In situ measurements of sound velocities and densities across the orthopyroxene → high-pressure clinopyroxene transition in MgSiO$_3$ at high pressure

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Abstract

Using acoustic measurement interfaced with a large volume multi-anvil apparatus in conjunction with in situ X-radiation techniques, we are able to measure the density and elastic wave velocities ($V_P$ and $V_S$) for both ortho- and high-pressure clino-MgSiO$_3$ polymorphs in the same experimental run. The elastic bulk and shear moduli of the unquenchable high-pressure clinoenstatite phase were measured within its stability field for the first time. The measured density contrast associated with the phase transition OEN $\rightarrow$ HP-CEN is 2.6–2.9% in the pressure of 7–9 GPa, and the corresponding velocity jumps are 3–4% for P waves and 5–6% for S waves. The elastic moduli of the HP-CEN phase are $K_S = 156.7(8)$ GPa, $G = 98.5(4)$ GPa and their pressure derivatives are $K'_S = 5.5(3)$ and $G' = 1.5(1)$ at a pressure of 6.5 GPa, room temperature. In addition, we observed anomalous elastic behavior in orthoenstatite at pressure above 9 GPa at room temperature. Both elastic wave velocities exhibited softening between 9 and 13–14 GPa, which we suggest is associated with a transition to a metastable phase intermediate between OEN and HP-CEN.

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1. Introduction

Orthopyroxene is an important mineralogical constituent of petrological models of the Earth’s upper mantle. The reconstructive (or the first-order) phase transformation in MgSiO$_3$ enstatite at high pressure from orthorhombic (OEN, space group $P_{bca}$) to a monoclinic phase (HP-CEN, space group $C2/c$) would occur in the deeper portions of the upper mantle (e.g., Pacalo and Gasparik, 1990; Kanzaki, 1991). The density increase associated with this phase transition is estimated to be $\sim 3\%$ (Angel et al., 1992); those authors used Birch’s law relating velocities to densities to estimate an associated change in P wave velocity of $\sim 3\%$ across this transition. Furthermore, the pressure range for this transition at the mantle temperature coincides with the depths at which seismic studies have revealed discontinuities, such as the Lehmann or X-discontinuities (see cross-hatched region of Fig. 1; and discussion in Angel et al., 1992; Woodland and Angel, 1997; Woodland, 1998).
Fig. 1. Topology of the phase diagram for MgSiO$_3$ (after Gasparik, 1990), and the $P$--$T$ conditions for synthesis of the OEN and HP-CEN phases, and the acoustic experiments reported in this study (for Run T409 conditions, see Table 2). The solid square denotes the $P$--$T$ conditions for hot-pressed of the OEN polycrystalline specimens which are synthesized prior to the acoustic experiments. These polycrystalline OEN specimens are loaded into the acoustic cell (Fig. 2) and pressurized up to the maximum pressure of 17 GPa. The X-ray, image and acoustic data are collected during the compression (open circles). At the peak pressure, the OEN specimens are heated to transform the specimen to the HP-CEN phase (solid circle). After the specimen had been fully transformed to HP-CEN at 1000 $^\circ$C (during which the cell pressure reduced due to the relaxation of the pressure media, to $\sim$14 GPa), data for the HP-CEN phase were collected at room temperature as the cell pressure was decreased (see shaded filled circles, and data on "decompressed, after heating" in Tables 1 and 2). At each pressure point, the cell assembly is re-heated up to $\sim$900 $^\circ$C to minimize the macroscopic deviatoric stress imposed on the sample by cell assembly, the gray dashed lines with arrows are the $P$--$T$ paths of the heating/cooling cycles. The cross-hatched area presents the possible $P$--$T$ conditions of the phase transformation from OEN $\rightarrow$ HP-CEN in the upper mantle: the higher temperatures are for normal mantle conditions, whereas the lower temperatures are for cooler subduction zone environments. The dark, dashed line is the phase boundary of OEN $\leftrightarrow$ HP-CEN shifted by 10 mol% of Fe. See also discussion in Section 5.

However, the HP-CEN phase cannot be recovered at ambient conditions because it transforms to low-pressure clinopyroxene (LP-CEN, monoclinic, space group $P2_1/c$) on release of pressure at room temperature (Angel et al., 1992; Ross and Reynard, 1999). Therefore, the HP-CEN phase has to be synthesized in situ, followed by studying its thermoelastic properties within its stability field. To date, equation-of-state investigations have consisted of in situ X-ray studies (Angel et al., 1992; Shinmei et al., 1999) or computer modeling (Wentzcovitch et al., 1995; Mendelsohn and Price, 1997). The absence of direct measurements of sound velocities of the HP-CEN phase has made it difficult to ascertain whether the magnitude of the acoustic velocity or impedance contrast between the OEN and HP-CEN phases is sufficiently strong to produce an observable seismic signature.

Acoustic experiments basically measure travel times of sound waves in specimens and must be combined with techniques to monitor the specimen length under elevated conditions of pressure and temperature to obtain velocity data. This is especially important when the polycrystalline specimen is undergoing a first-order phase transition involving a volume change. Recently, we have adapted the X-radiographic imaging techniques for use in our simultaneous ultrasonic and in situ X-ray diffraction experiments to permit direct measurements of the specimen length under all experimental conditions (Kung et al., 2002; Li et al., 2004).

With the ultrasonic system interfaced with a large volume high-pressure apparatus in conjunction with in situ X-radiation techniques, we were able to measure the elasticity of both MgSiO$_3$-OEN and HP-CEN in a single experimental run. In this paper, we present the velocity jumps associated with this phase transformation at high pressures and room temperature. During the high pressure experiments, we also observed anomalous elastic behavior of the OEN phase above 9 GPa, at room temperature. We discuss briefly the potential application of these new experimental data to the interpretation of seismic models of the Earth upper mantle.

