NATROLITE FROM THE GREEN RIVER FORMATION, COLORADO, SHOWING AN INTERGROWTH AKIN TO TWINNING

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Abstract

Fine crystals of natrolite have been found in a drill core from the Green River Formation (Eocene) in the Piceance Creek basin, northwestern Colorado. The morphology, optical properties and cell dimensions are recorded for this natrolite. A regular intergrowth simulating twinning is described and a structural interpretation attempted. For comparison optical data, cell dimensions and an indexed powder pattern have been obtained for analyzed natrolite from San Benito County, California.

Provenance and Associations

In 1967 the Humble Oil and Refining Company drilled its East Willow Creek #1 Core Hole in Section 28, Twp, 4 S, R 96 W, in the Piceance Creek basin in Garfield County, Colorado. At depth 478.5′ the rock is "poor quality oil shale with vuggy breccia fragments containing prismatic crystals"; this is "near the base of the Mahogany zone in the Parachute Creek Member".[1] The geology of the area has been described by Donnell (1961). The "prismatic crystals" are natrolite and through the courtesy of Professor Charles Milton the writer received a small lot of these for study. All of the crystals will be preserved in the U. S. National Museum.

A great variety of authigenic silicate minerals has been recorded from the Green River Formation (Milton *et al.*, 1960) but natrolite is not among these. The only zeolites hitherto known in the Green River Formation are analcime which was recognized long ago by Bradley (1930) and the distribution of which in another part of the Formation has been studied in detail by Iijima and Hay (1968), also mordenite and clinoptilolite found by Goodwin and Surdam (1967) in zeolitized tuffs in the Tipton shale member in Wyoming.

The natrolite crystals received were free of matrix or accompanying minerals except for one crystal attached to the base of which were many minute analcime crystals. This is not surprising in view of the fact that analcitized tuffs are conspicuous in that part of the section in which the natrolite crystals were found (Donnell, 1961). The analcime crystals are minute trapezohedra ranging in diameter from 0.04 to 0.08 mm, similar in size to those pictured by Iijima and Hay (1968) and close to the average

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[1] Personal communication from William W. Sloan, Jr., dated April 23, 1970

size given by Bradley (1930, p. 3) for analcime in the oil-shale beds, though analcime crystals in what he called "crystal beds" reach "nearly 2 millimeters in diameter." The analcime attached to the natrolite has a refractive index 1.489 ± 0.001 and shows very slight birefringence, in agreement with Bradley's report of "feeble anomalous birefringence" and index "1.488 ± 2" and corresponding to the higher of the indices reported by Iijima and Hay who recorded 1.483 to 1.488 ± 0.002.

Morphology

All of the natrolite crystals received, varying from 0.4 to 3.3 mm in length and 0.15 to 0.78 mm in thickness, plus a few small satellites which could be detached without damage, 13 crystals in all, were measured with a Stoe 2-circle reflecting goniometer and the dimensions recorded. No general statement of the ratio of length to thickness can be made as only two of the crystals, one of these a satellite, are doubly terminated. However, the crystals with broken ends are mostly 4 to 5 times greater in length than thickness. Though natrolite is usually pictured with pseudo-tetragonal habit, these crystals are distinctly orthorhombic, the ratio of the b to the a dimension mostly being about 1.5 and attaining the value 2.7 in one case.

Like most natrolite crystals these are rather simple in habit but the combination of principal forms is one commonly found. The two doubly terminated crystals show the same forms at both ends; there is no morphological indication of the polarity of the c axis. Hence $\{hkl\}$ indices as here used must be taken to refer to $\{hkl\}$ or $\{hk\bar{l}\}$ or both.

The front pinacoid, a $\{100\}$ is generally the most conspicuous form. The side pinacoid, $b\{010\}$, usually has narrow faces or may be represented by only a single face and in one case is lacking. $\{110\}$, $\{111\}$ and $\{331\}$ are usually represented by full complements of faces, the two pyramids being about equally developed. On three crystals faces of $\{311\}$ are also present and on one crystal the form is fully developed. Associated with $\{311\}$ are faces of very steep pyramids in the $\{0\bar{1}1\}$ zone, the form $\{14 \cdot 1 \cdot 1\}$ having been surely identified on two crystals. Other pyramidal forms are represented only by an occasional face, sometimes not surely identifiable. Faces corresponding to about twenty prism forms were tentatively indexed but besides the unit prism only $\{310\}$, $\{210\}$ and $\{120\}$ were found on three or more crystals.

