JOESMITHITE: A NOVEL AMPHIBOLE CRYSTAL CHEMISTRY

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Abstract

Joesmithite, a 9.885 (15), b 17.875 (18), c 5.227 (5) Å, β 105.67 (17)°, $P2/a$, is a beryllo-silicate clinoamphibole with composition $(Ca,Pb)Ca_2(Mg,Fe^{2+},Fe^{3+})_5[Si_6Be_2O_{22}](OH)_2$, $Z = 2$. One out of four tetrahedra in the asymmetric unit is occupied by beryllium, at the cross-linking site in one of the pyroxene chain sub-units. The A site is not centered but displaced 0.6 Å along the two-fold rotor and toward the beryllate tetrahedron.

It is suggested that a coupled relationship exists between A' (the off-centered A site) and Be, a condition ensuring reasonable charge balance around their mutual anions. The A' and Be atomic species lower the symmetry of the crystal: though joesmithite is topologically akin to the C-centered clinoamphiboles, its chemical contents are somewhat different. The lower symmetry induced by these atomic species probably accounts for the unequal octahedral cation distribution, which was assessed by least-squares analysis of three-dimensional single-crystal X-ray data.

Introduction

Joesmithite, a new mineral discovered by the author three years ago, proved to be related to the clinoamphibole mineral group. This mineral has been previously reported in two papers, one which describes the species for the first time (Moore, 1968a), the other which presents a preliminary account of its crystal structure (Moore, 1968b). A comprehensive analysis of its crystal chemistry on the basis of conventional X-ray diffraction techniques revealed some interesting features which add new knowledge to amphibole crystal chemistry. Though topologically joesmithite has a clinoamphibole structure, it possesses a remarkable topochemistry, with ordering of Si^{4+} and Be^{2+} over tetrahedral sites and a statically occupied off-centered A site occupied by large cations, principally Ca and Pb.

Joesmithite occurs as a rare skarn product from the famous Långban orebody in the province of Värmland, Sweden. It is associated with well-crystallized iron and manganese silicate skarns which have been impregnated with Pb and Be, resulting in a mineral paragenesis of bewildering complexity. Joesmithite occurs as black prismatic crystals associated with hematite, magnetite, schefferite and calcite.

Experimental Procedure

According to the analysis reported in Moore (1968a), the joesmithite crystal cell in Table 1 contains $Pb_{0.6}Ba_{0.1}Ca_{4.6}Mn_{0.8}$-$Fe^{2+}_{0.8}Mg_{4.6}Fe^{3+}_{3.4}Al_{0.3}Si_{13.8}Be_{0.1}(O_{39.7}OH_{14.5})$. Analysis of the metals present was performed by Ing. B. Rajandi of the Swedish Geological Survey (Stockholm) according to the quantitative emission spectrographic technique, using Be as the internal standard. Water and iron oxidation grade determinations were by Mr. A. Parwel of the Swedish Natural History Museum (Stockholm). A problem arose since some Be was detected in joesmithite during the preliminary qualitative analysis; the reported amount of Be was uncertain but it was believed to be below 0.5 percent.

From a single crystal of $0.09 \times 0.17 \times 0.15$ mm in dimensions, 3,426 independent integrated intensities were gathered on a *Pailred* automated diffractometer to $2\vartheta = 70°$ using monochromatized $MoK\alpha$ radiation, with [010] as the rotation axis. Rotation about the symmetry axis allows for accurate crystal alignment, but has the disadvantage of permitting possible overlapping reflections between levels as a result of the long axial translation. 1,041 data proved to be "zero intensity" including systematically extinct reflections and reflections with

Table 1. Joesmithite. Crystal Cell

a	9.885(15) Å
b	17.875(18)
c	5.227(5)
β	105.67(17)°
V	889.3 Å³
Z	1
space group	$P2/a$

Formula: $Pb_{0.8}Ca_{5.2}Fe_{4.8}Mg_{4.9}Al_{0.3}Si_{12.0}Be_{4.0}O_{44}(OH)_4$.

negative $I_{(obs)}$ (after background subtraction) and 781 were rejected due to asymmetric backgrounds (backgrounds which deviated in excess of 25 percent of their average value). Since these exclusions were essentially random over reciprocal space, the ensuing analysis was confined to the remaining 1,604 reflections, which were subjected to polyhedral transmission factor correction followed by the usual geometrical conversions to obtain observed $|F_o|$.

