Stability of orthoenstatite at high temperature and low pressure

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ABSTRACT

Experimental evidence for the stability of synthetic Ca-bearing orthoenstatite near 1400 °C at atmospheric pressure in the system MgSiO₃-CaMgSiO₃ is difficult to reconcile with other experimental results, given present thermodynamic models for pyroxenes on that join. The hypothesis that the phase stable under these conditions is not ordinary orthoenstatite, but is instead a structurally and mineralogically distinct phase, has been tested by optical, SEM, and TEM studies of crystals synthesized at 1370 °C and 1 atm, combined with a single-crystal X-ray structure refinement at 25 °C and with X-ray powder diffractometry at 25 °C and 1425-1440 °C. The results indicate that (1) the structure assumed by the quenched phase at room temperature is that of ordinary orthoenstatite and (2) the structure above 1400 °C is at least very similar to, and probably identical to, that of ordinary orthoenstatite and does not match the derivative structures seen at that temperature for analogous compositions of MgSiO₃-LiScSiO₃ pyroxenes.

INTRODUCTION

The first reports of the appearance of an orthopyroxene-like Ca-bearing phase stable on the join MgSiO₃-CaMgSiO₃ near 1400 °C at 1 bar (Schwab and Jablonski, 1973; Foster and Lin, 1975) were confirmed by the careful determination of its liquidus field in the system MgSiO₃-CaMgSiO₃-SiO₂ by Longhi and Boudreau (1980). Although ensuing investigations have repeatedly confirmed the existence of this phase at low pressures and high temperatures (e.g., Jenner and Green, 1983; Biggar, 1985; Carlson, 1988), the identification of this material as orthoenstatite appears to contradict other experimental evidence and thermodynamic analysis. The principal difficulty lies in reconciling the breakdown near 1000 °C and 1 atm of orthoenstatite to protoenstatite + diopside, with the possible regeneration of orthoenstatite near 1400 °C and 1 atm by reaction of protoenstatite + pigeonite (Fig. 1). Schreinemakers' analysis of phase relations near the invariant point at which all four pyroxenes are stable (cf. Jenner and Green, 1983, p. 154; Biggar, 1985, p. 57–58; Carlson, 1985, p. 409–410; Carlson, 1988, Fig. 1) demonstrates that it is not possible for both of the above reactions to occur stably on the 1-atm isobar unless their reaction boundaries in P-T projection are strongly curved, which is unexpected for solid-solid reactions among these closely related pyroxene structures.

Jenner and Green (1983) attempted to resolve these contradictions by postulating 1-atm phase relations in which the assemblage protoenstatite + diopside was presumed to be nowhere stable; Biggar (1985) attempted the same by postulating 1-atm phase relations in which the assemblage orthoenstatite + diopside was presumed to be nowhere stable. Subsequently, however, experiments by Carlson (1985, 1986b, 1988) indicated that both assemblages are stable on the 1-atm isobar (Fig. 1). This result has forced a search for alternative explanations. The three most evident, considered in turn below, are (1) errors in the experimental determinations of phase equilibria; (2) thermochemical properties for low-Ca pyroxenes inconsistent with present thermodynamic models; and (3) the hypothesis that the phase stable near 1400 °C is a previously unrecognized pyroxene polymorph, structurally and mineralogically distinct from ordinary orthoenstatite. This article emphasizes data bearing upon the third of these possibilities. The designation "orthopyroxene" (Opx) is used here to refer to the phase stable near 1400 °C on the 1-atm isobar, whereas "orthoenstatite" (Oen) is reserved for reference to the familiar orthorhombic pyroxene, known to coexist with diopside at low temperatures on the 1-atm isobar and over large ranges of temperature at elevated pressures.

