

## The synthesis and crystal structure of a magnesium–lithium–scandium protopyroxene

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### Abstract

Crystals of protopyroxene solid solution,  $\text{Li}_x\text{Sc}_x\text{Mg}_{2-x}\text{Si}_2\text{O}_6$ ,  $0.1 \leq x \leq 0.35$ , were grown, in solvents of the system  $\text{Li}_2\text{O}-\text{V}_2\text{O}_5-\text{MoO}_3$ , by cooling from 1350 to 650° at 1.5°C per hour. The crystals are transparent, euhedral, and prismatic, elongate parallel to  $c$  and up to  $15 \times 4 \times 3$  mm in size, with well-developed  $\{010\}$ ,  $\{110\}$ , and  $\{121\}$  faces. The cell edges used for structure analysis are:  $a = 9.251$ ,  $b = 8.773$ , and  $c = 5.377\text{\AA}$ . Long-exposure X-ray precession photographs showed no diffraction maxima inconsistent with space group  $Pbcn$  and no evidence of stack disorder. The crystal structure was refined from 1507 measured X-ray intensities, of which 826 were greater than  $3\sigma$  of the background intensity. Refinements of the structure in space groups  $P2_1cn$ ,  $Pb2n$ ,  $Pbc2_1$ , and  $P2/c$  yielded structures which did not differ significantly from that in space group  $Pbcn$ . The structure is ordered with all of the  $\text{Sc}^{3+}$  in  $M1$  and all of the  $\text{Li}^+$  in  $M2$ .

### Introduction

Protoenstatite is the stable form of  $\text{MgSiO}_3$  between approximately 1000° and 1540°C. On cooling below 1000°C it breaks down rapidly to a disordered mixture of ortho- and clinoenstatite (Brown and Smith, 1963; Smyth, 1973).

Due in part to its instability at lower temperature, single crystals of protopyroxene large enough for an X-ray structure determination have not been found in nature or made in the laboratory. Polysynthetically-twinned clinopyroxenes, which presumably originated by inversion from protopyroxene during rapid cooling, have been described in several meteorites (Binns, 1970; Dodd, 1974; Dodd *et al.*, 1975) and from a terrestrial porphyritic volcanic rock from Cape Vogel, Papua (Dallwitz *et al.*, 1966).

Atlas (1952) postulated that the space group is  $Pbcn$ , and the structure was determined by Smith (1959, 1969) from powder data. Sadanaga *et al.* (1969) reported a structure determination from 47 X-ray intensities measured from a single crystal at 1000°C. Smyth (1971) reported a structure refinement from 187 observed intensities measured from precession films taken at 1100°C, and noted numer-

ous violations of the  $b$ -glide diffraction symmetry. He reported the space group as  $P2_1cn$ ; however, the material studied showed significant stacking disorder, and he suggested that the violation of  $b$ -glide symmetry may have arisen from the stack disorder. Because of the difficulty of obtaining a well-crystallized specimen, the structure has never been refined from single-crystal intensity data obtained at room temperature, and the standard errors in all protopyroxene structures reported in the literature are relatively large. Further, as Thompson (1970) suggested that the ideal space group for the proto structure should be  $P2_1cn$ , there remains the question of the true space group of the protopyroxene structures.

### Crystal synthesis

During experiments of doping orthoenstatite with transition elements using a high-temperature solvent (Ito, 1975), it was found that  $\text{Sc}^{3+}$ , when coupled with  $\text{Li}^+$ , stabilizes protoenstatite structure at room temperature. Subsequent phase-equilibrium studies of the join  $\text{MgSiO}_3-\text{LiScSi}_2\text{O}_6$  showed that, using pure oxides as starting materials, a substantial field of stability for quenchable protopyroxene exists at sub-

Table 1. Crystal-growth data for Li,Sc-bearing protopyroxene, (Li,Sc,Mg)SiO<sub>3</sub>.

