

Roweite, $\text{CaMn}^{2+}_2(\text{OH})_4[\text{B}_4\text{O}_7(\text{OH})_2]$: Its Atomic Arrangement

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Abstract

Roweite, $4\text{Ca}_2\text{Mn}^{2+}_2(\text{OH})_4[\text{B}_4\text{O}_7(\text{OH})_2]$, a 9.057(1), b 13.357(2), and c 8.289(1) Å, space group *Pbam*, possesses a rather peculiar crystal structure. Condensed Mn-O octahedra at $z = 0$ link along b by sharing edges and along a by sharing corners to form $[\text{Mn}^{2+}(\text{OH})_2\text{O}]$ sheets. The oxygen in these sheets is shared with $[\text{B}_4\text{O}_7(\text{OH})_2]^{4-}$ polyanions located between the sheets at $z = \frac{1}{2}$. This polyborate tetramer consists of two tetrahedra and two triangles and has a linkage topologically identical to that in the $[\text{B}_4\text{O}_6(\text{OH})_4]^{2-}$ polyanion found in the structure of borax.

Me-O averages are Mn(1)-O 2.20, Mn(2)-O 2.22, Mn(3)-O 2.21, B(1)^[43]-O 1.48, B(2)^[43]-O 1.48, B(3)^[63]-O 1.37, and Ca^[63]-O 2.46 Å.

The extensive condensation of the octahedral fraction and the occurrence of borax-like polyanions are consistent with the paragenesis of roweite, which has crystallized in a basic environment.

Introduction

Recently, we have been investigating borates which have crystallized at intermediate to high temperatures. In addition, our investigations on transition metal complexes in mineralogical systems have led to investigations on the crystal structures of roweite and sussexite, the former structure which we report.

Roweite was described as a new species by Ber- man and Gonyer (1937) from a single specimen whose source is the famous hydrothermal vein paragenesis of the Franklin, New Jersey, zinc mines. The species occurred as a narrow veinlet mixed with thomsonite (?) cutting franklinite-zincite-willemitite ore. The authors proposed the formula $\text{H}_2\text{MnCa}(\text{BO}_3)_2$ or $\text{MnCa}(\text{BO}_2)_2(\text{OH})_2$.

Our experience with borates in basic mineral assemblages has led us to conclude that the type of borate polyanion cannot be easily predicted, nor can a correct crystal-chemical formula be proposed with certitude without a crystal structure analysis. This results from the dual role of the $(\text{OH})^-$ anion in the structure: either directly attached as a terminus to a boron atom or bound as a ligand to the transition metal fraction which is not immediately associated with the borate polyanion. Thus, Moore and Ghose (1971) showed that the seamanite formula is $\text{Mn}^{2+}_3(\text{OH})_2[\text{PO}_4][\text{B}(\text{OH})_4]$; and an unpublished study on sussexite by P.B.M. shows that its formula is $\text{Mn}^{2+}_2(\text{OH})[\text{B}_2\text{O}_4(\text{OH})]$.

Experimental

A small single crystal of roweite was kindly supplied by Drs. R. C. Erd and L. F. Aristarain, who determined and refined the cell parameters which we quote in this study (Table 1). We collected 3300 data to $2\theta = 65^\circ$ of the $k = 0$ - to 16-levels on a PAILRED automated diffractometer utilizing graphite monochromator and $\text{MoK}\alpha$ radiation. The half-angle scan was 2.4° , scan rate $2.5^\circ/\text{minute}$, 20 second background counting times on each side of the peak. Conventional geometric computation and averaging of symmetry-related peaks led to 1685 independent $|F(\text{obs})|$. Owing to the small crystal size and low linear absorption coefficient ($\mu = 36.9 \text{ cm}^{-1}$), we did not correct for absorption.

Structure Determination and Refinement

Patterson synthesis and β - and γ -general syntheses (Ramachandran and Srinivasan, 1970) led to a progressive determination of the roweite structure; because of the profound sheet-like distribution of the heavy Mn atoms in the xy -plane, the weaker contributions of the borate fraction were located with difficulty.

