

The Crystal Structures of Forsterite and Hortonolite at Several Temperatures Up to 900°C

JOSEPH R. SMYTH,¹ AND ROBERT M. HAZEN

Department of Geological Sciences, Harvard University,
Cambridge, Massachusetts 02138

Abstract

The crystal structures of a pure synthetic forsterite and a natural metamorphic manganoan hortonolite have been refined from three-dimensional intensity data obtained at 20°, 300°, 600°, and 900°C. Both structures show a zero or slightly negative expansion of silicon-oxygen distances compared with large positive expansions of the octahedral cation-oxygen distances with increasing temperature. The hortonolite refinements indicate a slight preference of Fe, possibly as Fe²⁺, for the smaller *M1* site. This preference appears to increase with increasing temperature.

Introduction

The olivines are minerals of vast geologic and geophysical importance. A detailed knowledge of the crystal structure at elevated temperatures has several potential applications to mineralogic as well as geophysical research. From accurate crystal structure data, one should be able to calculate crystal field splitting energies which would lead to a better understanding of the optical absorption spectra of olivines at high temperatures. Mineralogically, the question of Mg, Fe ordering over non-equivalent *M1* and *M2* sites in olivine has received much attention in recent research. Of recent crystallographic studies, Finger (1971) reports a slight preference of Fe for the smaller *M1* site in a lunar olivine from rock 10020 and a volcanic olivine from Australia, both of which have rapid cooling histories. Wenk and Raymond (1971) report a preference of Fe for *M1* in a lunar olivine but a reverse preference of Fe for *M2* in metamorphic forsterites. Birle *et al* (1968) report no detectible ordering in two igneous olivines, but the occupancies of the octahedral sites were not refined directly.

For the current study, two specimens were selected, a pure synthetic forsterite and a natural hortonolite ($\text{Mg}_{0.75}\text{Fe}_{1.10}\text{Mn}^{2+}_{0.15}\text{SiO}_4$) from a sillimanite-grade metamorphic environment. The first specimen was chosen to show the effects of temperature on a pure end-member. The second was selected

to show the effects of a transition metal as a function of temperature and also to determine if any ordering of Fe and Mg over the *M1* and *M2* sites truly occurs in the forsterite-fayalite system. This specimen is an intermediate olivine from a very slowly-cooled environment and was selected as the most likely specimen to show ordering, if such exists.

This study was begun in midsummer, 1972, and the results presented here are preliminary to further study and refinement. Because of their potential use to other investigators, we have decided to present our available data for inclusion with other papers on high temperature crystallography.

Experimental Procedures

A fragment of colorless, transparent synthetic forsterite about (2mm)³ in size was obtained from Dr. Al Duba. The material was grown from a melt by Crystal Products Division, Union Carbide Corporation, and is the same as that used by Kumazawa and Anderson (1969) for study of elastic properties. The latter authors give the composition as that of a pure forsterite plus 0.16 wt percent MnO (see Table 1), and refractive indices as: $\alpha = 1.6368 \pm 0.0004$, $\beta = 1.6517 \pm 0.0001$, $\gamma = 1.6694 \pm 0.0002$.

A small chip of approximate dimensions 450 × 300 × 250 μm was selected for study. The crystal showed {010} and {100} and its long axis was approximately parallel to *a*. The crystal was mounted in air directly on the join of a Pt-Pt 10 percent Rh thermocouple (wire diameter 44 μm) by natural adhesion to hot platinum. Using Nb-filtered Mo radi-

¹ Present address: The Lunar Science Institute, 3303 Nasa Road 1, Houston, Texas 77058.

