

The cell dimensions and space-group of pinnoite.

By H. P. STADLER, B.Sc.

[Communicated by F. A. Bannister, read June 6, 1946.]

PINNOITE, first described by Staute¹ in 1884, is straw-yellow, granular to faintly fibrous. It occurs in the upper kainite layers at Stassfurt, and is found associated with earthy boracite from which it is freed by washing with water. The analysis corresponds to the formula $\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, and Staute assumes the mineral to be an alteration product of boracite, $6\text{MgO} \cdot \text{MgCl}_2 \cdot 8\text{B}_2\text{O}_3$. Groth classes pinnoite together with $\text{CaO} \cdot \text{B}_2\text{O}_3$ as a hydrated metaborate.² This assumption does not seem justified, as will be pointed out later.

Although the mineral appears crystalline, the individual crystals are so firmly intergrown, and the material is so brittle that Staute never succeeded in isolating a crystal with developed faces. This was done later by Luedecke.³ He ascribes tetragonal symmetry with pyramidal hemihedrism to pinnoite, and from goniometric measurements deduced an axial ratio $c/a = 0.7609$. On the specimen available for the X-ray examination discussed in this paper, no crystal with faces could be found. Homogeneous-looking fragments were examined under the microscope. Those that showed no inclusions or wavy extinction were then submitted to X-ray examination by Laue photographs in order to eliminate intergrown crystals. The single-crystal fragments finally selected had to be set entirely by the double oscillation technique. Rotation photographs, using unfiltered Fe or filtered Cu radiation, were obtained about [001], [110], [100], and [201]. A complete set of oscillations (15°) was taken about [110], and absent spectra were specially looked for by long-exposure 5° oscillations about [001], [100], and [201]. The systematic absences so found were $h00$ for h odd, and $00l$ for l odd. The X-ray symmetry $4/m$ is apparent from the oscillation photographs, and was confirmed by a Laue photograph along c . This, together with the halving of $00l$, fixes the space-group as $C_4^3 = P4_2$ or $C_{4h}^2 = P4_2/m$. The halving of $h00$ was not required by the space-group, and may be confined to lower orders.

¹ H. Staute, Ber. Deutsch. Chem. Gesell., 1884, vol. 17, part 2, p. 1584.

² P. Groth, Chemische Krystallographie. Leipzig, 1908, vol. 2, p. 735.

³ O. Luedecke, Zeits. Naturwiss. Halle, 1885, vol. 58, p. 646.

Rough values of the cell dimensions were found from the layer-line distances of the rotation photographs. More accurate values were then obtained by measuring up high-order equatorial reflections with the film in Straumanis position.¹ This eliminates film-shrinkage errors. Absorption of X-rays by this light material is small, and its effect in high orders completely negligible. In this way values $a = 7.617 \pm 0.002 \text{ \AA}$. and $c = 8.190 \pm 0.002 \text{ \AA}$. were obtained.² They give an axial ratio $c/a = 1.075$, which is in good agreement with Luedecke's value, if the different choice of axes is taken into account: thus $c'\sqrt{2} = 1.076$. Assuming four molecules per unit cell, the calculated specific gravity is 2.290, in agreement with Larsen's value³ of 2.29.

The atoms lie in general positions so that all x and z parameters are indeterminate, and a full analysis would be required to find the structure. With no heavy atoms in the molecule this would be an arduous task. The structure of $\text{CaO} \cdot \text{B}_2\text{O}_3$ has, however, been determined by Zachariasen and Ziegler.⁴ According to these authors the B_2O_4 ion is composed of BO_3 triangles. It is thus a chain-ion of the pyroxene type. Since all the atoms of the BO_3 triangle lie in one plane, which also contains the chain propagation direction, CaB_2O_4 shows a marked birefringence of 0.14, whereas that of pinnoite is only 0.01; the length of the repeat unit of the metaborate chain is 4.3 \AA ., which is far removed from either of the cell dimensions of pinnoite. The double repeat of 8.6 \AA . may possibly be fitted into the cell as regards dimensions, but it would have to lie in special positions and symmetry considerations make this impossible.

An alternative to regarding pinnoite as a metaborate would be to write the formula as $\text{Mg}(\text{H}_2\text{BO}_3)_2 \cdot \text{H}_2\text{O}$, i.e. as an acid orthoborate, but there seems to be no positive evidence in support of such a formula. In fact, the behaviour on dehydration opposes both these structures. No water at all is given off below 180° C., suggesting that all the water is present in the form of OH groups. The intermediate products of dehydration showed the same powder pattern as pinnoite on a background of heavy scatter, so that no intermediate crystalline phases appear to be present. This condition of the total absence of water of

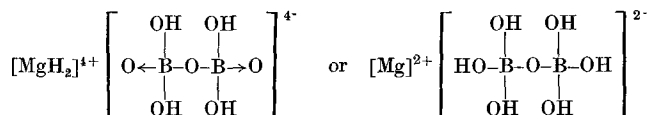
¹ M. J. Buerger, X-ray crystallography. New York, 1942, p. 394.

² The conversion factor used being $1 \text{ kX} = 1.00202 \text{ \AA}$.

³ E. S. Larsen and H. Berman, Microscopic determination of nonopaque minerals. Washington, 1934, p. 70.

⁴ W. H. Zachariasen and G. E. Ziegler, Zeits. Krist., 1932, vol. 83, p. 354. [M.A. 5-316.]

hydration would be fulfilled by the electronically balanced, but otherwise hypothetical:



As such, it would be the salt of an acid $\text{H}_8\text{B}_2\text{O}_7$, which has neither been described in its free state nor in the form of a salt. In conclusion, therefore, it can only be said that X-ray and chemical evidence make it most unlikely for pinnoite to be a metaborate, but that further work will be required to assign a definite structure to this mineral.

Acknowledgements.—The experimental work was carried out at the British Museum of Natural History, with the aid of a research studentship of Birkbeck College. The author wishes to express his thanks to the authorities of the British Museum of Natural History, especially the Keeper of Minerals, Dr. W. Campbell Smith, for granting him facilities to work at the museum, and for providing specimens and materials, and to Mr. F. A. Bannister and Dr. G. F. Claringbull for their constant advice, without which this paper could not have been written.