

SARCOPSID: ITS ATOMIC ARRANGEMENT

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ABSTRACT

The atomic arrangement of sarcopsid was determined from a combinatorial map based on an olivine-shaped cell, utilizing 680 symmetry independent single crystal reflections. The parameters were refined to $R(hkl) = 0.087$. Crystal cell parameters are $2(\text{Fe}_{0.78} \text{Mn}_{0.21} \text{Mg}_{0.01})_2 (\text{PO}_4)_2$, a 10.437(22), b 4.768(9), c 6.026(8) Å, $\beta = 90.0^\circ$, space group $P2_1/a$, calculated density 3.94 gm/cm³.

The structure can be derived from olivine through ordering of vacancies, resulting in cation-occupied octahedral edge-sharing trimers which corner-link to form a three-dimensional arrangement. The $(\text{PO}_4)^{3-}$ tetrahedron shares two of its edges with the octahedra and is oriented in a manner akin to olivine.

Interatomic averages are $M(1)-\text{O}$ 2.18, $M(2)-\text{O}$ 2.16 and $\text{P}-\text{O}$ 1.54 Å. The $\text{P}-\text{O}(3)$ 1.59 Å distance is unusually long and is a result of electrostatic oversaturation of cations about O(3). The $M-\text{O}$ and $\text{O}-\text{O}'$ polyhedral distances in sarcopsid, triphylite, and fayalite can be easily compared with the aid of Schlegel diagrams, which reveal trends compatible with simple electrostatic arguments.

INTRODUCTION

The crystal chemistry and paragenesis of primary and secondary pegmatite phosphates, especially of the first transition series cations, is a complex mineralogical problem. Traditional studies, based solely on chemical analyses, optical properties, and physical characters, are fraught with uncertainties on account of variable oxidation states of transition metal cations, exsolution textures, the frequent presence of water and hydroxyl ligands, and relatively complex crystal cells. A better understanding of their paragenetic tree requires careful pruning. The best method available is three-dimensional crystal structure analysis directed toward key compounds.

Professor D. R. Peacor and I are presently undertaking a detailed study on the paragenetic relationships among primary phosphates and their oxidation products such as alluaudite, triphylite-lithiophilite, heterosite-purpurite, graftonite-beusite, griphite, triplite-zwieselite, triploidite-wolfeite, sarcopsid, and arrojadite-dickinsonite. A detailed study of the alluaudite structure and crystal chemistry has recently been published by Moore (1971). The present study is an extension of the general problem towards clarifying the crystal chemistry of sarcopsid. Details of the sarcopsid crystal chemistry, including its exsolution textures with graftonite, triphylite, and other phases, shall

be held in abeyance and included in our general study. I refer readers to the investigation by Hurlbut (1965) as an introduction to the problem.

Allusion to a structure determination of sarcopside appeared in an abstract of Mrose and Appleman (1961) who state that "...; the Fe atoms in sarcopside occupy the same positions as the Li and Mn atoms in lithiophilite." However, this is not sufficient information toward deriving an unambiguous cation distribution for sarcopside. Apparently, a more detailed account of that study has not materialized and it proved necessary to regard the sarcopside atomic arrangement as unknown.

EXPERIMENTAL

Single crystal sarcopside suitable for accurate three-dimensional study is difficult to obtain. The species has only been observed as exsolution lamellae which are usually crinkled and/or polysynthetically twinned. In 1970, I collected broad sarcopside lamellae exsolved from large triphylite cleavages from the Bull Moose pegmatite, near Custer, South Dakota. Splitting of the lamellae revealed that a few sarcopside fragments showed smooth cleavage surfaces. After much effort, a fragment, nearly a cube in outline and measuring 0.09 mm on an edge, was secured and revealed Weissenberg photographs about the *b*-axis with no evidence of polysynthetic twinning.

