

Thermal pressure in the laser-heated diamond-anvil cell: An X-ray diffraction study

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Abstract: Using X-ray diffraction with synchrotron radiation, we have studied the pressure changes induced by laser heating on samples compressed in a diamond-anvil cell. The method has been to compare experimentally observed phase transitions of Mg₂SiO₄ and SiO₂ polymorphs with well-constrained phase diagrams and equations of state reported in the literature. Our results clearly demonstrate an increase of pressure in the laser hot spot with respect to the nominal pressure measured from the ruby fluorescence at room temperature. At 2200 ± 100 K, for instance, wadsleyite has been synthesized from forsterite at a nominal pressure of 11 GPa, which is 4 GPa lower than the reported transition pressure. In addition, the measured high-pressure, high-temperature molar volumes of forsterite and wadsleyite appear much smaller than those calculated from available thermoelastic data. Taking into account this pressure increase, we reconcile conflicting experimental determinations of the coesite-stishovite transition made with multi-anvil press and diamond-anvil cell. The pressure change induced by laser heating is a function of the product of the thermoelastic coefficients α (thermal expansion) and K_T (bulk modulus) of the sample. We thus stress the need for an internal pressure standard, such as Pt, Au or MgO for determining equations of state and phase equilibria under the P-T conditions prevailing in the Earth's mantle and core.

Key-words: diamond-anvil cell, laser heating, diffraction, thermal pressure, high-pressure phases, SiO₂, Mg₂SiO₄.

Introduction

Experiments performed in the laser-heated diamond-anvil cell (DAC) have played an important role in deciphering the constitution and physical properties of the Earth's deep interior. A major milestone was the first synthesis of what appears to be the Earth's most abundant mineral, namely (Mg,Fe)SiO₃-perovskite (Liu, 1974). In addition to being used extensively for mineral syntheses, the DAC has proven to be a convenient tool for determining physical properties and equations of state up to more than 100 GPa. For silicate perov-

skites or even iron alloys, these measurements have now been made up to pressures higher than that of the core-mantle boundary (Knittle & Jeanloz, 1989; Mao *et al.*, 1990; Boehler, 1993). A most satisfying aspect is the good agreement found between bulk moduli determined at room temperature in this way for (Mg,Fe)SiO₃ perovskite and those obtained at lower pressures with techniques such as X-ray diffraction in a multi-anvil press (Funamori & Yagi, 1993; Wang *et al.*, 1994; Utsumi *et al.*, 1995) or Brillouin scattering (Yeganeh-Haeri, 1994).

In contrast, considerable discrepancies are a major feature of the reported observations made at high temperatures with laser-heated DAC. For instance, published melting temperatures of MgSiO_3 perovskite vary from 2500 to 4000 K at 50 GPa (Knittle & Jeanloz, 1989; Zerr & Boehler, 1993). As this melting curve represents an upper bound to the geothermal gradient in the lower mantle, such discrepancies have considerable geophysical implications. Improvements have been made regarding temperature measurements. Despite the difficulties associated with the steep pressure and temperature gradients present in the DAC, the actual uncertainties of temperatures determined from thermal emission spectra of the samples are lower than 150 K (Shen & Lazor, 1995). Still, important results using laser-heated DAC remain controversial, as for example the SiO_2 phase diagram reported by Serghiou *et al.* (1995) in apparent disagreement with multi-anvil experiments (Zhang *et al.*, 1993, 1996).

Beside the increase in accuracy of the temperature measurements, little has been done to investigate the pressure changes during laser heating in the DAC. Because the chamber volume is tightly constrained, partial isochoric heating could produce a pressure increase in the sample chamber. Heinz (1990) calculated that pressure increases of 40–60% of the thermodynamic values could result in an elastic medium. He also suggested that thermal pressure could relax and that X-ray diffraction experiments with synchrotron radiation could be used to resolve the effects of relaxation and pressure increase. A recent paper using *in situ* X-ray diffraction (Fiquet *et al.*, 1996) indeed indicates that significant increase of pressure could occur in the laser hot-spot.

