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**Elastic behaviors of silicate materials at
deep mantle pressures**

Doctoral dissertation

by

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Chapter 1: Overview

1-1. Elastic measurements at deep mantle pressures

Elastic behavior in silicate materials at high pressures is fundamental information to understand the Earth's mantle. Because materials can not be obtained, observed seismic velocities in the Earth's deep interior need to be compared to sound velocity of constituent rocks of the Earth's deep interior at high pressure-temperature conditions to know chemical composition of the Earth's interior. Moreover, the compressibility and density of silicate materials are controlled by elastic behavior, therefore, elastic behavior also important parameters for density and the sink-float of materials at the Earth's deep interior.

Generally, there are three methods to measure the elastic properties of sample under extremely high pressures with static compressional condition, ultrasonic method, Brillouin scattering method, and inelastic X-ray scattering method.

In ultrasonic method, sample length is divided by detected delay time of reflective pulse the ultrasonic probe passed through the sample to obtain sound velocities of

sample. This method is applicable to not only transparent specimen but also not transparent specimen, however, the volume of sample has lower limit constrained by the wavelength of ultrasonic probe ($\sim 500 \mu\text{m}$ at the frequency of 10 MHz), therefore, ultrasonic method is applicable to piston-cylinder apparatus and multi-anvil cell, however, not easy to apply to diamond anvil cell (Bass, 2007).

Brillouin scattering method is known as an inelastic light scattering. This method would be optimized method to measure the transparent materials such as silicates at the deep mantle pressures, because this method is applicable to diamond anvil cell, and allows high accuracy data because this method need not extrapolations to obtain sound velocities. The details of this method are described in the next section.

Inelastic X-ray scattering method is one of the inelastic light scattering methods such as Brillouin scattering method. By this method, the dispersion of phonon at ultrahigh frequency is obtained ($\sim 20 \text{ meV}$). This method is also applicable to the microsize sample such as in diamond anvil cell. The most focusable point on this method is that not only transparent specimen but also not transparent specimen, for example, iron and highly iron-containing materials, are available (Fiquet et al., 2004). However, to obtain sound velocities, the extrapolation in phonon dispersion curve to the longer wavelength region is necessary.

Consequently, Brillouin scattering method might be the optimum method in order to obtain elastic properties of transparent silicate materials entire the Earth's mantle pressures.

1-2. Brillouin scattering measurement

When incident light is introduced into transparent materials, a part of incident photo is scattered with migration of energy and momentum by phonon of acoustic mode among the material (Born and Huang, 1954; Polian, 2003). The energy migration is controlled by the law of conservation of energy, therefore, the frequency shift in scattering light is expressed with following equation;

$$\hbar\nu_s = \hbar\nu_i \pm \hbar\omega \quad (1.1)$$

where ν_s is frequency of scattering light and ν_i is that of incident light, and ω is that of acoustic phonon among sample. Here, there are two processes in energy migration. If the acoustic phonon obtains energy by incident beam and the scattered light is modulated to lower frequency than the incident beam, the process is called “Stokes process”. If contrary energy migration and frequency shift in scattered light occurred, the process is “anti-Stokes process”. We can see that the quantity of frequency shift in

scattering light is equal to the frequency of acoustic phonon. The migration of momentum is expressed as;

$$\hbar \vec{k}_s = \hbar \vec{k}_i \pm \hbar \vec{q} \quad (1.2)$$

where k_s and k_i is the wavevector of scattering and incident light, respectively, and q is wavevector of the acoustic phonon. In Brillouin scattering, difference in the wavelength and wavenumber of between incident and scattering light can be assumed as zero because the modulation of wavelength and wavenumber by the acoustic phonon is negligible. Then, if the angle between the wavevector of incident beam and that of scattering light is defined as 2Φ , which is called as scattering angle, we can obtain following relation;

$$|\vec{q}| = 2n|\vec{k}| \sin \phi \quad (1.3)$$

where n is refractive index of the sample and $|\vec{k}|$ is the wavenumber of incident and scattering light. Here, we can obtain the velocity of the acoustic phonon as follows;

$$V = \frac{\omega}{|\vec{q}|} = \frac{\omega \lambda}{2n \sin \phi} \quad (1.4)$$

where V is sound velocity of sample and λ is the wavelength of incident beam. Hence, the sound velocity can be obtained by frequency shift in scattering light, scattering angle, refractive index of sample and the wavelength of incident beam. Because the frequency of this scattering light is very close to the elastic scattering light (Rayleigh

scattering), Fabry=Perot interferometer is chosen as a detector of frequency shift. This scattering is widely used to measure the elastic behavior of transparent materials, including silicate materials, under extreme conditions such as high pressure and high temperature conditions because both probe and detector does not need to be touched to the specimen under such untouchable condition, and this method is also applicable to the transparent specimen in diamond anvil cell because diamond windows are also transparent to visible light, therefore, the incident light can be introduced to the specimen. Present day, in order to measure sound velocities of samples in diamond anvil cell, two geometries, back scattering geometry and platelet geometry are employed. Schematic figure is shown in Fig. 1-1a and Fig. 1-1b. In particular, platelet geometry should be described in more detail, because this geometry does not need the refractive index of sample under extreme conditions in order to obtain sound velocities. In parallel multilayer, the product of refractive index and $\sin \Psi$, where Ψ is scattering angle, is constant because of Snell's law. Therefore, the refractive index of sample in diamond anvil cell is expressed as follows;

$$n = \frac{\sin \theta}{\sin \phi} \quad (1.5)$$

where θ represents external scattering angle. Combining Eq.(1.4) and Eq.(1.5), we can obtain the equation;

$$V = \frac{\omega\lambda}{2 \sin \theta} \quad (1.6)$$

Eq.(1.6) shows that with platelet geometry, sound velocities of sample in diamond anvil cell under extreme condition can be obtained without refractive index (Whitfield et al., 1976). The schematic figure of the geometry application of platelet geometry to diamond anvil cell is shown in (Fig. 1c).

The first significant improvement for application to geophysical science of Brillouin scattering method is conducted to single crystalline quartz with a diameter of ~0.3 mm by Weidner and his co-workers at ambient pressure (Weidner et al., 1975). Soon after, Whitfield et al. (1976) developed the application to diamond anvil cell and tested with the measurements of well-known sound velocities of single crystalline NaCl at high pressure in platelet geometry, however, the pressure is limited up to 3.5 GPa. The increment of deviatoric stress in the sample chamber with increasing pressure had hindered the expansion of the available pressure to the lower mantle condition for the long time. Murakami et al. (2007a) overcame this barrier by the optimizing of *in-situ* synthesis and annealing with CO₂-laser heating and prospered Brillouin scattering measurements for polycrystalline MgSiO₃ perovskite up to 96 GPa. Present available pressure of sound velocity measurements with Brillouin scattering method is up to 172 GPa in silicate minerals (Murakami et al., 2007b) and above 200 GPa in silicate glasses

(Murakami and Bass 2010; 2011), therefore, sound velocity measurements entire the Earth's mantle pressures (~135 GPa) is available.

1-3. The seismic anomalies at the lowermost mantle

The lowermost mantle is the most significant thermal and chemical boundary layer in the Earth's interior. Knowledge of the lowermost mantle is quite important to understand physical and chemical evolution of the Earth's history. Therefore, the interpretation of seismic structure in this region based on elastic properties by experimental method is necessary for understanding the evolution of the Earth's interior. However, seismic observations showed quite complex horizontal heterogeneities in this region as described below.

Fig. 1-2 shows the fluctuation of seismic velocities at the depth of 2790 km. There are three significant seismic heterogeneities in the lowermost mantle (Masters, 2000). First one is large cumulates laid under the central Pacific and southern Africa region, which shows about 3 % slower shear wave velocity and faster bulk sound velocity than average shear and bulk sound velocity, respectively, and is called Lager Low Shear Velocity Provinces (LLSVPs). LLSVPs are laid beneath the slower shear and

longitudinal velocity region, therefore, LLSVPs are interpreted as the origin of upwelling in mantle convection. These regions show anti-correlation between bulk and shear velocity, therefore, the cause of this seismic anomaly cannot be explained as a simply fluctuation of temperature. Second one is observed under the LLSVPs with a thickness of ~ 40 km and shows strongly slower shear velocity. These regions are called Ultra-Low Velocity Zones (ULVZs). The origin of ULVZs is interpreted as a partial melting of mantle rocks because of such strong reductions of seismic velocities (Garnero et al., 2008). Third one is laid beneath circum-Pacific region. This region shows faster shear wave velocity and slower bulk sound velocity than average seismic velocities, and this region is laid just beneath the trench. This seismic anomaly also cannot be explained by only temperature fluctuation because of the anti-correlation between shear wave velocity and bulk sound velocity.

There are some prospected sources of these seismic anomalies, however, all the candidates have no conclusive evidences, mainly because of the lacking of elastic properties of candidate materials at the lowermost mantle pressure. Piled Mid Ocean Ridge Basalt (MORB) is one of the feasible candidate sources of LLSVPs, because MORB is produced by the igneous activity at the mid ocean ridge, and subducted significant volume through the geological time, therefore, it is easy to explain such large

volume of chemical anomalies (Hernlund and Hauser, 2008; Ohta et al., 2008), however, because the elastic properties of constituent minerals at lowermost mantle pressure is lacking, the identification of this large anomaly has not been done yet. Recently, Labrosse et al (2007) suggested the solidification model of early Earth's mantle. Silicate melt denser than coexisting solid generates large Basal Magma Ocean (BMO) during fractional solidification of mantle just after Earth's formation. Then, BMO produces denser sluggish cumulates by solidification, and one part of BMO survives just on the core mantle boundary till present time because of slow crystallization. According to this BMO model, both LLSVPs and ULVZs can be explained uniformly as the sluggish cumulates and remnant silicate melt on the CMB, respectively, however, the feasibility of this model is still under debated, because the information of iron concentration to silicate melt during fractional crystallization and compressional behavior of silicate melts at high pressure-temperature conditions is not known well. Phase transition in MgSiO_3 perovskite to post-perovskite is one of the plausible candidates for explanation of the faster shear velocity anomaly beneath circum-Pacific region, because the bulk and shear wave velocity of MgSiO_3 post-perovskite is expected to become slower and faster than MgSiO_3 perovskite (Wentzcovitch et al., 2006; Murakami et al. 2007b), respectively. However, the D'' seismic discontinuity, which is expected as a result of the

MgSiO₃ perovskite to post-perovskite phase transition, exists in globally, at least, not only beneath circum-Pacific region (Van der Hilst et al., 2006). Hence, this phase transition is expected to occur globally so the influence of this phase transition in sound velocities would be also manifested in globally. Additionally, the degree of anomalies on seismic velocities seems to be not homogeneous. Therefore, only this phase transition can not explain this seismic anomaly.

Although there are other candidate sources than described above, anyway, the elastic properties at high pressure in candidate materials at the lower mantle pressures are necessary to identify those seismic anomalies.

1-4. Overview

Chapter 2 shows the aggregate shear wave velocity of tetragonal CaSiO₃ perovskite obtained by Brillouin scattering measurements. This material is one of the major constituent minerals in the pyrolytic lower mantle and subducted MORB (Hirose, 2006). The results show that this material has about 15 % slower shear velocity than average mantle minerals, MgSiO₃ perovskite and MgO (Murakami et al., 2007b; 2009) at lower mantle pressures, although bulk sound velocity of tetragonal CaSiO₃ perovskite shows

almost similar value to MgSiO_3 perovskite and slightly larger value than MgO . Based on this analysis, if tetragonal perovskite is stable in the lower mantle, or high-temperature cubic CaSiO_3 perovskite shows similar elastic behavior as Tsuchiya (2011) showed, bulk sound velocity and shear velocity of subducted Ca-depleted rocks, for example, harzburgite, would take slightly slower bulk sound velocity and faster shear velocity than average mantle, respectively. Additionally, Brillouin scattering measurement at limited high-pressure and temperature was conducted in Appendix 1. The results show larger temperature dependency in shear modulus and shear velocity than MgSiO_3 perovskite and MgO (Murakami et al., 2012). Therefore, shear velocity reduction by CaSiO_3 perovskite would be enhanced at high temperature. (However, experimental pressure-temperature range is quite limited so sound velocity measurements at various pressures and temperatures are needed to discuss more accurate effect in elasticity of CaSiO_3 perovskite.)

In Chapter 3, I show shear wave velocity of iron-bearing MgSiO_3 glass from 15 GPa to 113 GPa and relatively Mg-poor and Ca-rich basalt glass from 45 GPa to 77 GPa. Present glasses are employed as analogue materials of corresponding silicate melts. I found shear wave velocity anomaly around 60 GPa in iron-bearing MgSiO_3 glass. Similar anomaly is reported in ferropericlase by accompanying effect with spin

transition of iron (Marquardt et al., 2009; Murakami et al., 2012; Wu et al., 2013), therefore, this anomaly would be interpreted as a result of spin transition of iron among iron-bearing MgSiO_3 glass. In contrast, Mg-poor and Ca-rich basalt glass shows no anomaly in shear wave velocity. Hence, spin transition is not expected in basaltic glass.

In chapter 4, I show both compressional and shear wave velocities of iron-bearing MgSiO_3 glass from 15.5 GPa to 52.3 GPa and alumina-bearing MgSiO_3 glass from 11.2 GPa to 52.9 GPa. These velocity data lead bulk sound velocity, Poisson's ratio, and quantity of elastic density increase with increasing pressure at high pressure. Using with these parameters, density and elastic moduli up to mid lower mantle pressure are estimated. The behavior of both the Poisson's ratio and other elastic moduli of present two glasses at high pressure up to 53 GPa is very similar to that of MgSiO_3 glass and SiO_2 glass. It indicates the influence of iron to the structural change with increasing pressure in silicate glasses and melts would be very small or negligible. Additionally, the density is calculated by the aggregate of bulk sound velocity, however, this evaluation of density would be minimum because the sound velocities at high frequency such as Brillouin scattering regime would not reflect the volume change by structural change, therefore, the estimation of structural effect for density change with increasing

pressure is necessary to estimate the density of silicate glasses and melts at high pressure condition more accurately.

In chapter 5, implications and future perspectives are discussed based on the results in chapter 2~4.

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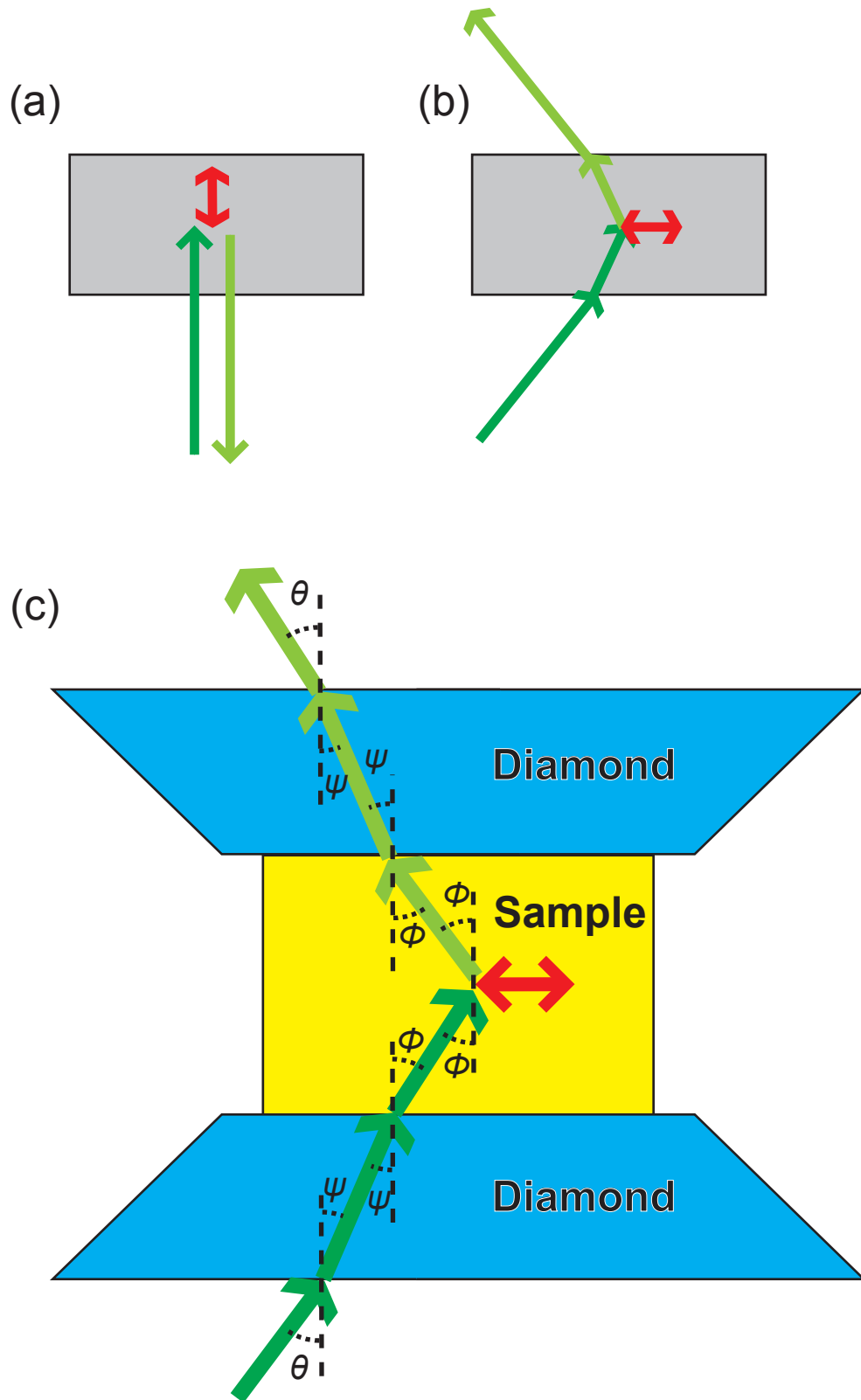


Fig. 1-1 Schematic figure of Brillouin scattering measurement in (a) backscattering geometry, (b) platelet geometry and (c) the application to diamond anvil cell. Dark green arrows represent incident beam, light green arrows denote scattering light, and red arrows is the acoustic phonon.

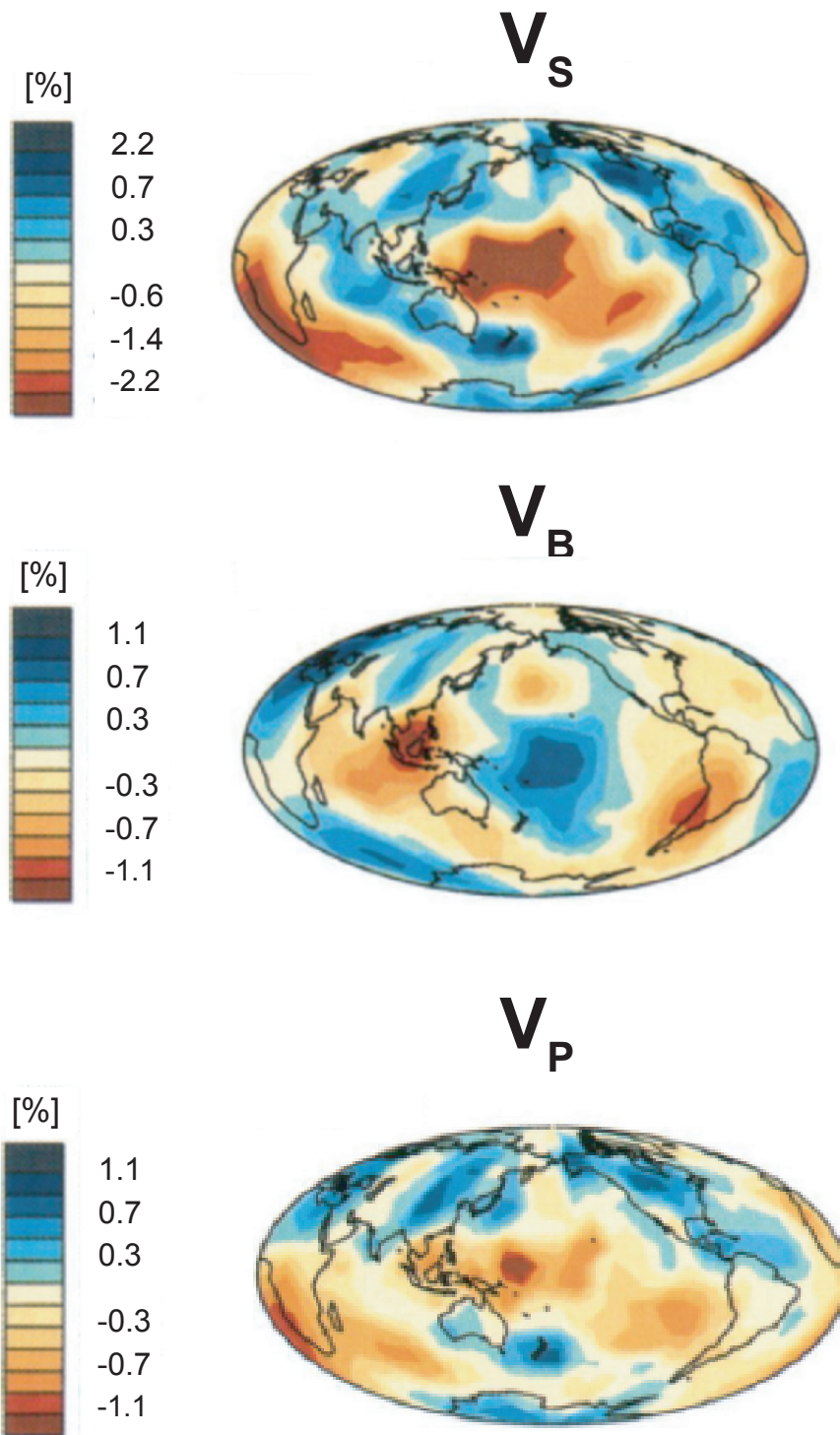


Fig. 1-2 Lateral seismic anomaly of shear velocity, bulk sound velocity, and compressional velocity at the depth of 2790 km by Masters et al. (2000).

We can see anti-correlation between shear velocity and bulk sound velocity beneath the central Pacific and south Africa (LLSVs), and circum-Pacific region.

Chapter 2: Sound velocity measurements of CaSiO_3 perovskite to 133 GPa and implications for lowermost mantle seismic anomalies

Abstract

In this chapter, the measurements of aggregate shear velocity (V_S) of CaSiO_3 perovskite (CaPv) at high pressure (P) between 33 and 133 GPa and room temperature (T) on the basis of Brillouin spectroscopy are reported. The sample had a tetragonal perovskite structure throughout the experiments. The measured P – V_S data show the shear modulus and its pressure derivative at ambient condition to be $G_0 = 115.8$ GPa and $G' = 1.20$, respectively. The zero-pressure shear velocity is determined to be $V_{S0} = 5.23$ km/sec, in good agreement with the previous estimate inferred from ultrasonic measurements on $\text{Ca}(\text{Si,Ti})\text{O}_3$ perovskite at 1 bar. Our experimental results are also generally consistent with earlier calculations on tetragonal CaPv. According to the very recent predictions, such tetragonal CaPv has similar velocities to the cubic phase. These indicate that shear and longitudinal velocities of CaPv are much lower than those of the other lower mantle minerals such as MgSiO_3 -rich perovskite and ferropericlase. While primitive mantle includes certain amount of CaPv, a depleted peridotite (former

harzburgite) layer in subducted oceanic lithosphere is deficient in CaPv and enriched in ferropericlasite in the lower mantle. Such harzburgite exhibits 0.9 % faster V_S and 0.7 % slower bulk sound velocity (V_B) than the primitive mantle at lowermost mantle P - T conditions. The observed fast V_S and slow V_B anomalies in the D'' layer underneath the circum-Pacific region may be attributed in large part to the presence of subducted harzburgitic materials.

2-1. Introduction

CaSiO₃ perovskite (CaPv) is an important mineral in both transition zone and lower mantle. Its mineral proportions are supposed to be about 5 and 25 vol% in pyrolitic mantle and subducted mid-oceanic ridge basalt (MORB) materials, respectively, under the lower mantle conditions (e.g. Kesson et al., 1998; Murakami et al., 2005; Hirose et al., 2005). Therefore, the elastic properties of CaPv is greatly important to interpret the seismic wave velocity structure in the lower mantle. First principles calculations by Karki and Crain (1998) demonstrated that sound velocities of cubic CaPv, in particular shear velocity, are much faster than MgSiO₃ perovskite. Karato and Karki (2001)

argued that the high shear to longitudinal wave velocity heterogeneity ratio observed in the deep lower mantle can be reconciled with the variation in the abundance of CaPv in addition to the Fe/(Mg+Fe) ratio.

It is known that CaPv adopts cubic perovskite structure at high temperature, while it slightly distorts to tetragonal symmetry with decreasing temperature (e.g., Stixrude et al., 1996; Shim et al., 2002; Akber-Knutson et al., 2002; Kurashina et al., 2004; Caracas et al., 2005; Adams and Oganov, 2005). The *P-T* condition of such tetragonal-cubic phase transition is still under debate (Li et al., 2006; Stixrude et al., 2007; Komabayashi et al., 2007). While earlier theoretical works predicted that such minor structural distortion from ideal cubic structure reduces the shear modulus considerably by ~30% (Li et al., 2006; Stixrude et al., 2007), the most recent calculations by Tsuchiya (2011) demonstrated that sound velocities of tetragonal CaPv are comparable to those of the cubic phase.

Despite its importance in the lower mantle, sound velocities of CaPv were measured at high pressure only up to 12 GPa by ultrasonic method (Li et al., 2004). In addition, sound velocity measurements were performed only on CaTiO₃ and Ca(Si_{0.5}Ti_{0.5})O₃ perovskites at 1 bar (Sinelnikov et al., 1998), because CaPv is unstable at ambient condition. In this study, we synthesized pure CaSiO₃ perovskite at high pressure in a

laser-heated diamond-anvil cell (DAC) and subsequently measured its shear velocity by Brillouin spectroscopy. The measurements were made with increasing pressure from 33 to 133 GPa at room temperature. With previously reported bulk modulus of CaPv, longitudinal velocity (V_p) is also estimated to deep lower mantle pressures.

2-2. Experimental method

High-pressure Brillouin scattering measurements were conducted at room temperature in a symmetric DAC with 60 degrees angular aperture (see Murakami et al., 2009a for details). We used CaSiO_3 gel as a starting material, which was dehydrated completely by heating to 1273 K in a furnace beforehand. The powder of the starting material and NaCl pressure medium were loaded into a hole in a rhenium gasket (NaCl : CaSiO_3 : NaCl = 1 : 4 : 1 in thickness). They were compressed to high pressure with flat 300 μm culet (<60 GPa) or beveled 150 μm culet (>60 GPa) diamond anvils. Polycrystalline CaPv sample was synthesized *in situ* in a DAC from the amorphous starting material by heating with a carbon dioxide laser. Typical x-ray diffraction (XRD) pattern is shown in Fig. 2-1. We observed a splitting of cubic 200 peak at ~14

degrees of two-theta angle, indicating a tetragonal distortion for all the samples at room temperature (Shim et al., 2002; Komabayashi et al., 2007). However, our experiment pressures were only 6 points and not enough to establish a reliable equation of state of CaPv so we employed the previous results by Ricolleau et al. (2009) for fitting present sound velocity data as we will show later. After each pressure increment, the sample was thermally annealed by heating to ~ 1300 K for 2 min with the carbon dioxide laser in order to minimize the deviatoric stress in the sample. All the pressures in the samples were determined from the unit-cell volume of B2-type NaCl (Sata et al., 2002).

We have collected Brillouin spectra from polycrystalline CaPv at 33 to 133 GPa in two separate runs. Diode-pumped laser with a wavelength of 532 nm (Verdi V2, Coherent, 200-600 mW) was introduced to the sample as an incident laser. The scattered light was collected into a Sandercock-type six-pass tandem Fabry-Perot interferometer (Sandercock, 1982). All measurements were performed in platelet geometry (Whitfield et al., 1972), and the scattering angle ($2\theta \approx 50$ degrees) was calibrated by using BK₇ glass as a standard (Yoneda and Song, 2005).

In order to obtain the sound velocity of isotropic aggregate of the sample, four to twelve Brillouin spectra were collected at a single pressure condition on different orientations by rotating the sample around the compression axis (chi-axis). The

collecting time for a single Brillouin scattering spectrum was 5 to 24 hours. The peaks from shear acoustic mode of CaPv were clearly observed in each spectrum (Fig.2-2). The individual raw Brillouin spectra were fitted with a Gaussian peak function to determine the peak positions. The evaluated peak positions of all spectra at a given pressure were averaged including Stokes and anti-Stokes peaks. For more experimental details, see Murakami et al. (2009a).

2-3. Result

We obtained the sharp Brillouin peaks for shear acoustic mode of CaPv over the entire pressure range explored, although longitudinal mode overlapped with the diamond peak. Representative spectra collected at 33 and 80 GPa are shown in Fig. 2-2. The peaks from NaCl pressure medium were not found in all the measurements, probably due to its small thickness. The aggregate shear velocities of tetragonal CaPv measured in this study are summarized in Table 2-1 and plotted as a function of pressure in Fig. 2-3. They are slightly lower than the values obtained for tetragonal CaPv at 0 K by first-principles calculations (Stixrude et al., 2007; Tsuchiya, 2011)

(Table 2-2), and considerably lower than the predictions for cubic CaPv at equivalent pressure (Karki and Crain, 1998; Stixrude et al., 2007), except the very recent calculations by Tsuchiya (2011); This paper showed results of calculation for supercells of tetragonal and cubic CaPv, and claimed that the elasticities between them were very similar and both of them were much lower than Karki and Crain (1998). However, extrapolation of our high-pressure V_S data to ambient pressure is consistent with previous estimate at 1 bar based on the velocities of CaTiO_3 and $\text{Ca}(\text{Si}_{0.5}\text{Ti}_{0.5})\text{O}_3$ perovskites measured by ultrasonic method (Sinelnikov et al., 1998) (Fig. 2-3).

In order to obtain the adiabatic shear modulus at zero pressure, G_0 , and its pressure derivative, G' , present P - V_S data were fitted to the third-order Eulerian finite strain equations:

$$\rho V_S^2 = G = G_0(2f + 1)^{\frac{5}{2}} \left\{ 1 - \left(5 - \frac{3K_S G'}{G_0} \right) f \right\} \quad (2.1)$$

where

$$f = \frac{1}{2} \left\{ \left(\frac{\rho}{\rho_0} \right)^{\frac{2}{3}} - 1 \right\} \quad (2.1)$$

ρ is density, and K_S is adiabatic bulk modulus (subscript zero denotes the value at zero pressure) (Birch, 1938). K_S is considered to be very similar to isothermal bulk modulus, K_T , at room temperature. Because our experimental pressures were too few as noted before, we used $\rho_0 = 4.23 \text{ g/cm}^3$, $K_{T0} = 244 \text{ GPa}$, and its pressure derivative, $K' = 4$ from

recent experimental results (Ricolleau et al., 2009). The fitting provided $G_0 = 115.8(20)$ GPa and $G' = 1.20(2)$ (Fig. 2-4, Table 2-2). The reported K_{T0} values of CaPv widely ranged from 232 to 325 GPa (Tamai and Yagi, 1989; Wang et al., 1996; Shim et al., 2000). Nevertheless, such variations change G_0 and G' by less than 1% and 25%, respectively. The G_0 of tetragonal CaPv obtained here is slightly lower than the previous calculations of $G_0 = 128$ GPa at $T = 0$ K by Stixrude et al. (2007). Conversely, present value is in good agreement with $G_0 = 112(5)$ GPa estimated on the basis of measurements of CaTiO_3 and $\text{Ca}(\text{Si}_{0.5}\text{Ti}_{0.5})\text{O}_3$ perovskites by Sinelnikov et al. (1998). The present G' value is also slightly lower than the previous calculations of $G' = 1.36$ by Stixrude et al. (2007) for tetragonal CaPv.

Both $G_0 = 116$ GPa and $G' = 1.20$ of CaPv are substantially lower than $G_0 = 173$ GPa and $G' = 1.56$ determined for MgSiO_3 perovskite based on similar Brillouin spectroscopy measurements (Murakami et al., 2007). Furthermore, they are smaller than those of other lower mantle minerals such as MgO periclase (Murakami et al., 2009b) and SiO_2 stishovite (Karki et al., 1997). As a consequence, shear velocity of tetragonal CaPv is much slower than those of other typical lower mantle minerals; ~16% slower than MgSiO_3 perovskite at 120 GPa and 300 K (Fig. 2-5). With K and ρ from the previous experiments by Ricolleau et al. (2009), we also calculated the longitudinal

velocity of tetragonal CaPv as a function of pressure (Fig. 2-6). The results show considerably slower V_p for CaPv than those of other lower mantle phases.

2-4. Discussion

2-4-1. Comparison with theoretical predictions

Present measurements are generally consistent with earlier theoretical calculations on tetragonal CaPv (Stixrude et al., 2007; Tsuchiya, 2011) (Fig. 2-3, Table 2-2). Our data show slightly lower velocities, possibly because the crystal structure of tetragonal CaPv in the present experiments might be different from that in the calculations. Stixrude et al. (2007) and Tsuchiya (2011) calculated the velocities of tetragonal CaPv with $I4/mcm$ space group, because $I4/mcm$ is predicted to be the most thermodynamically stable crystal structure at $T = 0$ K. Nevertheless, theory also reported that the energy differences between several different tetragonal structures are very small, suggesting a formation of another tetragonal phase under small shear stress in high-pressure

experiments as well as inside the Earth (Caracas et al., 2005; Adams and Oganov, 2006).

