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Compressibility of omphacite to 60 kbar: Role of vacancies

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ABSTRACT

Compressibilities of two *C2/c* omphacites from kyanite eclogite xenoliths in South African kimberlites have been measured. Both omphacites are approximately Jd_{58} in composition, but one of the crystals contains 6.5% M2-site vacancies, whereas the other contains only 1.7%. Cell parameters were determined at six pressures between 1 bar and 60 kbar on three single crystals (two omphacites and a nearly pure, natural diopside standard) mounted together in a Merrill-Bassett diamond anvil cell, on a four-circle X-ray diffractometer. Relative compression of the three pyroxenes could be measured precisely because pressure was the same for all crystals. Linear regression analysis of the data yields volume compressibilities of 0.75, 0.70, and 0.65 (all ± 0.01) $Mbar^{-1}$ for diopside, vacancy-rich omphacite, and vacancy-poor omphacite respectively. Both omphacites are significantly less compressible than diopside, consistent with the stiffer elastic moduli of jadeite. The vacancy-poor omphacite is significantly less compressible than the vacancy-bearing pyroxene of similar jadeite content. Greatest differences in axial compression among the three crystals occur parallel to **b** and may be accounted for by different distortions of the M2 sites, where the cation vacancies appear to occur.

INTRODUCTION

In order to refine geophysical and geochemical models of the upper mantle, it is necessary to have accurate equation-of-state data for mantle minerals. Although diopside-rich pyroxenes are the dominant clinopyroxenes in olivine-rich nodules derived from the upper mantle, jadeitic pyroxenes are a major component of eclogite, the high-pressure equivalent of basalt, and are the principal host phase for Na in the upper mantle. Recent geochemical and geophysical models of the mantle also incorporate significant amounts of eclogite (e.g., Anderson and Bass, 1984). However, relatively little is known about the physical properties of eclogite or its primary phases under mantle conditions.

Jadeitic pyroxenes found in mantle eclogite inclusions in kimberlite commonly contain significant M2-site vacancies (Sobolev et al., 1968; Smyth, 1980; McCormick, 1986). The vacancy component in omphacite, referred to as Ca-Eskola component ($Ca\square Al_2Si_4O_{12}$), appears to be stabilized by high pressure, as noted by the phase-equilibria studies of Khanukhova et al. (1977) and Gasparik (1984) and as suggested by the reduced cell volumes of nonstoichiometric pyroxenes (McCormick, 1986; Wood and Henderson, 1978).

High-pressure structural studies were performed on natural diopside by Hazen and Finger (1981) and Levien and Prewitt (1981). Elastic constants have been measured on a number of single crystals of end-member clinopyroxenes by Brillouin scattering (e.g., Levien et al., 1979; Kandelin and Weidner, 1988a, 1988b; Weidner and Vaughan, 1982; Hong and Vaughan, 1987). However, no attempt has been made to measure compressibilities of single crystals of jadeite or omphacite to upper-mantle pressures. Elastic properties of a single crystal of one of the omphacitic pyroxenes described in this study have recently been measured (Bhagat et al., 1988), and a full description of these data is currently in preparation (J. Bass, personal communication).

In order to refine estimates of the compressibility of natural omphacitic pyroxene, and in particular to assess the effect of vacancies, we have undertaken the measurement of cell parameters of diopside and two mantle-derived omphacites at a number of pressures to 60 kbar. The two omphacites are very similar in composition with the exception that one contains far more M-site vacancies than the other. The effect of pressure on vacancies in complex silicates is unknown. It was our intention, therefore, not only to estimate the compressibility of pyroxene on the jadeite-diopside join, but also to evaluate the effects of M-site vacancies on the compressibility by direct comparison of vacancy-rich and vacancy-poor omphacites.