In this work, our main aim was to make use of well-known phase transformations and thermoelastic parameters of Mg_2SiO_4 and SiO_2 polymorphs to investigate the physical conditions prevailing in a laser-heated DAC. More specifically, we have investigated possible pressure changes upon heating from comparisons with reference data and thermodynamic models, taking into account the accuracy of both pressure and temperature measurements. To avoid possible pitfalls besetting the optical observations made in previous phase-equilibria studies in DAC, we have used X-ray diffraction to detect phase transformations and also to obtain quantitative information on volume changes during laser heating at high pressure.

Experiments

We used a membrane diamond-anvil cell with a large optical aperture (Chervin *et al.*, 1995) mounted with type IIa diamond anvils with 500- μm culets. The starting materials were pure synthetic pressed polycrystalline discs for forsterite and finely polished single crystals for quartz. Samples 15–20 μm thick were loaded in the 200 μm hole drilled in stainless-steel gaskets pre-indented to a thickness of 60 μm . High-purity dry argon was introduced cryogenically before closing the pressure chamber to obtain a cell assembly similar to those used by Fiquet *et al.* (1996).

All experiments were made at the ID9-BL3 beam line of the European Synchrotron Radiation Facility (Grenoble, France). Energy-dispersive X-ray diffraction patterns were typically recorded in 3 minutes with a Canberra pure Ge solid-state detector between 7 and 100 keV at a 2θ angle of 6.808° , as determined from the reflections of MgO , gold and copper standards. A sample-detector distance of about 1 m, a 100- μm detector entrance slit and 2 stages of 2θ defining slits were used to obtain a resolution close to the theoretical limit of the detector (about $5 \cdot 10^{-3}$). The X-ray beam was collimated to $20 \cdot 20 \mu\text{m}^2$ by two slit stages, *i.e.*, to a size much smaller than that of the hot spot (typically 60–70 μm in diameter) obtained by focusing of the 120 W sealed-tube wave guide CO_2 laser on the sample. This difference in size minimizes the thermal gradient across the hot-spot volume sampled by the X-ray beam.

Pressures and temperatures were measured with the optical set-up described elsewhere (Fiquet *et al.*, 1996). Pressures (referred to as *nominal pressures* in the following) were measured before and after heating from the fluorescence emission of ruby grains placed at the edge of the gasket hole. We considered as reliable only those experiments for which the ruby pressure was similar before and after laser heating. When the pressure changed, the chamber volume had varied and we could not define a nominal pressure. We also recorded during heating the fluorescence of a ruby chip away from the hot spot (see Fiquet *et al.*, 1996), and only observed a moderate increase (about 0.5 GPa) of the ruby pressure. We believe that such a measurement cannot reveal any pressure change in the sample during the laser heating for the simple reason that the ruby grains were not placed where such an effect can appear (*i.e.* inside the laser hot spot).

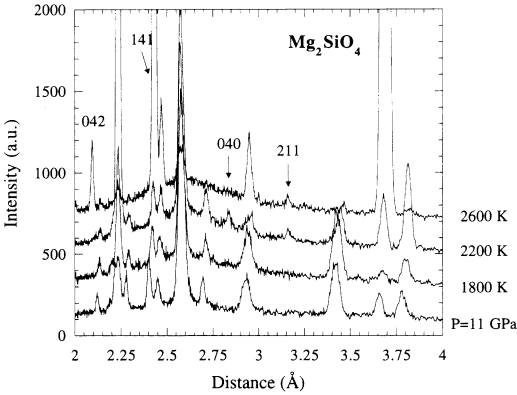


Fig. 1. Diffraction patterns of laser-heated forsterite at a nominal pressure of 11 GPa showing at 2600 K partial transformation to wadsleyite, as evidenced by its 042, 141, 040 and 211 Bragg reflections.

Neglecting the pressure and temperature dependencies of the emissivity, we calculated temperatures from least-squares fits of the data to Wien's approximation of Planck's radiation function (Heinz & Jeanloz, 1987; Boehler & Chopelas, 1991). The spectral response of the optical system was determined from the thermal emission of forsterite heated at its melting point with a heating-wire cell (Richet *et al.*, 1993). To monitor possible temperature variations, we recorded up to 10 black-body spectra while acquiring the diffraction patterns. Within the small X-ray-diffracting zone of the sample, major temperature or pressure gradients were absent as indicated by the fact that the widths of the reflections were identical to the room pressure and temperature values (see Fig. 1, as well as Fig. 4 and 5).

