A Partially Disordered Natrolite: Relationships between Cell Parameters and Si–Al Distribution

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Abstract

The crystal structure refinement of a natrolite from Gulacs Hill (Hungary) [$Na_{16}Al_{16}Si_{24}O_{80}.16H_2O$, cell parameters $a = 18.354$ (10), $b = 18.587$ (10), $c = 6.608$ (4) Å] shows a partial disorder in the (Si,Al) distribution of about 30% in all the tetrahedral sites ($R = 5.4$, $R_w = 5.2\%$ for 463 observed reflections). The relationships between cell parameters and the degree of disorder are discussed in relation to the present findings and to those available in the literature. There is an increase of 0.027 Å in the c parameter in going from the ordered to the disordered phase; the $b - a$ difference, which is zero in the disordered phase, increases to 0.35 Å in the ordered one. The rotation and twisting of the tetrahedral chain, under the influence of Na, are responsible for the $b - a$ difference.

Introduction

The crystal structure of the fibrous zeolite natrolite was postulated by Pauling (1930). Taylor, Meek & Jackson (1933) determined the atomic positions, Meier (1960) confirmed and refined the structure, Torrie, Brown & Petch (1964) determined the H positions from neutron diffraction data, and Peacor (1973) refined the structure at four different temperatures, which were low enough to avoid dehydration. From these structure determinations and refinements a fully ordered (Si,Al) distribution was evident. Krogh Andersen, Danø & Petersen (1969) described a tetragonal natrolite from Greenland. Pabst (1971) distinguished between orthorhombic pseudotetragonal natrolite with space group *Fdd*2 and tetragonal natrolite with space group *F*$\bar{4}$*d*2 and attributed the different symmetries to a disordered (Si,Al) distribution in the tetrahedra of the framework.

Further findings of tetragonal natrolite (Guseva, Men'shikov, Romanova & Bussen, 1975; Chen & Chao, 1980; D. Pongiluppi, private communication) showed that this mineral is not rare (but it is not as common as orthorhombic natrolite). Unfortunately, in all the samples of tetragonal natrolite there were no crystals suitable for a single-crystal X-ray study; therefore, Pabst's hypothesis could not be verified.

On the other hand, the accurate determinations of the cell parameters of orthorhombic natrolites give a $b - a$ difference of about 0.35 Å, a value which is consistent with a fully ordered (Si,Al) distribution, as suggested by Pauling (1930) and confirmed by Meier (1960) and Peacor (1973).

Natrolite from Gulacs Hill, Topolca, Hungary, has been found to have a $b - a$ difference as low as 0.23 Å (see Table 1). This anomalous value could be due to (*a*) exchangeable cation content very different from the normal value and the consequent different distortion of the tetrahedral chain, or (*b*) a partially diordered (Si,Al) distribution in the tetrahedral sites [there are three independent T sites, usually coded Si(1), Si(2) and Al: the Si/Al ratio could be different in the three T sites].

The first hypothesis can be ruled out on the basis of the chemical analysis.

The purpose of this work is to verify from a structure refinement of the Gulacs Hill natrolite whether the Al percentage is the same in both Si sites and to investigate the relationships between cell parameters and order–disorder in the tetrahedral sites.

Experimental

Electron microprobe analysis of the Gulacs Hill natrolite was carried out on an ARL-SEMQ instrument in the wavelength dispersive mode at 15 kV, with a 0.2 μA beam current and a defocused beam (spot size ~20 μm). Six analyses showed high chemical homogeneity of the sample with normal values for natrolite (see Table 1).

X-ray data collection and the determination of the cell parameters (see Table 1) were carried out on a prismatic crystal (0.10 × 0.06 × 0.03 mm) using a Philips PW 1100 diffractometer (Mo $K\alpha$ radiation) at the Istituto di Mineralogia, Università di Perugia.

Systematic absences indicate the space group of ordered natrolite (*Fdd*2). 886 unique reflections were collected, 463 of which with $F_o > 5\sigma(F_o)$ were considered observed and used in the refinement.

Table 1. *Crystallographic and chemical data of the Gulacs Hill natrolite*

		wt %		Atoms per unit cell
$a = 18.354$ (10) Å	SiO_2	46.55	Si	24.16
$b = 18.587$ (10)	Al_2O_3	25.77	Al	15.77
$c = 6.608$ (4)	Fe_2O_3	0.00	Fe^{3+}	0.00
$V = 2254$ Å^3	MgO	0.00	Mg	0.00
Space group: $Fdd2$	CaO	0.47	Ca	0.26
Schematic formula:	SrO	0.00	Sr	0.00
$Na_{16}Al_{16}Si_{24}O_{80}.16H_2O$	BaO	0.00	Ba	0.00
Si/Al = 1.532	Na_2O	15.44	Na	15.54
$E^* = -1.9\%$	K_2O	0.01	K	0.01
	H_2O†	11.76	H_2O	20.36
	Total	100.00	O	80.00

$$*E = \frac{(Al + Fe^{3+}) - [Na + K + 2(Mg + Ca + Sr + Ba)]}{[Na + K + 2(Mg + Ca + Sr + Ba)]} \times 100.$$

† Calculated as the difference from 100.00.