Phase equilibria

It is unlikely that the 1-atm phase equilibria are in serious error. Apparently conflicting evidence arises from three particular features of the phase-equilibrium exper-
Fig. 1. Phase equilibria on the join Mg$_2$Si$_2$O$_6$-CaMgSi$_2$O$_6$ showing split stability field for phase(s) Oen and Opx. From Carlson (1988); supersolidus equilibria after Longhi and Boudreau (1980).

ments, but none is especially suspect. (1) The stable existence of Opx near 1400 °C seems incontrovertible, given the excellent agreement among several recent studies on the extent of stability of the phase (cf. Fig. 6 of Carlson, 1988). (2) Equilibrium at 1295 ± 10 °C among protoenstatite, pigeonite, and diopside is confirmed by the reversed experimental data of Carlson (1988), which correspond closely to synthesis data at higher temperatures from several sources (cf. Biggar, 1985). (3) Likewise, equilibrium at 1005 ± 10 °C among protoenstatite, orthoenstatite, and diopside is confirmed by the reversed experimental data of Carlson (1988), which have been replicated, with identical results, using plumbate solvents (Carlson, 1988). These experiments corroborate the earlier synthesis results of Atlas (1952) and Boyd and Schairer (1964). Thus, although the rejection of any one of these three features would eliminate the apparent contradictions, all seem to be firmly based in experiment.

Thermodynamic analysis

It is possible that the thermodynamic properties of low-Ca pyroxenes in Mg$_2$Si$_2$O$_6$-CaMgSi$_2$O$_6$ are sufficiently unusual, and consequently poorly enough understood, to account for the split stability field for Oen shown in Figure 1. So far, however, no thermodynamic model for phase relations in this system has been able to reconcile that feature of the equilibria to the wealth of other experimental data in this system. The thermochemistry of pyroxenes in this system is extremely well constrained by reversed experimental data over the range 850-1600 °C and 1 atm-60 kbar and has been repeatedly modeled, with increasingly sophisticated thermodynamic formulations (e.g., Lindsley et al., 1981; Nickel and Brey, 1984; Carlson and Lindsley, 1988). Although the most recent of these models is capable of quantitatively reproducing all other features of the experimental phase equilibria, it does not generate an appropriate stability field at high temperature for Oen at 1-atm pressure. As detailed in Carlson and Lindsley (1988, p. 248) and as illustrated in Figure 2 by the location of the equilibrium “Oen = Pen + Pig,” the assemblage protoenstatite + pigeonite is computed to be stable instead of orthoenstatite in the appropriate range of temperature and composition. There is no certainty that the thermodynamic formulation employed in these models is sufficiently complex to account for unusual thermodynamic properties of the low-Ca pyroxenes. Nevertheless, the fact remains that no modeling attempt so far has succeeded in accommodating the split stability field for Oen while simultaneously fitting the large amount of other data in this system.

Hypothesis of a distinct polymorph

The incompatibility between the experimental findings and present thermodynamic models focuses attention on a third possible explanation for the observations: perhaps the phase stable near 1400 °C is not ordinary orthoenstatite at all, but is instead a distinct entity. Such a hypothesis, if true, would reconcile the otherwise incompatible observations (cf. Carlson, 1985, p. 410-411). Although Longhi and Boudreau (1980) considered this possibility, they rejected it on the basis of the similarity of room-temperature X-ray powder-diffraction patterns of Oen and Opx.

The hypothesis is rendered somewhat more attractive, however, by the recognition of unusual derivative pyroxene structures in the analogous system Mg$_2$Si$_2$O$_6$-LiScSi$_2$O$_6$. At temperatures below about 1400 °C, the Mg$_2$Si$_2$O$_6$-LiScSi$_2$O$_6$ join comprises a sequence of phases isosstructural with protoenstatite, orthoenstatite, pigeonite, and diopside (cf. Fig. 1 of Takéuchi et al., 1984), but with the structural variations extended over a wider range of compositions. Intriguingly, however, at temperatures near 1400 °C, a series of derivative structures appears for compositions near the magnesian end member (Takéuchi, 1978; Takéuchi et al., 1977, 1984). The derivative structures are characterized by planar slabs of material with C2/c clinopyroxene structure, varying with composition from 44.7 to 55.4 Å wide; these slabs are connected by narrow (~3-Å-wide) planar sheets of cross-linking octahedral sites (all vacant) and tetrahedra (30% vacant).
Successive slabs are reoriented relative to one another by glide operations. Variation in the width of the slabs allows these structures to maintain exact pyroxene stoichiometry over a range of compositions.