Results

Equations of state

We recorded the diffraction patterns of either forsterite or wadsleyite (also called β -spinel) as a function of temperature at nominal ruby pressures of 6.5 to 22 GPa. In both cases, 6 to 12 reflections with d -spacing ranging from 1.8 to 5.2 Å were used for orthorhombic cell-parameter calculations. The measured volumes and temperatures were obtained with errors smaller than 0.5% and 150 K, respectively. The experimental thermal expansion

Table 1. Mean experimental volume expansion [$\Delta V/(V\Delta T)$] calculated from the X-ray diffraction results (on single phases only).

	Nominal pressure (GPa)	Number of HT measurements	Mean α 10^6 K^{-1}
Forsterite	6.8	4	11.4
	7.5	4	14.4
	9.8	5	10.1
	10.0	5	9.8
Wadsleyite	14.2	5	6.4
	18.0	3	6.0
	20.5	2	2.7
	22.0	1	3.0

decreases with increasing nominal pressure (Table 1, Fig. 2), as expected from the negative value of $(\partial K_T/\partial T)_P$ of forsterite (see Table 2). However, the volumes measured at high temperature appear far too low compared to the values calculated for the given nominal pressures and temperatures from:

$$\left(\frac{\partial \alpha}{\partial P}\right)_T = \frac{1}{K_T^2} \left(\frac{\partial K_T}{\partial T}\right)_P \text{ with } \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad (1)$$

Where K_T is the isothermal bulk modulus obtained from the literature (Table 2).

For forsterite, the measurements yield a relative volume change [$\Delta V/(V\Delta T)$] of about $14 (\pm 2) \cdot 10^{-6} \text{ K}^{-1}$ at 6.5 GPa. The disagreement is obvious with the mean thermal expansion of $\alpha = 30 \cdot 10^{-6} \text{ K}^{-1}$, calculated at the same pressure between 300 to 2500 K from available thermoelastic parameters (Anderson *et al.*, 1991). Likewise, we obtain an experimental relative volume change (slope in Fig. 2) of $6 (\pm 1) \cdot 10^{-6} \text{ K}^{-1}$ for wadsleyite at 14.2 GPa, which is at variance with $\alpha = 15 \cdot 10^{-6} \text{ K}^{-1}$ as calculated from the data of Table 2. We thus conclude that the molar volumes are not those expected for these minerals, an effect similar to that reported for MgO by Fiquet *et al.* (1996). As mentioned in that study, this effect cannot be accounted for by errors in either the temperature or volume measurements, but points instead to a pressure increase in the hot part of the sample during experiments.

Table 2. Summary of thermoelastic parameters.

	α^* (10^6 K^{-1})	K_{T0} (GPa)	K'	$(\partial K_T / \partial T)_P$ (GPa/K)	θ_D (K)	γ	αK_T (MPa/K)
forsterite ¹	39.5	129	4.0	-0.024	762	1.15	4.4
wadsleyite ²	37.7	174	4.0	-0.027	952	1.30	5.3
quartz ³	24.0	37	6.4	-	570	0.66	2.3
coesite ⁴	7.5	96	8.4	-	675	0.33	1.5

* Mean thermal expansions between 300 to 2000 K. For quartz, the calculation takes into account the volume change of the α to β phase transition. High-temperature values: ¹Anderson *et al.* (1991), ²Suzuki *et al.* (1980) and Fei *et al.* (1992). γ is calculated assuming $C_v = 3nR$ at 2000 K. This value agrees with $\gamma = 1.26$ as determined by Suzuki *et al.* (1980). ³Dorogokupets (1995), Kuskov & Fabrichnaya (1987). ⁴Kuskov & Fabrichnaya (1987) and Swamy & Saxena (1994).

