

basalt to deeply-weathered bauxite profiles would be expected to neutralize the effects of possible variations in the composition and/or structure of the parent material.

REFERENCES

- BATES, T. F. (1952) Interrelationships of structure and genesis in the kaolinite group. *Problem in Clay and Laterite Genesis, Symp., A.I.M.M.*, New York, 144-153.
 HANLON, F. N. (1945) The bauxites of New South Wales. *Jour. Roy. Soc. N.S.W.* **78**, 94-112.
 LOUGHNAN, F. C. AND P. BAYLISS (1961) The mineralogy of the bauxite deposits near Weipa, Queensland. *Am. Mineral.* **46**, 209-217.
 OWEN, H. B. (1954) Bauxite in Australia. *Bur. Mineral. Res. Bull.* **24**.

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CELL DIMENSIONS OF DEHYDRATED NATROLITE

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Dehydration studies of natrolite ($\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$) have been carried out by a number of researchers in the past to delimit its dehydration temperature using DTA and thermogravimetric methods (Milligan and Weiss, 1937; Koizumi and Kiriyaama, 1953; Peng, 1955). However, with regard to structural change accompanying the dehydration, little has been done. In view of this, the present work was carried out in the hope of obtaining data on the cell dimensions of dehydrated natrolite and perhaps also information concerning possible mechanism of dehydration.

Two furnace attachments were constructed to be used with the Unicam type oscillation and the Buerger precession cameras, respectively (Dent and Taylor, 1956; Smith and Brown, 1959). A specially constructed cassette was employed in the oscillation method. The cassette had a slit having a width of 4.00 cm, and film was wrapped outside. Natrolite crystals used in the experiment were selected from the Genth Collection of the Pennsylvania State University. The crystals were needle-shaped, 1.0 mm in length and 0.3 mm in cross-section. The locality of the crystals was given as Bergen Hill, N. J. The chemical composition of natrolite from the same locality is given below (Hey, 1932):

SiO_2	47.22	K_2O	1.27
Al_2O_3	26.94	CaO	1.05
Na_2O	14.45	H_2O	9.28
		Total	100.21

The number of cations and water molecules per unit cell, assuming 80 oxygen atoms will be:

Si	23.92	K	0.82
Al	16.10	Ca	0.52
Na	14.29	H ₂ O	15.68

Crystals were rotated around the c axis in the oscillation method, and the same axis was set parallel to the x -ray beam in the precession technique.

Natrolite dehydrates at 300° C., which is in good agreement with the thermogravimetric data. On dehydration, natrolite becomes disordered as evidenced by the streaks seen in Figs. 1 and 2. No progressive development of diffuse streaks was observed in the course of raising temperature, indicating that two molecules of water (in the formula of natrolite) were lost simultaneously. In this respect, the water molecules in natrolite should be more properly termed as water of crystallization rather than zeolitic water.

The unit cell dimensions of dehydrated natrolite were found to be:

$$\begin{aligned} a &= 16.34 \pm 0.04 \text{ \AA} \\ b &= 17.09 \pm 0.04 \text{ \AA} \\ c &= 6.60 \pm 0.02 \text{ \AA} \\ \gamma &= 90^\circ \pm 2' \end{aligned}$$

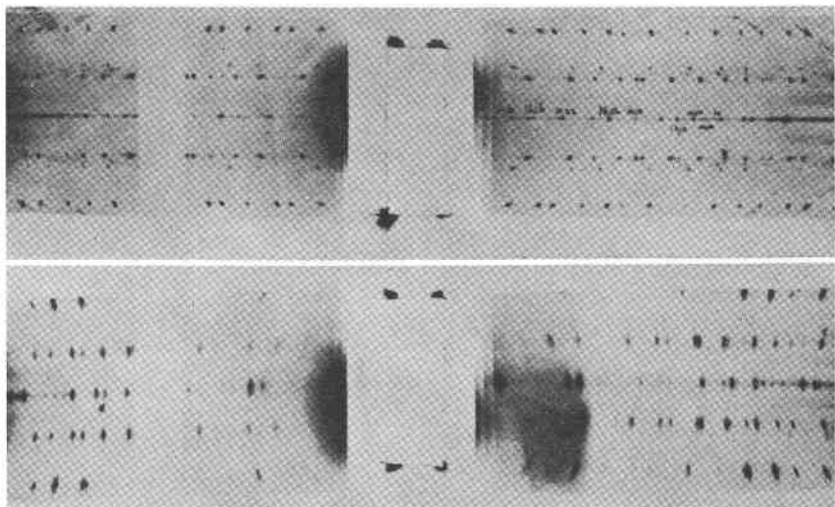


FIG. 1. Back-reflection oscillation photographs (taken with the cassette as described in the text) of natrolite and dehydrated natrolite.

(a) Upper. Natrolite, taken at 290° C., c -axis rotation. CuK α radiation, 8 hrs, x -ray || a axis. Central opening is for collimator.

(b) Lower. Dehydrated natrolite, taken at 305° C., 9 hrs. The rest same as in Fig. 1a.