The resulting derivative structure has two features that would make it, or some closely related structure, appealing as an alternative for magnesian compositions in Mg$_2$Si$_2$O$_6$-CaMgSi$_2$O$_6$. First, the high vacancy content would account for the restriction of the derivative structure to high temperature and low pressure. Second, an ordinary clinopyroxene (CPX) structure can be transformed into the derivative structure “by a mechanism of cooperative atomic movements in the CPX structure which in effect leads to the polysynthetic twinning of the CPX structure” (Tak6uchi, 1978, p. 176), in much the same way that protoenstatite can be transformed by minimal atomic repositioning into repetitively twinned clinoenstatite. This close relationship between alternative atomic positions might make the derivative structures (or, more likely, similar structures based on slabs of Pbcn orthopyroxene) good candidates for either producing orthoenstatite-like X-ray patterns directly, or for inversion to orthoenstatite on cooling via an unquenchable phase transition.

Consequently, in order to test the hypothesis that the high-temperature Opx phase is distinct from Oen, and perhaps related to the derivative structures in Mg$_2$Si$_2$O$_6$-LiScSi$_2$O$_6$, we have attempted to characterize it by optical, X-ray, SEM, and TEM methods.

**CHARACTERIZATION OF THE HIGH-TEMPERATURE PHASE**

**Synthesis and chemical analysis**

To synthesize crystals of sufficient size and suitable quality, the high-temperature solvent technique of Carlson (1986a) was employed. A sealed Pt capsule, containing equal weights of reactant glass and solvent with the compositions specified in Table 1, was maintained at 1370 ± 5 °C in a vertical quench furnace for 24 h and then dropped into water. A small chip of the charge was removed for analysis by electron microprobe, and the remainder was leached of quenched solvent-rich melt by immersion for 10–15 min in 4% HCl. Optical examination, X-ray powder diffraction, and microprobe analysis demonstrated that the crystalline run products consisted of 10 to 30-μm forsterite euhedra, 100 to 300-μm prisms of protoenstatite inverted to clinoenstatite (0.92 wt% CaO), 20 to 40-μm subhedral crystals of pigeonite (3.11 wt% CaO), and 50 to 300-μm euhedra of Opx. Both Opx and (to a lesser extent) protoenstatite commonly encompass tiny rounded inclusions of forsterite; other inclusions are rare.

Electron-microprobe analysis was performed by wavelength-dispersive techniques on a Jeol Superprobe 733, using an accelerating voltage of 15 kV, a sample current of 15 nA on brass, and counting intervals of 60 s on both peaks and backgrounds. Standards were NBS standard reference material #470 (glass K412) for Mg, Si, and Ca, and synthetic crystalline V$_2$O$_5$ for V; data reduction employed the empirical correction scheme of Albee and Ray (1970). The average of analyses at 25 randomly distributed points on seven grains of orthopyroxene in the run appears in the rightmost column of Table 1. That analysis is consistent with the range of compositions reported for this phase in other studies, as summarized in Biggar (1985).

**Optical measurements**

Crystals of Opx are distinguished from other phases in the run by their large size, gem clarity, and very pale blue color. It was therefore possible to extract crystals for optical, X-ray, SEM, and TEM analysis by hand-picking with forceps.

