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Sodium Silicate Hydrates. IV. Location of Hydrogen Atoms in $Na_2O.SiO_2.6H_2O$ by Neutron Diffraction*

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The hydrogen atoms in the silicate $Na_2O.SiO_2.6H_2O$ were located using neutron diffraction. The Si–O and Na–O bond lengths obtained from the refinement are compared with those given in the original X-ray structure determination, and also with the results of a completely new X-ray structure determination performed utilizing a chip from the crystal used for neutron diffraction. Some comments are made on the accuracy of the various results.

Introduction

The crystal structures of several silicates of empirical formula $Na_2O.SiO_2.xH_2O$ have been determined [for $x=5$ by Jost & Hilmer (1966); for $x=6$ and $x=9$ by Jamieson & Dent Glasser (1966*b*, 1967)]. All have been shown to contain isolated silicate tetrahedra which are presumed to have the formula $SiO_2(OH)_2^{2-}$; therefore, their constitutional formulae may be written: $Na_2(H_2SiO_4).(x-1)H_2O$.

In the case of $Na_2(H_2SiO_4).8H_2O$, the silicon atoms lie on twofold-symmetry axes and Si–O bond lengths are 1·59 and 1·67 Å. Jamieson & Dent Glasser assumed the latter to be the Si–OH bonds, a conclusion supported by the O–Si–O angles. In $Na_2(H_2SiO_4).5H_2O$, which crystallizes in space group $P2_1$, the silicon atoms do not lie on a symmetry axis; bond lengths determined in the earlier paper are given in Table 1 (X-ray 0). In this case they do not fall into two clearly defined categories; the distribution of bond lengths is very similar to that found by Jost & Hilmer (1966) for $Na_2(H_2SiO_4).4H_2O$. Therefore, it was much more difficult to assign positions to the hydrogen atoms; they were tentatively assumed to be bonded to O(3) and O(4), partly by analogy with the isostructural germanate and partly from a consideration of the probable hydrogen-bonding scheme. Nevertheless, the hydrogen positions remained in doubt, and it seemed possible that they might be statistically distributed. Since excellent large single crystals $Na_2(H_2SiO_4).5H_2O$ were available, it was decided to use neutron diffraction to resolve the question.

Experimental

A large (about 3 × 3 × 5 mm) well-formed crystal of $Na_2(H_2SiO_4).5H_2O$ was selected and mounted with its largest dimension (crystallographic *b*) parallel to the rotation axis. Cell dimensions used were $a=11·43$, $b=5·96$, $c=6·34$ Å, $\beta=102·1°$, corresponding to those quoted by Jamieson & Dent Glasser (1966*a*) which were calculated from powder data. These dimensions differ slightly from those used by Jamieson & Dent Glasser (1967), which we now believe were slightly in error.

Intensities of 503 independent *hkl* reflexions were measured using the Hilger–Ferranti automatic neutron diffractometer at the Atomic Energy Research Establishment, Harwell, England. Output from the diffractometer was converted to a set of structure amplitudes using a program written by N. A. Curry for the Chilton Atlas computer. Structure factors were calculated using parameters for Na, Si and O from the original X-ray analysis. A three-dimensional difference map gave positions for all hydrogen atoms. After several cycles of least-squares refinement (diagonal-block approximation, using an Elliott 803 computer; details are given below), the shifts in the non-hydrogen parameters were sufficient to cast doubt on the accuracy of the original (X-ray) determination.

Consequently a completely new set of X-ray data was obtained, using a small chip from the crystal used for the neutron-diffraction analysis. This was irregularly shaped, but more or less equant in dimensions. Using a Hilger and Watts automatic linear diffractometer, intensities of 1316 independent reflexions were measured; they were converted to structure factors in the usual way. No correction was made for absorption, which was believed to be small, since the radiation used was Mo $K\alpha$ and only light atoms were involved. Errors believed to be due to extinction were eliminated during refinement.

Calculations on the Elliott 803 computer were made with the use of programs kindly made available by Daly, Stephens & Wheatley (1963), and also programs *PBRM*3 and *PBRM*4 written by G. A. Mair of the Royal Institution, which combine structure-factor least-squares (block diagonal) calculations with bond-length and bond-angle calculations. Later, an ICL 4/50 computer became available and subsequent calculations were performed on it, using programs written by Dr F. R. Ahmed and collaborators of the National Reaearch Council of Canada, and adapted for use on

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Table 1. *Bond lengths and angles*

