and are connected to the protonated amino and imino groups through hydrogen bonds. Such a packing is obviously consistent with the ionic character of the crystal. As to the planar conformation of the molec-

ule, it should be considered that in the case of spermine both a planar and a skewed conformation have been established for different salts. Therefore the possibility cannot be excluded that also protonated spermidine molecules may adopt a skewed conformation characterized by *gauche* state of the bonds connecting the carbon atoms to the amino nitrogens. In view of the probably small energy differences between the two conformations in the case of spermine it may be inferred that under appropriate conditions a skewed conformation of spermidine may also be expected. This might be the case when spermidine interacts with DNA in solution and therefore the same model proposed to explain the mechanism of the interaction between DNA and spermine (Liquori, to be published) may be easily extended to spermidine.

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Sodium Silicate Hydrates. II. The Crystal Structure of $Na_2O \cdot SiO_2 \cdot 9H_2O$

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The crystal structure of $Na_2O \cdot SiO_2 \cdot 9H_2O$ has been determined by X-ray structure analysis, using three-dimensional data. The silicon atoms are shown to be surrounded tetrahedrally by four oxygen atoms; the tetrahedra are not linked through a common atom. Each sodium atom is coordinated by six oxygen atoms at the corners of a distorted octahedron; the octahedra share edges to produce helical chains. An attempt to locate hydrogen atoms was unsuccessful, but consideration of bond lengths and angles leads to the conclusion that two hydrogen atoms are probably attached to each silicon-oxygen tetrahedron, and that the constitutional formula is therefore $Na_2(H_2SiO_4) \cdot 8H_2O$.

Introduction

$Na_2O \cdot SiO_2 \cdot 9H_2O$ is orthorhombic, *Ibca*, with $a = 11\cdot74$, $b = 17\cdot03$, $c = 11\cdot60$ Å, $Z = 8$ (see part I, Jamieson

& Dent Glasser, 1966). The uncertainty about the nature of the anion (discussed in part I) made a structure determination seem worth while.

Experimental

The crystals used in this study were prepared as described in part I. Those selected for intensity measurements were in the form of rectangular plates [usually lying on (010)] whose longest dimension was never greater than 0.2 mm.

X-ray Weissenberg photographs were taken of $hk0$, $hk1$, . . . $hk5$ and $0kl$ and $1kl$ with Cu $K\alpha$ radiation and multiple-film packs. Intensities were estimated visually by comparison with a standard intensity strip prepared from one strong reflexion. The relative intensities, corrected for Lorentz and polarization factors, were converted to an approximately absolute scale by Wilson's statistical method, which gave also an approximate value for the overall temperature factor. No corrections were made for absorption or extinction.

All processing of data and crystallographic calculations were carried out on an Elliott 803 computer, using the programs of Daly, Stephens & Wheatley (1963), whose kindness in making them available is gratefully acknowledged.

Interpretation of Harker sections in the space group $Ibca$

The Harker section at $z=0$ of the three-dimensional Patterson synthesis has the form shown in Fig. 1(ii). Each fourfold peak at $(x, y, 0)$ has related eightfold peaks at $(\frac{1}{2}-x, \frac{1}{2}, 0)$ and $(\frac{1}{2}, \frac{1}{2}-y, 0)$. The non-Harker background can be minimized by comparing $P(x, y, 0)$ with $\frac{1}{2}P(\frac{1}{2}-x, \frac{1}{2}, 0)$ and $\frac{1}{2}P(\frac{1}{2}, \frac{1}{2}-y, 0)$; the minimum of the three values is replaced at $(x, y, 0)$. This provides a 'minimized' Harker section [Fig. 1(iii)]. Sections at $x=0$ and $y=0$ have the same form and can be treated similarly.