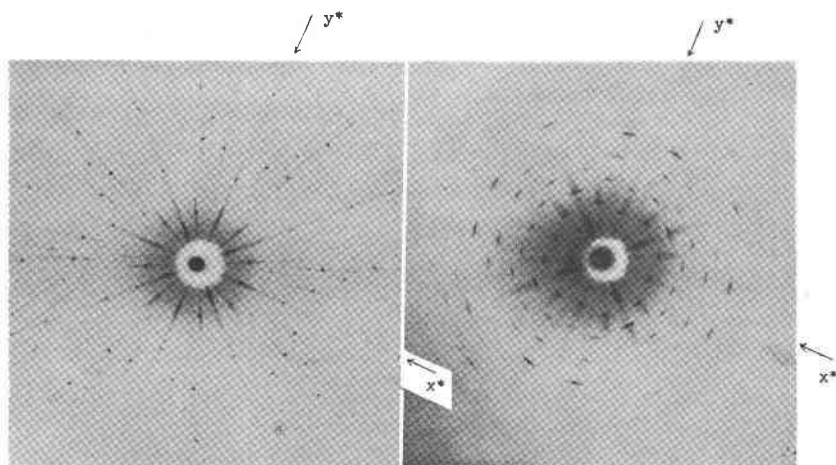


FIG. 2. Precession photographs.

(a) Left. Natrolite, (hk0), MoK α radiation, 2 hrs.

(b) Right. Dehydrated natrolite, (hk0), 12 hrs. Note the disappearance of high-angle reflections, indicating high thermal motion.

The shrinkage of the cell dimensions of dehydrated natrolite, thus, amounts to 10.7 per cent of the a axis, 8.3 per cent of the b axis; no change in the c axis was observed.

Indexing of the precession diagrams showed that the space group is $Fmm2$, $F222$ or $F2$. The distribution of intensities on the precession photographs (especially among weak spots) indicated monoclinic symmetry. Furthermore, in the space group of natrolite, $Fdd2$ (Pauling, 1930; Meier, 1960), there is neither a mirror plane parallel to, nor a two-fold axis perpendicular to the c axis. It is extremely unlikely that these new symmetry elements will be introduced after a simple transformation. Therefore, the most probable space group is monoclinic $F2$. The face-centered lattice is preserved, thus making c axis as the unique axis and the monoclinic angle γ .

The abatement of the cell size of dehydrated natrolite can easily be explained structurally. In the crystal structure of natrolite, there are essentially two types of linkage. One is the bonding between the tetrahedral groups, each group consisting of 3SiO_4 and 2AlO_4 , to form a rigid chain (two oxygen atoms are shared by the neighboring groups in this type of linkage) in the direction of the fiber axis ($=c$). The other, in the directions perpendicular to c , is more weakly linked by single oxygen bridges. Hence the structure is liable to distortion in the directions perpendicular to the fiber axis. The result obtained in this experiment clearly demon-

strated this susceptibility. In contrast to this situation in fibrous zeolites, of which natrolite is a representative, robust three-dimensional network zeolites (for example, chabazites) are self-supporting, in the sense that structural polyhedra are not only tightly bonded clusters of tetrahedra but they are also linked to the other polyhedra by multiple oxygen bridges, leading to a framework which shows minimal lattice changes during and after dehydration. Smith (1962) reported the cell dimensions of dehydrated chabazite as: $a=9.37 \text{ \AA}$, $\alpha=92^\circ 01'$, compared with the unhydrated-cell dimensions of $a=9.45 \text{ \AA}$, $\alpha=94^\circ 28'$. In terms of the cell volume, the diminution is only about two per cent for chabazite as compared to 18 per cent in the case of natrolite.

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REFERENCES

- DENT, L. S. AND H. F. W. TAYLOR (1956) An attachment for high-temperature single-crystal x -ray work. *Jour. Sci. Instruments*, **33**, 89–91.
- HEY, M. H. (1932) Natrolite and metanatrolite. *Mineral. Mag.* **22**, 243–289.
- KOIZUMI, M. AND R. KIRIYAMA (1953) Structural changes of some zeolites due to thermal dehydration. *Osaka Univ., Japan, Sci. Rept.* **2**, 65–85.
- MEIER, W. M. (1960) Crystal structure of natrolite. *Zeit. Krist.* **113**, 430–444.
- MILLIGAN, W. O. AND H. B. WEISER (1937). The mechanism of the dehydration of zeolites. *Jour. Phys. Chem.* **41**, 1029–1040.
- PAULING, L. (1930) The structure of some sodium and calcium aluminosilicates. *Proc. Nat. Acad. Sci.* **16**, 453–459.
- PENG, C. J. (1955) Thermal analysis study of the natrolite group. *Am. Mineral.* **40**, 834–856.
- SMITH, J. V. (1962) Crystal structures with a chabazite framework. I. Dehydrated chabazite. *Acta Cryst.* **15**, 835–844.
- AND W. M. BROWN (1959) X -ray precession photography at temperatures up to 1300°C . (abs). *Internatl. Cryst. Union*, 57.