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TABLE 1. Microprobe analyses and end-members for clinopyroxenes

	Diopside*	SBB-1**	SDC-1
	Weight percent oxides		
SiO_2	55.7	57.09(0.39)	55.55(0.35)
TiO_2	n.d.	0.36(0.05)	0.19(0.05)
Al_2O_3	0.07	19.83(0.25)	18.26(0.19)
Cr_2O_3	0.00	0.06(0.04)	n.d.
FeO	0.09	2.45(0.10)	1.24(0.04)
MgO	18.8	4.01(0.08)	5.78(0.08)
MnO	0.00	0.03(0.03)	n.d.
CaO	26.0	7.80(0.15)	10.41(0.18)
Na_2O	0.02	9.05(0.21)	8.60(0.13)
K_2O	n.d.	0.07(0.02)	0.01(0.01)
Total	100.7	100.75	100.04
	Mole percent end-members		
$NaCrSi_2O_6$	0.00	0.16	—
$NaFeSi_2O_6$	0.14	0.00	0.00
$NaAlSi_2O_6$	0.00	59.97	57.89
$KAlSi_2O_6$	—	0.31	0.04
$CaTiAl_2O_6$	—	0.93	0.50
$CaAl_2SiO_6$	0.00	2.49	6.15
$Ca_{0.5}AlSi_2O_6$	0.00	12.97	3.50
$CaMnSi_2O_6$	0.00	0.09	—
$Ca_2Si_2O_6$	49.78	9.32	15.17
$Mg_2Si_2O_6$	50.15	10.24	14.96
$Fe_2Si_2O_6$	0.00	3.51	1.80

Note: esd's in parentheses are based on 18 and 5 analyses for SBB-1 and SDC-1, respectively.

* Analysis from Finger and Ohashi (1976).

** Analysis from McCormick (1986).

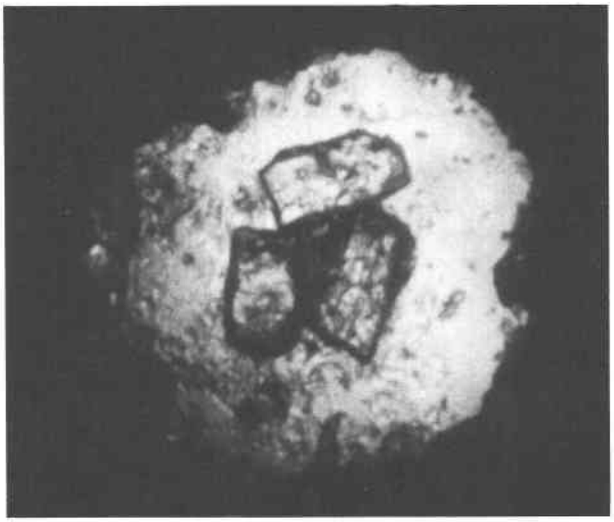

Fig. 1. Photomicrograph of three pyroxene crystals in diamond cell at 47 kbar. Diameter of the compressed gasket is approximately 300 μm.

EXPERIMENTAL METHODS

In order to make a direct comparison of the relative compression of the pyroxenes, the error on pressure determination can be eliminated by using a multiple crystal mount in the diamond cell (Hazen, 1981). Three single crystals, each measuring approximately 50 × 50 × 100 μm, were used in the study (Fig. 1). Diopside from Twin Lakes, California, was included as a standard, and the two omphacites (SBB-1 and SDC-1) were selected from kyanite eclogite inclusions in kimberlite from the Bellsbank Fissures, South Africa (Bobbejaan and Dan Carl mines). The Twin Lakes diopside was described in previous elevated *P-T* studies by Finger and Ohashi (1976) and Hazen and Finger (1981). The structure and chemistry of the vacancy-bearing pyroxene, SBB-1, has been described by McCormick (1986).

TABLE 2. Site occupancies of omphacite crystals

		Occupancy	
Site	Element	SBB-1*	SDC-1**
T	Si	0.979(4)	0.964(2)
T	Al	0.021(4)	0.036(2)
M1	Al	0.758(6)	0.676(3)
M1	Ti + Cr	0.011(2)	0.005(1)
M1	Mg	0.179(2)	0.283(3)
M1	Fe	0.052(2)	0.036(1)
M2	Ca	0.286(4)	0.387(8)
M2	Na	0.601(14)	0.579(7)
M2	Mg	0.026(2)	0.016(3)
M2	Fe	0.019(2)	0.000(1)
M2	Vac.	0.065(12)	0.017(5)

Note: Estimated errors in the last figure are shown in parentheses.

* Estimated from 18 microprobe analyses, X-ray structure refinements, and ALCHEMI measurements (McCormick, 1986).

