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Sound velocities across calcite phase transitions by Brillouin scattering spectroscopy

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Abstract

Calcite ($CaCO_3$) is widely considered an important carbon carrier in the Earth's interior. Laboratory measurements of the velocities and elastic properties of calcite are important for understanding the deep carbon cycle. The sound velocities of calcite were determined up to 10.3 GPa at ambient temperature by Brillouin scattering spectroscopy. Dramatic decreases in the velocity of compressional wave (Vp) and shear wave (Vs) and abrupt increases in the Vp anisotropy (Ap) and maximum Vs anisotropy (Asmax) were detected across the phase transition from $CaCO_3$-I to $CaCO_3$-II. Dramatic increases in the Vp and Vs and an abrupt decrease in Ap were observed across the phase transition from $CaCO_3$-II to $CaCO_3$-III. The phase transition from $CaCO_3$-I to $CaCO_3$-II may potentially explain the Gutenberg discontinuity at 51 km in the Izu-Bonin region. The Vp and Vs values of calcite were rather low. Our new results combined with literature data suggest that the rather low velocities of $CaCO_3$ could potentially explain the low-velocity zone occurring in

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Keywords: Brillouin scattering; sound velocity; elasticity; $CaCO_3$; high-pressure.

Introduction

Carbonates play an important role in the transport and storage of carbon in the Earth's crust and mantle (Dasgupta and Hirschmann 2010; Sanchez-Valle et al. 2011). Calcite is widely considered one of the most important carbonates in the Earth's interior. Recent experimental and theoretical studies have shown that its high-pressure phase remains stable under lower mantle pressure and temperature conditions (Dorfman et al. 2018; Liu et al. 2016; Oganov et al. 2006, 2008; Ono et al. 2007; Li et al. 2018). The existence of calcite in the mantle is also proven by the occurrence of its inclusion in diamonds at corresponding depths (Brenker et al. 2007; Kaminsky et al. 2009; Tschauner et al. 2018). Additionally, sound velocities and elastic properties are important for understanding the structure of the Earth's interior and the causes of some abnormal behaviors (e.g., seismic wave discontinuities and low-velocity zones) (Mao et al. 2010; Duffy et al. 1995; Bayarjargal et al. 2018; Marcondes et al. 2016). Laboratory measurements of the velocities and elastic properties of calcite are thus important for determining the deep carbon cycle and identifying potential carbonate-rich regions in the Earth's interior.

Calcite crystallizes in the trigonal crystal system with space group $R\bar{3}c$ (referred to as $CaCO_3$-I) under ambient conditions. It undergoes a series of structural phase transitions into $CaCO_3$-II, $CaCO_3$-III, and $CaCO_3$-VI at ~1.5, ~2.1, and ~15.0 GPa, respectively (Catalli 2005; Liu et al. 2016; Merlini et al. 2012). There are numerous experimental and theoretical reports on the velocity and elasticity of calcite. However, these studies are mainly concentrated on low-pressure measurements with ultrasonic interferometry or high-pressure conditions modeled through theoretical calculation

(Almqvist et al. 2010; Grady et al. 1978; Juneja and Endait 2017; Thanh and Lacam 1984; Peselnick and Robie 1963; Stekiel et al. 2017; Wang 1966; Zhao et al. 2009; Huang et al. 2017; Bayarjargal et al. 2018). Furthermore, some data on properties at ambient pressure and/or high-temperatures based on Brillouin scattering spectroscopy have been reported (Chen et al. 2001; Lin 2013). Therefore, we investigated the high-pressure velocities of natural calcite up to 10.3 GPa at ambient temperature by Brillouin scattering spectroscopy.

Methods

Natural single-crystal calcite (Iceland spar) samples were obtained from Guizhou, China. The composition was measured by electron microprobe analyses (JXA-8230, 15 kV and 10 nA, Northwest University, China), which indicated a homogeneous chemical composition of $CaCO_3$ with less than 0.4 mol% Mg. For simplification, we refer to it as $CaCO_3$. Single-crystal samples with optical clarity, surface smoothness, and parallelism of less than 30' were chosen for Brillouin scattering measurements.