Figure 1 is an axonometric drawing of a typical crystal. Table 1 gives the calculated angles for the surely established forms only. The maximum departure of observed coordinate angles for the principal forms from calculated angles, as established by measurements on the five best crystals, does not exceed 4'.
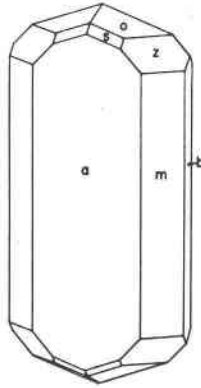
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Fig. 1. Axonometric drawing of an idealized natrolite crystal with typical habit of crystals from the Green River Formation, Colorado. Coordinates of picture plane are ϕ 70°, ρ 80°.

OPTICAL PROPERTIES, CELL DIMENSIONS
AND SPECIFIC GRAVITY

In Table 2 are summarized the optical properties, cell dimensions and specific gravity of the natrolite from The Green River Formation and of the natrolite which constitutes the matrix of benitoite from San Benito County, California, described by Louderback (1909) with analysis by Blasdale. This natrolite has a composition very close to that calculated

TABLE 1. NATROLITE ANGLE TABLE

Orthorhombic; pyramidal $mm2$
$a:b:c = 0.9812:1:0.3534;$[1] $p_0:q_0:r_0 = 0.3602:0.3534:1$
$q_1:r_1:p_1 = 0.9812:2.7764:1;$ $r_2:p_2:q_2 = 2.8297:1.0192:1$

	Forms	ϕ	$\rho = C$	ϕ_1	$\rho_1 = A$	ϕ_2	$\rho_2 = B$
b	010	0°00′	90°00′	90°00′	90°00′	—	0°00′
a	100	90 00	90 00	—	0 00	0 00	90 00
n	120	27 00	90 00	90 00	63 00	0 00	27 00
m	110	45 33	90 00	90 00	44 27	0 00	45 33
t	210	63 52	90 00	90 00	26 08	0 00	63 52
l	310	71 53	90 00	90 00	18 07	0 00	71 53
o	111	45 33	26 46	19 28	71 15	70 11	71 36
s	311	71 53	48 40	19 28	44 28	42 47	76 30
z	331	45 33	56 33	46 40	53 27	42 47	54 14
	14·1·1	85 59	78 49	19 28	11 53	11 13	86 04

[1] Axial elements based on cell dimensions determined for natrolite from Green River Formation, Garfield County, Colorado, from single crystal X-ray data.

Table 2. Physical Properties of Natrolite

	1		2	
Refr. Ind.	589 mμ	486	589	486
α	1.4775 ± 0.0010	1.482 ± 0.002	1.477 ± 0.003	1.484 ± 0.003
β	1.4810	1.487	1.482	1.489
γ	1.4895	1.496	1.489	1.496
orientation	X‖a, Y‖b		X‖a, Y‖b	
2V	(+) 62° (white light)		(+) moderate to large	
	measured directly		not measured	
dispersion	$v > r$, slight			
Cell dimensions				
a	18.285 ± 0.008 Å		18.288 ± 0.008	
b	18.636 ± 0.008		18.627 ± 0.008	
c	6.586 ± 0.003		6.580 ± 0.003	
$a:b:c$	0.9812:1:0.3534		0.9818:1:0.3533	
Specific gravity				
obs.	2.25 ± 0.01		2.241 ± 0.005	
calc.	—		2.248	

1. Natrolite from Green River Formation, Colorado. Sp. gr. determined by suspension of crystals in a bromoform-ethanol mixture simultaneously checked by Westphal balance.

