Anomalous Elastic Properties of Coesite at High Pressure and Implications for the Upper Mantle X-discontinuity

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Abstract

Compressional and shear wave velocities of coesite have been measured using ultrasonic interferometry in a multi-anvil apparatus up to 12.6 GPa at room temperature for the first time. While the P wave velocity increases continuously with pressure, the S wave exhibits an anomalous softening and the velocity decreases continuously with pressure. Finite strain analysis of the data yielded $K_{S0} = 103.6(4)$ GPa, $G_0 = 61.6(2)$ GPa and $K_0' = 2.9(1)$, $G_0' = 0.3(1)$ for the bulk and shear moduli and their pressure derivatives, respectively. The anomalous elastic behavior of coesite results in large velocity and impedance contrasts across the coesite - stishovite transition, reaching ~39% and ~48% for P and S wave velocity contrasts, and ~70% and 78% for P and S wave impedance contrasts, respectively, at pressure ~ 8 GPa, with P and S wave velocity perturbations showing no apparent dependence on depths (i.e., $d\ln V_{(P \text{ or } S)}/dh \sim 0$) within 8-12 GPa. These unusually large contrasts and depth independent characteristics render the transition between the two silica polymorphs one of the most plausible candidates for the cause of the seismically observed X-discontinuity. The current P and S wave velocity perturbation dependences on the SiO₂ content, $d(\ln V_P)/d(\text{SiO}_2) \sim 0.43 \text{ (wt\%)}^{-1}$ and

$d(\ln V_S)/d(\text{SiO}_2) \sim 0.60 \text{ (wt\%)}^{-1}$, can serve as a geophysical probe to track ancient subducted eclogite materials to gain insights on the geodynamics of the mantle.

Keywords: Coesite; Elastic properties; Ultrasonic interferometry; High pressure; X-discontinuity

1. Introduction

Coesite is a polymorph of silica with the monoclinic structure and space group $C2/c$. It was first synthesized by L. Coes, Jr. in 1953 at high pressure and high temperature and was later identified in Coconino sandstone at Meteor Crater, Arizona by Chao et al. in 1960. Coesite (or pseudomorphs) has also been found in metamorphic rocks in subduction or collision zones and eclogite xenoliths (Smith 1984; Wang et al., 1989; Butler et al., 2013). Since coesite forms at pressures and temperatures above 2.5 GPa and 700 °C, this suggests that these non-impact generated coesite were from depths greater than 75 km in the upper mantle. The occurrence of coesite in eclogitic assemblages is thought to be one of the best indicators of metamorphism at ultra-high pressure (UHP). Under higher pressures (~300 km depth), coesite transforms into another high-pressure phase of silica (stishovite) with the rutile structure (Stishov and Popova, 1961). As a consequence of the increase of coordination number from four to six, stishovite has much larger density (4.287 g/cm³) than coesite (2.909 g/cm³) and quartz (2.648 g/cm³) (Smyth and McCormick, 1995).

From static compression X-ray diffraction studies on powders (Bassett and Barnett, 1970) and single crystals (Levien and Prewitt, 1981; Angel et al., 2001; 2003), the crystal structure of coesite has been investigated up to 9.6 GPa and anomalous

compression behavior was reported, namely, an accelerated increase in incompressibility with pressure (Angel et al., 2003). Anomalies under high pressure have also been observed in Raman and infrared spectroscopy data (Hemley, 1987; Williams et al., 1993), which led to the proposal that coesite may undergo a crystalline - crystalline phase transition at 22-25 GPa, and become amorphous above 30 GPa. Very recently, a single crystal Raman spectroscopy study by Černok et al. (2014) revealed two phase transitions at ~23 GPa and 35 GPa, respectively; however, no amorphization of coesite was observed up to 51 GPa at room temperature in the latter study.

The reported values of the bulk modulus of coesite range from 96 to 126 GPa; for comparison, measured acoustic values for the bulk modulus of stishovite range from 305 GPa to 346 GPa (e.g., Mizutani et al., 1972; Weidner et al., 1982; Li et al., 1996b). The large contrasts in bulk modulus and density between coesite and stishovite are believed to produce large velocity and impedance contrasts between the two phases, such that if there is free silica in the upper mantle, the transformation from coesite to stishovite may offer a plausible explanation for the seismic discontinuity around 300 km depth in the upper mantle known as the X-discontinuity (Revenaugh and Jordan, 1991; Deuss and Woodhouse, 2004; Williams and Revenaugh, 2005; Schmerr et al., 2013). To further evaluate this hypothesis, the elasticity of coesite and stishovite at pressures and temperatures relevant to the Earth's upper mantle are required. While single-crystal or powder compression studies with X-ray diffraction provide valuable information on the structural behavior, density, and bulk modulus at high pressure, they provide no information on the behavior of the shear elastic properties. Prior to the current study, shear properties for coesite were only limited to those at ambient conditions from

previous Brillouin scattering experiments on single crystal (Weidner and Carleton, 1977) and ultrasonic experiments on polycrystalline specimens [see data of Liebermann (1976) cited in Weidner and Carleton (1977), and of Mizutani et al. (1970) cited in Akimoto (1972)]. Even though acoustic data at high pressures are available for stishovite from ultrasonic (Li et al., 1996b) and Brillouin scattering (Jiang et al., 2009) studies, the lack of direct acoustic measurements for the shear properties (i.e. shear wave velocity and shear modulus) of coesite at high pressures has greatly undermined the assessment of the physical properties across the coesite - stishovite transition for its implications for the X-discontinuity in previous studies.

