

# *In Situ* Elasticity Measurements of Unquenchable MgSiO<sub>3</sub> Clinoenstatite at Upper Mantle Conditions

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## Introduction

A phase transformation from orthorhombic (orthoenstatite [OEN], space group Pbc<sub>a</sub>) to monoclinic symmetry in (Mg,Fe)SiO<sub>3</sub>, a common constituent of the Earth's crust and upper mantle, is likely to occur in the deeper portion of the upper mantle [1, 2]. Angel et al. [3] confirmed that the clinoenstatite phase above 8 GPa is an unquenchable, high-pressure, monoclinic phase (high-pressure clinoenstatite [HP-CEN], space group C2/c). Because of its unquenchable nature, the HP-CEN phase has to be synthesized within its stability field in order to study its elasticity. To date, the elasticity of HP-CEN has not been measured; such measurements are limited by the techniques available.

For determining the elasticity at corresponding conditions by using an ultrasonic technique, the length of the specimen is a key parameter. Recently, the installation of x-radiography for ultrasonic measurement, combined with *in situ* x-ray diffraction, has made it possible to monitor the length change of the sample during an experiment and to measure the travel times ( $t_{(P,S)}$ ) and density of the sample simultaneously [4]. By using the state-of-art experimental setup, we were able to measure the elasticity of unquenchable HP-CEN. In this study, we present results on the measured elasticity of HP-CEN at high pressure and temperature for the first time.

## Methods and Materials

Ultrasonic measurements at high pressures and temperatures, in conjunction with synchrotron x-radiation, were performed on polycrystalline specimens of MgSiO<sub>3</sub>-clinoenstatite in a 1000-ton, multianvil apparatus with a T-cup module (T-25) [5]. Round-trip travel times (2t) of both P and S waves were collected by using a transfer function (TF) method [6]. In these experiments, high-pressure clinoenstatite was transformed at ~13 GPa and ~1000°C for 2 hours *in situ* from the well-sintered MgSiO<sub>3</sub> orthoenstatite that was synthesized prior to the acoustic experiments. After the transformation of the specimen to the high-pressure clinoenstatite was complete, its elasticity was measured along a series of heating and cooling cycles as the pressure was slowly decreased down to ~6 GPa. At each of these positions in pressure and temperature (P-T) space, energy-dispersive x-ray diffraction spectra were collected for both the

specimen and NaCl, yielding direct determinations of the specimen volume and cell pressure, respectively. By using the measured travel times from ultrasonics, specimen lengths from x-radiography, densities from x-ray diffraction spectra, elastic wave velocities ( $V_P$  and  $V_S$ ), and elastic moduli ( $K_S$  = bulk modulus and  $G$  = shear modulus) could be calculated at all experimental conditions.

## Results

The unit cell volumes of HP-CEN (from run T409) that were obtained were plotted as a function of pressure from a range of 6 to ~14 GPa and temperature up to 1000°C (Fig. 1). These data were used to estimate the high-temperature thermal expansion by using a modified high-temperature Birch-Murnaghan equation (e.g., see Eq. 2 in Ref. 7). The refined specimen cell volume at 6.5 GPa and room temperature was 385.567 Å<sup>3</sup>, which was in good agreement with our observed value of 385.626 Å<sup>3</sup>. We constrained the bulk modulus and its pressure derivative by using the acoustic data that were collected simultaneously and converted to isothermal values ( $K_T = 158$  GPa,  $K_T' = 5.3$  at 6.5 GPa and 300K) to obtain the thermal expansivity  $\alpha(T)$  and temperature derivative of the isothermal bulk modulus. We obtained a result of  $\alpha(T) = [0.64(3) \times 10^{-5}] + [3.14(50) \times 10^{-8}] T$  and  $(\partial K_T / \partial T) = -0.033(5)$  GPa K<sup>-1</sup>.

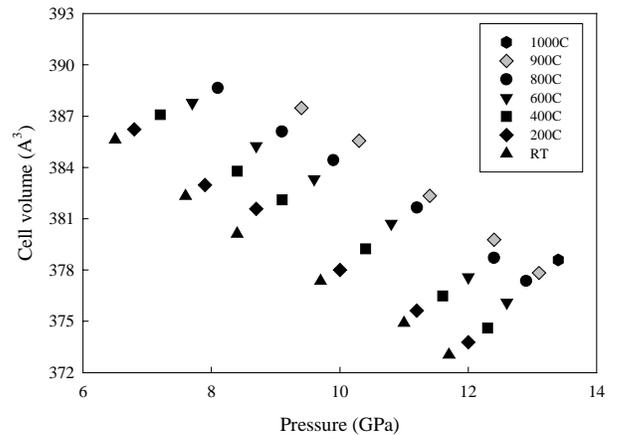


FIG. 1. Unit cell volumes at high pressure and high temperature for the HP-CEN phase from run T409.

The compressional (P) and shear (S) wave velocities of runs T354 and T409 were determined from the measured travel times and specimen lengths and plotted as a function of pressure at high temperature (Fig. 2). Both the P and S waves from the two runs exhibited a systematic increase with increasing pressure along the various isotherms, and they also exhibited strong linearity. The elastic velocities determined from the two runs and the two specimens at high temperature were comparable; the large difference in the velocity between the two runs was ~0.5% at a temperature of 800°C and at high pressure.

