

The crystal structure of natrolite*

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With 5 figures

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Auszug

Eine genaue Strukturbestimmung von Natrolith, $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$, mittels Fourier-Synthesen und der Methode der kleinsten Quadrate führte zu einer Bestätigung der von PAULING und TAYLOR vorgeschlagenen Struktur. Wasserstoffbrücken von 2,85 bzw. 2,99 Å Länge verbinden die Wassermoleküle mit Sauerstoffatomen des Alumosilikatgerüsts. Die Strukturbestimmung lieferte folgende Atomabstände: $1,62 \pm 0,01$ Å für die tetraedrische Si—O-Bindung, $1,75 \pm 0,02$ Å für die tetraedrische Al—O-Bindung und $2,37 \pm 0,02$ Å für die Na—O-Bindung.

Die Öffnungen zwischen benachbarten Ketten der Faserzeolithe formen ziemlich weite Kanäle, die die Struktur durchziehen. Die beobachteten Austauschvorgänge sind auf diese Kanäle zurückzuführen und nicht, wie dies lange vermutet wurde, auf die viel engeren, parallel zur Faserachse verlaufenden Kanäle.

Abstract

The structure of natrolite, $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$, proposed by PAULING and TAYLOR has been confirmed and refined by Fourier and least-squares methods using three-dimensional data obtained with $\text{CuK}\alpha$ radiation. The water is linked to oxygen atoms of the framework by hydrogen bonds having a length of 2.85 and 2.99 Å, respectively. The refined structure gives interatomic distances of 1.62 ± 0.01 Å for the tetrahedral Si—O bond, 1.75 ± 0.02 Å for the tetrahedral Al—O bond, and 2.37 ± 0.02 Å for the Na—O bond.

The openings between neighboring chains of the fibrous zeolites provide a system of open, intersecting channels. The dehydration and cation exchange phenomena must be attributed to these channels and not, as has long been supposed, to the much narrower channels parallel to the fiber axis.

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Introduction

The general features of many zeolite structures are sufficiently well known to provide possible explanations of their molecular-sieve and cation-exchange properties. More precise information about these structures is needed, however, to gain a full understanding of the nature of these porous crystals. Natrolite, a representative member of the fibrous zeolites, appeared to be well suited for a precise x-ray investigation with modern methods in order to further our knowledge of zeolite structures.

The structure of natrolite, $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$, was first proposed by PAULING (1930). It consists of characteristic chains of AlO_4 and

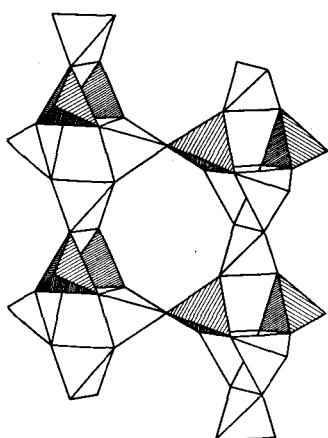


Fig. 1

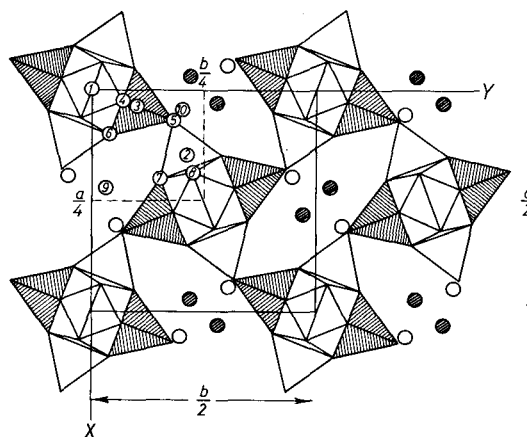


Fig. 2

Fig. 1. The chains in natrolite. The lower SiO_4 tetrahedra of a chain are linked to the upper AlO_4 tetrahedra (shaded) of neighboring chains.