2-4-2. Effect of variation in CaPv abundance on seismic velocities

Present results indicate that the presence of tetragonal CaPv considerably reduces both shear and longitudinal velocities in lower mantle pressures at 300 K (Fig. 2-5 and 2-6). When we apply the elasticities of CaPv at 300 K to lower mantle conditions, we have to consider which phase is stable at lower mantle conditions. Komabayashi et al. (2007) and Stixrude et al. (2007) suggested the cubic-tetragonal phase boundary is laid at about 550 K and 1500~2200 K, respectively in lower mantle pressure, and both of them showed that the stable phase at lower mantle condition is cubic. On the other hand, Li et al. (2006) suggested tetragonal-cubic phase boundary is on much higher temperature than both of them, and showed the stable phase is tetragonal. In addition, theoretical study by Tsuchiya (2011) found that sound velocities of cubic CaPv are very similar to those of the tetragonal phase (only ~3% slower in tetragonal CaPv at 30 GPa), in contrast to earlier predictions that the cubic CaPv has much faster velocities than tetragonal CaPv (Karki and Crain, 1998; Stixrude et al., 2007) (Fig. 2-3). Tsuchiya

(2011) attributed such a discrepancy to insufficient structural relaxations in earlier calculations. Consequently, the existent phase of CaPv under lower mantle condition is still under debate, so we calculated both tetragonal CaPv and cubic CaPv at high temperature. In order to calculate tetragonal CaPv at high temperature, we used the formalism by Stixrude and Lithgow-Bertelloni (2005) and the recent compilation of thermal parameters given in Xu et al. (2008), and to calculate cubic CaPv, we used the ratio of shear modulus of tetragonal CaPv and cubic CaPv in Stixrude et al., (2007) at each pressure and multiplied to shear modulus of tetragonal CaPv at 300 K, and employed those formalism and thermal parameters. With the results of previous Brillouin spectroscopy measurements at high pressures and 300 K (Murakami et al., 2007, 2009b), we made similar calculations for the high-temperature sound velocities of MgSiO₃ perovskite and MgO periclase as well. The effects of Al₂O₃ and FeO impurities in MgSiO₃-rich perovskite and ferropericlase are also considered according to Xu et al. (2008), except that bulk modulus of FeO end-member is from recent compression experiments by Sata et al. (2010). The aggregate velocities of multiple-phase assemblage are obtained by the Voigt–Reuss–Hill averaging method.

Let us first consider the effect of variation in the amount of CaPv with respect to MgSiO₃ perovskite on seismic wave velocities in the lowermost mantle. When we add

10 vol% tetragonal CaPv to pure MgSiO₃ perovskite at 120 GPa and 1500 K, shear and longitudinal velocities diminish by 1.9 and 0.8%, respectively, from those for MgSiO₃ perovskite (Fig. 2-7), and cubic CaPv, those velocities increase by 0.4% and negligible, respectively. On the other hand, an increase in temperature by 600 K from 1500 K also reduces the V_S of MgSiO₃ perovskite by 1.7% and the V_P by 1.0%. The shear to longitudinal wave heterogeneity ratio ($\Delta V_S/\Delta V_P$) caused by a simple addition/subtraction of tetragonal CaPv is thus very similar to that produced by temperature fluctuation in the lowermost mantle.

Chemical heterogeneity is, however, more complex in natural systems and may be distinguishable from thermal anomaly in seismology. The oceanic lithosphere includes large proportion of depleted peridotite called harzburgite. Such harzburgite typically contains <0.5 wt% CaO, because Ca-rich pyroxene is consumed at small degree of partial melting beneath oceanic ridges. The subducted harzburgite consists of 72 vol% (Mg_{0.94}Fe_{0.06})SiO₃ perovskite and 28 vol% (Mg_{0.90}Fe_{0.10})O ferropericlae in the lower mantle without any CaPv (Irifune and Ringwood, 1987). On the other hand, primitive mantle (pyrolitic) material includes 77 vol% (Mg_{0.86}Fe_{0.10}Al_{0.04})(Si_{0.96}Al_{0.04})SiO₃ perovskite, 16 vol% (Mg_{0.86}Fe_{0.14})O ferropericlae, and 7 vol% CaSiO₃ perovskite (Hirose, 2002). The calculations of acoustic velocities show $V_S = 7.23$ km/sec, $V_P =$

13.50 km/sec, and $V_B = 10.64$ km/sec for harzburgite, whereas $V_S = 7.16$ km/sec, $V_P = 13.52$ km/sec, and $V_B = 10.69$ km/sec for pyrolite with tetragonal CaPv at 120 GPa and 2500 K, and $V_S = 7.27$ km/sec, $V_P = 13.60$ km/sec, and $V_B = 10.69$ km/sec for that with cubic CaPv. The results with tetragonal CaPv indicate 0.9% faster V_S , 0.02% slower V_P , and 0.7% slower V_B for harzburgite. The higher shear velocity and lower bulk sound velocity in harzburgitic material are mainly attributed to the lack of CaPv and the enrichment in ferropericlasite, respectively. On the other hand, with cubic CaPv, 0.7% slower V_S , and 0.7% V_B slower for harzburgite. The summary is shown in table 3.

Global seismic tomography has demonstrated the fast V_S and slow V_B anomalies in the lowermost mantle underneath the circum-Pacific region (Masters et al., 2000; Trampert et al., 2004). According to the theoretical predictions (e.g., Iitaka et al., 2004; Oganov and Ono, 2004), phase transition from perovskite to post-perovskite could be the source of such heterogeneities in shear and bulk sound velocities. High-temperature elasticity calculations by Wentzcovitch et al. (2006) show 2.0% faster V_S and 0.8% slower V_B for post-perovskite than for perovskite. Observed lateral heterogeneities of up to +2% ΔV_S and -1% ΔV_B underneath the circum-Pacific region can therefore be explained by the presence of post-perovskite if it exists only in this specific area. However, the D'' seismic discontinuity, which is most likely attributed to the perovskite

to post-perovskite phase transition (see a review by Hirose, 2006), is observed not only in the circum-Pacific region but also in a hot region beneath the central Pacific (Lay et al., 2006). Moreover, van der Hilst et al. (2007) reported a widespread shear velocity increase in the D'' layer underneath Central and North America, which extends to both slow and fast regions in seismic tomography. These suggest that post-perovskite may be present globally, at least not only in cold areas. The low temperature anomaly in the circum-Pacific region causes thick post-perovskite layer and thus contributes to a certain extent to fast V_S and slow V_B heterogeneities; however, the thicker post-perovskite layer alone cannot explain the magnitude of observed anomalies. It is naturally expected that a large amount of subducted harzburgitic materials exist in the lowermost mantle underneath the circum-Pacific region, which also contributes to the cause of such V_S and V_B anomalies when CaPv takes tetragonal form in the lower mantle. However, it is necessary to reveal more mineral physic properties, especially in temperature effect for modeling the chemical heterogeneities in the lowermost mantle more preciously. It should be constrained with measurements of elastic properties for the constituent minerals at lowermost mantle condition.

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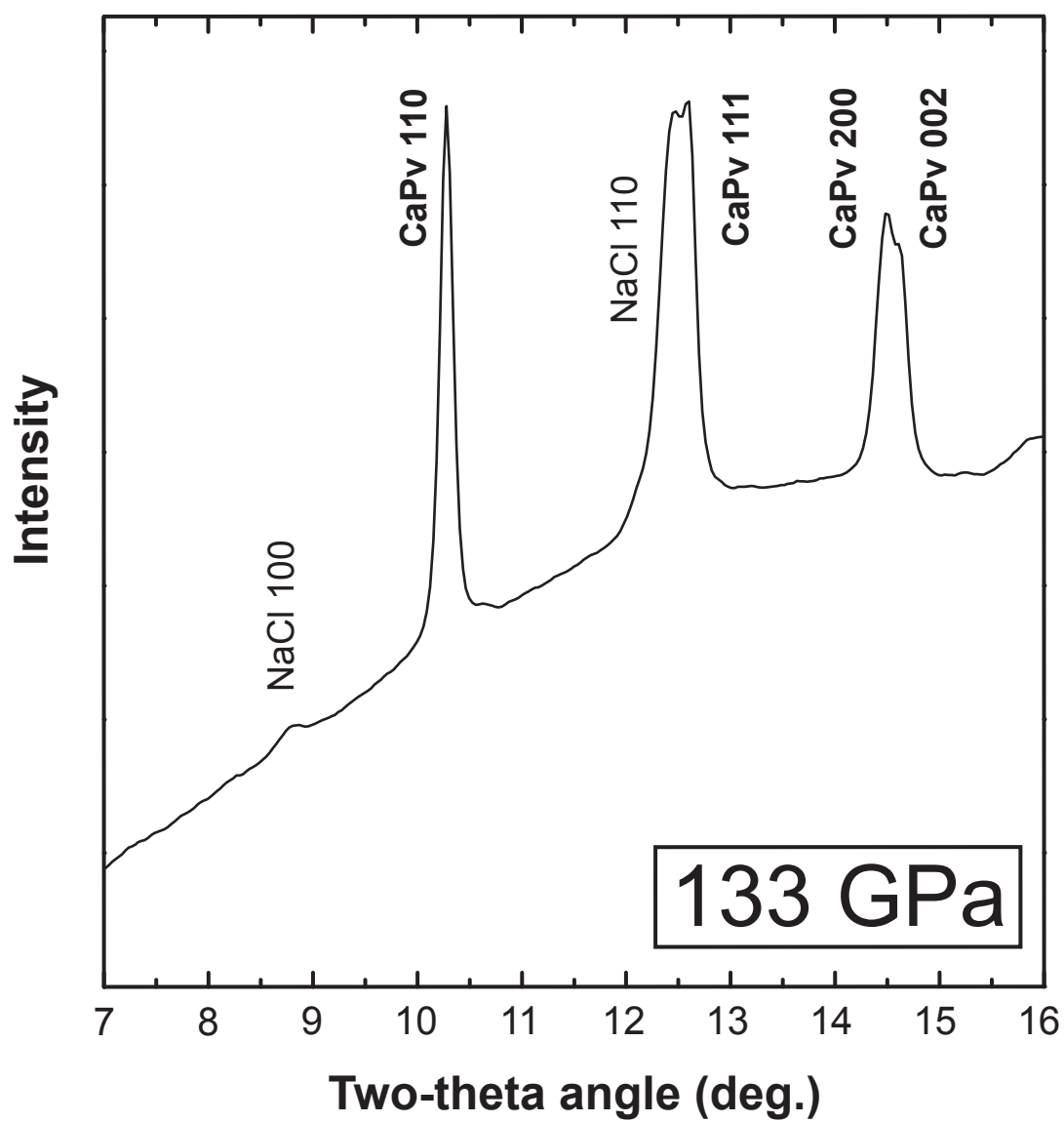


Fig. 2-1 Typical XRD pattern of CaPv obtained at 133 GPa and 300 K. Peak splitting around 14.5 degrees indicates the tetragonal distortion of perovskite structure.

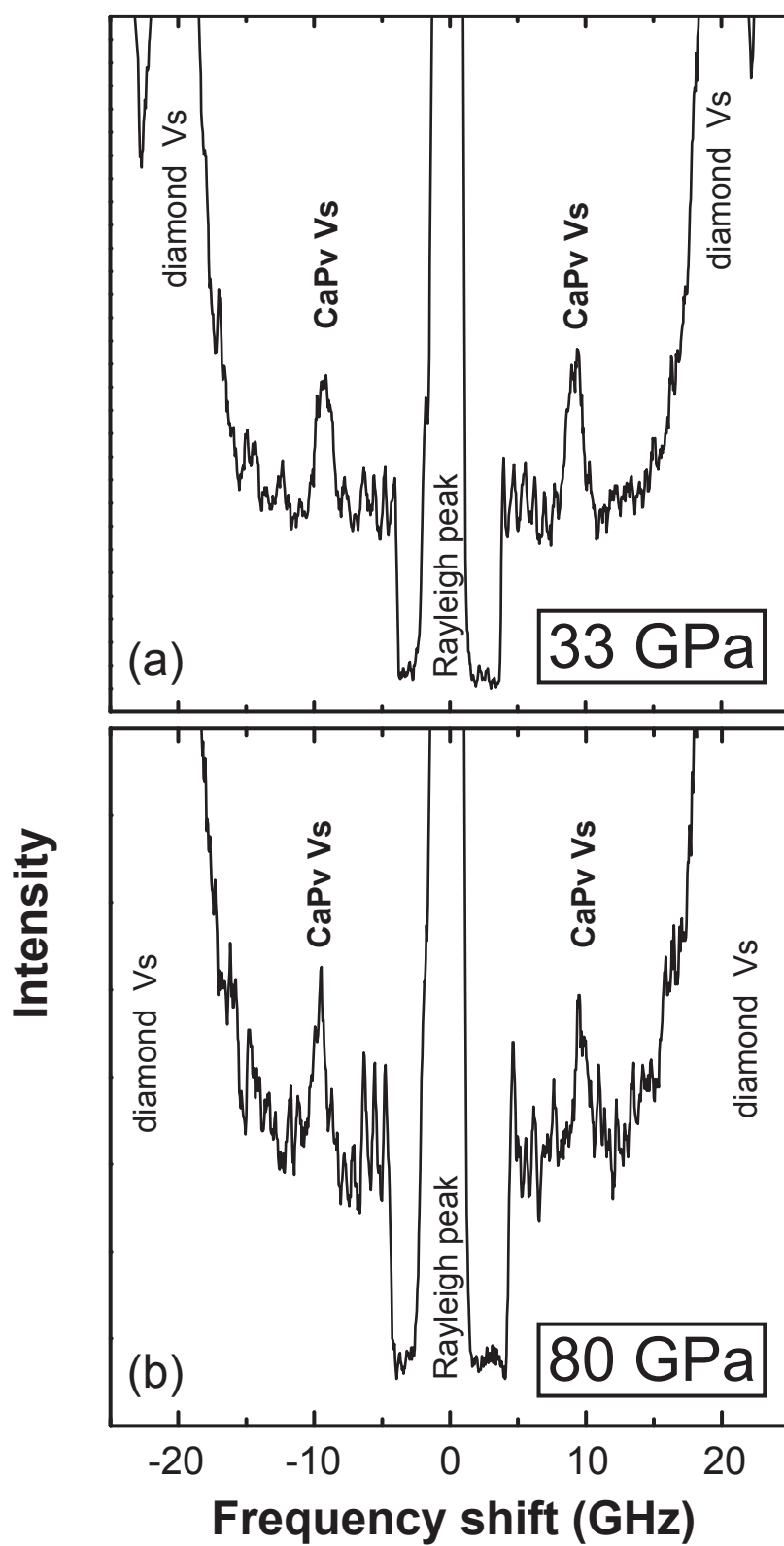


Fig. 2-2 Brillouin spectra of CaPv collected at (a) 33 GPa and (b) 80 GPa.

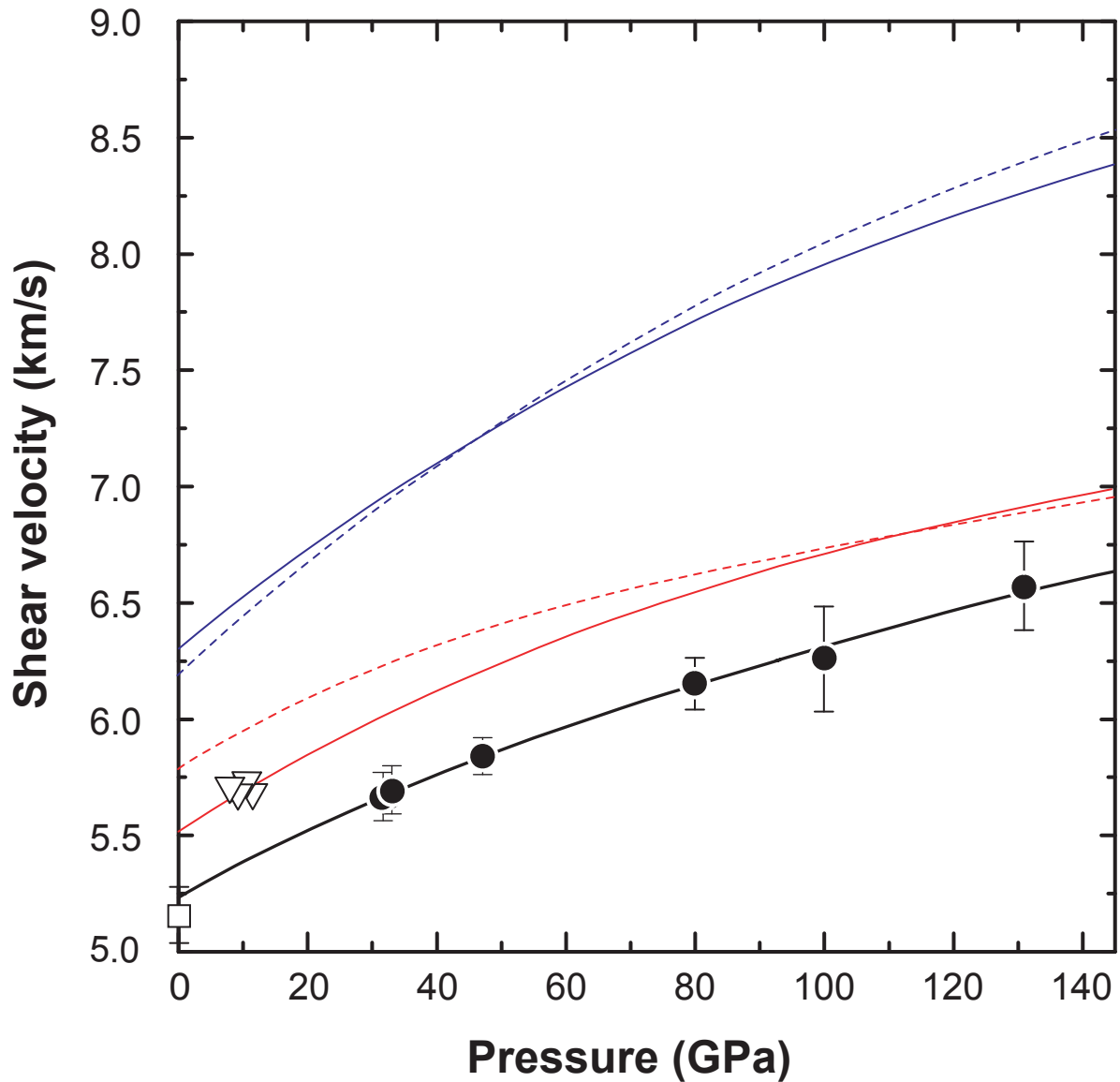


Fig. 2-3 Shear velocity of CaSiO₃ perovskite (solid circles) obtained in this study compared with the previous ultrasonic measurements at high pressures (open triangles) (Li et al., 2004) and the value inferred from measurements on Ca(Si,Ti)O₃ perovskites at 1 bar (open squares) (Sinelnikov et al., 1998). Blue and red curves represent earlier predictions for cubic and tetragonal CaSiO₃ perovskite, respectively. Blue broken line, Karki and Crain (1998); solid lines, Stixrude et al. (2007); red broken line, Tsuchiya (2011).

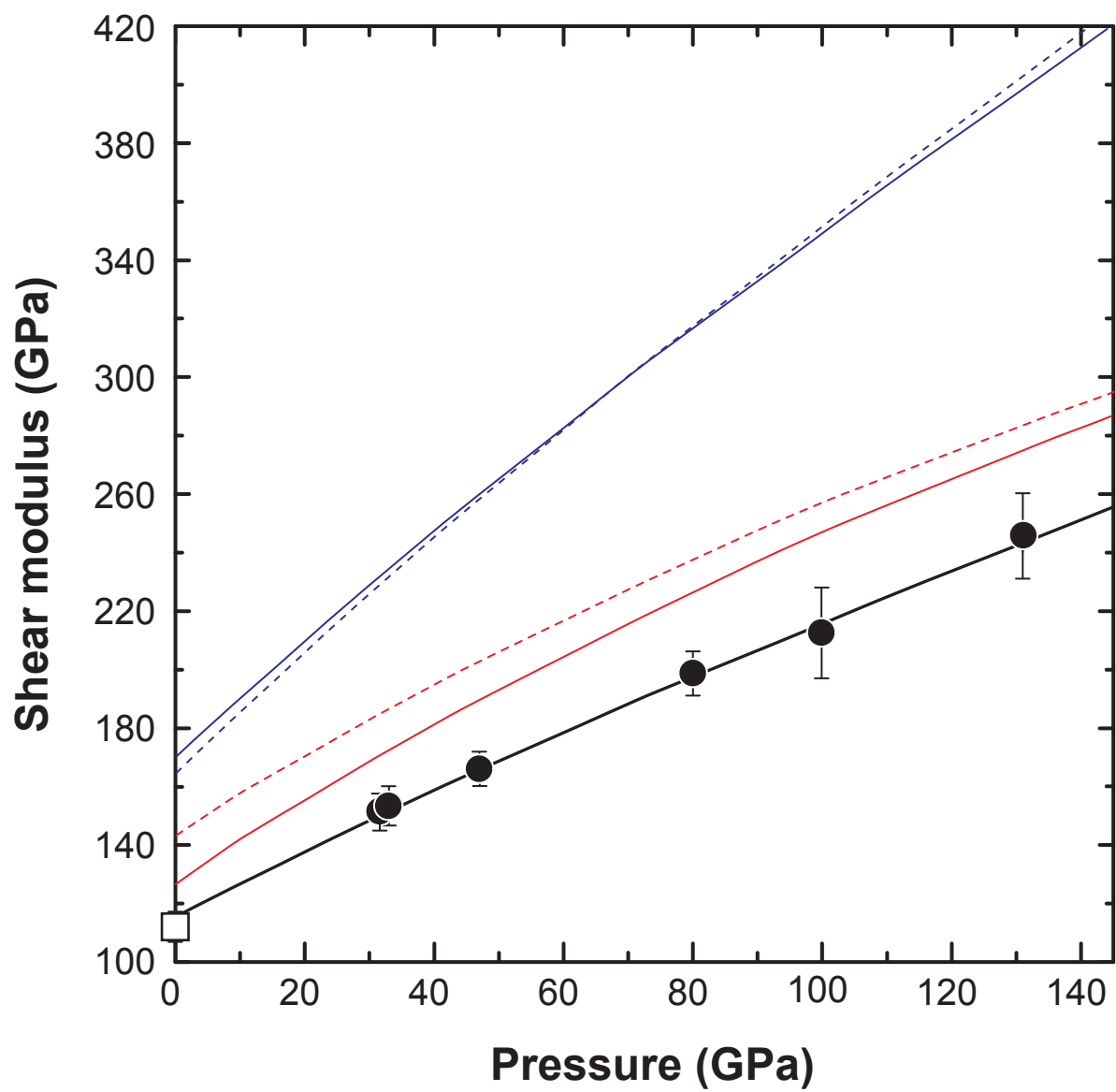


Fig. 2-4 Shear modulus of CaSiO_3 perovskite obtained in this study. Symbols and curves are same as Fig. 3.

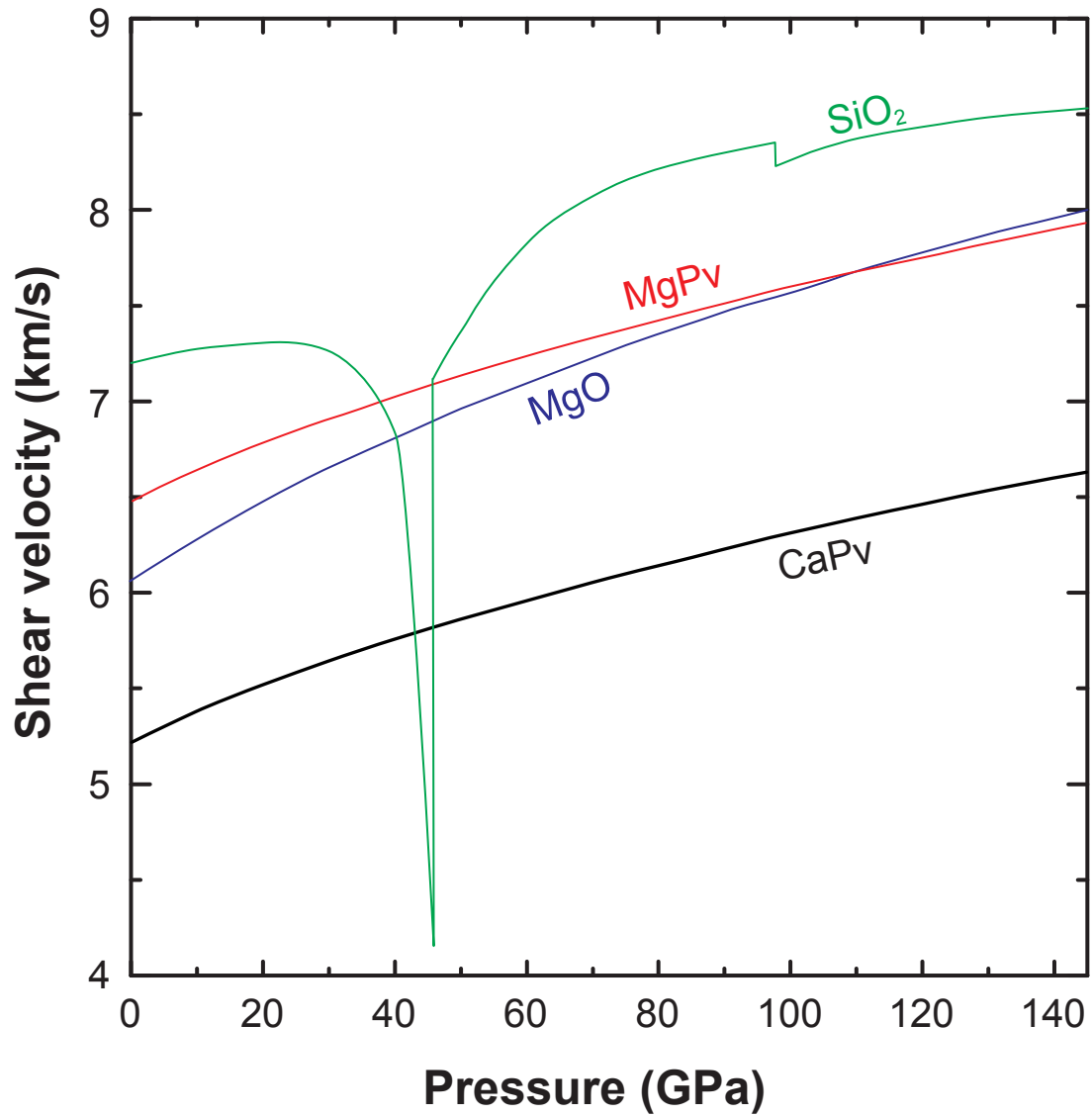


Fig. 2-5 Measured (300 K) or calculated (0 K) shear velocities of typical lower mantle minerals at high pressures. Black, CaSiO_3 perovskite (this study); red, MgSiO_3 perovskite (Murakami et al., 2007); blue, MgO (Murakami et al., 2009b); green, SiO_2 phase (Karki et al., 1997).

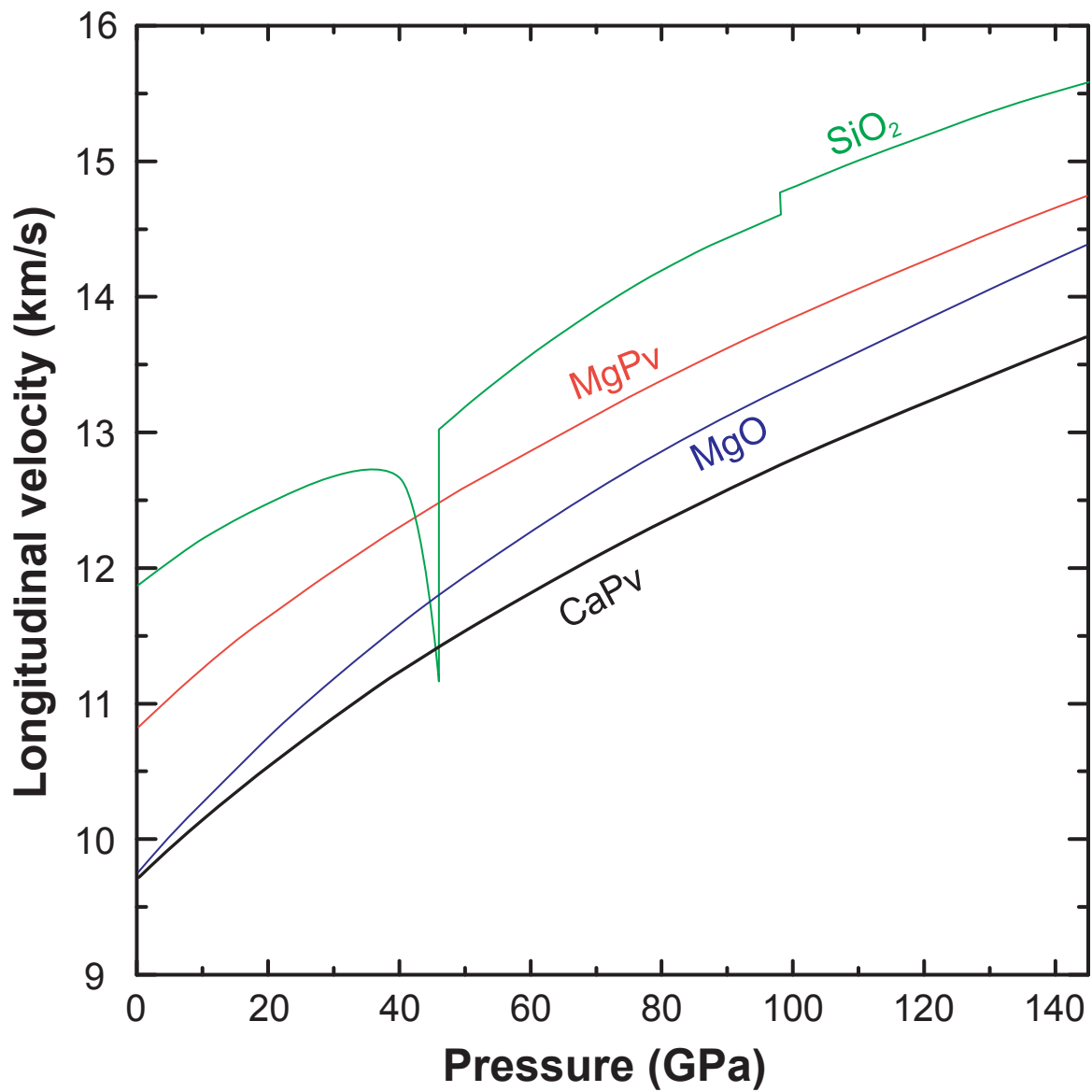


Fig. 2-6 Experimental (300 K) or computed (0 K) results of longitudinal velocities of typical lower mantle minerals at high pressures. Curves are same as Fig. 5.

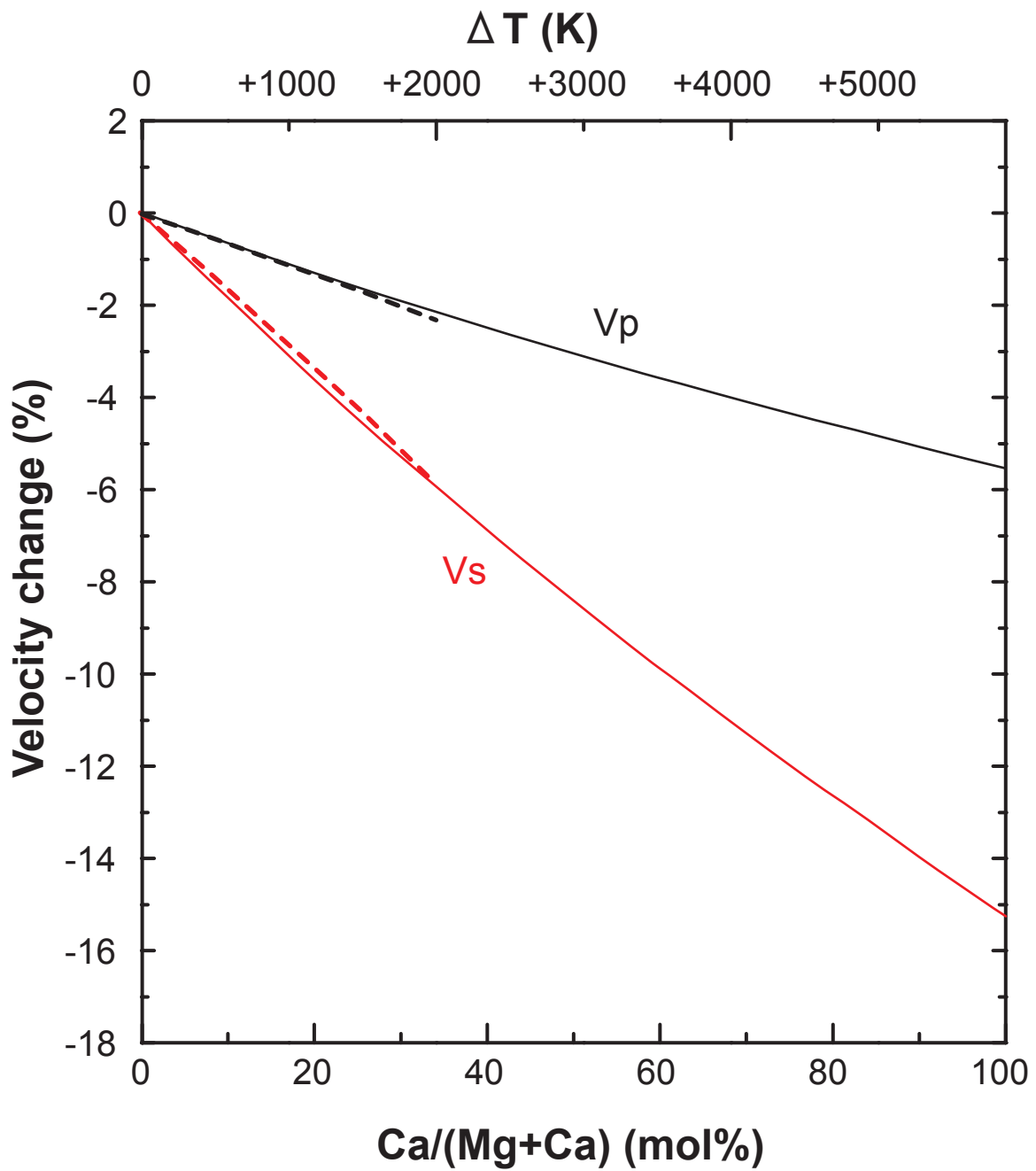


Fig. 2-7 Velocity changes due to addition of CaSiO_3 perovskite to MgSiO_3 perovskite (solid curves) and the increase in temperature from 2000 K (broken lines). See text for details.