** Estimated from five microprobe analyses. All Fe is assumed to be in M1.

The diamond cell used for this study was a standard Merrill-Bassett type as described by Hazen and Finger (1982). An Inconel gasket with a 350-μm hole was used, and the pressure medium was a 4:1 methanol : ethanol mixture that remains hydrostatic to pressures well in excess of those achieved in this experiment (Piermarini et al., 1973). The pressure was measured both before and after each set of cell determinations by using the shift of the R1 fluorescence line from several small ruby chips included in the cell.

The only modifications to standard single-crystal diamond-cell techniques were made because of the need to identify reflections from three crystals of very similar lattice parameters. This identification was achieved by loading one crystal at a time onto just one half of the cell plus the Inconel gasket. The crystal(s) and gasket were held in place by a smear of petroleum jelly applied to the face of the diamond anvil. After addition of each crystal the half-cell was mounted on a precession camera and a precession photograph was taken ($\mu = 15°$) with unfiltered Mo radiation. Comparison of successive photographs identified the crystal to which strong low-angle reflections belonged. In mounting the three crystals, it is important to load each crystal as close to the center of the cell as possible, without moving the previously mounted crystals, in order to reduce centering errors in the diffractometer.

With all three crystals loaded, the half-cell was transferred to an automated Picker four-circle diffractometer with a Mo tube ($K\alpha_1$ wavelength = 0.7093 Å). Several low-angle reflections from each crystal were found with

Table 3. Unit-cell parameters of diopside and omphacites at various pressures

	1 bar	14 kbar	24 kbar	34 kbar	47 kbar	60 kbar
Diopside						
a	9.7479(5)	9.7125(7)	9.6895(7)	9.6625(8)	9.6360(9)	9.6127(12)
b	8.924(1)	8.884(2)	8.855(2)	8.822(2)	8.794(2)	8.757(4)
c	5.2499(4)	5.2302(5)	5.2186(5)	5.2031(8)	5.1876(7)	5.1758(11)
β	105.823(5)	105.655(8)	105.556(7)	105.448(9)	105.356(10)	105.266(13)
V	439.38(6)	434.57(8)	431.36(8)	427.63(10)	423.88(11)	420.30(18)
$V - V_0$		−4.81(10)	−8.02(10)	−11.75(12)	−15.50(12)	−19.08(19)
$(V - V_0)/V_0$		−0.0109(2)	−0.0183(2)	−0.0267(3)	−0.0353(3)	−0.0434(4)
V/V_0		0.9891(2)	0.9817(2)	0.9733(3)	0.9647(3)	0.9566(4)
SBB-1 omphacite (vacancy rich)						
a	9.5000(10)	9.4680(9)	9.4440(10)	9.4169(7)	9.3900(10)	9.3614(19)
b	8.657(1)	8.624(2)	8.606(2)	8.581(1)	8.555(3)	8.515(4)
c	5.2413(8)	5.2237(5)	5.2122(7)	5.1974(5)	5.1822(9)	5.1669(14)
β	107.240(10)	107.107(8)	107.030(10)	106.916(6)	106.820(10)	106.662(18)
V	411.70(10)	407.65(9)	405.08(11)	401.80(6)	398.50(14)	394.55(19)
$V - V_0$		−4.05(13)	−6.62(15)	−9.90(12)	−13.20(17)	−17.15(21)
$(V - V_0)/V_0$		−0.0098(3)	−0.0161(4)	−0.0240(3)	−0.0321(4)	−0.0417(5)
V/V_0		0.9902(3)	0.9839(4)	0.9760(3)	0.9679(4)	0.9583(5)
SDC-1 omphacite (vacancy poor)						
a	9.525(2)	9.491(2)	9.469(1)	9.445(3)	9.415(2)	9.392(2)
b	8.683(5)	8.657(5)	8.640(3)	8.618(9)	8.591(5)	8.555(4)
c	5.239(1)	5.225(2)	5.213(1)	5.199(2)	5.183(1)	5.170(2)
β	107.01(2)	106.89(2)	106.79(1)	106.68(3)	106.60(2)	106.51(2)
V	414.33(24)	410.81(26)	408.29(16)	405.39(44)	401.74(25)	398.32(21)
$V - V_0$		−3.52(35)	−6.04(29)	−8.94(50)	−12.59(35)	−16.01(32)
$(V - V_0)/V_0$		−0.0085(9)	−0.0146(7)	−0.0216(12)	−0.0304(8)	−0.0386(8)
V/V_0		0.9915(9)	0.9854(7)	0.9784(12)	0.9696(8)	0.9614(8)