Silicon–oxygen tetrahedron

Lengths (Å)	X-ray 0	X-ray I	X-ray II	Neutron diffraction
Si–O(1)	1·640 (7)	1·604 (4)	1·597 (4)	1·599 (9)
Si–O(2)	1·623 (7)	1·608 (4)	1·612 (4)	1·591 (9)
Si–O(3)	1·712 (7)	1·682 (4)	1·691 (4)	1·698 (8)
Si–O(4)	1·646 (8)	1·648 (4)	1·657 (5)	1·672 (9)
O(1)–O(2)	2·767 (9)	2·721 (5)	2·721 (5)	2·714 (8)
O(1)–O(3)	2·679 (9)	2·646 (5)	2·651 (6)	2·667 (8)
O(1)–O(4)	2·632 (9)	2·605 (6)	2·610 (6)	2·637 (9)
O(2)–O(3)	2·718 (9)	2·670 (5)	2·681 (5)	2·650 (8)
O(2)–O(4)	2·701 (9)	2·674 (5)	2·680 (6)	2·676 (9)
O(3)–O(4)	2·704 (9)	2·695 (6)	2·704 (6)	2·706 (10)
Angles (°)				
O(1)–Si–O(2)	116·0 (3)	115·8 (2)	116·1 (2)	116·6 (5)
O(1)–Si–O(3)	106·1 (3)	107·3 (2)	107·4 (2)	108·0 (4)
O(1)–Si–O(4)	106·5 (3)	106·5 (2)	106·7 (2)	107·4 (5)
O(2)–Si–O(3)	109·2 (3)	108·5 (2)	108·5 (2)	107·4 (5)
O(2)–Si–O(4)	111·4 (4)	110·4 (2)	110·1 (2)	110·2 (5)
O(3)–Si–O(4)	107·3 (4)	108·1 (2)	107·7 (2)	106·8 (4)

Sodium–oxygen octahedra

Lengths (Å)	X-ray 0	X-ray I	X-ray II	Neutron diffraction
Na(1)–O(5)	2·43 (1)	2·424 (5)	2·416 (6)	2·445 (13)
Na(1)–O(6)	2·49 (1)	2·438 (5)	2·444 (5)	2·447 (12)
Na(1)–O(7)	2·50 (1)	2·456 (5)	2·444 (5)	2·486 (12)
Na(1)–O(8)	2·48 (1)	2·445 (5)	2·453 (6)	2·468 (13)
Na(1)–O(8′)	2·37 (1)	2·351 (5)	2·356 (5)	2·346 (12)
Na(1)–O(9)	2·39 (1)	2·350 (5)	2·346 (5)	2·369 (12)
Na(2)–O(3)	2·52 (1)	2·524 (5)	2·526 (5)	2·558 (13)
Na(2)–O(3′)	2·57 (1)	2·541 (4)	2·531 (5)	2·526 (12)
Na(2)–O(4)	2·29 (1)	2·305 (5)	2·304 (5)	2·321 (12)
Na(2)–O(5)	2·80 (1)	2·816 (5)	2·806 (6)	2·791 (13)
Na(2)–O(7)	2·58 (1)	2·549 (5)	2·551 (5)	2·553 (12)
Na(2)–O(9)	2·39 (1)	2·375 (5)	2·374 (5)	2·373 (12)

Hydrogen bonding

Lengths (Å)	X-ray 0	X-ray I	X-ray II	Neutron diffraction
O(2)–O(3′)	2·89 (1)	2·882 (5)	2·875 (6)	2·871 (9)
O(2)–O(4′)	2·67 (1)	2·628 (5)	2·613 (6)	2·607 (9)
O(1)–O(5)	2·75 (1)	2·765 (6)	2·767 (6)	2·747 (8)
O(1)–O(6)	2·67 (1)	2·670 (6)	2·677 (6)	2·657 (9)
O(1)–O(7)	2·60 (1)	2·643 (6)	2·650 (6)	2·629 (9)
O(1)–O(8)	2·90 (1)	2·874 (5)	2·873 (6)	2·851 (8)
O(2)–O(5)	2·76 (1)	2·738 (6)	2·744 (6)	2·733 (9)
O(2)–O(9)	2·77 (1)	2·742 (6)	2·738 (6)	2·74 (1)
O(4)–O(9)	3·18 (1)	3·157 (6)	3·156 (6)	3·131 (9)
O(5)–O(8)	2·91 (1)	2·872 (6)	2·875 (7)	2·898 (9)
O(6)–O(7)	2·76 (1)	2·756 (6)	2·759 (7)	2·743 (9)
O(6)–O(7′)	3·04 (1)	3·010 (6)	2·999 (7)	2·995 (9)

Hydrogen bonding – neutron diffraction

Lengths (Å)			
O(3)–H(3)	0·95 (1)	O(2)---H(3)	1·93 (1)
O(4)–H(4)	0·93 (1)	O(2)---H(4)	1·68 (1)
O(5)–H(52)	0·93 (1)	O(1)---H(52)	1·82 (1)
O(6)–H(61)	1·01 (1)	O(1)---H(61)	1·65 (1)
O(7)–H(72)	0·94 (1)	O(1)---H(72)	1·69 (1)
O(8)–H(82)	0·92 (1)	O(1)---H(82)	1·94 (1)
O(5)–H(51)	0·94 (1)	O(2)---H(51)	1·79 (1)
O(9)–H(92)	0·97 (1)	O(2)---H(92)	1·78 (1)
O(9)–H(91)	0·89 (2)	O(4)---H(91)	2·24 (2)
O(8)–H(81)	1·00 (1)	O(5)---H(81)	1·92 (1)
O(7)–H(71)	0·95 (1)	O(6)---H(71)	1·79 (1)
O(6)–H(62)	0·96 (1)	O(7)---H(62)	2·03 (1)