2. Experimental procedures

2.1. Specimens

Polycrystalline specimens of OEN were synthesized and hot-pressed from a starting material of MgSiO$_3$ glass prior to the acoustic experiments (details see Flesch et al., 1998; synthesis conditions denoted by closed square in Fig. 1). X-ray diffraction patterns have shown the final hot-pressed specimens
to be orthoenstatite (Fig. 6a). The density of polycrystalline specimens was \( \sim 3.18 \text{ g cm}^{-3} \) (99.3% of the single-crystal X-ray density of 3.20 g cm\(^{-3}\)). The sound velocities of specimens at ambient conditions were determined to be 8.00(5) km s\(^{-1}\) for P waves and 4.83(1) km s\(^{-1}\) for S waves; these values are within 1% of the isotropic velocities derived from the single-crystal data of Weidner et al. (1978) and Jackson et al. (1999).

Due to its unquenchable nature, HP-CEN was synthesized in situ at high pressure and temperature during the acoustic measurements. We used the well-sintered OEN specimen from the prior experiment (described above) as the starting material. The OEN specimen was loaded in the acoustic cell assembly (Fig. 2); after compression to 17 GPa at room temperature (Fig. 1, open circles), the cell was heated up to \( \sim 1000 \degree \text{C} \) at 13 GPa for 2 h to transform into HP-CEN phase (Fig. 1, closed circle).

### 2.2. Ultrasonics

Two-way travel times of ultrasonic waves through the specimens were determined using a transfer function (TF) method that has recently been developed in our laboratory (see details in Li et al., 2002, 2004). With this new system, the travel times can be measured using either the pulse echo overlap (PEO) or phase comparison method. Li et al. (2002, 2004) have demonstrated that the travel times deduced from both methods are comparable; in this study the PEO method was employed. In our experiments, dual-mode LiNbO\(_3\) transducers (10\(^\circ\) rotated Y-cut) were used to generate and receive the ultrasonic signals; these transducers generate both longitudinal and transverse acoustic signals with unspecified polarization of the transverse signal (see details in Kung et al., 2002; Sinelnikov et al., 2004).

The ultrasonic measurements at high pressure were performed using a 1000-ton, Kawai type multi-anvil apparatus with a T-cup module (now named the T-25 apparatus; for details, see Uchida et al., 2002) in conjunction with in situ X-radiation techniques at the 13ID beamline at the Advanced Photon Source of the Argonne National Laboratory. The octahedral ultrasonic cell assembly (Fig. 2) was modified from that used by Li et al. (1998); a cylindrical graphite furnace with end disk was inserted into an octahedron of semi-sintered MgO, with salt (NaCl) and MgO cups filling the space between the specimen and the furnace. The purpose of the NaCl was to provide an isotropic environment and also to serve as a pressure calibrant; the NaCl was mixed with BN to suppress grain growth at high temperature. On one end of the cell assembly, an alumina rod served as an acoustic buffer rod, located between the WC cube and specimen; this buffer rod was surrounded by brass foil to provide electrical contact between the WC cube and the graphite furnace. On the other end of the cell, a Mo-alloy ring provided the other furnace electrode. The remaining space inside the MgO octahedron was filled with a zirconia sleeve and rings (in run T354). The temperature was measured by a thermocouple, which was inserted from the edge of the MgO octahedron and located at the bottom of the specimen, inside of the NaCl cup. Two gold foils (2-microns thick, not shown in the diagram) were inserted at both ends of the specimen as the image markers; the foil between the Al\(_2\)O\(_3\) and specimen was also used to improve the mechanical coupling.
other furnace electrode. The remaining space inside the MgO octahedron was filled with zirconia sleeve and rings. The temperature was measured by a thermocouple (W3%Re/W25%Re), which was inserted from the edge of the MgO octahedron and located at the bottom of the specimen, inside of the NaCl cup. The specimen lengths used in this study were ~1 mm.

2.3. X-ray diffraction

The energy-dispersive X-ray method was employed using white radiation to collect diffraction spectra for both the NaCl as the pressure marker (collecting at the position behind the specimen) and the MgSiO$_3$ specimen (including OEN, HP-CEN and LP-CEN phases). The determination of unit cell parameters of the specimen was refined using the program package GSAS (general structure analysis system, Larson and Von Dreele, 1988). The entire diffraction pattern was used to refine simultaneously for both specimen and NaCl (contributed from the surrounding sleeve, see Fig. 2). As starting models for refinements in the Rietveld mode at different pressure conditions, we used the structural data of Ghose et al. (1986) for the OEN phase (Fig. 6a, ambient conditions before compression), of Angel et al. (1992) for the HP-CEN phase (Fig. 6c, at 9.7 GPa after transformation at high $P$ and $T$), and of Ohashi (1984) for the LP-CEN phase (Fig. 6b, as recovered at ambient conditions after the high P–T experiment). Final values of lattice parameter were obtained by a Le Bail refinement (Le Bail et al., 1988) in which least-square fitting of the diffraction profile was achieved by minimization of the difference between the observed and synthetic patterns.