Successive refinements of atomic coordinates and isotropic thermal vibration parameters led to $R(hkl) = (\sum ||F(\text{obs})| - |F(\text{calc})||) / (\sum |F(\text{obs})|)$ in Table 2.

TABLE 1. Data for Roweite, $\text{Ca}_2\text{Mn}^{2+}_2(\text{OH})_4[\text{B}_4\text{O}_7(\text{OH})_2]$

<i>Pbcm</i>	$a = 9.057(1) \text{ \AA}$	$b = 13.357(2) \text{ \AA}$	$c = 8.289(1) \text{ \AA}$	$z = 4$
Specific gravity	2.935(5); Density (calc) 2.962			

*Cell parameters and specific gravity are from Drs. R. C. Erd and L. Aristarain (private communication). The density was computed from the ideal formula.

We note that a substantial fraction (about 70 per cent) of all 1677 non-equivalent reflections were very weak because of the heavy atom substructure $a' = a/2$ and $b' = b/4$, and the remaining weak scatterers in the structure; consequently, the *R*-index for all reflections appears to indicate a poorly refined structure. However, the 682 very weak reflections are less than twice the background error.

Secondary extinction correction was applied to the refinements using the form factor tables of Cromer and Mann (1968) for Mn^{2+} , Ca^{2+} , and O^{1-} and of Onken and Fischer (1968) for B^{2+} . The full-matrix least-squares refinement proceeded from a locally modified version, adapted to the IBM 360 computer, of the familiar ORFLS program of Busing, Martin, and Levy (1962).

Table 3 lists the atomic coordinates and isotropic thermal vibration parameters, and Table 4 summarizes $|F(\text{obs})|$ and $F(\text{calc})$ values.

Description of the Structure

Topology and geometry

Roweite possesses a rather curious structure which can be described on the basis of two well-defined, although linked, fractions. The anionic group, $[\text{B}_4\text{O}_7(\text{OH})_2]^{4-}$, is a polyborate tetramer consisting of two triangles and two tetrahedra with a linkage topologically identical to that of the tetramer in

TABLE 2. Roweite. *R*(*hkl*) Dependence on *F*(*hkl*)

<i>F</i> (<i>hkl</i>)	Number of Reflections	<i>R</i> (<i>hkl</i>)
0 to 12	682	0.52
12 to 36	675	0.20
37 to 73	225	0.06
74 to 121	71	0.05
122 -	24	0.04
All reflections	1677	0.16
Above 36	320	0.06

borax. The structure of borax $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$, as determined by Morimoto (1956), differs in containing two additional terminal hydroxyl groups while the terminal O(6) in roweite is an oxide anion. This results from the weak bonding of the (OH)⁻ groups to Na⁺ cations in borax while in roweite O(6) is also bonded to two Mn²⁺ cations in octahedral coordination and to one Ca²⁺ cation in eight-fold coordination. Figure 1 reveals the $[\text{B}_4\text{O}_7(\text{OH})_2]^{4-}$ group, and Figure 2 shows these poly-anions centered at $z = 0.50$ and linked by the CaO_8 polyhedra to form a rather open sheet.

The second principal motif of this rather queer structure is an infinite sheet of condensed Mn²⁺-O octahedra centered at $z = 0$ and shown in Figure 3. The octahedra are linked parallel to the *b*-axis by edge-sharing, and the repeat unit in this direction is the sum of four octahedral edges ($13.36/4 = 3.34 \text{ \AA}$). The octahedra link via corners along the *a*-direction so that this direction is the sum of four Mn-O distances ($9.06/4 = 2.26 \text{ \AA}$). This sheet has average composition $\frac{2}{3} [\text{Mn}^{2+}(\text{OH})_2(\text{O}_\text{B})]$, where $\text{O}_\text{B} = \text{O}(6)$, the anion associated with the borate fraction. It corresponds, when idealized, to a sheet of octahedra perpendicular to the [110] direction in the cubic closepacking. Predicting the correct borate anion for roweite *a priori* would have been very uncertain indeed!