High-pressures were generated by a pair of 400 μm diamond culets. The sample chamber was composed of a rhenium gasket with a pre-indented thickness of ~70 μm and a drilled hole of ~160 μm. A volume ratio of 4:1 methanol and ethanol mixture was applied as the pressure transmitting medium for all experiments. Ruby powders and a single-crystal platelet with a thickness of ~40 μm were loaded into the sample chamber. Four independent experiments were conducted in this study. Pressures were determined by the quasi-hydrostatic ruby scale (Mao et al. 1986). The pressure uncertainties were ±0.1 GPa below 2 GPa and ±0.3 GPa between 3 and 10.3 GPa, which were estimated from the pressure measured before and after the collection of the Brillouin spectra.

Brillouin scatting spectra were collected by a Sandercock-type six-pass tandem

Fabry-Perot interferometer (TFP-2, JRS Scientific Instruments) equipped with a photomultiplier detector (Count-10B, Laser Components) and a diode-pumped laser with a wavelength of 532 nm (Verdi G2, Coherent) as an excitation source. A 60° symmetric scattering geometry was adopted in all experiments. The Brillouin scattering system was calibrated before the measurements with BK7 glass and deionized water (Sanchez-Valle et al. 2013; Yoneda and Song 2005). The aggregate velocities were calculated as follows:

$$V_i = \frac{\Delta w_i \lambda}{2\sin(\theta/2)}, \quad (1)$$

where V_i is the sound velocity (subscript i represents the P wave or S wave), $\Delta\omega_i$ is the measured Brillouin shift, λ represents the incident wavelength, and θ represents the angle between the incident and scattered orientations.

Results and discussion

Sound velocities and elastic properties of calcite at high-pressure

The sound velocities of calcite were determined up to 10.3 GPa at ambient temperature in a 0.3-3 GPa pressure interval by Brillouin scattering spectroscopy. The 19 sets of Brillouin scattering spectra were collected in the $(10\bar{1}1)$ plane, with 10° intervals for each pressure. The intensities of the compressional wave velocity (Vp) and shear wave velocity (Vs) varied with crystallographic direction. A representative Brillouin scattering spectrum for single-crystal calcite at 1.8 GPa and 300 K is shown in Figure 1. Although calcite has the property of birefringence, given the experimental uncertainty, its effect on velocity can be neglected based on the analysis in a previous study (Chen et al. 2001).

The Vp and Vs velocities of single-crystal calcite as a function of the azimuthal angle measured from the $(10\bar{1}1)$ cleaved plane at 0.3 GPa, 1.8 GPa, and 10.3 GPa are

shown in Figure 2. The Vp and Vs values varied significantly as a function of the azimuthal angle at each pressure, indicating strong elastic anisotropies of the mineral at different phases. However, the change trends of these velocities were obviously different from each other. A comparison of the velocities at 0.3 and 1.8 GPa reveals that the latter velocities were obviously less than the former velocities. The abnormal decrease in the Vp and Vs velocities at 1.8 GPa corresponded to a different structure of calcite (i.e., $CaCO_3$-II ($P2_1/c$)) (Merrill and Bassett 1975). Furthermore, the change trends of the velocities at 1.8 GPa and 10.3 GPa were obviously different, especially for Vp. At 10.3 GPa, the Vp value strictly varied as a sine or cosine trend with the azimuthal angle, which corresponded to the $CaCO_3$-III phase, and it crystallized in the triclinic space group $P\bar{1}$ (Merlini et al. 2012).

Based on the density and 19 sets of velocity data for the calcite at each pressure, the six elastic constants of calcite were calculated by a genetic algorithm using the Christoffel's equations (Chen et al. 2006; Redfern and Angel 1999). This method has been successfully used to calculate the elastic constants of magnesite, dolomite, Zn(2-methylimidazolate)$_2$ (Chen et al. 2006; Tan et al. 2012), and rhodochrosite (Zhao et al. 2018). The error for each elastic constant is estimated by calculating the variations of misfit as a function of the specific Cij (Chen et al. 2006).