Structure refinement

Atomic scattering factors for half-ionized atoms (Cromer & Mann, 1968) were used. Extinction and anomalous-scattering corrections were not applied. Owing to the small dimensions of the crystal and the low value of μ (0.69 mm^{-1} for Mo $K\alpha$ radiation), an absorption correction was not applied. Starting co-ordinates were from Peacor (1973). Some least-squares cycles of anisotropic refinement indicated full occupancy of the Na and W sites and gave final values of $R = 5.4$, $R_w = 5.2\%$ for the observed reflections, with weights assigned according to counting statistics. The

Table 2. *Atomic coordinates and equivalent isotropic thermal parameters with standard deviations for the Gulacs Hill natrolite*

$$B_{eq} = \tfrac{4}{3} \sum_i \sum_j \beta_{ij}\, \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
Si(1)	0	0	0	0.71
Si(2)	0.1540 (1)	0.2112 (1)	0.6245 (7)	0.70
Al	0.0378 (1)	0.0944 (1)	0.6180 (6)	0.56
O(1)	0.0230 (3)	0.0689 (3)	0.8664 (12)	1.29
O(2)	0.0701 (3)	0.1816 (3)	0.6140 (12)	0.81
O(3)	0.0980 (3)	0.0354 (3)	0.5050 (11)	1.05
O(4)	0.2079 (3)	0.1533 (3)	0.7285 (11)	1.21
O(5)	0.1799 (3)	0.2278 (3)	0.3907 (13)	1.55
Na	0.2213 (2)	0.0305 (2)	0.6207 (8)	1.64
H_2O	0.0577 (3)	0.1895 (4)	0.1150 (14)	2.33

positional and isotropic thermal parameters are given in Table 2, interatomic distances and bond angles in Table 3.*

Discussion

Fig. 1 shows a clinographic projection of the natrolite tetrahedral chain and its connection with an adjacent one. Fig. 2 shows an orthogonal projection of the natrolite structure on (001).

Table 3. *Interatomic distances* (Å) *and angles* (°) *for the Gulacs Hill natrolite*

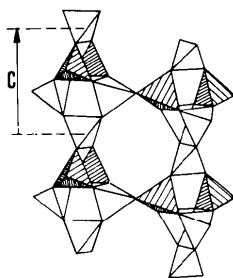| Si(1) tetrahedron			Si(2) tetrahedron			Al tetrahedron	
Si(1)—O(1)	1.612 (7) [×2]		Si(2)—O(2)	1.636 (6)		Al—O(1)	1.730 (8)
Si(1)—O(5)	1.641 (7) [×2]		Si(2)—O(3)	1.626 (6)		Al—O(2)	1.726 (6)
Average	1.627		Si(2)—O(4)	1.616 (6)		Al—O(3)	1.727 (6)
			Si(2)—O(5)	1.645 (8)		Al—O(4)	1.733 (6)
O(1)—O(1)	2.698 (11)		Average	1.631		Average	1.729
O(1)—O(5)	2.627 (9) [×2]						
O(1)—O(5)	2.640 (9) [×2]		O(2)—O(3)	2.858 (8)		O(1)—O(2)	2.813 (9)
O(5)—O(5)	2.704 (11)		O(2)—O(4)	2.691 (7)		O(1)—O(3)	2.825 (9)
			O(2)—O(5)	2.641 (9)		O(1)—O(4)	2.876 (9)
O(1)—Si(1)—O(1)	113.6 (5)		O(3)—O(4)	2.665 (8)		O(2)—O(3)	2.858 (8)
O(1)—Si(1)—O(5)	107.7 (3) [×2]		O(3)—O(5)	2.683 (9)		O(2)—O(4)	2.691 (7)
O(1)—Si(1)—O(5)	108.4 (3) [×2]		O(4)—O(5)	2.676 (9)		O(3)—O(4)	2.665 (8)
O(5)—Si(1)—O(5)	111.0 (5)						
			O(2)—Si(2)—O(3)	106.7 (3)		O(1)—Al—O(2)	109.0 (3)
Na polyhedron			O(2)—Si(2)—O(4)	111.7 (3)		O(1)—Al—O(3)	109.6 (3)
			O(2)—Si(2)—O(5)	107.2 (4)		O(1)—Al—O(4)	112.3 (3)
Na—O(2)	2.614 (6)		O(3)—Si(2)—O(4)	110.6 (4)		O(2)—Al—O(3)	111.7 (3)
Na—O(2)	2.524 (6)		O(3)—Si(2)—O(5)	110.2 (3)		O(2)—Al—O(4)	105.1 (3)
Na—O(3)	2.391 (6)		O(4)—Si(2)—O(5)	110.3 (3)		O(3)—Al—O(4)	109.1 (3)
Na—O(4)	2.404 (7)						
			Si(2)—O(5)—Si(1)	143.7 (4)		Si(1)—O(1)—Al	141.1 (4)
Na—H$_2$O	2.340 (8)		Si(2)—O(2)—Al	129.7 (3)		Si(2)—O(3)—Al	138.9 (4)
Na—H$_2$O	2.383 (9)		Si(2)—O(4)—Al	136.8 (4)			