	No. 1*	No. 2
CHARGE COMPOSITION		
Sc <sub>2</sub> O <sub>3</sub>	0.186g	0.186g
MgO	0.515	0.685
SiO <sub>2</sub>	0.807	1.595
Li <sub>2</sub> CO <sub>3</sub>	7.350	0.850
V <sub>2</sub> O <sub>5</sub>	2.08	1.836
MoO <sub>3</sub>	11.70	--
GROWTH CONDITIONS		
Soaking temperature	990°C	1350°C
Soaking time	14 days	2 days
Cooling rate	1.5°C per hour	1.5°C per hour
Cut off temperature	650°C	870°C
Platinum crucible	30 ml	30 ml
Products	Colorless, transparent prismatic crystals of protopyroxene + cracked protopyroxene + metastable olivine.	Large, transparent, v. faintly greyish blue prismatic crystals of protopyroxene. Single phase.
Maximum size of protoenstatite	5 x 1 x 0.4 mm	15 x 4 x 3 mm
Yields	Undetermined	2.00g
Flux impurities	V <sub>2</sub> O <sub>5</sub> 0.30wt% by AA MoO <sub>3</sub> 0.05wt%	V <sub>2</sub> O <sub>5</sub> 0.57wt% (Probe) 0.69wt% (AA)

\*The crystal used for structure work was obtained from this run.

solidus temperature. The protopyroxene solid-solution series is complete at 1250°C between MgSiO<sub>3</sub> and (Li,Sc)<sub>0.35</sub>Mg<sub>0.65</sub>SiO<sub>3</sub>, but is not quenchable if the content of (Li,Sc)SiO<sub>3</sub> is less than 10 mole percent. Since no primary liquidus for protopyroxene was found, the crystal growth was effected using the high-temperature solvents lithium vanadomolybdate (Grandin de L'Eprevier, 1972; Ito, 1975) and lithium vanadate, LiVO<sub>3</sub>.

Crystal growth can be achieved over a wide range of temperature (1350° to 650°C) and charge-to-flux ratios (charge/flux 10/1–1/10). Experimental details of two typical runs are tabulated in Table 1. The crystals thus obtained are up to 15 × 4 × 3 mm in size and are transparent and prismatic with well developed {010}, {110}, and {121} faces (Fig. 1). The crystals are elongate parallel to *c*, and are commonly euhedral without defect or inclusion.

Incorporation of the flux components, particularly LiVO<sub>3</sub>, in the crystal lattice was anticipated, since LiVO<sub>3</sub> was found to be isostructural with monoclinic pyroxene (Shannon and Calvo, 1973). Faster cooling, *i.e.*, rapid crystallization, will introduce as much as several mole percent LiVO<sub>3</sub>, but if cooling is controlled to less than 1.5°C per hour the amount of vanadium oxide can be kept below 0.5 weight percent.

Lithium molybdate alone did not yield satisfactory growth, due to the lack of sufficient solubility.

### X-ray studies

Unit-cell dimensions of three analyzed protopyroxenes were refined using powder-diffraction data (Table 2). X-ray powder data for Li<sub>0.174</sub>Sc<sub>0.174</sub>Mg<sub>0.625</sub>Si<sub>0.988</sub>O<sub>3</sub> are indexed and given in Table 3. Variations of the cell dimensions are consistent with the compositional changes. The *c* axis length remains almost unchanged throughout the solid-solution series, the *a* edge shows a small change, and the *b* dimension increases markedly with the increase in Li,Sc content. The observed changes of the cell edges are consistent with the silicate chains being stretched to the maximum in the *c* direction.

