

An X-ray examination of mordenite (ptilolite).

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I. *Introduction.*

THE structures of the fibrous zeolites edingtonite, thomsonite, and natrolite (with scolecite and mesolite) were determined by X-ray methods some years ago [1], and it was suggested shortly afterwards by M. H. Hey and F. A. Bannister in a private communication to one of us (W.H.T.) that 'ptilolite', another zeolite of fibrous habit, might prove to have a similar structure. An X-ray rotation photograph about the needle axis indicated a unit-cell dimension along the needle axis of approximately 7.5 Å., quite different from the axis c 6.6 Å. characteristic of the fibrous zeolites previously examined, and no further examination of 'ptilolite' was made at that time. We have now determined the unit cell and space-group of this crystal, and further work is in progress with a view to the complete analysis of the structure. This paper presents an account of the experimental data which we have obtained.

In the meantime a certain confusion in the naming of the mineral has been removed by the work of Hey and Bannister in the course of their systematic investigation of zeolites. In works of reference (for example, Dana's 'System of Mineralogy', Hintze's 'Handbuch der Mineralogie') the name mordenite is applied to a platy zeolite similar in habit and composition to heulandite, while ptilolite is applied to a zeolite of fibrous habit; and the platy 'mordenite' has also been named clinoptilolite by Schaller [2]. Hey and Bannister [3] have shown, however, that the platy mordenite (clinoptilolite) is structurally identical with heulandite, and is merely a silica-rich variety of that mineral; while the original fibrous mordenite of How is structurally identical with (fibrous) ptilolite, and is quite different from heulandite. They therefore, on grounds of priority, apply the name mordenite to the fibrous zeolite commonly known as ptilolite. This nomenclature is adopted in the present paper.

II. *Experimental Data.*

We have examined ptilolite from San Piero in Campo, Elba, Italy (B.M. 1914,321), mordenite from Aros, Isle of Mull, Scotland (B.M. 47614), and flokite from Iceland (B.M. 1932,1297). The appearance, under the microscope, of crystals from Elba and from Mull indicates that twinning

or parallel growth is common, and this is confirmed by the nature of the X-ray diffraction-spots obtained on rotation photographs. The X-ray data quoted below have been obtained from small crystal fragments selected because of their apparent freedom from twinning and parallel growth.

(i) *Specific Gravity*.—The specific gravities of small fragments of mordenite from Elba and Mull have been determined by flotation in a mixture of chloroform and bromoform: they are 2.15 ± 0.01 (Elba) and 2.12 ± 0.01 (Mull). According to Callisen [4] the specific gravity of flokite is 2.102.

(ii) *Pyroelectricity*.—The results of pyroelectric tests by the method of cooling in liquid air are inconclusive. Some specimens show a fairly definite, though weak, effect; other specimens from the same locality show no trace of the effect. In every case where the effect is observed, the electric charges are located at the ends of the needle axis, which is therefore the polar axis. Different specimens may perhaps be expected to yield inconclusive results from pyroelectric tests since parallel growths and twin growths are common.

(iii) *Symmetry*.—The crystals selected as being free from parallel growth and twinning are lath-shaped fragments with dimensions of the order $1 \times 0.2 \times 0.05$ mm. The extinction on the plate face of the crystal is parallel or nearly parallel to the needle axis, and the extinction on a section perpendicular to the needle axis is parallel to the plate face. The symmetry may therefore be assumed to be approximately orthorhombic with the *c*-axis [001] parallel to the needle axis, and with the plate face as pinakoid (100).

A Laue photograph taken with the X-ray beam normal to the plate face and so parallel to the assumed orthorhombic *a*-axis [100] shows reflection planes parallel and perpendicular to the needle axis, i.e. parallel to planes (010) and (001) in the assumed orthorhombic cell. Further confirmation of the orthorhombic symmetry is obtained in numerous oscillation photographs.

In some crystal fragments the extinction on the plate face (orthorhombic (100)) is not quite parallel to the needle axis: this departure from straight extinction would suggest that the true symmetry is monoclinic and only pseudo-orthorhombic. In a private communication Mr. F. A. Bannister informs us that his X-ray data conform to the requirements of orthorhombic symmetry, but that the extinction on the plate face may be inclined to the needle axis by as much as 4° , the extinction-angle apparently varying with the chemical composition.

It is therefore probable that the true symmetry is monoclinic, but that the structure is very closely pseudo-orthorhombic; the departure from the higher symmetry is too small to be revealed by X-ray methods, but is shown by the highly sensitive optical properties. Such pseudo-symmetry is frequently observed in complex structures of this type [5].

(iv) *Unit cell and space-group*.—The axial lengths of the orthorhombic unit cell, deduced from measurements on oscillation photographs obtained from a crystal from Mull, are a 18.25 ± 0.1 , b 20.35 ± 0.1 , c 7.50 ± 0.05 Å., the c -axis being the needle axis, the (100) plane the plate face of the crystal.

All reflections (hkl) are absent if $(h+k)$ is odd, and the cell is therefore centred on the c face (001). Also, reflections ($h0l$) are absent if either h or l is odd, reflections ($0kl$) are absent if k is odd, present when l is either odd or even, and reflections ($hk0$) are present when h and k are either both odd or both even, absent if $(h+k)$ is odd. Possible space-groups [6] are therefore $D_{2h}^{17} = Cmc$, $C_{2v}^{12} = Cmc$, and, with interchange of a - and c -axes, $C_{2v}^{16} = Ama$. If the last space-group is selected, the polar axis is normal to the plate face of the crystal; the pyroelectric tests indicate, however, that if the crystal is truly polar the needle axis must be the polar axis, and it is therefore probable that the space-group is $C_{2v}^{12} = Cmc$, assuming, of course, that the symmetry is orthorhombic.