The adiabatic bulk and shear moduli (Ks and G), were calculated by the Voigt-Reuss-Hill averages (Meister and Peselnick 1966) using the derived elastic constants. The derived bulk and shear moduli (K_0 and G_0) under ambient conditions were 78.2 and 32.6 GPa, respectively, which were in agreement with previous results (see Table S1) (Chen et al. 2001; Lin 2013). Then the aggregate Vp and Vs were calculated by the following equations:

$$V_{\mathrm{p}} = \sqrt{\frac{Ks + \frac{4}{3}G}{\rho}}, \quad (2)$$

$$Vs = \sqrt{\frac{G}{\rho}}, \quad (3)$$

The elastic constants and aggregate sound velocity properties of calcite in the form of $CaCO_3$-I at high-pressure are shown in Table 1. The monoclinic structure of $CaCO_3$-II and the triclinic structure of $CaCO_3$-III have thirteen and twenty-one independent elastic constants, respectively, which are difficult to accurately calculate by the genetic algorithm method. This method is better used to calculate the elastic constants in orthorhombic and higher symmetry crystals.

To characterize the change trends of the velocities, as a reference, a simple average of the 19 sets of velocities at each pressure was taken as the average velocity of the calcite, as shown in Figure 3. A large discrepancy (~0.6 km/s) was apparent between the aggregate Vp and average Vp values in the $CaCO_3$-I phase, while a smaller difference was observed between the aggregate Vs and average Vs values. Dramatic decreases in Vp (-16.0%) and Vs (-18.9%) were detected across the phase transition from $CaCO_3$-I to $CaCO_3$-II, while dramatic increases in Vp (+6.6%) and Vs (+20.2%) were detected across the phase transition from $CaCO_3$-II to $CaCO_3$-III. Sharp decreases in all elastic constants and the bulk modulus of calcite were reported to occur in the phase transition from $CaCO_3$-I to $CaCO_3$-II based on ultrasonic interferometry (Thanh and Lacam 1984; Singh and Kennedy 1974). The Vp decrease (-16.0%) across the phase transition from $CaCO_3$-I to $CaCO_3$-II in this study is in good agreement with the value of -19.0% reported based on ultrasonic interferometry (Wang 1966), although there is an obvious velocity discrepancy between these two methods. The average velocities measured in this study are almost identical to the

values obtained via theoretical calculation (Marcondes et al. 2016). To some extent, the change trends of the average velocities can represent the aggregate velocities. The approximate aggregate Vp and Vs values of $CaCO_3$-II were calculated based on this assumption.

The anisotropy factors for Vp and Vs are defined as follows:

$$A_p = 2\times\left(V_{P,\max} - V_{P,\min}\right)/\left(V_{P,\max} + V_{P,\min}\right)\times 100\%, \quad (4)$$

$$A_s = \left(V_{s2} - V_{s1}\right)/Vs\times 100\%, \quad (5)$$

where Vp,max and Vp,min represent the maximum and minimum Vp values of the mineral, respectively; Vs1 and Vs2 are two orthogonally polarized Vs values; and Vs represents the aggregate Vs value. The anisotropy factors of Ap and Asmax of calcite are a function of pressure and are shown in Figure 4. The extrapolated Ap and Asmax values are 24.3% and 61.4%, respectively, under ambient conditions, and these values are consistent with those in a previous study (Chen et al. 2001). The anisotropies of calcite in the different phases were considerably different, and the Ap and Asmax of $CaCO_3$-II were much larger than those of $CaCO_3$-I and $CaCO_3$-III. Similarly, a theoretical analysis implies that there are considerable differences in the anisotropies of different phases of $CaCO_3$ (Marcondes et al. 2016, Huang et al. 2017). The Ap and Asmax were generally stable at ~23% and ~62% in the structure of $CaCO_3$-I, respectively. Abrupt increases in Ap (+40.9%) and Asmax (+58.4%) were detected across the phase transition from $CaCO_3$-I to $CaCO_3$-II. Within $CaCO_3$-II, the Ap ranged from 31.3% to 32.0%, and Asmax ranged from 76.2% to 96.8%. Furthermore, across the phase transition from $CaCO_3$-II to $CaCO_3$-III, an abrupt decrease in Ap (-65.0%) was detected, and the Ap subsequently increased slowly to the maximum pressure in this study.