Starting with the atomic coordinates in Moore (1968b), full-matrix atomic coordinate and cation site preference refinements converged to

$$R_{hkl} = \frac{\sum ||F_0| - |F||}{\sum |F|} = 0.15.$$

A three-dimensional difference synthesis yielded a small but significant density at the tetrahedral site, believed to be unoccupied by Moore (1968b). This was ascribed to Be, and that atomic species was added to the list of atomic constituents. The refined site multiplicities allowed for judicious choice of scattering tables, prepared from the tabulated data for half-ionized species in *International Tables for X-ray Crystallography, Vol. 3* (MacGillavry and Rieck, 1962, pp. 202–207). It was assumed that each cation site was fully occupied and the equipoint rank number was used as an upper bound for the site multiplicities. Successive full-matrix atomic coordinate and isotropic temperature factor refinment using a local modification of the program of Busing, Martin and Levy (1962) for the IBM 7094 computer, converged to $R_{hkl} = 0.128$. Since the list of parameters was already quite extensive, no attempt was made to assess anisotropic thermal motion. Final atomic coordinates, the site occupancies, and isotropic temperature factors are listed in Table 2. F_o-F_o data are given in Table 3[1].

[1] For a copy of Table 3, order NAPS Document #00453 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th Street, New York, N.Y. 10001; remitting $1.00 for microfiche or $3.00 for photocopies.

TABLE 2. JOESMITHITE ATOMIC COORDINATES, SITE OCCUPANCIES, AND ISOTROPIC TEMPERATURE FACTORS

Atom	Species Present	x	y	z	B(Å²)
M(1)	$0.32Mg+0.68Fe^{3+}$	3/4	0.3416(4)	1/2	0.72(6)
M(1')	$0.85Mg+0.15Al$	3/4	.1624(5)	1/2	.19(9)
M(2)	$1.0Fe^{3+}$	3/4	.4275(3)	0	.53(5)
M(2')	$0.74Mg+0.26Fe^{2+}$	3/4	.0751(3)	0	.69(9)
M(3)	$0.55Mg+0.45Fe^{2+}$	3/4	.2559(4)	0	.65(7)
M(4)	$1.0Ca$	1/4	.4589(4)	1/2	1.02(7)
M(4')	$1.0Ca$	1/4	.0300(4)	1/2	1.06(7)
A'	$0.60Ca+0.40Pb$	1/4	.2836(1)	0	1.17(3)
Si(1)	$1.0Si$	0.4620(5)	.0807(4)	0.1896(9)	.68(7)
Si(2)	$1.0Si$	.4714(5)	.1691(4)	.6951(10)	.82(7)
Si(3)	$1.0Si$	.4594(5)	.4228(4)	.1799(9)	.72(7)
Be	$1.0Be$	.4731(18)	.3315(13)	.6894(35)	.11(23)
O(1)		.6315(12)	.4253(9)	.2643(23)	.71(17)
O(2)		.6434(14)	.3430(10)	−.2231(26)	1.07(19)
O(3) =	OH^-	.6423(13)	.2517(10)	.2872(24)	.99(17)
O(4)		.6375(12)	.1635(9)	−.2236(23)	.66(16)
O(5)		.6318(11)	.0807(9)	.1896(22)	.55(15)
O(6)		.3810(13)	.4977(10)	.2105(25)	1.03(19)
O(7)		.4030(13)	.3858(10)	−.1198(25)	.92(18)
O(8)		.4115(14)	.3630(10)	.3779(27)	1.14(21)
O(9)		.4151(15)	.2513(10)	.7121(28)	1.47(21)
O(10)		.4054(13)	.1158(10)	−.1156(24)	.89(18)
O(11)		.4084(15)	.1363(10)	.3954(28)	1.32(22)
O(12)		.3839(14)	.0037(10)	.2093(27)	1.26(20)

