STUDIES OF BORATE MINERALS (II): *X*-RAY CRYSTALLOGRAPHY OF INYOITE AND MEYERHOFFERITE; *X*-RAY AND MORPHOLOGICAL CRYSTALLOGRAPHY OF $2CaO \cdot 3B_2O_3 \cdot 9H_2O$*

C. L. CHRIST, *U. S. Geological Survey, Washington 25, D. C.*

ABSTRACT

Inyoite is monoclinic, $P2_1/a$, $a_0=10.63$, $b_0=12.06$, $c_0=8.40_5$ Å, $\beta=114°02'$. $2CaO \cdot 3B_2O_3 \cdot 9H_2O$ is triclinic $P\bar{1}$, $a_0=7.04_6$, $b_0=9.45_2$, $c_0=7.41_2$ Å, $\alpha=101°21'$, $\beta=101°19'$, $\gamma=99°49'$. The findings of Switzer in Palache (1938) for meyerhofferite are confirmed. Powder patterns, partially indexed, are given for inyoite, meyerhofferite, and $2CaO \cdot 3B_2O_3 \cdot 9H_2O$.

INTRODUCTION AND ACKNOWLEDGMENTS

A systematic study of borate minerals has been continued in the present investigation with the determination of the *x*-ray crystallography of inyoite, $2CaO \cdot 3B_2O_3 \cdot 13H_2O$, the *x*-ray crystallography and morphology of the synthetic mineral $2CaO \cdot 3B_2O_3 \cdot 9H_2O$, and the redetermination of the *x*-ray crystallography of meyerhofferite, $2CaO \cdot 3B_2O_3 \cdot 7H_2O$. Results obtained on meyerhofferite were in excellent agreement with those previously reported by Switzer in Palache (1938). Powder patterns of the three compounds have been measured and partially indexed.

The work was undertaken primarily as a preliminary to the determination of the structures.

The writer is indebted to various colleagues in the U. S. Geological Survey: Waldemar T. Schaller furnished the crystals studied; Mrs. Joan R. Clark made many of the calculations and film measurements; Howard T. Evans, Jr., made the goniometric measurements on and the drawing of $2CaO \cdot 3B_2O_3 \cdot 9H_2O$ and also rendered much helpful advice; Fred A. Hildebrand prepared the powder patterns reported.

EXPERIMENTAL WORK

All of the crystals used were synthetic. Schaller (personal communication) has furnished the following description of the methods of preparation:

Inyoite (2:3:13). Grown on ulexite fragments placed in water and held at room temperature for about two months.

Artificial (2:3:9). Grown on ulexite fragments placed in water and held at 50° C. for approximately one month.

Meyerhofferite (2:3:7). Grown on ulexite fragments placed in water and held at 70–80° C. for approximately six months.

The inyoite crystals were colorless, transparent, tabular {001}, with {110} and {001} dominant, i.e., having essentially the habit described

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by Schaller (1916) for the crystals found at the original Inyo County, Calif., occurrence. The crystals of the $2CaO \cdot 3B_2O_3 \cdot 9H_2O$ were likewise colorless and transparent and are described by the drawing given in Figure 1. The crystal is flattened on $\{\bar{1}01\}$. In order of decreasing importance the forms observed are: g $\{\bar{1}01\}$, a $\{100\}$, b $\{010\}$, e $\{0\bar{1}1\}$, M $\{1\bar{1}0\}$, t $\{\bar{1}\bar{1}1\}$, s $\{1\bar{2}1\}$, and l $\{1\bar{2}0\}$. The last three are not shown on the drawing. The morphological study shows no evidence for assigning

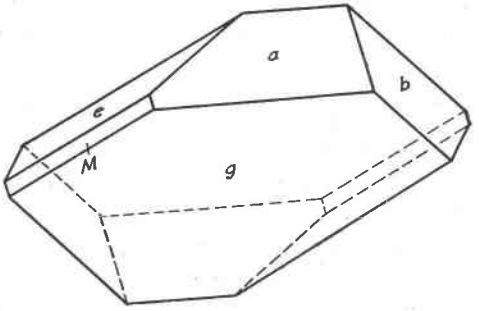

FIG. 1. Crystal of $2CaO \cdot 3B_2O_3 \cdot 9H_2O$ of typical habit (Evans, 1953 personal communication).

