Crystal chemistry of a high-pressure *C*2/*c* clinopyroxene with six-coordinated silicon

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ABSTRACT

A $(Ca_{0.36}Na_{0.56}Mg_{0.08})(Mg_{0.73}Si_{0.27})Si_2O_6$ clinopyroxene containing both four- and six-coordinated silicon was synthesized at 15 GPa and 1600 °C and its structure determined with single-crystal X-ray diffraction. Unlike the $Na(Mg_{0.5}Si_{0.5})Si_2O_6$ clinopyroxene that exhibits an ordered *P*2/*n* structure with octahedrally coordinated Mg^{2+} and Si^{4+} occupying two crystallographically distinct M1 sites (Angel et al. 1988), our sample possesses a *C*2/*c* symmetry and shows no detectable ordering between Mg^{2+} and Si^{4+} in the M1 site. The measured unit-cell parameters are $a = 9.5792(13)$, $b = 8.7588(12)$, $c = 5.2610(6)$ Å, $\beta = 107.199(3)°$, and $V = 421.7(2)$ Å^3. The crystal structure of the clinopyroxene reported in this study is comparable to that for omphacites formed under high temperatures and pressures.

INTRODUCTION

Pyroxenes are among the most important geological materials in the terrestrial planets. In the Earth's crust and upper mantle, they are stable in a wide range of pressure-temperature conditions and bulk compositions in magmatic and metamorphic environments (Prewitt 1980 and references therein). In the peridotitic upper mantle, pyroxenes occur with dominant enstatite and diopside components, representing major constituents of lherzolitic and harzburgitic rocks (e.g., Maaløe and Aoki 1977; McDonough and Rudnick 1998). In the subducted oceanic crust, clinopyroxenes are important constituents of high pressure rocks, but with a dominant jadeite component, reflecting the high Na-Al environment of metabasaltic and/or metasedimentary crustal settings (Carswell 1990 and references therein). Experimental studies have shown that clinopyroxene may be stable to pressures of 15–17 GPa in a typical upper mantle peridotite (e.g., Zhang and Herzberg 1994; Wang and Takahashi 2000), or to slightly higher pressures near 18 GPa in more simple chemical systems (e.g., Akaogi and Akimoto 1977; Canil 1994)

In spite of their stability to pressures in excess of 10 GPa, clinopyroxenes had long been assumed to contain silicon in tetrahedral coordination only. This assumption was disproved by Angel et al. (1988) (see also Gasparik 1988), who described a $Na(Mg_{0.5}Si_{0.5})Si_2O_6$ clinopyroxene (NaPx) that contains both 4- and 6-coordinated silicon. This pyroxene was synthesized at 15 GPa and 1600 °C and has a *P*2/*n* symmetry.

The existence of clinopyroxene with 6-coordinated silicon in natural mantle rocks was demonstrated by Wang and Sueno (1996), who reported an inclusion in diamond from a Chinese kimberlite (pipe No. 50, Liaoning province) with a composition 62.7 wt% SiO_2, 0.15 wt% Al_2O_3, 0.46 wt% FeO, 33.3 wt% MgO, 1.19 wt% CaO, 2.34 wt% Na_2O, 0.28 wt% K_2O, which can be

recalculated to a $NaPx_{16}En_{84}$ pyroxene solid solution. This finding indicates that parts of the Earth's upper mantle are characterized by an excess of sodium with respect to aluminum in the bulk, a situation not known to prevail in peridotitic portions of the upper mantle regularly sampled by xenoliths.