2. Natrolite from San Benito County, California. All data obtained on UC specimens M330 and M332, collected by Louderback. Analysis by Blasdale (Louderback, 1909) with corresponding ideal values for $Na_2Al_2Si_3O_{10} \cdot 2H_2O$ in brackets:—SiO_2 47.69 (47.39), Al_2O_3 27.14 (26.82), Na_2O 15.74 (16.31), H_2O 9.56 (9.48), sum 100.13% (100.00). This analysis was included by Foster (1965, Table 1, No. 11) in her study of compositions in the natrolite group. Blasdale reported the absence of Ti, Ba, Mn and K. X-ray spectrographic analysis by Robert N. Jack, using a G-1 standard and absorption corrections based on Blasdale's analysis, showed:—K_2O .034%, CaO .039, TiO_2 .010, MnO .002, BaO .003, SrO <.002, Br_2O <.002, Sp. gr. by Berman balance on four clear fragments from UC specimen M330.

from the formula $Na_2Al_2Si_3O_{10} \cdot 2H_2O$. Specimens of this natrolite are to be found in most large mineral collections. The properties of the Green River natrolite differ but slightly from those of the San Benito natrolite.

The optical properties were obtained from crystals mounted on goniometer heads as for goniometry or X-ray examination using a device similar to that described by Jones (1960). The optic angle was measured directly on crystals mounted to rotae on b. For crystals of low birefringence the direct measurement of $2V$ is far more accurate than calculation from indices. In the present case a change of β of 0.0005 involves a change in calculated $2V$ of nearly $5\frac{1}{2}°$, whereas the uncertainty of the direct measurement is surely no more than a degree or two.

One of the natrolite crystals was of such size and quality as to permit

partial determination of optical properties by the method of minimum deviation, using a natural prism formed by the faces (100) and ($\bar{1}$10). For wavelength 589 mμ this yielded 1.4891 for γ and 1.4781 for α, the latter calculated from α' by assuming the value of β obtained by the Jones method. These values differ by but 0.0004 and 0.0006 respectively from the values recorded in table 2 and may serve to support the estimated limits of error.

A Powder Pattern for Natrolite

Natrolite is represented in the ASTM Powder Diffraction File by card 3-0705 which is unindexed and from a commercial source, the data on the card being taken from various authors. Koizumi and Kiriyama (1953), Peng (1955), Meixner *et al.* (1956) and Neumann *et al.* (1957) have published unindexed powder patterns of natrolite without information on the materials examined. These agree only roughly with each other. Krogh Andersen *et al.* (1969) have recently published an indexed powder pattern of natrolite from Glen Farg, Scotland, Scotland, from which they derived the cell dimensions; a 18.276$\pm$0.003, b 18.637$\pm$0.002, c 6.583$\pm$ 0.001 Å, but they also fail to give further information on the matieral used. A calculated powder pattern for natrolite, based on the date of Meier (1960) has just been published by Borg and Smith (1969, pages 774–777).

A powder pattern of the San Benito County natrolite will be offered for inclusion in the X-Ray Diffraction File. For this pattern measured spacings were obtained from shrinkage corrected films made with Ni-filtered Cu radiation in a camera of 114.59 mm diameter. Intensities were estimated by comparison with a photographic strip of graded exposures. Spacings were calculated from the dimensions given in Table 2, using the POPA program of H.–R. Wenk and a CDC computer. Indexing was checked by comparing intensities with calculated F's of Meier (1960, table 3) supplemented by inspection of single crystal films. This powder pattern closely resembles that published by Krogh Andersen *et al.* mentioned above.

Characteristic Intergrowths

Hey (1932, p. 249) refers to twins of natrolite on (110) described by Stadtländer (1885, 113–122) and by Lacroix (1896). However, careful reading of these descriptions suggests that the intergrowths described may not have been twins on (110). Lacroix (1896, p. 424) refers to "rotation de 90° autour de l'axe vertical" and the material described by Stadtländer had previously been interpreted in a similar manner by von Koenen (1874), though Stadtländer preferred to consider the crystals to

be twins on (110), Lacroix cited a number of similar occurrences and also referred to fibrous uniaxial natrolite whose optical properties he considered to arise from such intergrowths in the manner postulated by Mallard. Brauns (1891, p. 67–69) in discussing these natrolite intergrowths clearly distinguished between twins on (110) and 90° rotation on c bringing a and b into coincidence and inclined towards the latter for the material described by von Koenen and Stadtländer. Recently truly tetragonal natrolite has been described by Krogh Andersen *et al.* (1969). Incidentally they refer to "a pseudo-uniaxial symmetry" arising by random orientation of a and b axes but do not seem to consider that this has any pertinence to the tetragonal natrolite.