Forms:	b	010	e	$0\bar{1}1$
	a	100	g	$\bar{1}01$
	M	$1\bar{1}0$		

less than holohedral symmetry to the crystal. The meyerhofferite crystals were colorless, transparent, prismatic elongated [001] with {100} dominant and {110} somewhat less dominant, i.e., having the habit given in figure 43 of Schaller's original description (1916).

The determination of the lattice type and the measurements of the lattice constants were made using a quartz calibrated precession camera with Mo/Zr ($\lambda_\alpha = 0.71069$ Å; $\lambda_{\alpha_1} = 0.70926$ Å) radiation. The precession films were corrected for vertical and horizontal shrinkage. The powder patterns were prepared in a 114.57 mm. diameter camera with Cu/Ni radiation. Shrinkage corrections were applied. The values of the axial

TABLE 1. CRYSTALLOGRAPHIC ELEMENTS OF INYOITE—$2CaO \cdot 3B_2O_3 \cdot 13H_2O$

Symmetry: Monoclinic; space group $P2_1/a$ (C_{2h}^5)		
Axial elements:		
$a_0 = 10.63$ Å	$\beta = 114°02'$	
$b_0 = 12.06$		
$c_0 = 8.40_5$		
	a:b:c: = 0.8814:1:0.6969	
$V = 984.1$ Å^3	$Z = 2$	Density (calc.) = 1.873

TABLE 2. CRYSTALLOGRAPHIC ELEMENTS OF $2CaO \cdot 3B_2O_3 \cdot 9H2O$

Symmetry: Triclinic; space group $P\bar{1}$ (C_i^1)

Axial elements:

$a_0 = 7.04_6$ Å	$\alpha = 101°21'$
$b_0 = 9.45_2$	$\beta = 101°19'$
$c_0 = 6.41_2$	$\gamma = 99°49'$

$a:b:c = 0.7455:1:0.6784$

Polar elements:

$a^* = 0.1483$	$\lambda = 76°13'$
$b^* = 0.1106$	$\mu = 76°14'$
$c^* = 0.1638$	$\nu = 77°26'$

$p_0:q_0:r_0 = 0.9055:0.6751:1$

Projection elements:

$x_0' = 0.2001$	$p_0' = 0.9508$
$y_0' = 0.2502$	$q_0' = 0.7089$

$\nu = 77°26'$

Cartesian matrices:

$v_1 = -0.2133$ $\quad v_2 = 0.9570$

Direct:

$$M = \begin{Vmatrix} 6.909 & -2.016 & 0 \\ 0 & 9.045 & 0 \\ -1.383 & -1.860 & 6.412 \end{Vmatrix} \text{ (in Å)}$$

Reciprocal:

$$M^{-1} = \begin{Vmatrix} 0.1447 & 0 & 0.0312 \\ 0.0323 & 0.1106 & 0.0390 \\ 0 & 0 & 0.1560 \end{Vmatrix} \text{ (in Å}^{-1}\text{)}$$

$V = 400.7$ Å^3 $\quad Z = 1$ $\quad$ density (calc.) $= 2.002$

lengths for inyoite and meyerhofferite are believed to be correct to 1.5 parts per 1000. The intervector angles are accurate to approximately 05′.

