

NOTES AND NEWS

TETRAHEDRAL BORON IN TEEPLEITE AND BANDYLITE

VIRGINIA ROSS AND JOHN O. EDWARDS, *Department of Chemistry,
Brown University, Providence, Rhode Island.*

The trivalent boron-oxygen radius ratio is 0.20 (Pauling, 1945) allowing boron either triangular or tetrahedral coordination. In the simple anhydrous borates, triangular coordination is very common; while in hydrous or hydroxy-borates and boro-silicates either tetrahedrally coordinated boron occurs alone or both types of coordination prevail as shown, for example, by Christ and Clark (1957). In the simple hydroxyl borates: teepleite, $\text{Na}_2\text{B}(\text{OH})_4\text{Cl}$ and bandylite, $\text{CuB}(\text{OH})_4\text{Cl}$, Fornaseri (1949, 1950, 1951) and Collin (1951) cited from *x*-ray analyses the presence of discrete tetrahedral $\text{B}(\text{OH})_4^-$ ions.

Natural teepleite was first described by Gale, Foshag and Vonsen (1939) as a mineral component of Borax Lake, California, resulting from the reaction of halite with borate-rich brine. Palache and Foshag (1938) previously had discussed the formation of bandylite as a secondary mineral in altered volcanic rock at Calama, Chile. *X*-ray Weissenberg analysis of teepleite was carried out by Switzer (Gale et al.). From single crystal studies of bandylite, Berman (Palache and Foshag) implied that the two minerals were characterized by the same space group symmetry, *P* 4/*n* *mm*. The correct space group of bandylite has since been shown by Collin to be *P* 4/*n*. Since no *x*-ray powder data have been published to facilitate the identification of these two species, they are given in Tables 1 and 2. The axial ratios of the two minerals differ by as much as 0.24 and their *x*-ray powder patterns are quite dissimilar. From the previous literature this distinction has not been made obvious.

The crystal structures of teepleite and bandylite are nevertheless similar, in that they have been found to consist of discrete $\text{B}(\text{OH})_4^-$ ions and octahedrally coordinated sodium and copper ions having four nearest neighbor oxygen atoms and two chlorine ions. The four sodium ions in teepleite are located at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$ (Fornaseri, 1949); in bandylite the copper ions are at $(0, \frac{1}{2}, 0.639)$ (Collin, 1951). The structure of bandylite proposed by Fornaseri (1950) was based upon the original space group and differed with respect to the orientation of the polyhedra in the basal plane.

The tetrahedral configuration about the boron in teepleite has now been confirmed by infra-red and nuclear quadrupole resonance studies at Brown. The Raman spectrum of the borate ion in aqueous solution was reinvestigated and compared to the vibrational frequencies of the

TABLE 1. X-RAY POWDER DIFFRACTION DATA FOR SYNTHETIC TEEPLEITE

CuK α (Corrected for camera radius and film shrinkage) Tetragonal, *Space Group* $P4/nmm$, $a_0=7.26\pm 0.01$ Å, $c_0=4.85\pm 0.01$ Å, $c/a=0.668$ (least squares analysis). $a_0=7.27$, $c_0=4.84$ Å, $c/a=0.666$ (Switzer).

I	<i>d</i> (meas)	<i>d</i> (calc)	<i>hkl</i>	I	<i>d</i> (meas)	<i>d</i> (calc)	<i>hkl</i>
4	5.13	5.13	110	7	1.815	1.815	400
0.5	4.86	4.85	001	5	1.761	1.763	222
6	4.03	4.03	011	7	1.709	1.711	330
2	3.63	3.63	200	8	1.659	1.655	411
5	3.52	3.53	111	5	1.619	1.617	003
8	2.90	2.91	021	3	1.578	1.578	013
10	2.697	2.700	121	7	1.539	1.542	113
5	2.565	2.567	220			1.540	421
0.5	2.425	2.425	002	5	1.476	1.477	023
5	2.295	2.300	102	6	1.446	1.447	213
		2.296	130	0.5	1.425	1.425	412
7	2.264	2.269	221	7	1.396	1.398	332
4	2.195	2.193	112			1.391	051
2	2.162	2.166	301	1	1.365	1.368	223
9	2.015	2.017	022			1.366	511
3	1.941	1.943	122	6	1.348	1.350	422
3	1.858	1.860	231	6	1.299	1.299	521

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR BANDYLITE, MINA QUETANA, CHILE

Film, Harvard Collection No. 5503, Cu-radiation, Ni-filter, (uncorrected for camera radius and film shrinkage). Tetragonal, $P4/n$, $a_0=6.19$ Å, $c_0=5.61$ Å, $c/a=0.906$ (Collin).