Table 1 (*cont.*)

Angles (°)	
O(3)-H(3)—O(2)	170 (1)
O(4)-H(4)—O(2)	175 (1)
O(5)-H(52)-O(1)	178 (1)
O(6)-H(61)-O(1)	175 (1)
O(7)-H(72)-O(1)	179 (1)
O(8)-H(82)-O(1)	170 (1)
O(5)-H(51)-O(2)	175 (1)
O(9)-H(92)-O(2)	171 (1)
O(9)-H(91)-O(4)	175 (1)
O(8)-H(81)-O(5)	164 (1)
O(7)-H(71)-O(6)	179 (1)
O(6)-H(62)-O(7)	179 (1)

Coordination of the water molecules

Lengths (Å)	X-ray 0	X-ray I	X-ray II	Neutron diffraction	Angles to H (°) (neutron diffraction)	
O(5)—Na(1)	2·43 (1)	2·424 (5)	2·416 (6)	2·45 (1)		
O(5)—Na(2)	2·80 (1)	2·816 (5)	2·806 (6)	2·79 (1)		
O(5)—O(1)	2·75 (1)	2·765 (6)	2·767 (6)	2·75 (1)		
O(5)—O(2)	2·76 (1)	2·738 (6)	2·744 (6)	2·73 (1)		
O(5)—O(8)	2·91 (1)	2·872 (6)	2·875 (7)	2·90 (1)		
Angles (°)						
Na(1)-O(5)-Na(2)	79·6 (3)	78·5 (1)	78·5 (2)	78·2 (4)		
Na(1)-O(5)-O(1)	129·2 (3)	128·3 (2)	128·6 (2)	127·8 (4)	Na(1)-O(5)-H(52)	129 (1)
Na(1)-O(5)-O(2)	113·0 (3)	113·7 (2)	113·7 (2)	113·1 (4)	Na(1)-O(5)-H(51)	113·1 (4)
Na(1)-O(5)-O(8)	88·2 (3)	90·0 (2)	89·9 (2)	88·4 (3)	Na(1)-O(5)-H(81)	88·8 (5)
Na(2)-O(5)-O(1)	88·4 (3)	87·3 (2)	87·5 (2)	88·7 (3)	Na(2)-O(5)-H(52)	89·9 (9)
Na(2)-O(5)-O(2)	90·9 (3)	91·3 (2)	91·3 (2)	91·9 (3)	Na(2)-O(5)-H(51)	90·4 (9)
Na(2)-O(5)-O(8)	161·4 (3)	162·2 (2)	162·1 (2)	160·5 (4)	Na(2)-O(5)-H(81)	164·4 (5)
O(1)—O(5)-O(2)	116·3 (3)	116·1 (2)	115·9 (2)	117·7 (3)	H(52)-O(5)-H(51)	113·5 (1·2)
O(1)—O(5)-O(8)	110·2 (3)	110·5 (2)	110·5 (2)	110·7 (3)	H(52)-O(5)-H(81)	105·1 (1·0)
O(2)—O(5)-O(8)	81·0 (3)	80·8 (2)	80·8 (2)	80·4 (3)	H(51)-O(5)-H(81)	87·5 (9)
Lengths (Å)						
O(6)—Na(1)	2·49 (1)	2·438 (5)	2·444 (5)	2·45 (1)		
O(6)—O(1)	2·67 (1)	2·670 (6)	2·677 (6)	2·66 (1)		
O(6)—O(7)	2·76 (1)	2·765 (5)	2·759 (7)	2·74 (1)		
O(6)—O(7′)	3·04 (1)	3·010 (6)	2·999 (7)	2·99 (1)		
Angles (°)						
Na(1)-O(6)-O(1)	111·7 (3)	112·2 (2)	111·9 (2)	111·9 (4)	Na(1)-O(6)-H(61)	113·8 (9)
Na(1)-O(6)-O(7)	110·7 (3)	111·1 (2)	111·2 (2)	111·1 (4)	Na(1)-O(6)-H(71)	110·2 (6)
Na(1)-O(6)-O(7′)	109·6 (3)	111·0 (2)	111·2 (2)	110·5 (4)	Na(1)-O(6)-H(62)	111·8 (9)
O(1)—O(6)-O(7)	97·9 (3)	98·3 (2)	98·3 (2)	98·8 (3)	H(61)-O(6)-H(71)	100·7 (9)
O(1)—O(6)-O(7′)	107·0 (3)	105·9 (2)	106·0 (2)	106·2 (3)	H(61)-O(6)-H(62)	102·4 (1·1)
O(7)—O(6)-O(7′)	118·2 (3)	117·6 (2)	117·6 (2)	117·5 (3)	H(62)-O(6)-H(71)	117·3 (9)
Lengths (Å)						
O(7)—Na(1)	2·50 (1)	2·456 (5)	2·444 (5)	2·49 (1)		
O(7)—Na(2)	2·58 (1)	2·549 (5)	2·551 (5)	2·55 (1)		
O(7)—O(1)	2·60 (1)	2·643 (6)	2·650 (6)	2·63 (1)		
O(7)—O(6)	2·76 (1)	2·756 (6)	2·759 (7)	2·74 (1)		
O(7)—O(6)	3·04 (1)	3·010 (6)	2·999 (7)	2·99 (1)		
Angles (°)						
Na(1)-O(7)-Na(2)	82·9 (3)	83·3 (2)	83·2 (2)	82·2 (4)		
Na(1)-O(7)-O(1)	145·9 (4)	145·3 (2)	145·5 (2)	145·1 (4)	Na(1)-O(7)-H(72)	145·5 (8)
Na(1)-O(7)-O(6)	105·0 (3)	106·6 (2)	106·6 (2)	105·6 (4)	Na(1)-O(7)-H(71)	106·3 (9)
Na(1)-O(7)-O(6′)	83·2 (3)	83·0 (2)	83·3 (3)	82·7 (3)	Na(1)-O(7)-H(62)	82·8 (5)
Na(2)-O(7)-O(1)	93·0 (3)	92·5 (2)	92·1 (2)	92·8 (3)	Na(2)-O(7)-H(72)	92·6 (8)
Na(2)-O(7)-O(6)	102·5 (3)	103·1 (2)	102·9 (2)	103·6 (4)	Na(2)-O(7)-H(71)	104·3 (9)
Na(2)-O(7)-O(6′)	162·5 (4)	161·6 (2)	161·8 (2)	160·2 (4)	Na(2)-O(7)-H(62)	160·5 (5)
O(1)—O(7)-O(6)	108·9 (4)	107·9 (2)	107·7 (2)	109·1 (3)	H(72)-O(7)-H(71)	108·0 (1·2)
O(1)—O(7)-O(6′)	92·5 (3)	91·9 (2)	92·1 (2)	92·3 (3)	H(72)-O(7)-H(62)	92·7 (8)
O(6)—O(7)-O(6′)	91·4 (3)	92·6 (2)	92·6 (2)	92·8 (3)	H(71)-O(7)-H(72)	91·8 (9)