Fig. 2. (001) projection of the natrolite structure. The repeat distances are $a/2$ and $b/2$ in this projection. The AlO_4 tetrahedra have been shaded. The notation used for the atoms of the asymmetric unit is as follows:

1. Si_I	3. Al	5. O_{II}	7. O_{IV}	9. Na
2. Si_{II}	4. O_I	6. O_{III}	8. O_V	10. H_2O

SiO_4 tetrahedra which are linked together in the way shown in Figs. 1 and 2. TAYLOR, MEEK and JACKSON (1933) subsequently determined the approximate locations of all the atoms in the structure. They calculated structure factors for a number of reflections and found good agreement with the observed values¹. This seemed to indicate that the

¹ The atomic coordinates given by TAYLOR *et al.* give a disagreement factor of 0.31 for the observable $hk0$ reflections.

structure was essentially correct. It was also demonstrated by TAYLOR (1934) that the chains found in natrolite can be linked in three different ways to give the structures of natrolite, thomsonite, and edingtonite.

Experimental work

The natrolite crystals used in this investigation were perfectly clear prisms of about 0.1 mm thickness from Aussig, Bohemia. Their composition was checked by a flamespectrometric determination of the cation content². The analysis gave $15.8 \pm 0.3\%$ Na₂O, which is only slightly below the expected value of 16.3% based on the formula. In addition 0.04% K₂O was found but no other cations such as calcium could be detected.

Unit cell and space group

The unit cell of natrolite is orthorhombic and contains 8 formula units of Na₂Al₂Si₃O₁₀ · 2 H₂O according to previous workers. Accurate cell dimensions were obtained from rotation photographs of the Straumanis type with the crystal rotating around the *c* axis. Values of *a* and *b* were calculated from high-angle reflections and the results plotted against sin²*θ* to allow for absorption and other corrections. The cell constant *c* was determined by means of the layer-line spacings. The cell dimensions obtained

$$\begin{aligned} a &= 18.30 \pm 0.01 \text{ \AA} \\ b &= 18.63 \pm 0.01 \text{ \AA} \\ c &= 6.60 \pm 0.02 \text{ \AA} \end{aligned}$$

are in agreement with the established values of *a* = 18.3, *b* = 18.6, and *c* = 6.6 Å. A different specimen of natrolite from Tick Canyon, California, gave the same cell constants within the limits of error.

The observed reflections clearly indicate a face-centered lattice, and the absence of reflections *h*0*l* and 0*k**l* with *h* + *l* ≠ 4*n* and *k* + *l* ≠ 4*n*, respectively, defines the space group as *C*_{2v}¹⁹—*Fdd*2. A weak spot corresponding to the forbidden reflection 402 gave rise to some doubt as to the correct space group in earlier investigations (HALLA and MEHL, 1930; HEY and BANNISTER, 1933). This weak reflection has also been observed and has been identified as a double reflection from the planes $\bar{1}11$ and $5\bar{1}1$ (Renninger effect).

² I am grateful to Mr. A. A. CHODOS, Division of Geological Sciences, California Institute of Technology, for practical assistance in the determination.

Intensity measurements

Intensities were obtained from equi-inclination Weissenberg photographs around [001] using filtered Cu radiation. A full set of three-dimensional data was collected using a small crystal of 0.08 mm thickness and 0.3 mm length. The use of the triple-film technique and long and short exposures produced an intensity range of about 1 to 6000. The intensities were estimated visually by comparison with standard intensity scales prepared with the same crystal. Only 15 of the 300 possible reflections with even indices were found to have intensities below the limit of observation. The intensity values were corrected for Lorentz and polarization factors in the usual way. Corrections for absorption effects were not applied.

The observed structure factors were initially placed on an absolute scale by the method of WILSON, which also provided a provisional temperature factor of 1.1 \AA^2 . The scaling factors were further adjusted in the course of the refinement by comparison with the calculated structure factors.

Verification and refinement of the structure

Procedure

The testing and first refinement of the structure were carried out with the use of the $hk0$ data because of the centrosymmetry of the (001) projection. The subsequent refinement in three dimensions was largely determined by the fact that the structure factors for reflections of the *even* layers can be reduced to

$$\left. \begin{aligned} A &= 16 \cos 2\pi hx \cos 2\pi ky \cos 2\pi lz \\ B &= 16 \cos 2\pi hx \cos 2\pi ky \sin 2\pi lz \end{aligned} \right\} \text{ for } h + k + l = 4n$$

and

$$\left. \begin{aligned} A &= -16 \sin 2\pi hx \sin 2\pi ky \cos 2\pi lz \\ B &= -16 \sin 2\pi hx \sin 2\pi ky \sin 2\pi lz \end{aligned} \right\} \begin{aligned} &\text{ for } h + k + l \\ &= 4n + 2 \end{aligned}$$

whereas the corresponding equations for reflections of the *odd* layers are considerably more complicated. The systematic refinement in three dimensions was therefore carried out by least-squares methods using the data from the even layers ($hk0$, $hk2$, and $hk4$) and the weighting system described by HUGHES (1941). Structure factors were finally calculated for the $hk1$ reflections to provide a check for the correctness of the z parameters which, strictly speaking, cannot be determined unambiguously on the basis of the even layers alone.