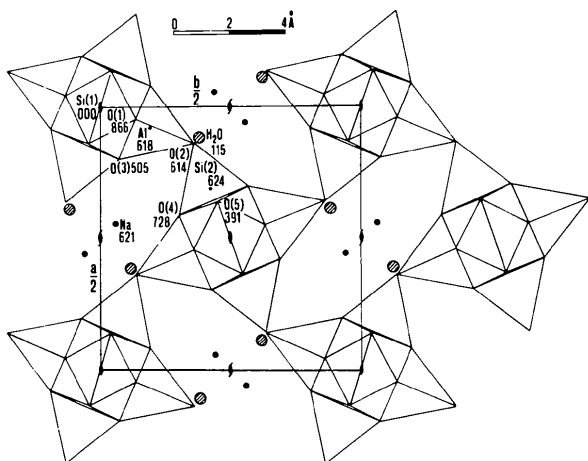Fig. 1. Clinographic projection of the natrolite tetrahedral chain, showing its connection with an adjacent one.

Fig. 2. Orthogonal projection of the natrolite structure on (001). Numbers give the heights of the atoms in thousandths of c.

Si–Al distribution

It is known that the mean T–O distances depend on the mineral and, in the same mineral, on the tetrahedral sites (Baur, 1978; Hill & Gibbs, 1979). Table 4 reports the values of the mean Si–O bond lengths derived from Baur's (1978) two regression equations, the measured T–O values for the Bergen Hill and Gulacs Hill natrolites and the corresponding values of

the degree of disorder in the tetrahedra. The values obtained from Baur's regression equations can be considered to be close to the true values, in spite of their high standard deviation (0·007 Å), for the following reasons: (1) the difference between the mean Si(1)–O and Si(2)–O bond lengths (0·003 Å) is justified by the fact that all the O atoms of the Si(2) tetrahedron are coordinated to a Na atom, whereas the O atoms of the Si(1) tetrahedron are not; (2) the mean values of all T–O distances, 1·669 (2) and 1·668 (1) Å for the Gulacs Hill and Bergen Hill natrolites respectively, are very close to the value of 1·666 Å found by both Jones (1968) and Ribbe & Gibbs (1969) for a Si/Al ratio of 3/2. The slope of the T–O bond-length curve as a function of Al/(Al + Si) (Jones, 1968; Ribbe & Gibbs, 1969) together with the mean T–O bond length found in the Gulacs Hill and Bergen Hill natrolites give values for Si–O which are very close to those derived from Baur's equations.

Baur's regression equations do not provide the mean Al–O bond length; this value was calculated from the Bergen Hill natrolite data in the following way; the mean distances for Si(1) and Si(2) tetrahedra exceed the calculated ones by 0·006 and 0·007 Å respectively; therefore, it may be assumed that the amount of Al is the same in both sites and that the difference between the mean T–O distance and the calculated Si–O distance for both Si sites is 0·0065 Å. Consequently, as the overall Si/Al ratio in natrolite is approximately 3/2 (Foster, 1965), the mean bond length for a fully ordered Al tetrahedron should be 0·0065 Å × 3/2 + 1·741 Å [where 1·741 Å is the mean T–O distance found in the Al tetrahedron of the Bergen Hill natrolite (see Table 4)].

With the assumption of a linear variation of the average T–O distance with the Si/Al ratio (Jones, 1968), the Al content in the three tetrahedra Si(1), Si(2) and Al is 5, 5 and 93% respectively for the Bergen Hill natrolite, with a standard deviation of less than 2%. Also, for the Gulacs Hill natrolite the mean T–O bond lengths show the same amount of Al in both Si

Table 4. T–O mean distances [(I)–(VII)] (Å) and degree of disorder [(VIII), (IX)] (%) in natrolites

	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	(IX)
Si(1)–O	1·612	1·610	1·611	1·612	1·668	1·617	1·627	5	12
Si(2)–O	1·614	1·614	1·614	1·612	1·668	1·621	1·631	5	12
Al–O			1·751	1·751	1·668	1·741	1·729	93	84

(I) Calculated from Baur's (1978) first equation.
(II) Calculated from Baur's (1978) second equation [the Si–O–T angles are from the Bergen Hill natrolite at 298 K (Peacor, 1973)].
(III) Values averaged between (I) and (II) [the Al–O distance is deduced from the data for the Bergen Hill natrolite at 298 K (Peacor, 1973)].
(IV) Averaged Si–O and Al–O distance.
(V) Averaged T–O distance for a fully disordered natrolite.
(VI) Experimental T–O distances for the Bergen Hill natrolite at 298 K.
(VII) Experimental T–O distances for the Gulacs Hill natrolite.
(VIII) Percentage of Al in the tetrahedra for the Bergen Hill natrolite at 298 K.
(IX) Percentage of Al in the tetrahedra for the Gulacs Hill natrolite.

tetrahedra, the Al content in the Si(1), Si(2) and Al sites being 12, 12 and 84% respectively (see Table 4), with a standard deviation of 2%.