Mg₂SiO₄ polymorphs

To probe better the increase of pressure in the laser hot spot, we performed *in situ* analysis of the phase transformation between the Mg₂SiO₄ polymorphs. According to the Mg₂SiO₄ phase diagram reported in Fei *et al.* (1990), due to the positive slope of the phase boundary, the forsterite is expected to transform into wadsleyite above about 14, 15, and 16 GPa for temperature of 1800, 2200 and 2600 K, respectively. When heating forsterite above 2200 ± 100 K with a CO₂ laser, however, we observed the 042, 141, 040 and 211 reflections of wadsleyite at a nominal room-temperature ruby-fluorescence pressure as low as 11.0 ± 0.7 GPa (Fig. 1). Other intense reflections of the β -phase were also present, but superimposed on those of forsterite. This partial transformation of

forsterite into wadsleyite is quite unexpected since forsterite should be stable up to around 15 GPa for this temperature. Hence, it indicates that the pressure in the heated part of the sample was about 4 GPa higher than the nominal pressure. Other experiments made at a starting nominal pressure of 13 ± 0.8 GPa also yielded a mixture of forsterite and wadsleyite above 1800 K, and pure wadsleyite was obtained only after heating at a higher nominal pressure of 14.2 ± 1 GPa. The forsterite to wadsleyite transition may thus act as a pressure buffer, with the 8 % volume decrease of the transition counterbalancing the pressure increase in the heated sample. Interestingly, we did not observe pure γ -spinel, probably because most experiments were made at too high temperatures for it to be stable.

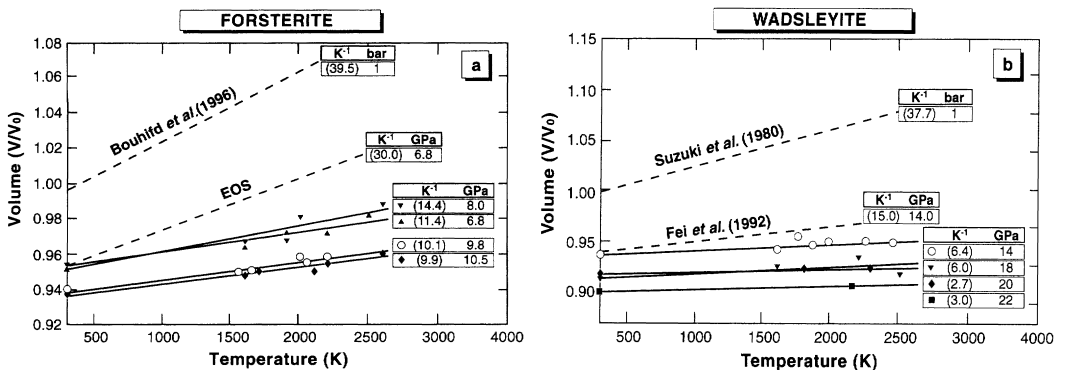


Fig. 2. Thermal expansion of forsterite (a) and wadsleyite (b) upon heating at various nominal pressure in the DAC (symbols and solid lines). We also reported those obtained at room pressure and calculated at 6.8 and 14 GPa for forsterite and wadsleyite, respectively, using the EOS given in the text and the parameters of Table 2 (dotted lines). For each series of experiments, the relative volume change $[\Delta V / (V \Delta T)]$ (K^{-1}) and nominal pressure (GPa) are given. The data point at 22 GPa nominal pressure was recorded just before decomposition of wadsleyite into perovskite and periclase.

SiO₂ polymorphs

The SiO₂ phase diagram (Fig. 3) also represents a useful reference to investigate pressure changes during the laser heating. With a quartz single crystal recovered after heating at 1840 ± 100 K at a nominal pressure of 2.0 ± 0.3 GPa, 3 weak quartz reflections were observed in the diffraction pattern in addition to those of argon. At 2210 ± 100 K, 9 reflections of quartz were observed along with 8 lines of coesite, showing that the transformation of quartz to a polycrystalline sample was accompanied by partial transformation to coesite (Fig. 4), although isobaric laser heating should keep the sample in the quartz stability field at this nominal pressure of 2.0 GPa. Indeed, according to the phase diagram (Fig. 3), minimum pressures of 3.7 and 3.9 GPa at 1840 and 2210 K, respectively are required to form coesite. Hence, pressure in the hot sample must again have been higher than the nominal one; the pressure increase is smaller than 1.7 GPa at 1840 K and is at least 1.9 GPa at 2210 K, whereas the 12 % volume decrease of the transformation also acts as a pressure buffer.