Hand calculations in the early stages of the refinement were followed by the use of the Datatron 205 electronic computer, at the California Institute of Technology, for the computation of Fourier syntheses, structure factors and least-squares parameter adjustments. The atomic scattering factors used in this study were those calculated by BERGHUIS *et al.* (1955) for Na and O, and TOMIE and STAM (1958) for Si and Al.

Testing of the structure

The positional parameters for the trial structure were derived on the basis of regular (Al,Si)O₄ tetrahedra of average dimension, and atomic scattering factors for Si were used in the beginning for both Si and Al positions in order to avoid any initial assumption about the Al—Si distribution. The positional parameters of the trial structure differed somewhat from the atomic coordinates given by TAYLOR, MEEK and JACKSON (1933). Calculated and observed structure factors for *hk0* gave an R_1 factor³ of 0.37 for the 96 observable reflections, and provided the signs for 68 reflections. A Fourier synthesis using these reflections confirmed the general features of the trial structure and suggested some parameter changes. After three stages of refinement by means of F_o and $(F_o - F_c)$ Fourier syntheses it was evident that the SiO₄ and AlO₄ tetrahedra are ordered in the way proposed by PAULING and TAYLOR. Definite sites were accordingly assigned to the Al and Si atoms in the subsequent refinement.

Two-dimensional refinement

Two more refinement cycles by means of difference syntheses and the use of individual isotropic temperature factors lowered R_1 to 0.214. Further refinement was achieved by least-squares calculations using all the *hk0* data. Individual isotropic temperature parameters were thereby used and shifts were also applied to the scaling factor. The R_1 factor was lowered to 0.077 in the course of seven such refinement cycles. The positional and temperature parameters obtained in this way are listed in Table 1.

Three-dimensional refinement

The three-dimensional refinement was also accomplished by means of the least-squares method. The *hk2* and *hk4* data were first refined independently in order to obtain sufficiently reliable values for the

³ Defined as $\sum |F_o| - |F_c| / \sum |F_o|$.

Table 1. Parameters obtained by the separate refinement of the layer-line data

		(hk0) refinement	(hk2) refinement	(hk4) refinement
(a) Positional parameters and <i>R</i> values				
Si _{II}	<i>x</i> ₂	0.1531	0.1535	0.1537
	<i>y</i> ₂	0.2114	0.2112	0.2116
	<i>z</i> ₂		0.6192	0.6172
Al	<i>x</i> ₃	0.0375	0.0375	0.0372
	<i>y</i> ₃	0.0937	0.0934	0.0934
	<i>z</i> ₃		0.6108	0.6118
O _I	<i>x</i> ₄	0.0225	0.0245	0.0234
	<i>y</i> ₄	0.0682	0.0688	0.0693
	<i>z</i> ₄		0.8508	0.8542
O _{II}	<i>x</i> ₅	0.0690	0.0712	0.0700
	<i>y</i> ₅	0.1840	0.1823	0.1826
	<i>z</i> ₅		0.6028	0.6004
O _{III}	<i>x</i> ₆	0.0987	0.0982	0.0987
	<i>y</i> ₆	0.0346	0.0345	0.0356
	<i>z</i> ₆		0.4965	0.4990
O _{IV}	<i>x</i> ₇	0.2060	0.2059	0.2064
	<i>y</i> ₇	0.1529	0.1525	0.1523
	<i>z</i> ₇		0.7270	0.7232
O _V	<i>x</i> ₈	0.1803	0.1782	0.1778
	<i>y</i> ₈	0.2266	0.2277	0.2283
	<i>z</i> ₈		0.3861	0.3847
Na	<i>x</i> ₉	0.2209	0.2206	0.2211
	<i>y</i> ₉	0.0302	0.0311	0.0308
	<i>z</i> ₉		0.6107	0.6123
H ₂ O	<i>x</i> ₁₀	0.0593	0.0579	0.0571
	<i>y</i> ₁₀	0.1874	0.1889	0.1886
	<i>z</i> ₁₀		0.1105	0.1100
	<i>R</i>	7.7%	7.0%	9.4%
(b) Thermal parameters <i>B</i> (in Å ²)				
Si _I		1.0	1.4	1.3
Si _{II}		0.8	1.1	1.1
Al		0.7	1.0	1.1
O _I		1.5	1.9	1.6
O _{II}		1.4	1.2	1.6
O _{III}		1.3	1.6	1.6
O _{IV}		1.0	1.3	1.4
O _V		1.5	2.2	1.6
Na		1.7	2.2	1.9
H ₂ O		2.9	2.9	2.4