If we define the degree of disorder in the Si(1), Si(2) and Al sites by means of the values Al[Si(1)]% × 5/2, Al[Si(2)]% × 5/2 and Si[Al]% × 5/3 respectively, where Al[Si(1)]% and Al[Si(2)]% are the percentages of Al in the Si(1) and Si(2) sites respectively and Si[Al]% is the percentage of Si in the Al site, there is a degree of disorder of about 30% in the three tetrahedral sites, *i.e.* $\frac{1}{3}$ of the maximum possible disorder.

Relationship between the degree of disorder and the c parameter

In what follows we assume that:

(1) the tetrahedra are regular, having equal $T-O$ and $O-O$ distances;

(2) the $T-O$ distance depends linearly on the Si/Al ratio and not on the T site, the structural influence being negligible, although it does exist (Table 4);

(3) the degree of disorder is the same for both Si sites and consequently it is coded Al[Si]% for both;

(4) for a fully ordered tetrahedron the Si—O distance is 1·612 Å (mean value between 1·611 and 1·614 Å in Table 4) and the Al—O distance is 1·751 Å.

With these assumptions the c parameter can be obtained from the following relationship (see Appendix A):

$$c = d_1(0\cdot86603 \cos \varphi - 0\cdot59194) + 5\cdot8959, \quad (1)$$

with $\sin \varphi = (13\cdot61920 - 5\cdot0d_1)/3\cdot46412d_1$ and $d_1 = 2\cdot6324 + Al[Si]\% \times 0\cdot2286$. In a fully ordered natrolite ($d_1 = 2\cdot6324$ Å), from (1) we have $c = 6\cdot616$ Å, whereas in a fully disordered natrolite ($d_1 = d_2 = 2\cdot7232$ Å) c increases to 6·644 Å.

The value of Δc as a function of the degree of disorder is shown in Fig. 3. This function can be approximated to a straight line with an error of less than 3% in the degree of disorder.

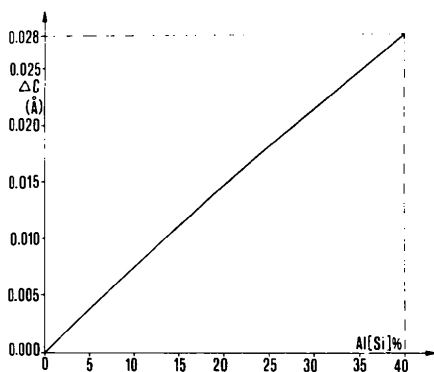The measured values of c are always lower than the corresponding calculated values. This difference is

Fig. 3. Δc as a function of Al[Si]%.

normally about 0·03 Å.* This difference can be explained by a compression of the Si(1) tetrahedron in the c direction as a consequence of the hydrogen bonds between the water molecule and the O(1) and O(5) oxygens. In fact, the measured values of the Al and Si(2) tetrahedra, both for the Bergen Hill and Gulacs Hill natrolites, in the c direction differ less than 0·02 Å from the calculated ones, whereas for the Si(1) tetrahedron this difference is about 0·06 Å. Therefore, we must decrease the calculated value of c by about 0·03 Å to relate it to the degree of disorder in the tetrahedral sites. It is obvious that the chemical composition influences the cell dimensions, although only to a small extent considering the great chemical homogeneity of natrolites (Foster, 1965). Unfortunately, a complete study relating the crystallographic and crystallochemical properties of natrolites does not exist. Consequently, the criterion for obtaining the degree of disorder in the tetrahedra from the value of the c parameter is only qualitatively useful. However, in view of the few good crystallographic data available, a variation range in the c parameter between 6·584 and 6·612 Å provides quite a good choice. In fact, the increase of the measured c parameter with the degree of disorder compares favorably with the calculated values.

Relationship between the degree of disorder and the b − a difference

Let l_1 be the O(2)—O(2) distance between the free vertices of the coupled Al tetrahedra and l_2 the O(2')—O(2') distance between the free vertices of the coupled Si(2) tetrahedra (see Appendix B);

$$l_1 = -1\cdot4495d_1 + 11\cdot1175$$
$$l_2 = d_1[1\cdot73205 \sin (\theta - \varphi) - 1\cdot5] + 6\cdot8080, \quad (2)$$

where $\theta = 70°32'$ is the dihedral angle of the tetrahedron and d_1 and φ are the values defined above. The values of l_1 and l_2 for a fully ordered natrolite, for a fully disordered natrolite, and for the Gulacs Hill and Bergen Hill natrolites are reported in Table 5.