The discovery that the clinopyroxene structure is capable of accommodating 6-coordinated silicon is of fundamental importance for our understanding of crystal-chemical behavior of minerals at high pressures and temperatures in general and chain silicates in particular (Finger and Hazen 1991). This is because a change in the silicon coordination from fourfold to sixfold in materials have significant effects on their physical and chemical properties, such as density, bulk modulus, and elastic moduli, and, consequently, on their pressure-temperature stability fields. In this paper, we report a $(Ca_{0.36}Na_{0.56}Mg_{0.08})(Mg_{0.73}Si_{0.27})Si_2O_6$ clinopyroxene synthesized at 15 GPa and 1600 °C. This pyroxene, like that examined by Angel et al. (1988), also contains a substantial amount of six-coordinated silicon, but possesses *C*2/*c* symmetry and displays no ordering between Mg^{2+} and Si^{4+} in the octahedral M1 sites.

EXPERIMENTAL PROCEDURES

The crystal used in this study was synthesized from a starting material with a composition of 68.6 wt% SiO_2, 12.7 wt% MgO, 10.5 wt% Na_2O, and 8.2 wt% CaO, which was prepared from a mix of high-purity (>99.99%) SiO_2, MgO, Na_2CO_3, and $CaCO_3$ by stepwise decarbonation, representing nominal $Na_{0.70}Ca_{0.30}(Mg_{0.65}Si_{0.35})Si_2O_6$. The high-pressure synthesis was carried out in a 1000t multi-anvil device using a 14/8 assembly (14 mm edge length of octahedron; 8 mm truncation of tungsten carbide cubes) with $LaCrO_3$ heater and a welded Pt_{100} (1.6 mm o.d.) sample container at the Bavarian Research Institute of Experimental Geochemistry and Geophysics, University of Bayreuth. Run conditions were 15 GPa and 1600 °C for a duration of 4 hours. Temperatures were measured with a W-WRe thermocouple, and pressure and temperature were computer-controlled during the entire run.

After the experiment, the sample capsule was retrieved from the assembly, embedded in epoxy resin and ground to expose the center of the experimental charge, which showed a mixture of clinopyroxene and quenched melt with some stishovite crystals (Fig. 1). The composition of the clinopyroxene was analyzed with an electron microprobe (JEOL JXA-8100) at the Institute of Mineralogy and
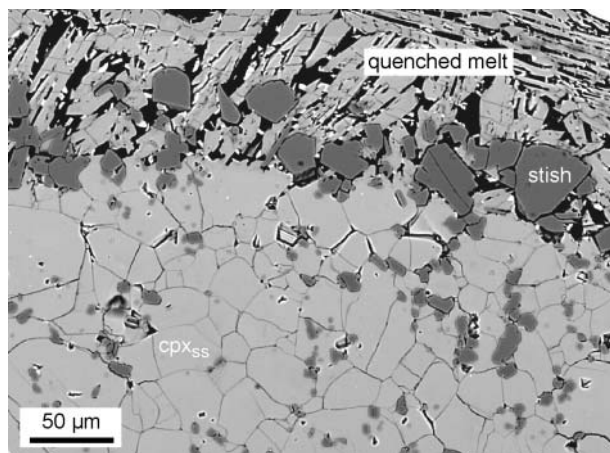
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FIGURE 1. Photomicrograph of the experimental products (15 GPa and 1600 °C).

TABLE 1. Averaged composition ($n = 10$) of $(Ca_{0.36}Na_{0.56}Mg_{0.08})(Mg_{0.73}Si_{0.27})Si_2O_6$

Oxide	wt%	Cation	Cation numbers*
SiO$_2$	65.54(85)	Si	2.27(1)
MgO	15.78(22)	Mg	0.82(1)
CaO	9.56(25)	Ca	0.36(1)
Na$_2$O	8.25(20)	Na	0.56(1)
Total	99.13(81)		4.01(3)

* Cation numbers were calculated based on 6 O^{2-} and normalized to 4 in the chemical formula. The estimated errors were based on the variation among the 10 point analyses.