The implication diagrams derived in this way [Fig. 1(iv)] are equivalent to unambiguous projections

of the electron density. However, ambiguity arises at a later stage in the problem as a result of not knowing which of four possible heights ($z, \frac{1}{2}-z, \frac{1}{2}+z, -z$) to assign to an atom at (x, y) . For n independent atoms in general positions, this leads to 4^{n-1} possible arrangements, even when all three projections are solved.

Structure determination

The unit cell contains $\text{Na}_{16}\text{Si}_8\text{O}_{96}\text{H}_{144}$. The general position in $Ibca$ is 16-fold; the silicon atoms must therefore lie on one of the five sets of special positions (unless there is some unusual sort of replacement or statistical distribution). Two of these sets lie on centres of symmetry, the others on the three sets of mutually perpendicular, non-intersecting twofold axes. In view of the well-known habit of silicon to adopt tetrahedral coordination in silicates, the latter seemed more probable; studies of Harker sections at $x=0, y=0$ and $z=0$ showed that it lay on $(x, 0, \frac{1}{4})$ with $x \approx \frac{3}{8}$. No other atoms were found in special positions, leaving seven independent non-hydrogen atoms to be located. The non-Harker background was initially considerable. After minimizing the sections, the seven most probable atomic positions were selected; overlap was troublesome in all three projections. At this stage no attempt was made to distinguish between oxygen and sodium; all seven atoms were treated as oxygen. Structure factors were calculated with scattering factors taken from *International Tables for X-ray Crystallography* (1962). The initial R index was about 55% for all three projections. A sequence of Fourier and difference synthesis refinements gradually reduced this figure to around 30%. At this stage, that part of the three-dimensional Patterson function lying within 2.6 Å of the origin was examined. The positions of the oxygen atoms forming a tetrahedron round the silicon atom were confirmed,

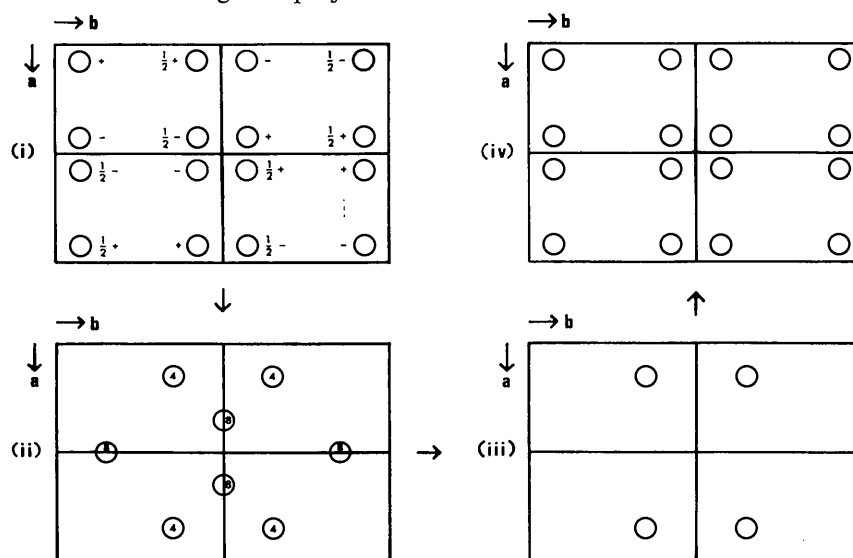


Fig. 1. (i) General positions in the space group $Ibca$. (ii) Harker section at $z=0$. Numerals indicate multiplicity of peaks. (iii) 'Minimized' Harker section. (iv) Implication diagram. The origin is chosen to correspond to (i).

and the positions of vector peaks corresponding to an interatomic distance of 2.3–2.4 Å (Na–O) suggested which of the five remaining atoms was sodium. With this information, the R value was quickly reduced to 26% for all reflexions having h , k and l all even, *i.e.* the structure invariants (whose structure factors are not affected by the ambiguity in assigning heights).