It is known (Gottardi, 1979) that the topological symmetry of natrolite is $I4_1/amd$, while its topochemical symmetry is $I4_1md$. The real symmetries of a fully ordered and a fully disordered natrolite are $Fdd2$ and $I\bar{4}2d$ respectively because of a rotation of the chain around its c axis, which changes the square section of the channels parallel to c into a diamond-shaped

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* We think that the most reliable unit-cell parameters are obtained by least-squares refinement from diffractometer powder data. According to the cell data of the natrolites (IX), (X), (XI) of Table 5 and 22 other natrolites obtained by this method by the authors (A. Alberti, D. Pongiluppi & G. Vezzalini, in preparation) c varies from 6·580 to 6·598 Å (mean 6·587 Å), a from 18·276 to 18·331 Å (mean 18·296 Å), b from 18·607 to 18·644 Å (mean 18·632 Å) and the $b - a$ difference from 0·289 to 0·360 Å (mean 0·335 Å).

Table 5. *Measured and calculated crystallographic data for natrolites*

	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)‡	(VIII)	(IX)	(X)	(XI)
a (Å)*	18·441	18·522	18·446	18·523	18·354	18·467	18·43	18·453	18·276	18·285	18·288
b (Å)*	18·701	18·522	18·446	18·523	18·587	18·649	18·71	18·681	18·637	18·636	18·627
c (Å)	6·615	6·642	6·619	6·635	6·608	6·625	6·52	6·619	6·583	6·586	6·580
l_1 (Å)	7·302	7·170			7·225	7·262	7·278	7·286			
l_2 (Å)	7·076	7·170			7·076	7·106	7·102	7·089			
ψ'[O(2)–O(2)]					24° 8'		24° 10'				
ψ''[O(2')–O(2')]					23° 56'		23° 56'				
a (Å)†	18·396	18·522				18·436		18·414			
b (Å)†	18·746	18·522				18·681		18·720			

(I) Calculated for a fully ordered natrolite.
(II) Calculated for a fully disordered natrolite.
(III) Measured for the tetragonal natrolite from Greenland (Krogh Andersen *et al.*, 1969).
(IV) Measured for the tetragonal natrolite from Mont St Hilaire (Chen & Chao, 1980); the high values of the parameters are justified by the high K₂O (1·12 wt%) content.
(V) Measured for the Gulacs Hill natrolite.
(VI) Calculated for the Gulacs Hill natrolite (Al[Si]% = 0·12).
(VII) Measured for the Bergen Hill natrolite.
(VIII) Calculated for the Bergen Hill natrolite (Al [Si]% = 0·05).
(IX) Measured for the Glen Farg natrolite (Krogh Andersen *et al.*, 1969).
(X) Measured for the Green River Formation natrolite (Colorado) (Pabst, 1971).
(XI) Measured for the S. Benito County natrolite (California) (Pabst, 1971).

* ψ angle 24° 2'. Parameters accounting only for the rotation of the chain.
† ψ angle 24° 2'. Parameters accounting for both the rotation and the twisting of the chain.
‡ The measured cell parameters are not in agreement with the other values reported in this table and with those we have found for many natrolites. This can be explained by the experimental method used (Weissenberg-geometry diffractometer).

section to allow a better coordination of the Na atoms. Figs. 7, 8 and 9 (Appendix *C*) show the natrolite framework projected onto (001) with its topochemical symmetry, displaying chain rotations of 24° (real symmetry) and 45°.

It is evident that *a* and *b* depend on the degree of (Si,Al) disorder and on the amount of rotation of the chain. With the assumption discussed in Appendix *C* we obtain

$$a = 2 \frac{l_2}{\sin (45° - \delta)} \cos (\psi + \delta),$$

$$(3)$$

$$b = 2 \frac{l_1}{\sin (45° + \delta)} \cos (\psi - \delta),$$

where $\delta = \arctan[(l_1 - l_2)/(l_1 + l_2)]$ and ψ is the angle of rotation of the chain around its axis. The calculated value of ψ is 24° 3' for the Bergen Hill natrolite and 24° 2' for the Gulacs Hill natrolite; therefore, it seems to be independent of the degree of disorder. The value of the ψ angle is in agreement with the value of 24° 6' obtained for the natrolite from Aroy (Norway) (Torrie *et al.*, 1964). Pauling (1930) calculated an angle of 24° 10'.