respective scaling factors. Four cycles of refinements were carried out for each layer, and the disagreement factors attained were $R_2 = 0.070$ for $hk2$ and $R_3 = 0.094$ for $hk4$. The results in Table 1 show satisfactory agreement, on the whole, between the positional parameters derived from the different layers. The discrepancies in the temperature parameters, if significant at all, seem to indicate errors in the scaling, and possibly some anisotropy in the thermal vibrations.

The data from the even layers were eventually combined for the final least-squares refinement. A total of 9 very strong reflections in the small-angle region were left out in this refinement since they appeared to be strongly affected by absorption or extinction. Average values for the parameters (from Table 1) lead to an R factor of 0.090 for the 284 observable reflections with even indices. Six stages of refinement eventually lowered R to 0.083. The last cycle did not indicate any

Table 2. *Final parameters*

Atom	Final atomic coordinates (With standard deviations)			B values (in \AA^2)	Corresponding coordinates given by TAYLOR <i>et al.</i> (1933)		
	x	y	z		x	y	z
Si _I	0	0	0	1.07	0	0	0
Si _{II}	0.1532 (0.0002)	0.2112 (0.0002)	0.6181 (0.0010)	1.00	0.153	0.208	0.625
Al	0.0376 (0.0002)	0.0936 (0.0002)	0.6119 (0.0011)	1.12	0.036	0.089	0.625
O _I	0.0227 (0.0004)	0.0683 (0.0004)	0.8594 (0.0024)	1.81	0.014	0.067	0.875
O _{II}	0.0704 (0.0004)	0.1824 (0.0003)	0.6011 (0.0023)	1.10	0.069	0.181	0.625
O _{III}	0.0986 (0.0004)	0.0346 (0.0004)	0.4997 (0.0020)	1.55	0.097	0.042	0.500
O _{IV}	0.2063 (0.0002)	0.1526 (0.0004)	0.7166 (0.0022)	1.24	0.208	0.153	0.750
O _V	0.1799 (0.0002)	0.2272 (0.0004)	0.3860 (0.0020)	1.83	0.183	0.236	0.375
Na	0.2208 (0.0003)	0.0305 (0.0002)	0.6120 (0.0016)	2.00	0.222	0.028	0.625
H ₂ O	0.0564 (0.0005)	0.1893 (0.0004)	0.1085 (0.0038)	2.50	0.069	0.181	0.125

further decrease in the inaccuracy total $\sum w(F_o - F_c)^2$. The scaling factors of the individual layers were still subject to small adjustments in the last stages of the refinement. The final parameters are given in Table 2 as compared with the values found by TAYLOR.

Comparison of observed $hk1$ structure factors with the calculated values using the final parameters showed good agreement (Table 3) and resulted in a disagreement factor of 0.077 for the 103 observable reflections in the first layer line. The correctness of the z coordinates could thus be confirmed.

An $hk0$ Fourier synthesis based on the signs calculated from the final parameters is shown in Fig. 3.

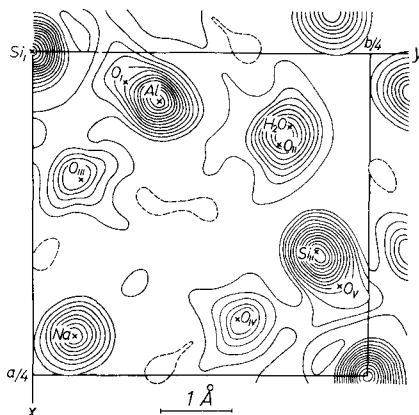


Fig. 3. Electron density projection along [001]. The contours are at intervals of 200 units = 2.35 e\AA^{-2} starting with zero (broken line).