It was necessary to obtain cell contents for the Bull Moose material. Consequently, an ARL electron microprobe analysis using olivines and triphylite as standards, was performed. These data were corrected for absorption and efficiency-of-generation effects. A powder pattern was prepared from a small homogeneous fragment which was finely ground and rolled with rubber cement to form a small bead. The reflections were carefully indexed using the three-dimensional single crystal intensity data as a guide, since the β -angle departs only slightly from 90° . Unfortunately, all sarcopsides examined in this study revealed a minor amount of another phase which appears to be a hydrothermally reworked product, occurring as brown films along joint fractures in the sarcopside. Additional powder diffraction lines are contributed by this phase and present study indicates that it is probably a new species. A powder pattern was then obtained from the same single crystal used in the structure analysis utilizing a 114.6 mm diameter Gandolfi camera. The intense and equally strong single crystal reflection pairs ($\bar{1}12$, 112) and ($\bar{2}22$, 222) showed no evidence of line splitting, indicating that $\beta = 90.00(15)^\circ$ within the error of the experiment since it was calculated that discernible line splitting would occur for deviations beyond $\pm 10'$ from 90° . Refinement of the initial cell parameters stated by Hurlbut (1965) was based on the indexed powder data from the standardized film of the Gandolfi camera. Crystal cell computations based on the probe analysis and the refined cell parameters are presented in Table 1.

1500 non-equivalent reflections of the *h0l-h6l* levels were collected on a PAILRED automated diffractometer to $2\theta = 65^\circ$ using MoK_α radiation and a graphite crystal monochromator. Due to the slightly crinkled surface of the crystal, 2.3° half-angle scans were necessary, with background counting times of 20 seconds on each side of the reflection.

The small size of the crystal and a relatively low linear absorption coefficient (77.0 cm^{-1}) did not necessitate absorption correction. The data were processed

TABLE 1. CRYSTAL CELL DATA FOR SARCOPSIDE

<u>a</u>	10.437 (22) Å
<u>b</u>	4.768 (9)
<u>c</u>	6.026 (8)
<u>β</u>	90.00 (15)°
<u>space group</u>	$P2_1/a$
<u>formula</u>	$(\text{Fe}_{0.78}\text{Mn}_{0.21}\text{Mg}_{0.01})_3 (\text{PO}_4)_2$
<u>Z</u>	2
<u>density (calc)</u>	3.94 gm/cm ³
<u>location</u>	Bull Moose Pegmatite, near Custer, South Dakota

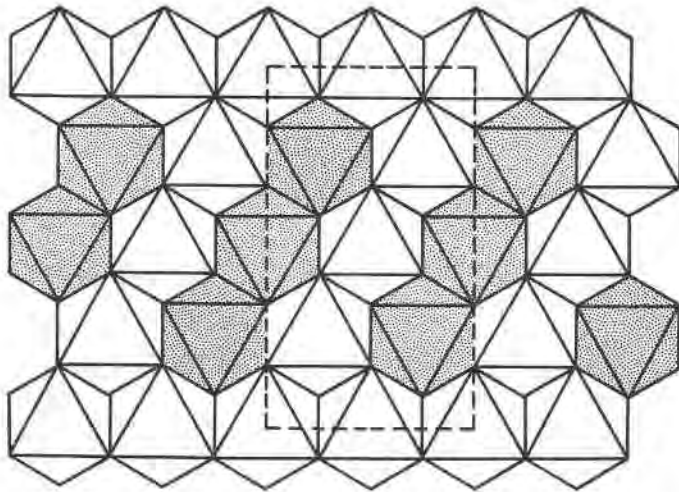
to obtain $F(obs)$. 680 reflections were greater than three times the background error and were the only ones used in the ensuing study. Included in the 900 "zero" reflections were the systematic absences which conformed to the uniquely determined $P2_1/a$ space group.