Several crystals (synthesis No. 1, Table 1) were selected for space-group determination by long-exposure precession photography. Using a large crystal (approximately 400 × 400 × 750 μm) and exposure times up to 100 hours with MoK $\alpha$  radiation (50 kV, 20 mA) on Ilford G film, each of the zero-level lattice planes showed no evidence of diffraction intensity violating space group *Pbcn* and no evidence of stacking disorder (*i.e.*, no streaks parallel to *a*\*). A smaller euhedral crystal (approximately 80 × 80 × 150 μm)

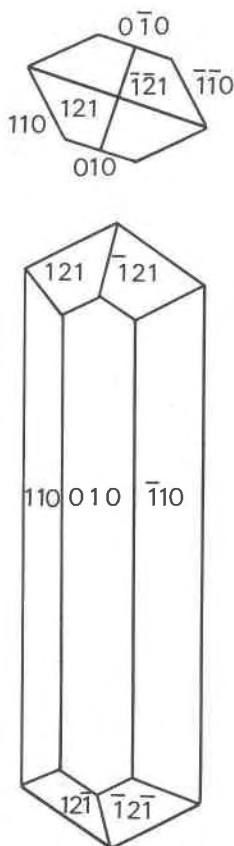


Fig. 1. Crystal morphology of the protopyroxene  $(\text{Li,Sc})_{0.2}\text{Mg}_{0.8}\text{SiO}_3$ . Drawing by A. Kampf, Department of Geophysical Sciences, University of Chicago.

was selected for X-ray intensity measurement and mounted on a Picker FACS-1 automated four-circle diffractometer. Cell edges were determined by least-squares refinement from automatic centering parameters of ten strong diffraction maxima with  $2\theta > 45^\circ$  ( $\text{MoK}\alpha$ ):  $a = 9.251(2)$ ,  $b = 8.773(2)$ ,  $c = 5.377(1)$  Å. Using monochromatic  $\text{MoK}\alpha$  radiation, 1507 symmetry-independent ( $Pbcn$ ) diffraction intensities were measured automatically, representing one octant of reciprocal space with  $2\theta < 75^\circ$ . Of these, 826 were greater than  $3\sigma$  of the background intensity.

### Structure refinement

All intensities were corrected for Lorentz and polarization effects. Using a calculated linear absorption coefficient of  $10.9 \text{ cm}^{-1}$ , maximum absorption was calculated at less than 10 percent, and the data were not corrected for absorption effects. All refinements of the structure models were done with the full-matrix, least-squares refinement program RFINE4 (Finger and Prince, 1975). Structure factors were

weighted according to  $1/\sigma_F^2$ , where  $\sigma_F$  is the standard deviation based on counting statistics as described by Burnham *et al.* (1971). Observations with intensities below the minimum observable level ( $3\sigma$ ) were rejected from the normal equations matrix during all stages of refinement. Atomic scattering factors used were those for fully ionized cations and  $\text{O}^{-1}$  (Cromer and Mann, 1968). Real and imaginary anomalous dispersion terms (Cromer and Liberman, 1969) were included in each cycle of refinement.

The initial atomic coordinates used were those given for pure protoenstatite at  $1100^\circ\text{C}$  (Smyth, 1973), and an arbitrary isotropic temperature factor of  $0.5 \text{ \AA}^2$  was assigned to each atom. The initial composition was assumed to be  $\text{Li}_{0.1}\text{Sc}_{0.1}\text{Mg}_{1.8}\text{Si}_2\text{O}_6$ , fully ordered with 10 percent Li in  $M2$  and 10 percent Sc in  $M1$ . In the first refinement cycle only the scale factor was varied, followed by two cycles with scale and atom coordinates varied, then two with scale, atom coordinates and isotropic temperature factors varied. The resulting temperature factors indicated that the original estimate of composition was in error, so the Sc content of  $M1$  and the Li content of  $M2$  were permitted to vary without constraint for two cycles. This refinement converged with an Li content of 0.31 for  $M2$  and an Sc content of 0.29 for  $M1$ . Since these two figures agree within  $2\sigma$ , and any disorder would cause the two to differ significantly, the two occupancies were set to 0.30 Li and Sc in  $M2$  and  $M1$  respectively. The composition determined on the basis of cell edges agrees well with this estimate (Table 2). With the  $M1$  and  $M2$  occupancies thus fixed, the structure was refined for three further cycles using anisotropic thermal parameters. These refinements converged with a final  $R$  of 0.053. The occupancies, atom coordinates, and anisotropic thermal

Table 2. Unit-cell dimensions of selected crystals in the synthetic protopyroxene solid-solution series:  $(\text{Mg}_{1-x}\text{Sc}_x)(\text{Mg}_{1-x}\text{Li}_x)\text{Si}_2\text{O}_6$ ;  $0 \leq x \leq 0.35$ .