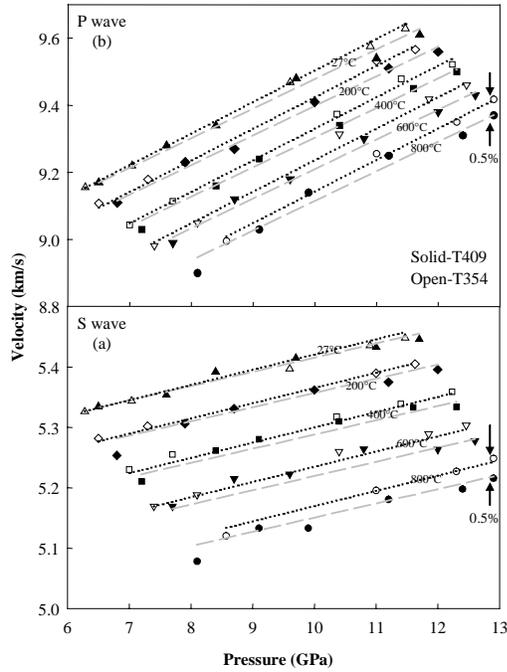


FIG. 2. Elastic wave velocities as function of pressure at high temperature for (a) S wave and (b) P wave. The solid symbols represent the data measured from run T409, and the open ones are from T354. The long (T409) and short (T354) dashed lines indicate fits to the observed data from using a linear dependence on pressure and temperature.

The bulk and shear moduli at high pressure and temperature were calculated from the measured P and S wave velocities and densities,  $K_S = \rho(V_P^2 - 4/3V_S^2)$  and  $G = \rho V_S^2$ . The bulk and shear moduli data were treated as a linear function of pressure and temperature to obtain the properties and temperature derivatives. The fitting results were  $K_S = 160(1)$  GPa,  $G = 99(1)$ ,  $\partial K_S/\partial P = 5.8(1)$ ,  $\partial G/\partial P = 1.5(1)$ ,  $\partial K_S/\partial T = -0.018(1)$ , and  $\partial G/\partial T = -0.015(1)$  at 6.5 GPa and at room temperature.

## Discussion

Enstatite (Mg-rich pyroxene) is a major component of the Earth's mantle. It may take up to ~20 modal % in regions with harburgitic or depleted bulk compositions [8]. Therefore, the high-pressure form of enstatite, HP-CEN, will be an important phase in the deep portion of the upper mantle before it is transformed into the garnet phase at a depth of 400 to ~450 km. Its low-pressure form, OEN, was considered to be a slow material when compared with the olivine phase, as indicated by the existing elasticity data [9]. The new measured elasticity for HP-CEN has brought into question whether this unquenchable high-pressure phase is another slow material when compared with the olivine phase in the upper mantle. To answer this question, we calculated the P and S wave velocities of HP-CEN and olivine along a 1600K adiabat at a pressure range of 6 to 14 GPa, corresponding to a depth of 250 to ~410 km. By using the thermoelastic properties of HP-CEN available from the current study and those of olivine (Fo<sub>90</sub>) available from high-pressure and high-temperature studies [10-12], elastic velocities could be computed in these phases as a function of pressure and temperature. The procedure was to first correct for the temperature by calculating the properties at 1600K. The next step was to extrapolate the properties adiabatically at a different pressure by using finite strain theory. The resultant P and S wave velocities for HP-CEN and olivine are plotted in Fig. 3. Of interest

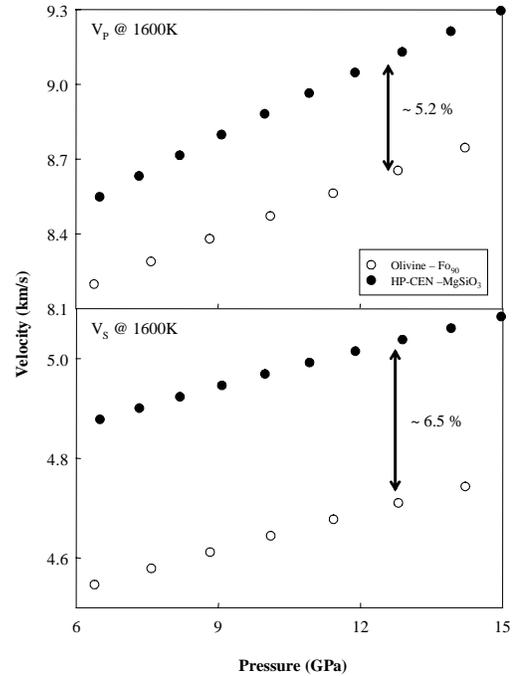


FIG. 3. Finite strain trajectories for P and S waves along a 1600K adiabat. The open symbols represent the olivine phase, and solid ones represent the HP-CEN phase.

is the fact that the elastic velocities of HP-CEN at high pressure and at 1600K are faster than those of olivine: ~5.2% for the P wave and ~6.5% for the S wave. From our demonstration, we conclude that the olivine phase would be the only slow phase in the deeper portion of the upper mantle (e.g., at a depth of 250 to ~400 km) in regions with harburgitic or depleted bulk mantle compositions.

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