After having completely transformed quartz into coesite at 5.2 GPa, coesite was compressed to 9.2 ± 0.5 GPa before being again laser-heated. Up to 2120 K, the reflections of only coesite and crystalline argon were present in the diffraction patterns. After heating at 2475 ± 100 K (Fig. 5),

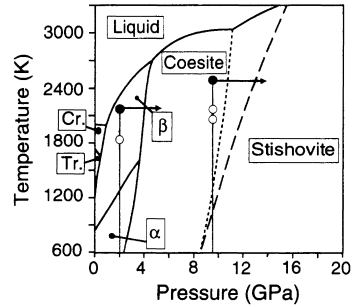


Fig. 3. Calculated phase diagram (solid lines) of the SiO₂ polymorphs after Swamy & Saxena (1994). Tr., Cr., α and β stand for tridymite, cristobalite, α-quartz and β-quartz, respectively. Note the disagreement between the coesite-stishovite phase boundary as determined at high temperature with a laser-heated diamond-anvil cell (Sergiou *et al.*, 1995; dotted line) and multi-anvil apparatus techniques (Zhang *et al.*, 1993, 1996; dashed line). Our results are represented by open circles which stand for runs where only quartz (2.0 GPa nominal pressure) and coesite (9.2 GPa nominal pressure) were found, whereas solid circles represent runs where mixtures of quartz-coesite or coesite-stishovite were observed.

the 7 most intense reflections of stishovite were observed, namely 101, 111, 210, 211, 220, 002 and 301, corresponding to interplanar distances from 2.4 to 1.2 Å. Complete transformation to sti-

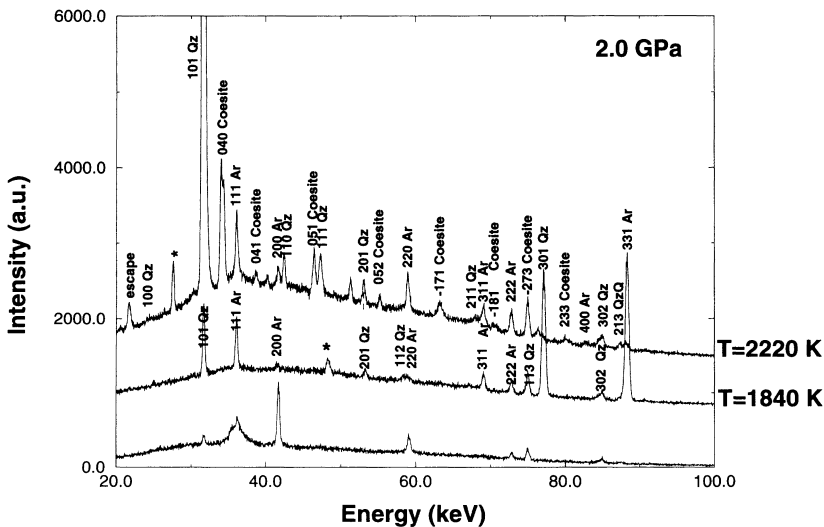


Fig. 4. Evolution of the diffraction patterns of quartz after heating to increasingly high temperatures at a nominal pressure of 2.0 GPa. Partial transformation to coesite, evidenced by the presence of 8 characteristic Bragg lines, is observed at temperatures higher than 2210 K. * stands for diffraction of sample environment.

shovite was observed as nominal pressure was eventually increased to 14.6 GPa. As shown in Fig. 3, these results are similar to recent DAC data (Serghiou *et al.*, 1995) and confirm the apparent disagreement with multi-anvil experiments which yield a phase boundary at higher pressures (Zhang *et al.*, 1993, 1996).

Discussion

Pressure increase

The basic question is in fact that of the stresses experienced by the sample while being heated in the DAC. It is usually assumed implicitly that isobaric conditions are achieved in a quasi-hydrostatic environment, that is, the pressure-transmitting medium relaxes the thermal pressure generated on heating. Simple calculations indicate, however, that a pressure increase in excess of 10 GPa can be produced within a laser-heated sample (Heinz, 1990). In this case, the experimental conditions would be closer to isochoric. However, the sample was not loaded in this study as modeled by Heinz. The sample was surrounded by molten argon, which probably resulted in a more homogeneous sample heating. Nevertheless, the important question is whether the cold pressure-transmitting medium (surrounding the molten argon) was able to relax the thermal pressure created in the hot zone.