SOLUTION OF THE STRUCTURE

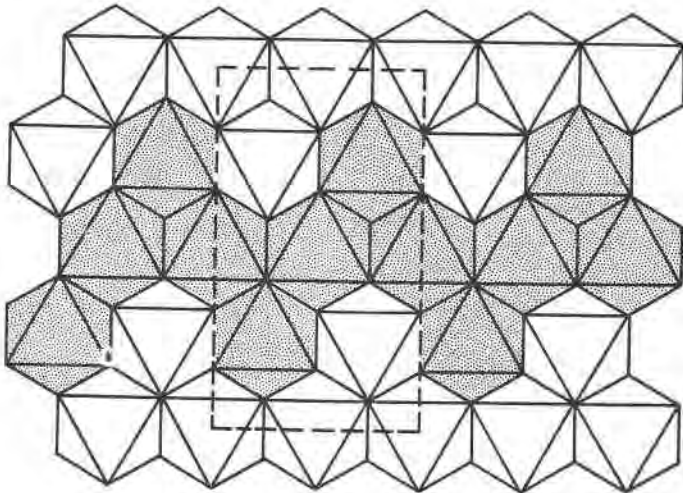
The marked similarity of the crystal cell parameters of sarcopside compared with triphylite-lithiophilite indicated a structure based upon hexagonal close-packed oxygen atoms. I have derived all possible octahedral and tetrahedral populations for given cationic stoichiometries and specified orthogonal cells based upon hexagonal close-packed two-octahedra level structures using a combinatorial topological technique. This technique has been briefly described in Moore (1968). For the cell of olivine dimensions and octahedral population stoichiometry, there exist five topologically distinct arrangements. Four of these arrangements are shown as polyhedral diagrams in Figure 1a-b and 2a-b. Only one arrangement possesses space group $P2_1/a$ and, if the assumption of close-packing is correct, it should represent the sarcopside arrangement. Since the sarcopside stoichiometry is $M:\text{O}$ (octahedral population: oxide anions) = 3:8, one set of octahedral populations on the inversion center must be vacant. Only one tetrahedral population scheme is possible, based on conventional electrostatic arguments. All independent atomic positions were derived from the combinatorial map in Figure 1a, whose initial coordinates are those for perfect close-packing without polyhedral distortions.

REFINEMENT

The initial model was submitted to full-matrix free parameter refinement using a local version of the program ORFLS for the IBM

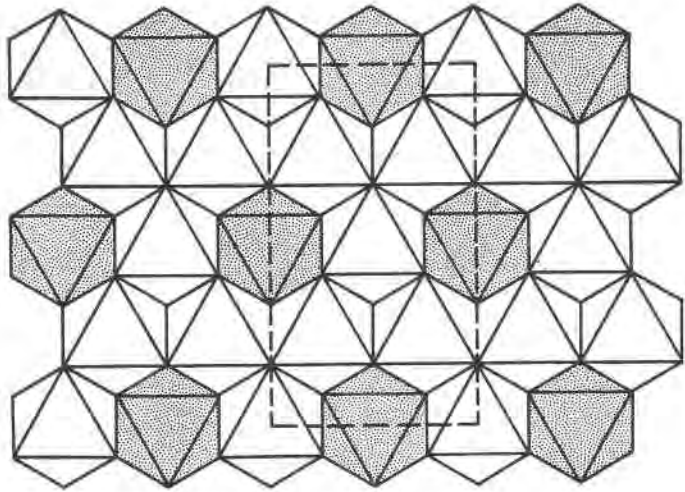


(a)

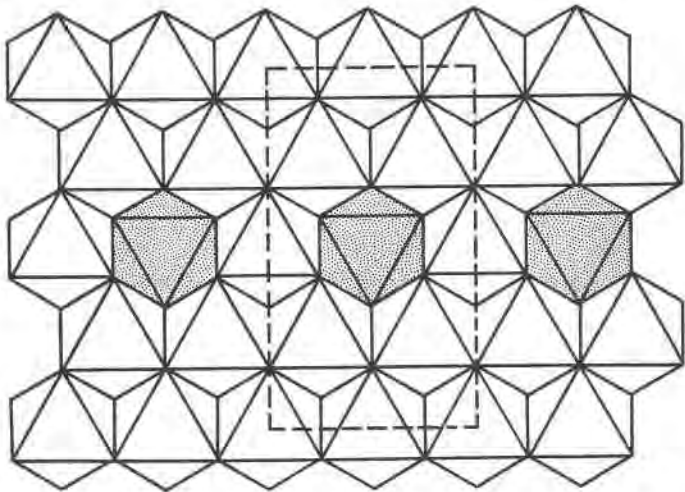


(b)

FIG. 1. Two of the five centrosymmetric combinatorial structures with $M:O = 1:2$ based on the olivine cell shape. Unstippled octahedral populations are at $y = 0$ stippled octahedral populations at $y = 1/2$. The b -axis is normal to the paper and the a - and c -axes are defined by right-handed convention. (a) Sarcopside, obtained by vacating octahedra at $(1/2, 0, 1/2)$ and $(0, 0, 1/2)$. The space group of the combinatorial structure is $P2_1/a$. (b) Olivine. In this orientation, the space group is Pnm . Vacating octahedra at $(0, 0, 0)$ and $1/2, 1/2, 0$ leads to sarcopside.