Table 1 (*cont.*)

Lengths (Å)						
O(8)—Na(1)	2·48 (1)	2·445 (5)	2·453 (6)	2·47 (1)		
O(8)—Na(1′)	2·37 (1)	2·351 (5)	2·356 (5)	2·35 (1)		
O(8)—O(1)	2·90 (1)	2·874 (5)	2·873 (6)	2·85 (1)		
O(8)—O(5)	2·91 (1)	2·872 (6)	2·875 (7)	2·90 (1)		
Angles (°)						
Na(1) -O(8)-Na(1′)	111·5 (3)	112·3 (2)	112·3 (2)	111·3 (4)		
Na(1) -O(8)-O(1)	112·8 (3)	113·6 (2)	113·3 (2)	114·0 (4)	Na(1) -O(8)-H(82)	109·4 (9)
Na(1) -O(8)-O(5)	107·2 (3)	108·3 (2)	108·1 (2)	107·6 (4)	Na(1) -O(8)-H(81)	104·3 (9)
Na(1′)-O(8)-O(1)	128·1 (3)	127·0 (2)	127·1 (2)	127·6 (4)	Na(1′)-O(8)-H(82)	128·5 (9)
Na(1′)-O(8)-O(5)	107·3 (3)	105·4 (2)	105·7 (2)	105·9 (4)	Na(1′)-O(8)-H(81)	98·4 (9)
O(1) —O(8)-O(5)	84·9 (3)	84·0 (2)	84·1 (2)	84·3 (2)	H(82) -O(8)-H(81)	100·9 (1·2)
Lengths (Å)						
O(9)—Na(1)	2·39 (1)	2·350 (5)	2·346 (5)	2·37 (1)		
O(9)—Na(2)	2·39 (1)	2·375 (5)	2·374 (5)	2·37 (1)		
O(9)—O(2)	2·77 (1)	2·742 (6)	2·738 (6)	2·74 (1)		
O(9)—O(4)	3·18 (1)	3·157 (6)	3·156 (6)	3·13 (1)		
Angles (°)						
Na(1)-O(9)-Na(2)	89·4 (3)	89·6 (2)	89·3 (2)	88·6 (4)		
Na(1)-O(9)-O(2)	123·3 (3)	124·2 (2)	124·7 (2)	124·5 (4)	Na(1)-O(9)-H(92)	121·2 (9)
Na(1)-O(9)-O(4)	114·2 (3)	113·8 (3)	113·9 (2)	114·6 (4)	Na(1)-O(9)-H(91)	114·8 (1·1)
Na(2)-O(9)-O(2)	96·7 (3)	96·9 (2)	97·0 (2)	96·5 (4)	Na(2)-O(9)-H(92)	101·1 (9)
Na(2)-O(9)-O(4)	122·9 (3)	121·8 (2)	121·7 (2)	121·8 (4)	Na(2)-O(9)-H(91)	125·2 (1·1)
O(2)—O(9)-O(4)	108·9 (3)	109·0 (2)	108·9 (2)	109·0 (3)	H(92)-O(9)-H(91)	105·9 (1·3)