Results

Standard deviations σ for the final atomic coordinates were calculated from the least-squares totals obtained in the last refinement cycle. They are listed with the coordinates in Table 2. The accuracy of the atomic positions of most atoms is around 0.005 \AA for the x and y coordinates and somewhat over 0.01 \AA for the z coordinates. The coordinates of the water molecules are by far the least accurate, with a σ -value of about 0.01 \AA for x and y , and 0.025 \AA for z .

Table 4 contains interatomic distances and bond angles together with estimated standard deviations. The standard deviations for the bond angles have values between 1° and 2° .

Table 3. Observed and calculated structure factors

h k l	$ F_o $	F_c	h k l	$ F_o $	F_c	h k l	$ F_o $	$ F_c $	h k l	$ F_o $	$ F_c $
0 4 0	201	241	10 18 0	31	25	1 21 1	14	20	13 3 1	91	91
0 8 0	186	-176	10 20 0	24	14	1 23 1	60	50	13 5 1	143	153
0 12 0	29	-25	12 0 0	39	-38	3 1 1	156	180	13 7 1	55	58
0 16 0	162	-166	12 2 0	30	26	3 3 1	44	42	13 9 1	112	97
0 20 0	40	36	12 4 0	181	194	3 5 1	271	314	13 11 1	87	75
0 24 0	21	28	12 6 0	118	121	3 7 1	69	58	13 13 1	79	78
2 2 0	166	191	12 8 0	28	26	3 9 1	64	60	13 15 1	48	45
2 4 0	165	178	12 10 0	50	42	3 11 1	82	82	13 17 1	< 14	12
2 6 0	92	-90	12 12 0	61	-58	3 13 1	81	80	13 19 1	22	19
2 8 0	74	79	12 14 0	64	-63	3 15 1	74	76	15 1 1	156	184
2 10 0	232	239	12 16 0	101	98	3 17 1	< 18	23	15 3 1	93	92
2 12 0	56	-52	12 18 0	34	-29	3 19 1	36	38	15 5 1	70	66
2 14 0	< 10	-12	12 20 0	31	-23	3 21 1	63	54	15 7 1	67	57
2 16 0	43	-35	14 2 0	36	-35	3 23 1	13	13	15 9 1	75	78
2 18 0	< 11	12	14 4 0	58	-53	5 1 1	199	219	15 11 1	89	86
2 20 0	< 10	3	14 6 0	218	232	5 3 1	272	299	15 13 1	39	33
2 22 0	117	104	14 8 0	29	28	5 5 1	10	12	15 15 1	53	47
4 0 0	170	194	14 10 0	16	14	5 7 1	29	28	15 17 1	52	42
4 2 0	143	-136	14 12 0	15	19	5 9 1	106	98	17 1 1	89	97
4 4 0	92	-88	14 14 0	71	62	5 11 1	26	23	17 3 1	< 18	11
4 6 0	55	54	14 16 0	43	-36	5 13 1	137	149	17 5 1	92	86
4 8 0	72	65	14 18 0	36	29	5 15 1	71	69	17 7 1	52	46