Note: Estimated errors in the last figure are shown in parentheses. V_0 and *V* refer to cell volume at 1 bar and to cell volume at elevated pressure, respectively.

the aid of the precession photographs. Orientation matrices were calculated from these initial reflections, and cell dimensions were determined from higher-angle reflections. The pressure fluid and the second half of the cell were not added until after room-pressure cells of all three crystals had been determined. Unit-cell parameters were determined at all pressures by constrained vector least-squares fit to the setting angles of 9 to 12 reflections ($35° < 2\theta < 45°$) from each crystal, measured by the method of King and Finger (1979) to eliminate effects of zero and crystal-centering errors.

RESULTS

Microprobe analyses and end-member calculations (Smyth, 1980) for each of the three crystals are presented in Table 1, and estimated site occupancies for the two omphacites are reported in Table 2. The site occupancies were estimated from microprobe analyses for SDC-1 and from a combination of electron microprobe, X-ray diffraction, and ALCHEMI results (McCormick, 1986) for SBB-1. Measured cell parameters at the various pressures are presented in Table 3. Variation of cell parameters with pressure is shown in Figure 2. Error estimates of 2 kbar in pressure determination are assumed in order to account for differences between our diopside data and those of Levien and Prewitt (1981). Linear regression applied to these measurements yields the linear compressibilities listed in Table 4. Pyroxene bulk moduli, calculated by fitting pressure-volume data to a Birch-Murnaghan equation of state with a pressure derivative (*K*′) of 4.0, are also given in Table 4. All three pyroxenes show compressibility along **b** to be greater than along **c**, with the least-compressible direction parallel to **a** sin β.

Relative changes in unit-cell volume with pressure are shown in Figure 3. The diopside is more compressible than omphacite, consistent with the stiffer bulk modulus of jadeite calculated by Kandelin and Weidner (1988b). There is a significant difference in the compression of the two omphacites, with the vacancy-rich pyroxene (SBB-1) being more compressible than the vacancy-poor pyroxene (SDC-1).

Table 4. Linear and volume compressibilities (Mbar^{-1}) and bulk moduli (Mbar) of clinopyroxenes

	Diopside*	SBB-1*	SDC-1*	Diopside**	Jadeite**
a sin β	0.194(5)	0.200(3)	0.191(4)	0.22	0.22
b	0.317(7)	0.259(6)	0.248(11)	0.40	0.24
c	0.247(7)	0.243(8)	0.226(6)	0.31	0.24
V	0.749(15)	0.696(12)	0.651(10)		
K†	1.22(2)	1.29(3)	1.39(4)	1.14(4)	1.43(2)

* Calculated from weighted linear regression of all pressure vs. unit-cell data. Second-order (P^2) terms are less than 2σ for all parameters.

** Calculated from elastic compliances of Levien et al. (1979) for diopside and from those of Kandelin and Weidner (1988b) for jadeite.

† Bulk moduli are calculated from least-squares fit of pressure vs. volume data to a Birch-Murnaghan equation of state (*K*′ assumed to be 4.0).