(a)



(b)

FIG. 2. Two other centrosymmetric combinatorial structures. The population schemes are interpreted as in Fig. 1 (a) Spinel derivative structure. The unstippled octahedra represent a slab of the spinel arrangement down the $[111]$ cube axis. (b) A novel arrangement, as yet unknown.

7094 computer, described by Busing, Martin and Levy (1962). Scattering curves included the values for Fe^{1+} , P^{3+} , and O^{2-} which are tabulated in MacGillavry and Rieck (1962). The trial model yielded $R(hkl) = \Sigma |F(\text{obs})| - |F(\text{calc})| / \Sigma |F(\text{obs})| = 0.52$. Six successive cycles of scale and atomic parameter refinement brought $R(hkl)$ down to 0.12, with the atomic parameter shifts within their limits of error. Three more cycles including scale factor, atomic parameter and isotropic thermal vibration refinement, converged to $R(hkl) = 0.087$. Throughout, no weighting scheme was used between the $|F(\text{obs})|$ and $F(\text{calc})$ data, and the overall scale factor converged to 0.886. A difference synthesis revealed that good positional convergences were attained. The relatively uniform and low isotropic thermal vibration parameters ($\text{O}^{2-} \sim 0.7 \text{ \AA}^2$) are representative of a structure based on oxygen close-packing.

The initial trial parameters and the final parameters and their errors are given in Table 2. To my knowledge, this is the first example of a structure solved from purely combinatorial techniques. Since all hexagonal close-packed two-layer structure types can be exhausted in this fashion, it implies that determinations of such structures are simple, if not trivial, problems. This is gratifying since other conventional techniques present difficulties as a result of the high parameter correla-

TABLE 2. SARCOPSIDE. INITIAL ATOMIC COORDINATES, FINAL ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS

(Estimated standard errors in parentheses)

	x_i	x_f	y_i	y_f	z_i	z_f	$B(\text{\AA}^2)$
M(1)	0	0.0000	0	0.0000	0	0.0000	0.58(4)
M(2)	1/4	.2830(2)	0	-.0134(6)	1/4	.2639(3)	.57(2)
P	$\sim 1/12$.1000(3)	3/8	.4341(7)	1/4	.2386(6)	.53(5)
O(1)	$\sim -1/12$	-.1042(10)	1/4	.2510(23)	-1/4	-.2159(18)	.71(15)
O(2)	$\sim -1/12$	-.0358(10)	1/4	.3147(23)	1/4	.2463(18)	.76(15)
O(3)	$\sim 1/6$.1620(10)	1/4	.2838(23)	0	.0291(17)	.78(15)
O(3a)	$\sim 1/6$.1822(10)	1/4	.3241(23)	1/2	.4296(17)	.69(14)

tions encountered in close-packed sequences. The $|F(obs)| - F(calc)$ data appear in Table 3.¹

DISCUSSION OF THE STRUCTURE

Sarcopside is based on hexagonal close-packed oxygen atoms in which $\frac{2}{3}$ ths of the octahedral and $\frac{1}{3}$ th of the tetrahedral voids are filled. It shares some features in common with the olivine (triphylite) structure type, including a similar orientation of the tetrahedra (compare Fig. 1a and 1b), but is distinct in consisting of octahedral edge-sharing trimers instead of the serrated chains. The trimers corner-link to those displaced $b/2$ and related by the axial glide and screw operations. The $(PO_4)^{3-}$ tetrahedron shares two edges with the octahedra, one associated with the $M(1)O_6$ octahedron and the other with $M(2)O_6$. Since sarcopside is a combinatorial derivative of the olivine cell shape, it should be possible to derive its structure by suppressing (and/or adding) olivine octahedral occupancies. This is achieved by vacating the populated octahedra at (000) and $(\frac{1}{2}, \frac{1}{2}, 0)$ in olivine. Thus, the statement that the Fe atoms in sarcopside occupy the same positions as Li and Mn in lithiophilite by Mrose and Appleman (1961) is correct, but does not allow for the unambiguous choice of ordering scheme. Based on the refinement of triphylite by Finger and Rapp (1970), where they showed that Li and Fe are ordered over the $\bar{1}$ and m point positions respectively, the chemical ordering relationship between triphylite and sarcopside must be



where \square is an ordered vacancy.

