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The crystal structure of natrolite*

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With 5 figures

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Auszug

Eine genaue Strukturbestimmung von Natrolith, $Na_2Al_2Si_3O_{10} \cdot 2H_2O$, 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 Alumosilikatgerüstes. Die Strukturbestimmung lieferte folgende Atomabstände: 1,62 ± 0,01 Å für die tetraedrische Si—O-Bindung, 1,75 ± 0,02 Å für die tetraedrische Al—O-Bindung und 2,37 ± 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, $Na_2Al_2Si_3O_{10} \cdot 2H_2O$, proposed by Pauling and Taylor has been confirmed and refined by Fourier and least-squares methods using three-dimensional data obtained with Cu$K\alpha$ 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, $Na_2Al_2Si_3O_{10} \cdot 2\ H_2O$, was first proposed by PAULING (1930). It consists of characteristic chains of AlO_4 and 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 values[1]. This seemed to indicate that the

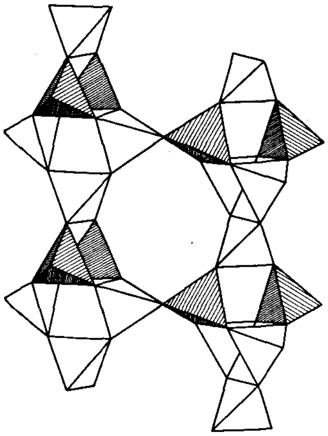

Fig. 1

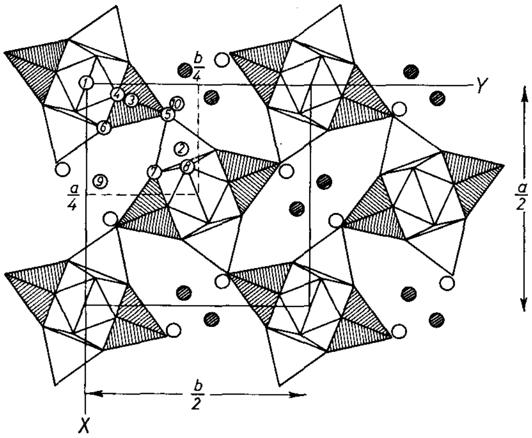

Fig. 2

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

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[1] The atomic coordinates given by TAYLOR *et al.* give a disagreement factor of 0.31 for the observable *hk*0 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 content[2]. The analysis gave $15.8 \pm 0.3\%$ Na_2O, which is only slightly below the expected value of 16.3% based on the formula. In addition 0.04% K_2O 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 $Na_2Al_2Si_3O_{10} \cdot 2\,H_2O$ 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 $\sin^2\theta$ to allow for absorption and other corrections. The cell constant c was determined by means of the layer-line spacings. The cell dimensions obtained

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

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 $h0l$ and $0kl$ with $h + l \neq 4\,n$ and $k + l \neq 4\,n$, respectively, defines the space group as C_{2v}^{19}—$Fdd2$. 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).

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[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 Å^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

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

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 Tomiie 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 $(\mathrm{Al,Si})\mathrm{O}_4$ 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 factor[3] 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 SiO_4 and AlO_4 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

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[3] Defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$.