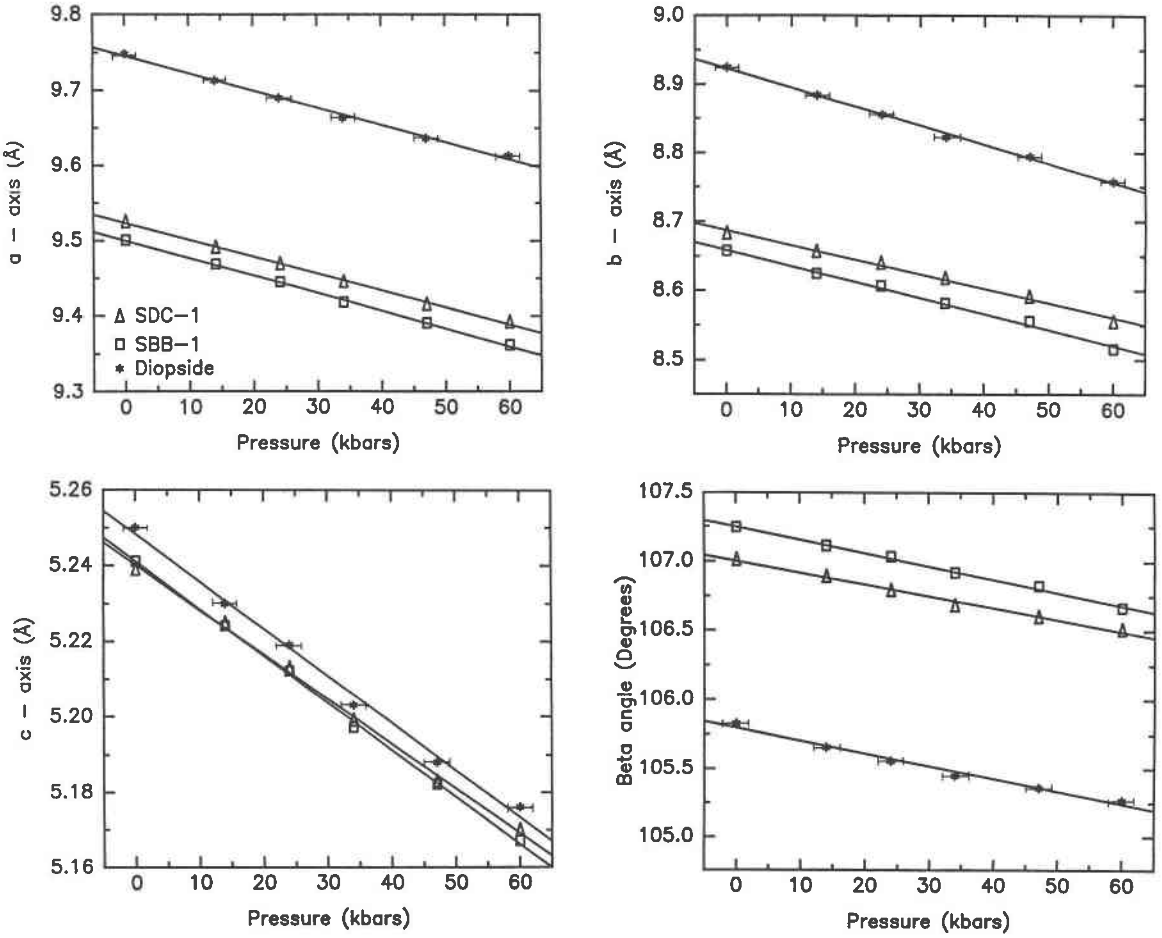

Fig. 2. Variation of pyroxene unit-cell parameters with pressure. Error bars of ±2 kbar on pressure determinations are shown on the diopside curve; symbol size exceeds estimated errors on cell parameters.

Discussion

Are differences in compressibilities of the two omphacites due to vacancies or some other compositional feature? The most significant difference in composition (Table 2) is in the vacancy content: 6.5% in SBB-1 compared with 1.7% in SDC-1. The other major differences are that SBB-1 has more M-site Al and correspondingly less Mg in M1 and less Ca in M2 than SDC-1. This implies that SDC-1 actually has more of the diopside component and therefore should be slightly *more* compressible than SBB-1 were it not for the vacancies. SDC-1 has very slightly more Al in the T site. This difference would tend to affect the *c* parameter most strongly (McCormick, 1986), although no inferences can be made on the magnitude of the effect based on our current data.

For many structures, the thermal-expansion behavior is the inverse of the compressibility. This inverse behavior is shown to be qualitatively true for the pyroxenes examined in this study by comparing the compressibilities with end-member thermal-expansion measurements of Cameron et al. (1973). Diopside is much more compressible than omphacite and also has a much higher volume thermal expansion than jadeite. In addition, diopside shows expansion of $b > c > a \sin \beta$, which mimics the order of compressibilities in diopside and omphacite. Jadeite, however shows thermal expansion of $b > a \sin \beta > c$.