the ICL 4/50 by Mr J. S. Knowles of the Department of Computing, University of Aberdeen.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

Progress of the refinement

As explained before, parameters were partially refined using the Elliott 803 computer. But this was very slow, and all three sets of data were consequently transferred to the ICL 4/50 for final processing. Only these final stages are described.

Original X-ray data (whose refinement is hereafter referred to as X-ray I) and the parameters from the early refinements of the neutron-diffraction data were used at the start of the final stages. Hydrogen atoms were included but their positions were not refined. Expect for Na^+, neutral atoms were assumed. This assumption was subsequently tested by substituting the curves for O^- in O(1) and O(2), the oxygen atoms of the H_2SiO_4 group which are not directly bonded to hydrogen. The only shift found of any size was in the temperature factors of these two atoms, and this was barely greater than the estimated standard deviation. The initial R value for 1415 reflexions was 0·2207, which dropped to 0·0926 after four cycles. Inspection of the F_o/F_c values showed that six strong reflexions at low angles were apparently suffering from extinction; since the available computer programs had no facilities for refining extinction coefficients, these reflexions were omitted from subsequent least-squares cycles. Three further cycles for the remaining 1409 reflexions reduced the R value to 0·0801. (Here, as elsewhere, reflexions omitted from the least-squares refinement were not included in calculating the R value). An attempt at this stage to refine the hydrogen parameters was unsuccessful, and it was decided to refine the neutron-diffraction data further before proceeding.

Using parameters from the 7th cycle of X-ray I, refinement of all parameters (including those of hydrogen atoms) began on 505 independent reflexions utilizing the neutron-diffraction data. After two cycles R dropped from its initial value of 0·0998 to 0·0718. Inspection of the F_o/F_c values showed that two reflexions had been included twice, and three further reflexions that showed very poor agreement appeared to be in error. The two duplicates were removed, and the three poor agreements were omitted from the least-squares calculations. After performing a further refinement cycle on the remaining 500 reflexions, none of the positional shifts was greater than the corresponding e.s.d., but considerable trouble was experienced with coupling of the temperature factors with the scale factor. An error analysis suggested that the weighting scheme used (which was simply $w=1$) was satisfactory, but it indicated that two more reflexions (both strong and apparently suffering from extinction) should be omitted. This was done, and after the coupled oscillation of scale and temperature factors had been controlled by manipulating the partial shift factors, parameters finally converged to those given in Table 2. At one point in the refinement, temperature factors for H(72) and H(91), which are notably different from those of the other hydrogen atoms, were altered to bring them more in line with the others. After one cycle they had returned almost to their original values. In the final cycle, all shifts were less than 1/100 of the respective e.s.d's, and the final R value was 0·0564. No refinement of neutron-scattering factors was attempted.

Table 2. *Parameters obtained in the several refinements of* $Na_2(H_2SiO_4).5H_2O$

Figures in parentheses give the e.s.d.'s corresponding to the least significant digit.