TABLE 3. Roweite. Atomic Multiplicities, Atomic Coordinates, and Isotropic Thermal Vibration Parameters*

	<i>M</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (\AA^2)
Ca	8	0.2333(2)	0.1317(1)	0.2445(2)	0.87(3)
Mn(1)	2	.0000	.0000	.0000	1.03(5)
Mn(2)	2	.5000	.0000	.0000	1.30(9)
Mn(3)	4	.4803(2)	.2468(2)	.0000	1.04(4)
B(1)	4	.2097(16)	.3003(12)	.5000	1.14(20)
B(2)	4	.2331(13)	.4753(10)	.5000	.57(16)
B(3)	8	.3717(9)	.3793(7)	.2929(11)	.74(12)
O(1) = OH ⁻	4	.1143(11)	.2091(8)	.5000	1.39(16)
O(2) = OH ⁻	4	.1611(10)	.5719(7)	.5000	.87(13)
O(3)	4	.1287(9)	.3911(7)	.5000	.68(12)
O(4)	8	.3092(7)	.2924(6)	.3550(9)	1.33(10)
O(5)	8	.3287(7)	.4695(5)	.3533(9)	1.16(10)
O(6)	8	.4724(6)	.3740(5)	.1695(8)	.87(9)
O(7) = OH ⁻	4	.2383(10)	.0215(7)	.0000	1.06(14)
O(8) = OH ⁻	4	.2290(11)	.2373(8)	.0000	1.25(14)
O(9) = OH ⁻	8	.4862(7)	.1229(5)	.1642(9)	1.14(10)

*Estimated standard errors refer to the last digit.

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TABLE 4. Structure Factor Tables for Roweite*

h	k	l	$F(\text{obs})$	$F(\text{calc})$
0	0	0	100	100
0	0	1	100	100
0	0	2	100	100
0	0	3	100	100
0	0	4	100	100
0	0	5	100	100
0	0	6	100	100
0	0	7	100	100
0	0	8	100	100
0	0	9	100	100
0	0	10	100	100
0	0	11	100	100
0	0	12	100	100
0	0	13	100	100
0	0	14	100	100
0	0	15	100	100
0	0	16	100	100
0	0	17	100	100
0	0	18	100	100
0	0	19	100	100
0	0	20	100	100
0	0	21	100	100
0	0	22	100	100
0	0	23	100	100
0	0	24	100	100
0	0	25	100	100
0	0	26	100	100
0	0	27	100	100
0	0	28	100	100
0	0	29	100	100
0	0	30	100	100
0	0	31	100	100
0	0	32	100	100
0	0	33	100	100
0	0	34	100	100
0	0	35	100	100
0	0	36	100	100
0	0	37	100	100
0	0	38	100	100
0	0	39	100	100
0	0	40	100	100
0	0	41	100	100
0	0	42	100	100
0	0	43	100	100
0	0	44	100	100
0	0	45	100	100
0	0	46	100	100
0	0	47	100	100
0	0	48	100	100
0	0	49	100	100
0	0	50	100	100
0	0	51	100	100
0	0	52	100	100
0	0	53	100	100
0	0	54	100	100
0	0	55	100	100
0	0	56	100	100
0	0	57	100	100
0	0	58	100	100
0	0	59	100	100
0	0	60	100	100
0	0	61	100	100
0	0	62	100	100
0	0	63	100	100
0	0	64	100	100
0	0	65	100	100
0	0	66	100	100
0	0	67	100	100
0	0	68	100	100
0	0	69	100	100
0	0	70	100	100
0	0	71	100	100
0	0	72	100	100
0	0	73	100	100
0	0	74	100	100
0	0	75	100	100
0	0	76	100	100
0	0	77	100	100
0	0	78	100	100
0	0	79	100	100
0	0	80	100	100
0	0	81	100	100
0	0	82	100	100
0	0	83	100	100
0	0	84	100	100
0	0	85	100	100
0	0	86	100	100
0	0	87	100	100
0	0	88	100	100
0	0	89	100	100
0	0	90	100	100
0	0	91	100	100
0	0	92	100	100
0	0	93	100	100
0	0	94	100	100
0	0	95	100	100
0	0	96	100	100
0	0	97	100	100
0	0	98	100	100
0	0	99	100	100
0	0	100	100	100