TABLE 1. Formulae and Chemical Analyses in Wt Percent

| MgO | FeO | MnO | SiO ₂ | Other | Total |
|--|-------|------|------------------|--------|--------|
| Synthetic Forsterite*, Mg ₂ SiO ₄ | | | | | |
| 56.82 | -- | 0.16 | 43.02 | < 0.01 | 100.00 |
| Hortonolite**, Mg _{0.75} Fe _{1.10} Mn _{0.15} SiO ₄ | | | | | |
| 16.66 | 44.15 | 5.70 | 33.28 | -- | 99.79 |

* Synthetic forsterite, J. V. Smith, microprobe analysis as given by Kumazawa and Anderson (1969).

** Wet chemical analysis by L. H. Bauer of hortonolite from Franklin, N. J. as given by Frondel (1965).

ation on a Picker FACS-1 automated diffractometer, 1096 non-equivalent X-ray intensities were measured representing all symmetry-independent reflections of 2θ less than 80° . The crystal was then heated to $300^\circ \pm 20^\circ\text{C}$ using a heater described by Smyth (1972) and allowed to equilibrate for 24 hours. Increasing the 2θ scan speed from 1.0 to 2.0 degrees per minute, 663 non-equivalent intensities were measured within the succeeding 26 hours, representing all symmetry-independent intensities of 2θ less than 65° . Similar equilibration and data collection procedures were then employed at 600° and 900° . Details of intensity measurement procedures are presented in Table 2.

Specimens of a manganoan hortonolite from Franklin, New Jersey, were kindly provided by Professor Clifford Frondel of Harvard University. This olivine was described by Frondel (1965) as occurring with calcite, magnetite, and minor pyrrhotite in a

skarn zone associated with the Franklin Marble. The mineral is greenish black in color, with a strong vitreous to resinous luster. Cleavage is poorly developed, and cleavage fragments have a slight tendency to elongate along the c axis. The composition was determined by L. H. Bauer as Mg_{0.75}Fe_{1.10}Mn_{0.15}SiO₄ (see Table 1) and indices of refraction are given as $\alpha = 1.741$, $\beta = 1.772$ and $\gamma = 1.788$ (Frondel, 1965).

A fragment of hortonolite about $300 \times 300 \times 200 \mu\text{m}$ in size was mounted in an evacuated silica glass capillary as described by Smyth (1972). X-ray intensity measurement procedures were otherwise identical to those used with forsterite and the details are outlined in Table 2. During the 900° measurements, the capillary ruptured, the crystal having apparently reacted with the silica glass, and the crystal completely oxidized. The breakdown of the crystal occurred after some 180 intensities had been measured, as was evident by changes in the standard reflections monitored approximately once per hour.

Refinements

All sets of integrated intensities were corrected for Lorentz and polarization effects. Each intensity measurement was also corrected for absorption differences using numerical integration techniques (Burnham, 1966). All refinements of the structure models were done with a version of the full-matrix least-squares refinement program RFINE (Finger, 1969) modified for handling disk files on IBM 360 and 370 computers. All observations were weighted according to $\omega = 1/\sigma_F^2$ where σ_F is the standard deviation based

TABLE 2. Intensity Measurement and Refinement

| Crystal | Forsterite | | | | Hortonolite | | | |
|---------------------------------------|------------|-------|-------|-------|-------------|-------|-------|-------|
| | 20° | 300° | 600° | 900° | 20° | 300° | 600° | 900° |
| Intensity measurement | | | | | | | | |
| Radiation | Mo | Mo | Mo | Mo | Mo | Mo | Mo | Mo |
| Filter | Nb | Nb | Nb | Nb | Nb | Nb | Nb | Nb |
| Take-off angle | 3.2 | 3.2 | 3.2 | 3.2 | 3.2 | 3.2 | 3.2 | 3.2 |
| Ku/Ma | 36/16 | 36/16 | 36/16 | 36/16 | 38/18 | 38/18 | 38/18 | 38/18 |
| 2θ scan speed | 1.0 | 2.0 | 2.0 | 2.0 | 1.0 | 2.0 | 2.0 | 2.0 |
| 2θ max | 80 | 65 | 65 | 65 | 80 | 65 | 65 | 65 |
| Number measurements | 1096 | 663 | 676 | 686 | 1111 | 677 | 681 | 174 |
| Number observations ($I > 2\sigma$) | 956 | 569 | 564 | 565 | 903 | 527 | 516 | 100 |
| Refinement | | | | | | | | |
| No. of cycles isotropic | 3 | 2 | 2 | 2 | 4 | 3 | 3 | 3 |
| No. of cycles anisotropic | 6 | 2 | 2 | 2 | 4 | 4 | 4 | 8 |
| No. of refl. rejected ¹ | 24 | 7 | 6 | 8 | 15 | 11 | 9 | - |
| Final R | | .048 | .054 | .057 | .031 | .033 | 0.030 | .042 |