4 10 0	251	283	16 0 0	161	-155	5 17 1	81	77	17 9 1	57	59
4 12 0	201	203	16 2 0	< 11	-7	5 19 1	23	33	17 11 1	43	34
4 14 0	35	33	16 4 0	< 11	15	5 21 1	57	50	17 13 1	30	25
4 16 0	40	40	16 6 0	< 11	-7	5 23 1	51	55	17 15 1	48	45
4 18 0	66	-57	16 8 0	58	57	7 1 1	190	192	19 1 1	37	41
4 20 0	50	45	16 10 0	33	31	7 3 1	52	42	19 3 1	< 16	14
4 22 0	64	-51	16 12 0	106	98	7 5 1	25	26	19 5 1	23	27
6 2 0	111	-111	16 14 0	45	38	7 7 1	145	152	19 7 1	46	38
6 4 0	70	-75	16 16 0	167	162	7 9 1	117	109	19 9 1	81	80
6 6 0	169	-161	18 0 0	45	42	7 11 1	62	61	19 11 1	66	67
6 8 0	24	-19	18 2 0	19	15	7 13 1	17	28	19 13 1	34	32
6 10 0	133	125	18 4 0	112	101	7 15 1	76	71	21 1 1	27	27
6 12 0	91	-84	18 6 0	67	-60	7 17 1	55	50	21 3 1	66	60
6 14 0	254	261	18 8 0	24	21	7 19 1	49	47	21 5 1	44	45
6 16 0	< 11	11	18 10 0	23	19	7 21 1	55	61	21 7 1	50	53
6 18 0	127	121	18 12 0	< 6	-4	9 1 1	73	64	21 9 1	16	20
6 20 0	101	89	20 0 0	70	66	9 3 1	57	53	23 1 1	33	40
6 22 0	14	-9	20 2 0	< 10	5	9 5 1	104	102	23 3 1	27	33
8 0 0	162	-151	20 4 0	48	44	9 7 1	118	121	0 2 2	145	175
8 2 0	95	-101	20 6 0	71	-60	9 9 1	189	193	0 6 2	163	170
8 4 0	105	107	20 8 0	28	26	9 11 1	98	102	0 10 2	237	263
8 6 0	< 8	-5	20 10 0	16	-14	9 13 1	116	113	0 14 2	92	91
8 8 0	107	103	20 12 0	34	-28	9 15 1	108	100	0 18 2	78	85
8 10 0	89	83	22 0 0	100	93	9 17 1	78	68	0 22 2	66	60
8 12 0	< 10	-8	22 2 0	72	72	9 19 1	89	89			
8 14 0	< 11	-3	22 4 0	10	-8	9 21 1	29	26			
8 16 0	45	41	22 6 0	5	4	11 1 1	146	157	2 0 2	158	192
8 18 0	72	63	22 8 0	155	166	11 3 1	99	103	2 2 2	184	224
8 20 0	29	26	1 3 1	197	200	11 5 1	15	18	2 4 2	126	123
8 22 0	10	1	1 5 1	181	191	11 7 1	64	60	2 6 2	170	194
10 2 0	227	238	1 7 1	79	74	11 9 1	103	99	2 8 2	63	59
10 4 0	257	-287	1 9 1	147	156	11 11 1	121	129	2 10 2	50	47
10 6 0	149	153	1 11 1	74	72	11 13 1	98	95	2 12 2	142	149
10 8 0	58	-51	1 13 1	173	185	11 15 1	67	54	2 14 2	20	19
10 10 0	185	-192	1 15 1	126	127	11 17 1	46	42	2 16 2	17	18
10 12 0	46	-33	1 17 1	< 17	17	11 19 1	76	71	2 18 2	94	98
10 14 0	19	-12							2 20 2	73	73
10 16 0	44	-37				13 1 1	64	71	2 22 2	44	41