Let us first calculate the pressures that would bring the measured volumes in agreement with the values derived from the thermoelastic data listed in Table 2. As made previously for MgO (Fiquet *et al.*, 1996), we use a simple equation of state (EOS), *viz.*:

$$P(V, T) = P(V, 300) - \frac{\gamma}{V} E_{th}(300) + \frac{\gamma 3nRT}{V} \quad (2)$$

where n is the number of atoms per formula unit, $E_{th}(300)$ the thermal energy at 300 K calculated from a simple Debye model, and γ the Grüneisen parameter which, for simplicity reasons, is assumed to be constant. In eq. (2), $P(V, 300)$ is calculated with a Birch-Murnaghan equation of state and $E_{th}(T)$ can be taken as $3nRT$ since all experiments were made much above the Debye temperatures of the minerals. The pressures calculated with eq. (2) are compared with the pressures obtained from the ruby fluorescence in Fig. 6. Clearly, the differences between these two pres-

ures correlate linearly with the run temperatures, with a slope of $3.4 \cdot 10^{-3}$ and $4.7 \cdot 10^{-3}$ GPa/K for forsterite and wadsleyite, respectively.

As a limiting case, we also calculated the thermal pressures that would be obtained if heating were isochoric, *i.e.*, assuming $V(T) = V(300 \text{ K})$ in eq. (2). The thermal pressure would then increase with temperature by $5.2 \cdot 10^{-3}$ and $6.5 \cdot 10^{-3}$ GPa/K for forsterite and wadsleyite, respectively. Hence, the actual pressure increase responsible for the low volume expansion found in this study represents about 65 and 72 % of the isochoric values. For instance, without formation of wadsleyite a pressure increase of 18.5 GPa could develop at 2500 K in forsterite initially compressed at 11.0 GPa. Such a pressure increase is compatible with the phase transformation observed during laser heating of forsterite at 11 GPa (Fig. 1).

Reconciling our observations with the well-established quartz-coesite boundary (Fig. 3) requires a pressure rise of about 1.9 GPa in quartz heated to 2210 K at a nominal pressure of 2.0 GPa. This figure corresponds to a rate of pressure increase of $1.0 \cdot 10^{-3}$ GPa/K. Using again eq. (2) for SiO_2 polymorphs, and neglecting the small differences in thermoelastic parameters between α - and β -quartz, we calculate that pressure increases of 3.4 and 4.2 GPa would develop at 1800 and 2210 K under isochoric conditions. Comparing this slope of $1.9 \cdot 10^{-3}$ GPa/K with that of $1.0 \cdot 10^{-3}$ GPa/K derived from our experimental results, we conclude that the actual pressure increase would represent about 53 % of the isochoric value.

From this conclusion, the controversy between DAC and multi-anvil determinations of the coesite-stishovite is readily resolved. Serghiou *et al.* (1995) and Zhang *et al.* (1993, 1996) reported linear variations with temperature of the transition pressure, namely, $6.5 + 0.0022 \text{ T}(\text{°C})$ and $8.1 + 0.001 \text{ T}(\text{°C})$, respectively. The pressure discrepancy is thus 0.44 and 1.04 GPa at 2000 and 2500 K, respectively. With eq. (2) and the parameters of Table 2, we calculate that their phase-boundary determinations agree if a pressure increase of 36 % of the isochoric thermal pressure is considered in the laser-heating experiment.

Thermal pressure relaxation

In summary, we observed that pressure increases in laser-heated minerals depend on the mineral. About 36 and 72 % of the isochoric thermal pres-