The problem remained of knowing which height to assign to each atom. Although this could eventually have been solved by a combination of trial-and-error and chemical intuition, it was decided to extend the knowledge of signs to the three remaining parity groups by an application of direct methods. The authors gratefully acknowledge the help of Professor M. M. Woolfson and Dr G. Germain, both formerly of the Manchester College of Science and Technology, in this part of the work. Unitary structure factors were calculated for all reflexions, the twenty largest values of U for each parity group picked out, and two signs assigned arbitrarily. Signs for the remaining 58 terms were developed by repeated application of the relationship

$$s(h, k, l) \approx s(h', k', l') s(h+h', k+k', l+l'),$$

where s means *sign of* and \approx means *probably equals*. A simple probability expression was used to assess the reliability of the sign relationship in each case.

Using the signs thus determined, together with those already known, a three-dimensional Fourier synthesis was calculated. This showed clearly which of the possible atomic sites were correct. Structure factors could then be calculated for the full three-dimensional data.

The structure was refined by the method of least squares (diagonal-block approximation), the procedure used closely following that of Cruickshank, Pilling, Bujosa, Lovell & Truter (1961), incorporating the same weighting scheme and method of calculation of the estimated standard deviations. It became clear during the later stages of refinement that the strongest reflexions were suffering from extinction. No correction was made for this, but the four reflexions most affected were omitted from the later least-squares cycles, although included in the final calculation of the R index. Intensities too weak to be observed were, for the purposes of refinement, assigned a value of half the minimum observed intensity.

After eight least-squares cycles, the maximum shift in atomic coordinates was a quarter of the e.s.d., and