$\text{MgSiO}_3$	100*	89.4**	79.3***	62.5****
$a$	9.25	9.2534(11)	9.2470(18)	9.2522(5)
$b$	8.74	8.7500(13)	8.7679(23)	8.7917(6)
$c$	5.32	5.3289(11)	5.3306(15)	5.3441(6)
$V$	430.0	431.47 (11)	432.19 (13)	434.70 (6)

\* J. V. Smith (1959) hydrothermally synthesized by F. R. Boyd, Geophysical Laboratory.

\*\*  $\text{Li}_{0.53}\text{Sc}_{0.53}\text{Mg}_{0.94}\text{Si}_{1.999}\text{O}_6$ , wet chemical analysis by J. Ito (1976).

\*\*\*  $\text{Li}_{0.95}\text{Sc}_{0.95}\text{Mg}_{0.793}\text{Si}_{1.000}\text{O}_6$ , Electron microprobe analysis by I. M. Steele (1976).

\*\*\*\*  $\text{Li}_{1.74}\text{Sc}_{1.74}\text{Mg}_{0.225}\text{Si}_{1.998}\text{O}_6$ , Electron probe analysis by I. M. Steele (1976).

Table 3. X-ray powder diffraction data for the synthetic protopyroxene.

h	k	l	I/I <sub>0</sub>	d obs.	d calc.	h	k	l	I/I <sub>0</sub>	d obs.	d calc.
1	1	0	10	6.37	6.37	1	4	2	5	1.669	1.669
2	0	0	2	4.625	4.626	3	3	2	5	1.663	1.663
0	2	0	10	4.397	4.396	0	2	3	10	1.651	1.651
2	1	1	25	3.251	3.250	4	2	2	3	1.624	1.624
1	2	1	100	3.188	3.187	5	2	1	5	1.625	1.625
2	2	0			3.187						
3	1	0	90	2.910	2.910	4	4	0	8	1.594	1.593
1	3	0	10	2.793	2.794	2	4	2			1.594
2	2	1	30	2.736	2.737	2	5	1	3	1.571	1.571
1	0	2	15	2.565	2.567	6	0	0	3	1.542	1.542
1	3	1	10	2.475	2.476	3	5	0	1	1.528	1.528
2	0	2	10	2.314	2.314	4	4	1	2	1.527	1.527
3	2	1	2	2.282	2.283	5	3	1	35	1.501	1.502
0	2	2	2		2.283	1	3	3			1.502
2	3	1	8	2.246	2.246	5	1	2	5	1.499	1.499
2	1	2	10	2.239	2.238	0	6	0	3	1.465	1.465
3	3	0	5	2.124	2.124	1	5	2	2	1.451	1.451
4	1	1	5	2.063	2.063	5	2	2	1	1.438	1.438
1	4	1	10	1.985	1.985	6	2	1	10	1.404	1.404
3	3	1	10	1.974	1.974	0	4	3	2	1.385	1.384
3	1	2	10	1.969	1.968	6	0	2	2	1.336	1.336
4	2	1	5	1.910	1.912	6	3	1	15	1.322	1.322
2	4	1	3	1.860	1.861	1	0	4			1.322
3	2	2	3	1.835	1.835	6	1	2	10	1.321	1.320
5	1	0	5	1.811	1.811	7	1	0	1	1.308	1.307
4	0	2	3	1.749	1.749	1	6	2	5	1.273	1.273
1	5	0	5	1.727	1.727	2	1	4	5	1.270	1.270
4	3	1	20	1.719	1.719	2	6	2	5	1.238	1.237
4	1	2	5	1.715	1.715	1	5	3	5	1.240	1.240
3	4	1	2	1.697	1.697	7	1	2	2	1.174	1.174
0	4	2			1.697	8	0	0	2	1.156	1.156

Refined unit-cell dimensions are a 9.2522(5), b 8.7917(5), c 5.3441(6),  $\gamma$  434.70(4), Orthorhombic Pbcn Z = 8.