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

		($hk0$) *refinement*	($hk2$) *refinement*	($hk4$) *refinement*
(*a*) Positional parameters and R values				
$\mathrm{Si}_{\mathrm{II}}$	x_2	0.1531	0.1535	0.1537
	y_2	0.2114	0.2112	0.2116
	z_2		0.6192	0.6172
Al	x_3	0.0375	0.0375	0.0372
	y_3	0.0937	0.0934	0.0934
	z_3		0.6108	0.6118
O_{I}	x_4	0.0225	0.0245	0.0234
	y_4	0.0682	0.0688	0.0693
	z_4		0.8508	0.8542
O_{II}	x_5	0.0690	0.0712	0.0700
	y_5	0.1840	0.1823	0.1826
	z_5		0.6028	0.6004
$\mathrm{O}_{\mathrm{III}}$	x_6	0.0987	0.0982	0.0987
	y_6	0.0346	0.0345	0.0356
	z_6		0.4965	0.4990
O_{IV}	x_7	0.2060	0.2059	0.2064
	y_7	0.1529	0.1525	0.1523
	z_7		0.7270	0.7232
O_{V}	x_8	0.1803	0.1782	0.1778
	y_8	0.2266	0.2277	0.2283
	z_8		0.3861	0.3847
Na	x_9	0.2209	0.2206	0.2211
	y_9	0.0302	0.0311	0.0308
	z_9		0.6107	0.6123
H_2O	x_{10}	0.0593	0.0579	0.0571
	y_{10}	0.1874	0.1889	0.1886
	z_{10}		0.1105	0.1100
	R	7.7%	7.0%	9.4%
(*b*) Thermal parameters B (in Å^2)				
Si_{I}		1.0	1.4	1.3
$\mathrm{Si}_{\mathrm{II}}$		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
$\mathrm{O}_{\mathrm{III}}$		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_2O		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 Å^2)	Corresponding coordinates given by TAYLOR *et al.* (1933)		
	x	y	z		x	y	z
Si$_{\text{I}}$	0	0	0	1.07	0	0	0
Si$_{\text{II}}$	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$_{\text{I}}$	0.0227 (0.0004)	0.0683 (0.0004)	0.8594 (0.0024)	1.81	0.014	0.067	0.875
O$_{\text{II}}$	0.0704 (0.0004)	0.1824 (0.0003)	0.6011 (0.0023)	1.10	0.069	0.181	0.625
O$_{\text{III}}$	0.0986 (0.0004)	0.0346 (0.0004)	0.4997 (0.0020)	1.55	0.097	0.042	0.500
O$_{\text{IV}}$	0.2063 (0.0002)	0.1526 (0.0004)	0.7166 (0.0022)	1.24	0.208	0.153	0.750
O$_{\text{V}}$	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_2O	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 $\Sigma\, w(F_o - F_c)^2$. 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.

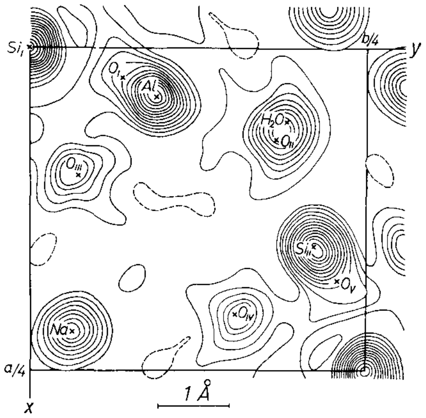

Fig. 3. Electron density projection along [001]. The contours are at intervals of 200 units = 2.35 eÅ^{-2} starting with zero (broken line).