Table 3 (continued)

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c
4	2	2	144	158	12	2	2	103	105	0	4	4	28	24	8	16	4	53	46
4	4	2	130	120	12	4	2	101	111	0	8	4	173	192	8	18	4	97	106
4	6	2	40	38	12	6	2	112	117	0	12	4	76	80					
4	8	2	148	161	12	8	2	34	38	0	16	4	107	115	10	2	4	40	41
4	10	2	115	108	12	10	2	16	12	0	20	4	51	45	10	4	4	188	200
4	12	2	96	106	12	12	2	10	8						10	6	4	44	37
4	14	2	142	151	12	14	2	35	83	2	2	4	73	78	10	8	4	31	26
4	16	2	78	82	12	16	2	36	35	2	4	4	123	129	10	10	4	126	140
4	18	2	79	74	12	18	2	56	51	2	6	4	110	118	10	12	4	51	43
4	20	2	102	111						2	8	4	170	191	10	14	4	60	64
4	22	2	71	68	14	0	2	112	126	2	10	4	25	19	10	16	4	21	18
					14	2	2	30	30	2	12	4	52	50	10	18	4	14	14
					14	4	2	137	154	2	14	4	48	46					
6	0	2	132	129	14	6	2	71	77	2	16	4	42	38	12	0	4	73	77
6	2	2	160	177	14	8	2	61	58	2	18	4	50	48	12	2	4	56	52
6	4	2	47	47	14	10	2	105	110	2	20	4	31	29	12	4	4	16	8
6	6	2	39	34	14	12	2	96	105						12	6	4	125	138
6	8	2	100	103	14	14	2	16	13	4	0	4	41	38	12	8	4	50	48
6	10	2	52	49	14	16	2	66	68	4	2	4	122	142	12	10	4	72	71
6	12	2	103	100	14	18	2	50	59	4	4	4	80	81	12	12	4	76	81
6	14	2	96	91						4	6	4	141	155	12	14	4	44	39
6	16	2	90	91	16	2	2	16	11	4	8	4	65	58	12	16	4	< 6	8
6	18	2	57	52	16	4	2	88	105	4	10	4	193	220					
6	20	2	70	70	16	6	2	84	86	4	12	4	18	16	14	2	4	60	64
6	22	2	37	36	16	8	2	30	31	4	14	4	34	29	14	4	4	24	24
					16	10	2	78	78	4	16	4	58	52	14	6	4	74	68
8	2	2	92	89	16	12	2	39	37	4	18	4	31	26	14	8	4	38	33
8	4	2	130	140	16	14	2	59	59	4	20	4	42	42	14	10	4	50	43
8	6	2	103	104	16	16	2	14	8						14	12	4	54	49
8	8	2	239	282						6	2	4	105	111	14	14	4	47	44
8	10	2	55	51	18	0	2	68	69	6	4	4	153	173					
8	12	2	54	56	18	2	2	87	98	6	6	4	148	164	16	0	4	125	137
8	14	2	77	78	18	4	2	61	64	6	8	4	36	33	16	2	4	34	29
8	16	2	57	53	18	6	2	59	64	6	10	4	18	13	16	4	4	46	42
8	18	2	52	51	18	8	2	39	40	6	12	4	124	130	16	6	4	47	49
8	20	2	40	39	18	10	2	56	58	6	14	4	70	71	16	8	4	26	21
10	0	2	215	238	18	12	2	40	41	6	16	4	34	32	16	10	4	< 7	0
10	2	2	42	38	18	14	2	42	49	6	18	4	13	9	16	12	4	< 6	8
10	4	2	128	133						6	20	4	91	96					
10	6	2	22	18	20	2	2	90	95						18	2	4	41	40
10	8	2	98	102	20	4	2	76	86	8	0	4	125	139	18	4	4	15	19
10	10	2	119	118	20	6	2	49	45	8	2	4	158	180	18	6	4	29	27
10	12	2	41	42	20	8	2	44	43	8	4	4	69	64	18	8	4	106	118
10	14	2	109	117	20	10	2	44	48	8	6	4	61	64	18	10	4	37	42
10	16	2	73	73						8	8	4	36	36					
10	18	2	74	67	22	0	2	60	62	8	10	4	27	25	20	0	4	51	53
10	20	2	32	25	22	2	2	27	25	8	12	4	59	59	20	2	4	23	26
					22	4	2	39	38	8	14	4	44	38	20	4	4	20	25

The following average interatomic distances calculated from the data in Table 4 are of particular interest:

Si—O : $1.62 \pm 0.01 \text{ \AA}$

Al—O : $1.75 \pm 0.02 \text{ \AA}$

Na—O : $2.37 \pm 0.02 \text{ \AA}$

Na—H₂O: $2.38 \pm 0.03 \text{ \AA}$.

Table 4. *Interatomic distances and bond angles calculated from the final parameters*