Final parameters

	Neutron diffraction (R=0·056)				X-ray I (R=0·071)				X-ray II (R=0·077)			
	x	y	z	B	x	y	z	B	x	y	z	B
Si	0·1271 (6)	0·0156 (*)	0·208 (1)	1·1 (1) Å^2	0·1260 (1)	0·0156 (*)	0·2091 (2)	1·33 (1) Å^2	0·1261 (1)	0·0156 (*)	0·2090 (2)	1·10 (2) Å^2
Na(1)	0·3836 (8)	0·462 (2)	0·926 (2)	1·7 (2)	0·3829 (2)	0·4657 (4)	0·9263 (4)	2·09 (3)	0·3823 (2)	0·4657 (4)	0·9253 (4)	1·93 (4)
Na(2)	0·1274 (8)	0·503 (2)	0·570 (2)	1·9 (2)	0·1263 (2)	0·5029 (5)	0·5653 (3)	2·42 (3)	0·1267 (2)	0·5031 (6)	0·5656 (5)	2·28 (4)
O(1)	0·2634 (5)	0·991 (1)	0·3328 (9)	1·3 (1)	0·2630 (3)	0·9919 (7)	0·3332 (5)	1·70 (5)	0·2624 (3)	0·9917 (7)	0·3325 (6)	1·49 (5)
O(2)	0·1010 (5)	0·987 (1)	−0·0468 (9)	1·6 (1)	0·1013 (3)	0·9881 (7)	−0·0487 (5)	1·70 (5)	0·1006 (3)	0·9883 (7)	−0·0495 (6)	1·55 (6)
O(3)	0·0453 (5)	0·818 (1)	0·3062 (9)	1·6 (1)	0·0475 (3)	0·8181 (7)	0·3089 (6)	1·72 (5)	0·0465 (3)	0·8186 (7)	0·3099 (6)	1·56 (6)
O(4)	0·0787 (5)	0·266 (1)	0·274 (1)	1·9 (1)	0·0804 (4)	0·2633 (7)	0·2743 (6)	2·13 (6)	0·0800 (4)	0·2649 (8)	0·2739 (7)	1·95 (6)
O(5)	0·2711 (6)	0·143 (1)	0·744 (1)	1·8 (1)	0·2742 (4)	0·1452 (8)	0·7486 (7)	2·46 (7)	0·2740 (4)	0·1464 (9)	0·7478 (7)	2·23 (7)
O(6)	0·4143 (5)	0·320 (1)	0·296 (1)	1·8 (1)	0·4139 (4)	0·3238 (8)	0·2945 (7)	2·43 (7)	0·4142 (4)	0·3239 (9)	0·2946 (7)	2·20 (7)
O(7)	0·3394 (5)	0·630 (1)	0·559 (1)	1·8 (1)	0·3388 (4)	0·6306 (8)	0·5633 (7)	2·36 (7)	0·3395 (4)	0·6307 (8)	0·5643 (7)	2·18 (7)
O(8)	0·4179 (5)	0·851 (1)	0·0585 (9)	1·8 (1)	0·4185 (4)	0·8511 (8)	0·0562 (6)	2·22 (6)	0·4184 (4)	0·8521 (8)	0·0560 (7)	2·13 (7)
O(9)	0·1852 (5)	0·557 (1)	0·948 (1)	1·8 (1)	0·1852 (4)	0·5578 (8)	0·9437 (6)	2·37 (7)	0·1854 (4)	0·5591 (8)	0·9438 (7)	2·01 (7)
H(3)	−0·0048 (9)	0·721 (2)	0·207 (2)	2·6 (2)								
H(4)	0·0125 (8)	0·337 (2)	0·189 (2)	2·3 (2)								
H(51)	0·209 (1)	0·087 (2)	0·809 (2)	3·1 (2)								
H(52)	0·268 (1)	0·087 (2)	0·607 (2)	2·9 (2)								
H(61)	0·361 (1)	0·190 (2)	0·314 (2)	2·9 (2)								
H(62)	0·493 (1)	0·258 (2)	0·344 (2)	2·9 (2)								
H(71)	0·366 (1)	0·525 (2)	0·467 (2)	3·1 (2)								
H(72)	0·3120 (8)	0·758 (2)	0·477 (2)	1·9 (2)								
H(81)	0·378 (1)	0·946 (2)	0·933 (2)	3·2 (2)								
H(82)	0·370 (1)	0·880 (2)	0·156 (2)	3·1 (2)								
H(91)	0·156 (1)	0·481 (2)	0·047 (2)	4·1 (3)								
H(92)	0·1617 (9)	0·712 (2)	0·962 (2)	2·7 (2)								

Original parameters (X-ray 0, R=0·111) (Jamieson & Dent Glasser, 1967)

	Coordinates (fractions of cell edge)			Isotropic temperature factor B
	x	y	z	
Si	0·1258 (2)	0·0156 (*)	0·2090 (3)	1·29 (2) Å^2
Na(1)	0·3828 (3)	0·4632 (8)	0·9264 (6)	2·10 (6)
Na(2)	0·1265 (3)	0·4999 (9)	0·5652 (6)	2·40 (6)
O(1)	0·2638 (5)	0·989 (1)	0·3362 (9)	1·4 (1)
O(2)	0·1017 (5)	0·989 (1)	0·951 (1)	1·4 (1)
O(3)	0·0482 (5)	0·813 (1)	0·312 (1)	1·5 (1)
O(4)	0·0807 (6)	0·261 (1)	0·279 (1)	1·7 (1)
O(5)	0·2730 (6)	0·145 (1)	0·745 (1)	2·3 (1)
O(6)	0·4130 (6)	0·321 (1)	0·301 (1)	2·3 (1)
O(7)	0·3383 (7)	0·634 (1)	0·562 (1)	2·5 (1)
O(8)	0·4190 (6)	0·854 (1)	0·058 (1)	2·2 (1)
O(9)	0·1841 (6)	0·553 (1)	0·944 (1)	2·2 (1)

* Since the origin of the cell is not fixed with respect to y in this space group, the y coordinate of the silicon atom was held constant to prevent oscillation of the entire set of y coordinates. The e.s.d. of this coordinate is therefore zero by definition. The y coordinates of Jamieson & Glasser's original data have been adjusted to the same origin.