DISCUSSION OF THE STRUCTURE

Crystal chemistry. The assigned site occupancies lead to the crystal cell formula $Pb_{0.8}Ca_{5.2}Fe_{4.8}Mg_{4.9}Al_{0.3}Si_{12.0}Be_{4.0}O_{44}(OH)_4$. It differs from the previously proposed formula in containing fewer hydroxyl ions, fewer silicon atoms, and an addition of substantial beryllium. The remaining atomic species are in satisfactory agreement with the results of chemical analysis and structure cell composition, after grouping Ba with Pb, Mn with Ca, and Al with Mg. It was stated elsewhere (Moore, 1968a) that the excess silicon reported in the analysis was doubtless due to the observable presence of minor grains of poikilitically included quartz. The chemical analyses of Be and OH^- in joesmithite are evidently in error. The water determination was obtained from only a few milligrams of pure crystals. Assuming 4Be in the unit cell of joesmithite, the total Be in weight percent computes to be only 1.8 percent! Since Be was used as the standard, this small quantity could be easily underestimated. The joesmithite formula can be ideally written in conformity with the clinoamphibole formula, that is

$$(Ca, Pb)Ca_2(Mg, Fe^{2+}, Fe^{3+})_5[Si_6Be_2O_{22}](OH)_2.$$
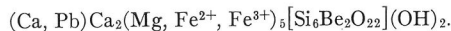
Topology and topochemistry. The joesmithite crystal structure is topologically equivalent to the clinoamphiboles, but chemically distinct for three important reasons: beryllium atoms are ordered over one out of four tetrahedral positions, such that the clinoamphibole mirror plane is destroyed; one octahedral site out of five is occupied almost exclusively by Fe^{3+}, whereas the four remaining sites possess mixed (Mg, Fe^{2+}, Fe^{3+}) showing unequal site preferences; the large (Ca, Pb) atoms are not ideally situated on the clinoamphibole A' site but displaced 0.6 Å away from it. These important chemical differences account for the doubling of the asymmetric unit contents and the pronounced lowering of symmetry. The topological equivalence, however, preserves the clinoamphibole-like cell translations.

Figures 1 and 2 are polyhedral diagrams of the joesmithite structure. Figure 1 shows the cross-linking tetrahedra in one of the pyroxene chain sub-units occupied by beryllium. Figure 2 shows the infrequently depicted approximately dense-packed wall common to the clinoamphiboles. This wall is comprised of edge-sharing octahedra alter-
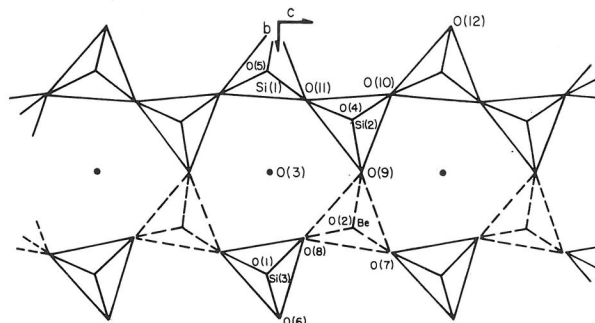

FIG. 1. The $[Si_6Be_2O_{22}]$ ribbon in the joesmithite crystal structure viewed down a^*. The Be atoms reside in the centers of the dashed tetrahedra. Note that they are the cross-linking tetrahedra in one of the pyroxene chain sub-units.

nately two and three in width which further edge-fuse to distorted square antiprisms.

The octahedral and square antiprism cations in the C-centered clinoamphiboles are designated $M(1)$, $M(2)$, and $M(3)$; and $M(4)$ sites respectively. In joesmithite, these sites degenerate into seven nonequivalent sites. With primes denoting the nonequivalent cations across the pseudo-mirror plane, unique cations in joesmithite can be obviously labelled $M(1)$, $M(1')$, $M(2)$, $M(2')$, $M(3)$, $M(4)$ and $M(4')$. Since the (Ca, Pb) atoms do not truly reside on the A site, they will be denoted as A'. The site preferences (Table 2) are $M(1) = 0.32$ Mg + 0.68 Fe^{3+}, $M(1') = 0.85$ Mg + 0.15 Al, $M(2) = 1.0$ Fe^{3+}, $M(2') = 0.74$ Mg + 0.26 Fe^{3+}, $M(3) = 0.55$ Mg + 0.45 Fe^{2+}, $M(4) = M(4') = 1.0$ Ca, and $A' = 0.60$ Ca + 0.40 Pb. These proposed distributions can only be approximate, although the substantial difference in scattering power between Mg and Fe allows for a reasonable estimate. The valence states over these sites were estimated from the average poly-hedral M-O distances listed in Table 4 in conjunction with the refined site populations, assuming initially Fe^{3+}-O 2.00, Al^{3+}-O 1.92, Mg-O 2.10, and Fe^{2+}-O 2.12 Å. Estimates based on these distances are admittedly crude since the assumed ideal M-O polyhedral distances can vary sub-stantially and since the tabulated M-O distances in joe-smithite have e.s.d.'s of 0.02 Å.