Phase diagram of $CaCO_3$

Because the phase diagram of $CaCO_3$ is fairly complicated and phase transitions are strongly dependent on temperature, the elastic properties of calcite at ambient temperature and high-pressure are carefully applied under high-temperature and high-pressure conditions. To further discuss the geophysical implications of a suitable pressure range, we constructed a phase diagram of $CaCO_3$ with showing estimated temperature and pressure conditions corresponding to relatively cold subduction zone based on the literature (Figure S1). According to synthesized phase diagram, calcite phases of $CaCO_3$-I, $CaCO_3$-II and aragonite should be stable in the cold subduction zone beneath NE Japan and Izu-Bonin (Figure S1). Raman spectroscopy in the calcite phases showed that $CaCO_3$-II is stable between 1.4 and 2.1 GPa at ambient temperature (Figure S2). This is consistent with the previous studies using Raman spectroscopy and X-ray diffraction measurements (Merlini et al. 2012; Hagiya et al. 2005; Liu et al. 2016; Bayarjargal et al. 2018). However, the stability field of $CaCO_3$-II should be slightly smaller at higher temperatures because of the negative Clausius-Clapeyron slopes of the phase boundary lines from $CaCO_3$-I to $CaCO_3$-II and from $CaCO_3$-II to aragonite (Pippinger et al. 2015, Liu et al. 2017). For the temperature and pressure conditions of the Izu-Bonin and NE Japan regions, $CaCO_3$-II is stable at pressures below ~1.7 GPa corresponding to 51 km depth, and then it transforms into aragonite at greater pressures. In contrast, $CaCO_3$-III may not exist under the relevant temperature and pressure conditions of the subduction zone beneath NE Japan and Izu-Bonin, since $CaCO_3$-III is stable at very low temperature condition. Accordingly, we will focus on the velocities of $CaCO_3$-I, $CaCO_3$-II and aragonite phases in the upcoming discussion.

Velocities and anisotropies of $CaCO_3$ and major upper mantle minerals at high-pressure

196 The velocities and anisotropies of $CaCO_3$ and major upper mantle minerals are
197 shown as a function of pressure in Figure 5. Comparisons are limited to room
198 temperature and high-pressure due to limited knowledge in the temperature effects on
199 the elastic properties of $CaCO_3$. Combined with the elastic properties of aragonite
200 reported previously (Huang et al. 2017; Liu et al. 2005; Marcondes et al. 2016),
201 $CaCO_3$ polymorphs have the lowest Vp and Vs values and the largest Ap and Asmax
202 values among the major upper mantle minerals over the entire pressure range (see
203 Figure 5).

204 **Velocities of the carbonated eclogite and peridotite models**

205 To further evaluate the effect of carbonate on the velocity of the major upper
206 mantle minerals, we calculated the velocities of eclogite and peridotite with and
207 without 10 wt.% $CaCO_3$ as reported previously (Bayarjargal et al. 2018). In terms of
208 mineral assemblage, the carbon-free eclogite model is 53.3 wt.% garnet and 46.7 wt.%
209 clinopyroxene, while the carbon-free peridotite model is 59.3 wt.% olivine, 12.8 wt.%
210 clinopyroxene, 11.4 wt.% orthopyroxene, and 16.5 wt.% garnet (Dasgupta and
211 Hirschmann 2006; Dasgupta et al. 2004; Yang et al. 2014). Here we modeled
212 velocities of hypothetical $CaCO_3$-rich mantle rocks, which are constructed by 90 wt.%
213 of eclogite/peridotite and 10 wt.% of $CaCO_3$. Compared to the carbon-free eclogite,
214 the Vp and Vs values decrease by 2.3% and 3.0% for $CaCO_3$-I, 3.6% and 4.4% for
215 $CaCO_3$-II, and 2.7% and 3.0% for aragonite, respectively. Velocities significantly
216 increase (Vp +1.3 % and Vs +1.4 %) during phase transition from $CaCO_3$-I to $CaCO_3$-
217 II. Similarly, the Vp and Vs values of the carbonated peridotite decrease by about 2-4 %
218 compared to normal peridotite (see Figure 6).

