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Effects of pressure on Mg-Fe ordering in orthopyroxene synthesized at 11.3 GPa and 1600 °C

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ABSTRACT

A single crystal of intermediate orthopyroxene, $(Mg_{0.56}Fe_{0.44})_2Si_2O_6$, has been recovered from a synthesis experiment at approximately 11 GPa and 1600 °C. This rapidly quenched crystal displays a high degree of disorder for orthopyroxene M1 and M2 octahedral sites ($K_d = 3.9$). Comparison with low-pressure orthopyroxene quenched from similar temperatures indicates that pressures corresponding to the Earth's mantle transition zone have little effect on Mg-Fe ordering between M1 and M2, unlike intracrystalline ordering in several other dense magnesium iron silicates.

INTRODUCTION

Ordering of Fe and Mg between the two octahedral sites of orthopyroxene $[(Mg,Fe)_2Si_2O_6]$ provides a sensitive marker for the thermal histories of a wide variety of rocks, including volcanic tephra (Johnston and Knedler, 1979), ophiolites (Skogby, 1992), granulites (Tribaudino and Talarico, 1992), charnockites (Saxena and Dal Negro, 1983), mantle xenoliths (Dyar et al., 1992), and meteorites (Molin et al., 1991). Consequently, the effects of equilibration temperature and cooling rate on the ordering behavior of orthopyroxene have received considerable attention (e.g., Ghose, 1965; Virgo and Hafner, 1969; Saxena and Ghose, 1971; Besancon, 1981; Ganguly, 1982; Saxena and Dal Negro, 1983; Anovitz et al., 1988; Saxena et al., 1989). These and other studies provide the basis for orthopyroxene geothermometry and geospeedometry.

In spite of the wide range of pressures under which orthopyroxenes can form, little attention has been paid to the influence of pressure on Mg-Fe ordering. This neglect is understandable, given the relatively small effect of ordering on orthopyroxene molar volume (Domeneghetti et al., 1985), as well as the difficulty of producing samples, especially single crystals, in the highest pressure range of orthopyroxene stability—from about 8 GPa for $FeSiO_3$ orthopyroxene (Ito and Matsui, 1977) to 17 GPa for $MgSiO_3$ (Sawamoto, 1987). Nevertheless, recent studies of high-pressure phases in the system MgO-FeO-SiO_2, including wadsleyite (Finger et al., 1993), anhydrous B (Hazen et al., 1992), and olivine (Aikawa et al., 1985), indicate that pressure may induce significant Mg-Fe ordering. We view the case of olivine as particularly noteworthy: Aikawa et al. (1985) have demonstrated a pronounced pressure-induced ordering in this phase, which typically displays almost complete disorder in crustal rocks. Pressure-induced ordering could play a significant role in cation distributions, phase equilibria, and element fractionations in the mantle. Ordering may also affect the elasticity (Weidner et al., 1982; Bass and Weidner, 1984) and thermochemical properties (Saxena and Ghose, 1971; Chatillon-Colinet et al., 1983) of orthopyroxene. Investigation of the effects of pressure on orthopyroxene ordering is thus warranted.

This study takes advantage of fine orthopyroxene single crystals of intermediate Mg-Fe composition that were inadvertently produced during efforts to obtain a suite of silicate spinel crystals. The resulting crystals, synthesized

TABLE 1. Refined orthopyroxene atomic coordinates, anisotropic thermal parameters, and equivalent isotropic thermal parameters

Atom	x	y	z	B_{eq}	β_{11}	β_{22}
M1	0.37566(4)	0.65433(6)	0.87255(11)	0.60(1)	0.00050(2)	0.00198(7)
M2	0.37783(3)	0.48396(5)	0.36615(9)	0.74(1)	0.00062(1)	0.00259(6)
SiA	0.27171(4)	0.34044(8)	0.05148(13)	0.54(1)	0.00041(2)	0.00189(8)
SiB	0.47378(4)	0.33632(9)	0.79433(13)	0.52(1)	0.00041(2)	0.00177(8)
O1A	0.18380(9)	0.33869(20)	0.04139(32)	0.71(3)	0.00041(5)	0.00292(22)
O2A	0.31110(10)	0.49979(20)	0.05281(31)	0.79(3)	0.00070(5)	0.00251(21)
O3A	0.30263(9)	0.23023(20)	−0.17567(34)	0.82(3)	0.00050(5)	0.00370(24)
O1B	0.56223(9)	0.33733(20)	0.79453(33)	0.73(3)	0.00041(5)	0.00294(22)
O2B	0.43342(9)	0.48406(20)	0.69513(34)	0.81(3)	0.00058(5)	0.00278(23)
O3B	0.44736(9)	0.20115(18)	0.59377(34)	0.75(3)	0.00053(5)	0.00282(22)

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at 11 GPa and 1600 °C and rapidly quenched from that high temperature, may be compared with similar samples equilibrated at low pressure. Thus, they provide a preliminary measure of high-pressure ordering behavior.