In this study, ultrasonic interferometric measurements on synthetic polycrystalline coesite have been conducted for the first time up to 12.6 GPa at room temperature. The densities and elastic bulk and shear properties are determined directly in the experimental pressure range. Combined with elasticity data for stishovite, the velocity and impedance contrasts between coesite and stishovite are precisely determined at high pressures and the implications for the seismic X-discontinuity are evaluated. In addition, the possibility of using this transition as a probe for ancient subducted oceanic materials in the mantle is explored.

2. Experiment methods

The polycrystalline specimen of coesite (S-3482) used in the current ultrasonic experiment was hot-pressed at 6.5 GPa and 920 °C for three hours in a 2000-ton uniaxial split-sphere apparatus (USSA-2000) in the High Pressure Laboratory at Stony Brook University using a commercial grade silicon dioxide powder as the starting material. The

hot-pressing experiment followed a specific P-T path designed to obtain a crack-free, fine-grained, and homogeneous coesite specimen (Gwanmesia and Liebermann, 1992); the recovered bulk sample was characterized by synchrotron X-ray diffraction, which revealed that the sample was nearly pure coesite with one extra small peak that can be indexed by (101) of quartz. The volume fraction of quartz was estimated to be ~1% from the intensity of the quartz peak observed in X-ray diffraction; this may cause an underestimation of ~0.25% for P and S velocities, which is within the current measurement uncertainties. The final dimensions of the sample after polishing were 1.807(1) mm in length and 2.710(10) mm in diameter. The bulk density of the sample was measured by the Archimedes' immersion technique using a single-crystal MgO as standard, yielding 2.92(2) g/cm³, which is in complete agreement with the density from X-ray diffraction (2.9213 g/cm³, Levien and Prewitt, 1981) within mutual uncertainties.

High-pressure ultrasonic interferometric experiment was performed in the 1000-ton uniaxial split-cylinder apparatus (USCA-1000) up to 12.6 GPa at room temperature. The cell assembly is similar to that in Li and Liebermann (2014). A dual mode LiNbO₃ transducer (50 MHz resonant frequency for P waves, and 30 MHz for S waves) was used to generate and receive both the compressional (P) wave and shear (S) wave signals simultaneously. Fig. 1 shows representative P wave signals at 5.6 GPa. An alumina buffer rod of 3.771(1) mm in length and 3.158(1) mm in diameter was inserted between the specimen and tungsten carbide (WC) anvil, allowing the specimen to be positioned at the center of the cell; the alumina buffer rod also serves as an in-situ pressure marker (see details below).

The travel times of P and S waves were obtained using the pulse echo overlap (PEO) method by overlapping the reflected echoes from the front and rear surfaces of the sample (e.g., B1 and S1 in Fig. 1). Details about the transfer function technique for data acquisition and processing have been discussed elsewhere (Li et al., 2002; 2004). The cell pressures were calculated from the S wave travel times of the alumina buffer rod by the equation $P=238.I*(I-t/t_0)$ that was derived in a previous study (Li et al., 2003), where P is cell pressure, t is the S wave travel time of the buffer rod, and t_0 is the S wave travel time at room pressure [for further details of the use of alumina as a pressure marker, see Li and Liebermann (2014), and Wang et al. (2014)]. The uncertainty in the pressure determined with alumina as the in-situ pressure marker is about 1%.

3. Results and Discussion

After the experiment, the sample length and diameter were 1.808(1) mm and 2.726(1) mm respectively, indicating that, within 0.6% uncertainty, the sample can be considered to have undergone elastic compression under pseudo-hydrostatic conditions in the entire course of the experiment. Therefore, the sample lengths under pressure can be reliably obtained using the method developed by Cook (Cook, 1957). We calculated the densities of the sample at high pressure from the length change derived from Cook's method together with $\frac{\rho_0}{\rho} = (\frac{l}{l_0})^3$. The bulk and shear moduli are calculated using the relationship $K_s = \rho \left(V_p^2 - \frac{4}{3} V_s^2 \right)$ and $G = \rho V_s^2$. All the experimental data up to 12.6 GPa are summarized in Table 1. The velocity and density data in the entire P-T range were then fitted to third-order Eulerian finite strain equations (Davies and Dziewonski, 1975) to obtain the bulk and shear moduli, as well as their pressure dependence at ambient

conditions. More details about the fitting procedures can be found in Li and Liebermann (2014).