In Table 2, the atomic positions are labelled to conform with adopted olivine nomenclature; since the general O(3) atom in olivine is not split by a mirror plane in sarcopside, the two independent analogous atomic positions are labelled O(3) and O(3a) respectively.

INTERATOMIC DISTANCES

The relationship of sarcopside with triphylite and the olivine structure type stimulates discussion on their relative interatomic distances.

¹To obtain a copy of Table 3, order NAPS Document #01668 from National Auxiliary Publications Service of ASIS, c/o CCM Information Corporation, 866 Third Avenue, New York, New York 10022, remitting in advance \$2.00 for microfiche or \$5.00 for photocopies, payable to CCMIC-NAPS.

A polyhedral representation of the sarcopside crystal structure showing its distorted polyhedra appears in Figure 3. To effectively compare individual polyhedral distances between sarcopside, triphylite, and fayalite, their Me—O and O—O' distances are featured as the Schlegel diagrams in Figure 4. Schlegel diagrams have been introduced as vehicles for interatomic distance parameters by Moore (1970); they reveal the maximum amount of information with the minimum of clutter and are well-suited for comparison of several polyhedra in tandem. The triphylite data were obtained from Finger and Rapp (1970) and the fayalite data from Birle, Gibbs, Moore, and Smith (1968).

Before advancing discussion on these diagrams, it is necessary to inquire about the electrostatic valence balances of cations coordinating to the anions for the three structures. These data are presented in Table 4. Only fayalite possesses electrostatic neutrality about each of the anions. In triphylite, O(1) and O(2) are slightly undersaturated whereas O(3) is oversaturated. In sarcopside, the differences are more extreme: O(1), O(2), and O(3a) are all slightly undersaturated whereas O(3) is severely oversaturated, with $\Sigma = 2.25$.

Such differences are manifest in the Me—O distances. The P—O(3) distances in sarcopside are longer than average, with P—O(3) 1.59 Å in sarcopside representing an unusually long P—O distance. Contribution to the O—O' edge distances results from the relationship among shared edges. The $T = O = M$ shared edge distances are particularly interesting and involve O(3)—O(3a) 2.43 and O(2)—O(3) 2.45 in

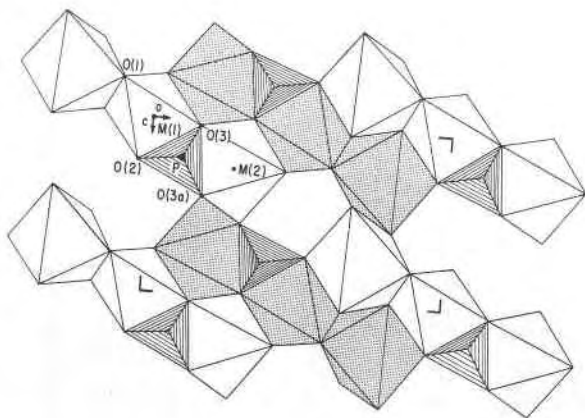


FIG. 3. Polyhedral diagram of the sarcopside arrangement showing actual distortions. Only the tetrahedral occupancies sharing edges above the octahedra at $y = 0$ are shown.