2.4. X-radiographic imaging

In the T-25 apparatus, the X-ray beam passes through the gaps between the WC anvils and then the cell assembly, and illuminates a fluorescent YAG crystal. The visible light generated by the YAG is reflected by a mirror into CCD camera where an image of the cell assembly is captured. A typical X-ray image of the cell assembly in our experiment is shown on the left panel of Fig. 3, consisting (from top to bottom) of the NaCl disk, gold foil, specimen, gold foil and Al$_2$O$_3$ acoustic buffer rod. The contrasting intensities at different regions were caused by the difference in the X-ray absorption of these materials. In this study, the

![Image](image_url)
Table 1
Elastic properties of polycrystalline MgSiO₃-enstatites (sample K628) at room temperature

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>Length (mm)</th>
<th>( c_P (\mu s) )</th>
<th>( c_S (\mu s) )</th>
<th>( V_P (\text{km/s}) )</th>
<th>( V_S (\text{km/s}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compression, before heating</strong></td>
<td></td>
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</tr>
<tr>
<td>0.5</td>
<td>1.096</td>
<td>0.272(1)</td>
<td>0.4518(1)</td>
<td>8.06</td>
<td>4.85</td>
</tr>
<tr>
<td>2.0</td>
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<td>0.4300(2)</td>
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<td>4.97</td>
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<td>0.4277(1)</td>
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<td>5.07</td>
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<td>6.1</td>
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<td>5.10</td>
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<td>5.12</td>
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<td>5.13</td>
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<tr>
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<td>HP-CEN</td>
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<td>0.2142(1)</td>
<td>0.3756(1)</td>
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<td>HP-CEN</td>
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<td>0.2138(2)</td>
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<td>HP-CEN</td>
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<td>HP-CEN</td>
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<td>1.023</td>
<td>0.2230(2)</td>
<td>0.3814(3)</td>
<td>9.14</td>
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<tr>
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<td>1.026</td>
<td>0.2252(1)</td>
<td>0.3830(1)</td>
<td>9.14</td>
</tr>
<tr>
<td>HP-CEN</td>
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<td>1.029</td>
<td>0.2272(1)</td>
<td>0.3856(2)</td>
<td>9.06</td>
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</table>

OEN, HP-CEN: the phases identified in first column were adjusted from run T409 at similar conditions. Anomaly: The region shows the elastic velocities anomaly behavior before the specimen subjected to heating. The uncertainty of the length measurement is 1 μm, resulting in <0.2% in P and S wave velocities.

X-ray absorption of specimen (MgSiO₃-enstatite) was similar to those of neighboring materials (Al₂O₃ and NaCl). Consequently, two gold foils (2-micron thick) were inserted at both ends of the specimen as the image markers; the foil between the Al₂O₃ and the specimen was also used to improve the mechanical coupling. A sequence of X-ray images were recorded during the course of collecting ultrasonic data at high pressures. The final image taken at ambient conditions when the press was opened at the end of the experiment, along with the measured length of the recovered specimen after the high-pressure run, provides the conversion factor between the image and the actual specimen dimensions (Kung et al., 2002; Li et al., 2004).

An output file of intensities along the specimen region was obtained for each image (e.g., right panel of Fig. 3), the specimen region is defined by the discontinuity in intensity at both boundaries, as demarcated by the gold foils. The specimen length change from one condition to another was measured by the change of pixels to obtain the best correlation of the two boundaries of the specimen. Then, using the conversion factor, the absolute specimen lengths at all experimental conditions were calculated (see Tables 1 and 2). Typically in this study, a change of 0.25 pixels can be resolved over a specimen dimension of about 550–700 pixels in this study. If the specimen length is directly measured from an image, it has a total uncertainty about 2–4 pixels, which gives 0.3–0.8% in precision.

3. Experimental data and analysis

Results from two acoustic experiments on MgSiO₃ in the T-25 apparatus (T354 and T409) are reported in this study. The acoustic experimental P-T paths are...
Table 2

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>Length (mm)</th>
<th>t &lt;sub&gt;p&lt;/sub&gt; (μs)</th>
<th>t &lt;sub&gt;s&lt;/sub&gt; (μs)</th>
<th>V&lt;sub&gt;p&lt;/sub&gt; (km/s)</th>
<th>V&lt;sub&gt;s&lt;/sub&gt; (km/s)</th>
<th>K&lt;sub&gt;S&lt;/sub&gt; (GPa)</th>
<th>G (GPa)</th>
<th>Volume (Å&lt;sup&gt;3&lt;/sup&gt;)</th>
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</thead>
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<td></td>
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<tr>
<td>OEN 0</td>
<td>1.093</td>
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<tr>
<td>OEN 1.0</td>
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<td>0.266(3)</td>
<td>0.4448(9)</td>
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<td>0.4360(5)</td>
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<td>4.96</td>
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<td>0.4173(3)</td>
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<td>5.10</td>
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<tr>
<td>HP-CEN 11.7</td>
<td>1.030</td>
<td>0.2176(1)</td>
<td>0.3828(5)</td>
<td>9.55</td>
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<td>102</td>
<td>390.114(103)</td>
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<td>1.030</td>
<td>0.2234(8)</td>
<td>0.3852(5)</td>
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<tr>
<td>HP-CEN 6.5</td>
<td>1.021</td>
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<td>0.3828(5)</td>
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<td>385.626(62)</td>
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<tr>
<td>LP-CEN 0</td>
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<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>416.796(55)</td>
</tr>
</tbody>
</table>

OEN, HP-CEN, LP-CEN: The first column shows the phase identified from X-ray diffraction patterns at different pressure condition. Due to poor-mechanical contact in the cell assembly at open press after high pressure run, there was no acoustic data available for LP-CEN phase. Anomaly: The region shows the elastic velocities anomaly behavior before the specimen subjected the heating, where the cell volumes of specimen were not extracted. ΔV is the fitting uncertainty obtained from the GSAS, not the experimental uncertainty. The estimated uncertainties in length and velocities are the same as those in Table 1. The uncertainties of K and G are ∼1 and 0.5%, assuming 0.1% uncertainty in density.