<i>Interatomic distances in Å</i>			
<i>SiO₄ tetrahedra:</i>			
Si _I -O _I	1.63 ± 0.01	O _I -O _I	2.67 ± 0.02
Si _I -O _V	1.62 ± 0.01	O _I -O _V	2.64 ± 0.02
Si _{II} -O _{II}	1.61 ± 0.02	O _V -O _V	2.70 ± 0.02
Si _{II} -O _{III}	1.62 ± 0.02	O _{II} -O _{III}	2.60 ± 0.02
Si _{II} -O _{IV}	1.60 ± 0.02	O _{II} -O _{IV}	2.66 ± 0.02
Si _{II} -O _V	1.64 ± 0.02	O _{II} -O _V	2.60 ± 0.02
		O _{III} -O _{IV}	2.67 ± 0.02
		O _{III} -O _V	2.68 ± 0.02
		O _{IV} -O _V	2.63 ± 0.02
<i>AlO₄ tetrahedra:</i>			
Al-O _I	1.73 ± 0.02	O _I -O _{II}	2.86 ± 0.02
Al-O _{II}	1.76 ± 0.02	O _I -O _{III}	2.82 ± 0.02
Al-O _{III}	1.73 ± 0.02	O _I -O _{IV}	2.91 ± 0.02
Al-O _{IV}	1.77 ± 0.02	O _{II} -O _{III}	2.88 ± 0.02
		O _{II} -O _{IV}	2.78 ± 0.02
		O _{III} -O _{IV}	2.86 ± 0.02
<i>Cations and water:</i>			
Na-O _{III}	2.36 ± 0.02	H ₂ O-O _I	2.86 ± 0.04
Na-O _{IV}	2.39 ± 0.02	H ₂ O-O _{II}	3.26 ± 0.04
Na-H ₂ O(1)	2.40 ± 0.03	H ₂ O-O _{III}	3.95 ± 0.04
Na-H ₂ O(2)	2.36 ± 0.03	H ₂ O-O _{IV}	3.45 ± 0.04
Na-O _{II} (1)	2.51 ± 0.02	H ₂ O-O _V	2.99 ± 0.04
Na-O _{II} (2)	2.62 ± 0.02		
Na-Na	3.65 ± 0.02		
<i>Bond angles</i>			
O _I -Si _I -O _I	110.5°	O _I -Al-O _{II}	110.5°
O _I -Si _I -O _V	108.2°	O _I -Al-O _{III}	109.5°
O _I -Si _I -O _V	108.6°	O _I -Al-O _{IV}	113.1°
O _V -Si _I -O _V	112.8°	O _{II} -Al-O _{III}	111.0°
		O _{II} -Al-O _{IV}	108.1°
O _{II} -Si _{II} -O _{III}	107.4°	O _{III} -Al-O _{IV}	109.6°
O _{II} -Si _{II} -O _{IV}	111.8°		
O _{II} -Si _{II} -O _V	106.7°	O _{III} -Na-O _{IV}	87.4°
O _{III} -Si _{II} -O _{IV}	111.7°	O _{III} -Na-H ₂ O(1)	92.2°
O _{III} -Si _{II} -O _V	110.8°	O _{IV} -Na-H ₂ O(2)	93.0°
O _{IV} -Si _{II} -O _V	108.8°	H ₂ O-Na-H ₂ O	141.7°
Si _I -O _V -Si _{II}	143.4°	O _I -H ₂ O-O _V	134.5°
Si _I -O _I -Al	162.3°		
Si _{II} -O _{II} -Al	129.1°		
Si _{II} -O _{III} -Al	138.7°		

Discussion of the structure

The aluminosilicate framework of natrolite has several interesting features. The dehydration and cation exchange phenomena have long been attributed to the channels parallel to the c axis (TAYLOR, 1934), which can easily be recognized in Fig. 2. The openings between neighboring chains (as shown in Fig. 1), however, provide an additional system of intersecting channels which are even more open. These channels have a minimum free diameter of 2.60 Å, whereas 2.08 Å is obtained for the corresponding width of the established channels parallel to the c axis. These data, however, do not represent limiting values for the size of exchangeable ions and molecules as in the case of rigid zeolite frameworks (e.g. BARRER and MEIER, 1958). The absence of a sieve action is due to the ability of the chains to rotate around the c axis to some extent, which changes the size of the openings. The observed changes in the cell constants a and b of ion-exchanged natrolite samples (HEY and BANNISTER, 1933) provide evidence for the changes in the orientation of the chains. Even so, it appears unlikely that sorption and exchange diffusion processes should take place along the narrower and much longer channels parallel to the fiber axis as has been supposed. The same applies to the related structures of thomsonite and edingtonite where the difference in the openness of the established channels ($\parallel c$) and the intersecting main channels ($\perp c$) is even more striking.

The ordered arrangement of the Al and Si atoms first proposed by PAULING (1930) has been fully confirmed. It is noteworthy that any other distribution of the Al and Si atoms in the unit cell would not only lower the symmetry but would also lead to neighboring AlO_4 tetrahedra with shared oxygen atoms requiring a bond of strength 0.5 for saturation. The requirements of the electrostatic valence rule, as well as extensive experimental evidence collected by LOEWENSTEIN (1954), appear to rule out such an arrangement (even in the presence of polyvalent cations). It may also be shown that the Al/Si ratio in natrolite cannot exceed the value of 2:3 in an ordered framework without Al—O—Al bonds⁴.

The average interatomic distances of 1.62 ± 0.01 Å for the Si—O bond and 1.75 ± 0.02 Å for the Al—O bond do not differ significantly from the values of 1.60 ± 0.01 Å and 1.78 ± 0.02 Å accepted by SMITH (1954). The Si—O bond length is in full agreement with the

⁴ A detailed account of the Al—Si distribution in fibrous zeolites will appear elsewhere.