Thus, $M(1)$-O 2.048, implies mixed Mg and Fe^{3+}; $M(2)$-O 2.013, Fe^{3+} and minor Mg; $M(2')$-O 2.068, Mg and Fe^{3+}; $M(3)$-O 2.091 Å, Mg and Fe^{2+}. $M(1')$-O 2.057 Å has electron density corresponding to Mg; perhaps this site accommodates the Al reported in the analysis. Again, it must be emphasized that the proposed distributions are crude estimates and their errors are probably in the range of 10–20 percent. Most important, the combination of site preference refinement and average M-O distances for $M(2)$ show that this site is essentially occupied by ferric iron.

The $M(4)$ and $M(4')$ sites are occupied by calcium in distorted oxygen square antiprisms, a topochemistry en-tirely akin to tremolite. As seen in Figure 1, the square an-tiprisms each share three edges with the octahedra in the walls and two edges with the highly irregular A'-O polyhe-dron. As with the inosilicate ribbons, the A'-O polyhedra cement the separated walls together along [010], forming flat sheets oriented parallel to {100}. Perhaps the most cu-rious feature of the joesmithite structure is the A' site. It is ten-coordinated with two distinct coordination shells. The inner shell includes six distances ranging from 2.56 to 2.59 Å and the outer shell consists of four distances rang-ing from 3.45 to 3.49 Å. The bonds to the outer coordina-tion shell are all on one side of the A' site. Deviations from the true C-centered clinoamphibole A-position were also noted by Papike, Clark and Huebner (1968) for a potassic richterite, K(NaCa)(Mg,Fe)$_5$ [(Si,Al)$_8$O$_{22}$] (OH,F)$_2$. In this crystal, the K atom occupies positions off the true A-
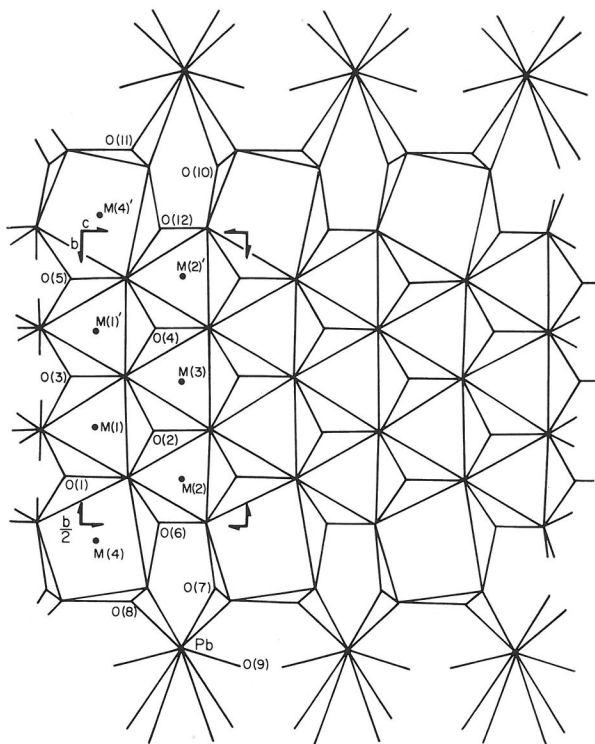

FIG. 2. Polyhedral diagram of the joesmithite wall down a^*. The A' (here designated Pb)—O bonds are drawn as spokes. This wall runs parallel to [001] and with the A'—O bonds forms flat sheets parallel to {100}. The primed oxygen atoms in Table 4 refer to the equivalent oxygens across the two-fold rotor. The primed metal positions in this diagram are not equivalent.

site which are not ordered. Thus, a clinoamphibole with full $C2/m$ symmetry is preserved on the average. This off-centering was attributed to average K-O distances which were reasonable for a split atom model but unrea-sonable for an atom at the A-site central point.