Analysis is by electron probe by Ian M. Steele as follows: SiO<sub>2</sub> 59.72, MgO 27.37, Sc<sub>2</sub>O<sub>3</sub> 10.35, Li<sub>2</sub>O 2.24(AA), Total 99.68 wt%.

Cu K $\alpha$  radiation with Si standard.

parameters of the final cycle of refinement are listed in Table 4. Cation-oxygen distances are listed in Table 5.

An attempt was made to refine the atom coordinates in each of the subgroup symmetries  $P2_1cn$ ,  $Pb2n$ ,  $Pbc2_1$ , and  $P2/c$  using isotropic thermal parameters. Each of these refinements yielded atom coordinates which did not differ from the positions in  $Pbcn$  by more than  $2\sigma$ . It was therefore concluded that the true space group of this material is  $Pbcn$ .  $F_{obs}$  and  $F_{calc}$  for the final cycle of refinement in space group  $Pbc2_1$  are available as Table 6.<sup>1</sup>

### Discussion

The results of this study permit several interesting speculations about pyroxene crystal chemistry. The cation radii of Li<sup>+</sup> and Sc<sup>3+</sup> are 0.74 and 0.73 Å compared with 0.72 Å for Mg<sup>2+</sup> (Shannon and Prewitt, 1969), so the effect of cation size should be relatively small for the substitution of 30 percent of these cations into M1 and M2. However the mean M-O distance for this protopyroxene is significantly larger and the mean Si-O distance significantly smaller than for either ortho- or low clino-enstatite. Since it is known that protoenstatite is not stable at room temperature, it seems reasonable to conclude

<sup>1</sup> To obtain a copy of Table 6 order document AM-77-059 from the Business Office, Mineralogical Society of America, 1909 K Street, N. W., Washington, D. C. 20006. Please remit \$1.00 in advance for the microfiche.

Table 4. Occupancies, atom coordinates, anisotropic, and equivalent isotropic temperature factors.

Parameter	M1	M2	Si	O1	O2	O3
Occupancy						
Li	0.00(3)	0.30(3)				
Sc	0.30(3)	0.00(3)				
Mg	0.70(3)	0.70(3)				
X	0	0	0.2935(2)	0.1199(3)	0.3736(4)	0.3493(3)
Y	0.0994(2)	0.2639	0.0900(2)	0.0908(3)	0.2504(4)	0.9831(4)
Z	3/4	1/4	0.0740(3)	0.0805(6)	0.0710(7)	0.3045(7)
Iso. B	0.54	0.93	0.46	0.46	0.78	0.73
$\beta$ 11	0.0015(2)	0.0027(4)	0.0011(1)	0.0014(3)	0.0025(4)	0.0013(3)
$\beta$ 22	0.0022(2)	0.0041(4)	0.0022(1)	0.0016(3)	0.0033(4)	0.0032(4)
$\beta$ 33	0.0037(5)	0.0053(11)	0.0028(3)	0.0035(9)	0.0042(10)	0.0065(12)
$\beta$ 12	.0	.0	-0.0002(1)	-0.0002(3)	-0.0009(4)	0.0002(3)
$\beta$ 13	-0.0004(3)	-0.0005(6)	0.0001(2)	-0.0001(6)	0.0003(7)	-0.0004(5)
$\beta$ 23	.0	.0	-0.0001(3)	0.0000(3)	0.0000(7)	0.0018(6)

Table 5. Cation-oxygen distances (Å) in Li-Sc protopyroxene with mean cation-oxygen distances in ortho- and clinoenstatite.