shown in Fig. 1. X-ray diffraction patterns of NaCl and specimen, and the travel times and length images of specimen were collected at high pressures, both before and after the OEN specimen transformed to the HP-CEN phase. The data were collected for the starting OEN phase while the pressure was increasing at room temperature to the maximum pressure of ∼17 GPa (see open circles in Fig. 1, data on “Compression, before heating” in Tables 1 and 2). At the peak pressures, the cell assembly was heated to transform the specimen to HP-CEN phase. After the specimen had been fully transformed to HP-CEN at 1000 °C (during which the cell pressure reduced due to the relaxation of the pressure media, to ∼14 GPa in Fig. 1), data for the HP-CEN phase were collected at room temperature as the cell pressure was decreased (see shaded filled circles in Fig. 1, data on “Decompression, after heating” in Tables 1 and 2). Following each reduction of pressure during the decompression cycle, the cell assembly was re-heated to ∼900 °C to minimize the deviatoric stress imposed on the specimen by the cell assembly. Data collection for the HP-CEN phase was terminated at ∼6 GPa, below which pressure the HP-CEN is known to transform to the LP-CEN phase (Angel et al., 1992; Ross and Reynard, 1999).

3.1. Travel time data

Before the OEN specimen was heated up and transformed to the HP-CEN phase, the travel times in OEN from both runs (T354 and T409) systematically decreased as a function of increasing pressure up to ∼9 GPa (see solid circles in Fig. 4, also Tables 1 and 2, travel times denoted as “OEN”). Above this pressure, however, both the P and S wave travel times began to increase as pressure was increased to ∼13 GPa, after which they decreased again (e.g., the P wave travel time data from run T354 shown by the gray circles in Fig. 4, travel times collected in this pressure range are denoted as “anomaly” in Tables 1 and 2). After the specimen was transformed to the HP-CEN phase, the
Fig. 4. Travel times of MgSiO$_3$-enstatite phases as a function of pressure at room temperature for P waves in run T354. The travel times of OEN decrease as the pressure is increasing up to 9 GPa (solid circles). Above 9 GPa, the travel times exhibit anomalous behavior, increasing as pressure is increasing, and then decreasing again above $\sim$13 GPa. The travel times collected for the HP-CEN phase increase with decreasing pressure during the decompression (open circles).

Travel times at room temperature increased systematically with decreasing pressure (Fig. 4, empty circles, travel times denoted as HP-CEN in Tables 1 and 2). The bond reverberations contributed by the two gold foils to the travel times for the OEN phase (2.5 ns for P waves and 5.2 ns for S waves) and for the HP-CEN phase (1.5 ns for P waves and 4.8 ns for S waves) were removed from the measured travel times; the corrected travel times are given in Tables 1 and 2.

3.2. Length changes in OEN and HP-CEN

The changes ($\Delta L/L_0$) for both OEN and HP-CEN phases at room temperature are plotted as a function of pressure (Fig. 5). On compression, the lengths of the OEN phase from runs T354 and T409 decrease with increasing pressure up to $\sim$17 GPa in a linear manner (see both solid and gray symbols); no anomalous behavior was observed. Thus, we conclude that the anomalous behavior of the acoustic travel times illustrated in Fig. 4 is due to changes in the elastic properties of the specimens.

The lengths of HP-CEN, measured at each pressure at room temperature after heating to 900 $^\circ$C following decompression are shown as empty symbols in Fig. 5.

Interestingly, the length changes in the HP-CEN phase specimens behave differently in runs T409 and T354. In run T409, the specimen length increases on reduction of pressure from 12 to 9 GPa; however, at pressures below 9 GPa, the lengths decrease continuously as the pressure decreases to 6 GPa. X-ray diffraction patterns in this pressure range clearly show that the specimen remained as the HP-CEN phase. Thus, we conclude that the shortening of the specimen length with decreasing pressure in run T409 is caused by plastic deformation induced when the sample is subjected to high temperatures between 9 and 6 GPa (see Fig. 1).

In run T354, the reduction of the specimen length associated with the phase transition from OEN to HP-CEN is twice that observed in run T409 at $\sim$12 GPa, but the length changes during subsequent decompression behave in a similar fashion as that in T409, but of smaller magnitude. We believe that this different behavior observed in runs T354 and T409 results from differences in the cell assemblies used in
these two runs. The ZrO$_2$ sleeve, inserted as a thermal insulator in run T354, was replaced by an MgO sleeve in run T409 in order to improve the transparency for X-ray. Differences in the thermoelastic and mechanical properties of these sleeves result in changes of the stress state on the sample at high pressure and temperature, which produces the different length change behavior observed above. However, the differing behavior observed in specimen lengths for the HP-CEN phases in runs T354 and T409 does not affect the measured wave velocities (see Fig. 8 and discussion below).

### 3.3. X-ray diffraction data

In both runs, the measured cell parameters of NaCl were used to determine the cell pressures using Decker’s (1971) equation of state; we estimate the precision of these cell pressures given in Tables 1 and 2 to be $\sim$0.1 GPa. X-ray diffraction patterns were also recorded for the MgSiO$_3$ specimens in runs T354 and T409 at all experimental conditions. For run T354, the intensity of X-ray diffraction patterns for the specimen was too weak to analyze because of the small entry slit size used and the contamination and strong absorption from the ZrO$_2$ thermal insulator surrounding the specimen.