¹Due to secondary extinction (see text)

on counting statistics as described by Burnham *et al* (1971). All observations below the minimum observable level (2σ) were rejected from the normal equations matrix during refinement of the model. Atomic scattering factors used are those given by Cromer and Mann (1968) for O^{2-} , Si^{4+} , Mg^{2+} , and Fe^{2+} , as derived from Hartree-Fock wave functions neglecting relativistic effects. In addition, both real and imaginary anomalous dispersion terms (*International Tables for X-ray Crystallography*, Vol. 3, p. 215) were included in the final two cycles of refinement of hortonolite at each temperature. Anomalous dispersion terms in forsterite are insignificant. Throughout all refinements, the chemistry was constrained to that given in Table 1.

The initial structure model used for the room temperature refinement of forsterite was that given by Birle *et al* (1968) for forsterite. The atomic coordinates and equivalent isotropic temperature factors obtained from the final cycle of refinement at room temperature were then used as the initial model for refinement of the structure at 300°C. The structure at each successive temperature was then refined from the previous structure in a similar manner. The atomic coordinates and isotropic temperature factors obtained from the final cycle of refinement of forsterite at room temperature were used as the initial model for the refinement of hortonolite at room temperature. The scattering curve for Fe^{2+} was used for the Fe + Mn component of the M1 and M2 sites and the total Fe plus Mn was split equally between M1 and M2. The high temperature structures of hortonolite were then refined in a manner

TABLE 3. Unit Cell Dimensions and Percent Thermal Expansion

| | a | b | c | v |
|--|-------|--------|-------|--------|
| Room temperature, unit cell (\AA or \AA^3) | | | | |
| Forsterite | 4.756 | 10.207 | 5.980 | 209.30 |
| Hortonolite | 4.798 | 10.387 | 6.055 | 301.80 |
| Percent thermal expansion* | | | | |
| Forsterite, 300° | 0.14 | 0.32 | 0.32 | 0.79 |
| 600° | 0.46 | 0.81 | 0.62 | 2.07 |
| 900° | 0.81 | 1.45 | 1.33 | 3.63 |
| Hortonolite, 300° | 0.22 | 0.31 | 0.41 | 0.95 |
| 600° | 0.51 | 0.66 | 0.76 | 1.95 |
| 900° | 0.83 | 1.01 | 1.33 | 3.05 |

* Determined from single crystal alignment data on a Picker Automated Diffractometer. Errors in unit cell dimensions estimated at one part per thousand.

similar to that of the forsterite refinements. In both structures, secondary extinction was found to affect the strongest intensities. Because our absorption correction program does not currently have a provision for calculating an extinction parameter for each reflection, the reflections most strongly affected were rejected from the normal equations matrix during refinement. Details of the refinement procedures including the number of intensities rejected because of extinction are outlined in Table 2. Fractional atomic coordinates and equivalent isotropic temperature factors for forsterite at each temperature are presented in Table 4. Occupancies, fractional coordinates and isotropic temperature factors for hortonolite are presented in Table 5. Because of the small amount of data for hortonolite at 900°C the errors are much larger than for the other refinements.