219 **Implications**

220 Discontinuities in seismic wave velocities are closely related to phase transitions,

rapid variations in chemical composition with depth, or changes in the degree of anisotropy (Stixrude 2015). Sharp increases in Vp (+2%) and Vs (+9%) from aragonite to $CaCO_3$-VII at 25 GPa (~690 km depth) and decreases in Vp (-12%) and Vs (-3%) from $CaCO_3$-VII to post-aragonite at 40 GPa (~1010 km depth) were previously determined based on density functional theory calculations (Bayarjargal et al. 2018). According to previous study (Bayarjargal et al. 2018), seismic wave velocities increase (Vp +0.4% and Vs +0.9%) upon aragonite to $CaCO_3$-VII phase transition at 25 GPa in pyrolite with 10 wt.% of $CaCO_3$, while these values largely decrease (Vp -4.7% and Vs -7.0%) during $CaCO_3$-VII to post-aragonite transition at 40 GPa. These data imply that the presence of $CaCO_3$ may contribute to the discontinuities at ~700 km and 930-1120 km (Bayarjargal et al. 2018; Yang and He 2015; Kaneshima 2013).

In this study, we measured the elastic properties of calcite at pressures up to 10.3 GPa and observed dramatic decreases in Vp (-16.0%) and Vs (-18.9%) across the phase transition from $CaCO_3$-I to $CaCO_3$-II, which occurred at ~1.4 GPa (42 km depth). If eclogite or pyrolite contain 10 wt.% of $CaCO_3$, seismic wave velocities significantly decrease by Vp -1.3% and Vs -1.4% upon the phase transition at 42 km depth (Figure 6). The sharp decreases in the Vp and Vs values of $CaCO_3$ across the phase transition may be related to the Gutenberg discontinuity at ~51(±10) km, where the Vs changes by -7.8%, as reported by seismic observations in the Izu-Bonin region (Revenaugh and Jordan 1991). On the other hand, we observed abrupt increases in Ap (+40.9%) and Asmax (+58.4%) across the phase transition. A small amount of calcite-type carbonates can significantly modify the seismic anisotropy of rocks (Valcke et al. 2006; Lin 2013). A strong, localized anisotropy is also considered to explain the Gutenberg discontinuity (Stixrude 2015; Gung et al. 2003). If calcite exists in the Izu-

Bonin region in a sufficient quantity, the phase transition from $CaCO_3$-I to $CaCO_3$-II may represent a possible explanation of the Gutenberg discontinuity at 51 km in this region.

A low-velocity layer has been observed in NE Japan, and it extends to 150 km depth beneath this region (Peacock 2003; Matsuzawa et al. 1986; Hasegawa et al. 1994). Under the relevant temperature and pressure conditions of the NE Japan region, the velocities of $CaCO_3$, including $CaCO_3$-I, $CaCO_3$-II, and aragonite, are much slower than those of the major upper mantle minerals up to at least 10 GPa (300 km depth) (see Figure 5 (a), (b)). As described above, we estimated sound wave velocities of mantle rocks (eclogite and peridotite) containing 10 wt.% of $CaCO_3$ (Figure 6). Results show that velocities significantly reduced by enrichment of $CaCO_3$ up to -4.4% compared to normal mantle. The presence of $CaCO_3$ at relevant depths in the NE Japan region may potentially explain the low-velocity zone observed in this region. In addition, a previous study suggested that the sound velocities of $CaCO_3$ in the post-aragonite phase were much lower than those of the major lower mantle constituent $MgSiO_3$, and the presence of $CaCO_3$ was considered a possible way to explain the existence of the low-velocity region in the bottom of the lower mantle (Marcondes et al. 2016). The rather low velocities and large anisotropies of carbonates (see Figure S3 and reference in (Marcondes et al. 2016)) can be considered potentially useful features for detecting carbonate-rich regions in the Earth's crust and mantle, which further improve our knowledge of the deep carbon cycle and seismic observations in the Earth's interior.