The values of the calculated *a* and *b* parameters, with a ψ angle of 24° 2', for fully ordered and disordered natrolites, and for the Bergen Hill and Gulacs Hill

natrolites are reported in Table 5. The experimental $b - a$ difference normally found for natrolite is higher than that calculated according to (3) (about 0·09 Å).* This discrepancy is due to the angle between O(2)–O(2) and O(2')–O(2') (Fig. 6 of Appendix *B*). This angle should be 90°, but actually differs by about 12'–14' from this value (see Table 5). This difference reflects the chain twisting caused by the tendency of the Na atom to achieve a better coordination. In fact Na coordinates two O(2) oxygens with very different distances and it pulls the far O to the closest possible position, considering it is bonded to Al and Si(2). This results in a stretching of the structure nearly parallel to **b** and a flattening nearly parallel to **a**. Obviously this twisting also depends on the degree of disorder and if the corresponding increase of the $b - a$ difference is a linear function of the degree of disorder we obtain the following relationships from the data of the Bergen Hill and Gulacs Hill natrolites (see Appendix *D*):

$$a = \frac{2l_2}{\sin (45° - \delta)} \cos (\psi + \delta)$$
$$- (1·0 - 2·5 \times \text{Al[Si]}\%) \times 0·045 \text{ Å};$$

$$(4)$$

$$b = \frac{2l_1}{\sin (45° + \delta)} \cos (\psi - \delta)$$
$$+ (1·0 - 2·5 \times \text{Al[Si]}\%) \times 0·045 \text{ Å}.$$
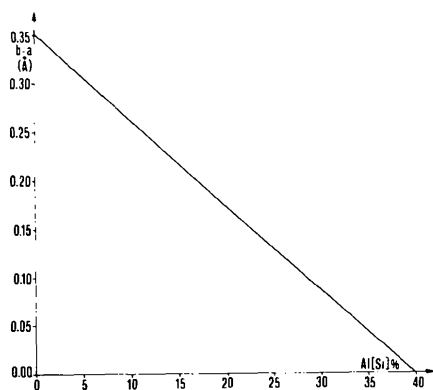
* See footnote on p. 784.

Fig. 4. $b - a$ as a function of Al[Si]%.

Table 5 reports the corrected values of the parameters and Fig. 4 shows the $b - a$ difference as a function of the degree of disorder. This function can be approximated to a straight line with a maximum error in the evaluation of the degree of disorder of less than 1%.

The measured values of a and b are always lower than the corresponding calculated values. This difference, due to the distortions in the structure, is normally around $0 \cdot 10$ Å (see Table 5).* However, the few good crystallographic data available show good agreement between the measured and calculated $b - a$ difference. Therefore, an evaluation can be made of the degree of disorder in the tetrahedral sites, which is more accurate than that obtainable from the value of the c parameter.

Conclusions

The comparison between the crystal refinement of the Gulacs Hill natrolite and the data of the Bergen Hill natrolite (Peacor, 1973) permits the following conclusions:

(1) the Gulacs Hill natrolite is partially disordered with a degree of disorder of 30% in comparison with 13% for the Bergen Hill natrolite;

(2) the degree of disorder is the same in both Si sites;

(3) the rotation angle of the chain around the c axis ($24° 2'$) does not depend on the degree of disorder;

(4) given the same chemical composition the c parameter depends on the degree of disorder in the tetrahedral sites, according to a nearly linear function, and increases by $0 \cdot 027$ Å with an increasing degree of disorder;

(5) the interaction between the Na^+ cation and the oxygens of the framework produces a rotation and a twisting of the chain. As a consequence a partially ordered Si–Al distribution causes a lowering of the symmetry, which is tetragonal when the degree of

* See footnote on p. 784.

disorder is 100% and becomes orthorhombic by the ordering process. The $b - a$ difference depends on the degree of disorder according to a nearly linear function and increases to $0 \cdot 35$ Å with a decreasing degree of disorder in the tetrahedral sites.

APPENDIX A

Let φ be the angle that the height of the internal face of the Si(2) tetrahedron forms with the chain axis (see Fig. 5), d_1 the O–O distance for Si(1) and Si(2) tetrahedra and d_2 the O–O distance for Al tetrahedra; the c parameter can then be calculated from the relationship

$$c = \overline{HH'} = d_1(\sqrt{2}/2 + \sqrt{3}/2 \cos \varphi) + d_2\sqrt{3}/2.$$

For fully ordered tetrahedra (Si–O $= 1 \cdot 612$, Al–O $= 1 \cdot 751$ Å) one obtains $d_1 = 2 \cdot 6324$ Å and $d_2 = 2 \cdot 8594$ Å. In general, $d_1 = 2 \cdot 6324 + $ Al[Si]% $\times 0 \cdot 2270$, where Al[Si]% is the percentage of Al in the Si(1) and Si(2) tetrahedra. Given Si/Al $= 3/2$ and as d_1 and d_2 vary linearly with the Al content, one obtains

$$3d_1 + 2d_2 = 13 \cdot 6160 \text{ Å}$$

or

$$d_2 = 13 \cdot 6160/2 - 3d_1/2 = 6 \cdot 8080 - 1 \cdot 5d_1;$$

$$c = (\sqrt{2}/2) d_1 + (\sqrt{3}/2) \cos \varphi d_1$$
$$+ 13 \cdot 6160\sqrt{3}/4 - (3\sqrt{3}/4) d_1$$