Thermal Expansion of Olivines

Olivine possesses orthorhombic symmetry, and thermal expansion may thus be completely charac-

TABLE 4. Atomic Fractional Coordinates and Isotropic Temperature Factors for Forsterite

| Atom | x | y | z | B |
|------------------|------------|-----------|-----------|----------|
| Room Temperature | | | | |
| M1 | 0 | 0 | 0 | 0.26(1) |
| M2 | 0.9915(2)* | 0.2774(1) | 1/4 | .22(1) |
| Si | .4262(1) | .0940(1) | 1/4 | .08(1) |
| O1 | .7657(3) | .0913(2) | 1/4 | .27(2) |
| O2 | .2215(4) | .4474(2) | 1/4 | .24(2) |
| O3 | .2777(2) | .1628(1) | 0.0331(2) | .27(2) |
| At 300°C | | | | |
| M1 | 0 | 0 | 0 | 0.60(4) |
| M2 | 0.9915(5) | 0.2780(2) | 1/4 | .57(4) |
| Si | .4257(4) | .0939(2) | 1/4 | .25(3) |
| O1 | .7657(10) | .0910(5) | 1/4 | .63(7) |
| O2 | .2177(10) | .4492(5) | 1/4 | .52(7) |
| O3 | .2806(7) | .1619(3) | 0.0347(6) | .59(5) |
| At 600°C | | | | |
| M1 | 0 | 0 | 0 | 1.17(5) |
| M2 | 0.9919(5) | 0.2785(2) | 1/4 | 1.14(5) |
| Si | .4257(3) | .0941(2) | 1/4 | 0.61(4) |
| O1 | .7637(9) | .0906(4) | 1/4 | 1.10(9) |
| O2 | .2178(9) | .4497(4) | 1/4 | 0.95(8) |
| O3 | .2822(6) | .1619(3) | 0.0352(5) | 1.10(6) |
| At 900°C | | | | |
| M1 | 0 | 0 | 0 | 1.77(7) |
| M2 | 0.9924(4) | 0.2795(2) | 1/4 | 1.69(6) |
| Si | .4263(3) | .0943(1) | 1/4 | 0.96(5) |
| O1 | .7631(8) | .0914(4) | 1/4 | 1.59(12) |
| O2 | .2178(8) | .4497(4) | 1/4 | 1.40(11) |
| O3 | .2843(5) | .1629(3) | 0.0359(5) | 1.72(8) |

* Parenthesized figures represent the estimated standard deviation (esd) in terms of least units cited for the value to their immediate left, thus 0.9915(2) indicates an esd of 0.0002.

terized by percent increases in the three mutually perpendicular cell edge lengths. Unit cell parameters are routinely measured in the orientation of single crystals prior to data collection on the automated diffractometer. Cell constants for forsterite and hortonolite were thus determined at 25, 300, 600 and 900°C. From these values were calculated percent thermal expansion from 25°C of *a*, *b*, *c* and volume for these two olivines (see Table 3). Data for forsterite and thermal expansion are in close agreement with the accepted values of Kozu *et al* (1934) and Skinner (1962). Similarly, thermal expansions of the manganoan hortonolite, while systematically greater, do not differ appreciably from previous determinations of intermediate iron-magnesium olivines

by Rigby *et al* (1945, 1946) as recorded in Clark (1966). Independent study of the manganese olivine, tephroite (Mn_2SiO_4) by one of us (RMH) yielded thermal expansions comparable to those of forsterite. Thus, it is assumed that the small Mn content of the olivine studied does not appreciably affect the temperature derivatives of unit cell lengths and volume.