For run T409, the X-ray patterns were collected on compression to 16.7 GPa, and after the phase transformation (i.e. on heating, specimens transformed to HP-CEN) on decompression from 11.7 to 6.5 GPa, as well as at ambient conditions before and after experiment (Fig. 6a–g). For both OEN (the starting phase, Fig. 6a) and low clinopyroxene (the final recovered phase, Fig. 6b) phases, data collected at ambient conditions yielded cell volumes of 832.9 Å$^3$ and 416.2 Å$^3$, respectively; in excellent agreement with published single-crystal data (832.76 Å$^3$ for OEN, Ghose et al., 1986, and 415.5 Å$^3$ for LP-CEN, Ohashi, 1984). From this comparison, we are confident that the energy dispersive diffraction patterns obtained using the cell assembly in T409 provide reliable equations of state data for both the OEN and HP-CEN phases at our experimental conditions. The cell volumes of OEN (below 10 GPa) and HP-CEN from run T409 are tabulated in Table 2, and were used to calculate the densities of OEN and HP-CEN at high pressures (Fig. 7). In Fig. 6d–g, we show the X-ray diffraction patterns of the OEN phase from run T409 in the pressure range from 9.6 to 16.8 GPa, the region in which the travel time data exhibited anomalous behavior (as shown in Fig. 4). Due to the complexity of X-ray diffraction patterns and observation of anomalous elastic behavior above 10 GPa to peak pressure before heating and transforming to HP-CEN (i.e. symbols in solid and gray in Fig. 8 and denoted as “anomaly” in Tables 1 and 2), we did not attempt to extract cell volumes for the polycrystalline specimen in this pressure range.

In previous experiments (e.g., Hugh-Jones and Angel, 1994; Angel and Jackson, 2002) single-crystals of the OEN phases were compressed to $\sim$8.5 GPa at room temperature with no indication of phase transition. The high pressure Raman studies (above 20 GPa, Chopelas, 1999; Serghiou et al., 2000; Lin, 2003) suggested a new phase appearing in a similar pressure range where we observed the anomalous elastic behavior; these authors suggested that the new phase might be HP-CEN. We have tried to evaluate whether the HP-CEN phase has begun to appear above 10 GPa at room temperature. However, many of the peak positions of HP-CEN overlap with those of OEN; it is therefore difficult to ascertain whether any new peaks of HP-CEN are appearing. On the other hand, the X-ray patterns collected at 9.6 and 11.8 GPa (Fig. 6d and e) indicated that the specimen retains a strong signature of OEN, at pressures where the travel time data started exhibiting the anomalous behavior. The most distinguishing feature in the X-ray diffraction patterns is the diminishing intensities of the OEN (3 2 1) and (5 1 1) peaks collected above 14 GPa; neither peak is observed in the diffraction pattern at the peak pressure of $\sim$17 GPa (Fig. 6f and g). On the basis of the crystal structure relationships, these peaks (3 2 1) and (5 1 1) of OEN should vanish if the specimen transformed to monoclinic symmetry (either C2/c or P2_1/c, for example, Fig. 6b and c). By contrast, the neighboring peak (6 1 0) of OEN, which corresponds to the (3 1 0) of the HP-CEN, should persist as shown in Fig. 6g. The existing X-ray diffraction data cannot give a definitive indication if the OEN phase began to transform to the HP-CEN phase at $\sim$17 GPa, room temperature.

Previous studies have shown that the HP-CEN phase (C2/c) would be transformed to LP-CEN (P2_1/c) on released of pressure at room temperature condition (Angel et al., 1992; Ross and Reynard, 1999); this version was also observed in our experiment (Fig. 6b...
Fig. 6. (a–c) X-ray diffraction patterns of MgSiO$_3$-enstatite collected in run T409; (a) starting specimen with the OEN structure at ambient conditions; (b) recovered specimen identified as LP-CEN at ambient conditions; (c) HP-CEN at 9.7 GPa after transforming from OEN. The red crosses and green line represent the observed and calculated spectra, respectively. Black, red and blue ticks represent the peak positions of NaCl, MgSiO$_3$-OEN and HP-CEN, respectively. (d–g) X-ray diffraction patterns from 9.6 to 16.8 GPa collected in run T409. Our X-ray data show that OEN (red indices) is as the dominant phase up to 17 GPa. It is difficult to verify if any new peaks of HP-CEN (blue indices) appear due to the overlap of the peak positions for the two phases. The most distinguishing feature is that the intensities of the (3 2 1) and (5 1 1) peaks of OEN are decreasing.
Fig. 6. (Continued).
Fig. 7. Densities of OEN and HP-CEN as function of pressure at room temperature. The densities of OEN (solid diamonds) and HP-CEN (open diamonds) measured at high pressures in our study are in good agreement with Hugh-Jones et al. (1994) and Angel and Jackson (2002) (OEN, crosses), and Angel et al. (1992) and Angel and Hugh-Jones (1994) (HP-CEN, open circles). However, the densities of HP-CEN derived from Shinmei et al. (1999) (gray triangles) are somewhat higher at all pressures. The density jump associated the phase transformation OEN → HP-CEN is 2.6–2.9%, from 7 to 9 GPa. The gray broken lines are the best fits to the OEN and HP-CEN data obtained in this study.

To provide us with a specimen recovered at ambient conditions after being subjected to a similar pressure range without heating (as in the acoustic experiment described above, before heating), we conducted an in situ X-ray experiment in the diamond anvil cell (DAC) up to 15.5 GPa using OEN as the starting material; following compression, the specimen was decompressed, all at room temperature. Interestingly in the DAC experiment, we observed that the intensity of peaks (3 2 1) and (5 1 1) of OEN were also decreasing at high pressures, but increased during the depressurization. The recovered specimen exhibited OEN symmetry in the X-ray diffraction pattern. We also examined the recovered specimen using Raman spectroscopy to compare with a fresh OEN specimen. The Raman spectra from both specimens presented identical features representative of the OEN phase; this is consistent with the previous Raman studies of OEN at high pressure (Serghiou et al., 2000; Lin, 2003). From our DAC experiment, we infer that the OEN phase in our acoustic experiments did not transform to the HP-CEN (C2/c) phase while being pressurized up to 15.5 GPa; had this occurred, the recovered specimen in the DAC experiment should have been the LP-CEN phase (P21/c).