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 Å for the x and y coordinates and somewhat over 0.01 Å for the z coordinates. The coordinates of the water molecules are by far the least accurate, with a σ-value of about 0.01 Å for x and y, and 0.025 Å 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	$\lvert F_o \rvert$	F_c
0	4	0	201	241
0	8	0	186	−176
0	12	0	29	− 25
0	16	0	162	−166
0	20	0	40	36
0	24	0	21	28
2	2	0	166	191
2	4	0	165	178
2	6	0	92	− 90
2	8	0	74	79
2	10	0	232	239
2	12	0	56	− 52
2	14	0	< 10	− 12
2	16	0	43	− 35
2	18	0	< 11	12
2	20	0	< 10	3
2	22	0	117	104
4	0	0	170	194
4	2	0	143	−136
4	4	0	92	− 88
4	6	0	55	54
4	8	0	72	65
4	10	0	251	283
4	12	0	201	203
4	14	0	35	33
4	16	0	40	40
4	18	0	66	− 57
4	20	0	50	45
4	22	0	64	− 51
6	2	0	111	−111
6	4	0	70	− 75
6	6	0	169	−161
6	8	0	24	− 19
6	10	0	133	125
6	12	0	91	− 84
6	14	0	254	261
6	16	0	< 11	11
6	18	0	127	121
6	20	0	101	89
6	22	0	14	− 9
8	0	0	162	−151
8	2	0	95	−101
8	4	0	105	107
8	6	0	< 8	− 5
8	8	0	107	103
8	10	0	89	83
8	12	0	< 10	− 8
8	14	0	< 11	− 3
8	16	0	45	41
8	18	0	72	65
8	20	0	29	26
8	22	0	10	1
10	2	0	227	238
10	4	0	257	−287
10	6	0	149	153
10	8	0	58	− 51
10	10	0	185	−192
10	12	0	46	− 33
10	14	0	19	− 12
10	16	0	44	− 37
10	18	0	31	25
10	20	0	24	14
12	0	0	39	− 38
12	2	0	30	26
12	4	0	181	194
12	6	0	118	121
12	8	0	28	26
12	10	0	50	42
12	12	0	61	− 58
12	14	0	64	− 63
12	16	0	101	98
12	18	0	34	− 29
12	20	0	31	− 23
14	2	0	36	− 35
14	4	0	58	− 53
14	6	0	218	232
14	8	0	29	28
14	10	0	16	14
14	12	0	15	19
14	14	0	71	62
14	16	0	43	− 36
14	18	0	36	29
16	0	0	161	−155
16	2	0	< 11	− 7
16	4	0	< 11	15
16	6	0	< 11	− 7
16	8	0	58	57
16	10	0	33	31
16	12	0	106	98
16	14	0	45	38
16	16	0	167	162
18	2	0	45	42
18	4	0	19	15
18	6	0	112	101
18	8	0	67	− 60
18	10	0	24	21
18	12	0	23	19
18	14	0	< 6	− 4
20	0	0	70	66
20	2	0	< 10	5
20	4	0	48	44
20	6	0	71	− 60
20	8	0	28	26
20	10	0	16	− 14
20	12	0	34	− 28
22	2	0	100	93
22	4	0	72	72
22	6	0	10	− 8
22	8	0	5	4
				$\lvert F_c \rvert$
1	3	1	155	166
1	5	1	197	200
1	7	1	181	191
1	9	1	79	74
1	11	1	147	156
1	13	1	74	72
1	15	1	173	185
1	17	1	126	127
1	19	1	< 17	17
1	21	1	14	20
1	23	1	60	50
3	1	1	156	180
3	3	1	44	42
3	5	1	271	314
3	7	1	69	58
3	9	1	64	60
3	11	1	82	82
3	13	1	81	80
3	15	1	74	76
3	17	1	< 18	23
3	19	1	36	38
3	21	1	63	54
3	23	1	13	13
5	1	1	199	219
5	3	1	272	299
5	5	1	10	12
5	7	1	29	28
5	9	1	106	98
5	11	1	26	23
5	13	1	137	149
5	15	1	71	69
5	17	1	81	77
5	19	1	23	33
5	21	1	57	50
5	23	1	51	55
7	1	1	190	192
7	3	1	52	42
7	5	1	25	26
7	7	1	145	152
7	9	1	117	109
7	11	1	62	61
7	13	1	17	28
7	15	1	76	71
7	17	1	55	50
7	19	1	49	47
7	21	1	55	61
9	1	1	73	64
9	3	1	57	53
9	5	1	104	102
9	7	1	118	121
9	9	1	189	193
9	11	1	98	102
9	13	1	116	113
9	15	1	108	100
9	17	1	78	68
9	19	1	89	89
9	21	1	29	26
11	1	1	146	157
11	3	1	99	103
11	5	1	15	18
11	7	1	64	60
11	9	1	103	99
11	11	1	121	129
11	13	1	98	95
11	15	1	67	54
11	17	1	46	42
11	19	1	76	71
13	1	1	64	71
13	3	1	91	91
13	5	1	143	153
13	7	1	55	58
13	9	1	112	97
13	11	1	87	75
13	13	1	79	78
13	15	1	48	45
13	17	1	< 14	12
13	19	1	22	19
15	1	1	156	184
15	3	1	93	92
15	5	1	70	66
15	7	1	67	57
15	9	1	75	78
15	11	1	89	86
15	13	1	39	33
15	15	1	53	47
15	17	1	52	42
17	1	1	89	97
17	3	1	< 18	11
17	5	1	92	86
17	7	1	52	46
17	9	1	57	59
17	11	1	43	34
17	13	1	30	25
17	15	1	48	45
19	1	1	37	41
19	3	1	< 16	14
19	5	1	23	27
19	7	1	46	38
19	9	1	81	80
19	11	1	66	67
19	13	1	34	32
21	1	1	27	27
21	3	1	66	60
21	5	1	44	45
21	7	1	50	53
21	9	1	16	20
23	1	1	33	40
23	3	1	27	33
0	2	2	145	175
0	6	2	163	170
0	10	2	237	263
0	14	2	92	91
0	18	2	78	85
0	22	2	66	60
2	0	2	158	192
2	2	2	184	224
2	4	2	126	123
2	6	2	170	194
2	8	2	63	59
2	10	2	50	47
2	12	2	142	149
2	14	2	20	19
2	16	2	17	18
2	18	2	94	98
2	20	2	73	73
2	22	2	44	41