RESULTS

The results obtained from the *x*-ray single crystal study of inyoite are given in Table 1. The ratio of the axial elements and the value of the β-angle obtained in the *x*-ray work for inyoite are in excellent agreement with those obtained from morphological studies by Poitevin and Ellsworth (1921):

Present work	$a:b:c = 0.8814:1:0.6969$	$\beta = 114°02'$
Poitevin and Ellsworth	$a:b:c = 0.8833:1:0.6950$	$\beta = 114°01'$

The value of the *x*-ray density is 1.873. Schaller (1916) obtained 1.875 by the suspension method on Inyo material.

The crystallographic elements obtained from the *x*-ray work on $2CaO \cdot 3B_2O_3 \cdot 9H_2O$ are collected in Table 2. The formulas given by Evans (1948) were used in the calculations. The specific gravity of this compound was determined on the Berman balance to be 2.00. This value agrees well with the *x*-ray value of 2.002.

TABLE 3. COMPARISON OF X-RAY RESULTS FOR INYOITE, $2CaO \cdot 3B_2O_3 \cdot 9H_2O$, MEYERHOFFERITE, AND COLEMANITE

Mineral	Inyoite	Artificial	Meyerhofferite*	Colemanite**
Composition	$2CaO \cdot 3B_2O_3 \cdot 13H_2O$	$2CaO \cdot 3B_2O_3 \cdot 9H_2O$	$2CaO \cdot 3B_2O_3 \cdot 7H_2O$	$2CaO \cdot 3B_2O_3 \cdot 5H_2O$
System	Monoclinic	Triclinic	Triclinic	Monoclinic
Space Group	$P2_1/a$ (C_{2h}^5)	$P\bar{1}$ (C_i^1)	$P\bar{1}$ (C_i^1)	$P2_1/a$ (C_{2h}^5)
Z	2	1	1	2
a	10.63 Å	7.04$_6$ Å	6.61 Å	8.743 Å
b	12.06	9.45$_2$	8.35	11.264
c	8.40$_5$	6.41$_2$	6.49	6.102
α	(90°00′)	101°21′	90°00′	(90°00′)
β	114°02′	101°19′	101°31′	110°07′
γ	(90°00′)	99°49′	86°55′	(90°00′)
Volume	984.1 Å^3	400.7 Å^3	350.5 Å^3	564.2 Å^3
density (calc.)	1.873	2.002	2.118	2.419
a:b:c: (*x*-rays)	0.8814:1:0.6969	0.7455:1:0.6784	0.792:1:0.777	0.7762:1:0.5418
Vol./0-atom	20.5 Å^3	20.0 Å^3	19.5 Å^3	17.6 Å^3

* Switzer in Palache (1938) (original kX units converted to Å).
** Christ (1953).

The present study completes the determination of the crystallographic elements of the known members of the series: $2CaO \cdot 3B_2O_3 \cdot xH_2O$, where $x = 13$, 9, 7, and 5. The pertinent data on the four members of the series are collected in Table 3. One of the most interesting results of this comparison is that there is a progressive decrease in the volume occupied per oxygen atom with decreasing water content. In the case of colemanite the 17.6 Å^3 per oxygen atom is about the value expected if the structure is determined by the nearly close-packing of oxygen atoms (Christ, 1953). It is apparent that in the higher hydrates the percentage of oxygen atoms in nearly close-packing decreases. It is planned to study the thermal analysis for this series as an aid, and in addition, to the structural analysis.

The partially indexed powder patterns for inyoite, $2CaO \cdot 3B_2O_3 \cdot 9H_2O$, and meyerhofferite are given in Tables 4 to 6.