The P and S wave velocities as a function of pressure are plotted in Fig. 2. For comparison, the P and S wave velocities of the bench-top measurement and those calculated from the elastic moduli K_0 and G_0 derived from the finite-strain fit are also included, as well as the ultrasonic data from Liebermann (1976), and the single crystal Brillouin scattering data from Weidner and Carleton (1977) on coesite. Fig. 2 indicates that whereas the P wave velocity of coesite increases steadily with pressure in the experiment pressure range (Fig. 2a), consistent with the behavior of most mantle minerals, the S wave velocities (Fig. 2b) exhibit a monotonic decrease up to the peak pressure of the current experiment. This feature of coesite, although different from other mantle minerals such as olivine and diopside whose shear wave velocity increases monotonically with pressure in the current experimental pressure range (e.g., Li et al., 1996a; Li and Neuville, 2010), has been observed in spinels (e.g., Zou et al., 2013), as well as in orthopyroxene (Kung et al., 2004) and hydrous stishovite under higher pressures (Lakshtanov et al., 2007). In many cases, such anomalies are often followed by phase transitions or amorphization with further increase in pressure (e.g., Karki et al., 1997a, 1997b; Carpenter and Salje, 1998). The decrease of shear wave velocity in coesite, which is related to the shear modulus G , may result from the softening of the shear elastic constant C_{44} that was reported to decrease with increasing pressure (Kimizuka et al., 2008).

The P and S wave velocities at room pressure and temperature derived from this study are 7.97(1) km/s and 4.59(1) km/s, respectively. As shown in Table 2, these results

are nearly identical to the directly measured bench-top values on the same specimen reported in Michaut (2001). Using ultrasonic pulse transmission method, Mizutani et al. (1970) reported the P wave velocity for coesite to be 7.6 km/s (later revised to 7.53 in Akimoto 1972; not plotted in Fig. 2), which is about 5-6% lower than our data. The differences are probably caused by the quality of the sample used in different experiments. Liebermann (1976) reported the velocities of P and S waves to be 7.92 km/s and 4.55 km/s, respectively, which are in remarkable agreement with our data. A single crystal study on coesite using Brillouin scattering by Weidner and Carleton (1977) yielded the VRH averages of $V_P = 8.19$ km/s, $V_S = 4.59$ km/s from their best model, and $V_P = 7.86$ km/s, $V_S = 4.69$ km/s from an alternate model. While our V_P falls within the range of the two models, the V_S from our experiment is indistinguishable from their best model and slightly lower (about 2%) than their alternate model. The average velocity derivatives with respect to pressure are $dV_P/dP = 0.027$ km/s/GPa and $dV_S/dP = -0.013$ km/s/GPa for P and S waves, respectively; these results are significantly different from the corresponding values for other mineral phases in lithospheric mantle of peridotitic and/or eclogitic compositions, such as those for olivine ($dV_P/dP \sim 0.07$ km/s/GPa, Li et al., 1996a), diopside ($dV_P/dP \sim 0.08$ km/s/GPa, Li et al., 2010), and orthopyroxene ($dV_P/dP \sim 0.10$ km/s/GPa; Kung et al., 2004). In addition, the negative dV_S/dP of coesite yields a fast increase of V_P/V_S from ~ 1.75 at ambient conditions to 1.88 at ~ 12.6 GPa. All of these distinct features of coesite can be important geophysical signatures to distinguish the subducted oceanic crust stagnant in the upper mantle.

The elastic moduli K_S and G as a function of pressure are plotted in Fig. 3. The uncertainties in the bulk and shear moduli are approximately 0.5%. The adiabatic bulk

modulus increases systematically over the entire pressure range, while the shear modulus increases to about 12 GPa, then decreases slightly, which may mark the onset of a pressure-induced amorphization or phase transition above 20 GPa as suggested in previous Raman and Infrared data of coesite (Hemley, 1987; Williams et al., 1993). A recent single-crystal Raman spectroscopy study by Černok et al. (2014) has reported that coesite does not become amorphous at least up to 52 GPa; instead, it undergoes two phase transitions at ~23 GPa and ~35 GPa. Clearly, acoustic experiments to higher pressure than the current peak pressure will help to further understand the behavior of coesite as these transitions are approached.

The volume change as a function of pressure observed in our experiment, as well as single-crystal experiment data from Angel et al., (2001) and Levien and Prewitt, (1981), are compared in Fig. 4. Our data extend the highest pressure from 9.6 GPa to 12.6 GPa, and more importantly, show excellent consistency with those of single-crystal studies under hydrostatic pressures. This provides strong evidence that our experiments have been carried out under nearly hydrostatic conditions, which in turn provides further confirmation about the reliability of the current length determination using Cook's method and the resulted velocities.