Six of the Colorado natrolite crystals were examined by means of single crystal X-ray diffraction, oscillation, Weissenberg and precession methods being used. Three of these crystals, all of such size that the entire crystal was within the X-ray beam, showed a type of intergrowth akin to twinning not previously studied by X-ray methods. In each case the c axes of two lattices are parallel or nearly so while the b axis of one coincides with the a axis of the other and vice versa. In one case alignment is sensibly perfect as shown by the enlargement of one quadrant of an khO precession pattern (Fig. 2). This best example occurs in a crystal which is doubly terminated. Initially morphological evidence of the intergrowth was overlooked. In measurement with c normal to the rotation axis of the goniometer for recording pyramidal faces at both ends the ϕ and ρ angles for (111) differ by only 21', as can be seen from the values in the last four columns of Table 1, recalling that the supplement of 70° 11', 19° 49', can be taken as ϕ in the last setting. Two faces of {111} were measured at each end. The average values for their coordinate angles at one end are 19° 25', 71° 12' and at the other end 19° 51', 71° 34'. The coordinate angles for the faces of {331}, measured at one end only, are in agreement.

The intergrowth can be explained nicely on the basis of the structure of natrolite. A segment of this structure, projected onto (001), is shown in Figure 3. It consists of columns parallel to c which may be taken to have the composition $Si_3Al_2O_{10}$. These share corners, O_{II} atoms (nomenclature of Meier, 1960), with adjoining columns at two levels within one repeat distance for each colum at points designated A, A', B, B', etc. Except for the shading that indicates Al-centered tetrahedra the departure of the structure from tetragonal symmetry would scarcely be discernible in the drawing. The columnar habit, {110} cleavage and frequent fibrous character of natrolite indicate that the strongest bonding is within the columns. The vector A-A' is symmetrically equivalent to B-B' (by d glide in x, 3/8, z indicated in the drawing by the conventional symbol). If the structure to the upper right of A-A' is rotated clockwise on c by 90° and
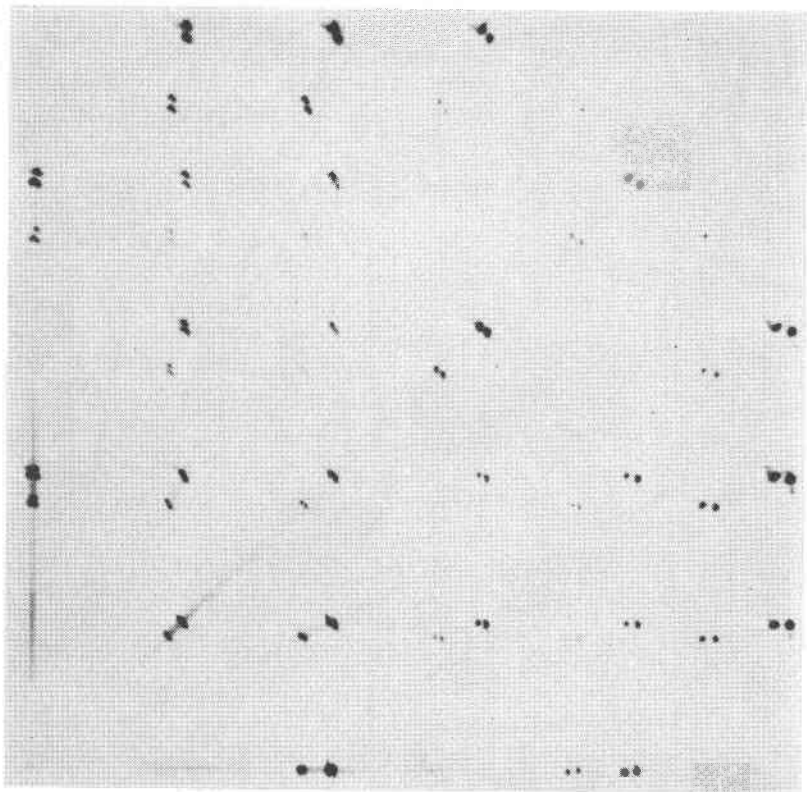
FIG. 2. One quadrant of an *hk*0 precession pattern of a regularly intergrown pair of natrolite crystals. Pattern made with unfiltered Cu radiation. Enlargement 2×.

attached at the lower right of B-B′ a of one part will coincide with b of the other and c will be in common. This would be in accord with the view of Lacroix cited above.