Fig. 2. P-T projections of calculated univariant reactions involving protoenstatite, orthoenstatite, pigeonite, and diopside (from Carlson and Lindsley, 1988), illustrating calculated stability of protoenstatite + pigeonite in place of orthoenstatite near 1400 °C and 1 bar. Bold lines depict ternary equilibria in CaO-MgO-SiO$_2$; lighter lines depict binary equilibria among the Ca-free end members. Equilibria are computed from a thermodynamic model constrained by experimental data indicated by rectangles and by additional data extending to 1600 °C and 60 kbar. Calculated supersolidus equilibria (metastable relative to silicate melts) at T > ~1400 °C and P < ~5 kbar are omitted.
mounts yielded several near-centered optic-axis figures, confirming the biaxial positive character of the phase and allowing estimation of the 2V as ~50°. These figures also display distinct optic-axis dispersion about the acute bisectrix of the sense r > v. The refractive indices α and γ were measured on uncrushed grains in immersion liquids using the dispersion-matching technique (Emmons and Gates, 1948). For wavelengths near Na, these indices are 1.654 and 1.661, respectively, with errors estimated at ±0.001; both indices show dispersion n_r - n_c of approximately 0.017. The refractive index β was determined to be 1.658 ± 0.001 using immersion liquids and a crystal mounted on a spindle stage. These indices are in good agreement with determinations of birefringence calculated from measured thicknesses and retardations observed on oriented crystal fragments. All of the above optical properties are indistinguishable from those measured on Oen, the familiar orthoenstatite phase.

X-ray powder diffractometry at 25 °C

Four samples were examined by X-ray powder diffractometry at room temperature in this study; all were synthesized at atmospheric pressure and at temperatures from 1295 to 1370 °C in experiments similar to the synthesis run described above. These Opx compositions were chosen for analysis, despite the fact that they are probably metastable (cf. Carlson, 1988, p. 240), because they extend the range of measured CaO contents upward to near 3 wt%. All four samples produced diffraction patterns that could be satisfactorily indexed on the orthoenstatite structure. Unit-cell dimensions were refined from these powder patterns by a least-squares technique modified from that of Appleman and Evans (1973).

Cell dimensions from this study are compared in Figure 3 to data from several other sources. Formerly, only one measurement of cell parameters for the high-temperature Opx phase was available (filled diamonds). It falls well off the trend of the low-temperature Oen data (open squares and open triangles) and therefore was regarded as possible evidence for a distinct polymorph (cf. Fig. 3 of Carlson, 1985). The new determinations of cell parameters for Opx in this study (filled circles) fall closely on the trend of the Oen data and indicate that the data represented by the filled diamonds are discrepant. If the diamonds are disregarded, all data fall along a single trend, whether for crystals synthesized in the high-temperature Opx field (filled symbols) or for those synthesized under P-T conditions at which Oen is stable (open symbols).

Fig. 3. Variations in unit-cell parameters at 25 °C with composition for Oen (shown by open symbols, synthesized at low temperatures and/or high pressures) and for Opx (shown by filled symbols, synthesized at high temperatures and 1-bar pressure). Shapes of symbols indicate sources of data: triangles from Hawthorne and Ito (1971); squares from Warner and Luth (1974); diamonds from Longhi and Boudreau (1980); and circles from this study.

Structure refinement at 25 °C on quenched crystal

To rule out the possibility that the quenched crystals possessed a derivative structure with differences from orthoenstatite too subtle to be revealed in powder-diffraction spectra, a single-crystal structure refinement at 25 °C was performed. The crystal selected for the refinement was gem-clear and subhedral, approximately 100 × 100 × 150 μm. Unfortunately, all of the large crystals contain inclusions of forsterite; the one chosen contained two rounded inclusions, each about 5 μm in diameter.