Table 2-1

Measured aggregate shear velocities and shear moduli of CaPv

Pressure (GPa)	V_s (km/s)	G (GPa)
31.6(4)	5.67(10)	151.4(55)
33.0(2)	5.70(10)	153.4(56)
47.1(3)	5.84(8)	165.9(45)
80.1(15)	6.15(11)	198.9(71)
100.6(20)	6.26(33)	212.5(153)
133.3(15)	6.57(20)	245.8(142)

Numbers in parentheses are standard deviations in the last digit(s).

Table 2-2

Comparison with previous studies on CaPv

Source	G_0 (GPa)	G'	V_{p0} (km/s)	V_{s0} (km/s)	Remarks
<i>Experiments</i>					
This study	115.8(20)	1.20(2)	9.70(4) ^a	5.23(4)	Brillouin spectroscopy
Sinelnikov et al. (1998)	112(5)		9.24(13)	5.16(12)	ultrasonic method
<i>Theory</i>					
Karki and Crain (1998)	164		10.3	6.2	cubic structure
Xu et al. (2008)	157	2.2	10.3	6.1	cubic structure
Stixrude et al. (2007)	171		10.4	6.3	cubic structure
	127		9.9	5.6	tetragonal structure
Tsuchiya (2011)	144.1		10.1	5.8	tetragonal structure

Numbers in parentheses are standard deviations in the last digit(s).

^a Only the uncertainty in shear modulus is considered for error estimate.

Table 2-3

Acoustic velocities of pyrolitic and harzburgitic materials at 120 GPa and 2500 K

	V_S (km/s)	V_P (km/s)	V_B (km/s)		(vol.%)	K (GPa)	G (GPa)	ρ (g/cm ³)
Pyrolite	7.17	13.54	10.72	MgPv ^b	78	643.4	288.9	5.429
				Fp ^c	15	530.9	268.4	5.526
				CaPv	7	653.6	212.9	5.443
Harzburgite ^a	7.25	13.54	10.64	MgPv ^d	72	642.5	287.0	5.378
	+1.22%	-0.02%	-0.77%	Fp ^e	28	530.7	273.5	5.389

^a Difference in velocity from pyrolite is shown in the bottom column.^b (Mg_{0.86}Fe_{0.10}Al_{0.04})(Si_{0.96}Al_{0.04})SiO₃ perovskite, ^b (Mg_{0.86}Fe_{0.14})O, ^c (Mg_{0.94}Fe_{0.06})SiO₃ perovskite, ^d (Mg_{0.90}Fe_{0.10})O

Chapter 3: Shear velocity measurements of iron-bearing MgSiO_3 glass and basaltic glass at the lower mantle pressure

Abstract

High-pressure Brillouin scattering measurement were conducted in $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass and mid ocean ridge basalt (MORB) glass containing 9 wt.% FeO. Shear wave velocity of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass was obtained from 15.5 GPa up to 113.0 GPa. Present shear wave velocity of both silicate glasses is slower than that of MgSiO_3 glass. Shear velocity anomaly is observed around 60 GPa in $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass. This anomaly is excellently similar to shear velocity anomaly previously reported in ferropericlase by spin transition of iron. In contrast, there are no significant anomalies in MORB glass up to 76.9 GPa, which indicates spin transition in iron among MORB glass would not occur, therefore, no iron concentration is expected if subducted MORB solved. Additionally, present relatively Mg-poor and Ca-rich MORB glass shows significantly slower shear wave velocity than that of Mg-rich and Ca-poor MORB glass at lower mantle pressure. It indicates that magnesium molar fraction in MORB melt shows higher elastic moduli, and lower compressibility in the lower mantle.

3-1. Introduction

The properties of silicate melt at high pressure controls the behavior of silicate melt in the Earth's deep interior through Earth's history, especially just after terra forming since large part of the mantle should be melted. Nomura et al., (2011) found that the ratio of iron concentration over coexisting perovskite phase suddenly increases at 76 GPa, therefore, iron-rich, denser melt could be generated at the depth more than 1800km, and would build Basal Magma Ocean (BMO) (Labrosse et al. 2007). The iron-rich BMO, would discharge magnesium and silicon during solidification. Therefore, the iron-rich, denser, therefore, slower sound velocity materials should be concentrated at the D'' layer with the horizontal heterogeneities, and the remnants of the BMO could content the large low shear velocity provinces (LLSVPs). Additionally, the melting remnants, or crystalline FeO-rich materials would be laid under the LLSVPs as ultra-low velocity zones (ULVZs), hence, the seismological structural heterogeneities at the D'' layer could be explained uniformly. For the cause of iron-concentration to the silicate melt, Nomura et al ., (2011) suggested the spin-crossover of iron among the silicate melts, based on the X-ray Emission Spectroscopy (XES) measurements for the $(\text{Mg}_{0.95}\text{Fe}_{0.05})\text{SiO}_3$ glass. Their observation shows high spin state iron transforms to low

spin state completely between 59 GPa to 77 GPa. However, more recently, Gu et al.(2012) demonstrated XES and Mössbauer spectroscopic experiments for $(\text{Mg}_{0.80}\text{Fe}_{0.20})\text{SiO}_3$ glass, and suggested spin-transition in high iron content silicate glass occurs more gently than low iron content silicate glass and the iron in silicate glass does not transform to low spin state from high spin state. Similar conclusion was also shown in Prescher et al., (2014) and Mao et al., (2014). Moreover, Andrault et al. (2012) showed contrasting result to Nomura et al. (2011) that the iron distribution coefficient between melt and coexisting crystalline phase does not drop with melting experiments in chondritic composition entire lower mantle pressure. Therefore, the cause of rapidly reduction in iron distribution coefficient between perovskite and coexisting melt, and the formation of BMO caused by rapidly increase of iron concentration to silicate melt in the Earth's formation is still under controversial. Apropos, some accompanying effects with spin transition were reported in ferropericlase, for example, anomalous volume and bulk modulus reduction (Li et al., 2005; Fei et al., 2007; Wentzcovitch et al., 2009), anomalous electrical conductivity behavior (Lin et al., 2006; Ohta et al., 2014), increase in optical absorption coefficient (Goncharov et al., 2006; Kepller et al., 2007), and anomaly in shear wave velocity (Lin et al., 2007; Crowhurst et al., 2008; Marquardt et al., 2009; Murakami et al., 2012; Wu et al., 2013). These anomalous behaviors in

physical properties also expected to be manifested if spin crossover occurs in iron-bearing MgSiO_3 glass, which is an analog for silicate melt.

On the other hand, possibility of subducted MORBs melting is suggested by previous high pressure experiments (Andrault et al., 2014). The fate of molten MORBs at depth is controlled by its density. MORBs also contains iron, therefore, spin transition and accompanying anomalous behaviors are also imagined.

3-2. Experimental method

$(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass was synthesized by quenching melt from 1931 K in $\text{CO}_2\text{-H}_2$ gas-mixing furnace. The oxygen fugacity in the high-temperature furnace was controlled to be slightly above the iron-wüstite buffer, in which iron in the melt completely turn to ferrous iron. Mid ocean ridge basalt glass was also synthesized by quenching melt from $\text{CO}_2\text{-H}_2$ gas-mix furnace. The composition of present MORB glass was aligned to the ratio of main components (SiO_2 , MgO , FeO , Al_2O_3 , CaO , and Na_2O) in ARP74 (Fujii and Bougault, 1983) by the ratio of SiO_2 , MgCO_3 , Fe_2O_3 , Al_2O_3 , CaCO_3 and Na_2CO_3 . These oxides were placed 6 hour in temperature-controlled furnace

with a maximum temperature of 870 K, in order to eliminate carbon, then, well-mixed, and put in an oven again in order to remove water. This slag was hanged by a platinum wirer and put in a furnace. These glass samples were analyzed with EDS and FE-EPMA in order to confirm that the sample was glass without any quench-crystals, and its chemical compositions were correct. X-ray diffraction measurements also confirm the material was amorphous phase. The result of MORB glass is shown in Table 3-1 with comparison previous studies.

Present high-pressure Brillouin scattering measurements were conducted in diamond anvil cells with 60 degree- angular aperture. Incident laser beam with a wavelength of 532 nm (Verdi V2, coherent) was focused and introduced into sample chamber with a radius of $\sim 20 \mu\text{m}$. The employed laser power was 600 mW. Scattered light was directed into 6-mirror tandem Fabry=Perot interferometer (Sandercock, 1982). All the measurements were conducted with platelet geometry. The scattered angle was employed 50 degree, and calibrated by the compressional velocity of BK₇ standard glass (Yoneda and Song, 2005). Then, sound velocities were obtained by following relationship;

$$V_i = \frac{\Delta\omega_i \lambda}{2 \sin\left(\frac{\theta}{2}\right)} \quad (3.1)$$

where V_i is velocity, $\Delta\omega_i$ is observed frequency shift by Fabry-Perot interferometer, λ is the wavelength of incident laser, θ is scattering angle (Whitfield et al., 1976), and subscription i denotes i^{th} wave mode. Exposure time was 3~ 24 hour. Pressures were determined by Raman T_{2g} mode of diamond anvils (Akahama and Kawamura, 2004). To ensure that there were no large deviatric pressure gradient in sample chamber, the pressure determinations were conducted at least 3 points around Brillouin incident beam irradiated at each single pressure point. Typical pressure difference in sample chamber was within 1 GPa. All the Brillouin peaks were fitted by Gaussian function. The evaluated Stokes and anti-Stokes peak positions were averaged and employed as a obtained peak position. In order to avoid not completely relaxation in sample camber by pressure increment, an interval of at least 8 hour was taken between pressure increment and Brillouin scattering measurement at all the pressure increment.

3-3. Result

Clear Brillouin peaks of shear wave mode for $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass were obtained from 15.5 GPa to 113.0 GPa, and for MORB glass were from 45.5 GPa to 76.9 GPa.

Exemplary spectra are shown in Fig. 3-1, Fig. 3-2, Fig. 3-3, and Fig. 3-4. Peaks from compressional wave velocity above 52.9 GPa in $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass, and entire pressure range of this measurements in MORB glass is not observed, perhaps masked by huge shear velocity peaks of diamond anvils. The full-width half maximum of shear wave peak at 15.5 GPa was 0.53 GHz and that at 113.0 GPa was 0.59 GHz in $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass, and 0.43 GHz at 45.5 GPa and 0.35 GHz at 76.9 GPa. No significant increase entire present experimental pressure range is observed in both two glasses. This behavior of full-width half maximum indicates that Brillouin scattering signals were not influenced by deviatoric large pressure gradient in sample chamber, because this value is expanded by pressure gradient in environment. Obtained shear wave velocities of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass and MORB glass are summarized in Table 3-1 and Table 3-2, respectively. The aggregates shear wave velocities are plotted in Fig. 3-5 with that of previous MgSiO_3 glass for comparison (Sanchez-Valle and Bass, 2010; Murakami and Bass, 2011). The shear wave velocity of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass is typically ~5% slower than that of MgSiO_3 glass entire the experiment pressure range. Around 60 GPa, we can see a shear wave velocity anomaly in $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass. Shear wave velocity increases about 300 m/s from 57.3 GPa to 61.2 GPa, and its

pressure dependency decreases from 16 m/s/GPa to 7 m/s/GPa. In contrast, no significant anomalies are observed in MORB glass.

3-4. Discussion

3-4-1. Elastic anomaly in present silicate glasses and possibility of spin transition

Present shear wave velocities of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass from 15.5 GPa to 113.0 GPa are slightly slower than those of pure MgSiO_3 glass (Sanchez-Valle and Bass, 2010; Murakami and Bass, 2011). Generally, shear wave velocity defined by $V_S = (G/\rho)^{1/2}$ where G represents shear modulus and ρ is density, therefore, this reduction would be caused by the larger density in $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass than MgSiO_3 glass because of increasing in iron content.

At around 60 GPa, the aggregate shear wave velocity of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass has anomaly behavior that increase rapidly about 0.3 km/s from 57.3 GPa to 60 GPa, and decrease its pressure derivative from to above 60 GPa. Murakami et al., (2012) found similar shear wave anomaly around 50 GPa in $(\text{Mg}_{0.92}\text{Fe}_{0.08})\text{O}$ by Brillouin scattering

measurement, that rapidly increase in shear wave velocity with increasing pressure, and decrease its pressure dependency above the pressure. This anomaly was interpreted as a result of spin transition in polycrystalline ferropericlaase. Marquardt et al. (2009) also found such anomaly by spin crossover in single crystalline ferropericlaase. The comparison of shear velocity profile of ferropericlaase and that of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass by this study is shown in Fig. 3-6. We can see the excellently similar shear velocity behavior between ferropericlaase and $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass. Such behavior is also predicted by ab-initio calculation (Wu et al., 2013). Therefore, this shear wave velocity anomaly in $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass would be interpreted as an accompanied effect with spin transition of iron among the silicate glass.

In contrast, present result in MORB glass does not show such shear velocity anomalies. This observation indicates spin transition would occur moderately enough to negligible in elasticity, or not occur in this pressure range.

3-4-2. Composition dependence of elasticity in MORB glass

Recently, the other high-pressure Brillouin scattering measurements of MORB glass were conducted by Wu et al. (2014). Their results of shear wave velocity were shown in Fig. 3-7 with present result for comparison. Although both two studies have no shear wave velocity data from 20 GPa to 40 GPa, we can see significant shear wave velocity discrepancy between the results of this study and Wu et al. (2014). It is conceivable that the difference in composition of MORB glass, especially the molar ratio of MgO and CaO yields this discrepancy in shear wave velocity. Schilling et al. (2001) showed elastic behaviors of silicate glasses in pseudo-ternary anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) – diopside ($\text{CaMgSi}_2\text{O}_6$) – forsterite (Mg_2SiO_4) system by Brillouin scattering measurements, and found that magnesium-rich glasses show relatively higher bulk and shear moduli among basaltic composition. They interpreted higher bonding strength between network-forming tetrahedra formed by SiO_4 and AlO_4 , and magnesium than the other network modifying cations such as calcium. It is good agreement with the result of *ab-initio* calculation (Hauser et al., 1998). Based on this analysis, it was speculated that basaltic glasses, and melts show smaller both pressure and temperature dependency in volume with increasing MgO content (Schilling et al., 2001). Moreover, *ab-initio*

calculation suggested that the coordination number of Mg-O and Ca-O would be different among diopside ($\text{CaMgSi}_2\text{O}_6$) liquid at high pressures, therefore, the function of Mg and Ca would be different and the contribution to shear modulus and compressibility might be also different (Sun et al., 2011).

On the other hand, V_s is the function of both density and shear modulus as described. With the analysis above, we can speculate both bulk and shear moduli increase with increasing pressure relatively faster and density increase relatively slower in Mg-rich and Ca-poor silicate glass, and contribution of both of them drives shear wave velocity in higher pressure faster. Therefore, the significantly slower shear wave velocity of present MORB glass would be caused by the difference in the molar fraction of MgO and CaO, and indicates that shear modulus, compressibility and density of MORB melt in the lower mantle decrease with increasing MgO molar ratio. However, information is too poor about MORB glasses and melts in various composition at the lower mantle pressures, therefore, systematic experiments in various Mg/Ca ratio is needed.

3-4-3. Geophysical implications

Present result in $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass by Brillouin scattering measurements shows shear velocity anomaly around 60 GPa, and this anomaly would be interpreted as a result of spin transition. This analysis supports to Nomura et al., (2011) that pressure-induced spin crossover in iron-bearing MgSiO_3 glass occurs between 59 GPa to 70 GPa. Therefore, it is plausible that the rapidly increase in iron concentration to silicate melt rather than coexisting perovskite at 76 GPa is caused by the change of spin state in iron among silicate melt. In contrast, no shear wave velocity anomalies are observed in results of MORB glass. Therefore, rapidly increase in iron concentration to melt such as in $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ melt would not occur in MORB melt during present pressure range.

Brillouin scattering measurements were conducted at SPring-8 (proposal no. 2013B0087, 2014A0080, and 2014B0080)

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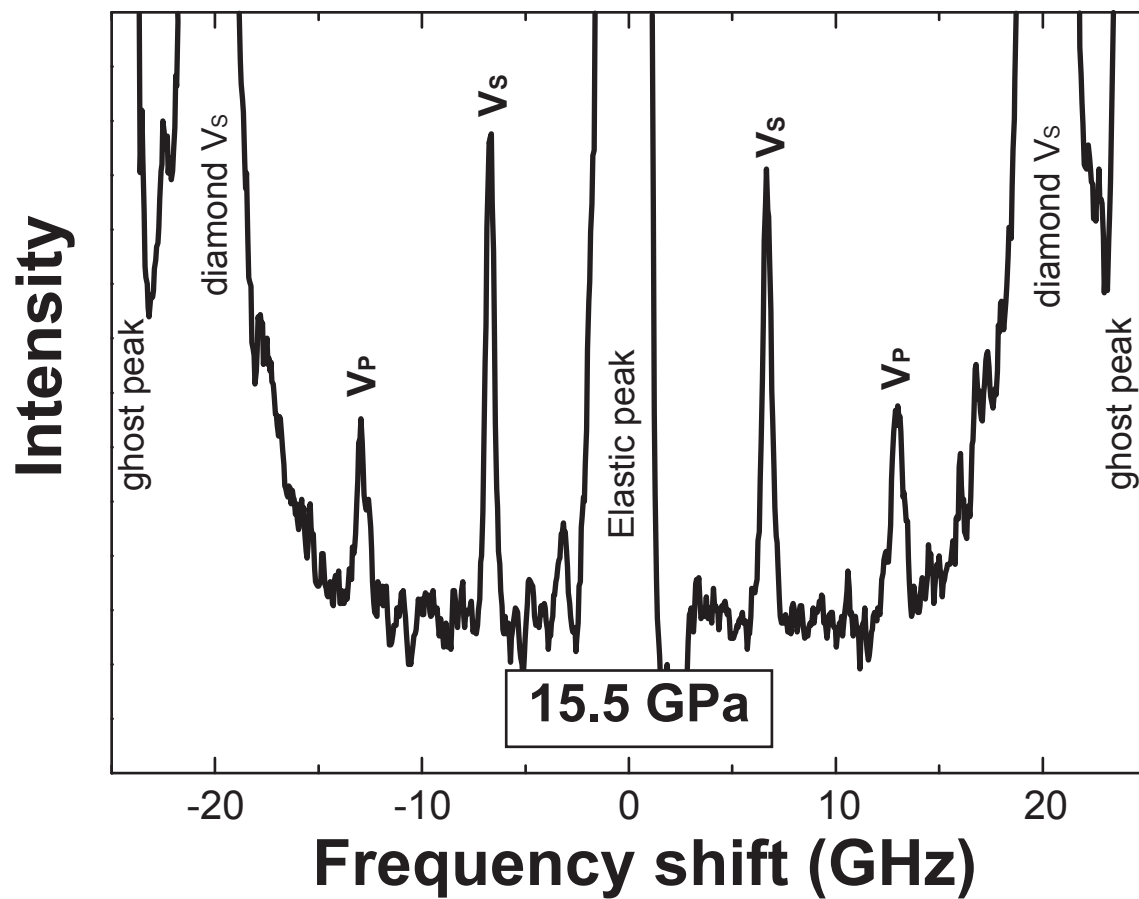


Fig. 3-1 Brillouin spectrum of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass at 15.5 GPa.

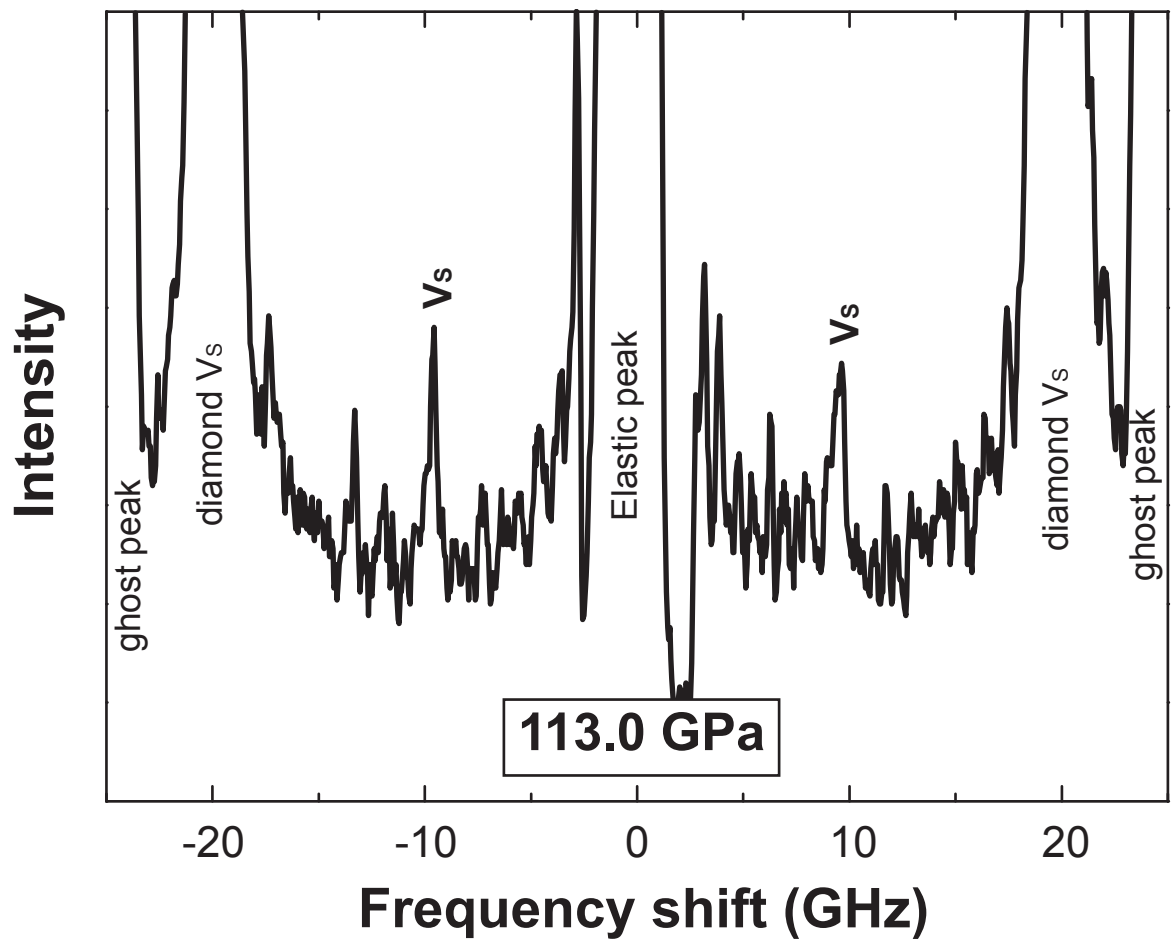


Fig. 3-2 Brillouin spectrum of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass at 113.0 GPa.

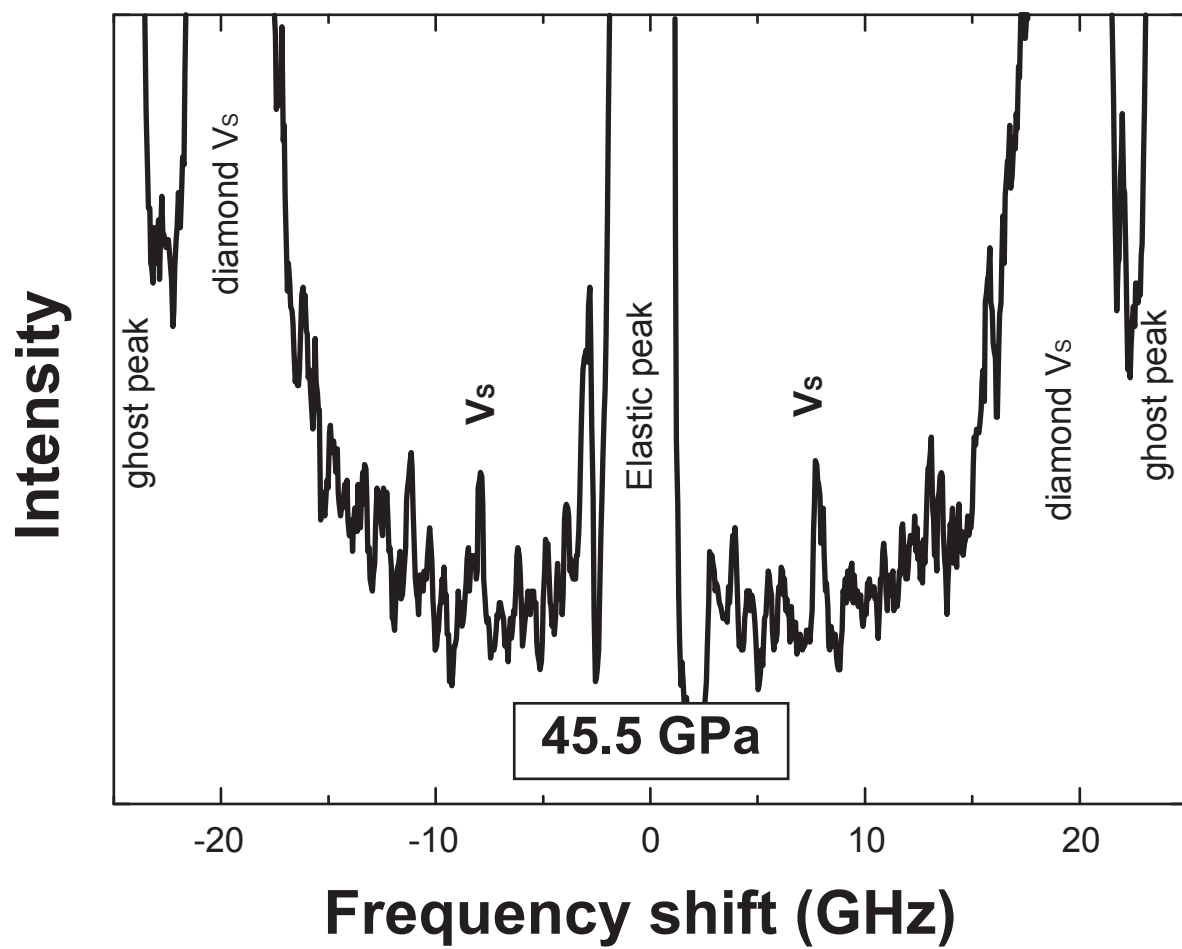


Fig. 3-3 Brillouin spectrum of MORB glass at 45.5 GPa.

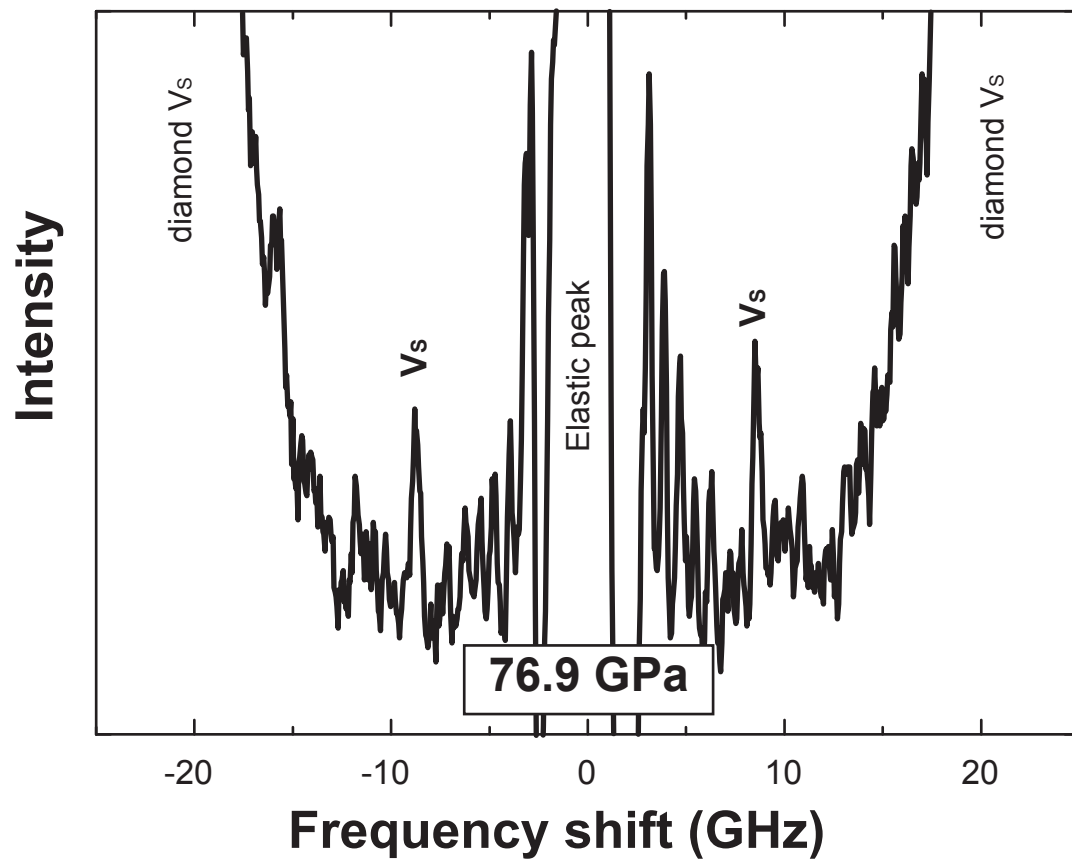


Fig. 3-4 Brillouin spectrum of MORB glass at 76.9 GPa.

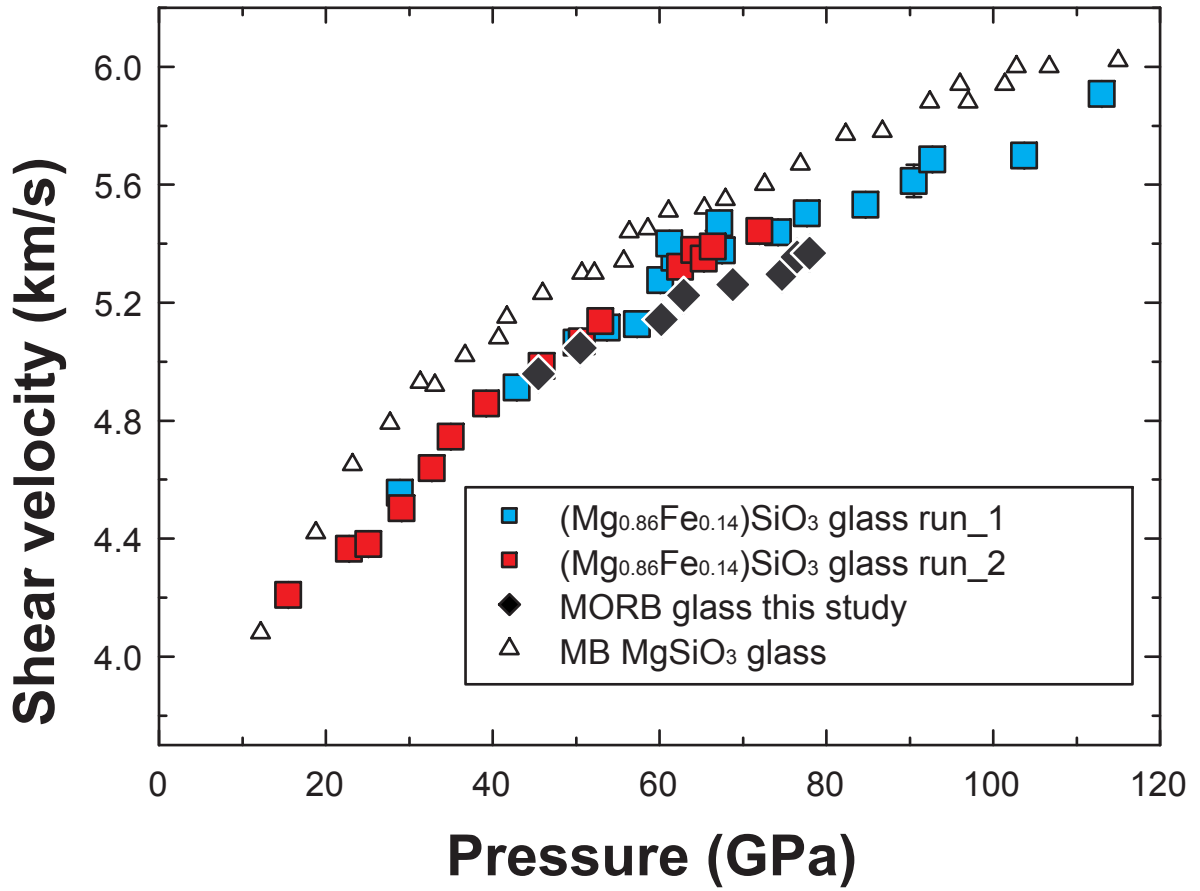


Fig. 3-5 Shear wave velocity of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass, (square), MORB glass (black diamond), and MgSiO_3 glass by Murakami and Bass (2011) (open triangle). In $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass, the symbols of run_1 are colored light blue and symbol of run_2 are colored red.