Tetrahedron		M1 Octahedron		M2 Polyhedron	
Atoms	Distance	Atoms	Distance	Atoms	Distance
Li-Sc Protopyroxene					
Si - 01	1.607(3)	M1 - 01	2.085(4)	M2 - 01	2.086(4)
Si - 02	1.591(3)	M1 - 01	2.199(4)	M2 - 02	2.078(4)
Si - 03	1.630(3)	M1 - 02	2.003(4)	M2 - 03	2.393(4)
Si - 03	1.658(3)				
<u>&lt;Si - 0 &gt;</u>	<u>1.622(3)</u>	<u>&lt;M1 - 0 &gt;</u>	<u>2.096(4)</u>	<u>&lt;M2 - 0 &gt;</u>	<u>2.186(4)</u>
Orthoenstatite*					
<Si - 0 >	1.636	<M1 - 0 >	2.070	<M2 - 0 >	2.158
Clinoenstatite**					
<Si - 0 >	1.634	<M1 - 0 >	2.078	<M2 - 0 >	2.142

\* Morimoto and Koto (1969).

\*\* Ohashi and Finger (1976).

that  $\text{Li}_{0.3}\text{Sc}_{0.3}\text{Mg}_{1.4}\text{Si}_2\text{O}_6$  protopyroxene is also metastable at 20°C, based on the analogy with protoenstatite and the somewhat anomalous cation-oxygen distances. Protoenstatite breaks down to a disordered mixture of ortho- and low clino-enstatite by an autoepitaxial inversion. Smyth (1973) argued that the simplest mechanism for this inversion involves an exchange of *M1* and *M2* cations, and that chemical ordering of *M1* and *M2* cations should inhibit the autoepitaxial inversion mechanism. It seems likely that this Li-Sc protopyroxene is a further example of the inversion mechanism being inhibited by cation ordering in the *M1* and *M2* sites.

Another significant result of this work is that the true space group of well-crystallized protopyroxene is indeed *Pbcn*, as originally proposed by Atlas (1952). The protoenstatite studied at 1100°C by Smyth (1971) showed diffraction maxima violating the *b*-glide symmetry. However, that material also showed evidence of stacking disorder, characterized by reciprocal lattice streaks parallel to *a*\*. Further, the disorder was diffracting coherently with the proto structure and showed up as anomalous electron density in Fourier maps of the structure. Also, Smyth (1971) was unable to refine the structure successfully in space group *P2<sub>1</sub>cn*. It seems reasonable to speculate that the violations of the *b*-glide symmetry in that structure are likely to have resulted from stacking

disorder which was diffracting coherently with the structure, and not from a systematic reverse kinking of the silicate chains as suggested by Thompson (1970) for the ideal protopyroxene structure.

### Conclusions

There are four firm conclusions which may be drawn from this study of Li-Sc protopyroxene. The first is that protopyroxenes may be synthesized directly from the melt, using lithium molybdovanadate or lithium vanadate fluxes. Second, Li-Sc protopyroxenes containing more than about 10 percent  $\text{LiScSi}_2\text{O}_6$  can be quenched. Third, the structure of a protopyroxene with a composition of  $\text{Li}_{0.3}\text{Sc}_{0.3}\text{Mg}_{1.4}\text{Si}_2\text{O}_6$  grown by slow cooling down to 600°C is nearly completely ordered with  $\text{Sc}^{3+}$  in *M1* and  $\text{Li}^+$  in *M2*. Fourth, the space group of this well-crystallized protopyroxene is *Pbcn*.

### Acknowledgments

The first author is indebted to the Deutsche Forschungsgemeinschaft for a temporary research position at the University of Marburg, during which this study was performed. Manuscript preparation has been supported by the Los Alamos Scientific Laboratory. The crystal synthesis part of this work has been carried out in the Materials Research Laboratory of the University of Chicago, funded by the National Science Foundation. The authors thank Dr. Ian M. Steele for his electron probe analyses, and Dr. A. R. Kampf for the morphological diagram of the protopyroxene crystal.