While the X-ray I refinement was in progress, refinement of the new set of X-ray data (hereafter referred to as X-ray II) was started. Refinement of the non-hydrogen atoms began, utilizing final parameters from X-ray I for the non-hydrogen atoms and positional parameters from the second cycle of the neutron-diffraction refinement for the hydrogen atoms, but giving them a uniform temperature factor ($B=3{\cdot}5$). It was subsequently shown, as might be expected, that the X-ray refinement was insensitive to small changes in any hydrogen parameters. After three cycles the initial R value of 0·1362 dropped to 0·0901, and at this point the data were critically examined for poor agreements. It was found that the poor agreements corresponded exclusively to the strong reflexions, and again the cause appeared to be extinction. Accordingly, the 14 poorest agreements were omitted from subsequent calculations, together with one other very weak one listed as zero, probably by error. After two further refinement cycles, the R value reduced to 0·0768, and all positional shifts were less than the corresponding e.s.d's; but coupled oscillations existed in the scale and temperature factors, although not as severe as with the neutron-diffraction data. An error analysis suggested that the weighting scheme was somewhat unsatisfactory, and the parameters were changed accordingly (weighting schemes used are discussed later). This produced some significant shifts in the positional parameters and caused an initial slight rise in the R value, which subsequently reduced again to 0·0771; at this value the refinement converged. A further error analysis showed that the weighting scheme was now satisfactory. Replacement of the hydrogen parameters by those from the final cycle of the neutron-diffraction data caused no significant shifts in any other parameters; all shifts were less than $\frac{1}{5}$ of the corresponding e.s.d's in the final cycle. Final parameters for the non-hydrogen atoms are given in Table 2.

Further attention was now focused on the X-ray I refinement which was continued using the final hydrogen parameters from the neutron-diffraction refinement. As before, no significant shifts were produced by this change, but an error analysis at this point again suggested a change in the weighting scheme and the removal of a further 14 reflexions showing unsatisfactory agreement; as before, the cause of the trouble was believed to be extinction. These changes produced a number of significant shifts in the positional parameters. A subsequent error analysis showed that this final weighting scheme was satisfactory, and after performing three further cycles on the remaining 1392 reflexions, the refinement converged at $R=0{\cdot}0705$. All