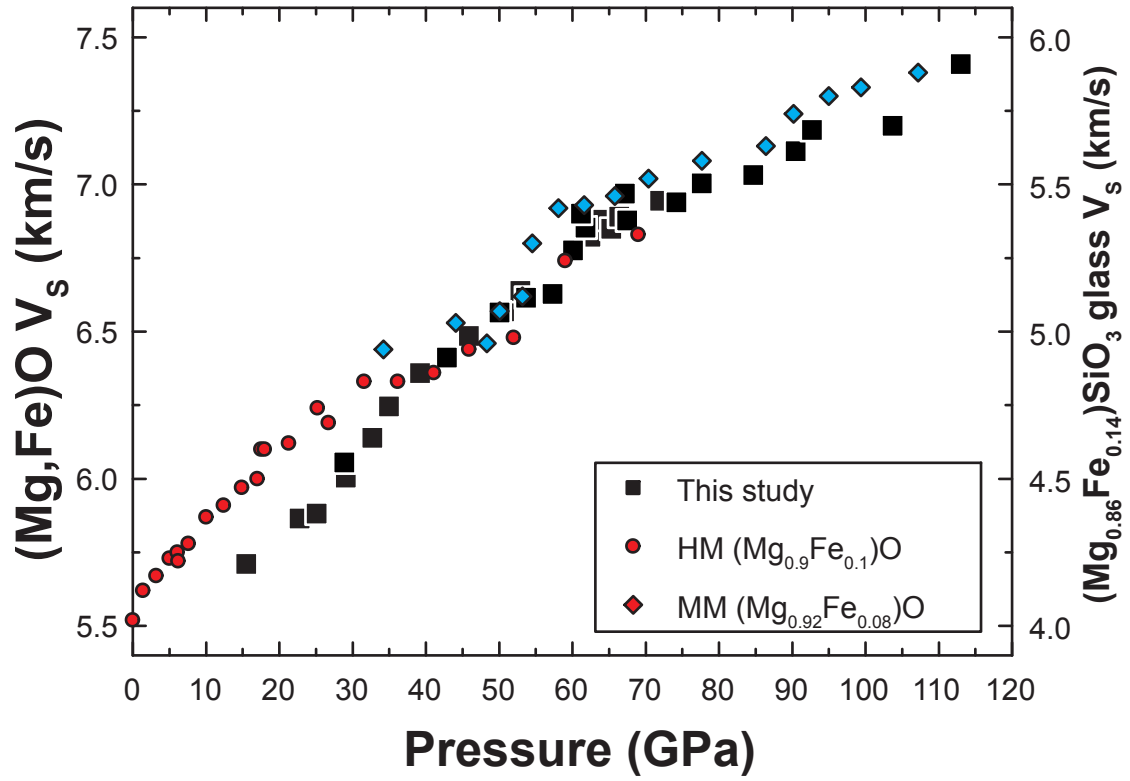


Fig. 3-6 Comparison of shear wave velocity between present (Mg_{0.86}Fe_{0.14})SiO₃ glass and previous ferropericlase by Marquardt et al. (2009) (red circle) and Murakami et al. (2012) (light blue diamond). The Symbols of present shear wave velocities are plotted by adding 1.5 km/s.

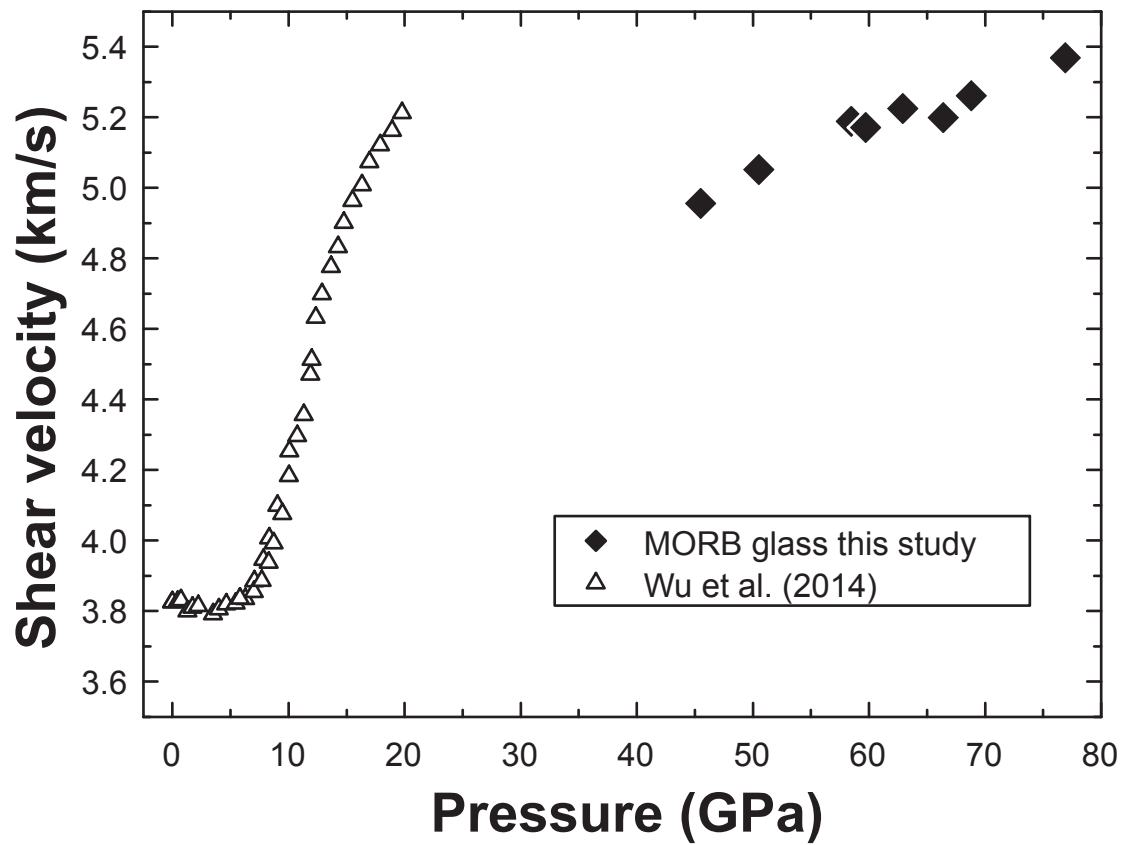


Fig. 3-7 Comparison of shear wave velocity between present relatively Mg-poor, Ca-rich MORB glass and previous Mg-rich, Ca-poor MORB glass by Wu et al. (2014).

Table 3-1

Weight ratio of oxide components in MORB glass analyzed by Energy Dispersive X-ray spectroscopy (EDS)

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Cr ₂ O ₃	NiO	H ₂ O	total
Ths study	50.9		12.5	7.72		8.94	14.0	3.31						97.40
Fujii and Bougault (1983)	50		15.5	8.05	0.17	10.5	13.3	2.1	0.13	0.14				99.9
Wu et al. (2014)	48.3	1.08	15.1	8.54	0.12	12.4	8.68	2.1	2.12		0.11	0.07	0.46	99.1

All the ratios are written in a percentage.

Table 3-2Summary of results in (Mg_{0.86}Fe_{0.14})SiO₃ glass

Pressure (GPa)	V _s (k m/s)
<i>run 1</i>	
28.9	4.56(1)
42.9	4.91(1)
50.1	5.06(1)
53.7	5.11(1)
57.3	5.13(1)
60.1	5.28(1)
61.8	5.35(1)
61.2	5.40(1)
67.5	5.38(1)
67.2	5.47(1)
74.2	5.44(1)
77.7	5.50(2)
84.7	5.53(1)
90.5	5.61(5)
92.7	5.68(2)
103.7	5.70(4)
113.0	5.91(1)
<i>run 2</i>	
15.5	4.21(1)
22.8	4.36(1)
25.1	4.38(2)
29.1	4.50(4)
32.7	4.64(4)
35.0	4.75(1)
39.2	4.86(1)
45.9	4.98(1)
50.7	5.07(3)
52.9	5.13(2)
62.5	5.32(3)
64.2	5.38(3)
65.3	5.35(3)
66.4	5.39(4)
72.0	5.44(3)

Numbers in parentheses indicate uncertainty in the last digit(s).

Table 3-3
Summary of results in MORB glass

Pressure (GPa)	V _s (km/s)
45.5	4.96(1)
50.5	5.05(1)
58.5	5.19(1)
59.7	5.17(3)
62.9	5.23(3)
66.4	5.20(1)
68.8	5.26(1)
76.9	5.37(1)

Numbers in parentheses indicate uncertainty in the last digit(s).

Chapter 4: Density estimation of iron-bearing MgSiO_3 glass and alumina-bearing MgSiO_3 glass to lower mantle pressure

Abstract

High-pressure Brillouin scattering measurements of iron-bearing MgSiO_3 glass and alumina-bearing MgSiO_3 glass were conducted. Compressional and Shear wave velocities, Poisson's ratio were obtained up to mid-lower mantle pressure, and elastic density increase with increasing pressure were obtained by bulk sound velocity. Elastic behavior of both iron-bearing and alumina-bearing MgSiO_3 glass is similar to SiO_2 and MgSiO_3 glasses, it indicates the structural change in both present two glasses is very similar to SiO_2 and MgSiO_3 glasses. By sound velocities and density, elastic moduli were calculated. Densities of silicate glasses were extrapolated and compared to crystalline lower mantle minerals. The comparison of the density of iron-containing silicate glass and that of average mantle minerals indicates that both highly iron-concentration to melt and anelastic density change in SiO_2 component due to the structural change, such as short range order coordination number increment in Si-O atom, at Brillouin frequency regime would be necessary for occurrence of density excession in silicate melt than coexisting crystalline solids.

4-1. Introduction

Structure and density of silicate melts at high pressure and high temperature is fundamental information to understand evolution and migration of magmas in the Earth and Earth-like planetary interior. However, information of structure and density of silicate melts at high pressure, especially in lower mantle pressures is quite limited. The reasons can be roughly separated to two, keeping high temperature condition above melting temperature of silicate in high pressure sample chamber during measuring physical properties is very difficult, and X-ray diffraction measurements can not apply directly as crystalline phases. Directly structural and density measurements of silicate melts under static compression at lower mantle pressure are reported only X-ray diffraction measurement analyzed with Ashcroft–Langreth formalism for molten MORB (Sanloup et al., 2013), however, this method would be quite difficult to apply silicate melts of wide composition range, because of its complex chemical composition. Silicate glasses are used as a good analogue to silicate melts because of structural similarity (Wolf and McMillan, 1995), and relatively lower technical barrier because silicate glasses can exist at ambient temperature.

It is well known that the density of silicate melts and glasses strongly depends on the behavior of SiO_2 melt and glass because their network is based on Si-O network (Henderson et al., 2006). The compressional behavior of SiO_2 glass is complex. Its density after decompressed from higher pressure than 8~9 GPa at room pressure is denser than that before compressed, called as densification (Grimsditch, 1984). The origin of densification is accounted for structural change of the silicate glasses with increasing pressure. Additionally, SiO_2 glass transforms to newly 6-fold structure above 20 GPa and this 6-fold structure is hard to quench to ambient pressure (Williams and Jeanloz, 1988). Recently, the behavior of this “reversal densification” was revealed above 20 GPa by X-ray absorption measurements and X-ray diffraction analysis (Sato and Funamori, 2008; 2010). Even if details are still controversial, previous studies are summarized that the compressional behavior of SiO_2 glass can be separated to six pressure regimes. (1)The density increases following to elastic manner as a single phase between 0 GPa and 9 GPa. (2)From 9 GPa to 13 GPa, compressional behavior is following to anelastic manner that the density of silica glass during decompression is higher than during compression. This anomalous density behavior is due to the pressure-induced deformation in SiO_4 -tetrahedra structure among the intermediate range order. This densification proceeds continuously up to 13 GPa. (3)From 13 GPa to 20

GPa, completely densified glass is compressed following to elastic manner in a single phase. The completely densified glass shows also elastic manner below 13 GPa (Wakabayashi et al., 2011). (4) From 20 GPa to 35 GPa, newly “reversible densification” caused by different mechanism from described above is observed. The density rapidly increases with increasing pressure due to the continuous short-range order coordination transition. As a result of this short-range order transition, the average coordination number of Si-O atoms increases from 4 to 6, and SiO_4 tetrahedra transform to SiO_6 octahedra. (5) Above 35 GPa, the density also increases following to elastic manner in a single-phase. Although *in-situ* measurements of density is limited up to 55 GPa in SiO_2 glass (Sato and Funamori, 2008), we can speculate that this density behavior would be kept at least up to 100 GPa because the structure is also kept up to 100 GPa (Sato and Funamori, 2010). (6) Above 140 GPa, newly structural change and densification is expected because of the anomalous increasing in shear velocity with increasing pressure obtained by Brillouin scattering measurements (Murakami and Bass, 2010). This anomalous increasing in shear velocity is also observed in MgSiO_3 glass (Murakami and Bass, 2011). Murakami and Bass suggested the shear velocity anomaly is caused by the coordination number increasing in Si-O atom from 6 to higher than 6, and might become 8, however, direct structural measurements are never conducted above 100 GPa.

Because the structure of glasses reflects corresponding liquid, those structural densification would also occur in silicate melts (Funamori and Sato, 2010). In fact, the increment in coordination number between Si and O from 4 to 6 is also reported in molten basalt at nicely consistent pressure range to SiO_2 glass (Sanloup et al., 2013). Therefore, structural change and compressibility of silicate glasses at high pressure is important information to understand those of silicate melts.

Elastic wave velocities would also give information of its structure and elastic density change with increasing pressure (Zha et al., 1994; Rouxel, 2008, Murakami and Bass, 2010; 2011). It was conducted density estimation by integration of bulk sound velocity up to 33.4 GPa in MgSiO_3 glass (Sanchez-Valle and Bass, 2010), and up to 20 GPa in hydrous MORB glass (Wu et al., 2014). Here this study performed high-pressure Brillouin scattering measurements in iron-bearing MgSiO_3 glass and deduced elastic density increasing, in order to evaluate the density and sink-float of iron-containing silicate melts in lower mantle pressures. Additionally, the elasticity of alumina-bearing MgSiO_3 glass is also measured in order to know the effect of alumina in structure and elastic compressibility of alumina-bearing silicate melts.

4-2. Experimental method

(Mg_{0.86}Fe_{0.14})SiO₃ glass was synthesized by quenching melt from 1931 K in CO₂-H₂ gas-mixing furnace. The oxygen fugacity in the high-temperature furnace was controlled to be slightly above the iron-wüstite buffer, in which iron in the melt completely turn to ferrous iron. The glass sample was analyzed with FE-EPMA in order to confirm that the sample was glass without any quench-crystals, and its chemical composition was (Mg_{0.86}Fe_{0.14})SiO₃. X-ray diffraction measurements also confirm the material was amorphous phase.

High pressure Brillouin scattering measurements were conducted in diamond anvil cell (DAC) with 60-degree angular aperture. A rhenium gasket pre-pressed to the thickness of 50 μm was drilled a hole with the radius of 40 μm as a sample chamber, and pre-pressed glass specimen without any pressure medium was loaded into the sample chamber. The culet radius of the diamond anvils was 120 ~ 300 μm . In order to reduce the masking region by the peak of shear wave velocity of diamond anvils, the crystal orientation of the opposing diamond anvils were equalized each other. Before pressure increment, the diamond anvil cells were put in a vacuum oven with a temperature of 430 K, at least 6 hour in order to remove water from sample chamber. Pressure in the

sample chamber was determined with the Raman T_{2g} shift of diamond anvil (Akahama and Kawamura, 2004). At each pressure point, several measurements for pressure determination were conducted around where the Brillouin incident laser was irradiated. Typical pressure deviation was within 1 GPa. Brillouin scattering measurements were conducted with Brillouin scattering measurement system at SPring-8 BL10XU (Murakami et al., 2009). A Sandercock-type 6-mirror pass tandem Fabry-Perot interferometer (Sandercock, 1983) was used as a analyzer of scattered light, and a diode-pump laser (Verdi V2, Coherent) with a wavelength of 532 nm was used as incident probe beam. All the Brillouin spectra were obtained in platelet geometry, and the scattering angle (~ 50 degree) was calibrated with BK7 glass standard (Yoneda and Son, 2005). An incident laser power of 200 ~ 600 mW was employed. The incident beam was focused to a diameter of ~ 20 μm and introduced to sample chamber. In platelet geometry, sound velocity is obtained with following equation (Whitfield et al., 1976);

$$V_i = \frac{\Delta\omega_i \lambda}{2 \sin\left(\frac{\theta}{2}\right)} \quad (4.1)$$

where V is sound velocity, $\Delta\omega$ is frequency shift observed, λ is wavelength of incident beam, θ is scattering angle, and subscription i denotes vibration mode. For $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass, measurement was performed in a single run, and for 14 mol%

Al_2O_3 -bearing MgSiO_3 glass, sound velocity measurements were conducted with 2 separated runs. At all the single pressure condition, at least 2 measurements on different orientations by rotating around compression axis were conducted. The exposure time for a single Brillouin scattering spectrum was 3 ~ 24 hour. To determine peak positions of all the individual raw Brillouin spectra, Gaussian peak function was fitted with those spectra. The evaluated peak positions of all spectra at a given pressure were averaged including Stokes and anti-Stokes peaks.

4-3. Result

Sharp Brillouin peaks of glass sample from both shear and compressional wave velocities were obtained from 15.5 GPa up to 52.9 GPa in $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass and from 11.2 GPa to 53.5 GPa in 14 mol % Al_2O_3 -bearing MgSiO_3 glass. Representative spectra pattern is shown in Fig. 4-1, Fig. 4-2, Fig. 4-3, and Fig. 4-4. There are no significant broadenings in full width of half maximum were observed in shear Brillouin peaks. It means that deviatoric shear stress increment in the sample chamber did not occur during pressure increment. In both compositions, the peaks from compressional wave velocity were masked by huge peaks from shear wave velocity of diamond anvils

above 53.5 GPa, even using the orientation of the pair of diamond anvils sandwiching the sample equalized, in order to minimize the masked region, and measuring along the (100) orientation of diamond anvils, which direction shows the fastest shear wave velocity. Therefore, the pressure range of available for compressional velocity observation was limited to 52.9 GPa in $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass and 53.5 GPa in 14 mol % Al_2O_3 -bearing MgSiO_3 glass. The result of compressional, and shear velocity is plotted in Fig. 4-5 and Fig. 4-6, respectively. At 25 GPa, the shear and compressional wave velocity of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass was ~5% and ~6% slower than those of MgSiO_3 glass, respectively (Sanchez-Valle and Bass, 2010; Murakami and Bass, 2011).

At these pressure both shear and compressional velocities obtained, bulk sound velocity, V_B and Poisson's ratios, ν of the glasses were calculated directly by both compressional and shear velocities with following relation;

$$V_B = \sqrt{V_P^2 - \frac{4}{3}V_S^2} \quad (4.2)$$

$$\nu = \frac{1}{2} \left(1 - \frac{1}{\left(\frac{V_P}{V_S}\right)^2 - 1} \right) \quad (4.3)$$

where V_P and V_S represents compressional and shear wave velocity, respectively. The aggregate of V_B and ν is plotted in Fig. 4-7 and Fig. 4-8, respectively. At 15.5 GPa, Poisson's ratio of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass is 0.324, and increased to about 0.335 at 30

GPa. Above 30 GPa, the Poisson's ratio seems to be nearly constant up to 52.9 GPa in $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass. In 14 mol% Al_2O_3 -bearing MgSiO_3 glass, this value is 0.297 at 11.2 GPa and is also increase to about 0.335 at 30 GPa, and become nearly independent to pressure.

To obtain density of glass at high pressure, following relation was employed;

$$\rho(P) = \int_{P_0}^P \left(\frac{\gamma}{V_B^2} \right) \partial P - \rho(P_0) \quad (4.4)$$

where P_0 is standard pressure, γ is the ratio between K_S and K_T where K_S is adiabatic bulk modulus and K_T is isothermal bulk modulus. Generally, we can assume that γ is ~ 1 under ambient temperature for the silicate materials. Therefore, we can obtain the density of any silicate materials under high pressure by the bulk sound velocity profile under high pressure and the density under ambient condition, without X-ray diffraction measurements. From this point on, referred K_S and K_T in K for simplify. For density of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass at ambient condition, following method was employed. First, the molar volume of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{O}$ virtual glass were calculated with the fellow relation, $V_0 = 12.44 + 1.11z \text{ cm}^3/\text{mol}$ for $(\text{Mg}_{1-z}\text{Fe}_z)\text{O}$ virtual glass, where V_0 is molar volume of virtual $(\text{Mg}_{1-z}\text{Fe}_z)\text{O}$ glass (Funamori and Sato, 2010). Then, molar volume of SiO_2 ($23.81 \text{ cm}^3/\text{mol}$ by Schilling et al., 2001) was added to that of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{O}$ virtual glass following to ideal molar mixing model (Stebbins et al., 1984; Schilling et

al., 2001). This value, 36.41 cm³/mol was used as the molar volume of (Mg_{0.86}Fe_{0.14})SiO₃ glass. After that, formula weight of (Mg_{0.86}Fe_{0.14})SiO₃ were divided by the molar volume of (Mg_{0.86}Fe_{0.14})SiO₃ glass to estimate the density. At last, 2.878 g/cm³ was obtained as the density of (Mg_{0.86}Fe_{0.14})SiO₃ glass at ambient pressure. The bulk sound velocity of (Mg_{0.86}Fe_{0.14})SiO₃ glass at ambient pressure was estimated also following to ideal molar mixing model as follows. The molar bulk modulus of virtual (Mg_{0.86}Fe_{0.14})O glass at ambient pressure is 118 GPa by Funamori and Sato (2010), and that of SiO₂ is 47.4 GPa by Schilling et al. (2001). Then, the bulk modulus of (Mg_{0.86}Fe_{0.14})SiO₃ glass is estimated 82.7 GPa, and its bulk sound velocity at ambient pressure is deduced 5.36 km/s with following relation; $V_B = (K/\rho)^{1/2}$. In 14 mol% Al₂O₃-bearing MgSiO₃ glass, similar process was employed to obtain its density and bulk sound velocity in ambient condition. The integration of $1/V_B^2$ for estimating the density under high pressure was deduced with following equation;

$$\int_{P_0}^P \left(\frac{1}{V_B^2} \right) dP \cong \sum_i \frac{\left(\frac{1}{V_B^2} \right)_i (P_{i+1} - P_i) + \left(\frac{1}{V_B^2} \right)_{i+1} (P_{i+1} - P_i)}{2} \quad (4.5)$$

The subscription i denotes i^{th} pressure point from standard pressure, and $i = 0$ means the standard pressure. Fig. 4-9 is a schematic picture to explain this calculation. Because $1/V_B^2$ would be monotone decreasing with pressure, the maximum estimation of density change with increasing pressure from P_i to P_{i+1} are given by the taller rectangle in Fig.

4-9, which has a horizontal edge length of $P_{i+1}-P_i$ GPa and a vertical edge length of $(1/V_B^2)_i$ g/cm³/GPa. Similarly, the minimum estimation are by the shorter rectangle, which has a horizontal edge length of $P_{i+1}-P_i$ GPa and a vertical edge length of $(1/V_B^2)_{i+1}$. The square of the trapezoid gives the average of density increment between P_{i+1} and P_i . Therefore, this systematic uncertainty of density should be increasing with the pressure because the difference between maximum and minimum estimation is increasing with increasing pressure. However, the uncertainty of density is within 5 % at 52.9 GPa. The $1/V_B^2$ as a function of pressure is shown in Fig. 4-10. In this study, sound velocities data from 0 GPa to 15 GPa is lacking. Because the structural transition in the silicate glasses were expected (Zha et al., 1994; Sanchez-Valle and Bass, 2010), some deviatric increment of the density and anomaly in sound velocities would occur between 0 GPa to 15 GPa, therefore, present calculation can not consider the details of such deviatric increments of density. However, $1/V_B^2$ of MgSiO₃ glass in previous study (Sanchez-Valle and Bass, 2010) showed almost monotone decreasing trend with pressure (Fig. 4-10). Therefore, the elastic density increment would become within the maximum and minimum density increment estimation shown above.

With obtained density, bulk modulus and shear modulus at each pressure point were obtained by following relation,

$$G = \rho V_s^2 \quad (4.6)$$

$$K = \rho \left(V_p^2 - \frac{4}{3} V_s^2 \right) \quad (4.7)$$

The obtained aggregate elastic moduli were fitted with third-order Eulerian finite strain equations;

$$K = K_0(1 + 2f)^{\frac{5}{2}} \left[1 + (3K'_0 - 5)f + \frac{27}{2} (K'_0 - 4)f^2 \right] \quad (4.8)$$

$$G = (1 + 2f)^{\frac{5}{2}} [G_0 + (3K_{T0}G'_0 - 5G_0)f + (6K_{T0}G'_0 - 24K_0 - 14G_0 + 9K_{T0}K'_{T0})f^2] \quad (4.9)$$

where

$$f = \frac{\left(\frac{\rho_0}{\rho} \right)^{2/3} - 1}{2} \quad (4.10)$$

G_0 is shear modulus and K_0 is bulk modulus at ambient pressure, and G' is pressure derivative of shear modulus and K' is that of bulk modulus, and ρ_0 is density at ambient pressure. From least-square regression analysis, $K' = 4.46$, $G_0 = 32.6$ GPa, and $G' = 1.61$ was deduced, with fixed K_0 of 82.7 GPa obtained by ideal mixing model as described. Thereby, the Poisson's ratio under ambient condition is 0.326. The correlation coefficient between third order Eulerian finite strain model of bulk and shear modulus and observed corresponding modulus was 0.9954 and 0.9916, respectively. In 14 mol % Al_2O_3 -bearing MgSiO_3 glass, both bulk and shear moduli at ambient pressure are 87.4 GPa and 445 GPa, respectively. These parameters are deduced with ideal

mixing model and molar elastic property by Schilling et al (2001). Then, regression analysis gives $K' = 3.67$ and $G' = 1.32$. Young's moduli of present silicate glasses at high pressure are also deduced. The aggregates density, bulk, shear, and Young's modulus is shown in Fig. 4-11, Fig. 4-12, Fig. 4-13, Fig. 4-14, respectively. All the velocity, density and elasticity data of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass and 14 mol% Al_2O_3 -bearing MgSiO_3 glass were summarized in Table 4-1 and Table 4-2, respectively.

4-4. Discussion

4-4-1. Poisson's ratio and the structure of silicate glass

Zha et al. (1994), and Sanchez-Valle and Bass (2010) reported that the aggregate Poisson's ratio of SiO_2 and MgSiO_3 glass have a trend that increasing from ambient pressure to ~20 GPa, and saturating with the pressure-increment to 50 GPa, at about 0.33, respectively. In $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass, this property is 0.326 at ambient pressure. This value is abnormally higher than typical silicate glasses at ambient pressure (0.15~0.28), however, the cause of this abnormal value will be discussed below. At 15 GPa, this property is 0.326 and is increase to about 0.34 at 30 GPa, then, becomes

independent against pressure up to 52.9 GPa. Therefore, above 20 GPa, the Poisson's ratio of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass follows similar trend to SiO_2 and MgSiO_3 glass. Such similar behavior on Poisson's ratio of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass to that of MgSiO_3 and SiO_2 glass indicates the influence of iron is very small in structural change with increasing pressure above 15 GPa, because elastic behavior would strongly depend on its structural change. In 14 mol % Al_2O_3 -bearing MgSiO_3 glass, the profile of Poisson's ratios seems to be also following to the trend of other silicate glass above 11.2 GPa.

Poisson's ratio is good indicator for ductility. Generally, metallic materials take this value between 0.25 and 0.35, and liquid materials take 0.5. Therefore, the ductility of both Fe-bearing MgSiO_3 glass and 14 mol% Al_2O_3 -bearing MgSiO_3 glass is very close to usual metals, as discussed in Zha et al. (1994) and Sanchez-Valle and Bass (2010) for silica glass and MgSiO_3 glass, respectively.

Makishima and Mackenzie (1975) established calculation model of elastic properties and Poisson's ratio of oxide glasses by dissociation energies and packing densities of consist oxide components, based on the Gruneisen's first rule. According to this calculation model, Poisson's ratio can be deduced by only packing density defined as;

$$\nu = 0.5 - \frac{1}{7.2V_t} \quad (4.11)$$

where V_t is packing density defined as

$$V_t = \rho \frac{\sum_i f_i V_i}{\sum_i f_i M_i} \quad (4.12)$$

where f_i , M_i , V_i is molar fraction per single formula, formula weight, and packing factor of i^{th} component. V_i which has $A_x B_y$ chemical formula is defined as;

$$V_i = \frac{4}{3} \pi N_A (x r_A^3 + y r_B^3) \quad (4.13)$$

where N_A is the Avogadro's number and r_A , r_B represent the ionic radii. According to these relation between packing density, ionic radii and Poisson's ratio, elastic density change above 25 GPa is interpreted as a result of shrinking in ionic radii among silicate glasses rather than structural deformation, because Poisson's ratio are nearly constant.

4-4-2. Density and Elastic moduli

For MgSiO_3 glass by Sanchez-Valle and Bass (2010), the bulk modulus and shear modulus, and Poisson's ratio were reported as 78.4 GPa, 41.1 GPa, and 0.277, respectively. It is slightly (~5 %) larger in bulk modulus of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass than that of MgSiO_3 glass, and ~20 % smaller in shear modulus. This discrepancy is interpreted by difference of the estimation method between bulk and shear modulus in $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass. Previous studies reported the kink of shear and compressional wave velocities at 2 ~ 10 GPa, which the sound velocities below this pressure are

decreasing or consistent with increasing pressure, and those above this pressure are increasing relatively more rapid than those in below pressure (Zha et al., 1994; Sanchez-Valle and Bass 2010). The shear modulus in of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass in ambient pressure is obtained by the fitting with the data of high pressure sound velocities above 15 GPa, which pressure is over the pressure of reported kinks. On the other hand, the bulk modulus is calculated by ideal mixing model with the data in ambient pressure. Therefore, the shear modulus of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass in ambient pressure seems to be significantly smaller than pure MgSiO_3 glass. This reduction in obtained shear modulus of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass is the cause of abnormally higher Poisson's ratio than typical silicate glasses in ambient pressure.. The pressure derivative of bulk modulus and shear modulus of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass is 4.49 and 1.45, respectively. Although the pressure derivative of shear modulus is almost equal to that of pure MgSiO_3 glass, the derivative of bulk modulus is about 18 % smaller. This discrepancy indicates that the difference in the bulk modulus between iron-bearing and pure MgSiO_3 glass becomes larger with increasing pressure, so the difference in compressibility of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass also becomes larger with increasing pressure than that of pure MgSiO_3 glass. Therefore, the difference in the density between $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass and pure MgSiO_3 glass might be larger with increasing pressure.

Because pressure derivative of density can describe only with bulk sound velocity as follows;

$$\left(\frac{\partial \rho}{\partial P}\right)_T = \frac{1}{V_B^2} \quad (4.14)$$

difference in bulk sound velocity of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass and MgSiO_3 glass also indicates the enhancing of density gap with increasing pressure as the gap of pressure derivative of bulk modulus. If the elastic properties could be extrapolated up to the lowermost mantle pressure, the density of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass would become 0.36 g/cm^3 denser at 135 GPa. This value is about 4 times larger than the difference at ambient pressure.

Above 30 GPa, the elastic density change would be caused by shrinking distances between cation and oxygen rather than structural change, as discussed above. Therefore, the difference in density increasing quantity with increasing pressure would be as a result of difference in easiness of density increase by shrinking of Fe-O bond length and of Mg-O bond. In fact, $1/V_B^2$ value by equation of state of periclase is smaller than that of wüstite, indicates the contribution of shrinking distance between Mg-O in density change is smaller than between Fe-O. The $1/V_B^2$ value of 14 mol% Al_2O_3 -bearing MgSiO_3 glass is also smaller than that of MgSiO_3 glass above 11.2 GPa. This reduction would be explained as a result of the difference in ionic radii between Si^{4+} (0.26 Å) and

Al^{3+} (0.38 Å) (Shannon and Prewitt, 1969), because Al^{3+} is quite larger than Si^{4+} , the easiness of shrinking distance between Al-O *bond would be larger than that between Si-O bond.

4-4-3. Geophysical implication

The densities of the glass deduced by present high-pressure Brillouin scattering measurements are extrapolated with third-order Eulerian finite strain equation, and plotted in Fig. 4-15. The extrapolated density profiles of silicate glasses are compared with that of mixture between $(\text{Mg}_{0.92}\text{Fe}_{0.08})\text{SiO}_3$ perovskite and $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{O}$ with a volume amount ratio of 8:2 as average mantle density profile in 300 K in order to evaluate the sink-float of silicate melts at the lower mantle. The density of $(\text{Mg}_{0.92}\text{Fe}_{0.08})\text{SiO}_3$ perovskite and $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{O}$ is calculated with elastic properties by Xu et al.(2008). Let us consider the iron-concentration during fractional crystallization just after the Earth's formation. Nomura et al. (2011) demonstrated the Fe-Mg distribution coefficient between melt and $(\text{Mg,Fe})\text{SiO}_3$ perovskite defined as $K_D = (\text{Fe}^{\text{Pv}}/\text{Mg}^{\text{Pv}})/(\text{Fe}^{\text{melt}}/\text{Mg}^{\text{melt}})$ suddenly decrease from 0.226 to 0.071 at 76 GPa. This decrement in iron distribution coefficient corresponds increase of Fe/(Fe+Mg) from

0.25 to 0.55 in (Mg,Fe)SiO₃ melt coexisting with (Mg_{0.92}Fe_{0.08})SiO₃ perovskite. In order to evaluate density profiles of high iron containing melt coexisting with (Mg_{0.92}Fe_{0.08})SiO₃ perovskite, ideal molar volume mixing model in molar volume are employed (Bottinga and Weill, 1970). The molar volume of (Mg_{1-x}Fe_x)SiO₃ glass is described as

$$V_{(Mg_{1-x}Fe_x)SiO_3} = x (V_{(Mg_{0.86}Fe_{0.14})SiO_3} - V_{MgSiO_3})/14 + V_{MgSiO_3} \quad (4.15)$$

where $V_{(Mg_{0.86}Fe_{0.14})SiO_3}$ and V_{MgSiO_3} is molar volume of glass for corresponding compositions, respectively, deduced by

$$V_{(Mg,Fe)SiO_3} = M_{(Mg,Fe)SiO_3} / \rho_{(Mg,Fe)SiO_3} \quad (4.16)$$

where $\rho_{(Mg,Fe)SiO_3}$ is density of glass for corresponding compositions. Then, the density of high iron-containing glass is evaluated as

$$\rho_{(Mg_{1-x}Fe_x)SiO_3} = M_{(Mg_{1-x}Fe_x)SiO_3} / V_{(Mg_{1-x}Fe_x)SiO_3} \quad (4.17)$$

This density profile of appropriate iron-contain glass is also shown in Fig. 4-15 as dashed pink line. The density of highly iron concentrated glass is not reached to that of crystalline phases consisting average mantle.