Conclusions

Although these data are of a preliminary nature only, several important conclusions can be drawn. As can be seen from Table 6, the silicon-oxygen interatomic distances show practically no change with increasing temperature while the oxygen bonds to

TABLE 5. Atomic Fractional Coordinates, Isotropic Temperature Factors, and M1 and M2 Occupancies for Hortonolite

| Atom | x | y | z | B | Occupancy Fraction* | |
|-------------------------|-------------|-----------|------------|----------|---------------------|-------|
| | | | | | (Fe + Mn) | (Mg) |
| <u>Room Temperature</u> | | | | | | |
| M1 | 0 | 0 | 0 | 0.44(2) | 0.639(2) | 0.361 |
| M2 | 0.9867(1)** | 0.2792(1) | 1/4 | .33(2) | .611 | .389 |
| Si | .4287(2) | .0957(1) | 1/4 | .33(1) | | |
| O1 | .7661(5) | .0918(2) | 1/4 | .49(2) | | |
| O2 | .2127(6) | .4514(2) | 1/4 | .50(2) | | |
| O3 | .2844(4) | .1633(2) | 0.0357(3) | .55(3) | | |
| <u>At 300°C</u> | | | | | | |
| M1 | 0 | 0 | 0 | 1.02(3) | 0.641(3) | 0.359 |
| M2 | 0.9876(2) | 0.2797(1) | 1/4 | 0.81(4) | .609 | .391 |
| Si | .4284(3) | .0957(1) | 1/4 | .69(3) | | |
| O1 | .7649(8) | .0921(4) | 1/4 | .98(3) | | |
| O2 | .2135(9) | .4524(4) | 1/4 | .91(3) | | |
| O3 | .2847(6) | .1631(2) | 0.0375(5) | 1.04(4) | | |
| <u>At 600°C</u> | | | | | | |
| M1 | 0 | 0 | 0 | 1.52(3) | 0.661(3) | 0.339 |
| M2 | 0.9878(2) | 0.2802(1) | 1/4 | 1.23(3) | .589 | .411 |
| Si | .4289(3) | .0958(1) | 1/4 | 0.96(3) | | |
| O1 | .7632(7) | .0926(3) | 1/4 | 1.29(4) | | |
| O2 | .2123(7) | .4514(3) | 1/4 | 1.37(3) | | |
| O3 | .2853(5) | .1631(2) | 0.0370(4) | 1.48(4) | | |
| <u>At 900°C</u> | | | | | | |
| M1 | 0 | 0 | 0 | 2.37(7) | 0.662(4) | 0.338 |
| M2 | 0.994(8) | 0.2799(2) | 1/4 | 1.69(7) | .588 | .412 |
| Si | .445(15) | .0959(5) | 1/4 | 1.06(9) | | |
| O1 | .814(62) | .0882(14) | 1/4 | 2.64(6) | | |
| O2 | .210(12) | .4503(9) | 1/4 | 0.89(14) | | |
| O3 | .280(10) | .1615(6) | 0.0447(12) | 1.84(14) | | |

* Occupancies calculated assuming 100% M1 and M2 occupancy, and $\Sigma(\text{Fe} + \text{Mn}) = 1.25$ per 4 oxygens.

** Parenthesized figures represent the esd in terms of least units cited for the value to their immediate left, thus 0.9867(1) indicates an esd of 0.0001.