* Note the orientation a 9.057 Å, b 8.289 Å, c 13.357 Å; column heads are k , l , $F(\text{obs})$, and $F(\text{calc})$.

Interatomic distances

Polyhedral metal-oxygen averages include Mn(1)-O, 2.20; Mn(2)-O, 2.22; Mn(3)-O, 2.21; B(1)^[4]-O, 1.48; B(2)^[4]-O, 1.48; and B(3)^[3]-O, 1.37 Å. These averages are all typical values for the cations and their associated coordination polyhedra, as revealed in many recently determined crystal structures. In addition, the Ca²⁺ cation possesses eight-fold coordination by oxygens, residing in a highly distorted square antiprism. It shares its O(1)-O(2)^{iv} and O(7)-O(8) edges on the mirror planes, resulting in columns which run parallel to the z -direction. The Ca-O distances range between 2.39 and 2.59 Å with a polyhedral average of 2.46 Å. In the

Mn-O octahedral sheet, two independent sets of shared edges occur: O(6)^l-O(6)ⁱⁱⁱ, 2.81 Å; and O(9)-O(9)^v, 2.72 Å. These distances are the shortest for their polyhedra, as observed in Table 5, which lists the polyhedral distances.

Electrostatic valence balances and hydrogen bonds

Table 6 lists the electrostatic valence balances of cations about the anions, with Σ corresponding to the sum of cation charge divided by coordination number for the ensemble of cations about each anion. $\Delta\Sigma$ is the deviation from neutrality. M is the anion multiplicity. For a neutral crystal, the sum of $(\Delta\Sigma)(M) = 0.00$. Deviations are then tested by the interatomic distance observations. We prefer to neglect the O-H

and O...H contributions in this table and treat (OH)⁻ as a single negative species. The effects of the presence of H are then looked for via the deviation.

The existence of hydrogen bonds is severely limited by the geometrical constraints of the sheets at $z = 0$ and $1/2$. Based on cations other than hydrogen, the only example of extreme deviation from neutrality is O(3) with $\Delta\Sigma = -0.50$. It probably receives two hydrogen bonds: O(2)-H...O(3), 2.67; and O(9)-H...O(3), 3.07 Å. Even so, O(3) remains undersaturated by $1/2 - 1/6 - 1/6 = 1/6$ e.s.u. which may contribute to the shorter-than-average B-O(3) distance. O(7) and O(8) may form reciprocal bonds since O(7)-H...H-O(8), which equals 2.88 Å, is the line across the open space in the octahedral sheets. The configuration O(7)-H...O(8)-H 2.88 Å provides the O(8)-H...O(7)-H 3.81 Å distance which is too long. A better alternative is O(8)-H...O(4) 3.12 Å. Finally, there is O(1)-H...O(4) 3.01 Å. This would require that O(4) is in fact oversaturated since it receives two rather long bonds from O(1)-

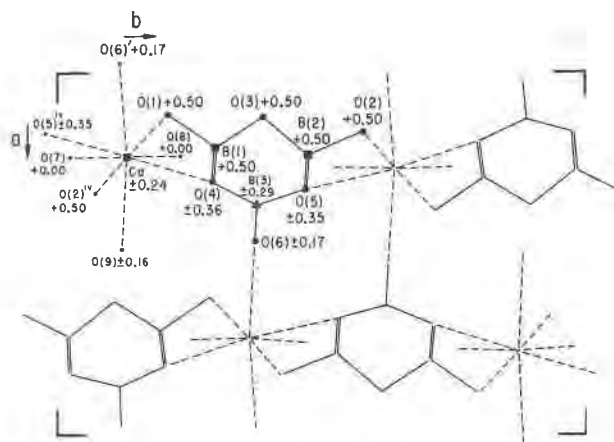


FIG. 2. Spoke diagram showing the borate tetramers (solid lines) and the linking CaO₆ polyhedra (dashed lines). Heights are given as fractional coordinates in z . Atoms are labelled according to Tables 3 and 5.