In Table 2, we compare our data for the bulk (K) and shear (G) moduli and their pressure derivatives of coesite with previous acoustic, static compression and theoretical studies. Among static compression studies, single-crystal data up to 5.19 GPa by Levien and Prewitt (1981) predicted the lowest bulk modulus ($K_T = 96$ GPa) together with a highest value for the pressure derivative ($K_T' = 8.4$). The pressure derivative of bulk modulus of 8.4 is much higher than our data of $K_0' = 2.9$ as well as those compared in

Table 2. The wide discrepancy may result from the different pressure ranges and hydrostaticity in these experiments as well as the well-known trade-off between K_T and K_T' in equation-of-state fit. For more details about the trade-off between K_T and K_T' , see Kung et al. (2001). Using single-crystal X-ray diffraction and hydrostatic compression up to 9.6 GPa, Angel et al. (2001) observed an anomalous compression behavior around 3.5 GPa, and a fourth order equation of state analysis yielded $K_T = 100.8$ GPa, $K_T' = 1.8$, and a positive second pressure derivative of $K'' = +0.057$ GPa⁻¹. Our results in Fig. 3a appear to indicate that there is indeed a non-negative second pressure derivative for the bulk modulus of coesite. The current third order finite strain analysis yielded an implied value of K'' of -0.039 GPa⁻¹, when fitted with 4th order; a positive value of $+0.094$ GPa⁻¹ ($K_0 = 104.8$ GPa, $K_0' = 2.2$). The close agreement between the current data and those of Angel (2001) can be also seen in the Fig. 4. The bulk and shear moduli calculated by VRH average using the reported elastic constants from DFT study of Kimizuka et al. (2008) are $K_0 = 95.9$ GPa and $G_0 = 55.2$ GPa, respectively. Comparisons with these experimental studies show that our experiment provides the most self-consistent and complete information on the elasticity of coesite for its simultaneous determination of bulk and shear moduli and their pressure derivatives.

4. Implications for seismic discontinuities in upper mantle

4.1 Velocity and impedance contrasts between coesite and stishovite

Compared to stishovite, coesite has lower pressure derivatives for both the bulk and shear moduli, and this is especially pronounced for the shear modulus. By using the elastic parameters and their pressure derivatives for stishovite (Li et al., 1996b; Jiang et

al., 2009), P and S wave velocities of stishovite under the same pressures as those in the current experiment were calculated by fitting to the third-order Eulerian equation of state (Davies and Dziewonski, 1975). Previous ultrasonic measurements up to 3 GPa by Li et al. (1996b) yielded pressure derivatives for stishovite of $K_0' = 5.3$, $G_0' = 1.8$, which are higher than the VRH values ($K' = 4.0$ and $G' = 1.1$) reported by Jiang et al. (2009) from single crystal Brillouin scattering study to 12 GPa. As a result, in the pressure range of 0-6 GPa the velocities calculated using elasticity data from Li et al. (1996b) and Jiang et al. (2009) differ by 1.6-0.5% for P wave and 2.5-1.5% for S wave, respectively; a close examination indicated that the nearly pressure-independent P wave velocities and the negative pressure dependence in S wave velocities in Jiang et al. (2009) between 0 and 6 GPa are somewhat different from all previous observations from ultrasonic measurements (Mizutani et al., 1972; Li et al., 1996b), polycrystalline Brillouin scattering study (Asahara et al., 2013), and theoretical studies using density functional theory (Karki, 1997a) and Landau theory (Carpenter et al., 2000). Thus, the velocities calculated using the elasticity data of Li et al. (1996b) were used in the current calculation as well as subsequent discussions. Compared to those calculated using data from Jiang et al. (2009) in the pressure range of interest to the X discontinuity from 8 to 12 GPa, the velocities only differ by +0.2 to -0.4% and +1.2 to +0.6% for P and S waves, respectively, and can be considered to be within mutual uncertainties.

From these data, the velocity and impedance (ρV ; ρ = density, V = velocity) contrasts between coesite and stishovite as a function of pressure at room temperature are obtained and compared in Fig. 5. In the current study, the contrasts are defined by

$$C = \frac{A(St.) - A(Co.)}{(A(St.) + A(Co.))/2} \times 100\% \quad (1)$$

where C is the contrast, A represents velocity or impedance, St.: stishovite, and Co.: coesite. The figures indicate that P wave velocity contrasts are about 39% and nearly independent of pressure within the current experimental pressure range, while S wave contrast increases from ~43% at room pressure to ~49% at 12.6 GPa. The resultant impedance contrasts are even larger, reaching 69-73% for P wave and ~78% for S wave, due to contributions from both the large velocity and density contrasts between coesite and stishovite. The velocity and impedance contrasts of S waves are greater than those of P waves, and this feature becomes more pronounced at higher pressures. This is a consequence of the larger pressure derivative contrast for the shear modulus as compared with the bulk modulus between coesite and stishovite. In comparison with that (~ 9-11%) (Li and Liebermann, 2014) across the phase transition of olivine to wadsleyite, the velocity contrasts of coesite-stishovite transition are 4-5 times higher; such large velocity and impedance contrasts are believed to be the highest among all phase transitions of mantle minerals, making coesite - stishovite the most efficient phase transition in producing seismically detectable velocity jumps at mantle depths.