TABLE 2. Summary of crystal data and refinement results

Structural formula	$(Ca_{0.36}Na_{0.56}Mg_{0.08})(Mg_{0.73}Si_{0.27})Si_2O_6$
Formula weight	206.71
Crystal size (mm^3)	$0.05 \times 0.05 \times 0.06$
Space group	$C2/c$ (No. 15)
a (Å)	9.5792(13)
b (Å)	8.7588(12)
c (Å)	5.2610(6)
β (°)	107.199(3)
V (Å^3)	421.7(2)
Z	4
ρ_{calc} (g/cm^3)	3.256
λ (Å)	0.71069
μ (mm^{-1})	1.48
θ range for data collection	0 to 29
No. of reflections collected	2367
No. of independent reflections	527
No. of reflections with $I > 2\sigma(I)$	457
No. of parameters refined	50
R(int)	0.031
Final R factors [$I > 2\sigma(I)$]	$R_1 = 0.028$, $wR_2 = 0.075$
Final R factors (all data)	$R_1 = 0.033$, $wR_2 = 0.077$
Goodness-of-fit	1.112

Petrology, University of Innsbruck. Analytical conditions were 15 kV acceleration voltage and 20 nA beam current with counting times of twenties and tens on peaks and backgrounds, respectively. The following standards were used: Mg and Si: pure synthetic MgO and SiO$_2$; Na: natural jadeite; Ca: natural bytownite. Raw counts were corrected using the PRZ correction procedure. The averaged composition of the crystal based on the 10 analysis points is listed in Table 1.

Based on optical examination, three nearly cube-shaped crystals with the largest dimensions ranging from 0.04 to 0.06 mm were selected and a Bruker Smart CCD X-ray diffractometer equipped with graphite-monochromatized Mo$K\alpha$ radiation was used for data collection. A hemisphere of three-dimensional X-ray diffraction data was collected with frame widths of 0.3° in ω and 30 s counting time per frame (see Table 2 for the experimental details). The data were analyzed to locate peaks for the determination of the unit-cell parameters. All reflections were indexed based on a monoclinic unit cell. Since all three crystals gave similar cell parameters, only the results from the crystal with the best data quality are presented. An empirical correction for X-ray absorption was made using the program SADABS (part of the Bruker program SAINT). Examination of reflection data revealed a C-lattice with the possible space group Cc or $C2/c$. Equivalent reflections were merged into a set of 527 independent reflections ($R_{int} = 0.031$), out of which 457 had $I_{obs} > 2\sigma(I_{obs})$.

The initial structure model for the crystal was taken from that for the SBB-2H omphacite studied by Oberti and Caporuscio (1991), because of the similarities in unit-cell parameters and Na/(Ca + Na) ratios between the two samples. The structure was refined based on $C2/c$ symmetry with the program SHELX97. All atoms were refined with anisotropic thermal displacement parameters. Based on the chemical composition determined with electron microprobe analysis, the following site occupancies were assumed during the refinements: (0.36 Ca^{2+} + 0.56 Na$^+$ + 0.08 Mg^{2+}) in the M2 site, (0.73 Mg^{2+} + 0.27 Si^{4+}) in the M1 site, and 2.0 Si^{4+} in the tetrahedral site. The resultant R_1 factor is 0.028 for the observed reflections and 0.033 for all independent reflections. No significant peaks were revealed in difference Fourier maps at convergence of the refinement. As there is a small amount of Mg in the M2 site, a refinement of the structure with the split-M2 sites was also attempted, but it did not produce a meaningful displacement factor for the M2' site. Final atomic coordinates and anisotropic thermal displacement parameters are presented in Table 3 and selected bond distances in Table 4. Structure factors for $(Ca_{0.36}Na_{0.56}Mg_{0.08})(Mg_{0.73}Si_{0.27})Si_2O_6$ are given in Table 5.[1]

RESULTS AND DISCUSSION

The most prominent feature of the $(Ca_{0.36}Na_{0.56}Mg_{0.08})(Mg_{0.73}Si_{0.27})Si_2O_6$ clinopyroxene structure is the presence of 0.27 Si^{4+} (apfu) in the M1 octahedral site. Thus far, only one pyroxene with

[1] For a copy of Table 5, Document item AM-05-018, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the American Mineralogist web site at http://www.minsocam.org.