However, this density estimation of silicate glasses might give only minimum estimation of density, because structural unrelaxation at Brillouin frequency regime (~10 GHz) is expected above 9 GPa. The density is governed by the “relaxed” bulk

modulus, which is measured by pressure-volume relation, or sound velocities with enough long time period. If the period time is not enough long for the structural relaxation, “unrelaxed” bulk modulus would be measured, and the “unrelaxed” bulk modulus is significantly higher than relaxed bulk modulus, and the density deduced by unrelaxed bulk modulus becomes smaller (Ghosh et al., 2014). Above 9 GPa, the densification by structural rearrangement occurs and structural relaxation time would become significantly longer, therefore, the density estimation of silicate glasses might be underestimated. In fact, the density of SiO₂ glass obtained by X-ray absorption method shows great increase in density between 10 GPa to 40 GPa, although the density calculated with bulk sound velocities above 10 GPa by Brillouin scattering measurement (Zha et al., 1994) had no such a significant increase. The density of MgSiO₃ glass by Brillouin scattering measurement (Sanchez-Valle and Bass, 2010) and *ab-initio* calculation (Ghosh et al., 2014) also have a similar gap as the densities of SiO₂ glass, and structural change is also expected above 12 GPa by coordination transition from 4-fold to 6-fold in Si-O in MgSiO₃ glass (Lee et al., 2009). Thus, the density of silicate glass, including present iron-bearing MgSiO₃ glass, by Brillouin scattering would be minimum estimation (Zha et al., 1994; Sanchez-Valle and Bass, 2010). Additionally, we can only speculate that thermal expansion of silicate glasses and melts

would be higher than corresponding crystals based on that of ambient pressure (Lange and Carmichael, 1987), therefore, it is hard to estimate the effect of temperature increasing accurately. Consequently, now we can discuss the existence of density crossover between silicate melt and average mantle phases very roughly, and this discussion would not be able to give conclusive claims. However, based on the discussion above, we can claim that the structural effect in silicate glasses and melts for density change with increasing pressure is very important to estimate density more accurately.

Brillouin scattering measurements were conducted at SPring-8 (proposal no. 2013B0087, 2014A0080, and 2014B0080)

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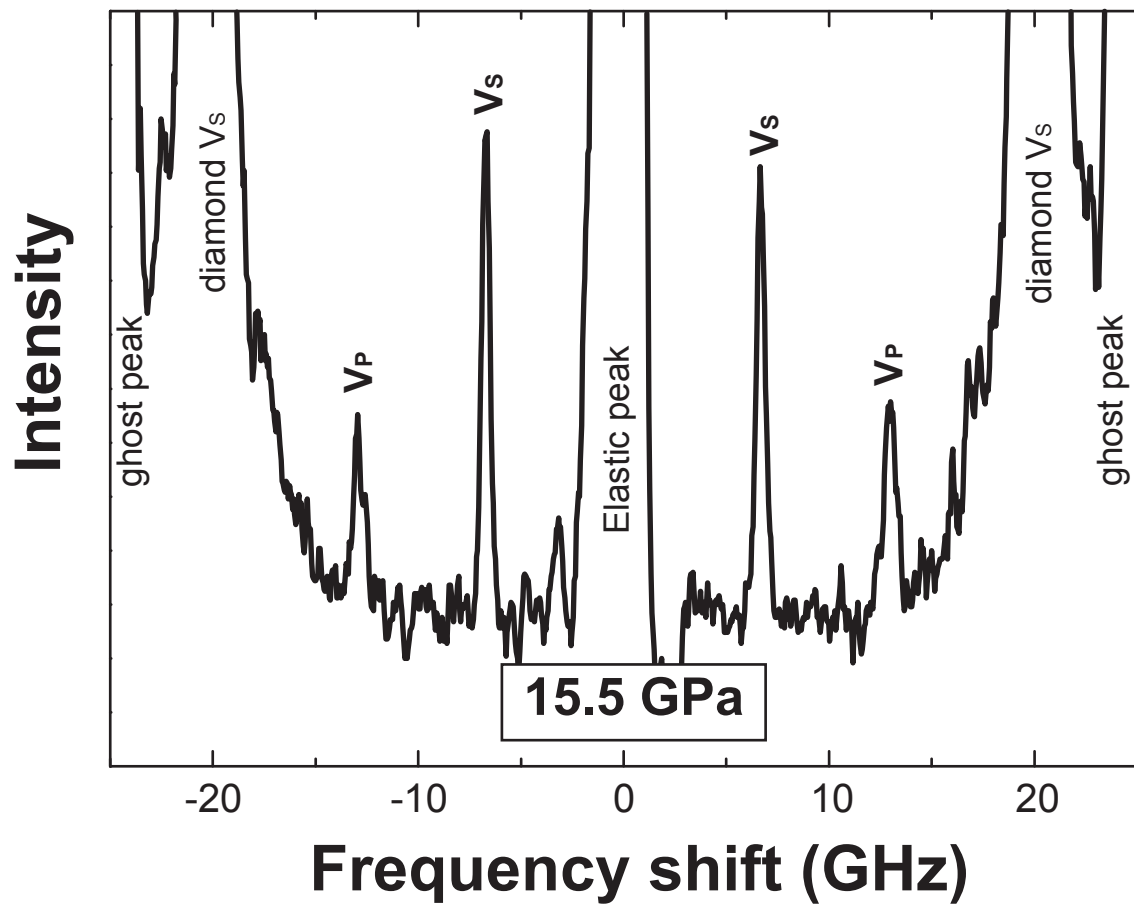


Fig. 4-1 Brillouin spectrum of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass at 15.5 GPa.

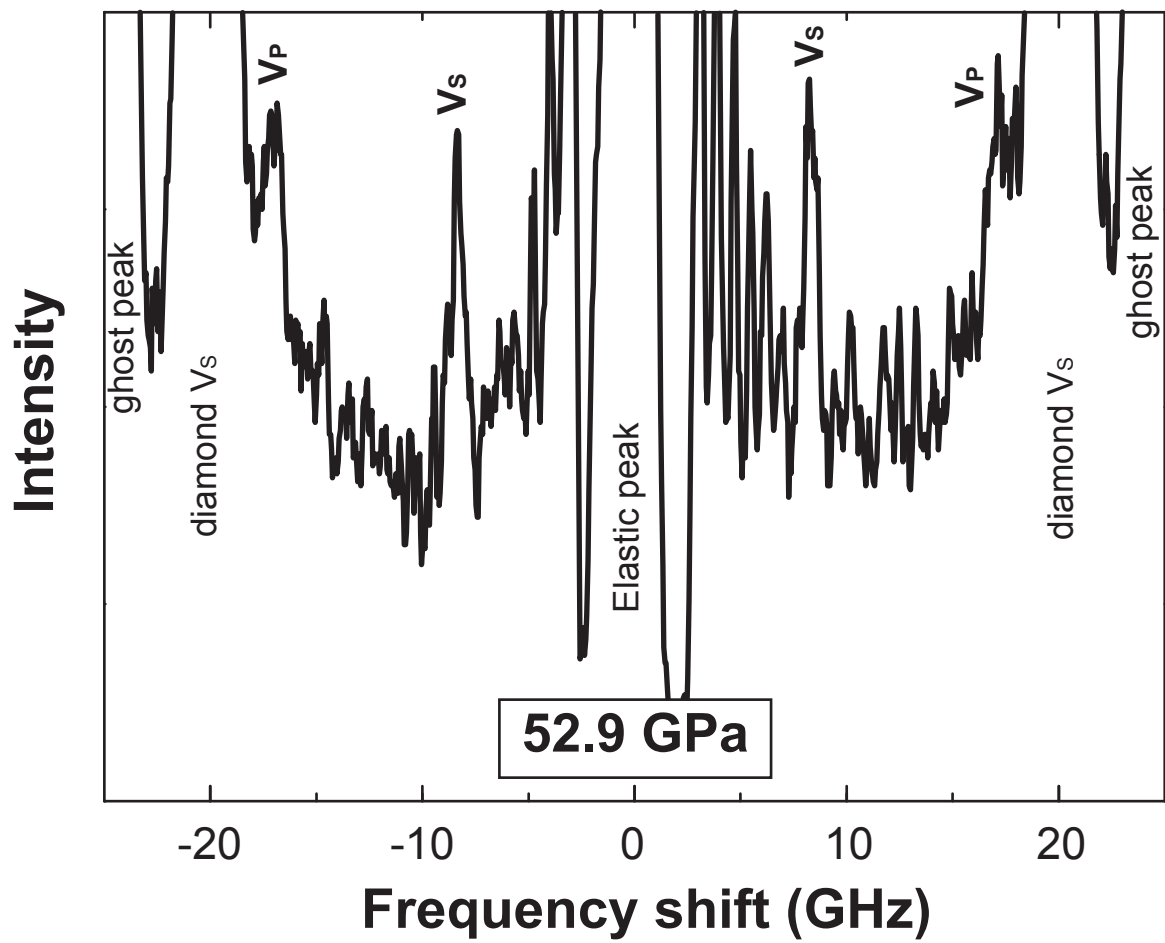


Fig. 4-2 Brillouin spectrum of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass at 52.9 GPa.

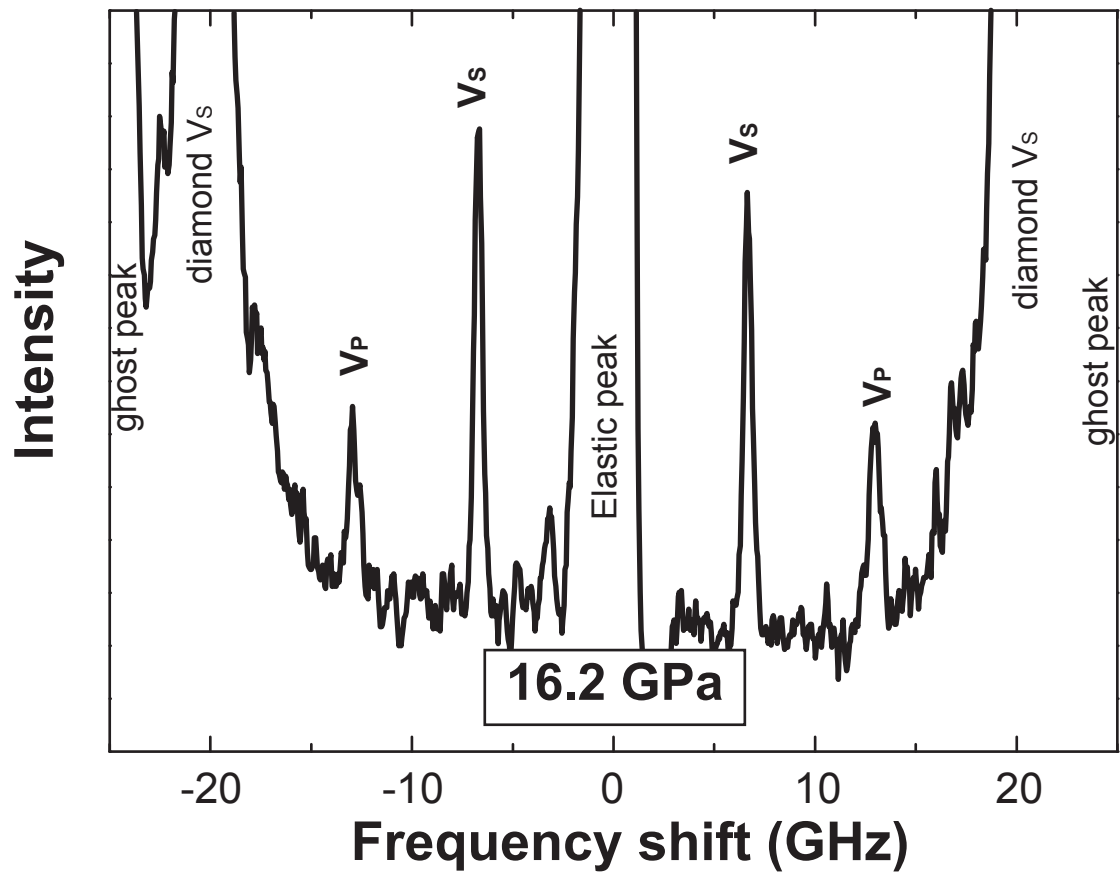


Fig. 4-3 Brillouin spectrum of 14 mol% Al_2O_3 -bearing MgSiO_3 glass at 16.2 GPa.

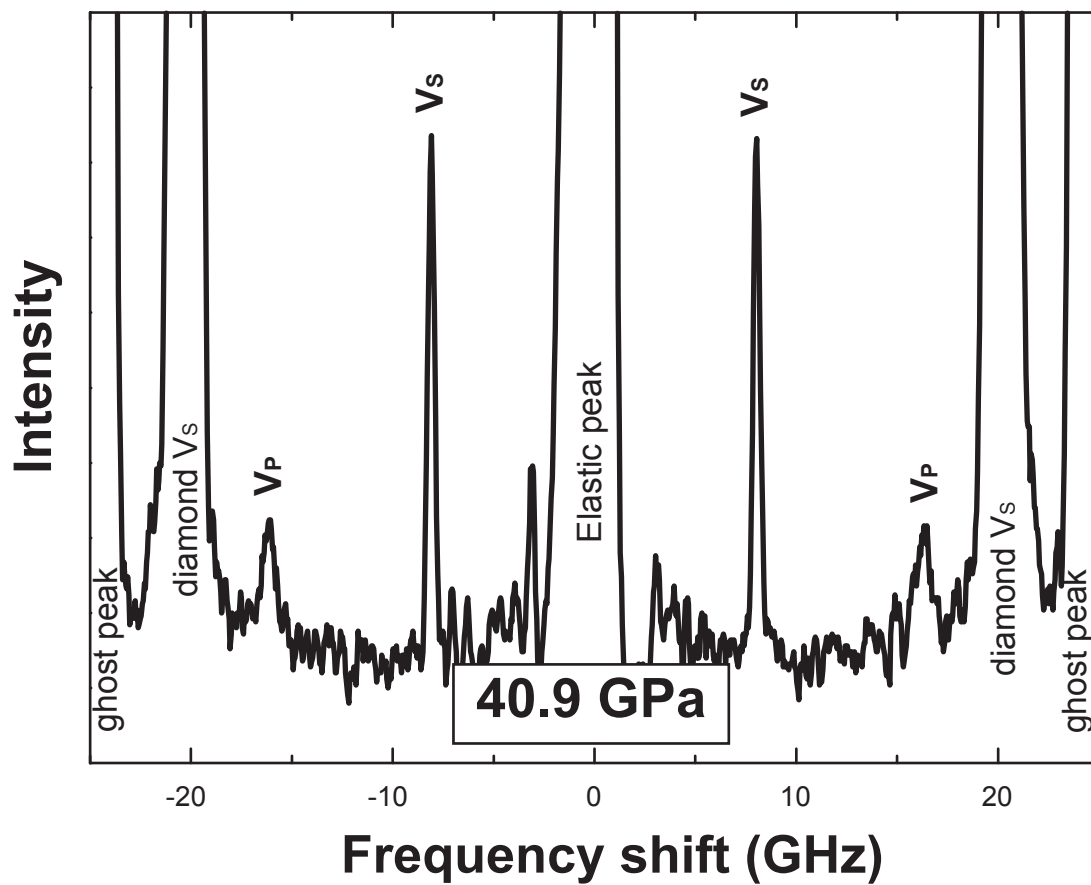


Fig. 4-4 Brillouin spectrum of 14 mol% Al_2O_3 -bearing MgSiO_3 glass at 40.9 GPa.

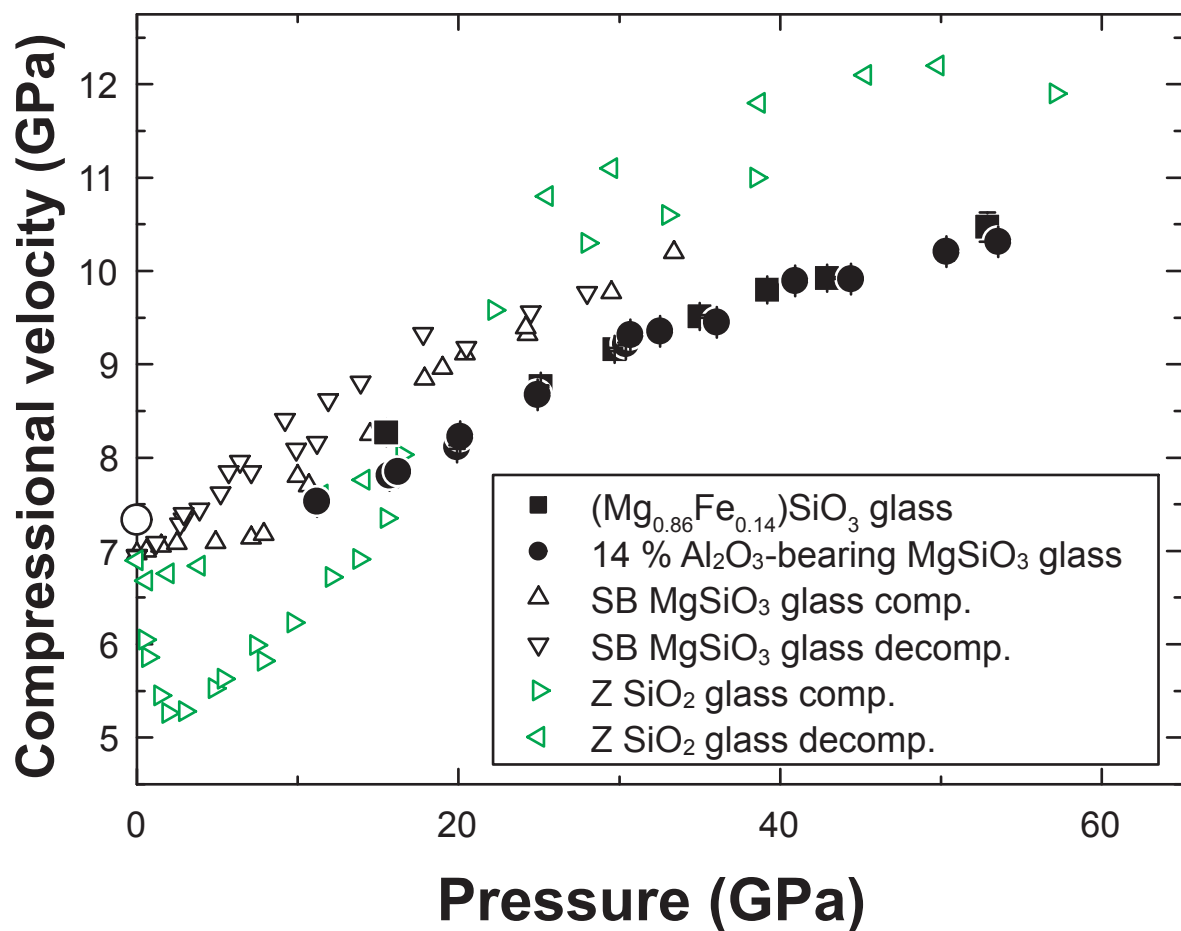


Fig. 4-5 Compressional wave velocity of (Mg_{0.86}Fe_{0.14})SiO₃ glass (black square), 14 mol% Al₂O₃-bearing MgSiO₃ glass (black circle), MgSiO₃ glass during compression (upward open triangle) and decompression (downward open triangle) by Sanchez-Valle and Bass (2010), SiO₂ glass during compression (rightward open triangle) and decompression (leftward open triangle) by Zha et al. (1995), and 14 mol% Al₂O₃-bearing MgSiO₃ glass calculated by ideal mixing model at ambient pressure (open circle).

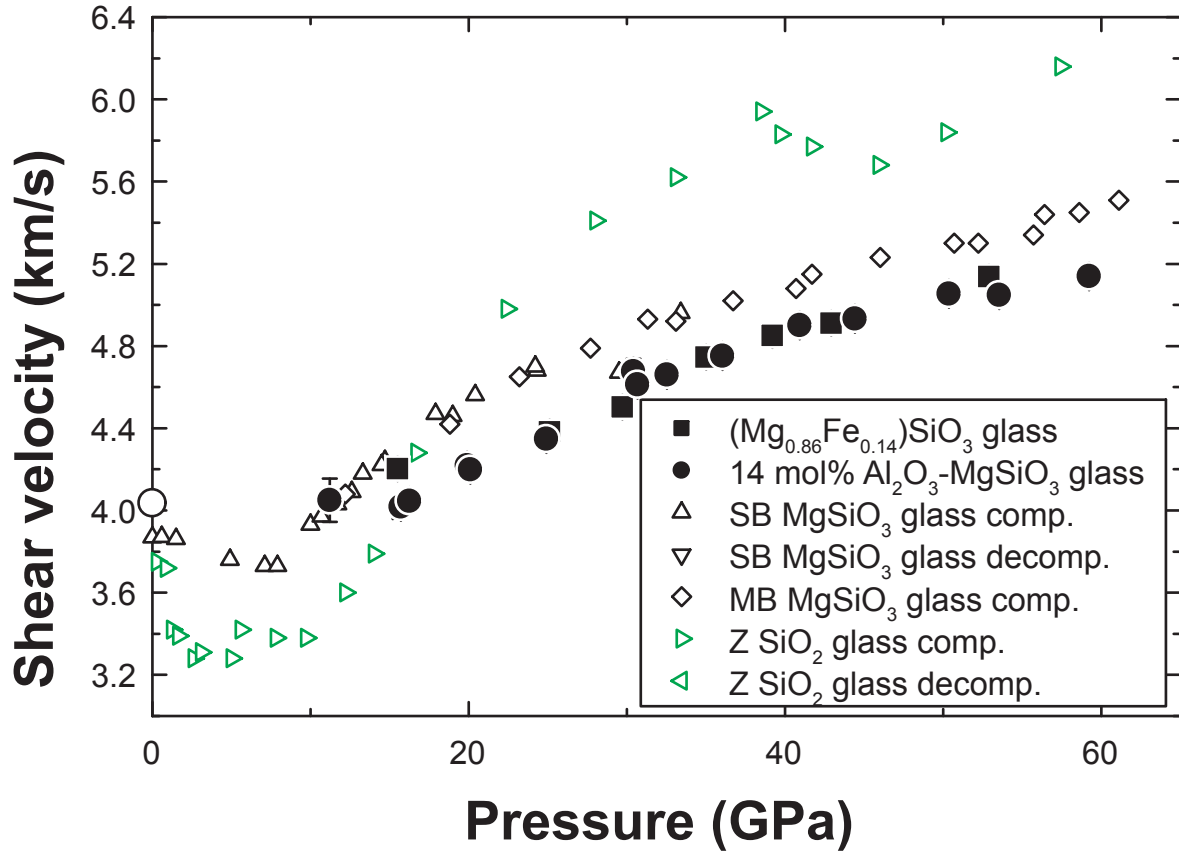


Fig. 4-6 Compressional wave velocity of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass (black square), 14 mol% Al_2O_3 -bearing MgSiO_3 glass (black circle), MgSiO_3 glass during compression (upward open triangle) and decompression (downward open triangle) by Sanchez-Valle and Bass (2010), during compression by Murakami and Bass (2011) (open diamond), SiO_2 glass during compression (green rightward open triangle) and decompression (green leftward open triangle) by Zha et al. (1995), and 14 mol% Al_2O_3 -bearing MgSiO_3 glass calculated by ideal mixing model at ambient pressure (open circle).

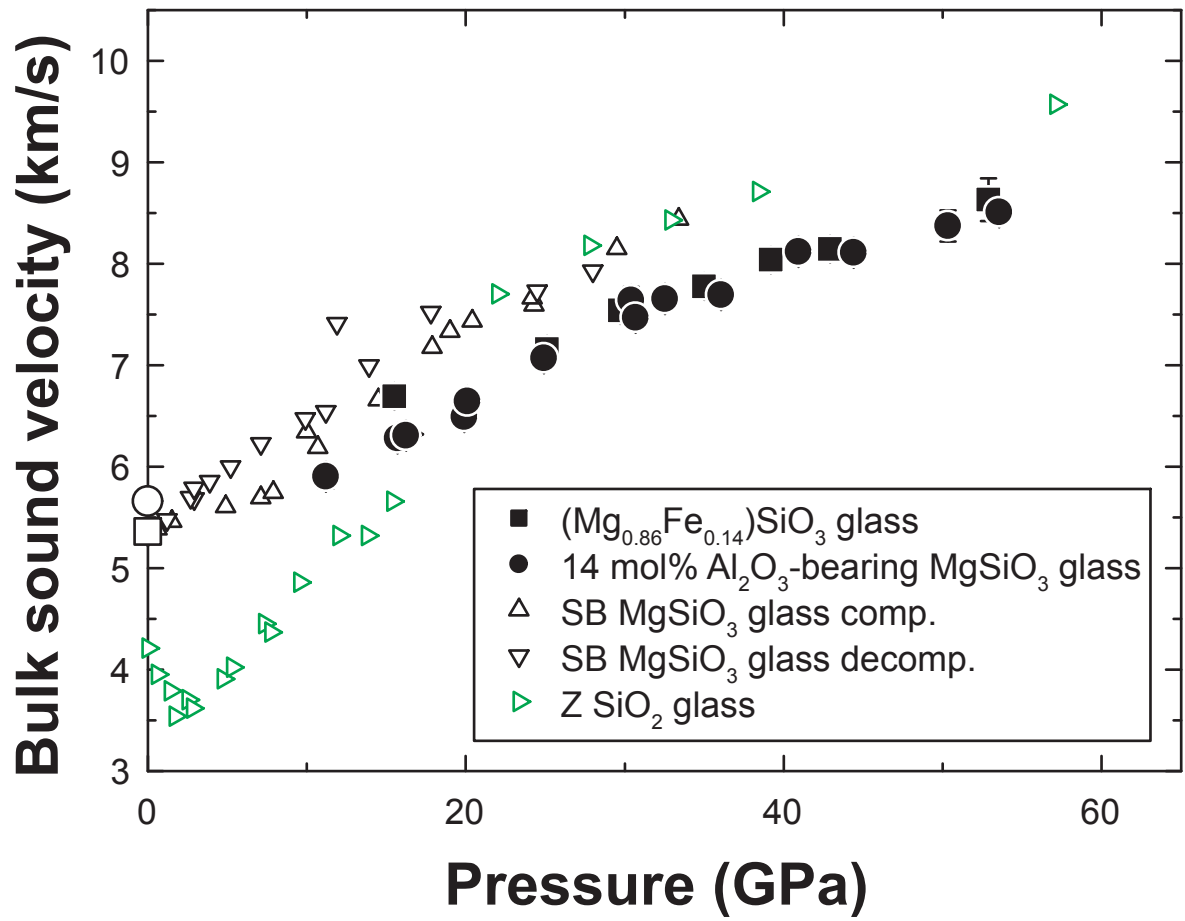


Fig. 4-7 Bulk sound velocity of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass (black square), 14 mol% Al_2O_3 -bearing MgSiO_3 glass (black circle), MgSiO_3 glass during compression (upward open triangle) and decompression (downward open triangle) by Sanchez-Valle and Bass (2010), SiO_2 glass by Zha et al. (1995) (green rightward open triangle), and $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass calculated by ideal mixing model (open square), 14 mol% Al_2O_3 -bearing MgSiO_3 glass calculated (open circle).

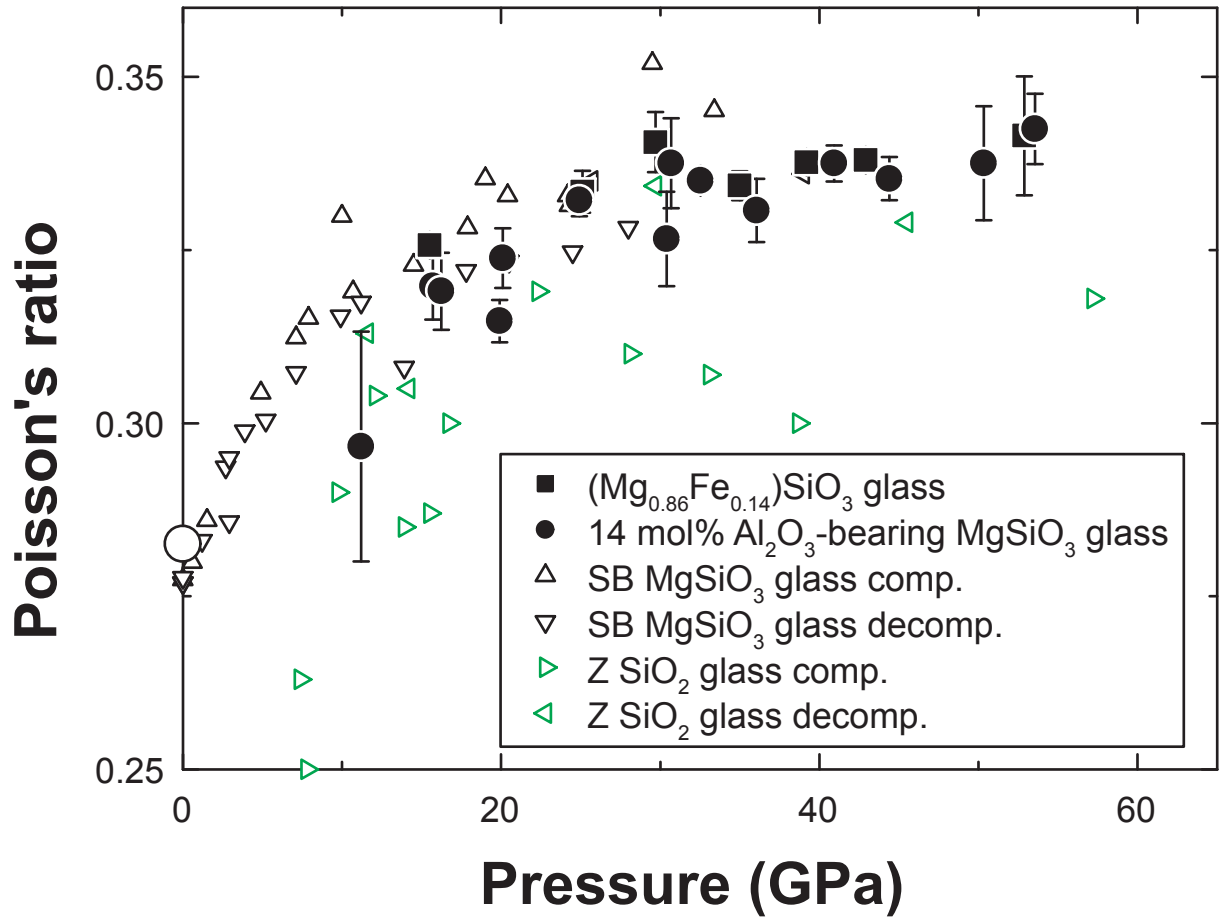


Fig. 4-8 Poisson's ratio of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass (black square), 14 mol% Al_2O_3 -bearing MgSiO_3 glass (black circle), MgSiO_3 glass during compression (upward open triangle) and decompression (downward open triangle) by Sanchez-Valle and Bass (2010), SiO_2 glass during compression (rightward open triangle) and decompression (leftward open triangle) by Zha et al. (1995), and 14 mol% Al_2O_3 -bearing MgSiO_3 glass calculated by ideal mixing model at ambient pressure (open circle).