There appears to be little question that only the inner coordination shell should be considered when computing electrostatic valence balances about the anions. The com-puted electrostatic valence balances for the anions in Table 5 show some surprising features. O(3), with $\Sigma = 1.00$ is clearly the hydroxyl group. O(12), O(2) and O(6) are highly undersaturated with $\Sigma = 1.58$, 1.67 and 1.75 respec-tively. In every instance save $M(2)$-O(2), the M-O and T-O distances are the shortest for their polyhedra; indeed, the highly undersaturated O(12) anion has especially short distances, with $M(2')$-O 2.034, $M(4')$-O 2.313, and Si(1)-O 1.582 Å. These results are consistent with the interpreta-tion that only O(3) is an hydroxyl anion, whereas all the others are oxide anions.

A coupled relationship exists between A' and Be. The A' position is shifted 0.6 Å away from the clinoamphibole A site, along the twofold rotor and in the direction of the Be atom. Three anions—O(7), O(8) and O(9)—are associated

TABLE 4. JOESMITHITE. M-O, T-O, AND O-O' INTERATOMIC DISTANCES

(e.s.d's are M-O, Si-O ± 0.017, O-O' ± 0.023, Be-O ± 0.025 Å)

M(1)		M(1')		M(2)		M(2')		M(3)		A'	
2 M(1)-O(2)	2.009 Å	2 M(1')-O(4)	2.050	2 M(2)-O(6)	1.975	2 M(2')-O(12)	2.034	2 M(3)-O(2)	2.055	2 A'-O(9)	2.559
2 -O(3)	2.055	2 -O(5)	2.052	2 -O(2)	2.025	2 -O(5)	2.075	2 -O(3)	2.066	2 -O(7)	2.560
2 -O(1)	2.080	2 -O(3)	2.070	2 -O(1)	2.040	2 -O(4)	2.095	2 -O(4)	2.152	2 -O(8)	2.594
										2 -O(11)	3.453
average	2.048 Å		2.075		2.013		2.068		2.091	2 -O(10)	3.493
[a]1 O(3)-O(3)'	2.631	[a]1 O(3)-O(3)'	2.631	[a]1 O(2)-O(2)'	2.687	[a]1 O(4)-O(4)'	2.757	[a]1 O(2)-O(2)'	2.687	average of	
[a]2 O(2)-O(1)'	2.723	[a]2 O(4)-O(3)'	2.778	[a]2 O(1)-O(2)'	2.723	[a]2 O(5)-O(4)'	2.798	[a]1 O(4)-O(4)'	2.757	all ten:	2.932
[a]2 O(2)-O(3)'	2.764	[a]2 O(4)-O(5)'	2.798	2 O(1)-O(6)	2.798	2 O(5)-O(12)	2.892	[a]2 O(3)-O(2)'	2.764	average of	
[b]1 O(1)-O(1)'	2.905	[b]1 O(5)-O(5)'	2.848	2 O(2)-O(6)	2.866	1 O(12)-O(12)'	2.943	[a]2 O(3)-O(4)'	2.778	inner six:	2.571
2 O(2)-O(1)	3.031	2 O(4)-O(3)	3.015	[b]2 O(1)-O(6)'	2.963	[b]2 O(5)-O(12)'	2.995	2 O(3)-O(4)	3.090	average of	
2 O(2)-O(3)	3.033	2 O(4)-O(5)	3.019	2 O(1)-O(2)	2.971	2 O(4)-O(12)	2.998	2 O(3)-O(2)	3.129	outer four	3.473
2 O(1)-O(3)	3.105	2 O(5)-O(3)	3.079	1 O(6)-O(6)'	3.006	2 O(5)-O(4)	3.010	1 O(4)-O(2)	3.208		
	2.904		2.905		2.861		2.924		2.948		