the composition Na(Mg$_{0.5}$Si$_{0.5}$)Si$_2$O$_6$ (NaPx) has been reported to contain six-coordinated silicon (Angel et al. 1988). In that structure, the octahedrally coordinated Mg^{2+} and Si^{4+} cations are completely ordered into two crystallographically distinct sites, M1 (=Mg) and M1(1) (=Si), due to the large difference in their sizes and charges. The M1 and M1(1) octahedra alternate along the c direction to form an edge-shared octahedral chain. As a consequence, the symmetry of the structure is $P2/n$ rather than $C2/c$, even though the sample was synthesized at high temperature (1600 °C and 15 GPa) and quenched rapidly after the experiment, which would be expected to stabilize the $C2/c$ structure in omphacitic clinopyroxenes (Carpenter 1981). In contrast, despite the substitution of a substantial amount of Si^{4+} for Mg^{2+} in the octahedral site, our clinopyroxene sample maintains the $C2/c$ symmetry with no detectable ordering between the two cations, a structure that is comparable to that for omphacites formed under high temperatures and pressures (e.g., Carpenter 1981; Oberti and Caporuscio 1991). Nevertheless, it is unclear whether the $C2/c$ structure of our sample is stabilized by the lower amount of Si^{4+} (0.27 apfu) in the octahedral site than that (0.5 apfu) in NaPx (Angel et al. 1988), the substitution of a considerable amount of larger Ca^{2+} for Na$^+$ in the M2 site, or the coupled effects of both factors. In general, the smaller and more charged cations in the M1 site are thought to have more influence on the clinopyroxene structure than the larger and less charged M2 cations whose main function seems to fill large cavities and balance the charges (e.g., Rossi 1988). More investigations are needed to define the relative composition-temperature-pressure stability field of the $P2/n$ and $C2/c$ clinopyroxenes that contain six-coordinated silicon.

TABLE 3. Atomic coordinates and anisotropic displacement parameters for $(Ca_{0.36}Na_{0.56}Mg_{0.08})(Mg_{0.73}Si_{0.27})Si_2O_6$

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
M2	0	0.2989(1)	1/4	0.0199(7)	0.0118(6)	0.0110(6)	0	−0.0008(4)	0	0.0154(5)
M1	0	0.9052(1)	1/4	0.0095(8)	0.0092(8)	0.0083(8)	0	0.0017(5)	0	0.0092(6)
Si	0.2887(1)	0.0925(1)	0.2316(1)	0.0096(4)	0.0102(4)	0.0077(4)	−0.0010(2)	0.0029(2)	0.0005(2)	0.0091(2)
O1	0.1123(2)	0.0820(2)	0.1352(4)	0.0109(10)	0.0309(12)	0.0221(11)	−0.0084(8)	0.0048(8)	0.0048(7)	0.0213(5)
O2	0.3608(2)	0.2560(2)	0.3108(4)	0.0281(11)	0.0114(9)	0.0145(9)	−0.0012(7)	0.0055(8)	−0.0011(7)	0.0182(4)
O3	0.3517(2)	0.0132(2)	0.0038(3)	0.0129(9)	0.0177(10)	0.0089(8)	−0.0041(7)	0.0044(7)	0.0007(7)	0.0129(4)

The disordering between Si^{4+} and Mg^{2+} in an octahedral site is not common (see Finger and Hazen 1991 for a review) and has only been observed in a tetragonal $MgSiO_3$ garnet crystal synthesized at 17 GPa and 1800 °C, in which there are two octahedral sites, one with a composition of $(Mg_{0.2}Si_{0.8})$ and the other $(Mg_{0.8}Si_{0.2})$ (Angel et al. 1989). Thus, the M1 site in our sample exhibits the greatest disordering between Si^{4+} and Mg^{2+} of all magnesium silicates so far examined.