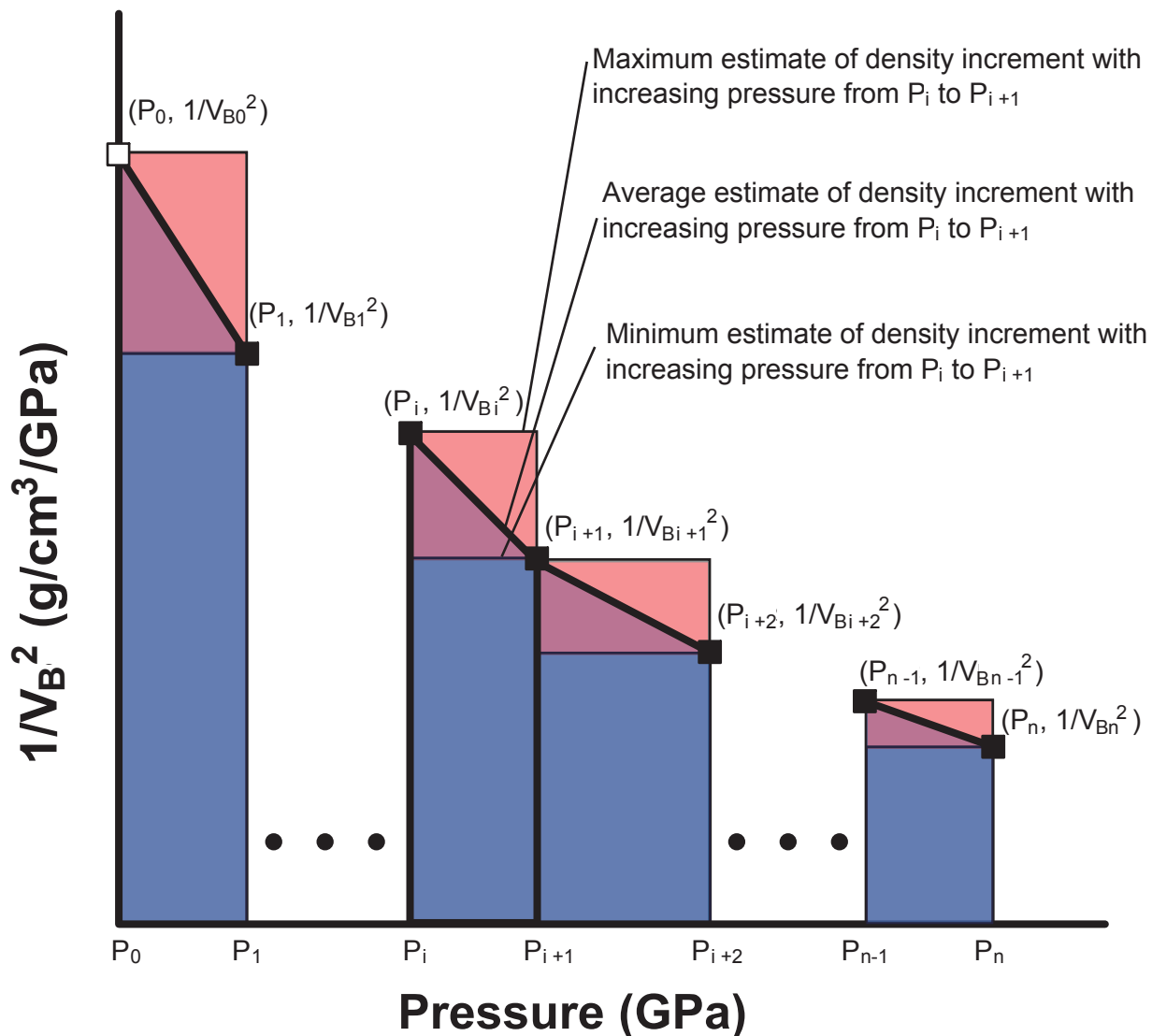


Fig. 4-9 Schematic figure for explaining integration of $1/V_B^2$ in order to estimate density integration. The taller pink rectangles represent maximum estimation of density change with increasing pressure from P_i to P_{i+1} , shorter purple one is minimum estimation, and gray trapezoids are the average of density change. In this study, densities at high pressure are employed the sum of average estimations, and errors are obtained by the difference in the sum of average estimation and maximum, minimum estimation.

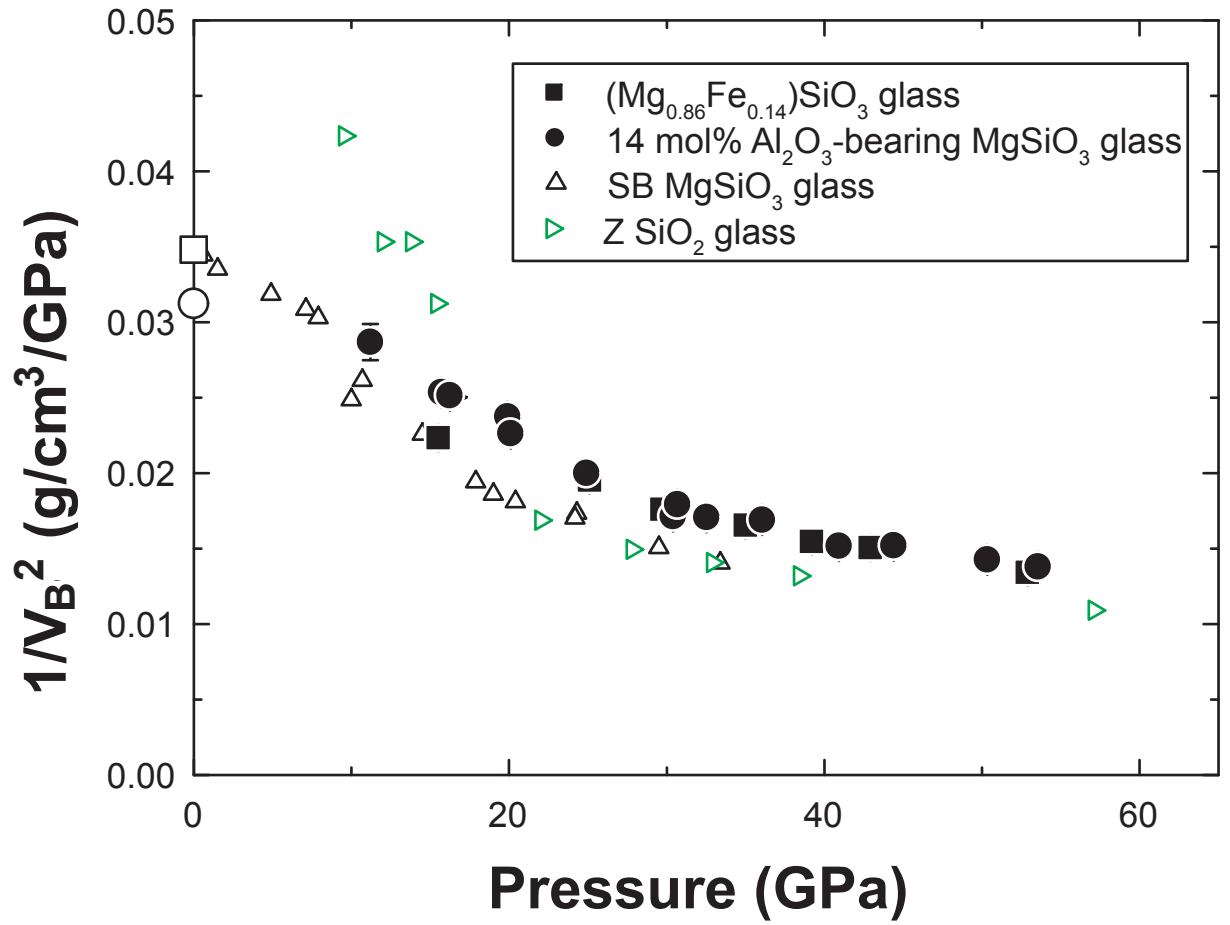


Fig. 4-10 $1/V_B^2$ value of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass (black square), 14 mol% Al_2O_3 -bearing MgSiO_3 glass (black circle), MgSiO_3 glass during compression (upward open triangle) and decompression (downward open triangle) by Sanchez-Valle and Bass (2010), SiO_2 glass during compression (rightward open triangle) and decompression (leftward open triangle) by Zha et al. (1995), and 14 mol% Al_2O_3 -bearing MgSiO_3 glass calculated by ideal mixing model at ambient pressure (open circle).

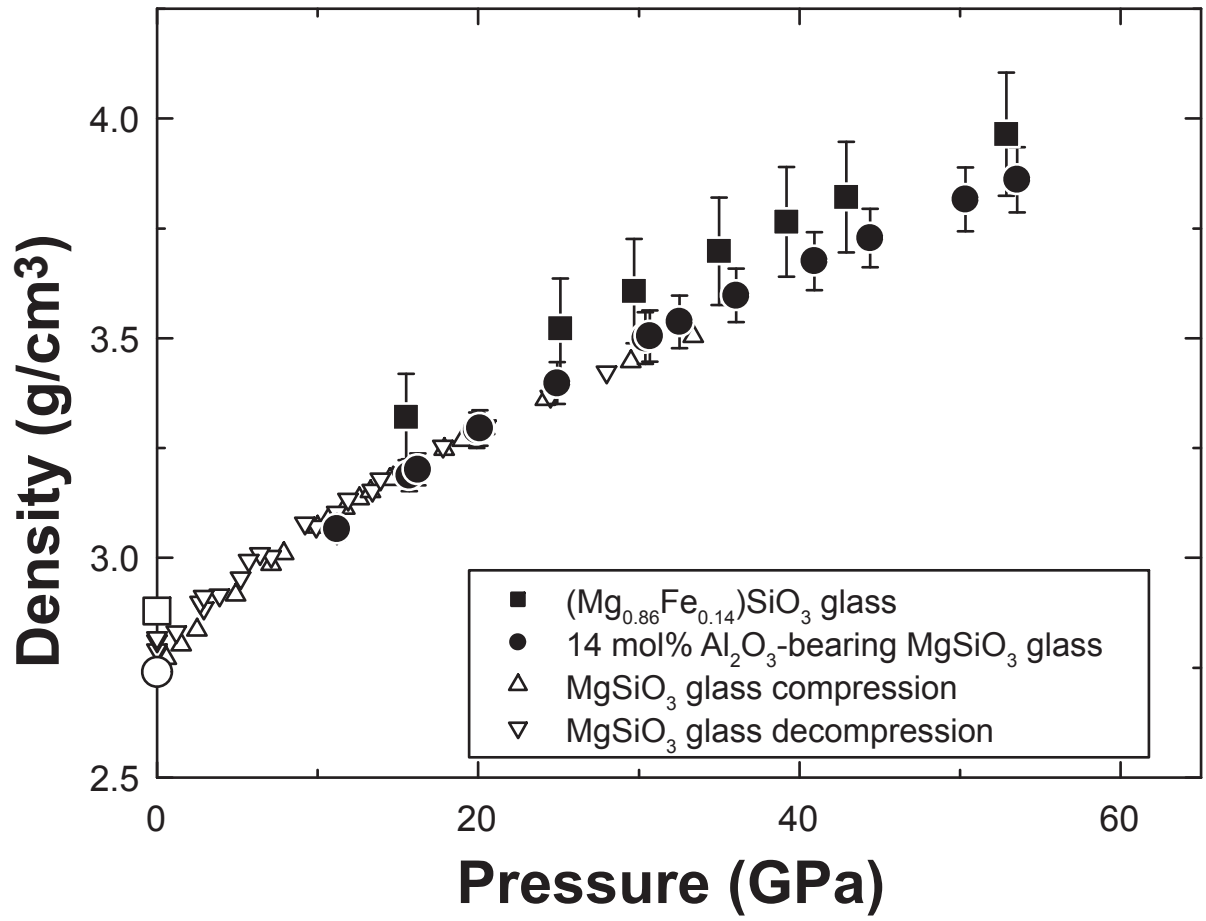


Fig. 4-11 Density of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass (black square), 14 mol% Al_2O_3 -bearing MgSiO_3 glass (black circle), MgSiO_3 glass during compression (upward open triangle) and decompression (downward open triangle) by Sanchez-Valle and Bass (2010), and $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass calculated by ideal mixing model at ambient pressure (open square), 14 mol% Al_2O_3 -bearing MgSiO_3 glass by ideal mixing model at ambient pressure (open circle).

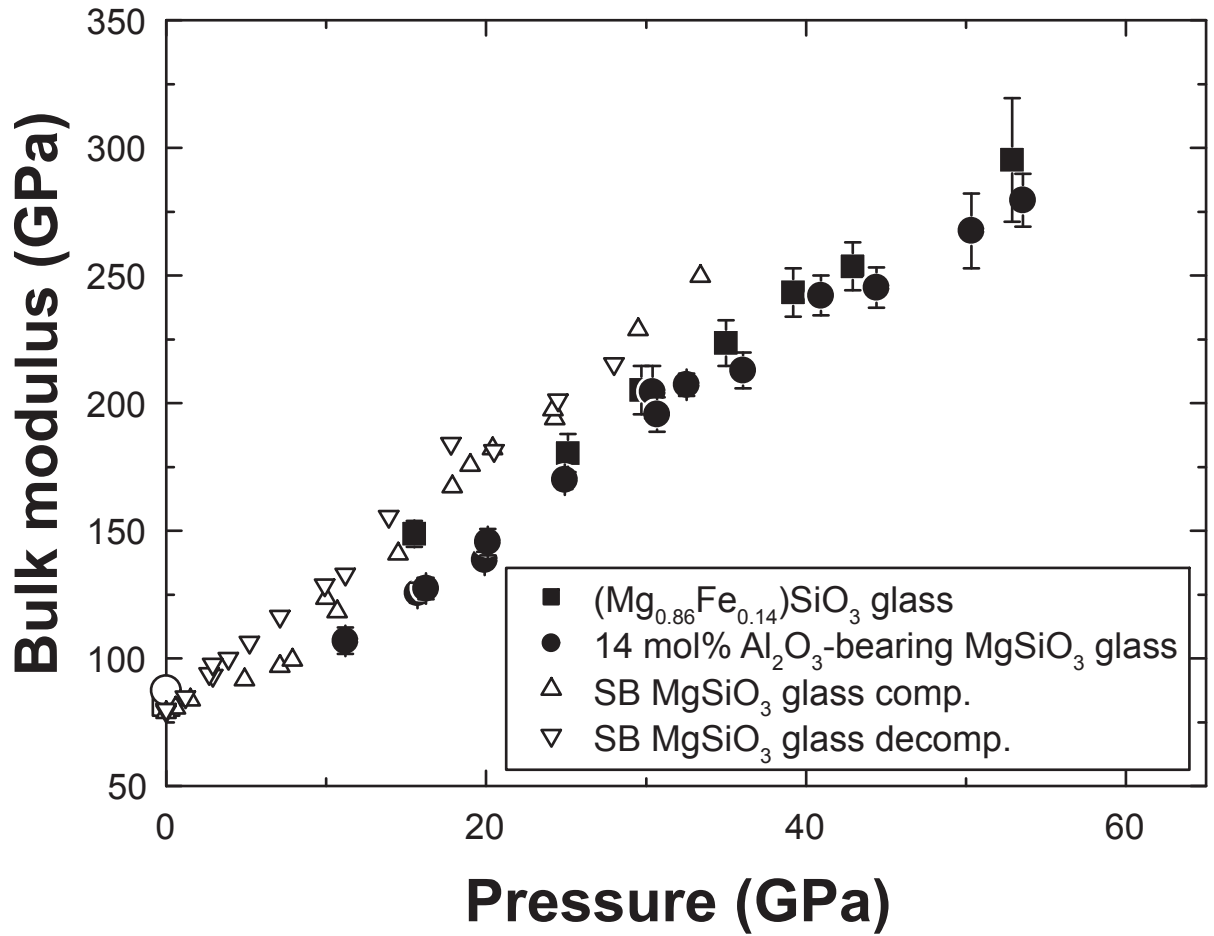


Fig. 4-12 Bulk modulus of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass (black square), 14 mol% Al_2O_3 -bearing MgSiO_3 glass (black circle), MgSiO_3 glass during compression (upward open triangle) and decompression (downward open triangle) by Sanchez-Valle and Bass (2010), and $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass calculated by ideal mixing model at ambient pressure (open square), 14 mol% Al_2O_3 -bearing MgSiO_3 glass by ideal mixing model at ambient pressure (open circle).

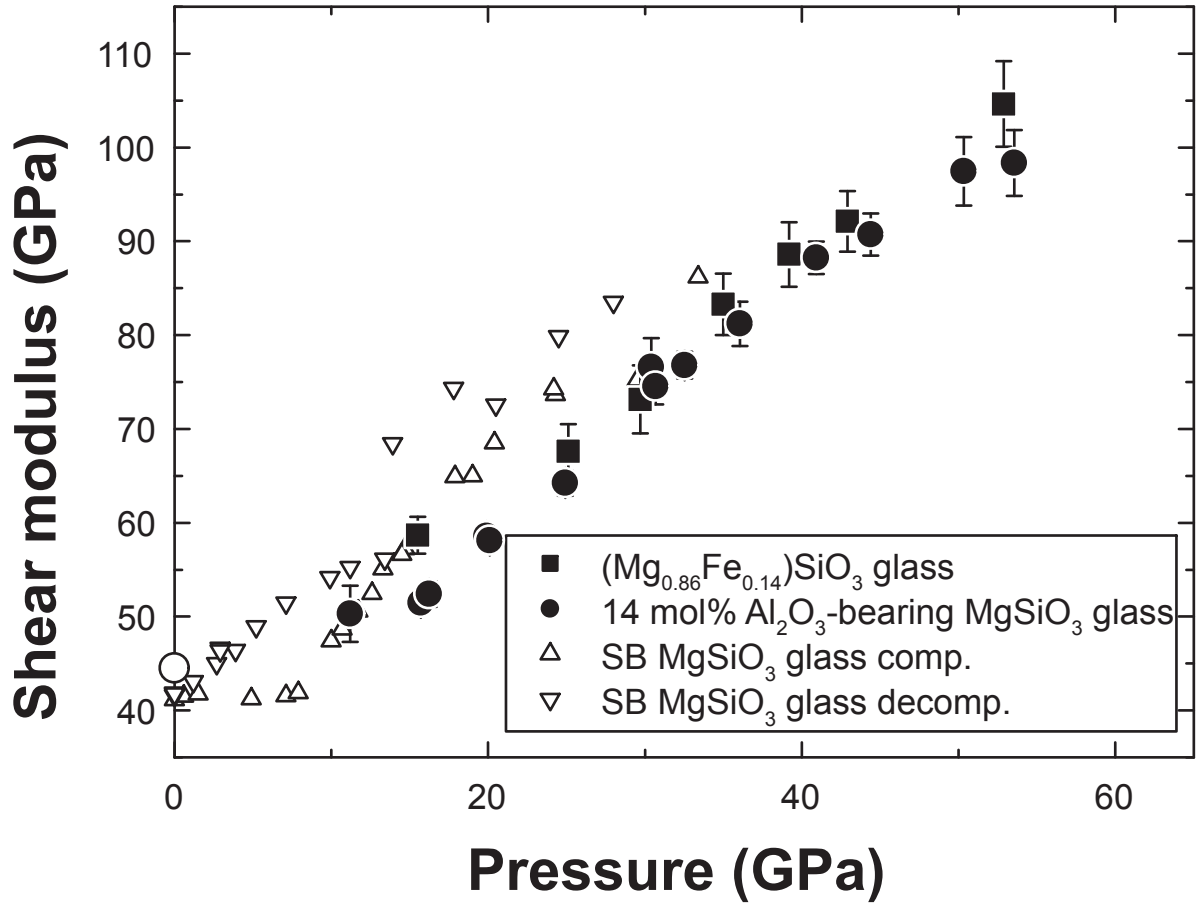


Fig. 4-13 Shear modulus of (Mg_{0.86}Fe_{0.14})SiO₃ glass (black square), 14 mol% Al₂O₃-bearing MgSiO₃ glass (black circle), MgSiO₃ glass during compression (upward open triangle) and decompression (downward open triangle) by Sanchez-Valle and Bass (2010), and (Mg_{0.86}Fe_{0.14})SiO₃ glass calculated by ideal mixing model at ambient pressure (open square), 14 mol% Al₂O₃-bearing MgSiO₃ glass by ideal mixing model at ambient pressure (open circle).

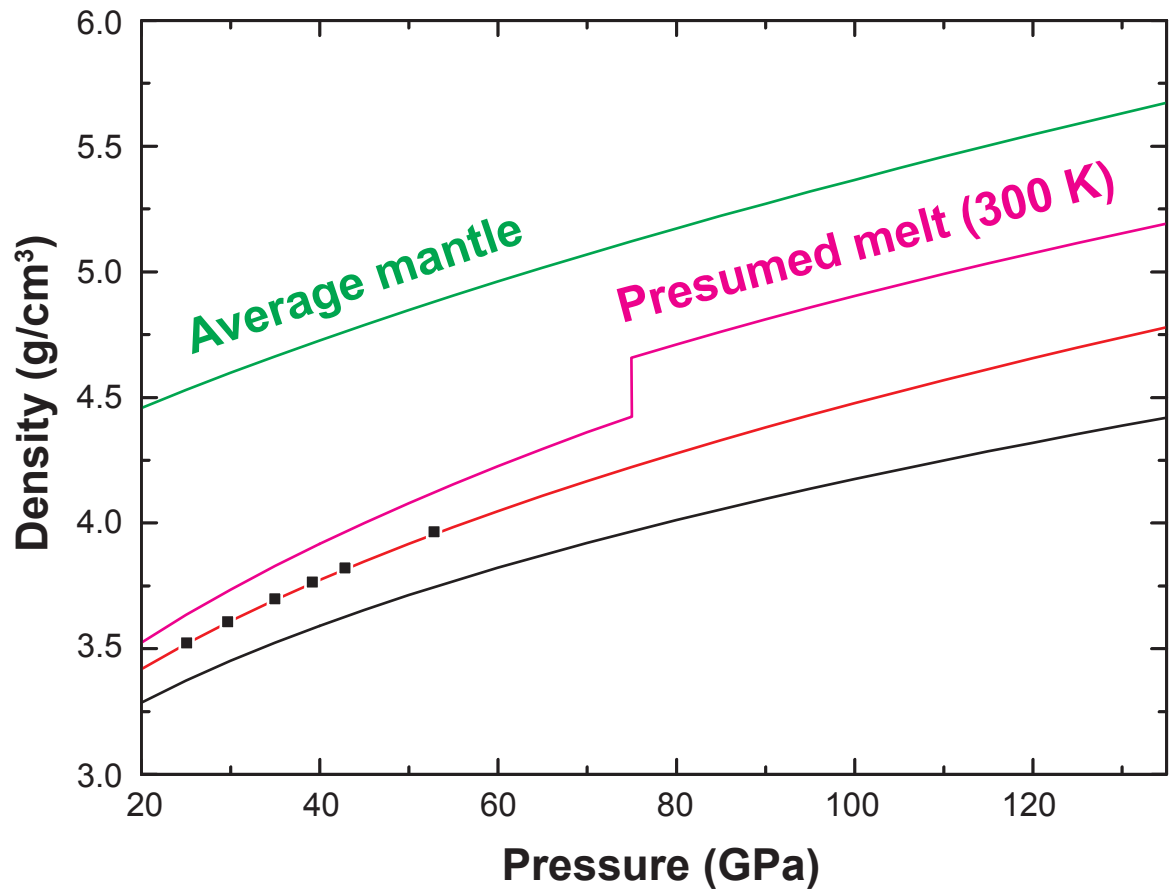


Fig. 4-15 Density of the $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass (red line), MgSiO_3 glass (black line), appropriate iron-containing MgSiO_3 glass (pink line), and crystalline average mantle rock (green line). The black square is obtained density in $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass by present Brillouin scattering measurements.

Table 4-1Summary of the results in (Mg_{0.86}Fe_{0.14})SiO₃ glass

Pressure (GPa)	V _s (km/s)	V _p (km/s)	V _B (km/s)	Poisson's ratio	ρ (g/cm ³)	K (GPa)	G (GPa)	Young's modulus (GPa)
0	3.36 ^c	6.62 ^c	5.36 ^a	0.326 ^c	2.878 ^a	82.7 ^a	32.5 ^b	86.2 ^c
15.5	4.20(1)	8.26(1)	6.69(2)	0.326(1)	3.321(97)	148.7(51)	58.7(20)	155.6(65)
25.1	4.38(2)	8.76(2)	7.15(3)	0.333(3)	3.522(111)	180.4(74)	67.6(29)	180.3(108)
29.7	4.50(3)	9.15(1)	7.53(5)	0.341(4)	3.607(116)	205.1(95)	73.2(36)	196.1(137)
35	4.74(2)	9.51(1)	7.77(3)	0.334(2)	3.697(120)	223.5(90)	83.3(33)	222.2(117)
39.2	4.85(1)	9.79(1)	8.03(1)	0.338(2)	3.765(123)	243.3(95)	88.6(34)	237.0(111)
42.9	4.90(1)	9.92(1)	8.14(2)	0.338(1)	3.821(124)	253.5(94)	92.1(34)	246.5(107)
52.9	5.13(3)	10.47(15)	8.62(20)	0.342(1)	3.964(133)	95.2(242)	104.6(46)	280.7(394)

Numbers in parentheses indicate uncertainty in the last digit(s).

^a Calculated by ideal mixing model.^b Obtained by regression analysis above 15 GPa.^c Calculated by bulk modulus and density by ideal mixing model and shear modulus by regression analysis above 15 GPa.

Table 4-2Summary of the results of 14 mol % Al₂O₃-bearing MgSiO₃ glass

Pressure (GPa)	V _S (km/s)	V _P (km/s)	V _B (km/s)	Poisson's ratio	ρ (g/cm ³)	K (GPa)	G (GPa)	Young's modulus (GPa)
0	4.04 ^a	7.33 ^a	5.66 ^a	0.283 ^a	2.73 ^a	87.4 ^a	44.5 ^a	114.1 ^a
<i>run 1</i>								
11.2	4.05(11)	7.53(2)	5.90(12)	0.297(17)	3.066(27)	106.9(51)	50.3(30)	130.4(168)
15.7	4.02(1)	7.81(4)	6.28(6)	0.320(5)	3.188(36)	125.7(39)	51.5(10)	135.9(75)
19.9	4.22(1)	8.11(2)	6.49(4)	0.315(3)	3.291(40)	138.6(33)	58.6(11)	154.0(61)
24.9	4.35(2)	8.67(1)	7.07(3)	0.332(2)	3.398(48)	169.9(37)	64.2(13)	171.1(58)
30.7	4.61(2)	9.31(9)	7.47(7)	0.338(6)	3.505(59)	195.5(67)	74.5(19)	190.6(136)
35.5	4.70(9)							
39.6	4.82(4)							
<i>run 2</i>								
16.2	4.05(3)	7.85(4)	6.31(7)	0.319(6)	3.201(37)	127.4(41)	52.4(13)	138.3(86)
20.1	4.20(1)	8.22(6)	6.65(8)	0.324(4)	3.296(41)	145.5(51)	58.1(10)	153.8(87)
30.4	4.61(6)	9.31(1)	7.64(13)	0.327(7)	3.500(59)	204.3(102)	76.6(31)	212.6(187)
32.5	4.66(1)	9.35(1)	7.65(2)	0.335(1)	3.537(60)	207.2(44)	76.8(14)	205.0(55)
36.1	4.75(3)	9.45(4)	7.69(7)	0.331(5)	3.597(61)	212.8(71)	81.2(24)	216.1(128)
40.9	4.90(1)	9.89(5)	8.12(7)	0.338(3)	3.675(66)	242.2(75)	88.3(17)	236.1(110)
44.4	4.93(2)	9.91(4)	8.11(6)	0.335(3)	3.7281(67)	245.3(80)	90.7(24)	242.3(120)
50.3	5.05(5)	10.21(9)	8.37(15)	0.338(8)	3.816(73)	267.5(146)	97.5(36)	260.7(278)
53.5	5.05(4)	10.31(4)	8.51(9)	0.343(5)	3.861(74)	279.5(95)	98.4(35)	264.1(178)
59.2	5.14(1)							

Numbers in parentheses indicate uncertainty in the last digit(s).

^a Calculated by ideal mixing model.

Chapter 5: General discussion

5-1. CaSiO_3 perovskite

In chapter 2, I demonstrated sound velocity measurements of CaSiO_3 perovskite, which material would be concentrated in basaltic, and depleted in harzburgitic rocks at the lower mantle, respectively. I revealed tetragonal CaSiO_3 perovskite has much slower shear wave velocity than pyrolitic mantle entire lower mantle pressures although previous compressibility measurements shows comparable or slightly superior bulk modulus to other mantle minerals (Shim et al., 2000). It indicates that relatively Ca-rich rock shows similar or slightly higher bulk sound velocity and slower shear wave velocity than average mantle rocks and Ca-poor rock (Murakami et al., 2007; 2009; 2012). Therefore, harzburgitic rock is possibility source of the heterogeneity beneath circum-Pacific region at the lowermost mantle. However, cubic CaSiO_3 perovskite is presumed as a Ca-rich silicate phase in the lower mantle because of the high temperature. Tsuchiya (2011) reported that cubic CaSiO_3 perovskite shows similar shear wave velocity to tetragonal phase by theoretical calculation, but there are no

experimental evidences. Therefore, high-temperature measurements are necessary for understanding more accurate role of shear wave velocity of CaSiO_3 perovskite in the lower mantle. In Appendix 1, shear velocity of CaSiO_3 perovskite is obtained at high temperature up to 800 K generated by external heating diamond anvil cell as described below, however, experimental pressure and temperature conditions were quite limited. For high-pressure and high-temperature measurements, there are two candidate methods. First one is heating with CO_2 laser during exposure time. Murakami et al (2012) reported shear wave velocity of MgSiO_3 perovskite and MgO at 2700 K with this method. However, the temperature gradient in the sample chamber is expected large ($\sim 10\%$). The other one is using with external heating diamond anvil cell. In this method, high-temperature is generated by electrical heating with a resistive heater around sample chamber, therefore, the spatial and temporal temperature fluctuation in the sample chamber is small ($< 5\text{ K}$).

5-2. Identifying the sources of seismic anomalies in the lower mantle

The remnant of Basal Magma Ocean (BMO), which is the gravitationally stable layer formed by dense melt beneath crystalline mantle with relative smaller density than

dense melt, is one of the probable sources of LLSVPs and ULVZs (Labrosse et al., 2007). In order to form BMO, the density of silicate melt must exceed that of coexisting solid phase during solidification at the deep interior. Nomura et al. (2011) found the rapidly increase in the ratio of iron concentration to silicate melt above 76 GPa. This increase would drive silicate melt denser than coexisting solid phases. Nomura et al. (2011) also found the spin transition of iron among $(\text{Mg}_{0.95}\text{Fe}_{0.05})\text{SiO}_3$ glass, as analog material of silicate melt, at the corresponding pressure by X-ray emission spectroscopy measurement and suggested the rapidly increase of iron concentration to melt phase. Based on this result, Nomura et al. (2011) suggested the source of LLSVP is iron-rich cumulates and of ULVZ is still molten, extremely high iron containing melt or crystalline wüstite. However, other measurement with relatively iron-rich MgSiO_3 glass reported spin transition would not complete even if lower most mantle pressure (Gu et al., 2012, Prescher et al., 2014). In chapter 3, I reported the shear wave velocity of $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass up to 113.0 GPa. I found anomaly in shear wave velocity around 60 GPa. Similar anomaly is reported in ferropericlase, which is clarified the occurrence of spin transition around 55 GPa (Marquardt et al., 2009; Murakami et al., 2012). Therefore, my result supports that the shear velocity anomaly around 60 GPa,

which is corresponding to the spin transition pressure Nomura et al., (2011) reported, would be as a result of spin transition.

If the gravitic possibility of BMO model is high, sound velocities of sluggish cumulate and remnant dense melt should be compared with the observed seismic velocities in order to identify both LLSVPs and ULVZs. The knowledge of chemical composition and mineral proportion of sluggish cumulate and remnant dense melt are required to estimate sound velocities of the sluggish cumulates. The chemical composition could be evaluated by phase diagram among MgO-FeO-SiO₂ components entire the lower mantle pressures. The melting experiments at the lower mantle pressure conditions would be necessary to draw the phase diagram, however, little is reported because of the difficulty of melting experiments in silicates at high pressure.

Piled MORB is also one of the most plausible candidates of LLSVPs as the sluggish remnants of BMO, because substantial volume of MORB is generated and subducted into the Earth's deep interior through geological time, therefore, one is easy to explain such large volume of seismic anomaly (Hernlund and Hauser, 2008; Ohta et al., 2008). Subducted MORB at the lowermost mantle condition is expected to contain MgSiO₃ perovskite, CaSiO₃ perovskite, aluminous-rich phase and α PbO₂-type SiO₂ phase (Hirose, 2006), therefore, elastic properties of all these four phases at high-pressure is

necessary to evaluate the existence. However, the lack of shear velocity data of SiO_2 phase and aluminous-rich phase at the lowermost mantle pressure by experimental method prevents the estimation of the elastic behavior of subducted MORB. In particular, the elasticity of αPbO_2 -type SiO_2 phase by experimental method are never reported, in contrary the sound velocity of stishovite, CaCl_2 -type SiO_2 phase (Asahara et al., 2013), and aluminous-rich phase (Dai et al., 2013) is already measured at relatively lower pressure regime than the lowermost mantle. Because this phase is stable above 120 GPa (Murakami et al., 2003), it is quite difficult to synthesize this material at high-pressure on capable condition for Brillouin scattering with CO_2 laser heating. There are two subsist methods for measure the elastic behavior of this material. First one is employing cristobarite as a starting material. Dubrovinsky et al. (2001) reported that αPbO_2 -type SiO_2 phase appeared above 80 GPa with a starting material of cristobarite by residential heating diamond anvil cell experiment. Other experiments also reported the appearance of αPbO_2 -type SiO_2 phase at relatively lower pressure than its stable pressure conditions if cristobarite is used as a starting material (Tsuchida and Yagi, 1989; Prakapenka et al., 2004). Another one is using inelastic X-ray scattering method. To apply inelastic X-ray scattering method, the sample is not implied to be transparent, therefore, laser absorber for YAG laser or fiber laser such as platinum is available to be mixed in the sample as

Murakami et al. (2003) already employed to synthesize αPbO_2 -type SiO_2 phase at the pressure above 120 GPa.