TABLE 6. Metal-to-Oxygen Interatomic Distances*

| Atoms | 25°C | 300°C | 600°C | 900°C |
|--------------------|-------|-------|-------|-------|
| <u>Forsterite</u> | | | | |
| (2) M1-01 | 2.085 | 2.091 | 2.101 | 2.116 |
| (2) -02 | 2.069 | 2.080 | 2.087 | 2.097 |
| (2) -03 | 2.132 | 2.140 | 2.153 | 2.180 |
| Mean M1-0 | 2.095 | 2.104 | 2.113 | 2.131 |
| (1) M2-01 | 2.183 | 2.199 | 2.220 | 2.237 |
| (1) -02 | 2.051 | 2.057 | 2.066 | 2.068 |
| (2) -03 | 2.216 | 2.231 | 2.245 | 2.258 |
| (2) -03 | 2.067 | 2.073 | 2.082 | 2.086 |
| Mean M2-0 | 2.133 | 2.144 | 2.156 | 2.165 |
| (1) Si-01 | 1.615 | 1.614 | 1.615 | 1.615 |
| (1) -02 | 1.654 | 1.636 | 1.636 | 1.649 |
| (2) -03 | 1.635 | 1.624 | 1.623 | 1.628 |
| Mean Si-0 | 1.635 | 1.625 | 1.624 | 1.630 |
| <u>Hortonolite</u> | | | | |
| (2) M1-01 | 2.112 | 2.124 | 2.138 | 2.211 |
| (2) -02 | 2.106 | 2.111 | 2.120 | 2.161 |
| (2) -03 | 2.188 | 2.194 | 2.203 | 2.205 |
| Mean M1-0 | 2.135 | 2.143 | 2.154 | 2.192 |
| (1) M2-01 | 2.216 | 2.229 | 2.241 | 2.437 |
| (1) -02 | 2.094 | 2.102 | 2.104 | 2.050 |
| (2) -03 | 2.275 | 2.277 | 2.291 | 2.240 |
| (2) -03 | 2.071 | 2.089 | 2.091 | 2.165 |
| Mean M2-0 | 2.167 | 2.177 | 2.184 | 2.216 |
| (1) Si-01 | 1.619 | 1.619 | 1.612 | 1.599 |
| (1) -02 | 1.646 | 1.642 | 1.644 | 1.693 |
| (2) -03 | 1.630 | 1.625 | 1.632 | 1.631 |
| Mean Si-0 | 1.629 | 1.626 | 1.633 | 1.631 |

* Values represent bond distances uncorrected for thermal motion. Standard errors were not calculated but are estimated at one part per thousand except for hortonolite at 900° where standard error is approximately 1 part per hundred.

divalent metal cations show large increases with increasing temperature. This is in good agreement with work done on orthopyroxene by Smyth (1973) and other work done on silicates at high temperatures (Smyth, 1971; Smyth and Burnham, 1972; Brown *et al.*, 1972; Papike *et al.*, 1972; Cameron *et al.*, 1972; Sueno *et al.*, 1972).

If one believes the standard errors calculated for the Fe occupancies of M1 and M2 by RFIN in Table 5, there is a significant preference of Fe and/or Mn for M1, the smaller of the two octahedral sites. At 600°C, it appears that there is an even greater preference of Fe (and/or Mn) for M1. An increase of order with increasing temperature and a preference of Fe for the smaller of two octahedral sites are both contrary to what would be expected by analogy with orthopyroxene. The most likely explanation for this unexpected behavior is that the preference for M1 is by Fe³⁺ rather than Fe²⁺. Duba (1972) reports wet chemical analyses of olivines containing up to

0.5 wt percent Fe₂O₃. The increase in order with temperature would then be due to a slight oxidation from the residual oxygen in the capillary when sealed. The M1 octahedra form edge-sharing chains parallel to *c*, while the M2 sites are attached alternately to either side of the chain in the (100) plane. A strong preference of Fe³⁺ for M1 is likely to affect the conductivity more strongly than a preference for M2 and may help explain the strong dependence of electrical conductivity of olivine on fugacity of oxygen (Duba and Nicholls, 1973) and the fact that conductivity is highest in the *c*-direction (Duba, 1972).

These data presented here are preliminary only, and further work is in progress. Anisotropic temperature factors, complete bond angles and thermal corrections to bonds are available from the authors on request.

Acknowledgment

This work was supported by NSF grant GA-12852 through Professor C. W. Burnham of Harvard University. Typing and preparation of the manuscript were supported by the Lunar Science Institute.