M(4)		M(4')		Be		Si(1)		Si(2)		Si(3)	
2 M(4)-O(6)	2.340	2 M(4')-O(12)	2.313	Be-O(2)	1.632	Si(1)-O(12)	1.582	Si(2)-O(4)	1.580	Si(3)-O(6)	1.575
2 -O(7)	2.509	2 -O(5)	2.423	[d]-O(9)	1.663	-O(5)	1.615	[d]-O(9)	1.593	[c]-O(8)	1.634
2 -O(1)	2.532	2 -O(11)	2.604	[c]-O(7)	1.677	[c]-O(11)	1.647	[c]-O(10)	1.638	-O(1)	1.638
2 -O(8)	2.553	2 -O(10)	2.653	[c]-O(8)	1.688	[c]-O(10)	1.671	[c]-O(11)	1.639	[c]-O(7)	1.647
	2.483		2.498		1.665		1.629		1.613		1.623
				O(9)-O(7)	2.573	O(12)-O(11)	2.548	O(10)-O(11)	2.590	O(6)-O(8)	2.551
				O(9)-O(8)	2.646	O(11)-O(5)	2.661	O(9)-O(10)	2.594	O(7)-O(8)	2.612
				O(8)-O(2)	2.673	O(10)-O(5)	2.662	O(11)-O(4)	2.625	O(1)-O(8)	2.648
				O(7)-O(8)	2.680	O(12)-O(10)	2.671	O(9)-O(11)	2.628	O(1)-O(7)	2.679
				O(7)-O(2)	2.685	O(10)-O(11)	2.688	O(10)-O(4)	2.646	O(6)-O(7)	2.689
				O(9)-O(2)	2.734	O(12)-O(5)	2.740	O(9)-O(4)	2.646	O(6)-O(1)	2.739
					2.665		2.662		2.622		2.653

[a] Edges shared between octahedra.
[b] Edges shared between octahedra and square antiprisms.
[c] T-O-T' oxygens in [[pyroxene]] chain.
[d] T-O-T' oxygens bridging across [[pyroxene]] chains.

both with A' and Be. Since Be contributes only about half the charge that Si does, these anions would be extremely undersaturated if the A site were occupied instead of A'. In other words, the off-centered A' site stabilizes the joesmithite crystal by contributing to the coordination sphere about O(7), O(8) and O(9). This off-centered A' site and the ordered Be atoms must also influence the octahedral walls. Though there does not appear to be any obvious explanation for the occupation of the $M(2)$ site principally by Fe^{3+}, the highly unequal distribution of Fe over the oc-

tahedral sites reflects the asymmetry induced in the walls by the A' and Be atoms.

Is lead a necessary constituent of the A' site? Since this site is mixed, with atom fractions approximating 0.6 Ca and 0.4 Pb, it would appear that the presence of lead is fortuitous. The A' site most likely accommodates divalent cations by reason of electrostatic charge balance about nearest neighbor anions. The inner six average A'-O distances of 2.57 Å suggest that Pb^{2+}, Ca^{2+} and Ba^{2+} would be likely candidates for this site.

TABLE 5. JOESMITHITE. ELECTROSTATIC VALENCE BALANCES (Σ)

			Σ[a]	Σ, no A'
O(1)	$M(1)+M(2)+M(4)+Si(3)$	2(+)/6+3/6+2/8+4/4	2.08(+)	
O(2)	$M(1)+M(3)+M(2)+Be$	2(+)/6+2/6+3/6+2/4	1.67(+)	
O(3)=OH⁻	$M(1)+M(3)+M(1')$	2(+)/6+2/6+2/6	1.00(+)	
O(4)	$M(3)+M(1')+M(2')+Si(2)$	2/6+2/6+2/6+4/4	2.00	
O(5)	$M(1')+M(2')+M(4')+Si(1)$	2/6+2/6+2/8+4/4	1.92	
O(6)	$M(2)+M(4)+Si(3)$	3/6+2/8+4/4	1.75	
O(7)	$M(4)+A'short+Be+Si(3)$	2/8+2/6+2/4+4/4	2.08	1.75
O(8)	$M(4)+A'short+Be+Si(3)$	2/8+2/6+2/4+4/4	2.08	1.75
O(9)	$A'short+Be+Si(2)$	2/6+2/4+4/4	1.83	1.50
O(10)	$A'long+M(4')+Si(1)+Si(2)$	0+2/8+4/4+4/4	2.25	
O(11)	$A'long+M(4')+Si(1)+Si(2)$	0+2/8+4/4+4/4	2.25	
O(12)	$M(4')+M(2')+Si(1)$	2/8+2/6+4/4	1.58	

[a] Values marked (+) have average charge slightly in excess of values given.