Subducted early crustal layer, and KREEP-like liquid are also suggested as candidates of the explanation for the LLSVPs (Boyet and Carlson, 2005; Tolstikhin et al., 2006; Tackly, 2012). Additionally, non-negligible quantity of continental crust is also expected to sink into the deep Earth's interior through the Earth's history (Rino et al., 2004; Yamamoto et al., 2009). The location of these depleted rocks in the Earth's interior is important for the understandings of not only chemical structure but also the location of radiogenic heat source in the Earth's interior, because these depleted rocks is enriched long-lived radioactive elements such as ^{40}K , ^{232}Th , ^{235}U , and ^{238}U . Therefore, the estimation of sound velocities of continental crust, early crust, and KREEP-like rock at the lower mantle condition is also necessary to discuss the source of seismic heterogeneities at the lowermost mantle and thermochemical evolution of the Earth's interior. However, little is known about the constituent phases and mineral proportion of these rocks entire the lower mantle conditions. Only those of continental crust up to 28 GPa, corresponding to the depth of 880 km, is reported by experimentally (Ishii et al., 2012). Hence, the identification of the constituent minerals and mineral proportion of those rocks under the lower mantle conditions is required.

5-3. Other future perspective

In chapter 2,3, and 4, signals of compressional wave velocity are not obtained in all the spectra of CaSiO_3 perovskite, MORB glass, and the measurements of Al_2O_3 -bearing MgSiO_3 glass and $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_3$ glass above 53 GPa because of the large masks by shear mode of diamond anvils on the signals of compressional velocity of samples in Brillouin spectra. Seismic observation of compressional velocity is also very strong probe for the Earth's deep interior. Moreover, it is also important to obtain compressional velocity for construction of primary pressure marker, which is determined the pressure without any other pressure markers calibrated by shock wave experiments, because it is necessary to obtain compressional velocity, shear velocity and density of materials simultaneously. Therefore, compressional velocity at high pressure should be also measured by experimentally. Brillouin scattering measurement with backscattering geometry has possibility to overcome. Zha et al (1994) and Zha et al (2000) reported the compressional wave velocity of SiO_2 glass and MgO around 12 km/s, which velocity corresponds to shear wave velocity of diamond, with Brillouin

scattering measurements in 135 degree scattering geometry, respectively. In the backscattering geometry, the amplitude of the shear modes become significantly smaller, including the shear mode of diamond, thereby, the signals of compressional mode of sample would be observed relatively easier than platelet geometry. However, in order to obtain wave velocities, the refractive index of sample under extreme condition is required, because the frequency shift depends on not only velocity but also the refractive index in backscattering geometry (Bass, 2007). To know this parameter, Zha et al. (1994) and Zha et al. (2000) used the frequency shift in both reflection scattering and 135° scattering light. Further details are described in Zha et al. (1994).

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APPENDIX 1: High-pressure and high-temperature Brillouin scattering measurements of CaSiO₃ perovskite

Abstract

High-pressure and temperature Brillouin scattering measurements at 60 GPa and 300 K to 800 K with external heating diamond anvil cell revealed tetragonal CaSiO₃ perovskite has relatively larger dependency on shear modulus and shear wave velocity than MgSiO₃ perovskite and MgO at 60 GPa. This larger dependency indicates that if tetragonal CaSiO₃ perovskite exists stably at the lower mantle conditions, the reduction of shear velocity which predicted in chapter 1 (Kudo et al., 2012) would be enhanced.

A1-1. Introduction

CaSiO₃ perovskite was found in 1975 by Li et al., and its crystal structure was believed to be cubic under ambient temperature. However, Shim et al. (2002) reported the

structure of this material was slightly distorted from cubic structure. Additionally, Kurashina et al. (2004) and Komabayashi et al. (2007) found that CaSiO_3 perovskite takes distorted form under ambient temperature and cubic under high temperature condition by experimental studies. Theoretical studies supported this structure relation (Stixrude et al., 1996), but the phase boundary is laid in significantly higher temperature than experimental suggestions (Stixrude et al., 2007). The shear modulus of both two CaSiO_3 perovskites were also predicted by theorem, however, the results were controversially. Stixrude et al. (2007) suggested the “shear softening”, only shear modulus is significantly decreased and there are no anomalies in bulk modulus, occurs only in the distorted and lower temperature phase, and about 30 % slower shear velocity of tetragonal CaSiO_3 perovskite than cubic CaSiO_3 perovskite. On the other hand, Tsuchiya (2011) suggested the “shear softening” also occurs in non-distorted and higher temperature phase. Additionally, ferroelasticity, which is a phenomenon that the shear strain enhances in a spontaneous way and shear modulus reduce to zero, is expected at the neighborhood pressure-temperature condition to phase boundary as a critical phenomenon (Carpenter et al., 2006). Despite such important phenomena are expected, shear wave velocity was revealed only ambient temperature condition with experimental method (Kudo et al., 2012).

A1-2. Experimental method

High-pressure and high-temperature Brillouin scattering measurements were conducted with external-heating diamond anvil cell. A rhenium sheet as a gasket was pre-pressed to a thickness of 50 μm , and drilled a hole with a laser beam machine as a sample chamber. The radius of the sample chamber was ~ 80 μm . CaSiO_3 -gel was employed as a starting material. The gel was prepressed with a thickness of ~ 40 μm , and loaded into the sample chamber and sandwiched a couple of NaCl with a thickness of ~ 5 μm as a thermal insulator and pressure marker. The sample was compressed by a couple of diamond anvils with a culet size of 300 μm .

A platinum wirer with a radius of 100 μm was winded in a spiral configuration to a alumina tube as a resistive heater. This heater was put around the sample chamber. Temperature was determined with R-type thermocouple put by the sample chamber, and touched by a side of diamond anvil. In order not to short-circuit the thermocouple and rhenium gasket, the rhenium gasket, and leads from the thermocouple was covered with cement and narrow alumina tubes as an electrical insulator, respectively. The resistive heater was applied a voltage with stabilized power supply. During heating, this diamond anvil cell was hold by a holder with cooling function. In order to ensure no unexpected

increment or decrement of pressure during resistivity heating, pressure-temperature relation was determined with same configuration to Brillouin scattering measurements by *in-situ* NaCl volume obtained by X-ray diffraction several times (Fei et al., 2007). The pressure change with increasing temperature is shown in Fig. A1-1. We can see no significant pressure change with increasing temperature. The pressure deviation by temperature change is within 2 GPa. Therefore, we can assume that the pressure at high temperature in this measurement is independent on temperature.

Brillouin scattering measurements were conducted with Brillouin scattering measurement system in SPring-8 (Murakami et al., 2009a). A diode pumped laser with a wavelength of 532 nm (Verdi V2, coherent) was employed as incident beam. The laser power was 200 mW. All the measurements were conducted in platelet geometry. External scattering angle was ~50 degree calibrated by BK₇ standard glass (Yoneda and Song, 2005). In platelet geometry, sound velocity was obtained by following relationship;

$$V_i = \frac{\Delta\omega_i \lambda}{2 \sin\left(\frac{\theta}{2}\right)} \quad (\text{A1.1})$$

where V is velocity, $\Delta\omega$ is frequency shift, λ is wavelength of incident laser, θ is external scattering angle, and subscription i denotes i^{th} vibration mode (Whitfield et al.,

1976). Scattered light was analyzed by 6-pass tandem mirror Fabry=Perot interferometer (Sandercock, 1982).

CaSiO₃-perovskite was synthesized with CO₂ laser heating. The heating laser was introduced from single side of diamond window. Heating was conducted twice from different side. Each single heating time was 10 seconds. To ensure the CaSiO₃ perovskite succeed to be synthesized in the sample chamber, X-ray diffraction measurement was conducted at SPring-8 BL10XU. The diffraction pattern is shown in Fig. A1-2.

Measurement pressure was 60 GPa at 300 K and temperature was increased by resistive heating up to 600 K, 700 K, and 800K. Pressure and temperature points are shown in Fig. A1-3 with phase relationship in CaSiO₃ obtained by experiments (Komabayashi et al., 2007) and theorem (Stixrude et al., 2007). The relation between power output and temperature is shown in Fig. A1-4. Exposure time for single collection was typically 6 hour. To evaluate peak position, Gaussian function was fitted.

A1-3. Result and discussion

X-ray diffraction pattern shows clear signals by B2 phase of NaCl pattern and slightly broaden signals by CaSiO_3 perovskite. It indicates that CaSiO_3 perovskite has relatively smaller grain-size because of such a short heating time (20 second). However, the existence of CaSiO_3 perovskite in sample chamber is ensured.

Typical Brillouin spectrum at 60 GPa, 300 K is shown in Fig. A1-5, and 60 GPa, 600 K is in Fig. A1-6. Doublet peaks are observed around $\pm 9\text{GHz}$. Because NaCl phase would not appear around $\pm 9\text{GHz}$, corresponding to about 5.5 km/s, at 60 GPa, (Sinogeikin et al., 2006; Murakami, 2010), these peaks are from shear mode of CaSiO_3 perovskite or CaSiO_3 gel. Considering the higher frequency shifted peaks are consistent with shear velocity of CaSiO_3 perovskite at 300 K (Kudo et al., 2012), higher frequency shifted peaks are from CaSiO_3 perovskite and lower frequency shifted peaks are from starting material. This similar shear velocity of CaSiO_3 perovskite to previous research indicates the configuration in sample-chamber satisfies platelet geometry even starting material is coexisting.

Shear wave velocity with increasing temperature is summarized in table A1-1 and plotted in Fig. A1-7. Regression analysis gives $\partial V_s/\partial T = -0.31 \text{ m/s/K}$, $\partial \ln V_s/\partial T =$

-5.31×10^{-5} . Additionally, with $K_0 = 244$ GPa, $K' = 4$, $G_0 = 115.8$ GPa, $G' = 1.2$ (Ricolleau et al., 2009; Kudo et al., 2012), and $\gamma_0 = 1.89$, $q_0 = 0.9$, Debye temperature is 802 K (Xu et al., 2008), $\partial G/\partial T = -21$ MPa/K, $\partial \ln G/\partial T = -12.1 \times 10^{-5}$, $\eta_{s0} = 6.2$ is obtained with the formula by Stixrude and Lithgow-Bertelloni (2005) (See Appendix 2). Murakami et al. (2012) showed $\partial G/\partial T$ and $\partial V_s/\partial T$ is -15 MPa/K and -0.14 m/s/K in MgSiO_3 perovskite, and -13 MPa/K and -0.17 m/s/K in MgO at similar pressures (at 57 GPa in MgSiO_3 perovskite and at 61.8 GPa in MgO), respectively. Therefore, temperature dependency of shear modulus and velocity in CaSiO_3 perovskite would be significant larger than other mantle minerals. If tetragonal CaSiO_3 perovskite, which has significantly lower shear modulus than other mantle minerals, exist stably in lower mantle, this larger temperature dependency would enhance reduction of shear velocity in subducted Ca-rich rocks. The comparison is summarized in table A1-2.

The temperature of phase boundary suggested experimentally is about 550 K at 60 GPa (Komabayashi et al., 2007), therefore, CaSiO_3 perovskite at present temperature condition would be cubic phase. If shear softening in tetragonal CaSiO_3 perovskite is correct and phase boundary is laid around at the temperature of 550 K, we can observe shear velocity jump above 600 K. However, present result shows only decreasing with

temperature increasing. Therefore, the shear softening or/and phase boundary laid around 550 K may not be true.

Present pressure-temperature region is quite limited. The possibility of ferroelasticity is still not clarified. Hence, measurements in more expanded temperature-pressure region are necessary to understand more accurate role of this material in the Earth's deep interior.

Brillouin scattering measurements and X-ray diffraction measurements were conducted at SPring-8 (proposal no. 2011B0087, 2012A0087, 2012B0087, and 2013A0087)

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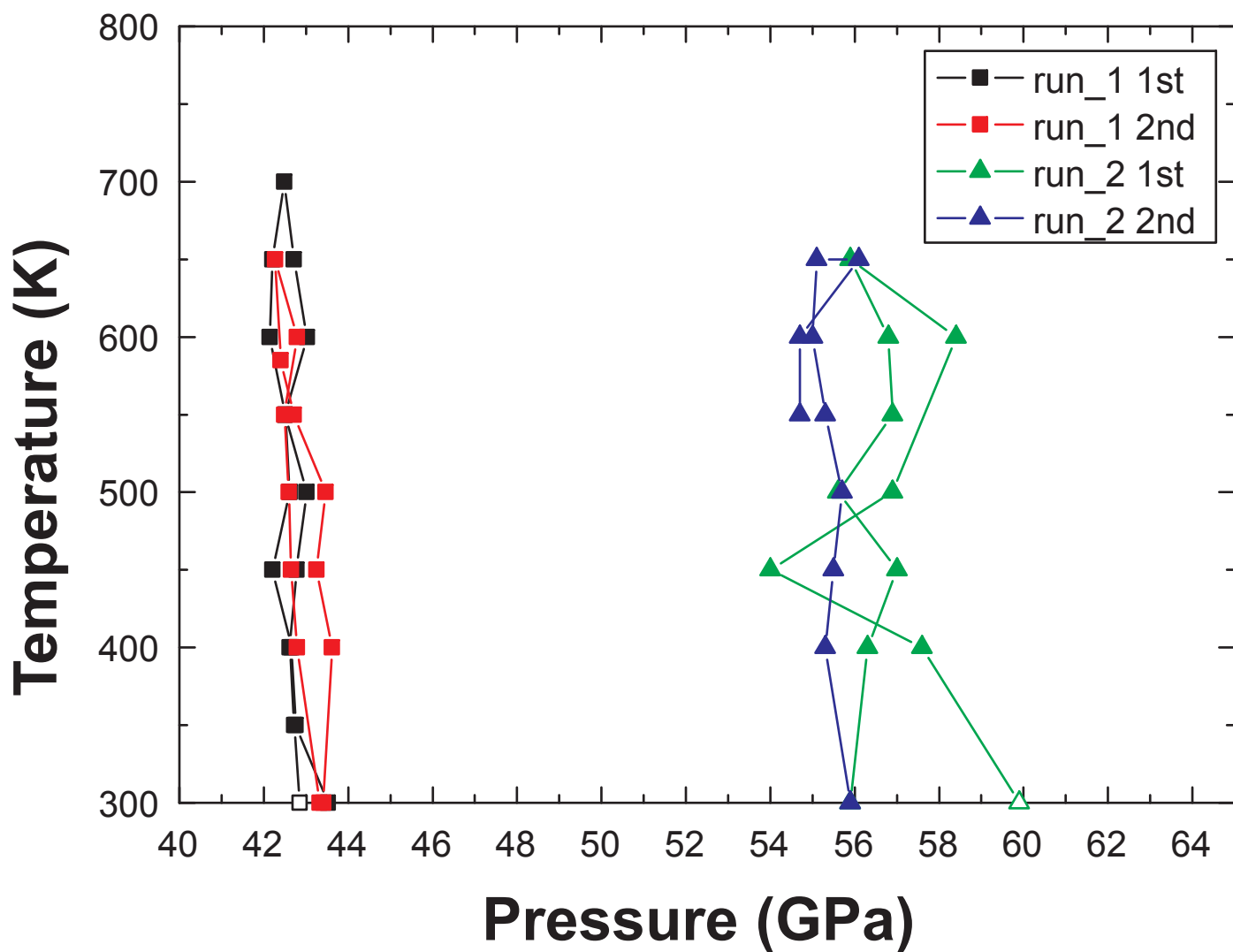


Fig. A1-1 Temperature-dependency of pressure in this heating system is shown.

There are two separated runs for determine the temperature dependency.

Open symbols represent initial pressure of both two runs.

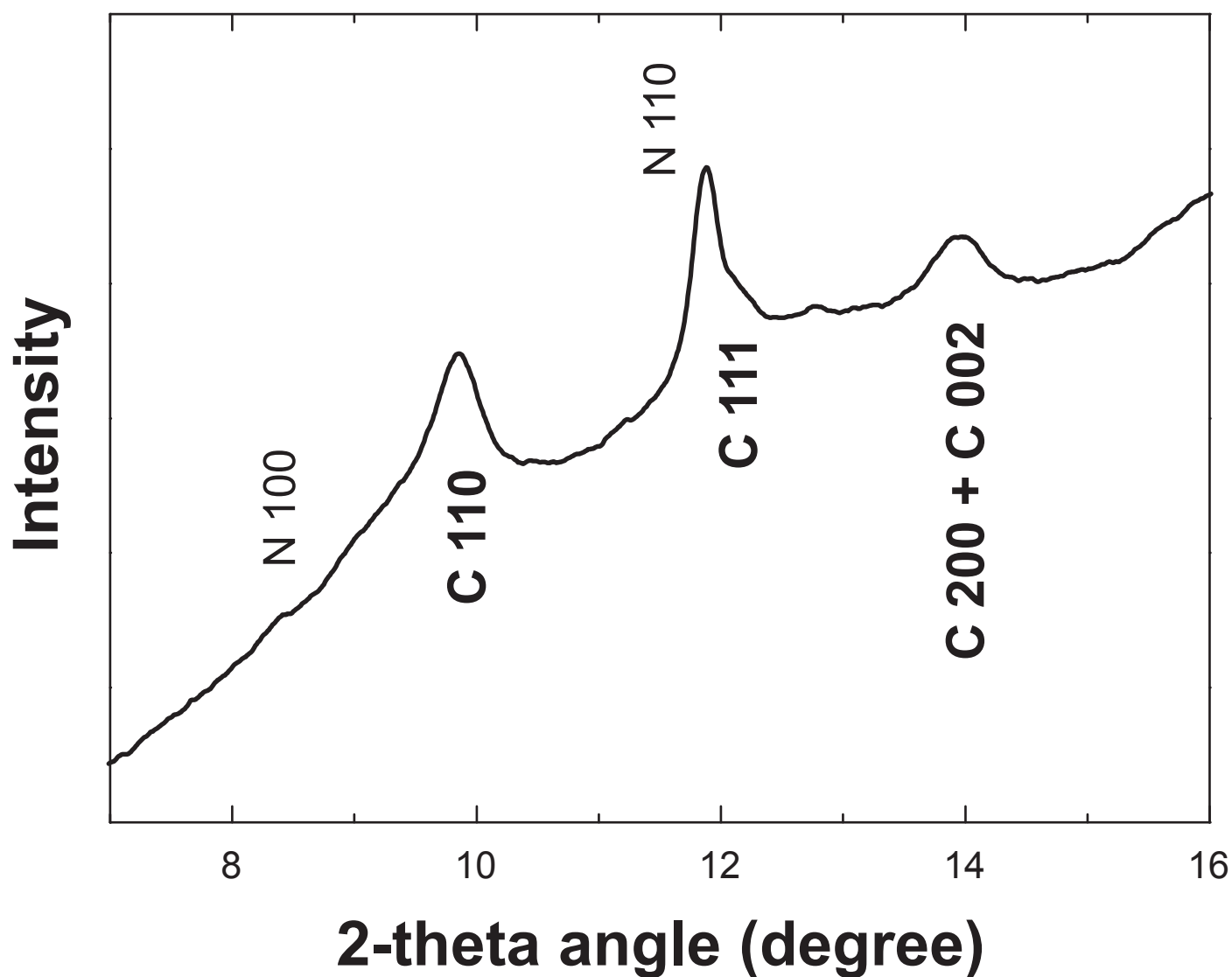


Fig. A1-2 X-ray diffraction pattern at 60 GPa, 300 K. Fine peaks from B2 phase of NaCl, and relatively broaden peaks from CaSiO_3 perovskite are observed. N denotes peaks from NaCl, and C denotes peaks from CaSiO_3 perovskite.

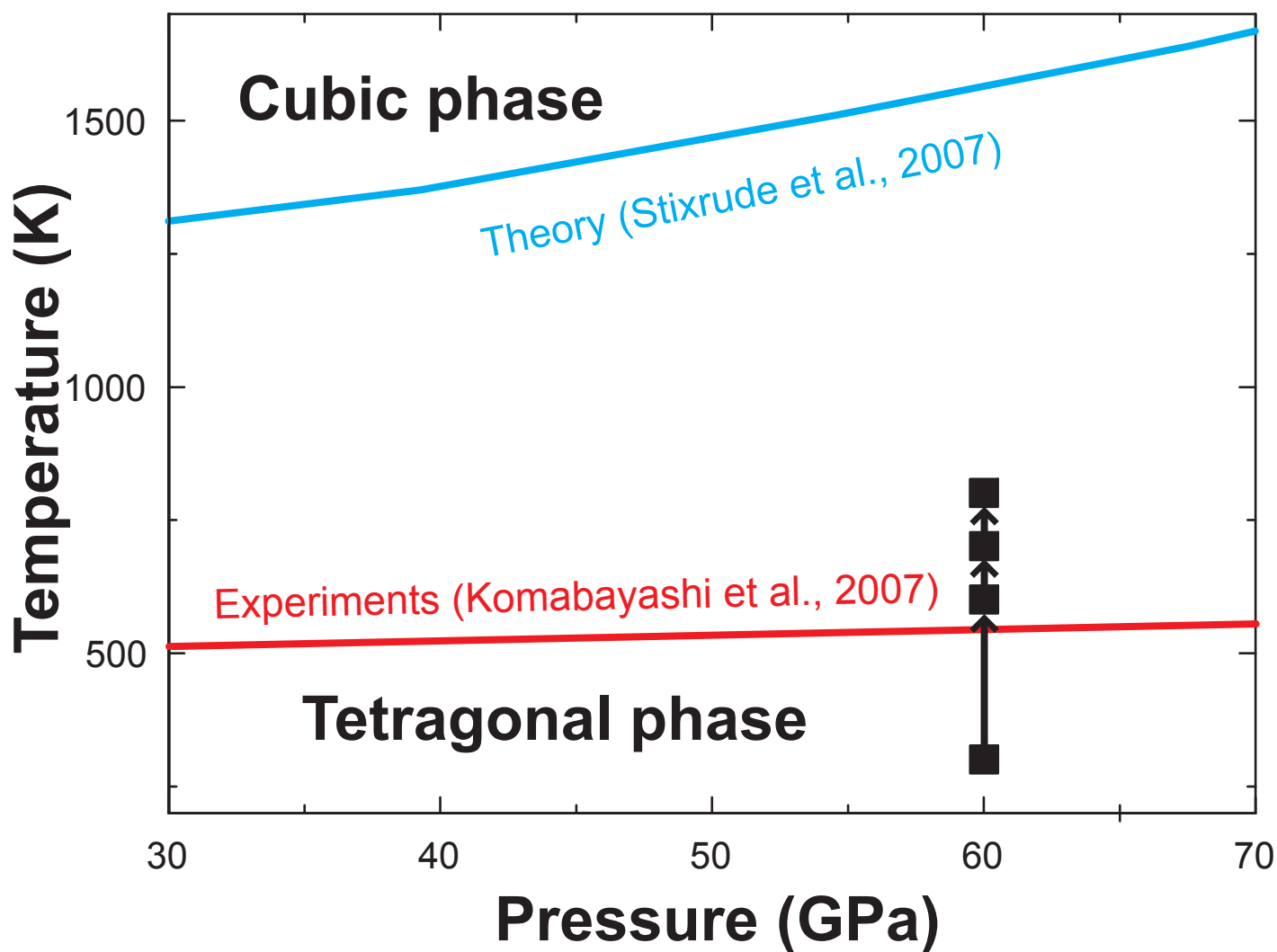


Fig. A1-3 Experimental pressure-temperature path with phase diagram of CaSiO_3 perovskite

Light blue and red line is suggested phase boundary between tetragonal-cubic CaSiO_3 perovskite with theoretical calculation (Stixrude et al., 2007) and experimental measurement (Komabayashi et al., 2007), respectively..

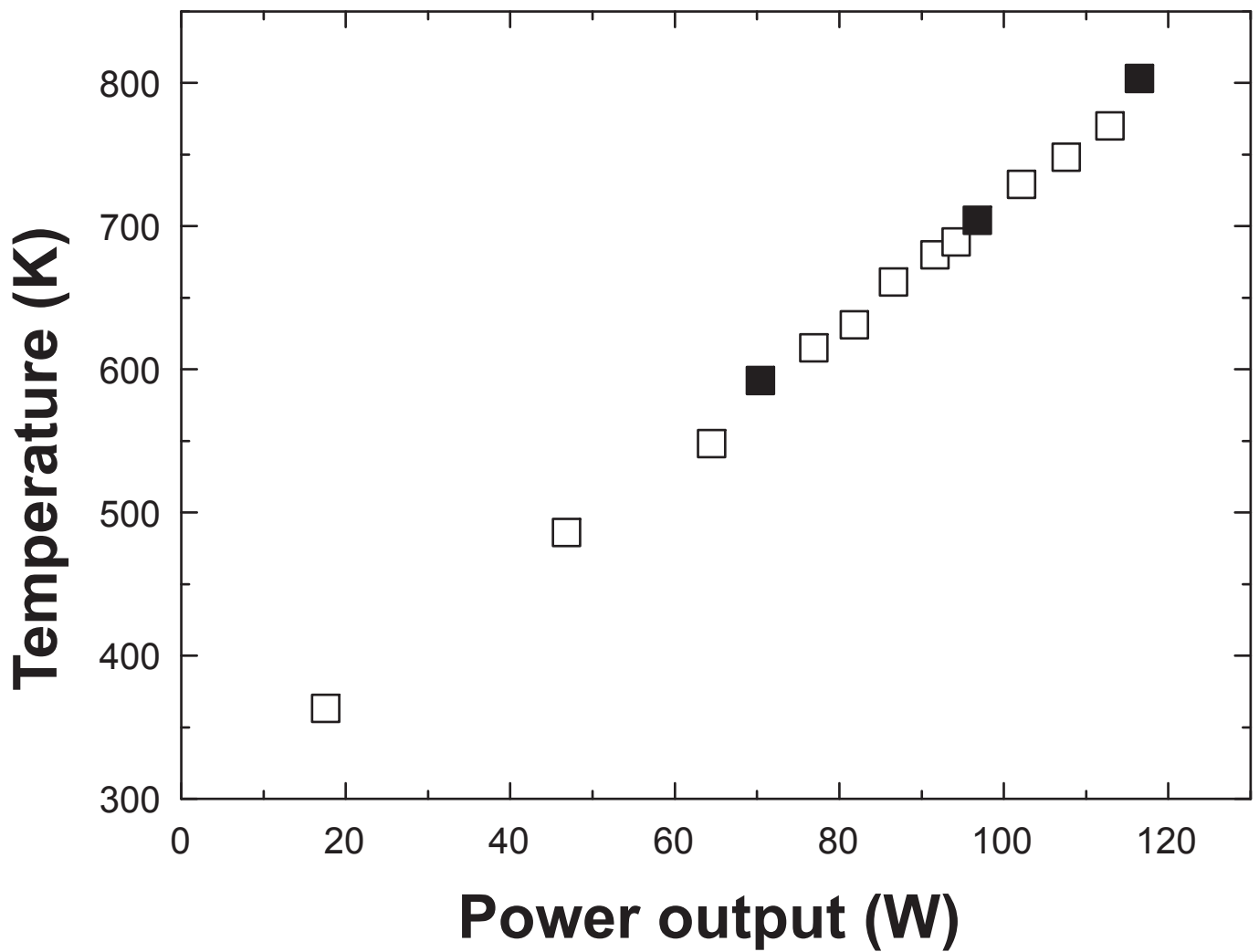


Fig. A1-4 Relationship between power supply and temperature is shown.

Closed symbols represent measurement condition of Brillouin scattering.

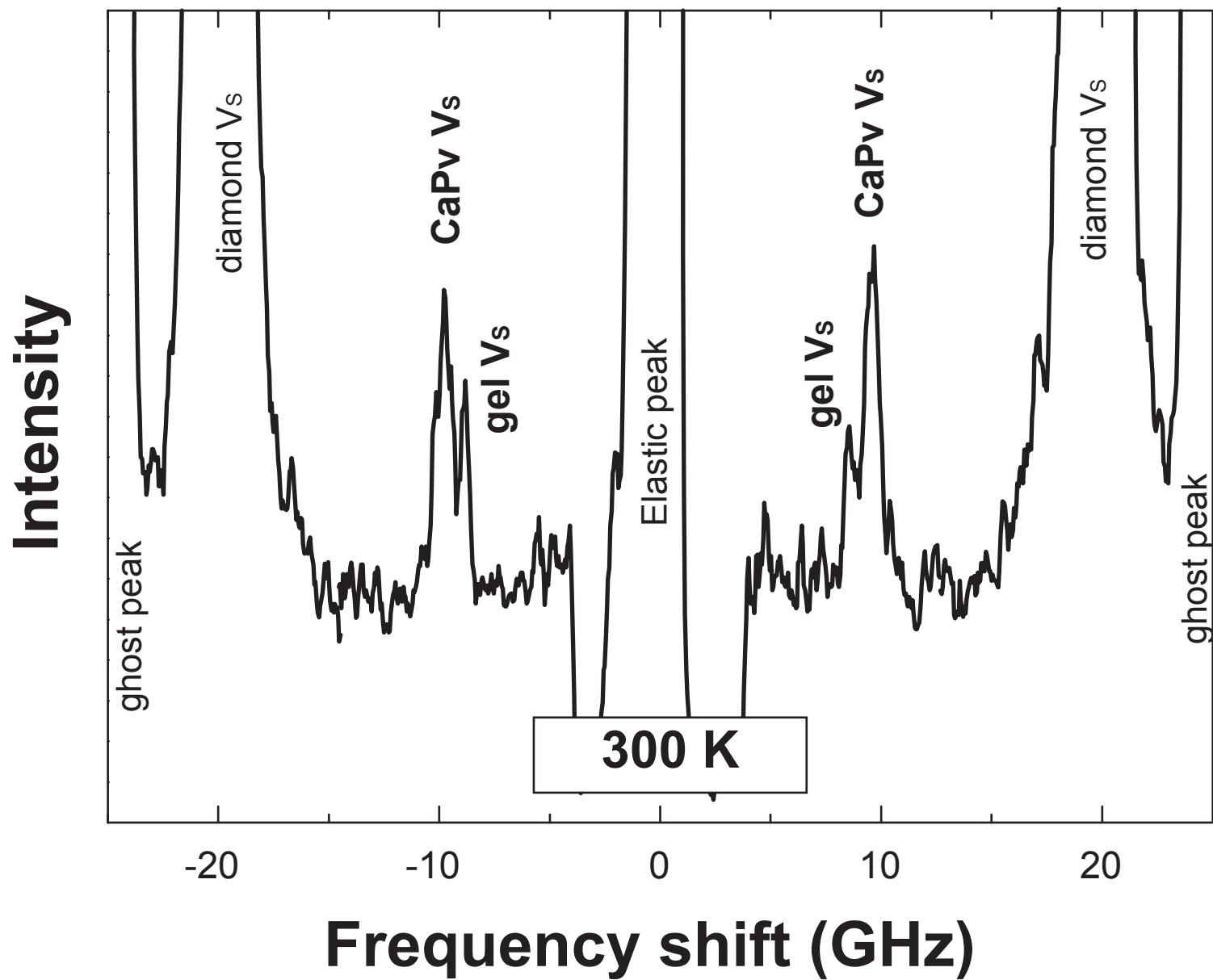


Fig. A1-5 Brillouin spectrum of CaSiO_3 perovskite at 60 GPa, 300 K.

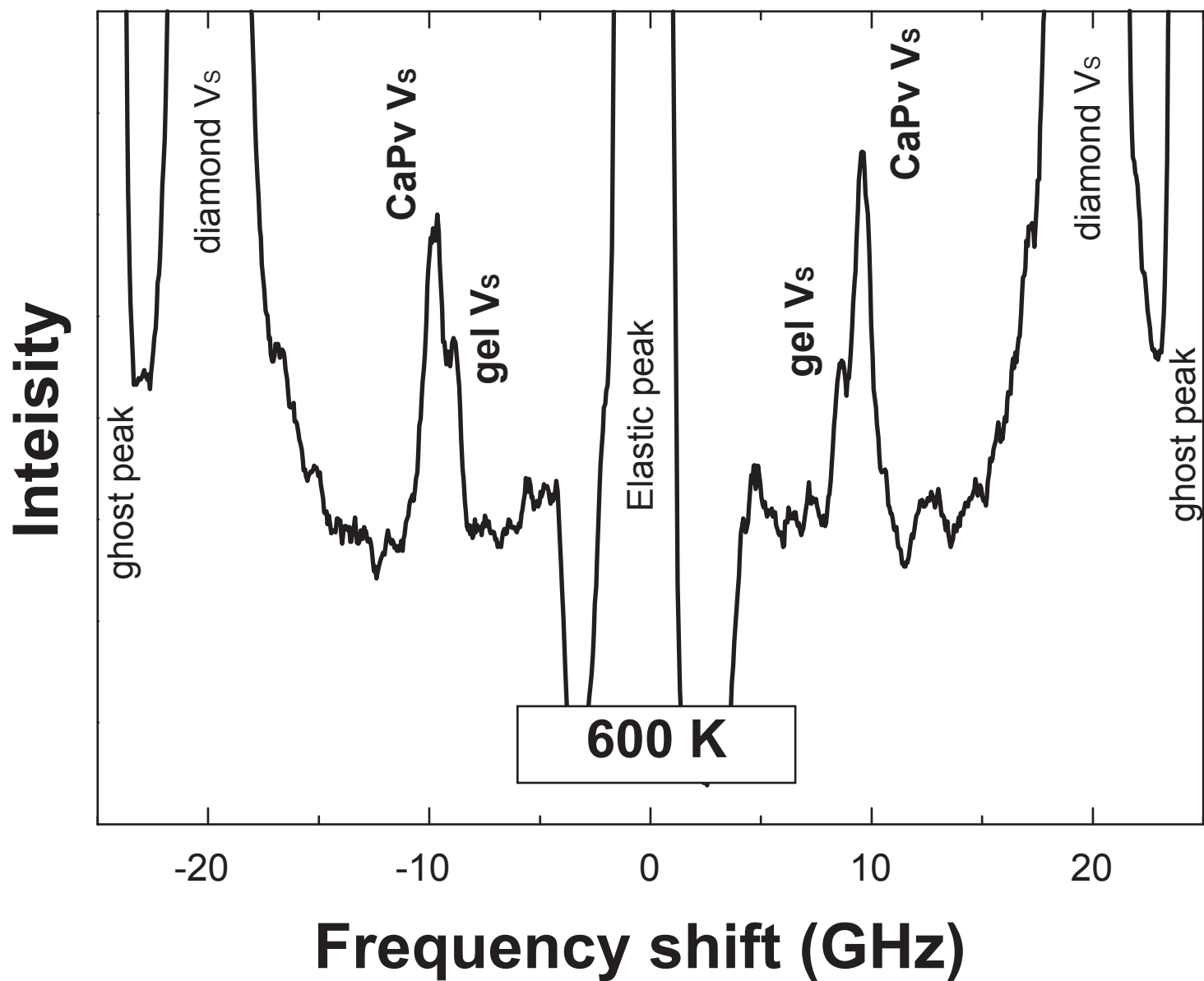


Fig. A1-6 Brillouin spectrum of CaSiO_3 perovskite at 60 GPa, 600 K.