I	<i>d</i>	<i>hkl</i>	I	<i>d</i>	<i>hkl</i>
10	5.59	001	4	1.394	
6	4.35	110	3	1.381	
5.5	4.13	101	2.5	1.330	
8	3.08	200	2	1.317	
3	2.80	002	2	1.265	
2	2.69	201	4B	1.137	
8	2.54	102	4B	1.130	
2	2.43	121	1	1.060	
4	2.18	220	0.5	1.030	
7	1.952	122	1	.983	
4	1.858		1	.976	
2	1.764		2	.955	
6	1.655		1	.922	
3	1.544		1	.883	
5	1.457		0.5	.875	

B = broad line.

infrared spectrum of teepelite and theoretical Heath-Linnett values (Edwards, Morrison, Ross and Schultz, 1955). For this purpose large crystals of teepelite were prepared by evaporation of a solution containing equal volumes of sodium borate and sodium chloride. Nuclear magnetic resonance analysis of synthetic teepelite using a field of 5,250 gauss and a Pound-Watkins recording spectrometer yielded a quadrupolar coupling constant, $eqQ=0.094\pm 0.001$ Mcps, corresponding to the resonance of tetrahedrally-coordinated B^{11} with an approximately isometric charge distribution.

Acknowledgment

The nuclear magnetic resonance analysis of teepelite was carried out through the courtesy of Professor P. J. Bray and G. O'Keefe of the Department of Physics, Brown University. The authors are grateful to Professor C. Fronzel for the preparation and loan of the x-ray diffraction powder photograph of bandylite from the Harvard University Collection. This research was supported by the U. S. Army Office of Ordnance Research.

REFERENCES

- CHRIST, C. L. AND CLARK, J. R. (1957), Nature of the polyions in some borate Minerals: Abstr., G.S.A. 38th Ann. Meet., *Bull. Geol. Soc. Amer.*, **68**, 1708.
- COLLIN, R. L. (1951), The crystal structure of bandylite, $CuCl_2 \cdot CuB_2O_4 \cdot 4H_2O$: *Acta Cryst.*, **4**, 204.
- EDWARDS, J. O., MORRISON, G. C., ROSS, V. F. AND SCHULTZ, J. (1955), The structure of the aqueous borate ion: *J. Am. Chem. Soc.*, **77**, 266.
- FORNASERI, M. (1949), La struttura cristallina della teepelite: *Period. Min.*, **18**, 103.
- (1950), La struttura cristallina della bandylite: *Period. Min.*, **19**, 159.
- (1951), Struttura di metaborati tetragonali e loro relazione cristallografiche: *La Ricerca Scientifica*, **21**, 3.
- GALE, A., FOSHAG, W. F. AND VONSEN, M. (1939), Teepelite, a new mineral from Borax Lake, California: *Am. Mineral.*, **24**, 48.
- PALACHE, C. AND FOSHAG, W. F. (1938), Antofagastite and bandylite, two new copper minerals from Chile: *Am. Mineral.*, **23**, 85.
- PAULING, L. (1945), *The Nature of the Chemical Bond*: Cornell University Press, 382.

THE AMERICAN MINERALOGIST, VOL. 44, JULY-AUGUST, 1959

NOTES ON A SECOND OCCURRENCE OF GROUTITE

CURT G. SEGELER, *Brooklyn, New York.*

The talc mines at Talcville, about 8 miles southeast of Gouverneur, New York have long attracted the attention of amateur mineral collectors and others. The prime reason for this interest is the lilac colored variety of tremolite (called hexagonite in some of the older textbooks)