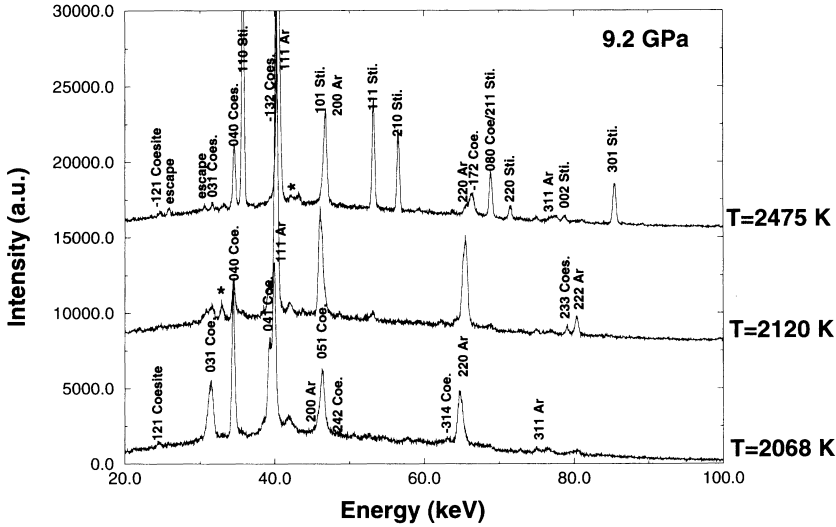


Fig. 5. Diffraction patterns showing the transformation at a nominal pressure of 9.2 GPa of coesite into stishovite, for which 7 reflections are observed after heating to 2475 K. * stands for diffraction of sample environment.

pressures were developed in coesite and wadsleyite, respectively. In fact, this percentage varies as a function of the product αK_T of the phase (Fig. 7, Table 3). This suggests that, for a similar heating (ΔT), the pressure increase is less well relaxed throughout the sample chamber when the thermal pressure ($\alpha K_T \Delta T$) is the highest. The reason lies probably in the deformation properties of the solid

pressure-transmitting medium, which is submitted to a strong temperature gradient for each particular heating ΔT . As suggested by the correlation drawn in Fig. 7, isobaric conditions would be achieved for the limiting case $\alpha K_T = 0$. In contrast, with a very large αK_T , large thermal pressures cannot be relaxed and the conditions become close to isochoric.

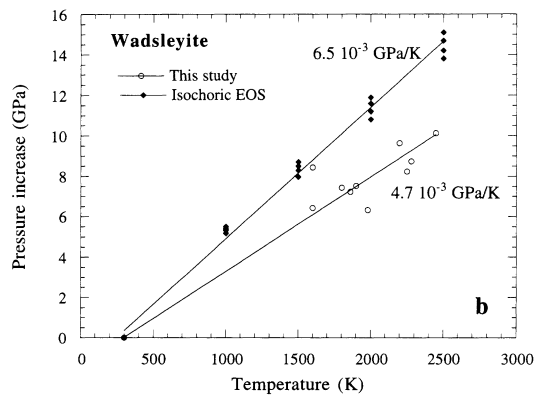
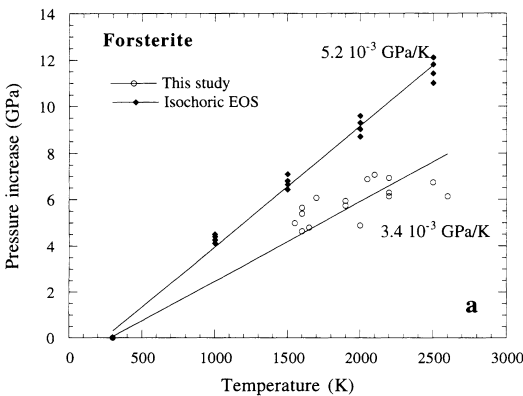


Fig. 6. Comparison of the pressure increases (open circles) needed to account for the too low high-temperature experimental volumes for forsterite (a) and wadsleyite (b), with thermal pressure calculated for isochoric equation of states at various temperatures and for nominal pressures between 1 bar and 15 GPa or 10 and 25 GPa for forsterite or wadsleyite, respectively (solid diamonds). Number indicates slopes (GPa/K). Pressure increases of about 65 and 72 % of the isochoric values are established during laser heating of forsterite and wadsleyite, respectively (Table 3).

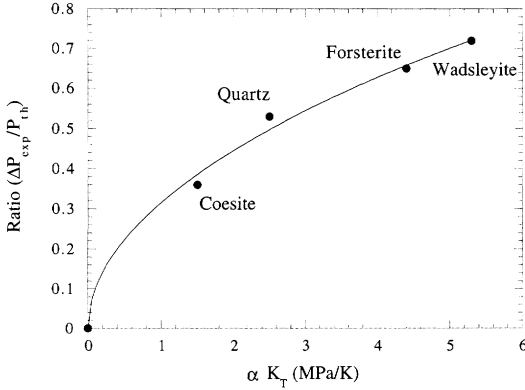


Fig. 7. Ratios of the experimental pressure increases (ΔP_{exp}) over isochoric thermal pressure value (P_{th}) as a function of αK_{T} for various heated material (see text). The correlation indicates that the thermal pressure is less well relaxed throughout the pressurized sample when the thermal pressure ($\alpha K_{\text{T}} T$) is the highest. For a given experimental time, stiffer materials are less relaxed than softer materials.