$$= d_1(0 \cdot 86603 \cos \varphi - 0 \cdot 59194) + 5 \cdot 8959.$$

As $(d_2 - d_1)/2 = \sqrt{3}/2 \sin \varphi d_1$,

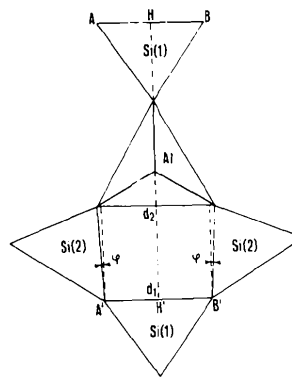$$\sin \varphi = (6 \cdot 8080 - 2 \cdot 5 d_1)/1 \cdot 7321 d_1.$$

Fig. 5. The natrolite chain projected on the Si(1)–Si(2)–Si(2) plane.

APPENDIX B

With d_1, d_2 and $\sin \varphi$ defined as in Appendix A, the distances l_1 and l_2 (see Fig. 6) can be calculated from the relationships

$$l_1 = O(2) - O(2) = d_1 + 2\sqrt{2/3}\, d_2$$

$$= d_1 + 2[0 \cdot 8165(6 \cdot 8080 - 1 \cdot 5\, d_1)]$$

$$= -1 \cdot 4495\, d_1 + 11 \cdot 1175,$$

$$l_2 = O(2') - O(2') = d_2 + 2\overline{AB}.$$

Let $\theta = 70° 32'$ (the dihedral angle of the tetrahedron):

$$\overline{AB} = d_1\sqrt{3}/2 \sin (\theta - \varphi);$$

therefore,

$$l_2 = 6 \cdot 8080 - 1 \cdot 5\, d_1 + d_1\sqrt{3} \sin (\theta - \varphi)$$

$$= 6 \cdot 8080 + d_1[1 \cdot 7321 \sin (\theta - \varphi) - 1 \cdot 5].$$

Fig. 7. Schematic projection on (001) of the natrolite structure in its topochemical symmetry.

APPENDIX C

The interaction between the Na^+ cation and the framework oxygens causes a rotation of the natrolite chain around its axis. Therefore, the schematic structure of Fig. 7 tends to transform, by a 45° rotation of the chain, into that of Fig. 8. However, in the real symmetry the rotation is only about 24° (Fig. 9). The transformation of the Fig. 7 structure into that of Fig. 8, through structures of the type described in Fig. 9, can occur in an infinite number of ways. Hence it is necessary to fix certain conditions. Let us assume that, when the chain rotates, point O (Fig. 10) runs along the straight line OD, so that the angle δ is constant; for a given degree of disorder, therefore

$$\tan \delta = \overline{OH}/\overline{DH} = (l_1 - l_2)/(l_1 + l_2),$$

$$\delta = \arctan [(l_1 - l_2)/(l_1 + l_2)].$$

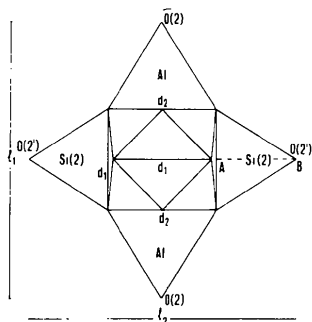Thus the angle δ is only a function of the degree of disorder.
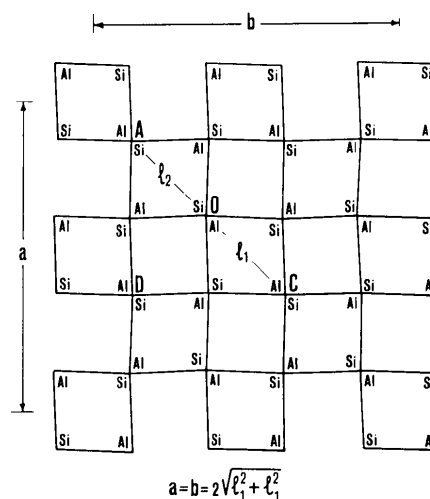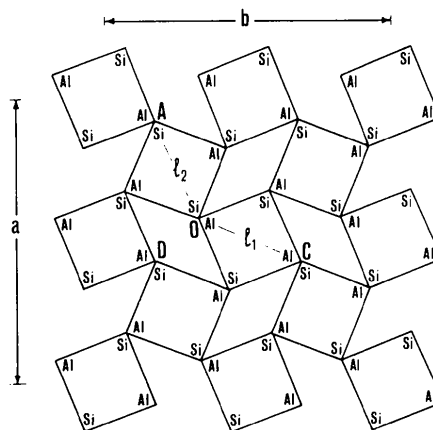