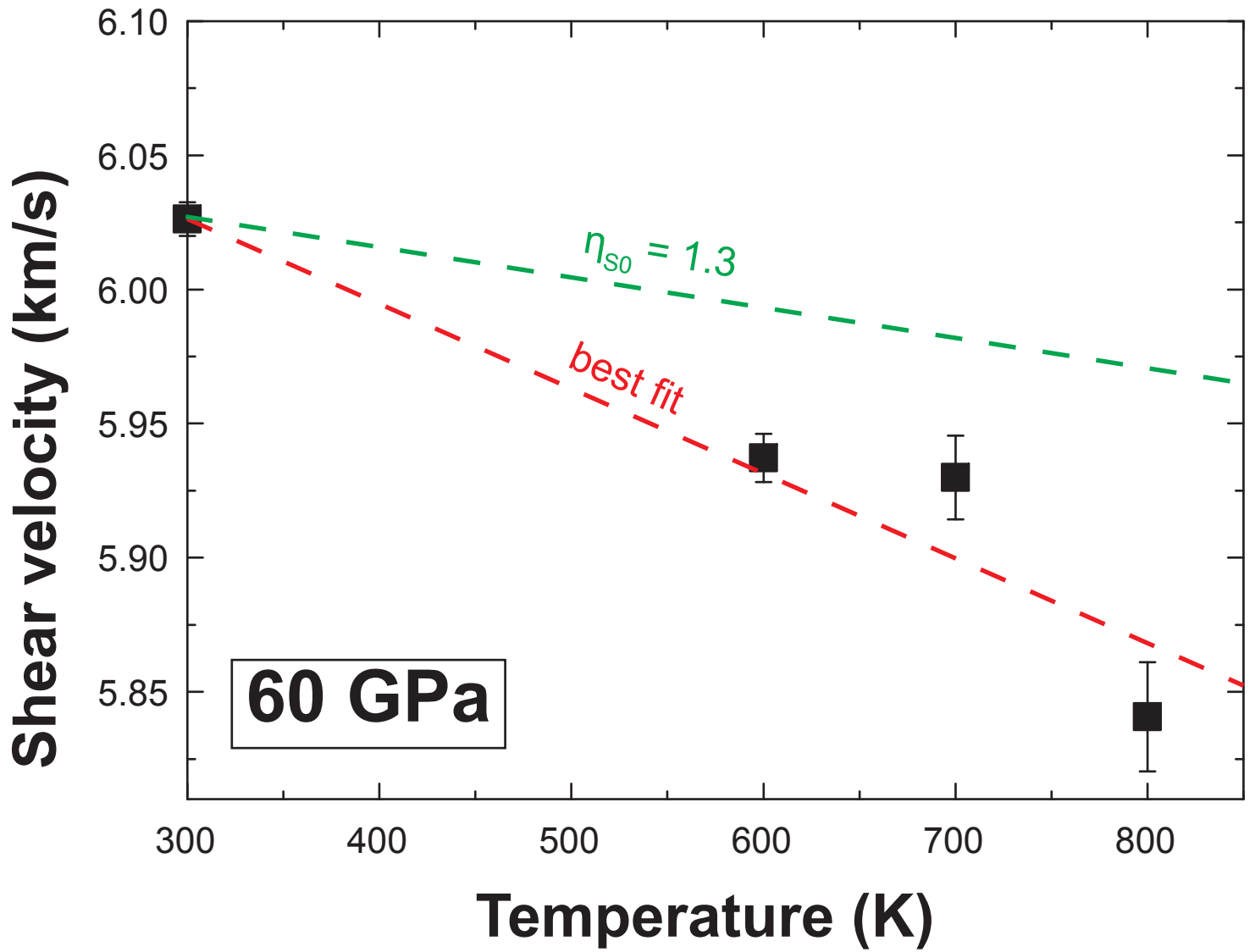


Fig. A1-7 Shear wave velocity of CaSiO_3 perovskite with increasing temperature at 60 GPa is shown. Dashed red line represents obtained temperature dependency by regression analysis, and dashed green line is calculation result with $\eta_{s0} = 1.3$ by Xu et al. (2008).

Table A1-1.

Summary of experimental result

T (K)	V_s (km/s)	ρ^a (g/cm ³)	G (GPa)
300	6.03(1)	5.034	183.0(6)
600	5.94(1)	5.013	176.9(6)
700	5.93(2)	5.005	176.0(12)
800	5.84(2)	4.996	170.4(12)

^a Calculated by Ricolleau et al. (2009) in cold part, and Xu et al (2008) in temperature dependency

Table A1-2

Comparison of temperature dependency

	$\partial G/\partial T$ (MPa/T)	$\partial V_s/\partial T$ (m/s/K)	η_{s0}
CaSiO ₃ perovskite (this study)	-21	-0.31	6.2
CaSiO ₃ perovskite (Xu et al., 2008)	-9	-0.11	1.3
MgSiO ₃ perovskite (Murakami et al., 2012)	-15	-0.14	2.4
MgO (Murakami et al., 2012)	-13	-0.17	3.0

APPENDIX 2: A sound velocity calculator for mantle pressure-temperature conditions, “thermo-elastic calculator”

A2-1. Introduction

Recent development in high-pressure experimental technique enables elastic measurements at the lower mantle pressures. The elastic behaviors of mantle constituent minerals were researched by X-ray diffraction measurements (Komabayashi et al., 2008; Sugimura et al., 2008; Sata et al., 2010; Imada et al., 2012; Noguchi et al., 2013), ultrasonic measurements (Li et al., 2004; Kono et al., 2010), Brillouin scattering measurements (Zha et al., 2000; Jackson et al., 2005; Murakami et al., 2007a; 2007b; 2009; 2012; Marquardt et al., 2009; Asahara et al., 2010; 2013; Kudo et al., 2012; Dai et al., 2013), inelastic x-ray scattering measurements (Fiquet et al., 2001; Lin et al., 2005) and so on. On the other hand, ab-initio calculations also revealed elastic behaviors in ultra-high pressures (Karki and Crain, 1998; Karki et al., 2001; Stixrude et al., 2007; Tsuchiya, 2011).

These results are frequently extrapolated or fitted with the formula by Stixrude and Lithgow-Bertelloni (2005), which is based on Eulerian finite strain equation and Mie-Gruneisen-Debye formulas. This program is for reproduce sound velocity of minerals in the mantle temperature condition by experimental or ab-initio calculation data and integrate with several average methods, with easy usage.

A2-2. Calculation method

This program has mainly three calculation faculties for calculating elastic properties of focused materials, or rocks at the lower mantle pressure and temperature condition. The first faculty is for solving the equation of state of focused material at the user-defined pressure-temperature condition, the second one is for calculating the elastic properties of focused material at the molar-volume and the user-defined temperature, and the last one is for calculating the elastic properties of the mixture, including solid solutions, at the user-defined mixing ratio of the mineral species. To calculate the elastic properties of the rocks, which is a mixture of mineral species, at the user-defined pressure-temperature condition or profile, we have to use all of these three faculties.

A2-2-1. Solving equation of states of focused material at user-defined P-T condition

This faculty can be implemented by below 3 steps.

The first step is to solve equation of state at given pressure (P_g) and standard temperature (T_s) which is generally employed as the lowest temperature of the measurements in the reference papers, and is typically room temperature, or 300K.

The parameter f was defined as a function of the ratio for the molar volume between given pressure and ambient pressure of the focused material, as follows:

$$f = \frac{1}{2} \left(\left(\frac{V}{V_0} \right)^{\frac{2}{3}} - 1 \right) \quad (\text{A2.1})$$

where V_0 is the molar volume of the focused material at ambient pressure and V is one at given pressure, therefore, f means the isotropic finite strain. Then, the pressure can express as a function of f , for example, third-order Birch-Murnaghan's equation of state by the parameter f as follows:

$$P(f, T_s) = \frac{3}{2} K_0 f (2f + 1)^{\frac{5}{2}} \left(1 + \frac{(3K' - 5)}{2} f \right) \quad (\text{A2.2})$$

where P is the calculated pressure. K_0 is bulk modulus, and K' is the pressure derivative at ambient pressure, for the focused material, respectively. In this program, pressure was described with three kinds of formulas, second-order Birch-Murnaghan's equation of state, third-order one, and Vinet's equation of state, which is expressed with logarithmic

function, and user can change the employing formula. Additionally, defined the function $F(f, T_s)$ as follows:

$$F(f, T_s) = P(f, T_s) - P_{g_n} \quad (\text{A2.3})$$

where P_{g_n} is the given pressure at standard temperature. At the first calculation, this pressure is employed as user defined pressure ($P_{g_0} = P_g$). The f value what fulfills $F(f, T_s) = 0$, define as f_c , should give the molar volume at given pressure and standard temperature, as following relationship;

$$V = V_0(1 + 2f_c)^{-\frac{3}{2}} \quad (\text{A2.4})$$

where V is molar volume of focused material at given pressure. In order to optimize xc, this program employed “regula falsi” method. After this, the obtained V is called as given volume, and obtained f_c is called as given finite strain.

The second step is calculating the thermal pressure, which is the pressure-increment with increasing temperature under keeping the molar volume condition.

To calculate thermal pressure, this program follows Mie-Gruneisen equation of state, which

$$P_{th} = \gamma \frac{\Delta U}{V} \quad (\text{A2.5})$$

where P_{th} is thermal pressure, γ is Gruneisen parameter and ΔU is the difference of internal-Energy of focused material between at user-defined temperature and at T_s . To

estimate ΔU , this program follows Debye model. Therefore, we can obtain P_{th} with γ , and Debye temperature (θ) at given volume. Following Stixrude and Lithgow-Bertelloni (2005), γ and θ is described as follows;

$$\gamma = \frac{1}{6} \frac{v_0^2}{v^2} (2f_c + 1) [a_{ii}^{(1)} + a_{ijjj}^{(2)} f_c] \quad (A2.6)$$

$$\theta = \theta_0 \left[1 + a_{ii}^{(1)} f_c + \frac{1}{2} a_{ijjj}^{(2)} f_c^2 \right]^{\frac{1}{2}} \quad (A2.7)$$

where

$$a_{ii}^{(1)} = 6\gamma_0 \quad (A2.8)$$

$$a_{ijjj}^{(2)} = -12\gamma_0 + 36\gamma_0^2 - 18\gamma_0 q_0 \quad (A2.9)$$

$$\frac{v^2}{v_0^2} = \left[1 + a_{ii}^{(1)} f_c + \frac{1}{2} a_{ijjj}^{(2)} f_c^2 \right] = \left(\frac{\theta}{\theta_0} \right)^2 \quad (A2.10)$$

where γ_0 , θ_0 , q_0 is Gruneisen parameter, Debye temperature, and volume derivative of Gruneisen parameter of focused material under ambient condition, respectively, and v is the frequency and given isotropic finite strain calculated in the previous step. Note that to obtain internal energy per a Avogadro's number of formula, we have to multiple the number of atoms per formula (n) to Debye energy because Debye energy only gives internal energy for a Avogadro's number (N_A) of atoms, and in a molar volume of focused materials, the number of atoms is $n \times N_A$.

The last step is to optimize the pressure at user-defined temperature to the given pressure. Since we obtain the molar volume at sum of given pressure and thermal

pressure, and user-defined temperature ($V(P_g + P_{th}, T_g)$), where T_g is user-defined temperature) through the passed two steps, we have to recalculate $V(P_g, T_g)$. In order to optimize the condition $(P_g + P_{th}, T_g)$ to (P_g, T_g) , the following recurrence relation is defined,

$$P_{g_{n+1}} = P_g - P_{th_n} \quad (n = 0, 1, 2, \dots) \quad (\text{A2.11})$$

where P_{th_n} is thermal pressure of n^{th} calculation, and P_{th_0} is the thermal pressure of first calculation. If the distance between $P_n + P_{thn}$ and P_g is smaller than defined threshold, this calculation is finished, elsewhere, return to step 1 with P_{gn} as P_{gn+1} . In this program, the defined threshold is 0.0001 GPa.

A2-2-2. Calculation of the elastic properties of focused material at the molar-volume and the user-defined temperature

In this step, calculating isothermal bulk modulus, adiabatic bulk modulus, shear modulus, density, and sound velocities of focused material under the user-defined pressure and temperature conditions as a function of given finite strain and temperature.

Following Stixrude and Lithgow- Bertelloni (2005), isothermal bulk modulus and shear modulus at given finite strain (f_c) and temperature (T_g) are described as following formula,

$$K_T(f_c, T_g) = K_{T0}(1 + 2f)^{\frac{5}{2}} \left[1 + (3K'_{T0} - 5)f + \frac{27}{2}(K'_{T0} - 4)f^2 \right] + (\gamma + 1 - 1)\gamma\rho\Delta U - \gamma^2\rho\Delta(C_V T) \quad (A2.12)$$

$$G(f_c, T_g) = (1 + 2f)^{\frac{5}{2}} [G_0 + (3K_{T0}G'_0 - 5G_0)f + (6K_{T0}G'_0 - 24K_0 - 14G_0 + 9K_{T0}K'_{T0})f^2] - \eta_S\rho\Delta U \quad (A2.13)$$

where

$$\eta_S = \gamma - \frac{1}{2} \frac{v_0^2}{v^2} (2f_c + 1)^2 a_S^{(2)} \quad (A2.14)$$

$$a_S^{(2)} = -2\gamma_0 - 2\eta_{S0} \quad (A2.15)$$

K_T and G is isothermal bulk modulus and shear modulus under user-defined pressure and temperature condition, K_{T0} and G_0 is isothermal bulk modulus and shear modulus under ambient condition, and K_{T0}' and G_0' is the bulk modulus and shear modulus derivative of pressure under ambient condition, respectively, $\Delta(C_V T)$ is the change in constant volume specific heat capacity with varying temperature at constant volume:

$$\Delta(C_V T) = T_g C_V(V, T_g) - T_g C_V(V, T_S) \quad (A2.16)$$

η_s is the shear strain derivative of γ and η_{s0} is η_s at ambient condition. To obtain $C_v(V,T)$, this program employed Debye model as step1. Then, adiabatic bulk modulus can be obtained with following relationship:

$$K_S = K_T + \gamma^2 \rho C_V T_g \quad (\text{A2.17})$$

where ρ is the density of focused material under user-defined pressure and temperature.

At last, the longitudinal, shear, and bulk sound velocity is described by bulk, shear moduli and density as follows,

$$V_P = \sqrt{\frac{K_S + \frac{4}{3}G}{\rho}} \quad (\text{A2.18})$$

$$V_S = \sqrt{\frac{G}{\rho}} \quad (\text{A2.19})$$

$$V_B = \sqrt{\frac{K_S}{\rho}} \quad (\text{A2.20})$$

respectively. Therefore, sound velocity of focused component at high-pressure and temperature can be deduced by inputting V_0 , formula weight (M), number of atoms per single formula (n), K_{T0} , K'_{T0} , G_0 , G'_0 , γ_0 , q_0 , η_{s0} .

A2-2-3. Calculating the elastic properties of the mixture

In this step, this program calculates elastic properties, density, and sound velocities of rocks, solid solutions as a mixture of mineral species calculated in step1 and 2. The molar volume fragment of i^{th} component is given as $c_i V_i$, where c_i is molar fragment of i^{th} component and V_i is molar volume of one at the user defined pressure and temperature. Then, the bulk density is deduced as

$$\rho_{bulk} = \frac{\sum_i \rho_i c_i V_i}{\sum_i c_i V_i} \quad (\text{A2.21})$$

where ρ_i is the density of i^{th} component. Then, elastic moduli were calculated by Reuss, Vohgt, and Hill average model, which is given as

$$E_{Reuss} = \sum_i c_i V_i E_i \quad (\text{A2.22})$$

$$E_{Vohgt} = \frac{1}{\sum_i \frac{c_i V_i}{E_i}} \quad (\text{A2.23})$$

$$E_{Hill} = \frac{E_{Reuss} + E_{Vohgt}}{2} \quad (\text{A2.24})$$

where E is bulk or shear modulus, subscription Reuss, Vohgt, Hill denotes the modulus of Reuss, Vohgt, and Hill average, respectively, and E_i is the elastic modulus of i^{th} component.

A2-3. Bench Mark

Bench marks with several materials were conducted. In MgO by Kono et al. (2010), this calculator reproduced excellently agreement value with experimental results at more than 100 pressure-temperature conditions. The maximum deviation from experimental value is no more than 0.6 %. The results are summarized in table A2-1. Shear velocity of the mixture of MgSiO_3 -perovskite by Xu et al. (2008) and tetragonal CaSiO_3 -perovskite by Kudo et al. (2012) mixture at 135 GPa and 3000 K condition as a function of molar amount ratio is shown in Fig. A2-1.

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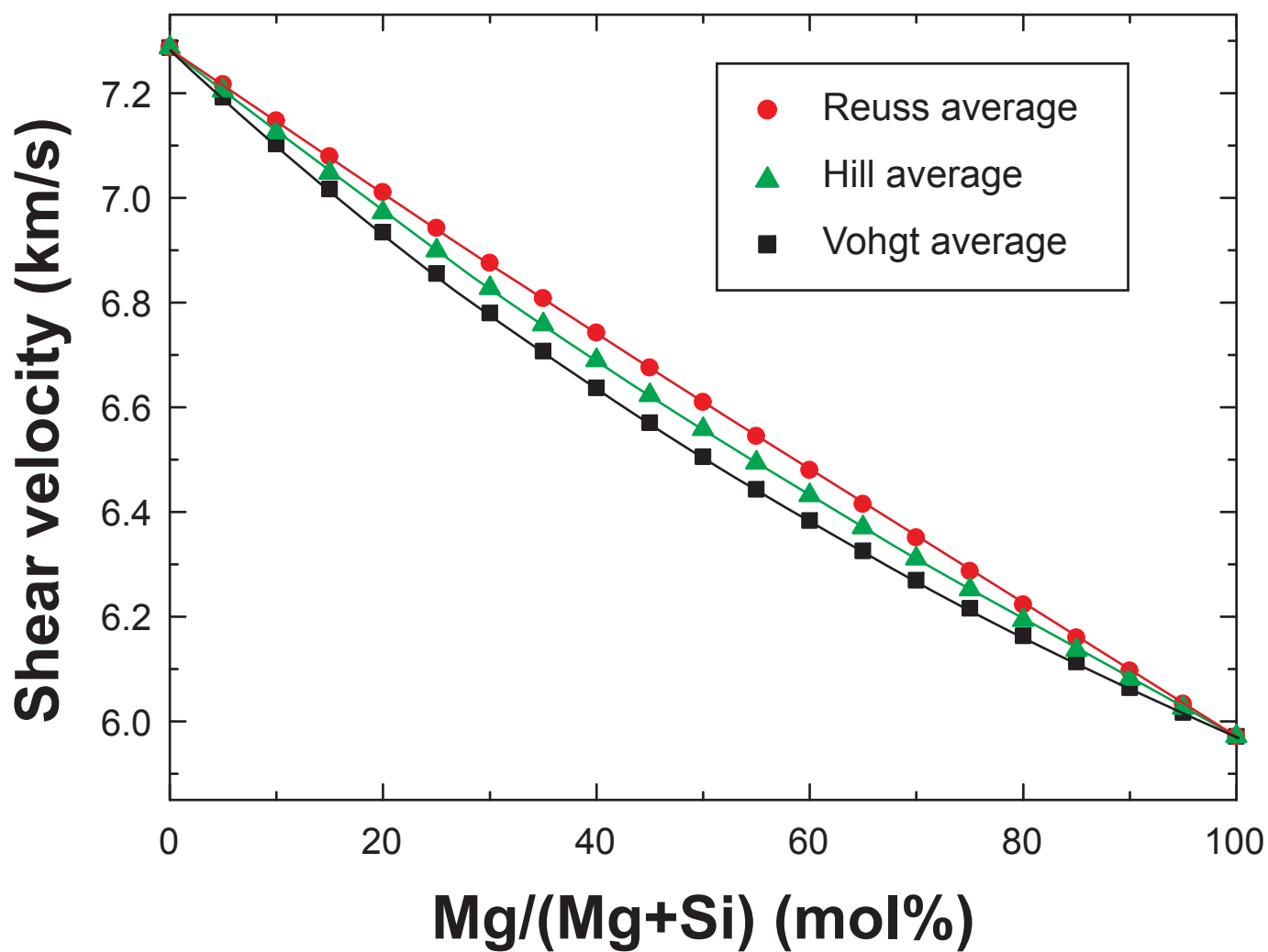


Fig. A2-1 The calculation result of mixture between MgSiO_3 perovskite and tetragonal CaSiO_3 perovskite by Reuss, Vohgt, and Hill average model.

Table A2-1

Comparison of the calculation results by this program and experimental results of MgO (Kono et al. 2010)

P (GPa)	T (K)	ρ (g/cm ³)	$\rho_{\text{calc.}}$ (g/cm ³)	$\rho/\rho_{\text{calc.}} - 1$ (%)	V_P (km/s)	$V_{P \text{ calc.}}$ (km/s)	$V_P/V_{P \text{ calc.}} - 1$ (%)	V_S (km/s)	$V_{\text{scal.}}$ (km/s)	$V_S/V_{S \text{ calc.}} - 1$ (%)
2.7	300	3.642	3.637	0.14	9.84	9.87	-0.28	6.07	6.08	-0.20
3.4	300	3.657	3.652	0.13	9.89	9.92	-0.32	6.10	6.11	-0.15
4.7	300	3.682	3.678	0.11	10.02	10.01	0.07	6.16	6.15	0.10
6.0	300	3.709	3.705	0.11	10.09	10.11	-0.20	6.21	6.20	0.14
6.1	300	3.711	3.706	0.13	10.11	10.11	-0.05	6.21	6.20	0.10
8.2	300	3.751	3.747	0.12	10.25	10.26	-0.08	6.28	6.27	0.10
8.6	300	3.759	3.755	0.12	10.30	10.29	0.13	6.29	6.29	0.04
9.3	300	3.772	3.768	0.12	10.30	10.33	-0.31	6.31	6.31	0.00
9.8	300	3.782	3.777	0.13	10.35	10.37	-0.15	6.33	6.33	0.05
10.7	300	3.799	3.794	0.13	10.42	10.43	-0.06	6.36	6.36	0.06
11.8	300	3.820	3.815	0.13	10.50	10.50	0.01	6.40	6.39	0.13
12.8	300	3.837	3.832	0.13	10.55	10.56	-0.09	6.42	6.42	-0.02
14.7	300	3.870	3.865	0.12	10.67	10.68	-0.06	6.47	6.48	-0.13
15.4	300	3.883	3.879	0.11	10.70	10.72	-0.21	6.51	6.50	0.14
16.2	300	3.896	3.891	0.13	10.75	10.76	-0.14	6.53	6.52	0.13
18.4	300	3.934	3.929	0.13	10.90	10.90	0.03	6.59	6.59	0.06
20.8	300	3.972	3.967	0.13	11.05	11.03	0.19	6.66	6.65	0.14
2.8	450	3.626	3.622	0.11	9.79	9.81	-0.21	6.00	6.03	-0.51
3.7	450	3.645	3.641	0.12	9.85	9.88	-0.29	6.05	6.06	-0.24
4.9	450	3.670	3.666	0.11	9.95	9.97	-0.19	6.10	6.11	-0.15
6.2	450	3.698	3.693	0.12	10.06	10.07	-0.07	6.16	6.16	0.03
8.7	450	3.747	3.742	0.13	10.23	10.24	-0.11	6.23	6.24	-0.23
9.5	450	3.761	3.757	0.11	10.25	10.29	-0.42	6.26	6.27	-0.16
10.9	450	3.788	3.784	0.12	10.37	10.39	-0.18	6.32	6.32	0.05
13.0	450	3.827	3.822	0.13	10.51	10.52	-0.13	6.37	6.38	-0.22
15.0	450	3.862	3.857	0.13	10.62	10.65	-0.25	6.42	6.44	-0.38
15.8	450	3.876	3.872	0.11	10.66	10.70	-0.36	6.47	6.47	0.01
16.4	450	3.886	3.882	0.11	10.74	10.73	0.06	6.51	6.49	0.36
18.8	450	3.927	3.922	0.12	10.87	10.87	-0.04	6.56	6.56	0.06
21.1	450	3.965	3.961	0.11	11.00	11.01	-0.07	6.63	6.62	0.12

3.1	600	3.613	3.608	0.13	9.73	9.76	-0.26	5.95	5.98	-0.48
4.0	600	3.632	3.628	0.12	9.81	9.83	-0.15	6.01	6.01	-0.07
5.2	600	3.658	3.653	0.13	9.90	9.92	-0.18	6.05	6.06	-0.17
6.6	600	3.688	3.683	0.13	10.02	10.02	-0.05	6.12	6.11	0.10
9.0	600	3.735	3.730	0.13	10.17	10.19	-0.23	6.18	6.20	-0.29
9.7	600	3.749	3.744	0.13	10.19	10.24	-0.52	6.21	6.22	-0.21
11.2	600	3.777	3.772	0.13	10.32	10.34	-0.22	6.27	6.27	-0.04
13.3	600	3.817	3.812	0.12	10.46	10.49	-0.24	6.32	6.34	-0.37
15.2	600	3.851	3.847	0.11	10.59	10.61	-0.16	6.38	6.40	-0.37
15.8	600	3.861	3.856	0.12	10.62	10.64	-0.19	6.45	6.42	0.46
16.6	600	3.876	3.871	0.14	10.67	10.69	-0.20	6.45	6.45	0.06
19.1	600	3.918	3.913	0.12	10.80	10.84	-0.37	6.51	6.52	-0.15
21.4	600	3.956	3.951	0.12	10.97	10.97	-0.03	6.58	6.59	-0.08
3.4	750	3.599	3.595	0.12	9.68	9.70	-0.17	5.90	5.92	-0.41
4.2	750	3.617	3.613	0.11	9.73	9.76	-0.35	5.94	5.96	-0.31
5.6	750	3.646	3.642	0.12	9.83	9.87	-0.39	5.98	6.01	-0.52
6.9	750	3.674	3.670	0.11	9.92	9.97	-0.50	6.05	6.06	-0.21
9.4	750	3.724	3.719	0.12	10.09	10.15	-0.58	6.12	6.15	-0.53
10.0	750	3.736	3.732	0.11	10.14	10.19	-0.52	6.16	6.18	-0.25
11.5	750	3.765	3.760	0.13	10.28	10.29	-0.14	6.23	6.23	0.06
13.6	750	3.806	3.801	0.13	10.42	10.44	-0.20	6.28	6.30	-0.31
15.6	750	3.841	3.836	0.13	10.53	10.56	-0.32	6.34	6.36	-0.34
16.4	750	3.855	3.850	0.13	10.60	10.61	-0.13	6.41	6.39	0.37
16.9	750	3.865	3.860	0.13	10.63	10.65	-0.17	6.38	6.40	-0.36
19.5	750	3.910	3.905	0.12	10.76	10.81	-0.44	6.46	6.48	-0.35
21.7	750	3.947	3.942	0.12	10.94	10.94	0.03	6.54	6.55	-0.11
3.7	900	3.583	3.579	0.12	9.61	9.63	-0.20	5.84	5.86	-0.42
4.6	900	3.603	3.599	0.12	9.68	9.70	-0.23	5.89	5.90	-0.20
7.3	900	3.662	3.658	0.12	9.87	9.92	-0.48	6.00	6.01	-0.20
9.7	900	3.712	3.708	0.12	10.04	10.10	-0.58	6.09	6.10	-0.23
10.3	900	3.724	3.720	0.12	10.09	10.14	-0.51	6.11	6.13	-0.26
11.8	900	3.753	3.748	0.13	10.24	10.24	-0.04	6.18	6.18	0.03
14.0	900	3.795	3.791	0.11	10.37	10.40	-0.26	6.22	6.26	-0.56
15.9	900	3.829	3.825	0.12	10.49	10.52	-0.26	6.30	6.32	-0.25
16.7	900	3.845	3.840	0.12	10.59	10.57	0.16	6.36	6.34	0.25

17.2	900	3.853	3.848	0.12	10.58	10.60	-0.21	6.33	6.36	-0.45
19.9	900	3.900	3.895	0.12	10.75	10.77	-0.16	6.44	6.44	-0.02
22.1	900	3.937	3.933	0.11	10.87	10.90	-0.26	6.48	6.51	-0.42
4.9	1050	3.588	3.584	0.11	9.60	9.64	-0.40	5.82	5.84	-0.40
7.7	1050	3.649	3.645	0.12	9.82	9.86	-0.43	5.94	5.96	-0.32
7.7	1050	3.651	3.647	0.12	9.82	9.87	-0.50	5.97	5.96	0.13
8.3	1050	3.663	3.659	0.12	9.87	9.91	-0.44	5.99	5.99	0.08
10.1	1050	3.699	3.695	0.11	9.99	10.04	-0.55	6.04	6.05	-0.21
10.6	1050	3.711	3.706	0.12	10.04	10.09	-0.46	6.06	6.07	-0.23
12.1	1050	3.741	3.736	0.13	10.18	10.19	-0.14	6.13	6.13	0.02
14.3	1050	3.783	3.778	0.13	10.33	10.35	-0.15	6.17	6.21	-0.58
16.2	1050	3.817	3.812	0.12	10.46	10.47	-0.08	6.26	6.27	-0.14
17.3	1050	3.837	3.833	0.11	10.55	10.54	0.10	6.29	6.31	-0.24
17.5	1050	3.842	3.837	0.12	10.54	10.56	-0.16	6.27	6.31	-0.69
18.2	1050	3.853	3.849	0.11	10.60	10.60	0.02	6.32	6.33	-0.23
20.3	1050	3.891	3.886	0.13	10.70	10.73	-0.27	6.39	6.40	-0.17
22.4	1050	3.927	3.923	0.11	10.84	10.86	-0.17	6.44	6.47	-0.40
5.4	1200	3.578	3.574	0.11	9.58	9.59	-0.11	5.79	5.79	-0.05
8.2	1200	3.640	3.636	0.11	9.79	9.82	-0.31	5.93	5.91	0.30
8.8	1200	3.653	3.648	0.13	9.81	9.87	-0.57	5.94	5.94	0.07
11.0	1200	3.698	3.694	0.12	10.00	10.03	-0.32	6.03	6.02	0.14
12.6	1200	3.730	3.725	0.12	10.14	10.15	-0.07	6.09	6.08	0.14
14.7	1200	3.772	3.768	0.11	10.27	10.30	-0.31	6.12	6.16	-0.66
16.5	1200	3.806	3.801	0.13	10.42	10.42	-0.01	6.23	6.22	0.13
17.7	1200	3.828	3.823	0.12	10.51	10.50	0.09	6.24	6.26	-0.36
17.9	1200	3.832	3.827	0.12	10.52	10.51	0.05	6.26	6.27	-0.16
20.8	1200	3.882	3.878	0.11	10.66	10.69	-0.32	6.33	6.36	-0.49
23.1	1200	3.922	3.917	0.12	10.81	10.83	-0.22	6.42	6.43	-0.20
8.7	1350	3.628	3.624	0.12	9.74	9.77	-0.27	5.89	5.86	0.54
9.1	1350	3.638	3.633	0.13	9.77	9.80	-0.32	5.89	5.88	0.22
11.4	1350	3.686	3.682	0.11	9.96	9.98	-0.20	5.98	5.97	0.16
12.9	1350	3.718	3.713	0.12	10.10	10.10	0.04	6.04	6.03	0.16
16.9	1350	3.794	3.790	0.11	10.37	10.37	-0.03	6.16	6.17	-0.23
17.9	1350	3.814	3.809	0.12	10.45	10.44	0.07	6.19	6.21	-0.33
18.1	1350	3.818	3.813	0.13	10.47	10.46	0.13	6.20	6.22	-0.28

21.0	1350	3.870	3.865	0.12	10.61	10.64	-0.32	6.28	6.31	-0.53
23.2	1350	3.908	3.904	0.11	10.76	10.78	-0.19	6.37	6.38	-0.21
9.1	1500	3.616	3.612	0.11	9.70	9.71	-0.14	5.84	5.80	0.61
9.7	1500	3.629	3.625	0.12	9.73	9.76	-0.30	5.84	5.83	0.19
11.8	1500	3.673	3.669	0.11	9.92	9.92	-0.04	5.93	5.92	0.24
13.4	1500	3.706	3.702	0.11	10.06	10.05	0.14	6.00	5.98	0.33
14.4	1500	3.728	3.724	0.12	10.14	10.12	0.15	6.02	6.02	-0.02
17.4	1500	3.785	3.781	0.12	10.33	10.33	-0.02	6.11	6.13	-0.32
18.5	1500	3.806	3.801	0.12	10.45	10.41	0.41	6.15	6.17	-0.31
21.5	1500	3.860	3.856	0.11	10.59	10.60	-0.12	6.25	6.27	-0.32
23.6	1500	3.897	3.892	0.12	10.72	10.73	-0.13	6.35	6.34	0.19
9.7	1650	3.607	3.603	0.12	9.66	9.67	-0.08	5.78	5.75	0.44
14.0	1650	3.699	3.695	0.10	10.05	10.01	0.37	5.95	5.94	0.21