Table 3 *(continued)*

h k l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h k l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h k l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h k l	$\lvert F_o \rvert$	$\lvert F_c \rvert$
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	113	108	12 10 2	16	12	0 20 4	51	43	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
6 0 2	132	129	14 4 2	137	154	2 14 4	48	46			
6 2 2	160	177	14 6 2	71	77	2 16 4	42	38	12 0 4	73	77
6 4 2	47	47	14 8 2	61	58	2 18 4	50	48	12 2 4	56	52
6 6 2	39	34	14 10 2	105	110	2 20 4	31	29	12 4 4	16	8
6 8 2	100	103	14 12 2	96	105				12 6 4	125	138
6 10 2	52	49	14 14 2	16	13	4 0 4	41	38	12 8 4	50	48
6 12 2	103	100	14 16 2	66	68	4 2 4	122	142	12 10 4	72	71
6 14 2	96	91	14 18 2	50	59	4 4 4	80	81	12 12 4	76	81
6 16 2	90	91				4 6 4	141	155	12 14 4	44	39
6 18 2	57	52	16 2 2	16	11	4 8 4	65	58	12 16 4	< 6	8
6 20 2	70	70	16 4 2	88	105	4 10 4	193	220			
6 22 2	37	36	16 6 2	84	86	4 12 4	18	16	14 2 4	60	64
			16 8 2	30	31	4 14 4	34	29	14 4 4	24	24
8 2 2	92	89	16 10 2	78	78	4 16 4	58	52	14 6 4	74	68
8 4 2	130	140	16 12 2	39	37	4 18 4	31	26	14 8 4	38	33
8 6 2	103	104	16 14 2	59	59	4 20 4	42	42	14 10 4	50	43
8 8 2	239	282	16 16 2	14	8				14 12 4	54	49
8 10 2	55	51				6 2 4	105	111	14 14 4	47	44
8 12 2	54	56	18 0 2	68	69	6 4 4	153	173			
8 14 2	77	78	18 2 2	87	98	6 6 4	148	164	16 0 4	125	137
8 16 2	57	53	18 4 2	61	64	6 8 4	36	33	16 2 4	34	29
8 18 2	52	51	18 6 2	59	64	6 10 4	18	13	16 4 4	46	42
8 20 2	40	39	18 8 2	39	40	6 12 4	124	130	16 6 4	47	49
			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 ± 0.01 Å

Al—O : 1.75 ± 0.02 Å

Na—O : 2.37 ± 0.02 Å

Na—H_2O: 2.38 ± 0.03 Å .

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

Interatomic distances in Å

SiO_4 tetrahedra:

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

AlO_4 tetrahedra:

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

Cations and water:

Na—O_{III}	2.36 ± 0.02	H_2O—O_I	2.86 ± 0.04
Na—O_{IV}	2.39 ± 0.02	H_2O—O_{II}	3.26 ± 0.04
Na—$H_2O(1)$	2.40 ± 0.03	H_2O—O_{III}	3.95 ± 0.04
Na—$H_2O(2)$	2.36 ± 0.03	H_2O—O_{IV}	3.45 ± 0.04
Na—$O_{II}(1)$	2.51 ± 0.02	H_2O—O_V	2.99 ± 0.04
Na—$O_{II}(2)$	2.62 ± 0.02		
Na—Na	3.65 ± 0.02		

Bond angles

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—$H_2O(1)$	92.2°
O_{III}—Si_{II}—O_V	110.8°	O_{IV}—Na—$H_2O(2)$	93.0°
O_{IV}—Si_{II}—O_V	108.8°	H_2O—Na—H_2O	141.7°
Si_I—O_V—Si_{II}	143.4°	O_I—H_2O—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 bonds[4].

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

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

recent results of 1.62 ± 0.01 Å found in danburite, $CaB_2Si_2O_8$, by Johansson (1959) and 1.61 ± 0.01 Å in coesite, the high-pressure form of silica, as determined by Zoltai and Buerger (1959). The somewhat low value for the Al—O bond distance seems to suggest some substitution of Al atoms by Si as indicated by the result of the alkali determination. It should be noted, however, that the observed difference is within the limits of error and thus does not represent sufficient evidence for any substitution of Al by Si. Moreover, the extensive analytical data reported by Hey and Bannister (1933) clearly indicate a fixed Al/Si ratio of 2:3.

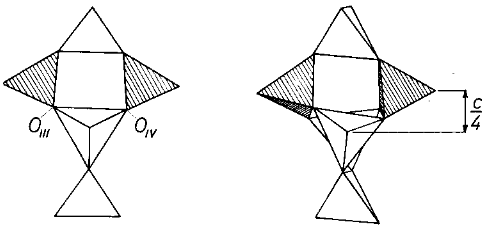

Fig. 4

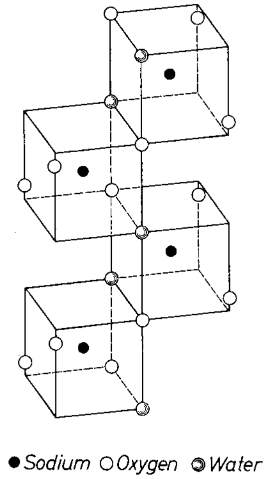

Fig. 5

Fig. 4. Ideal and distorted natrolite chain.