The resulting structure would have a continuously linked framework but at the points where the two orientations meet Al-centered tetrahedra would be juxtaposed contrary to relations in the ideal single crystal. One may imagine that an intergrowth of this sort may arise by a "mistake" in the growth of a crystal, an Al atom going into a position where there should be a Si, or a pair of columns being joined to another pair in the manner suggested. However, the azimuth of A-A′ projected onto (001) is 44° 3′. So, if A is placed at B and A-A′ rotated 90° it will be out of line with B-B′ by 1° 54′, or the separation at B′ will be about 0.3 Å. This discrepancy must be accommodated by adjustments within the framework distributed over eight tetrahedra or ca. 0.04 Å per tetrahedron, consid-
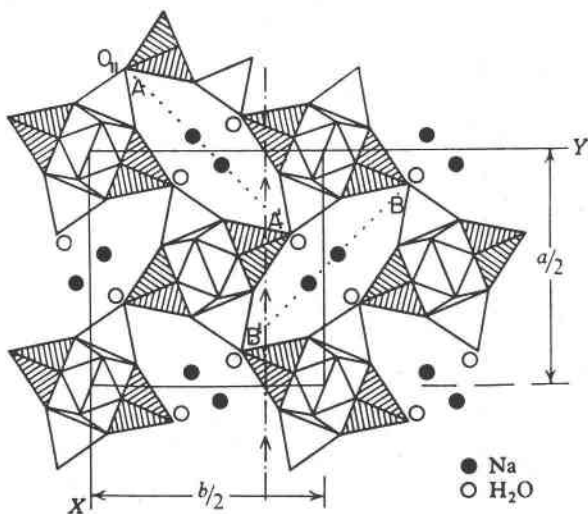
Fig. 3. Structure of natrolite projected onto (001). Modified from Meier (1960, fig. 2) as redrawn by Deer, Howie and Zussman (1963, vol. 4. fig. 110. p. 362). The Al tetrahedra are shaded. Space group $Fdd2$, cell content $8[Na_2(Si_3Al_2O_{10}) \cdot 2H_2O]$.

erably less than the variation of O-O distinces within a tetrahedron reported by Meier (1960, table 4). Two pairs of $Si_3Al_2O_{10}$ columns could fit together in the manner indicated with no more distortion than this. At a distance from the region where the juxtaposition of the two orientations is initiated the misfit would gradually increase due to the difference of about 1.8 percent between a and b. There would be only trifling changes in the bond angles from Al-O_{II}-Si to Al-O_{II}-Al and Si-O_{II}-Si, the precise amount of the changes depending on the manner in which the aforementioned adjustments take place.

One may also speculate as to the nature of the structure at the boundary in a (110) twin of natrolite. According to the conventional view of twinning one part is turned 180° on the normal to (110) relative to the other in such a twin. B-B' differs in azimuth from (110) by only 26' so that the twinning operation is practically equivalent to turning B-B' end for end. This also brings Al-centered tetrahedra together. Additionally the sense of the polar c axis in one part of the twin will be opposed to that in the other part. However, if twinning on (110) is regarded as involving reflection of the structure in the twin plane no such difference in the sense of the polar c will exist. Again some adjustment is required to fit the two parts of the structure together so that the $\{110\}$ planes of the two parts will be parallel. The a and b axes of the one part will diverge from the b and a axes of the other by only 1°2', the divergence of $hh0$ and $h\bar{h}0$ of the

two lattices in Figure 1. Probably the two cases can be distinguished with assurance only in favorable circumstances.

Aminoff and Broomé (1931, p. 376) suggested that the structure at the boundary of a twin must correspond to that of a polymorph or some other plausible structure. For instance, the structure at the composition surface of a sphalerite (111) contact twin has been shown to correspond to the wurtzite 2H, 4H or 6H structures (Pabst, 155, fig. 9). Krogh Andersen *et al.* (1969) have recently described tetragonal natrolite from Greenland. Its cell dimensions are a 18.446, c 6.619 Å, a being very close to the mean of a and b of ordinary orthorhombic natrolite. Presumably Si_{II} and Al are disordered in the tetragonal polymorph of natrolite. The juxtaposition of Al-centered tetrahedra (and Si_{II}-centered tetrahedra) in the postulated structure of {110} twins of natrolite or of the intergrowth described above corresponds to local disorder. Hence either of these cases may be considered to fulfill the requirement of Aminoff and Broomé as to the conditions at a twin boundary.

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