3.4. Data analysis

The compressional and shear velocities ($V_P$ and $V_S$) were calculated with measured travel times and the specimen lengths ($V = \frac{2l}{t}$) at different experimental conditions. The elastic moduli ($L$, $G$) at high pressures were also calculated from the $P$ and $S$ wave velocities and densities determined from the observed specimen volumes ($\rho = \frac{m}{V}$). Then, the measured elastic moduli at pressures are fitted to third- or fourth-order Eulerian finite strain equations:

$$L = \rho V_P^2 = \sqrt{S^2 \left[ L_1 + \frac{1}{2} L_2 (1 - S^2) + \frac{1}{4} L_3 (1 - S^2)^2 \right]},$$  \hspace{1cm} (1)

$$G = \rho V_S^2 = \sqrt{S^2 \left[ M_1 + \frac{1}{2} M_2 (1 - S^2) + \frac{1}{8} M_3 (1 - S^2)^2 \right]},$$  \hspace{1cm} (2)
Fig. 8. P and S wave velocities of MgSiO$_3$-enstatite as function of pressure at room temperature. The P and S wave velocities of OEN (solid symbols) measured up to 9 GPa in this study are reproducible between the two runs (T354 and T409). Data from a previous acoustic study (without X-rays) in our laboratory (Flesch et al., 1998) are in good agreement with our new data, within mutual uncertainties. Above 9 GPa (denoted as “anomaly” in Tables 1 and 2, symbols in gray), both the P and S wave velocities anomalously decrease with increasing pressure, reaching minimum values near 13 GPa, which are 5–6% below the trend at lower pressures. At pressure above 13 GPa, both velocities continue to increase with pressure. The elastic velocities of HP-CEN at high pressure (after transformation from OEN) also show very good agreement between the two runs. The velocity contrast associated the phase transformation OEN$_{below10\,GPa}$ → HP-CEN is 2–3% for P wave and 4.5–5.5% for S wave.

\[ G_0 = M_1, \]
\[ K_{\text{SO}} = L_1 - \frac{4}{3} G_0, \]  
\[ G_0 = \frac{1}{3} M_1 - M_2, \]  
\[ K_{\text{SO}}' = \frac{1}{3} L_1 - \frac{L_2}{K_{\text{SO}}}, \]  
\[ G_0' = \frac{1}{9} M_1 + 3(K_0' - 4)M_2 - 5(3K_0' - 5)L_1. \]  

following Davies and Dziewonski (1975) in terms of the linear compression \( S = (V_0/V)^{1/3} \), where the \( L_i \) and \( M_i \) are the fitting coefficients. When third-order equations are used, the high-order terms are ignored (i.e. \( L_3, M_3 \), see Kung et al., 2002). These fitting coefficients are used to calculate the \( K_{\text{SO}}, G_0, K_{\text{SO}}', G_0' \) via Eqs. (1)–(8) and the results are tabulated in Table 3. In this study, the density
Table 3
Elastic moduli and their pressure derivatives of MgSiO_3 enstatite at room temperature

<table>
<thead>
<tr>
<th>K_s (GPa)</th>
<th>G (GPa)</th>
<th>K'_s (GPa^-1)</th>
<th>G' (GPa^-1)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>OEN T409</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3E 107.4(28)</td>
<td>76.4(4)</td>
<td>7.2(7)</td>
<td>1.7(1)</td>
<td>Cook’s method</td>
</tr>
<tr>
<td>3E 108.7(37)</td>
<td>76.5(5)</td>
<td>6.6(7)</td>
<td>1.6(1)</td>
<td>X-ray data a</td>
</tr>
<tr>
<td>4E 103.6(12)</td>
<td>75.7(3)</td>
<td>2.5(1)</td>
<td>-1.59(17)</td>
<td>-0.29(3)</td>
</tr>
<tr>
<td>4E 101.1(22)</td>
<td>75.4(4)</td>
<td>2.4(2)</td>
<td>-2.03(34)</td>
<td>-0.39(5)</td>
</tr>
<tr>
<td>HP-CEN T409</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3E 155.9(22)</td>
<td>98.3(2)</td>
<td>5.4(6)</td>
<td>1.5(1)</td>
<td>X-ray data a</td>
</tr>
<tr>
<td>4E 156.7(8)</td>
<td>98.5(4)</td>
<td>5.5(3)</td>
<td>1.5(1)</td>
<td></td>
</tr>
</tbody>
</table>

a V_0 = 832.918 Å^3 and V_0 = 385.626 Å^3 are used in the finite-strain fit.
b The results of fourth-order finite-strain fit are re-performed. The only difference is the value of G', 1.4 in Flesch et al. (1998), and the rest values are comparable.

used in the equations can be obtained from the direct measurements of the cell volume or inferred from the method of Cook (1957).

4. Elasticity of MgSiO_3-enstatites at high pressure, room temperature

4.1. Elasticity of OEN and HP-CEN

The current experimental setup enables us to measure the elastic wave velocities and densities of the OEN and HP-CEN phases in the same experiment, and thereby directly compare their elastic properties. The densities of two phases were calculated from the P-V data in this study (T409, see Table 2) and are compared with those measured from previous studies in Fig. 7 (in all of which the phases were studied separately: Angel et al., 1992; Angel and Hugh-Jones, 1994; Hugh-Jones et al., 1994; Shinmei et al., 1999; Angel and Jackson, 2002). There is good agreement among most of the independent datasets; only the densities of HP-CEN derived by Shinmei et al. (1999) are somewhat higher at all pressures. We conclude that the density contrast between OEN and HP-CEN phases in pressure range of 7–9 GPa is between 2.6 to 2.9% in this study, which is compatible with that calculated at 7.9 GPa (2.7%) from the data of Angel et al. (1992) and Hugh-Jones et al. (1994).