Experimental conditions

Consistent with our own observations that argon was molten around the sample at high temperatures (Fiquet *et al.*, 1996), molecular dynamic simulations (Belonoshko, 1992) indicate that the melting temperature of argon increases from 700 to 1600 K between 5.3 and 18.7 GPa. Argon therefore produces a convenient hydrostatic pressure on the sample, in all the molten zone. In this pressure interval, argon melting is associated with a volume increase of only 2–3%; however, such a moderate increase could have significant consequences because it is similar to the expansion of minerals between 300 and 2000 K. Assuming a linear temperature gradient between the cold diamonds and the hot, 20- μm thick sample enclosed

in the 40- μm thick gasket, we estimate that the volume of melting of argon should represent less than one third of that of the heated sample. Hence, the effects of argon melting should be smaller than those of intrinsic thermal pressure of the sample. Experiments with other rare gases (with different melting volumes) would be useful to assess more precisely the relative importance of the sample thermal pressure and melting of the pressure-transmitting medium. In addition, the pressure increase developed in the hot zone (sample plus molten medium) could be more efficiently relaxed with a softer pressure-transmitting medium. Hence, the correlation apparent in Fig. 7 should be used only for samples with a similar cell configuration (using argon), and as a guide for assessing the pressure increase encountered during the laser heating in other pressure media.

Conclusion

Contrary to the assumption usually made, our phase-equilibria results as well as our high-temperature compression data for forsterite and wadsleyite clearly demonstrate that isobaric conditions are not maintained on laser heating in a DAC, corroborating preliminary results obtained for the equation of state of periclase (MgO) (Fiquet *et al.*, 1996) and Heinz (1990) calculations. Regardless of their origin, the pressure changes observed when a sample is laser-heated in a diamond-anvil cell cannot be neglected. Similarly, pressure increases have been observed in samples heated with a YAG laser without any pressure-transmitting medium (Andraut *et al.*, 1996). We have shown that these pressure changes depend on the thermoelastic parameters of the investigated compound and that, owing to the near constancy of the αK_{T} product, they are probably significant at all pressures.

Table 3. Summary of pressure calculations (data from Table 2). ΔP_{exp} is the pressure increase needed to reconcile experimental results with both theoretical EOS and phase diagrams. P_{th} is the isochoric thermal pressure. The last column is the ratio between experimental and isochoric pressure changes ($\Delta P_{\text{exp}}/P_{\text{th}}$).

	pressure range (GPa)	ΔP_{exp} (GPa/K)	P_{th} (GPa/K)	ratio
α -quartz	[2.0]	$1.0 \cdot 10^{-3}$	$1.9 \cdot 10^{-3}$	0.53
coesite	[8.0–12.0]	$0.5 \cdot 10^{-3}$	$1.4 \cdot 10^{-3}$	0.36
forsterite	[6.8–10.5]	$3.4 \cdot 10^{-3}$	$5.2 \cdot 10^{-3}$	0.65
wadsleyite	[14.–20.]	$4.7 \cdot 10^{-3}$	$6.5 \cdot 10^{-3}$	0.72

One can then wonder whether these pressure changes upon heating may be the cause for the controversies affecting some high-pressure phase-equilibrium determinations. In fact, this effect should be still more important for a transformation like melting, associated with a positive volume change whose effects add up to those of thermal pressure. Hence, this situation differs markedly from the formation of high-pressure phases, with a negative volume of transition, characterized by the "pressure buffering" observed in this study. It is probable that corrections should be applied. As an example, we have shown that conflicting data for the coesite-stishovite transitions can be reconciled quantitatively when pressure increases are taken into account in laser-heated DAC experiments.

Even though X-ray diffraction with synchrotron radiation is probably the best available technique for determining equations of state and phase equilibria under the P conditions prevailing in the Earth's mantle and core, it appears that without internal pressure standards the effects of stress relaxation and pressure increase cannot be sorted out properly.

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