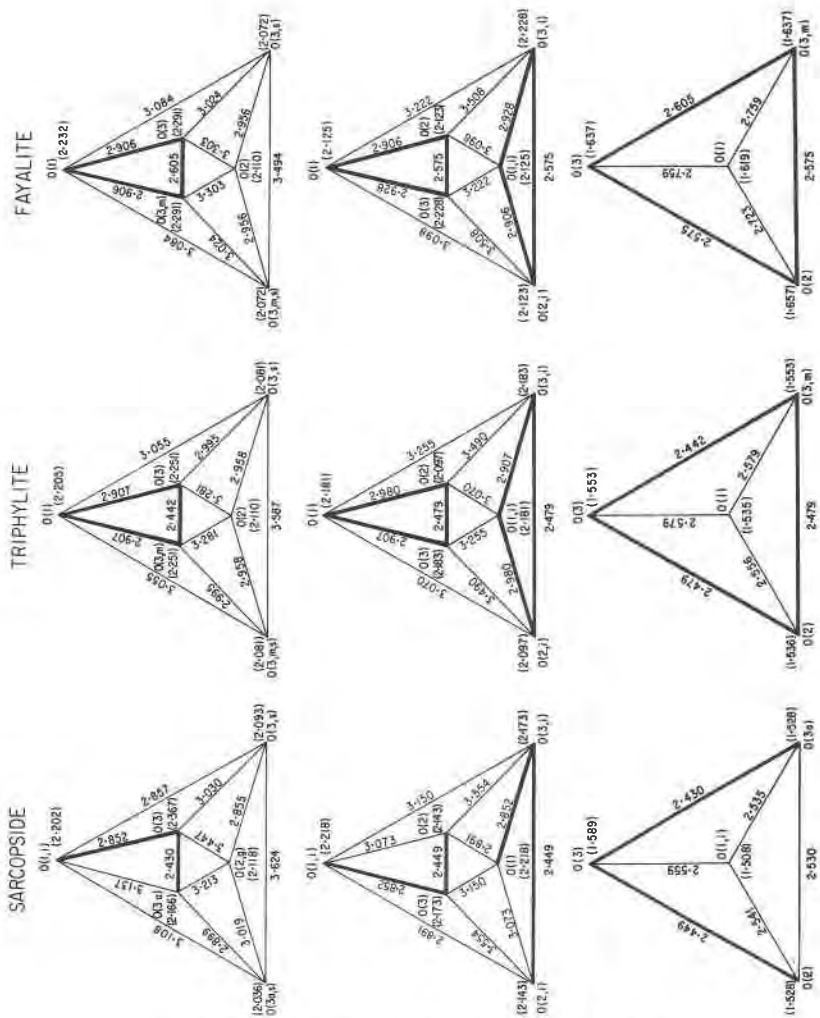


Fig. 4 Octahedral and tetrahedral interatomic distances in sarcopsite, triphylite and fayalite featured on Schlegel diagrams. The top row are the $M(2)$ and the middle row the $M(1)$ octahedra. Shared edges are drawn bold. Labeling of atoms with g , s , and i represent axial glide, screw and inversion operations performed on the coordinates in Table 2 and for the olivine structures in similar orientation.

Estimated standard errors for sarcopsite are $Me - O \pm 0.01 \text{ \AA}$ and $O - O' \pm 0.02 \text{ \AA}$.

TABLE 4. SARCOPSIDE, TRIPHYLITE AND FAYALITE. COMPARISON OF ELECTROSTATIC VALENCE BALANCES (Σ) OF CATIONS ABOUT ANIONS

	Sarcopside		Triphylite		Fayalite	
		Σ		Σ		Σ
O(1)	$2\text{Fe}^{2+}+\text{P}^{5+}$	1.92	$2\text{Li}^{+}+\text{Fe}^{2+}+\text{P}^{5+}$	1.92	$3\text{Fe}^{2+}+\text{Si}^{4+}$	2.00
O(2)	$2\text{Fe}^{2+}+\text{P}^{5+}$	1.92	$2\text{Li}^{+}+\text{Fe}^{2+}+\text{P}^{5+}$	1.92	$3\text{Fe}^{2+}+\text{Si}^{4+}$	2.00
O(3)	$3\text{Fe}^{2+}+\text{P}^{5+}$	2.25	$\text{Li}^{+}+2\text{Fe}^{2+}+\text{P}^{5+}$	2.08 (x2)	$3\text{Fe}^{2+}+\text{Si}^{4+}$	2.00(x2)
O(3a)	$2\text{Fe}^{2+}+\text{P}^{5+}$	<u>1.92</u>	-	<u>-</u>	-	<u>-</u>
		8.00		8.00		8.00

sarcopside; and O(3, m)—O(3) 2.44 and O(2)—O(3) 2.48 Å in triphylite. The mean O—O' 2.51 and 2.52 Å in sarcopside and triphylite respectively suggest that distortion of the highly charged and tightly bound (P^{5+}O_4) tetrahedral group by cation-cation repulsion effects is substantial. Distortion of the softer octahedra, is, of course, much more severe since the polyhedral edges are dependent on the geometrical restrictions of the hard tetrahedra. The average O—O' 3.00 for M(1) and O—O' 3.04 Å for M(2) in sarcopside; O—O' 3.04 Å for M(2) (=Fe) in triphylite; and O—O' 3.04 for M(1) and O—O' 3.05 Å for M(2) in fayalite reveal that average isopolyhedral isocationic edge distances are conserved among structures with similar topology and geometry. The major differences appear in the M—O distances, which largely depend on charge balance and cation-cation repulsion effects. Comparison between sarcopside, and the triphylite and fayalite structures is especially interesting. The M(2)O₆ octahedron in the olivine structures involves a mirror plane which divides the Schlegel diagram in Figure 4 vertically. In sarcopside, only one M = O = M shared edge is present and the mirror plane is destroyed. Instead, compensatory effects appear: the lone O(1, i)—O(3) 2.85 shared edge is shorter than the two O(1)—O(3) 2.91 Å shared edges related by the mirror plane in triphylite. Averaging the edge distances across the missing olivine mirror plane in sarcopside reveals distances roughly comparable with those found in triphylite and fayalite.