Our measured P and S wave velocities at room temperature for the OEN and HP-CEN phases (Table 1) are plotted as a function of pressure in Fig. 8a and b. We discuss initially the data for OEN below 9 GPa (denoted as “OEN” in Tables 1 and 2) and the data for HP-CEN between 6 and 12 GPa (denoted as HP-CEN in Tables 1 and 2). At pressure below 9 GPa at room temperature, both the P and S wave velocities of the OEN phase (T409, solid circles; T409, solid diamonds, Fig. 8) increase systematically as the pressure increasing, with good reproducibility between the two ultrasonic runs and the two specimens. The acoustic dataset from a previous study without in situ X-ray measurements (Flesch et al., 1998) are plotted in Fig. 8a and b for comparison. Both the P and S wave velocities in the two studies are in excellent agreement within the mutual uncertainties.

Elastic velocities of the HP-CEN phase measured in T354 and T409, plotted in Fig. 8a and b (empty symbols), are also remarkably consistent, even though the behavior of length changes between two runs was different after transformation (Fig. 5). These velocities can be treated as linear functions of pressure within the range of the data collected (6 to 12 GPa). The velocities of the HP-CEN and OEN phases define sub-parallel trends versus pressure above 6 GPa, with an
observed contrast of 3–4% for P waves and 5–6% for S waves.

Using densities converted from the measured unit-cell volumes and elastic wave velocities, the elastic bulk ($K_S$) and shear ($G$) moduli are calculated and presented in Table 2 and plotted in Fig. 9a and b. These data have been fit using the Eulerian finite strain equations given above, to both third and fourth order in strain. In our analyses, the linear compression, $S = (V/V_0)^{1/3} = (1 - 2\varepsilon)^{1/2}$, where $\varepsilon$ is strain), was obtained in two different ways: (1) direct measurement from X-ray diffraction data; and (2) from the measured travel time data following the method of Cook (1957), which has been widely used in ultrasonic studies performed without in situ X-ray techniques (e.g., Flesch et al., 1998). The results for the moduli and their pressure derivatives ($K_S'$, $K_S''$, $G'$, and $G''$) are given in Table 3, along with previous OEN dataset from Flesch et al. (1998). The elastic moduli of OEN parameters resulting from the two measures of linear compression $S$ are in good agreement and similar to those of Flesch et al. (1998). In both studies, the clear non-linear behavior of the velocities versus pressure illustrated in Fig. 8a and b is reflected in the requirement of using the fourth order finite-strain equations to adequately fit the moduli-pressure data.

Fig. 9. Elastic moduli of OEN and HP-CEN at high pressure. The diamond symbols present the result from run T409 (solid: OEN, open: HP-CEN). The dash gray lines are the best fits of our data. The open triangles are the data from Flesch et al. (1998). The elastic moduli measured from Flesch et al. (1998) and in this study are in good agreement. Both the bulk and shear moduli show non-linear behavior as a function of pressure. In contrast to OEN, the elastic moduli of HP-CEN exhibit a linear relationship with pressure in the pressure range for which data were collected (6–12 GPa). The difference in elastic moduli across the phase transformation is 16.5% for G and 2.3–5% for $K_S$. 
5.5 (3) and = Flesch et al., 1998 (Fig. 9, solid diamonds – this study, open triangles – 6.5–11.7 GPa, which can be fit to obtain 156.7(8) GPa (Fig. 9, open diamonds) in the pressure range of other hand, exhibit linear relationships with pressure

formation (see Carpenter and Salje, 1998; Carpenter (elastic softening) could be induced by a phase trans-

served in this study has reached the maximum value. We cannot be certain that the velocity reduction ob-

to the HP-CEN phase. Without further experiments, velocity increases associated with the transformation T354; this reduction is larger in magnitude than the

varies between the two acoustic runs, with the slower

runs T354 and T409; the degree of velocity reduction

and 14 GPa, and then begin to increase again. This anomalous velocity behavior was observed in both runs T354 and T409; the degree of velocity reduction varies between the two acoustic runs, with the slower rate of pressurization in T354 producing more pronounced velocity minima. In the pressure range from 9 to ∼13 GPa, the P and S wave velocities decrease by as much as 5.3% and 6.3%, respectively, i.e. in run T354; this reduction is larger in magnitude than the velocity increases associated with the transformation to the HP-CEN phase. Without further experiments, we cannot be certain that the velocity reduction ob-

served in this study has reached the maximum value.

The cause of such anomalous elastic behavior (elastic softening) could be induced by a phase trans-

formation (see Carpenter and Salje, 1998; Carpenter et al., 1998 for general review, references therein) or pressure-induced solid-state amorphization (SSA) due to structural or lattice instability (e.g. H2O, Gromitskaya et al., 2001). After carefully examining the X-ray diffraction patterns above 10 GPa, we did not observe any increase in the intensity of the background due to amorphization of OEN (Fig. 6f and g). In addition, none of the previous Raman studies (Chopelas, 1999; Serphious et al., 2000; Lin, 2003) suggests amorphization in the pressure range studied here. Thus, the possibility of OEN amorphization can be ruled out. The elastic softening of OEN is most likely caused by a phase transition. Although the proxy experiment in orthoferrosilite (FeSiO3, space group Pbca → C2/c clinoferrrosilite (Hugh-Jones et al., 1996) would suggest a phase transition from OEN to HP-CEN, such a transition can be ruled out in the case of our experiments for reasons cited above (Section 3.3). Neither does our X-ray evidence support the possible phase transition, Pbca → Cmca, suggested by Jackson et al. (2004), for their high tem-

perature experiments in MgSiO3 at room pressure. In the Pbca → Cmca phase transformation, the OEN (3 2 1) and (6 1 0) peaks should disappear, and the OEN (5 1 1) peak remain after the transition. This is different from the observation in our X-ray diffraction patterns; we observed that the OEN (3 2 1) and (5 1 1) peaks disappeared at high pressures (Fig. 6d–g). From our existing data, although it is difficult to determine the symmetry of the new phase, clearly this transition is reversible.