Fig. 5. The arrangement of the sodium ions and water molecules in natrolite (slightly idealized).

The undistorted natrolite chain built up of regular tetrahedra of the established size (Smith, 1954) has a repeat distance of 6.61 Å which is in good agreement with the observed value of $c = 6.60$ Å. The oxygen atoms O_{II} which provide the links for neighboring chains are at heights differing by 1.73 Å in the undistorted chain. The value required by the structure is $\frac{c}{4} = 1.65$ Å, however, which should give rise to some distortion of the chains. The bond angles listed in Table 4 show that the tetrahedra undergo some deformation as a result of this requirement. The deviations from regularity of the tetrahedra are mostly within the limits of error of this determination, however. By far the most significant irregularity, on the other hand, lies in the difference of the z parameters of O_{III} and O_{IV} (0.4997 and 0.4666 in the chain of Fig. 4). This difference indicates twisted chains as illustrated in Fig. 4. The requirement mentioned above as well as the electrostatic charge distribution discussed below may account for the twisting of the chains. The Si—O—(Si,Al) bond angles in natrolite (Table 4) are within the range of about 130°—160° normally observed in such structures.

The arrangement of the cations and water molecules in the zeolite is shown in Fig. 5. Each sodium atom has four nearest neighbors, two oxygen atoms (O_{III} and O_{IV}) at an average distance of 2.37 Å and two water molecules at an average distance of 2.38 Å. These interatomic distances are considerably shorter than the value of 2.6 Å found in earlier investigations (Pauling, 1930; Taylor *et al.*, 1933) and compare well with the value of 2.35 Å for the ionic Na—O bond length (Pauling, 1952). Two more oxygen atoms lie somewhat further away from the sodium atoms, the distances being 2.51 and 2.62 Å. These two oxygen atoms O_{II} have also to be considered in the estimation of bond strengths contributed by the central Na^+ ion. The bond strength contributions by Al^{3+} and Si^{4+} to the O^{2-} ions of the framework amount to 2.0 for O_V and 1.75 for O_I, O_{II}, O_{III}, and O_{IV}. Estimated values for the strength of the Na—O and H_2O—O bonds are listed in Table 5 and lead to bond strength totals of 2.1 for O_V, 2.05 for O_I, and 1.95 for O_{II}, O_{III} and O_{IV}. A satisfactory local balance of charges is thus obtained.

Table 5. *Electrostatic charge distribution around the sodium ions and water molecules*

Bond	Interatomic distance	Estimated bond strength
Na—O_{III}	2.36 Å	0.2
Na—O_{IV}	2.39 Å	0.2
Na—H_2O(1)	2.40 Å	0.2
Na—H_2O(2)	2.36 Å	0.2
Na—O_{II}(1)	2.51 Å	0.1
Na—O_{II}(2)	2.61 Å	0.1
H_2O—O_I	2.86 Å	0.3
H_2O—O_V	2.99 Å	0.1

The locations of the protons cannot be deduced with rigor. The interatomic distances between the water molecule and the surrounding oxygen atoms (Table 4) together with the electrostatic charge distribution just discussed, provide strong evidence that the water is linked to O_I and O_V by hydrogen bonds having a length of 2.85 and 2.99 Å respectively.

The dehydration of the zeolite causes some serious disturbances in the local charge balance. It seems likely that the Na^+ ion will tend to move towards O_I on dehydration in order to contribute to the charge balance on O_I. The resultant increase in the Na—O_{II} and other bond distances would have to be counteracted by some changes in the orientation of the chains. A careful examination reveals that this would lead to a decrease in the cell constants *a* and *b*. X-ray photographs of dehydrated crystals were found to be rather poor, unfortunately, owing to the tendency of the crystals to break up into bundles of fibers on dehydration. The photographs, nevertheless, revealed a small decrease in the cell constants *a* and *b* which was also observed by HEY and BANNISTER (1933). The shrinking of the natrolite lattice on dehydration thus appears to be a consequence of the requirements set forth by the electrostatic valence rule.

I would like to express my sincere thanks to Professor LINUS PAULING for suggesting this study, and for his kind interest and valuable advice during the course of this work. Thanks are also due to Drs. E. W. HUGHES, G. JOHANSSON, and W. BARCLAY KAMB for many helpful discussions. Finally, I wish to acknowledge the tenure of an Arthur Amos Noyes Fellowship.

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