4.2 X-discontinuity

The X-discontinuity in the upper mantle has been observed in a number of seismic studies, which indicate that there is a velocity contrast of 1.5%~4.8% for compressional and shear waves in the depth range of 250-350 km (e.g. Zhang and Lay, 1993; Deuss and Woodhouse, 2002; A. Li et al., 2002; Bagley and Revenaugh, 2008; Schmer et al., 2013; Shen et al., 2014; Chu et al., 2014). Unlike the discontinuities at 410 km and at 660 km, the X-discontinuity may not be a global feature; it has been observed typically in regions of active mantle dynamics, such as subduction zones and beneath

oceanic plates (Revenaugh and Jordan, 1991; Zhang and Lay, 1993; Gilbert et al., 2001; Deuss and Woodhouse, 2002; Bagley and Revenaugh, 2008), and stable continents, such as Australia and North America (Hales et al., 1980; A. Li et al., 2002; Chu et al., 2014), although a recent study suggested that it could be also a global feature (Shen et al., 2014). The X-discontinuity is often accompanied by a Lehmann-discontinuity at shallower depths (around 220 km) in the upper mantle (Revenaugh and Jordan, 1991; Deuss and Woodhouse, 2004), which has been proposed to be caused by the transition in deformation mechanism from dislocation to diffusion creep (e.g., Deuss and Woodhouse, 2004) or the dehydration of subducted sediment (Ono, 2007) contributing to its negative Clapeyron slope. In contrast to the L-discontinuity, the X-discontinuity is often attributed to phase transitions of minerals in the upper mantle. However, the depth range, geological setting, and velocity jump make it difficult to find an optimum explanation (e.g., Deuss and Woodhouse, 2004)

Several mechanisms have been proposed to explain the X-discontinuity. One earlier explanation, as suggested by Revenaugh and Jordan (1991), is the formation of hydrous phase A ($\text{Mg}_7\text{Si}_2\text{H}_6\text{O}_{14}$). However, phase A cannot explain this discontinuity because this phase is now known to become unstable above 1000 °C at 300 km depth and is limited to hydrous environment of cold subduction zones (Williams and Hemley, 2001; Komabayashi et al., 2005). Another mechanism is the transition of orthoenstatite (OEn, space group Pbca) to high-pressure clinoenstatite (HPCen, space group C2/c) (Woodland and Angel, 1997), which is characterized by velocity contrasts of 4% for P waves and 7.8% for S wave (Kung et al., 2005). Although OEn-HPCen transition can occur at the P-T conditions of the X-discontinuity (Fig. 6) and can be narrow enough to cause the seismic

reflection (Woodland, 1998), the impedance jump caused by this transition in a pyrolite composition (1-1.4% for S wave and 0.7-0.9% for P wave) is too small compared with the impedance contrast of 3%~8% at the X-discontinuity (see also Woodland, 1998; Matsukage et al., 2005; Li et al., 2014). To match the impedance contrast of the X-discontinuity observed by seismic studies, it would require 25-67% orthopyroxene in the upper mantle modal composition (Jacobsen et al., 2010); however, such high orthopyroxene contents (~30% or above) have only been observed in xenoliths and exposed massifs from southern Africa (e.g., Boyd and McCalister, 1976; see also Matsukage et al., 2005) and the Siberia craton (see Kelemen et al., 1998). The depleted mantle peridotite (harzburgite) in subduction zones, however, only has a moderate amount of orthopyroxene (~20%), and the corresponding impedance contrast is only about 1-2.2%. Moreover, in-situ synchrotron X-ray studies as well as previous “cook-and-look” experiments indicate that the OEn - HPCen transition can occur at depths up to ~275 km along a normal mantle adiabat or subduction geotherm (Akashi et al., 2009, see also Fig. 6); the incorporation of water shifts the transition to even shallower depths (Jacobsen et al., 2010). Thus, OEn - HPCen transition can be considered as a possible contributor, but most likely not the sole cause of the X discontinuity around 300 km depth.

Other mechanisms, such as the transformation of forsterite (Fo) and periclase (Per) to anhydrous phase B (Anh-B, $\text{Mg}_{14}\text{Si}_5\text{O}_{24}$), have also been proposed as a candidates to explain the X discontinuity (Ganguly and Frost, 2006). Despite the debate about the stability of Anh-B (see Bagley and Revenaugh, 2008; Ottonello et al., 2010), the current elasticity data at high pressures (e.g., Ottonello et al., 2010 and references therein) appear

to suggest that the corresponding impedance contrasts are comparable to those of OEn-HP-Cen transition for P and S waves; as a result, in order for Fo+Per → Anh-B to produce velocity changes comparable to those observed in seismic studies, a mechanism for generating substantial amounts of periclase would need to be demonstrated from both laboratory study and field observations.