The anomalous velocity behavior observed here, if associated with a phase transition, would be a sen-

tive tool to locate the transition point. In the cases of our acoustic experiments, the minima of the velocity anomalies can be interpreted as the transition point between 13 and 14 GPa (Fig. 8). In this pressure range, we also observed distinctive changes in the X-ray diffraction patterns, and the characteristic of the “new” phase was enhanced as pressure increases (see Section 3.3). The specimen remained in this new phase until being heated to 900 ºC at peak pressure and transforming to HP-CEN. No reversion to this phase was observed during the experimental conditions in run T409 (see Fig. 1 for experimental P-T path). This suggests that the new phase may be a metastable phase related to the kinetic process of the phase transition from OEN to HP-CEN at room temperature.

4.2. “Anomalous” behavior observed in the OEN phase above 9 GPa, before transformation to the HP-CEN phase

As shown in Fig. 8, at pressures above 9 GPa, both Vp and Vs (symbols in gray, denoted as “anomaly” in Tables 1 and 2) decrease dramatically with increasing pressure, reaching minimum values between 12 and 14 GPa, and then begin to increase again. This anomalous velocity behavior was observed in both runs T354 and T409; the degree of velocity reduction

peaks disappear at high pressures (Fig. 6d–g). From

our existing data, although it is difficult to determine the symmetry of the new phase, clearly this transition is reversible.

The anomalous velocity behavior observed here, if associated with a phase transition, would be a sen-
tive tool to locate the transition point. In the cases of our acoustic experiments, the minima of the velocity anomalies can be interpreted as the transition point between 13 and 14 GPa (Fig. 8). In this pressure range, we also observed distinctive changes in the X-ray diffraction patterns, and the characteristic of the “new” phase was enhanced as pressure increases (see Section 3.3). The specimen remained in this new phase until being heated to 900 ºC at peak pressure and transforming to HP-CEN. No reversion to this phase was observed during the experimental conditions in run T409 (see Fig. 1 for experimental P-T path). This suggests that the new phase may be a metastable phase related to the kinetic process of the phase transition from OEN to HP-CEN at room temperature.

5. Geophysical applications

Many seismic models of the Earth’s upper mantle show velocity discontinuities or unusual gradients in the depth range of 200–350 km (see Gaherty et al., 1999; Gu et al., 2001; Deuss and Woodhouse, 2002
and references therein); these include the Lehmann discontinuity at depths of about 220 km and the 260 km or X-discontinuity. The OEN to HP-CEN transition involves a significant density increase of ~3%, which has been suggested to be the cause of the seismic reflectors at depths between 200 and 300 km; such reflectors might be expected to be observed in an Earth of “depleted” mantle composition model (Angel et al., 1992; Woodland and Angel, 1997; Woodland, 1998). In the absence of velocity data for the HP-CEN phase, Angel et al. (1992) used Birch’s law to estimate the velocity changes associated with the OEN to HP-CEN phase transition (see also Woodland and Angel, 1997). In this study, we were able to measure the elasticity of both the OEN and HP-CEN in the same experiment and thus to evaluate the contrast of seismic properties between these two phases directly.

The density jump across the phase transformation is 2.6–2.9% at a pressure range corresponding to the depth of 200–300 km in the upper mantle. The corresponding velocity jump is 3–4% for P wave and 5–6% for S wave. Thus, the seismic impedance contrast \( Z_{HP-CEN} - Z_{OEN} \) is \( Z_{OEN} \times (Z_{HP-CEN} - Z_{OEN}) \), where \( Z \) is density \times velocity. For a depleted mantle composition model with ~20 modal% OEN (i.e. Ca-poor orthopyroxene, Jordan, 1978; Woodland, 1998) the expected seismic impedance contrast should be between 1 and 2% for P and S waves in the depth range 200–300 km. Based on unpublished data from our laboratory (Kung et al., 2002), we expect that the magnitude of these velocity and impedance increases would be reduced somewhat at high temperature. Such small velocity and impedance contrasts could be masked by the other geophysical processes or structures (Woodland, 1998) and thus not produce strong seismic reflections. Therefore, the OEN to HP-CEN phase transformation may not be a satisfactory explanation for seismic discontinuities observed at the depth range of 200–300 km.

In this study, we also observed, for the first time and unexpectedly, anomalous elastic behavior prior to the phase transition from the orthoenstatite \( \rightarrow \) HP-CEN at room temperature: both the P and S wave velocities reach a maximum value near 9 GPa and thereafter decrease on increase of pressure. Interestingly, an elastic softening behavior has also been observed in OEN at high temperatures and room pressure (Jackson et al., 2004). If anomalous elastic behavior were to be observed also at high pressure and high temperature, such a “softening” of the elasticity of the pyroxene component of mantle compositions may contribute to low-velocity zones or enhanced seismic discontinuity, which occurs at depths of ~220 km continental regions (Gaherty et al., 1999; Gu et al., 2001; Deuss and Woodhouse, 2002).

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