References

- BIRLE, J. D., G. V. GIBBS, P. B. MOORE, AND J. V. SMITH (1968) Crystal structures of natural olivines. *Amer. Mineral.* **53**, 807-824.
- BROWN, G. E., C. T. PREWITT, J. J. PAPIKE, AND S. SUENO (1972) A comparison of the structures of high and low pigeonite. *J. Geophys. Res.* **77**, 5778-5789.
- BURNHAM, C. W. (1966) Computation of absorption correction and the significance of end effect. *Amer. Mineral.* **51**, 159-167.
- , Y. OHASHI, S. S. HAFNER, AND D. VIRGO (1971) Cation distribution and atomic thermal vibrations in an iron-rich orthopyroxene. *Amer. Mineral.* **56**, 850-876.
- CAMERON, M., S. SUENO, AND J. J. PAPIKE (1972) High temperature crystal chemistry of acmite, hedenbergite and spodumene. (abstr.) *Geol. Soc. Amer. Abstr. Programs*, **4**, 466.
- CLARK, S. P. (1966) Handbook of Physical Constants. *Geol. Soc. Amer. Mem.* **97**, New York, N. Y.
- CROMER, D. T., AND J. B. MANN (1968) X-ray scattering factors computed from numerical Hartree-Fock wave functions. *Acta Crystallogr.* **24**, 321-324.
- DUBA, AL (1972) Electrical conductivity of olivine. *J. Geophys. Res.* **77**, 2483-2495.
- , AND I. A. NICHOLLS (1973) The influence of oxidation states on the electrical conductivity of olivine. *Earth Planet. Sci. Lett.* (in press).
- FINGER, L. W. (1969) Determination of cation distribution by least-squares refinement of single-crystal X-ray data. *Carnegie Inst. Washington Year Book*, **67**, 216-217.
- (1971) Ordering of cations in olivine. (abstr.) *Amer. Mineral.* **56**, 353-354.

- FRONDEL, C. (1965) Johannsenite and manganoan hortonolite from Franklin, New Jersey. *Amer. Mineral.* **50**, 780-782.
- KOZU, S., J. UEDA, AND S. TSURUMI (1934) Thermal expansion of olivine. *Proc. Imp. Acad. Japan*, **10**, 83-86.
- KUMAZAWA, M., AND O. L. ANDERSON (1969) Elastic moduli, pressure derivatives, and temperature derivatives of single-crystal olivine and single-crystal forsterite. *J. Geophys. Res.* **74**, 5961-5972.
- PAPIKE, J. J., C. T. PREWITT, S. SUENO, AND M. CAMERON (1972) Pyroxenes: comparison of chemical and thermal structural expansion (abstr.) *EOS*, **53**, 1134.
- RIGBY, G. R., G. B. H. LOVELL, AND A. T. GREEN (1945) The reversible thermal expansion and other properties of some calcium ferrous silicates. *Trans. British Ceram. Soc.* **44**, 37-52.
- , ———, AND ——— (1946) The reversible thermal expansion and other properties of some magnesian ferrous silicates. *Trans. British Ceram. Soc.* **45**, 237-250.
- SKINNER, B. J. (1962) Thermal expansion of ten minerals. *U. S. Geol. Surv. Prof. Pap.* **450D**, 109-112.
- SMYTH, J. R. (1971) Protoenstatite: a crystal structure refinement at 1100°C. *Z. Kristallogr.* **134**, 262-272.
- (1972) A simple heating stage for single-crystal diffraction studies up to 1000°C. *Amer. Mineral.* **57**, 1305-1309.
- (1973) An orthopyroxene structure up to 850°C. *Amer. Mineral.* **58**, 636-648.
- , AND C. W. BURNHAM (1972) The crystal structures of high and low clinohypersthene. *Earth Planet. Sci. Lett.* **14**, 183-189.
- SUENO, S., J. J. PAPIKE, C. T. PREWITT, AND G. E. BROWN (1972) The crystal structure of high cummingtonite. *J. Geophys. Res.* **77**, 5767-5777.
- WENK, H. R., AND K. N. RAYMOND (1971) Crystal structure refinements of four magnesium-rich olivines. (abstr.) *Geol. Soc. Amer. Abstr. Programs*, **3**, 748-749.

Manuscript received, October 30, 1972;
accepted for publication, December 18, 1972.