The M1 octahedron in the $(Ca_{0.36}Na_{0.56}Mg_{0.08})(Mg_{0.73}Si_{0.27})Si_2O_6$ structure has an average M1-O bond length of 2.010 Å and a polyhedral volume of 10.69 Å³. These values fit well into the linear relations defined by the MgO_6 and SiO_6 octahedra in the NaPx structure (Angel et al. 1988). However, owing to the edge-sharing between the MgO_6 and SiO_6 octahedra that are appreciably different in their geometry, the M1 octahedron (MgO_6) in $Na(Mg_{0.5}Si_{0.5})Si_2O_6$ (Angel et al. 1988) is much more distorted than that in our sample, as indicated by their octahedral angle variances (106.6 vs. 31.0) (Robinson et al. 1971).

Except for the presence of Si^{4+} in the M1 octahedron, the general structural features of our clinopyroxene are comparable to those of $C2/c$ omphacites studied by Oberti and Caporuscio (1991), especially the SBB-2H sample with the composition $[(Ca_{0.45}Na_{0.55})(Mg_{0.37}Fe_{0.03}Al_{0.60})(Si_{1.92}Al_{0.08})O_6]$. For comparison, listed in Table 4 are also the bond lengths and other polyhedral parameters for the SBB-2H omphacite. In addition, the O3-O3-O3 kinking angles of the silicate tetrahedral chains in the two pyroxene structures are also similar (~170°). Oberti and Caporuscio (1991) noted that the M2 polyhedral volume in $C2/c$ omphacites is a linear function of the constituent cation charge of the site, and so is the mean M1-O bond distance. Our data agree well with these relationships.

Intriguingly, the unit-cell c dimension [5.2610(6) Å] of our clinopyroxene sample is longer than that for any $C2/c$ omphacite (5.246–5.256 Å) examined by Oberti and Caporuscio (1991) or for any $P2/n$ omphacite (5.248–5.257 Å) by Rossi et al. (1983), but significantly shorter than that [5.274(1) Å] for the $Na(Mg_{0.5}Si_{0.5})Si_2O_6$ pyroxene (Angel et al. 1988). The increase of the c dimension with increasing octahedrally coordinated Si in clinopyroxenes is unexpected, as c tends to decrease nonlinearly with increasing the average M1 cation charge for clinopyroxenes along the Di-Jd join (Oberti and Caporuscio 1991; Rossi et al. 1983). In general, the c dimension of clinopyroxene is strongly affected by the sizes of the M1 octahedra and the SiO_4 tetrahedra. Yet, these parameters for our sample are comparable to those for the $C2/c$ omphacites studied by Oberti and Caporuscio (1991). Evidently, other possible factors, such as coulombic repulsion and site distortion, may come into play for the relatively long c dimension in pyroxenes containing six-coordinated Si (Oberti, personal communication).

Thompson et al. (2005) demonstrated that the unit-cell vol-

TABLE 4. Selected interatomic bond distances (Å) and polyhedral parameters

$(Ca_{0.36}Na_{0.56}Mg_{0.08})(Mg_{0.73}Si_{0.27})Si_2O_6$					
M1-O1 (×2)	1.997(2)	M2-O1 (×2)	2.349(2)	Si-O1	1.616(2)
M1-O1 (×2)	2.075(2)	M2-O2 (×2)	2.351(2)	Si-O2	1.591(2)
M1-O2 (×2)	1.960(2)	M2-O3 (×2)	2.476(2)	Si-O3	1.647(2)
		M2-O3 (×2)	2.763(2)	Si-O3	1.661(2)
Avg.	2.010	Avg. (8)	2.484	Avg.	1.629
PV*	10.69	PV (8)	25.22	PV	2.20
AV*	31.00			AV	20.86
QE*	1.0098			QE	1.0049
The SBB-2H omphacite† $(Ca_{0.45}Na_{0.55})(Mg_{0.37}Fe_{0.03}Al_{0.60})(Si_{1.92}Al_{0.08})O_6$					
M1-O1 (×2)	1.982	M2-O1 (×2)	2.376	Si-O1	1.623
M1-O1 (×2)	2.043	M2-O2 (×2)	2.390	Si-O2	1.594
M1-O2 (×2)	1.933	M2-O3 (×2)	2.450	Si-O3	1.647
		M2-O3 (×2)	2.715	Si-O3	1.661
Avg.	1.986	Avg. (8)	2.483	Avg.	1.631
PV	10.29	PV (8)	25.17	PV	2.21
AV	34.51			AV	24.09
QE	1.011			QE	1.006