TABLE 4. X-RAY POWDER DATA: INYOITE—$2CaO \cdot 3B_2O_3 \cdot 13H_2O$
Monoclinic $P2_1/a$; $a_0 = 10.63$, $b_0 = 12.06$, $c_0 = 8.40^5$ Å, $\beta = 114°02'$

Measured*		Calculated	
Cu/Ni	$\lambda = 1.5418$ Å		
I	d_{hkl}	d_{hkl}	hkl
71	7.59	7.563	110
6	5.98	6.030	020
18	4.72	4.745	$21\bar{1}$
		4.743	021
		4.695	111
13	3.85	3.841	002
9	3.71	3.714	130
		3.690	$21\bar{2}$
4	3.45	3.449	$12\bar{2}$
6	3.37	3.369	211
6	3.13	3.126	310
100	3.03	3.033	221
		3.015	040
13	2.775	2.779	$20\bar{3}$
		2.777	032
9	2.643	2.643	231
18	2.494	2.503	$013, 33\bar{2}$
		2.494	212
		2.483	132
3	2.410	2.406	321
25	2.286	2.287	241
		2.286	$23\bar{3}$
		2.281	$13\bar{3}$
4	2.185	2.190	410
		2.185	$25\bar{1}, 42\bar{2}$
		2.181	142
		2.180	151
13	2.098	2.102	$20\bar{4}$
		2.092	$15\bar{2}$
		2.090	420
9	2.049	2.055	$43\bar{1}$
		2.049	$25\bar{2}$
		2.044	$2\bar{3}3, 052$
6	1.972		
13	1.916		
18	1.880		
3	1.752		
4	1.605		
6	1.528		
6	1.441		
Plus additional weak lines.			

* Shrinkage correction negligible.

TABLE 5. *X*-RAY POWDER DATA: $2CaO \cdot 3B_2O_3 \cdot 9H_2O$
Triclinic $P\bar{1}$; $a_0=7.04_6$, $b_0=9.45_2$, $c_0=6.41_2$ Å
$\alpha=101°21'$, $\beta=101°19'$, $\gamma=99°49'$

Measured*		Calculated	
Cu/Ni	$\lambda=1.5418$ Å		
I	d_{hkl}	d_{hkl}	hkl
100	9.14	9.05	010
100	6.75	6.743	100
4	6.08	6.079	$\bar{1}10$
71	5.76	5.731	$0\bar{1}1$
50	5.20	5.181	$\bar{1}01$
6	4.88	4.916	110
50	4.56	4.564	$\bar{1}\bar{1}1$
71	4.19	4.207	$\bar{1}20$
		4.195	$1\bar{1}1$
13	4.07	4.070	101
25	3.59	3.587	$1\bar{2}1$
18	3.36	3.364	111
13	3.14		
35	3.08		
50	3.02		
18	2.966		
18	2.864		
50	2.807		
25	2.700		
9	2.594		
71	2.573		
13	2.463		
4	2.405		
6	2.369		
13	2.333		
13	2.268		
4	2.228		
18	2.157		
9	2.133		
35	2.104		
13	2.048		
9	2.005		
9	1.940		
9	1.911		
9	1.878		

Plus additional weak lines.

* Shrinkage correction negligible.

TABLE 6. *X*-RAY POWDER DATA: MEYERHOFFERITE—$2CaO \cdot 3B_2O_3 \cdot 7H_2O$
Triclinic $P\bar{1}$; $a_0=6.61$, $b_0=8.35$, $c_0=6.49$ Å*
$\alpha=91°00'$, $\beta=101°31'$, $\gamma=86°55'$

Measured**		Calculated	
Cu/Ni	$\lambda=1.5418$ Å		
I	d_{hkl}	d_{hkl}	hkl
100	8.39	8.33	010
100	6.51	6.49	001
		6.47	100
50	5.03	5.038	011
8	4.17	4.167	020
		4.141	101
18	3.65	3.670	$1\bar{1}1$
12	3.50		
35	3.30		
100	3.17		
18	3.09		
18	2.974		
nil	2.900		
18	2.641		
50	2.540		
50	2.520		
4	2.463		
25	2.149		
18	2.093		
18	2.072		
18	2.019		
18	1.988		
18	1.956		
18	1.928		
18	1.894		
Plus additional weak lines.			

* Original units in kX. Given here in Å. Error ± 0.02 Å.
** Shrinkage correction negligible.

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