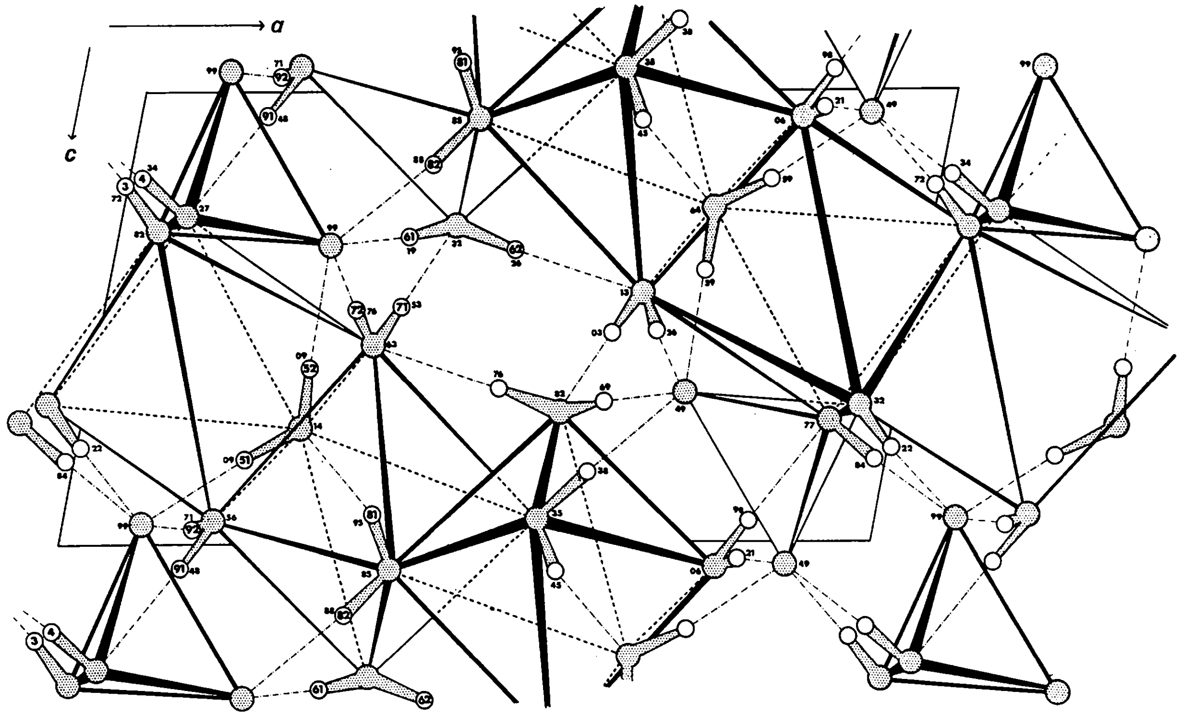

Fig. 1. Projection of the structure of $Na_2(H_2SiO_4).5H_2O$ on (010), adapted from Fig. 3 of Jamieson & Dent Glasser (1967). Open circles represent hydrogen atoms; shaded shapes represent oxygen atoms and their direct bonds to hydrogen. Hydrogen bonds are indicated by dot-dash lines. The remaining lines outline the coordination polyhedra about silicon and sodium (tetrahedra and octahedra respectively), but the central atoms are omitted. Figures within the open circles give the numbering of the hydrogen atoms of the asymmetric unit corresponding to Table 2; the numbering of the oxygen atoms can readily be deduced from that of the hydrogen atoms to which they are attached. The remaining numbers give the heights of the oxygen and hydrogen atoms in $b/100$.

shifts were then less than $\frac{1}{10}$ of the corresponding e.s.d's. Final parameters are given in Table 2.

Copies of the final F_o/F_c tables may be obtained from one of us (L.S.D.G.).

Discussion

Fig. 1, adapted from Jamieson & Dent Glasser (1967), shows the structure projected down **b** with the positions of the hydrogen atoms indicated. The hydrogen-bonding scheme proposed from the original X-ray structure analysis is confirmed, as is the conclusion that O(3) and O(4) of the SiO_4 group are, in fact, hydroxyl groups. The Si–O bond distances from all three of the later refinements correlate much more sensibly with this assignment.

There are still some discrepancies, from a comparison with the perfect, symmetry dictated, arrangement found in $Na_2(H_2SiO_4).8H_2O$, of 1·591 (8) and 1·672 (8)Å for Si–O and Si–OH, respectively. However, the mean values for Si–O and Si–OH in $Na_2(H_2SiO_4).5H_2O$ (calculated by combining X-ray I and X-ray II) work out to be 1·605 (3) and 1·669 (10) Å, respectively; these correlate reasonably well with the $Na_2(H_2SiO_4).8H_2O$ result.

All sets of results are at least consistent in suggesting that Si–O(3) is longer than Si–O(4) (although the difference is barely 3 × e.s.d. for the neutron-diffraction results); therefore one is justified in assuming that the effect is real and in considering what the explanation may be. Atom O(3) forms two bonds, of about average length, to Na(2) and one hydrogen bond of intermediate length to O(2). The only other close approach is to O(9) (> 3·0 Å), and this is definitely not a hydrogen bond. Atom O(4) forms one short bond to Na(2), one rather short hydrogen bond to O(2) and one very long hydrogen bond to O(9). Although this does provide some sort of explanation for the difference in bond lengths, it is by no means as clear cut as one would like.

All significant bond lengths and angles, together with those from the original structure analysis, are summarized in Table 1. Note that the excessively long hydrogen bond from O(4) to O(9), which is greater than 3·1 Å in all sets of results, involves H(91) which has a considerably higher temperature factor than the rest. Conversely, the hydrogen bond from O(1) to O(7) which is, for all sets of results, the shortest of those formed by water molecules involves H(72) which has an abnormally low temperature factor. All other hydrogen bonds formed by the water molecules lie between about 2·67 and 3·00 Å, and the temperature factors of the hydrogen atoms involved do not differ significantly. Examination of the two hydroxyl groups shows that the hydrogen bond formed by O(3) is longer than that formed by O(4). Considering all results, the difference is probably significant; the temperature factor for H(3) is larger than that for H(4), but the difference is not really significant.

Table 2 indicates that the final parameters for X-ray I and X-ray II agree within the limits of experimental error, whereas some of the X-ray I and X-ray 0 parameters differ significantly. Probably, the inclusion of some inaccurate data in the original refinement is largely responsible for this, and it is also likely that the different weighting schemes may have had some effect. In the original structure determination, the weighting scheme suggested by Cruickshank, Pilling, Bujosa, Lovell & Truter (1961) was used. We feel that this had tended to overweight the very weak reflexions, and that for diffractometer data, at least, it is preferable to use a scheme that gives maximum weight to the moderate reflexions and very little to the very weak and very strong ones. Accordingly, one of the alternative schemes provided by Dr F. R. Ahmed, and his collaborators was chosen for the final refinement. This sets $w = 1/\{1 + [(F_o - P_2)/P_1]^2\}$ and an appropriate choice of P_2 and P_1 was found to give an excellent distribution of $\sum w\Delta^2/n$ with both F_o and $\sin\theta$. It was noticed that changes in the values of P_1 and P_2 caused significant shifts in the atomic parameters, as did the omission of doubtful reflexions. Since the final X-ray I parameters agree far better with those from X-ray II than they did with the ones in the original structure determinations, it appears that the obtained values are more a function of refinement method than of any characteristics of the crystal from which the data were obtained.

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