Another possible cause for the X discontinuity, as suggested in previous studies, is the coesite-stishovite phase transition (e.g., Williams and Revenaugh, 2005; Schmerr et al., 2013). In contrast to the formation of the Anh-B transition which requires local enrichment of periclase, the coesite - stishovite requires free silica at upper mantle depths. It has been well accepted that free silica could come from the eclogitic assemblage formed by the subducted oceanic crust, as seen in the computed phase diagram of MORB in Fig. 6a from Ricard et al., 2005 (see also Irifune and Tsuchiya, 2007; Stixrude and Lithgow-Bertelloni, 2012, and Woodland et al., 2014). The former basaltic material, which comes from subduction or delamination of the oceanic crust, undergoes metamorphism with the formation of coesite at depth of ~80 km. A silica phase (coesite or stishovite) also forms in the subducted sediments and its proportions can be as high as ~20 wt% in the sedimentary layers (Ono, 2007; see also Ono, 1998). The presence of coesite at upper mantle depths has also been demonstrated by thermodynamic calculations for a variety of altered and unaltered basaltic compositions (Gubbins et al., 1994; Ghent et al., 2004); the discovery of coesite as inclusions in garnet and omphacite in eclogite xenoliths and collision zones in various localities (e.g., Smith 1984; Wang et al., 1989; Butler et al., 2013) may represent a observable manifestation of stable coesite in the upper mantle.

Previously, the velocity and impedance contrasts using the amounts of SiO₂ characteristic of basalts from MORB were estimated to be in 1-2.5% and 2-5% range, respectively (Williams and Revenaugh, 2005). Note that these previous estimations assumed a pressure independent Poisson's ratio in order to estimate the values of the shear modulus for coesite and under pressure. However, the current data in Table 2 indicate that Poisson's ratio increases monotonically from 0.25 at ambient pressure to 0.3 at 12 GPa; thus, the shear modulus of coesite was greatly overestimated in previous studies while the velocity and impedance contrasts were all underestimated. According to the current data (e.g., Fig. 5), within the pressure range of 8-12 GPa (corresponding to ~250-350 km depths), the velocity contrasts between coesite and stishovite are as high as ~39% for P wave and 48% for S wave, together with impedance contrasts of ~70% and ~78% for P and S waves, respectively. With such extreme contrasts between coesite and stishovite, even small amount of free silica (~5%) present in eclogite assemblages is capable of generating velocity and impedance contrasts comparable to those observed at the depths of X-discontinuity. To further evaluate this, we calculated the velocities and impedances of the (coesite+garnet) and (stishovite+garnet) systems using VRH averaging method (Watt et al., 1976), and obtained the property contrasts for velocity, density, and impedance across the coesite-stishovite transition with 4 to 20 wt% silica (Fig. 7a). For the MORB mineralogy with 14 wt% of coesite/stishovite as suggested by Ricard et al. (2005) (see Fig. 6), the velocity contrasts are about 5.8% for P wave, 7.3% for S wave, and the corresponding impedance contrasts are about 10.7% and 12.3%, respectively. These values are nearly twice as high as those reported for the X-discontinuity. To reproduce the seismically observed P and S wave impedance contrasts of 3-8% and

density increase of ~2.0%, the required amount of SiO₂ at these depths is 4-8 wt%, which is in remarkable agreement with the experimentally determined free silica content in MORB from petrological studies (e.g., Aoki and Takahashi, 2004) and thermodynamic calculations(e.g., Ghent, et al., 2004).

Thus, the existence of free silica in MORB, the depth range of the coesite-stishovite transition (Fig. 6), and the sharpness and magnitude of the velocity increase all make this transition a favorable explanation for the X-discontinuity. On the other hand, based on the analysis of the depth (h) and S wave velocity perturbations (dlnVs) around X-discontinuity at various tectonic settings, Deuss and Woodhouse (2004) concluded that the seismic data do not seem to reveal a Clapeyron slope that is consistent with any single phase transformation of mantle minerals. In fact, according to the current data within 8-12 GPa, both P and S wave velocity perturbations show no dependence on depths, i.e., $d\ln V_{(P \text{ or } S)}/dh \sim 0$, across the coesite-stishovite transition in eclogite from 250 to 300 km (Fig. 8). This appears to offer a reasonable explanation for the relationship between the depth and S wave velocity perturbations observed by Deuss and Woodhouse (2004); the sporadic locations of the X-discontinuity can then be reconciled by the silica phase from subducted eclogite materials and/or terrigenous materials that are transported into in the mantle due to disequilibrium mixing (e.g., Xu et al., 2008). In the event that some recycled eclogite reacts locally with surrounding peridotite to form orthopyroxene-rich peridotite (e.g., Yaxley and Green, 1998; Mallik and Dasgupta; 2012) under ambient mantle pressure and temperature conditions, the X-discontinuity may also contain contributions from the OEn- HPCen transition which can further widen the observed depth distribution.