Finally, I remark that unusually long compensating O—O' distances occur in the octahedra, whose trends are preserved in all three structures. The long O(3a, s)—O(3, s) 3.62; O(3, m, s)—O(3, s) 3.59 and 3.49 Å distances for sarcopside; triphylite, and fayalite respectively appear at the edge opposing the T = O = M edge in the M(2) octa-

hedra. The effect is particularly noticeable for the two phosphates on account of the smaller and more highly charged (PO_4) tetrahedra and the consequent violent compensation at the opposing free edge. For the $M(1)$ octahedra, the long distances are $\text{O}(2, i) - \text{O}(3)$ 3.55 and 3.51 Å for sarcopside and fayalite respectively. $M(1)$ in triphylite cannot be compared, since it is occupied by Li^+ .

SOME CURIOUS FEATURES OF TRIPHYLITE AND SARCOPSIDE

The average $\text{P}-\text{O}$ 1.54 Å distance in sarcopside is within the limit of error of the average observed for triphylite. The average $M-\text{O}$ distances among the three structures are $M(1)-\text{O}$ 2.18, $M(2)-\text{O}$ 2.16 Å in sarcopside ($M(1) + M(2) = (\text{Fe}_{0.79}\text{Mn}_{0.21})$); $M(1) (= \text{Li}) - \text{O}$ 2.15, $M(2) (= \text{Fe}_{0.76}\text{Mn}_{0.24}) - \text{O}$ 2.16 Å in triphylite; and $M(1)-\text{O}$ 2.16, $M(2)-\text{O}$ 2.18 Å in fayalite. These distances are sufficiently similar within the crystal and between crystals that no site preference scheme can be advanced solely on the X-ray evidence. In sarcopside, the isotropic thermal vibration parameters for $M(1)$ and $M(2)$ are identical within their error limits; the low Mg content in the crystal does not admit a site preference scheme.

It is odd that triphylite is an ordered crystal, judging from the marked similarity in the Li-O and Fe-O distances; the tendency toward extensive solid solution in fayalite-forsterite (where the Mg-O and Fe-O average distances differ more than those in triphylite); and the disordered character of (Na, Mn) in natrophilite, $\text{NaMn}(\text{PO}_4)$, as determined by Byström (1943). More detailed study on triphylite at high temperature will be necessary before adequate knowledge can be advanced regarding the relationships among the primary pegmatite phosphates, particularly those which display exsolution phenomena. This problem is presently being pursued.

The existence of sarcopside is puzzling. Calvo (1968), in his study on the graftonite structure, states "Since the two major components of graftonite, $\text{Mn}_3(\text{PO}_4)_2$ and $\text{Fe}_3(\text{PO}_4)_2$, crystallize with the graftonite structure, the fact that the sarcopside structure forms at all is curious." He advances the suggestion that Mg^{2+} may play a crucial role in the sarcopside structure. The present study indicates that if Mg^{2+} plays any role at all, it must be a very delicate and subtle one.

On this point, Nature appears to be telling us something. Sarcopside has never been observed as a primary crystal phase. All evidence indicates that it is an exsolution product, associated either with graftonite or triphylite. Its association with triphylite is particularly interesting since sarcopside is indisputably the exsolved phase, suggesting that triphylites at high temperature are at least partially disordered, ex-

tending our interest to the series $\text{Li}_2\text{Fe}_2(\text{PO}_4)_2 - \square \text{FeFe}_2(\text{PO}_4)_2$. It would appear that exsolution relationships play a crucial role in the stability of sarcopside. These questions Professor Peacor and I hope to answer in our detailed investigation on the primary phosphate studies presently in progress.

ACKNOWLEDGMENTS

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