The crystal was mounted on a Syntax P2, automated diffractometer, and data were collected for 2θ ≤ 60°, 0 ≤ h ≤ 25, 0 ≤ k ≤ 12, −7 ≤ l ≤ 7, using MoKα radiation monochromatized with a graphite crystal, λ = 0.71069 Å. The diffractometer was operated in the ω-scan mode with scan rates varying from 4° to 8° min−1. Four standard reflections (133, 352, 931, and 10.31), collected after each 100 reflections, varied less than ±1% in intensity. Omega scans of several peaks were symmetric with peak widths at half-height of about 0.3°. A least-squares refinement of 30 reflections whose 2θ values were precisely determined in the range 25–30° yielded the lattice parameters a = 18.280(2) Å, b = 8.834(1) Å, c = 5.197(1) Å. Measured intensities were transformed in the usual manner to structure amplitudes; no absorption correction was made. Es-
The atomic positional and thermal parameters ($\times 10^4$) for 25°C refinement measured intensities were averaged to give 1223 unique counting statistics. Equivalent reflections from the 2398 reflections considered observed on the basis that $F > 5\sigma(F)$. The refinement converged to $R = 0.0303$ ($\sigma_R = 0.0319$). A phase distinct from ordinary orthoenstatite exists at high temperature, but that it undergoes an unquenchable phase transition to Oen when cooled to room temperature. Scanning and transmission electron microscopic (SEM and TEM) observations bear on this possibility.

SEM and TEM observations

The data reported above leave open the possibility that a phase distinct from ordinary orthoenstatite exists at high temperature, but that it undergoes an unquenchable phase transition to Oen when cooled to room temperature. Scanning and transmission electron microscopic (SEM and TEM) observations bear on this possibility.

1 A copy of Table 3 may be ordered as Document AM-88-390 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit $5.00 in advance for the microfiche.
tending well into the grain were present prior to sample preparation. However, in all samples examined in this study, regardless of the method of preparation, defects occur both at grain edges and in grain interiors. Thus it appears that at least some of the defects are not artifacts of the preparation procedure.

Buseck and Iijima (1975) presented evidence that similar defects in natural Bamble bronzite are intergrowths of orthoenstatite and clinoenstatite induced by twinning during deformation by shear. In the synthetic samples, we observe many regions terminating entirely within the crystals that do not possess the 18-Å repeat distance characteristic of orthopyroxene. Only one lattice fringe is affected, consistent with the hypothesis that these regions are twin variants of orthopyroxene resulting in a clinoenstatite structure. It is possible that these regions originate from shearing during anisotropic contraction of the orthoenstatite on cooling. An alternative explanation, however, is that the thin lamellae represent growth defects on a growing (100) face. Optically visible striations on many of the crystals lend some support to the latter explanation. If such defects result from the normal growth of pyroxenes at elevated temperature, then the presence of these features, and of the parting that they induce, cannot alone be used as evidence for deformation. The measurement of clinoenstatite field widths, as suggested by Buseck and Iijima (1975), should be useful to distinguish between these two possibilities.

These defects, while numerous, occupy negligible volume and are spaced aperiodically. Consequently, they do not produce coherent scattering of X-rays and thus do not contribute, except as background, to the X-ray intensities measured in the refinement described previously. It is therefore not surprising to have obtained low values for $R$ in the X-ray structure refinement, even though defects are almost certainly present in the material used in the single-crystal diffraction study.

In addition to the (100) defects, domains of opposite contrast separated by curvilinear boundaries were observed, as in the two-beam dark-field image ($g = 832$) shown in Figure 5. Irregular domain boundaries within a mineral of such striking anisotropy are characteristic of a texture induced on quench. Unfortunately, the features produce very weak contrast and were therefore only rarely observed. Their nature and origin are consequently poorly defined, and their presence, although perhaps suggestive of the development of antiphase domains, can-

Fig. 4. Typical straight defects parallel to (100) in synthetic Opx. Short dimension of image = 0.15 μm.

Fig. 5. Microstructure in synthetic Opx, consisting of irregular domains of opposite contrast (rarely observed). Two-beam dark-field image; short dimension = 30 μm; $g = 832$. 
not be regarded as compelling evidence for a phase inversion during quench.