H and O(8)-H in addition to B(1), B(2), and Ca. Indeed, B(1)-O(4) and B(3)-O(4) are the longest distances for their polyhedra.

Summing up, we propose O(1)-H...O(4), O(2)-H...O(3), O(7)-H...O(8)-H, O(8)-H...O(4) and O(9)-H...O(3) as the most likely hydrogen bonds in the structure.

Paragenetic Settings for the Transition Metal Basic Borates

The basic borates seamanite, Mn²⁺₃(OH)₂[PO₄][B(OH)₄]; sussexite, Mn²⁺₂(OH)[B₂O₄(OH)]; and roweite, Ca₂Mn²⁺₂(OH)₄[B₄O₇(OH)₂] have all crystallized at moderate to low temperatures in basic

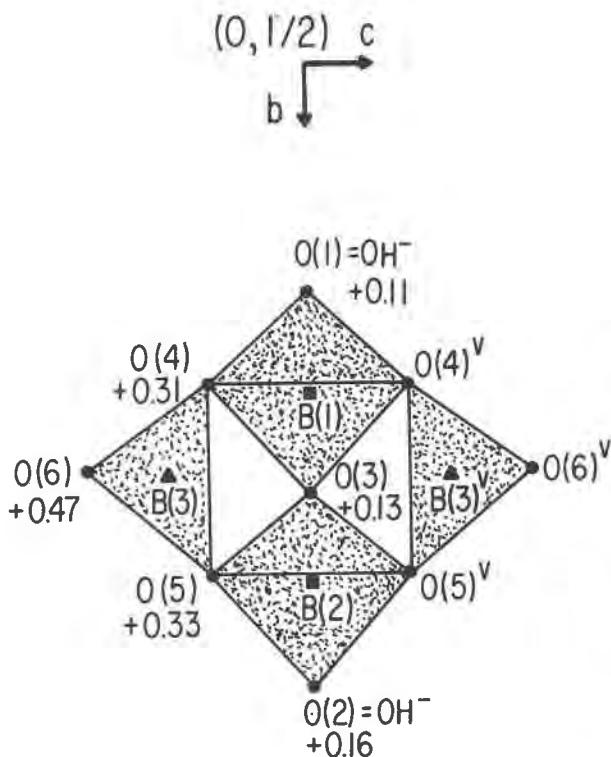


FIG. 1. Polyhedral diagram of the [B₄O₇(OH)₂]²⁻ tetramer down the a -axis. Heights are given as the x -coordinate. The diagram is referred to the locus at $b = 0$ and $c = 1/2$.

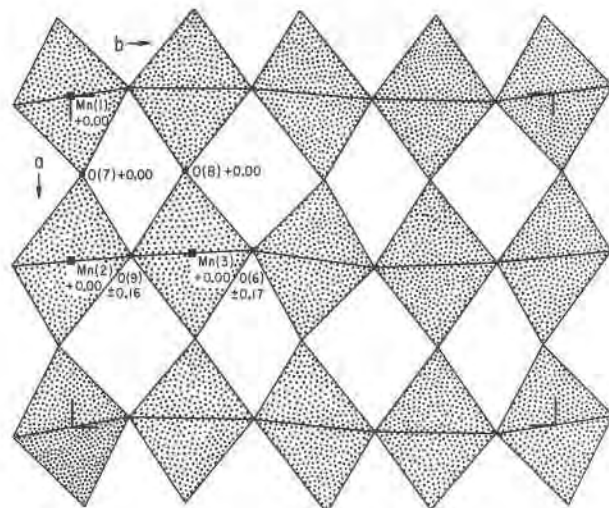


FIG. 3. Octahedral fraction of the roweite structure at $z = 0$. Atom locations are labelled according to Table 3.