Thus, the current data in Fig. 7 and the seismic data on the X-discontinuity offer a possible geophysical approach for probing and even quantifying the eclogitic materials at upper mantle depths. As seen in Fig. 7b, at 300 km depth both P and S wave velocity perturbations show a linear dependence on the SiO₂ content with $d(\ln V_P)/d(\text{SiO}_2) \sim 0.43 (\text{wt}\%)^{-1}$ and $d(\ln V_S)/d(\text{SiO}_2) \sim 0.60 (\text{wt}\%)^{-1}$. It should be noted that the above velocity and impedance calculations would be altered by only $\sim 0.1\%$ when the variation/discrepancy of the reported elasticity of majoritic garnet is taken into account. This suggests that the contrasts across the coesite-stishovite transition, as well as the subsequently derived $d(\ln V_P)/d(\text{SiO}_2)$ and $d(\ln V_S)/d(\text{SiO}_2)$, are insensitive to the elasticity (hence the composition) of the co-existing garnet in the subducting oceanic basalts. In the above discussion, we have assumed that the velocity and impedance contrasts between coesite and stishovite at room temperature are representative of those at high temperatures. It has been shown that, such as for the olivine-wadsleyite transition, the velocity contrasts at room temperature are in agreement with those along mantle temperatures within $\sim 1\%$ (e.g., Li et al., 1996a; 2014) due to the fact that $(\partial^2 V_P / \partial T \partial P)$ and $(\partial^2 V_S / \partial T \partial P)$ are both nearly zero (e.g., Liu et al., 2005; 2009); this has been proven to be true even when S wave exhibits an anomalously low dV_S/dP as demonstrated by a recent ultrasonic study on MgAl₂O₄ spinel (Zou et al., 2013). While simultaneous high pressure and temperatures are underway to obtain direct measurement of the velocity and impedance contrasts between coesite and stishovite under mantle conditions, the results in this paper may serve as an important diagnostic for tracking ancient subducted materials to gain insights about the dynamics of the mantle.

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Figure Captions

Fig. 1. Acoustic echoes observed for 50 MHz P waves at 5.6 GPa. A: anvil, B: buffer rod, S: sample, 1 represents the first echo train.

Fig. 2. P- and S-wave velocities of coesite as a function of pressure up to 12.6 GPa determined by ultrasonic measurements (blue diamonds) in the USCA-1000 multi-anvil apparatus; (a) P wave, (b) S wave. Data obtained using Cook's method and the full finite strain method are indistinguishable. Purple X is the bench-top velocities of our specimen (see Michaut, 2001). Red squares are ambient velocities calculated from elastic moduli from the finite strain fit. Also shown are the data of Liebermann (1976) - green triangle; single crystal data (yellow and blue circles) by Weidner and Carleton (1977) from Brillouin scattering.

Fig. 3. Adiabatic bulk (K) modulus and shear (G) modulus for coesite as a function of pressure up to 12.6 GPa determined by ultrasonic measurements in the USCA-1000 multi-anvil apparatus; (a) bulk (K) modulus, (b) shear (G) modulus.

Fig. 4. Calculated volume change of coesite as a function of pressure from our ultrasonic experiments (red squares). Blue triangles are from single-crystal study on coesite by Angel et al. (2001). Green diamonds are from Levien and Prewitt. (1981).

Fig. 5. Velocity and impedance (ρV) contrasts between coesite and stishovite as a function of pressure.

Fig. 6. (a) Phase diagram for MORB (from Ricard et al., 2005). (b) Phase boundaries for coesite-stishovite and OEn-HPC, superimposed with possible geotherms of continents, ocean, slab surface, and the interior of the slab (see Kirby et al., 1996;

Peacock, 2003). Phase boundaries for coesite-stishovite include those from Akaogi et al. (2011) and Zhang et al., (1996), and Liu et al. (1996); OEn-HPCen boundaries are representative of the works by Akashi et al. (2009); Woodland and Angel (1997), Ulmer and Stalder (2001) and Pacalo and Gasparik (1990). Fo+Per $\rightarrow$ Anh-B boundary is representative of the work by Ottonello et al. (2010).

Fig. 7. (a) P and S wave velocity, impedance and density contrasts of coesite-stishovite transition in MORB as a function of SiO₂ content at 10 GPa. (b) P and S wave velocity, and density jumps across coesite-stishovite transition at 10 GPa.

Fig. 8 Velocity increase across coesite-stishovite transition in eclogite at various depths for SiO₂ content range of 4-12%, showing $[d\ln V_{(P \text{ or } S)}/dh]_{\text{SiO}_2} \sim 0$. (a) V_P, (b) V_S.