(v) *Contents of the unit cell*.—The formula of ptilolite is given by Hintze (1897, vol. 2, p. 1824) as $(Ca, K_2, Na_2)Al_2Si_{10}O_{24} + 5$ (or 7) H_2O , while Callisen [4] gives as the formula of flokite $H_8(Ca, Na_2)Al_2Si_9O_{26} \cdot 2H_2O$ which is equivalent to $(Ca, Na_2)Al_2Si_9O_{22} \cdot 6H_2O$ when all the hydrogen is assumed to be present as water.

We have calculated the cell contents for flokite, on the basis of Callisen's published density and analysis [4], and assuming an orthorhombic unit cell with edges a 18.25, b 20.35, c 7.50 Å. The composition of flokite is SiO_2 67.69, Al_2O_3 12.43, CaO 2.65, MgO 0.09, Na_2O 4.36, $H_2O + 8.82$, $H_2O - 4.53$, total 100.57; the density is 2.102, and the unit cell therefore contains $Ca_{1.7}Na_{5.0}Al_{8.7}Si_{40.0}O_{97.2} + 26H_2O$.

Similarly, we have calculated the cell contents for the Elba mordenite (ptilolite) (B.M. 1914,321) assuming the same orthorhombic unit cell; the specific gravity is 2.15, and the composition as determined by D'Achiardi [7] is SiO_2 65.21, Al_2O_3 11.20, CaO 3.77, MgO trace, alkalis 6.07, $H_2O + 10.11$, $H_2O - 4.11$, total 100.47. The alkalis are not separated and are stated to consist mainly of sodium, with spectroscopic indications of potassium, lithium, and caesium. Assuming the alkali to be pure Na_2O the unit cell contains $Ca_{2.4}Na_{7.1}Al_{8.0}Si_{39.5}O_{96.9} + 28.4H_2O$.

Assuming the alkali to be pure K_2O the unit cell contains $Ca_{2.4}K_{4.7}Al_{8.0}Si_{39.5}O_{95.7} + 28 \cdot 4H_2O$. No analysis of the Mull mordenite is available.

Great accuracy is not claimed for the measurements of either specific gravity or unit cell dimensions, but the above calculations may be taken to indicate that the unit cell of mordenite contains a group ideally represented by $Ca_4Al_8Si_{40}O_{96} + 28H_2O$, i.e. four molecules of composition $CaAl_2Si_{10}O_{24} \cdot 7H_2O$. In the mineral, calcium is partly replaced by sodium and potassium, and the water content is variable, probably depending upon the vapour pressure of the surrounding atmosphere, as is suggested by Hintze (loc. cit.) in the case of ptilolite analyses made at Denver and at Washington.

III. Nature of the Structure.

In attempting to deduce the structure of mordenite two initial difficulties are encountered. In the first place, the optical properties indicate monoclinic symmetry, while the X-ray data conform to the requirements of orthorhombic symmetry. This difficulty is probably more apparent than real: it seems reasonable to suppose that the structure approximates very closely indeed to one of orthorhombic symmetry—so closely, in fact, that no difference can be detected by X-ray methods. Secondly, assuming orthorhombic symmetry, the choice of space-group depends upon the results of the pyroelectric tests; if the crystal is pyroelectric the space group is $C_{2v}^{12} = Cmc$, otherwise it is $D_{2h}^{17} = Cmcm$. By analogy with the case of thomsonite [1], it is legitimate to suggest that to a first approximation the structure may perhaps possess holohedral symmetry, the actual polar structure being only a slight distortion of the holohedral structure. Only after completion of the structure analysis will it be possible to decide this point.

It is highly probable that this zeolite structure is based on a framework of linked SiO_4 and AlO_4 tetrahedra, with water molecules and cations located in cavities existing within the relatively rigid framework. The unit cell contains 48 tetrahedra, and the symmetry of the crystal is low (even if holohedry is assumed), so that it is difficult to test the correctness of any assumed tetrahedron framework by comparing observed and calculated intensities of reflection. We have discovered one arrangement of 48 tetrahedra per unit cell, of the right dimensions, and possessing the holohedral symmetry of $D_{2h}^{17} = Cmcm$, but we have so far been unable to prove that this structure, or any slight modification of it, is capable of explaining the observed intensities of reflection. Further work is in progress.

IV. *Summary.*

Specimens of the fibrous zeolite mordenite (ptilolite) have been examined by X-ray methods, and the specific gravity and pyroelectric properties determined. Laue and oscillation photographs indicate that the structure possesses orthorhombic symmetry, and the unit cell, with edges a 18.25, b 20.35, c 7.50 Å., contains four molecules of composition $(\text{Ca}, \text{Na}_2, \text{K}_2)\text{Al}_2\text{Si}_{10}\text{O}_{24} \cdot 7\text{H}_2\text{O}$. The space-group is either $D_{2h}^{17} = Cmc$ or $C_{2v}^{12} = Cmc$; the pyroelectric tests are somewhat inconclusive, but indicate that the c -axis [001] is probably polar. The structure is probably based on a framework of linked tetrahedra.

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