hydrothermal vein assemblages. This is indicated by the frequent co-existence of pyrochroite, $\text{Mn}(\text{OH})_2$, with seamanite and sussexite, the latter assemblage being particularly well-developed in veins at Franklin, New Jersey. In such veins, basic manganese arsenates also occur. At Långban, Sweden, and at other related central Swedish deposits, the assemblage native lead-pyrochroite-basic Mn arsenates is persistent (Moore, 1971). Additional support of the rather basic character of such assemblages comes from Bricker (1965) who shows that the boundary between aquated Mn^{2+} in solution and pyrochroite lies at $\text{pH} \sim 10.8$ in the system $\text{Mn}-\text{O}_2-\text{H}_2\text{O}$ for activities of dissolved species about 10^{-6} . The field moves toward lower pH values as the concentration of Mn^{2+} increases, to around 9.5 at $a_{\text{Mn}^{2+}} = 10^{-4}$. According to Ingri (1963), the distribution of borate

polyanion species at pH between 9.5 and 11 consists of the tetrahedral $[\text{B}(\text{OH})_4]^-$ group, the $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ cluster of two tetrahedra and two triangles and smaller amounts of $[\text{B}_3\text{O}_3(\text{OH})_5]^{2-}$ (one triangle and two tetrahedra), $[\text{B}_3\text{O}_3(\text{OH})_4]^-$ (two triangles and one tetrahedron), and very little $[\text{B}(\text{OH})_3]^\circ$ triangles. At low temperatures, the amount of borate tetrahedra in the borate fractions increases with increasing pH. Thus, with increasing pH, borax (two tetrahedra and two triangles) condenses to form ulexite (three tetrahedra and two triangles) (Christ *et al.*, 1967). These chemical observations are all consistent with seamanite and roweite having formed under basic conditions. Sussexite, which consists of a dimer of two corner-sharing triangles, presumably formed at conditions which are less basic, although its structure and paragenesis do not allow any con-

TABLE 5. Roweite. Polyhedral Interatomic Distances**

Mn(1)		Mn(3)		B(1)		B(3)	
2 Mn(1)-0(7)	2.177(9) Å	2 Mn(3) -0(9)	2.143(7)	1 B(1)-0(3)	1.417(17)	1 B(3)-0(5)	1.364(12)
4 -0(6)'	2.207(7)	2 -0(6)	2.206(7)	1 -0(1)	1.493(18)	-0(6)	1.367(12)
average	2.197	1 -0(8)'	2.262(10)	2 -0(4)	1.506(16)	-0(4)	1.393(12)
		1 -0(8)	2.279(10)	average	1.481	average	1.375
		average	2.207				
2 0(6)'-0(6)'''	2.810(10)*			1 0(4)-0(4) ^v	2.404(10)		
4 0(6)'-0(7)''	3.082(12)			2 0(1)-0(4)	2.408(12)	1 0(4)-0(5)	2.372(10)
4 0(6)'-0(7)	3.118(12)	1 0(9) -0(9) ^v	2.722(10)*	2 0(3)-0(4)	2.420(12)	1 0(5)-0(6)	2.375(10)
2 0(6)'-0(6) ^{iv}	3.403(10)	1 0(6) -0(6) ^v	2.810(10)*	1 0(1)-0(3)	2.434(12)	1 0(4)-0(6)	2.395(10)
average	3.102	2 0(6) -0(8)'	3.096(12)	average	2.416	average	2.381
		2 0(8) -0(9)	3.101(12)				
		2 0(6) -0(8)	3.189(12)				
		2 0(8)' -0(9)	3.190(12)				
		2 0(6) -0(9)	3.356(10)				
		average	3.116				
		Ca					
		Ca-0(9)	2.388(7)				
		-0(5) ^{iv}	2.411(7)				
		-0(4)	2.431(7)	2 0(2) -0(5)	2.378(12)		
		-0(6)'	2.445(7)	2 0(3) -0(5)	2.420(12)		
		-0(2) ^{iv}	2.457(9)	1 0(5) -0(5) ^v	2.432(10)		
		-0(8)	2.469(10)	1 0(2) -0(3)	2.433(13)		
		-0(7)	2.506(9)	average	2.410		
		-0(1)	2.591(10)				
		average	2.462				
Mn(2)				B(2)			
4 Mn(2)-0(9)	2.136(7)			1 B(2) -0(2)	1.446(15)		
2 -0(7)	2.388(9)			1 -0(3)	1.469(15)		
average	2.220			2 -0(5)	1.495(14)		
				average	1.476		
2 0(9) -0(9) ^{iv}	2.722(10)*						
4 0(9) -0(7)	2.954(12)						
2 0(9) -0(9) ^{vi}	3.293(10)						
4 0(9) -0(7)''	3.435(12)						
average	3.132						