* PV = polyhedral volume (Å³); AV = angle variance; QE = quadratic elongation (Robinson et al. 1971).
† The data for the SBB-2H omphacite was taken from Oberti and Caporuscio (1991).

ume of the $C2/c$ pyroxenes is strongly correlated with the M1 cation size and suggested that the high-pressure behavior of the M1 octahedron dictates the compressibility of the whole structure. For example, the bulk moduli of the M1 octahedron and the whole structure are 111 and 116 GPa, respectively, for diopside, whereas they are 139 and 137 GPa for jadeite (Thompson et al. 2005). Thus far, the bulk modulus of the SiO_6 octahedron has only been determined from stishovite (Ross et al. 1990), which has a value of 331 GPa. If the linear correlation between the compressibilities of the M1 octahedron and the whole structure for the diopside-jadeite join holds, then the estimated bulk modulus for our clinopyroxene sample would be around 173 GPa, which may account for its high-pressure stability.

The only experimental study that has dealt specifically with clinopyroxenes containing 6-coordinated silicon was carried out by Gasparik (1989). This study investigated pyroxene solid solutions in the systems NaPx–En ($Mg_2Si_2O_6$), NaPx–En–Di ($CaMgSi_2O_6$), and NaPx–En–Jad ($NaAlSi_2O_6$), and revealed that NaPx can form solid solutions with En, Di, and Jad. Experiments in the system NaPx–En–Di produced a solid solution with the composition $NaPx_{28}Di_{38}En_{34}$, which has a diopside component similar to that in our sample ($NaPx_{56}Di_{36}En_8$). On the other hand, experiments in the system NaPx–En showed that NaPx with 1–2 mol% En-solid solution is stable between 8 and 15 GPa at 1400–1650 °C. Based on these data, Gasparik (1989) constructed a phase diagram, postulating a large miscibility gap between 8 and 15 GPa and an upper pressure stability limit of NaPx-En solid solutions near 15 GPa.

As noted by Angel et al. (1988), a key requirement for the stability of silica-rich sodium pyroxenes at high pressure and temperature is an excess of sodium with respect to aluminum in the bulk. In spite of this bulk compositional restriction, the existence of a NaPx-solid solution ($NaPx_{16}En_{84}$) in nature was documented by Wang and Sueno (1996). From the phase diagram for the system NaPx-En presented by Gasparik (1989), Wang and Sueno (1996) concluded that this natural NaPx-En solid solution must have been formed at pressures in excess of 16 GPa. Accordingly, the finding of the NaPx-En solid solution by Wang and Sueno (1996) suggests that the Earth's transition zone is sufficiently heterogeneous, with respect to bulk composition, to permit the stable existence of Na-rich and Al-poor pyroxenes.

ACKNOWLEDGMENTS

REFERENCES CITED

Akaogi, M. and Akimoto, S. (1977) Pyroxene-garnet solid-solution equilibria in the systems $Mg_4Si_4O_{12}$-$Mg_3Al_2Si_3O_{12}$ and $Fe_4Si_4O_{12}$-$Fe_3Al_2Si_3O_{12}$ at high pressures and temperatures. Physics of the Earth and Planetary Interiors, 15, 90–106.

Angel, R.J., Gasparik, T., Ross, N.L., Finger, L.W., Prewitt, C.T., and Hazen, R.M. (1988) A silica-rich sodium pyroxene phase with six-coordinated silicon. Nature, 335, 156–158.