EXPERIMENTAL

Single crystals of intermediate orthopyroxene were synthesized in a split-sphere anvil apparatus (USSA-2000, experiment 959) starting from a dried fayalite powder (Fe_2SiO_4). The starting material was surrounded by Re foil, which was in turn jacketed by MgO and a cylindrical $LaCrO_3$ heater (Gasparik, 1989). The sample was held at a maximum pressure of 11.3 GPa at 1600 °C for 3 h, and then rapidly quenched at high pressure by turning off the heater. In this procedure, temperature is estimated to decrease to below 500 °C in <1 s (Tibor Gasparik, personal communication), and so high-temperature ordering characteristics may be preserved. The core of this sample inside the Re capsule yielded poorly crystallized iron silicate spinel. A split in the capsule, however, produced a contact zone up to 2 mm wide of intermediate orthopyroxene, which apparently formed by reaction between the Fe_2SiO_4 sample and MgO packing material, although we are uncertain why a chain silicate should form under these circumstances. These crystals, which are up to 250 μm in diameter, are optically uniform and display sharp extinction.

Electron microprobe analyses of orthopyroxene crystals from this experiment reveal a range of Fe/(Fe + Mg) from about 0.41 to 0.53, although individual grains are compositionally uniform on a scale of 100 μm. The conditions of synthesis (11.3 GPa and 1600 °C) are near the high-pressure stability limit for this range of orthopyroxene composition. A thin, wedge-shaped single crystal, approximately 120 × 90 × 30 μm, was selected for structure analysis by X-ray diffraction.

Single-crystal X-ray data were obtained using a Rigaku AFC-5 diffractometer with rotating anode generator and graphite monochromatized Mo$K\alpha_1$ radiation ($\lambda = 0.7093$ Å). The crystal has an orthorhombic unit cell [space group *Pbca*; $Z = 8$; $a = 18.312(4)$, $b = 8.917(2)$, $c = 5.217(1)$ Å; calculated density = 3.564 g/cm³; $\mu_l = 38.0$ cm⁻¹]. The unit-cell volume, 851.8(4) Å³, corresponds to Fe/(Fe + Mg) ≈ 0.445, with ideal mixing between end-members $MgSiO_3$ (832.5 Å³) and $FeSiO_3$ (875.9 Å³) (Sasaki et al., 1982).

TABLE 1.—*Continued*

β_{33}	β_{12}	β_{13}	β_{23}
0.00461(20)	0.00003(4)	−0.00015(5)	0.00002(12)
0.00508(16)	−0.00013(3)	−0.00045(4)	0.00002(9)
0.00439(20)	−0.00010(4)	0.00002(5)	0.00011(13)
0.00412(21)	0.00004(4)	−0.00002(5)	0.00010(13)
0.00597(57)	−0.00001(10)	0.00006(14)	0.00015(37)
0.00590(60)	−0.00018(10)	0.00012(15)	0.00035(36)
0.00548(63)	−0.00004(9)	−0.00002(16)	−0.00176(33)
0.00647(57)	−0.00007(10)	−0.00002(14)	0.00061(37)
0.00693(63)	0.00008(9)	−0.00015(16)	0.00103(35)
0.00593(70)	−0.00001(8)	0.00009(16)	−0.00079(32)

Four octants of intensity data were measured to $2\theta = 60°$ [$(\sin\theta)/\lambda = 0.70$], using ω step scans, yielding 5644 measured reflections including standards. These data were averaged according to Laue symmetry *mmm* for all reflections, giving 1252 symmetrically independent structure factors (internal agreement 5.7%), of which 1024 were observed ($I \geq 2\sigma$; internal agreement for observed reflections 3.6%).

RESULTS

Structure refinement

We initiated the orthopyroxene structure refinement with parameters observed by Burnham et al. (1971) for an Fe-rich orthopyroxene ($Ca_{0.04}Mg_{0.26}Fe_{1.70}Si_2O_6$) sample. In addition to the scale factor and 30 variable atomic coordinates, we refined anisotropic temperature factors, an extinction parameter, and Fe/(Fe + Mg) for the crystal and both symmetrically distinct octhedral sites, M1 and M2 (Table 1). All atomic positions are within 0.04 Å of those for the Fe-rich sample described by Burnham et al. (1971).

The refinement converged to a weighted *R* ($R_w = \Sigma\, \sigma_F^{-2}(F_o - F_c)^2/\Sigma\, \sigma_f^{-2}F_o^2$) of 0.018, and unweighted *R* ($R = \Sigma\, \|F_o| - |F_c\|/\Sigma\, |F_o|$) of 0.051 for all 1252 independent data; $R = 0.037$ and $R_w = 0.018$ for 1012 data with $F_o > 2\sigma_F$. Refined positional and thermal parameters appear in Table 1. Bond distances and angles (Table 2) are similar to those reported in previous studies (Burnham et al., 1971; Sasaki et al., 1982; Domeneghetti and Steffen, 1992). The magnitudes and orientations of thermal vibration ellipsoids are close to those reported by Burnham et al. (1971), who emphasized the distinct thermal behavior of bridging vs. nonbridging O atoms.