## References

- Atlas, L. M. (1952) The polymorphism of  $MgSiO_3$  and solid state equilibria in the system  $MgSiO_3$ - $CaMgSi_2O_6$ . *J. Geol.*, **60**, 125-147.
- Binns, R. A. (1970) Pyroxenes from non-carbonaceous chondritic meteorites. *Mineral. Mag.*, **37**, 650-669.
- Brown, W. L. and J. V. Smith (1963) High temperature X-ray studies on the polymorphism of  $MgSiO_3$ . *Z. Kristallogr.*, **118**, 186-212.
- Burnham, C. W., Y. Ohashi, S. S. Hafner and D. Virgo (1971) Cation distribution and atomic thermal vibrations in an iron-rich orthopyroxene. *Am. Mineral.*, **56**, 850-876.
- Cromer, D. T. and D. Liberman (1968) Relativistic calculation of anomalous scattering factors for X-rays. *J. Chem. Phys.*, **53**, 1891-1898.
- and J. B. Mann (1968) X-ray scattering factors computed for numerical Hartree-Fock wave functions. *Acta Crystallogr.*, **24**, 321-324.
- Dallwitz, W. B., D. H. Green and J. E. Thompson (1966) Clinoenstatite in a volcanic rock from the Cape Vogel area, Papua. *J. Petrol.*, **7**, 375-403.
- Dodd, R. T. (1974) Petrology of the St. Mesmin chondrite. *Contrib. Mineral. Petrol.*, **46**, 129-145.
- , J. E. Grover and G. E. Brown (1975) Pyroxenes in the Shaw (L-7) chondrite. *Geochim. Cosmochim. Acta*, **39**, 1586-1594.
- Finger, L. W. and E. Prince (1975) *A system of Fortran IV Computer Programs for Crystal Structure Computations*, U. S. Natl. Bur. Stand. Technical Note 854.
- Grandin de L'Eprevier, A. (1972) *Synthese monocristeaux de forsterite,  $Mg_2SiO_4$ , par la methode des sels fondus*. These, La Faculté des Sciences d'Orleans, Orleans, France.
- Ito, J. (1975) High temperature solvent growth of orthoenstatite,  $MgSiO_3$ ; in air. *Geophys. Res. Letters*, **2**, 533-536.
- Morimoto, N. and K. Koto (1969) The crystal structure of orthoenstatite. *Z. Kristallogr.*, **129**, 65-83.
- Sadanaga, R., F. P. Okamura and H. Takeda (1969) X-ray study of the phase transformations of enstatite. *Mineral. J.*, **6**, 110-130.
- Shannon, R. D. and C. Calvo (1973) Crystal structure of  $LiVO_3$ . *Can. J. Chem.*, **51**, 265.
- and C. T. Prewitt (1969) Effective ionic radii in oxides and fluorides. *Acta Crystallogr.*, **B25**, 925-946.
- Smith, J. V. (1959) The crystal structure of protoenstatite,  $MgSiO_3$ . *Acta Crystallogr.*, **12**, 515-519.
- (1969) Crystal structure and stability of  $MgSiO_3$  polymorphs; physical properties and phase relations of Mg,Fe pyroxenes. *Mineral. Soc. Am. Spec. Paper*, **2**, 3-29.
- Smyth, J. R. (1971) Protoenstatite: a crystal structure refinement at 1100°C. *Z. Kristallogr.*, **134**, 262-274.
- (1973) Experimental study on the polymorphism of enstatite. *Am. Mineral.*, **59**, 345-352.
- Thompson, J. B. (1970) Geometrical possibilities for amphibole structures: model biopyriboles. *Am. Mineral.*, **55**, 292-293.

Manuscript received, April 18, 1977; accepted for publication, July 11, 1977.