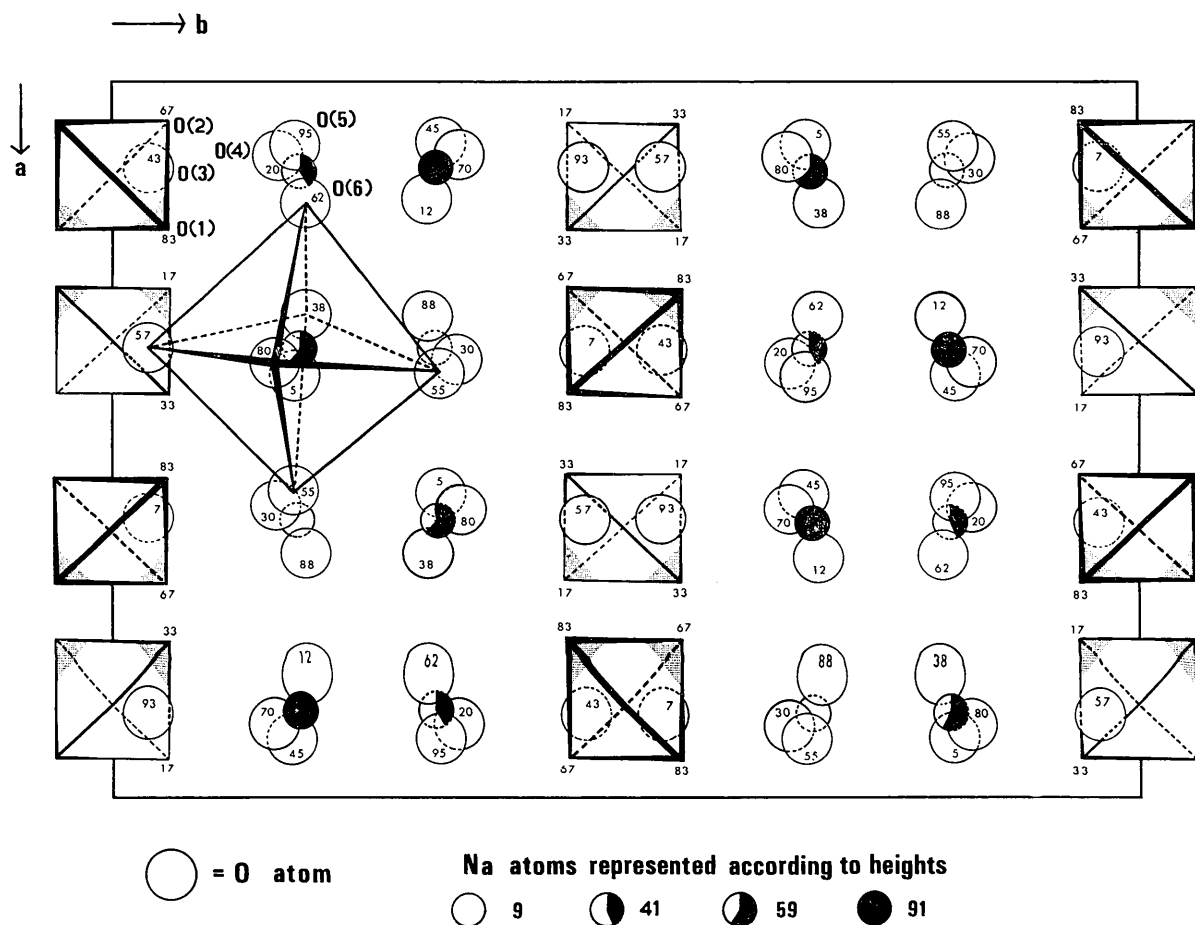


Fig. 2. Projection of the structure on (001). $(\text{H}_2\text{SiO}_4)^{2-}$ groups are represented by tetrahedra; shaded corners indicate probable positions of hydrogen atoms. One $\text{Na}(\text{H}_2\text{O})_6$ octahedron is outlined. z coordinates are in hundredths of the cell side.

the average shift only 0.08 of the average e.s.d., showing that the structure was refined as completely as the data would permit. The final R value was 15.7% for 694 reflexions (Table 1). Final parameters and estimated standard deviations are listed in Table 2.

Table 2. Final parameters for the non-hydrogen atoms of $\text{Na}_2\text{O} \cdot \text{SiO}_2 \cdot 9\text{H}_2\text{O}$

	Coordinates (fractions of cell edge) with e.s.d.'s $\times 10^4$ in brackets			Isotropic temperature factor $B(\text{\AA}^2)$ with e.s.d. in brackets
	x	y	z	
Si	0.3734 (2)	0	$\frac{1}{4}$	0.81 (0.06)
Na	0.1239 (3)	0.1822 (2)	0.4111 (4)	2.00 (0.08)
O(1)	0.2876 (6)	0.0560 (3)	0.1695 (7)	1.1 (0.1)
O(2)	0.4444 (6)	0.0564 (3)	0.3323 (7)	1.2 (0.1)
O(3)	0.1197 (6)	0.0365 (4)	0.4349 (8)	1.5 (0.1)
O(4)	0.1078 (6)	0.1607 (3)	0.2029 (7)	1.3 (0.1)
O(5)	0.4142 (6)	0.1774 (3)	0.0548 (8)	1.5 (0.1)
O(6)	0.3272 (6)	0.1894 (4)	0.3848 (8)	1.6 (0.1)

A three-dimensional difference synthesis was calculated in the hope of finding some indication of the positions of the hydrogen atoms, but this proved unsuccessful.

Description of the structure

Fig. 2 shows the structure projected on (001). Each silicon atom is surrounded by four oxygen atoms at the corners of a slightly distorted tetrahedron (Table 3(a); Fig. 3); these tetrahedra are isolated and do not share corners with one another. None of these oxygen atoms takes part in the coordination of the sodium atom.