Can a beryllium-tremolite analog of the joesmithite structure exist? This would imply the crystal cell exchange $\square^0(Si^{4+})_4 \rightarrow (Ca^{2+})_2(Be^{2+})_4(Y^+)_4$, where "$\square$" denotes the empty A site and "Y" the collection of required positive charge remaining. In the joesmithite crystal, Y is essentially Fe^{3+}. Indeed, the crystal cell of joesmithite would require four trivalent atoms distributed over the octahedral sites: the chemical analysis shows $Fe^{3+}_{3.4}Al_{0.3}$, in satisfactory agreement with this conclusion. Instructive in this respect would be an attempted synthesis of an aluminum-beryllium-tremolite with composition $Ca_3Al_2Mg_3$ $[Si_6Be_2O_{22}]$ $(OH)_2$. Such a compound, if it does exist, may be of potential interest to mineralogists since it could conceivably appear in beryllium-bearing pegmatites. It should be an isotype of joesmithite.

Joesmithite, a beryllo-silicate mineral allied to an important rock-forming mineral group, does not have particularly unusual status in silicate mineralogy. There are many examples of beryllium-bearing silicates which possess a simple relationship to important rock-forming silicates. Some of these pairs possess the same symmetry, such as osumilite and milarite, indialite and beryl, muscovite and bityite, and datolite and gadolinite. Others have a lower symmetry, such as åkermanite and leucophane. The status of beryllium-bearing vesuvianite is not known and further study will be required on this relationship. It would be interesting to examine these pairs in the light of electrostatic valence balance requirements, since the behavior of beryllium-bearing analogues might be predicted on this basis.

Distortions. Polyhedral distortions, aside from the effects of local electroneutrality, result largely from cation-cation repulsion effects. The most severe distortions are evident across shared polyhedral edges within the octahedral portion of the walls. Shared edges between octahedra are always the shortest distances for each of the polyhedra, clearly shown in Table 4. On the other hand, the effects of cationic repulsions are not nearly as severe when octahedra share edges with the square antiprisms and these shared edges have intermediate values for their octahedra, since the square antiprisms (and calcium atoms) are much larger polyhedra (cations) with much longer average M-O distances.

For the tetrahedra, the corners shared in the pyroxene chain components have the largest T-O distances. These oxygen atoms are consistently oversaturated relative to the surrounding cations. Some dilation is also doubtless caused by the relatively close Si-Si distances across the shared corners. Since the tetrahedra do not share edges with other polyhedra (excepting the large A'-O polyhedron), repulsions will appear as slight T-O dilations. Similar observations occur for the pyroxene chains in johannsenite (Freed and Peacor, 1967) where the corner-shared oxygens have T-O 1.683 and 1.693 Å with the free oxygens having T-O of 1.594 and 1.604 Å. It is difficult to state how much of these differences are due to T-T repulsion effects: since shared oxygens are electrostatically neutral with respect to silicon atoms, they are usually oversaturated, for at least one additional coordinating cation is present.

FURTHER DISCUSSION

Joesmithite is topochemically distinct from the C-centered clinoamphiboles because of the ordered off-centered A' site and ordered beryllium atoms in tetrahedral positions. This coupled relationship assures a crystal with statically occupied sites resulting in lower symmetry. On the other hand, as stated by Papike, *et al.* (1968) the A' site in the potassic richterite is not statically occupied since both sides of the true A site have identical topochemical neighborhoods, and a coupled relationship with silicon on one side is as likely as silicon on the other. Besides, on grounds of electrostatic charge balance, a one-sided coupled relationship is not necessary, whereas in joesmithite, ordered beryllium necessitates statically occupied A'.

But this does not explain why joesmithite is ordered. Indeed, the A'-Be coupled relationship could conceivably occupy both sides of the pseudo-mirror plane statistically, resulting in full $C2/m$ symmetry on the average. Several explanations can be offered for full ordering and lower symmetry in joesmithite. The A'-Be pair was coupled during incipient crystal growth, acting as a template and dictating the other cation distributions in the crystal. It is also possible that ordered Be in the joesmithite crystal may result in less violent crystal distortions than the average distribution over two sides of a mirror plane. Finally, the entropy effect of mixing A'-Be over pairs of sites randomly may be too great to assure stability of the crystal.

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