*0-0' shared edges.

**Estimated standard errors refer to the last digit. ' = $1/2 + x, 1/2 - y, z$; '' = $-x, -y, -z$; ''' = $1/2 + x, 1/2 - y, -z$; ^{iv} = $1/2 - x, 1/2 + y, z$; ^v = $x, y, -z$; ^{vi} = $-x, -y, z$ applied to the coordinates in Table 3.

TABLE 6. Roweite. Electrostatic Valence Balances (Σ)¹

anions	coordinating cations		Σ	$\Delta\Sigma$	$(\Delta\Sigma) (M)$
O(1) = OH ⁻	B(1) ^[4] + 2Ca	3/4 + 2(2/8)	1.25	+0.25	1.00
O(2) = OH ⁻	B(2) ^[4] + 2Ca	3/4 + 2(2/8)	1.25	+0.25	1.00
O(3)	B(1) ^[4] + B(2) ^[4]	3/4 + 3/4	1.50	-0.50	-2.00
O(4)	B(1) ^[4] + B(3) ^[3] + Ca	3/4 + 3/3 + 2/8	2.00	+0.00	0.00
O(5)	B(2) ^[4] + B(3) ^[3] + Ca	3/4 + 3/3 + 2/8	2.00	+0.00	0.00
O(6)	B(3) ^[3] + Ca + Mn(1) + Mn(3)	3/3 + 2/8 + 2/6 + 2/6	1.92	-0.08	- .64
O(7) = OH ⁻	Mn(1) + Mn(2) + 2Ca	2/6 + 2/6 + 2(2/8)	1.17	+0.17	+ .64
O(8) = OH ⁻	2Mn(3) + 2Ca	2/6 + 2/6 + 2(2/8)	1.17	+0.17	+ .64
O(9) = OH ⁻	Mn(2) + Mn(3) + Ca	2/6 + 2/6 + 2/8	0.92	-0.08	- .64
				sum	0.00

¹ Δ is the deviation from ideality ("overbonding"), M is the anion site multiplicity. In this calculation, OH⁻ is treated as a single species of charge -1.

clusions by analogy: sussexite is not only a dense-packed structure but apparently has also formed at higher temperatures than these other borates.

Even more interesting is the great tendency toward polymerization of the Mn(OH₂O)₆ octahedra with increasing pH. Among the sulfates, phosphates, and borates of manganese (2+), there are at least nine species which have definitely formed under acid conditions. All of these possess crystal structures where the Mn²⁺-O octahedron is highly aquated (such as hexa-aquo Mn²⁺) and not linked to other Mn²⁺-O octahedra. In the basic regime, however, no less than 25 species have been described—mostly basic arsenates of manganese—and the structures of these reveal a very high degree of polymerization of the octahedra. This would suggest that a large variety of elegant octahedral clusters probably exists among the basic manganous sulfates, phosphates, arsenates, and borates.

Acknowledgments

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