The compressibilities measured in this work may be compared to elastic moduli measured by single-crystal Brillouin spectroscopy. The linear compressibility in any particular direction in the crystal is directly related to the elastic compliances (Nye, 1957). In the case of monoclinic pyroxenes, the linear compressibilities are given by

$$\beta_1 = S_{11} + S_{12} + S_{13}$$
$$\beta_2 = S_{12} + S_{22} + S_{23}$$
$$\beta_3 = S_{13} + S_{23} + S_{33},$$

where the S_{ij} values are the elastic compliances and β_1, β_2, and β_3 are the adiabatic linear compressibilities parallel to **a** sin β, **b**, and **c**. These compressibilities have been calculated from the elastic compliances reported for diopside (Levien et al., 1979) and jadeite (Kandelin and

Weidner, 1988b) and are included in Table 4 for comparison. No corrections were made from adiabatic to isothermal compressibilities as these corrections are much less than the experimental uncertainties.

The measured isothermal linear compressibilities of all three crystals studied here are less than or equal to the values calculated from elasticity data for jadeite and diopside. Brillouin spectroscopy reveals compressibilities at room pressure; our values are averaged over 0–60 kbar, and the expected negative curvature of cell parameters with pressure will decrease the calculated average linear compressibility. The errors on pressure measurements, coupled with only six pressure-volume data points for each crystal, preclude meaningful calculation of this curvature. However, in terms of relative axial compressibilities, our data agree with data from Brillouin experiments.

Kandelin and Weidner (1988a) have argued that the axial compression in clinopyroxenes depends on the M-site chemistry: in Ca-rich pyroxenes, the M2 sites support the structure in the **a*** direction, whereas in Na-rich pyroxenes, the elastic properties are most strongly dependent on the chemistry of the M1 site. However, current data are insufficient to allow prediction of the elastic behavior of intermediate compositions based on M-site chemistry. The β_2 parameter, which is related to the off-diagonal elastic moduli c_{12} and c_{23}, is most sensitive to M-site chemistry (Kandelin and Weidner, 1988a) and varies the most among our samples.

CONCLUSIONS

Measured compressibilities of two omphacites and diopside indicate that omphacite ($\sim Jd_{58}$) is much less compressible than diopside, owing to the presence of the stiffer, less-compressible jadeite component in solid solution. The multicrystal, high-pressure mount enabled measurement of *relative* compressibilities of the two omphacites with three orders of magnitude greater accuracy than comparison of absolute compressibilities of the crystals determined in different experiments, because precision of unit-cell measurement is much higher than absolute pressure determination. Significantly higher compression was noted in vacancy-bearing omphacite than in nearly stoichiometric omphacite of otherwise similar composition. This observation is consistent with the conclusion that the vacancy-bearing pyroxenes are stabilized by pressure.

The **b** unit-cell direction is the most compressible, followed by **c** and **a** sin β. The **b** direction also has the highest thermal expansion, reflecting the inverse relation between compression and thermal expansion that has been observed in many structures (Hazen and Finger, 1982).

Although attempts were made to model the high-pressure structures by distance–least-squares (DLS) methods, in general the errors are too large to draw any conclusions regarding the differences between the stoichiometric and nonstoichiometric pyroxene structures. High-pressure structure refinements are necessary in order to determine the structural effects of increasing pressure on the jadeite and Ca-Eskola substitutions in clinopyroxene.

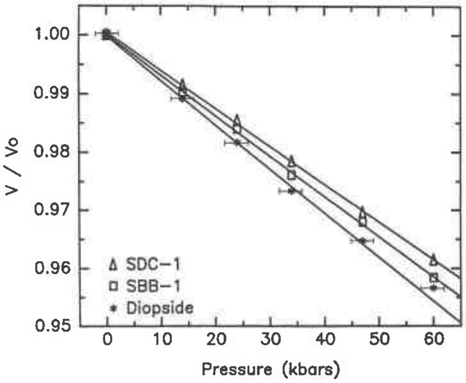

Fig. 3. Volume compression of clinopyroxenes as a function of pressure. Error bars of ±2 kbar on pressure determinations are shown on the diopside curve; symbol size exceeds estimated errors on V/V_0.

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