**X-ray powder diffractometry at 1425-1440 °C**

X-ray powder diffractometry was used to examine directly the structure of the Opx phase at temperatures above 1400 °C. Spectra were obtained using CuKα radiation over the range 10-70° 2θ, with powdered samples emplaced as an acetone slurry onto a Pt strip heater; the heater was equipped with a temperature controller calibrated against the melting points of NaCl, Ag, Au, and CaMgSi₂O₄. In addition to two Opx separates from the synthesis run described above, a specimen of natural bronzite from the Bamble, Norway, locality was also examined. After collecting an initial room-temperature spectrum, each sample was heated over an interval of about 1-2 min to 1440 °C and then held for 1-2 min. Each sample was then returned to room temperature and a final spectrum collected.

The high- and low-temperature spectra of the natural bronzite sample (which was immersed in an atmosphere of helium to prevent oxidation of Fe during the run) showed no marked differences, apart from the expected increase in cell parameters. Diffraction patterns of the synthetic material, however, showed distinct changes over time. The pattern run immediately after heating displayed broadened reflections of relatively low intensity. Two subsequent patterns, run after longer exposure to high temperature, both showed sharper and more intense reflections. These two spectra were nearly identical to each other, and although they closely resembled an orthoenstatite spectrum (as described in more detail below), both contained two diffraction maxima, of very low intensity, that are absent in the room-temperature spectrum very closely.

The high-temperature spectra strongly resemble the diffraction patterns of the natural orthoenstatite, suggesting that the structure of the phase at high temperature is closely related to that of Oen, if not identical to it. To attempt to determine whether the subtle differences that did appear are genuine indications of a difference in the high-temperature structure or are merely artifacts of the analysis, the powder pattern expected from end-member magnesian orthoenstatite at 1425 °C was calculated. The calculations were performed using the positional parameters of Hawthorne and Ito (1977), scattering factors for neutral atoms corrected for the real and imaginary parts of dispersion (International Tables for X-ray Crystallography, 1974), and cell parameters equal to those refined by a least-squares technique (after Appleman and Evans, 1973) from the observed 1425 °C powder pattern [in Å, a = 18.567(4), b = 8.954(2), c = 5.341(6)]. Table 4 compares the relative intensities of observed diffraction maxima with those calculated for the Oen structure at 1425 °C; except for 210, calculated maxima with I/I₀₀ < 1 are omitted. The quantitative agreement is excellent, except for (a) excess intensity in the 210, 400, and 800 maxima, which is reasonably accounted for as the result of preferred orientation on cleavage and parting planes; (b) insufficient intensity (by a factor of three or greater) in the...
the evidence is not entirely unambiguous, this investigation strongly indicates that the orthopyroxene-like phase stable in MgSiO₃–CaMgSiO₃ near 1400 °C at atmospheric pressure is identical to ordinary orthoeno-

Under the hypothesis that the high-temperature structure is indeed that of ordinary orthoenstatite, only two features of the powder-diffraction data remain unex-

Thermal expansion

If the high-temperature phase is indeed identical to Oen, then thermal-expansion coefficients calculated from the 25 °C and 1425 °C refinements of cell parameters should be consistent with those in the literature for other orthorhombic pyroxenes. The differences in cell parameters between 25 °C and 1425 °C generate mean linear coefficients of thermal expansion (in units of 10⁻³ per °C) of 1.12, 0.95, 1.98, and 4.14, for a, b, c, and volume, respectively. These values are similar in magnitude to those in the literature for other orthopyroxene.

Conclusions

Although the evidence is not entirely unambiguous, this investigation strongly indicates that the orthopyroxene-like phase stable in MgSiO₃–CaMgSiO₃ near 1400 °C at atmospheric pressure is identical to ordinary orthoeno-

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