Table 1. Experimental results for coesite up to 12.6 GPa at room temperature

Table 2. Comparison of the P and S wave velocity, density, and elastic moduli of coesite with previous experimental results and theoretical calculations

Highlights:

- V_s of coesite decreases monotonically with pressure
- Coesite-stishovite transition exhibits enormous velocity and impedance contrasts
- Phase transition of coesite to stishovite may explain the seismic X-discontinuity
- A geophysical probe to track ancient subducted eclogitic material is proposed

Fig.1

Fig.2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Table 1. Experimental results for coesite up to 12.6 GPa at room temperature

P(GPa)	$2t_p(\mu\text{s})$	$2t_s(\mu\text{s})$	$l(\text{mm})$	$\rho(\text{g/cm}^3)$	V/V_0	$V_P(\text{km/s})$	$V_S(\text{km/s})$	$K_S(\text{GPa})$	$G(\text{GPa})$
0.7	0.4499(3)	0.7854(3)	1.803(2)	2.94(1)	0.993(5)	8.01(1)	4.59(1)	106.3(6)	62.0(3)
1.7	0.4479(3)	0.7864(3)	1.797(2)	2.97(1)	0.984(5)	8.03(1)	4.57(1)	108.5(6)	62.0(3)
2.5	0.4459(3)	0.7859(3)	1.793(2)	2.99(1)	0.977(5)	8.04(1)	4.56(1)	110.4(6)	62.2(3)
4.1	0.4409(3)	0.7859(3)	1.785(2)	3.03(1)	0.964(5)	8.10(1)	4.54(1)	115.3(6)	62.5(3)
5.6	0.4369(3)	0.7849(3)	1.777(2)	3.07(1)	0.951(5)	8.14(1)	4.53(1)	119.3(6)	62.9(3)
7.1	0.4334(3)	0.7844(3)	1.770(2)	3.11(1)	0.940(4)	8.17(1)	4.51(1)	123.0(6)	63.3(3)
8.4	0.4299(3)	0.7844(3)	1.764(2)	3.14(1)	0.930(4)	8.21(1)	4.50(1)	126.8(7)	63.5(3)
9.4	0.4274(3)	0.7844(3)	1.759(2)	3.17(1)	0.923(4)	8.23(1)	4.48(1)	129.6(7)	63.7(3)
10.4	0.4244(3)	0.7844(3)	1.755(2)	3.19(1)	0.916(4)	8.27(1)	4.47(1)	133.0(7)	63.8(3)
11.2	0.4224(3)	0.7844(3)	1.751(2)	3.21(1)	0.910(4)	8.29(1)	4.46(1)	135.3(7)	64.0(3)
11.9	0.4204(3)	0.7849(3)	1.748(2)	3.23(1)	0.905(4)	8.32(1)	4.45(1)	137.8(7)	64.0(3)
12.6	0.4189(3)	0.7864(3)	1.745(2)	3.24(1)	0.901(4)	8.33(1)	4.44(1)	139.9(7)	63.8(3)

Table 2. Comparison of the P and S wave velocity, density, and elastic moduli of coesite with previous experimental results and theoretical calculations

Method		V_P (km/s)	V_S (km/s)	K_0 (GPa)	K_0'	G_0 (GPa)	G_0'	Max P (GPa)
(1) Ultrasonic ^a		7.92	4.53	105	-	59.9	-	0.75
(2) Ultrasonic ^a		7.53	4.19	97.2	-	51.3	-	1
(3) Brillouin Scattering ^a	Best model	8.19	4.59	113.7	-	61.6	-	0
	Alternate model	7.86	4.69	94.7	-	64.2	-	0
(4) Compression ^b		-	-	96	8.4	-	-	5.19
(5) Compression ^b		-	-	100.8	1.8	-	-	9.6
(6) Compression ^b		-	-	114	8 ^d	-	-	8.5
		-	-	126	4 ^d	-	-	
(7) DFT ^c		7.57	4.32	95.9	-	55.2	-	15
<i>Current study</i>								
(8) Ultrasonic ^a	Bench top	7.94(1)	4.58(1)	102.0(4)	-	61.0(2)	-	-
		7.97(1)	4.59(1)	103.6(4)	2.9(1)	61.6(2)	0.3(1)	12.6

^a Ks, ^b K_T, ^c 0 K, ^d assumed, $K_S = (1 + \alpha\gamma T) K_T$, $1 + \alpha\gamma T \approx 1.001$ with thermal expansion $\alpha = 6.9 \times 10^{-6} \text{ K}^{-1}$ (Fei, 1995), and Grüneisen parameter $\gamma = \frac{\alpha K_S}{C_p \rho}$, $C_p = 40.38 \text{ J/(mol} \cdot \text{K)}$ (Hemingway et al., 1998).

(1) Liebermann (1976)-see Weidner and Carleton (1977)

(2) Akimoto (1972)-also see Mizutani (1970)

(3) Weidner and Carleton (1977)

(4) Levien and Prewitt (1981)

(5) Angel et al. (2001)

(6) Bassett and Barnett (1970)

(7) Kimizuka et al. (2008)

(8) This study, see Michaut (2001) for bench-top measurement (number in parentheses are uncertainties in measured values)