The refined $Fe_{tot}/(Fe_{tot} + Mg)$ is 0.441, in agreement with the 0.445 value estimated from the unit-cell volume. As in all Fe-bearing orthopyroxenes, Fe orders preferentially into the M2 site, with 60% Fe, whereas M1 has only 28% Fe.

TABLE 2. Selected orthopyroxene interatomic distances and angles

M1 octahedron		M2 octahedron	
M1-O1A	2.043(2)	M2-O1A	2.147(2)
M1-O1A	2.160(2)	M2-O1B	2.109(2)
M1-O2A	2.045(2)	M2-O2A	2.046(2)
M1-O1B	2.171(2)	M2-O2B	1.996(2)
M1-O1B	2.078(2)	M2-O3A	2.365(2)
M1-O2B	2.069(2)	M2-O3B	2.523(2)
Mean M1-O	2.094	Mean M2-O	2.198
SiA tetrahedron		SiB tetrahedron	
SiA-O1A	1.611(2)	SiB-O1B	1.620(2)
SiA-O2A	1.594(2)	SiB-O2B	1.597(2)
SiA-O3A	1.640(2)	SiB-O3B	1.668(2)
SiA-O3A	1.656(2)	SiB-O3B	1.669(2)
Mean SiA-O3	1.625	Mean SiB-O3	1.639
Tetrahedral chains			
A chain		B chain	
SiA-SiA	3.067(1)	SiB-SiB	3.029(1)
SiA-O3A-SiA	137.0(1)	SiB-O3B-SiB	130.4(1)

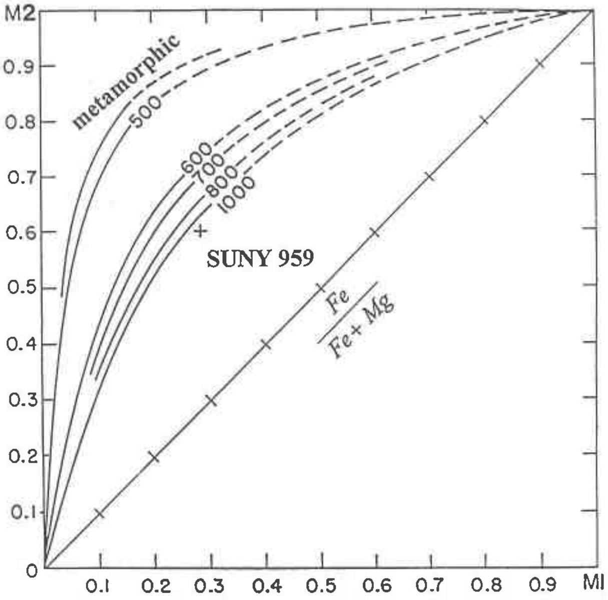

Fig. 1. The 11.3 GPa orthopyroxene single crystal described in this study plots slightly above the 1000 °C ordering isotherm of Virgo and Hafner (1969).

Effects of pressure on Mg-Fe ordering

Ordering between the M1 and M2 sites of orthopyroxene can be expressed as a distribution coefficient: $K_d = (X\mathrm{Fe}_{M2}/X\mathrm{Mg}_{M2})/(X\mathrm{Fe}_{M1}/X\mathrm{Mg}_{M1})$.

A completely disordered mineral has $K_d = 1$. Orthopyroxenes have two very different octahedral sites and thus may have significant Mg-Fe ordering. When equilibrated at low temperature, Fe strongly orders into the larger and more distorted M2 site, whereas Mg prefers the smaller and less distorted M1 site. Distribution coefficients >50 have been reported for slowly cooled natural samples (Tribaudino and Talarico, 1992) and samples annealed at temperatures near 500 °C, whereas samples equilibrated above 1000 °C and rapidly quenched more typically have K_d between 3 and 4 (Virgo and Hafner, 1969).

The high-pressure crystal of this study has $K_d = 3.9$, close to the maximum disorder observed in rapidly quenched synthetic orthopyroxenes and consistent with the degree of ordering expected for a sample quenched from 1600 °C at room pressure. Plotted on a nomogram of temperature vs. M1 and M2 Fe content (Virgo and Hafner, 1969; Shi et al., 1992), this sample lies above the 1000 °C equilibration curve (Fig. 1)—a temperature reflecting the rapid quench from 1600 °C of our sample.

Details of possible partial ordering during quenching from temperatures above 1000 °C remain an unresolved aspect of this and other high-pressure experiments. If quench rates for samples produced in multianvil experiments are significantly different from those of piston-cylinder or hydrothermal experiments, for example, then direct comparison of ordered states may prove difficult. Studies of ordering under different quench rates thus appear warranted. Nevertheless, all rapid quench methods appear to preserve ordering characteristic of temperatures in excess of 1000 °C. We conclude, therefore, that pressure does not induce significant Mg-Fe ordering in orthopyroxene.

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