Angel, R.J., Finger, L.W., Hazen, R.M., Kanzaki, M., Weidner, D.J., Liebermann, R.C., and Veblen, D.R. (1989) Structure and twinning of single-crystal $MgSiO_3$ garnet synthesized at 17 GPa and 1800 °C. American Mineralogist, 74, 509–512.

Canil, D. (1994) Stability of clinopyroxene at pressure-temperature conditions of the transition region. Physics of the Earth and Planetary Interiors, 86, 25–34.

Carpenter, M.A. (1981) Time-temperature-transformation (TTT) analysis of cation disordering in omphacites. Contributions to Mineralogy and Petrology, 78, 433–440.

Carswell, D.A. (1990) Eclogite Facies Rocks, 396 p. Blackie, London.

Finger, L.W. and Hazen, R.M. (1991) Crystal chemistry of six-coordinated silicon: a key to understanding the Earth's deep interior. Acta Crystallographica, B47, 561–580.

Gasparik, T. (1988) The synthesis of a new pyroxene-$NaMg_{0.5}Si_{0.5}Si_2O_6$ and garnet near the diopside-jadeite join. EOS, Transactions American Geophysical Union, 69, 500.

——— (1989) Transformation of enstatite-diopside-jadeite pyroxenes to garnet. Contributions to Mineralogy and Petrology, 102, 389–405.

Maaløe, S. and Aoki, K. (1977) The major element composition of the upper mantle estimated from the composition of lherzolites. Contributions to Mineralogy and Petrology, 63, 161–173

McDonough, W.F. and Rudnick, R.L. (1998) Mineralogy and composition of the upper mantle. In Hemley, R.J. Ed., Ultrahigh-Pressure Mineralogy: Physics and Chemistry of the Earth's Deep Interior, vol. 37, p. 139–164. Reviews in Mineralogy, Mineralogical Society of America, Washington, D.C.

Oberti, R. and Caporuscio, F.A. (1991) Crystal chemistry of clinopyroxenes from mantle eclogites: A study of the key role of the M2 site population by means of crystal-structure refinement. American Mineralogist, 76, 1141–1152.

Prewitt, C.T. (1980) Pyroxenes. vol. 7, 525 p. Reviews in Mineralogy, Mineralogical Society of America, Washington, D.C.

Robinson, K., Gibbs, G.V., and Ribbe, P.H. (1971) Quadratic elongation, a quantitative measure of distortion in coordination polyhedra. Science, 172, 567–570.

Ross, N.L., Shu, J., Hazen, R.M., and Gasparik, T. (1990) High pressure crystal chemistry of stishovite. American Mineralogist, 75, 739–747.

Rossi, G. (1988) A review of the crystal chemistry clinopyroxenes in eclogites and eclogite-facies rocks. In D.C. Smith, Ed., Eclogites and eclogite-facies rocks, p.237–270, Elsevier, Amsterdam.

Rossi, G., Smith, D.C., Ungaretti, L., and Domeneghetti, C. (1983) Crystal-chemistry and cation ordering in the system diopside-jadeite: A detailed study by crystal structure refinement. Contributions to Mineralogy and Petrology, 83, 247–258.

Thompson, R.M., Downs, R.T., and Redhammer, G.J. (2005) Model pyroxenes III: Volume of $C2/c$ pyroxenes at mantle P, T, and x. American Mineralogist, 90, in press.

Wang, W. and Sueno, S. (1996) Discovery of a NaPx-En inclusion in diamond: possible transition zone origin. Mineralogical Journal, 18, 9–16.

Wang, W. and Takahashi, E. (2000) Subsolidus and melting experiments of K-doped peridotite KLB-1 to 27 GPa: its geophysical and geochemical implications. Journal of Geophysical Research, 105, 2855–2868.

Zhang, J. and Herzberg, C. (1994) Melting experiments on anhydrous peridotite LKB-1 from 5.0 to 22.5 GPa. Journal of Geophysical Research, 99, 17729–17742.