Fig. 8. Schematic projection on (001) of the natrolite structure in its real symmetry (chains rotated by approximately 24°).
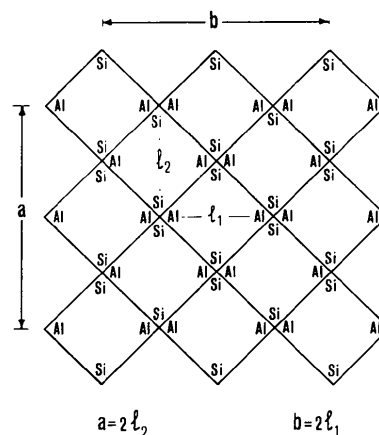

Fig. 9. Schematic projection on (001) of the natrolite structure when the chain is rotated by 45°.

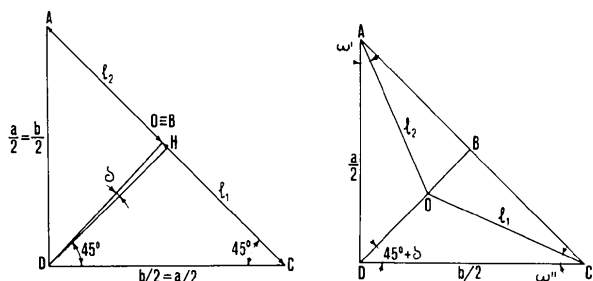Fig. 6. Projection of the chain on (001).

Fig. 10. Part of Fig. 7 showing the angle δ (left). Part of Fig. 8 showing the relationships between cell parameters and the angle of chain rotation (right).

The values of the parameters a and b as functions of the rotation angle ψ of the chains can be calculated. From Fig. 10 (left)

$$l_1/\sin (45° + \delta) = \overline{DO}/\sin 45°$$

$$l_2/\cos (45° + \delta) = \overline{DO}/\sin 45°$$

$$l_1/l_2 = \tan (45° + \delta) \quad \text{or} \quad \tan (45° + \delta) l_2/l_1 = 1.$$
(C1)

From Fig. 10 (right)

$$OD/\sin \omega'' = l_1/\sin (45° + \delta)$$

$$OD/\sin \omega' = l_2/\cos (45° + \delta)$$

and, consequently,

$$\sin \omega''/\sin \omega' = \tan (45° + \delta) l_2/l_1;$$

but $\tan (45° + \delta) l_2/l_1 = 1$ from equation (C1) and therefore $\omega'' = \omega' = \omega$. The a and b parameters can therefore be calculated from

$$a/2 = l_2 \sin (180° - 45° + \delta - \omega)/\sin (45° - \delta),$$

$$b/2 = l_1 \sin (180° - 45° - \delta - \omega)/\sin (45° + \delta);$$

let $\psi = 45° - \omega$ be the rotation angle of the chain around its c axis, then

$$a = 2l_2 \cos (\psi + \delta)/\sin (45° - \delta),$$

$$b = 2l_1 \cos (\psi - \delta)/\sin (45° + \delta).$$

APPENDIX D

The two values $O(2)-O(2')$ (see Appendix B) are obtained from

$$O(2)-O(2')^2 = [O(2)-O(2)/2]^2 + [O(2')-O(2')/2]^2$$
$$\pm 2[O(2)-O(2)/2][O(2')-O(2')/2]$$
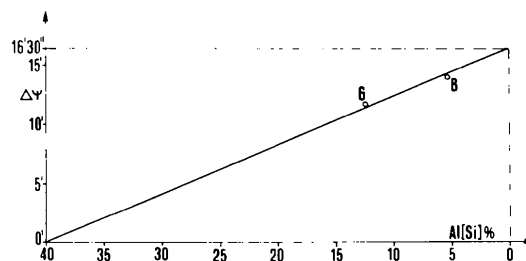$$\times \cos (90° + \Delta\psi).$$

Fig. 11. Difference $\Delta\psi = \psi' - \psi''$ as a function of Al[Si]%. B and G represent the Bergen Hill and Gulacs Hill natrolites respectively.

Since Al[Si]% = 0·0 for $\Delta\psi = 16'30''$ (see Fig. 11), $O(2)-O(2') = 5·0962$ Å and $O(2)-O(2') = 5·0718$ Å. Therefore, the values of a and b have to be modified by the value $4[(5·0962 - 5·0718)/2] \cos 24° 2' = 0·045$ Å. In general, the calculated values of a and b corrected for the rotation of the chain (Appendix C) and for the twisting of the chain are obtained from

$$a \text{ (Å)} = 2l_2 \cos (\psi + \delta)/\sin (45° - \delta)$$
$$- (1·0 - 2·5 \text{ Al[Si]}\%) 0·045,$$

$$b \text{ (Å)} = 2l_1 \cos (\psi - \delta)/\sin (45° + \delta)$$
$$+ (1·0 - 2·5 \text{ Al[Si]}\%) 0·045.$$

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