Table 3. Interatomic distances and bond angles

Primes and Roman numerals indicate atoms in different asymmetric units

(a) Silicon-oxygen tetrahedron

Bond distance		Bond angle	
Si—O(1)	1.672 \AA	O(1)—Si—O(1')	105.9°
Si—O(2)	1.591	O(1)—Si—O(2)	107.8°
		O(1)—Si—O(2')	108.0°
O(1)—O(1')	2.67	O(2)—Si—O(2')	116.9°
O(2)—O(2')	2.71		
O(1)—O(2)	2.64		
O(1)—O(2')	2.66		

(b) Sodium-oxygen octahedron

Na—O(3)	2.50 \AA	O(3) — Na—O(4)	87.6°
Na—O(4)	2.45	O(3) — Na—O(5')	86.0°
Na—O(5')	2.49	O(3) — Na—O(6 ^{iv})	87.0°
Na—O(5''')	2.46	O(3) — Na—O(6)	94.8°
Na—O(6 ^{iv})	2.44		
Na—O(6)	2.41	O(4) — Na—O(5'')	94.3°
		O(5'') — Na—O(6 ^{iv})	94.6°
		O(6 ^{iv}) — Na—O(6)	83.6°
		O(6) — Na—O(4)	87.6°
		O(5''') — Na—O(4)	106.8°
		O(5''') — Na—O(5'')	80.0°
		O(5''') — Na—O(6 ^{iv})	80.8°
		O(5''') — Na—O(6)	98.7°

Table 3 (cont.)

(c) Hydrogen bonds

O(1)—O(3')	2.80 \AA
O(1)—O(4)	2.79
O(1)—O(5)	2.87
O(2)—O(3 ^{iv})	2.82
O(2)—O(3 ^v)	2.86
O(2)—O(4'')	2.65
O(2)—O(6)	2.72
O(4)—O(6''')	2.85

Estimated standard deviations:

Si—O	0.008 \AA
Na—O	0.01 \AA
O—O	
Angles	0.4°

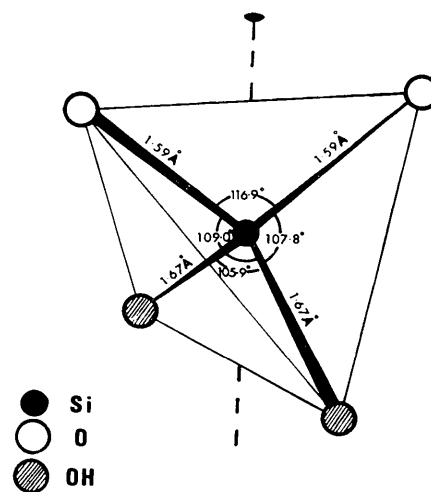


Fig. 3. Detail of $(\text{H}_2\text{SiO}_4)^{2-}$ tetrahedron.

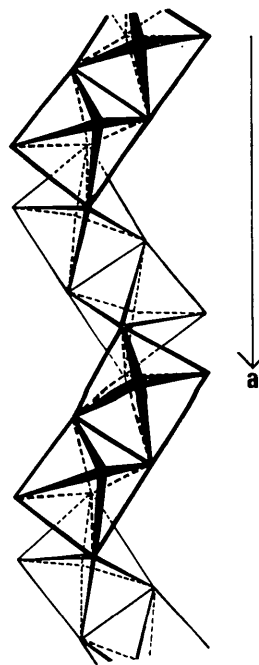


Fig. 4. $\text{Na}(\text{H}_2\text{O})_6$ octahedra sharing edges to form helical chains parallel to x .

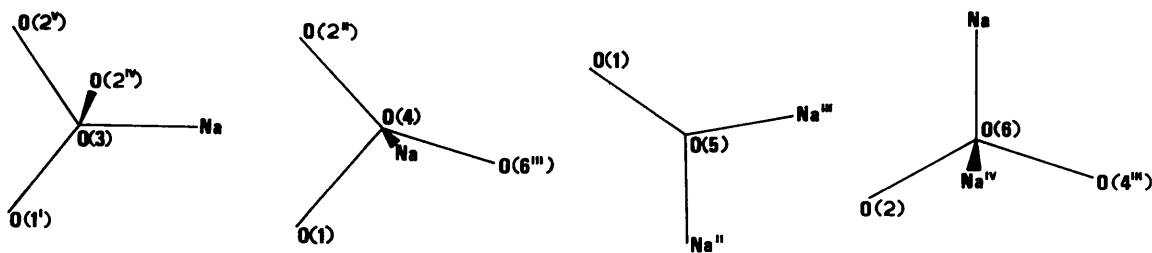


Fig. 5. Coordination of water molecules. The magnitudes of the angles are as follows:

O(1')—O(3)—Na	119.9°	O(1)—O(4)—Na	100.1°	Na''—O(5)—Na'''	97.1°	Na ^{iv} —O(6)—Na	96.2°
O(1')—O(3)—O(2 ^v)	90.8	O(1)—O(4)—O(2'')	95.6	Na''—O(5)—O(1)	117.5	Na ^{iv} —O(6)—O(2)	93.3
O(1')—O(3)—O(2 ^{iv})	132.0	O(1)—O(4)—O(6''')	108.7	Na'''—O(5)—O(1)	122.0	Na ^{iv} —O(6)—O(4''')	109.2
Na—O(3)—O(2 ^v)	89.5	Na—O(4)—O(2'')	108.1			Na—O(6)—O(2)	119.2
Na—O(3)—O(2 ^{iv})	121.3	Na—O(4)—O(6''')	101.4			Na—O(6)—O(4''')	110.8
O(2 ^v)—O(3)—O(2 ^{iv})	105.8	O(2'')—O(4)—O(6''')	137.6			O(2)—O(6)—O(4''')	122.0

The remaining oxygen atoms surround the sodium atoms, whose coordination is roughly octahedral [Table 3(b)]. The oxygen octahedra share edges, producing the helical chains shown in Fig. 4.

A study of the bond lengths shows that a system of hydrogen bonding links the oxygen atoms. None of the hydrogen bonds is as short as the 'short bonds' found in afwillite, $\text{Ca}_3(\text{SiO}_3\text{OH})_2\cdot 2\text{H}_2\text{O}$, by Megaw (1952). (This is the only other compound containing H_xSiO_4 groups whose structure has been accurately determined.) Table 3(c) lists those oxygen–oxygen distances which are presumed to represent hydrogen bonds. The coordination of O(3), O(4) and O(6) is roughly tetrahedral; the coordination of O(5) is more nearly triangular (Fig. 5). There is a fourth fairly close approach to O(5) by O(4) at 3.02 Å, but this seems too long to represent a hydrogen bond. With this exception, all O–O distances not listed in the table were greater than 3.35 Å.

O(3), O(4), O(5) and O(6) may conceivably be H_2O , H_3O^+ or OH^- . Since all are approximately the same distance from Na^+ , it seems unlikely that there is any great variation in the number of hydrogen atoms associated with each (although it is recognized that the hydrogen atoms may be statistically distributed). It seems plausible as a first approximation to treat all as H_2O . This leaves two hydrogen atoms to be associated with the SiO_4 tetrahedron. As Si–O(1) is significantly longer than Si–O(2), it seems likely that O(1) is in fact an OH group. This also agrees with the angular dis-

tortion of the tetrahedron (Table 3) the two remaining charged oxygen atoms apparently repelling one another (Fig. 3). These results may be compared with those of Megaw (1952) on afwillite. She found that in the HSiO_4 tetrahedra Si–OH was significantly longer than Si–O, although there appeared to be no significant angular distortion.

As suggested above, the hydrogen atoms may not be fixed in position, but may have a distribution such that some of the water molecules have a certain (OH)⁻ character, and others tend towards H_3O^+ . Whether or not this is the case, it seems that the formula may best be written as $\text{Na}_2(\text{H}_2\text{SiO}_4)\cdot 8\text{H}_2\text{O}$, supporting the infrared and extraction studies discussed in part I.

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