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Figure captions

Figure 1. A representative Brillouin spectrum of single-crystal calcite at 1.8 GPa and 300 K. The inserted picture represents the single-crystal calcite in a diamond anvil cell. R: Rayleigh peak. Vp and Vs stand for compressional and transverse velocities.

Figure 2. Vp and Vs velocities of single-crystal calcite as a function of the azimuthal angle measured from a cleaved (101) platelet. (a) $CaCO_3$-I, 0.3 GPa; (b) $CaCO_3$-II, 1.8 GPa; (c) $CaCO_3$-III, 10.3 GPa. The dotted lines represent the change trends of the velocities.

Figure 3. Vp and Vs velocities of calcite as a function of pressure at ambient temperature. The dashed lines represent the tentative trend of the average sound velocities.

Figure 4. Ap and Asmax Anisotropies of calcite as a function of pressure at ambient temperature. The dashed lines represent the tentative change trend of the anisotropies.

Figure 5. Pressure dependence of Vp (a) and Vs (b) velocities and Ap (c) and Asmax (d) anisotropies of $CaCO_3$ and major upper mantle minerals at 300 K. Black lines: calcite (Cal) (this study; Chen et al. 2001); dark cyan lines: aragonite (Arag) (Huang et al. 2017; Liu et al. 2005; Marcondes et al. 2016); olive lines: olivine (Ol) (Mao et al. 2015; Zha et al. 1998); green lines: garnet (Gt) (Duffy and Anderson 1989; Sinogeikin and Bass 2000); wine lines: clinopyroxene (Cpx) (Duffy and Anderson 1989; Sang and Bass 2014; Collins and Brown 1998; Zou et al. 2018); blues lines: orthopyroxene (Opx) (Chai et al. 1997; Duffy and Anderson 1989).

Figure 6. Vp and Vs velocities of eclogite and peridotite models with and without $CaCO_3$ at ambient temperature. (a) eclogite model; (b) peridotite model. In terms of mineral assemblage, the carbon-free eclogite model is 53.3 wt.% garnet and 46.7 wt.% clinopyroxene, while the carbon-free peridotite model is 59.3 wt.% olivine, 12.8 wt.%

clinopyroxene, 11.4 wt.% orthopyroxene, and 16.5 wt.% garnet (Dasgupta and Hirschmann, 2006; Dasgupta et al. 2004; Yang et al. 2014). The carbonated eclogite and peridotite models include 10 wt.% $CaCO_3$ ($CaCO_3$-I, $CaCO_3$-II, aragonite), respectively.

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523 Table 1. Single-crystal elastic properties of calcite in the $CaCO_3$-I phase under high-
524 pressure and ambient temperature conditions.

P (GPa)	0.3±0.1	0.7±0.1	1.0±0.1	1.3±0.1
C_{11} (GPa)	150.8±1.5	151.8±1.5	152.5±1.5	153.5±2.0
C_{33} (GPa)	90.2±3.0	93.9±3.5	93.8±3.5	94.3±4.0
C_{44} (GPa)	35.4±0.5	39.6±2.0	42.4±1.5	44.9±1.5
C_{12} (GPa)	63.2±2.5	66.7±2.5	71.2±2.5	73.8±3.0
C_{13} (GPa)	56.8±1.5	59.2±2.0	61.4±2.5	63.4±2.5
C_{14} (GPa)	20.0±0.5	20.6±0.5	21.1±0.5	21.7±1.0
Ks (GPa)	79.9±1.7	82.5±1.9	84.3±2.0	85.9±3.1
G (GPa)	32.8±1.6	34.1±2.3	34.1±2.1	34.5±2.5
V_P (km/s)	6.74±0.11	6.84±0.13	6.87±0.13	6.91±0.17
V_S (km/s)	3.47±0.02	3.53±0.03	3.52±0.03	3.54±0.04
Ap (%)	23.1	22.9	23.1	23.7
A_{Smax} (%)	61.5	61.6	61.7	61.2

525

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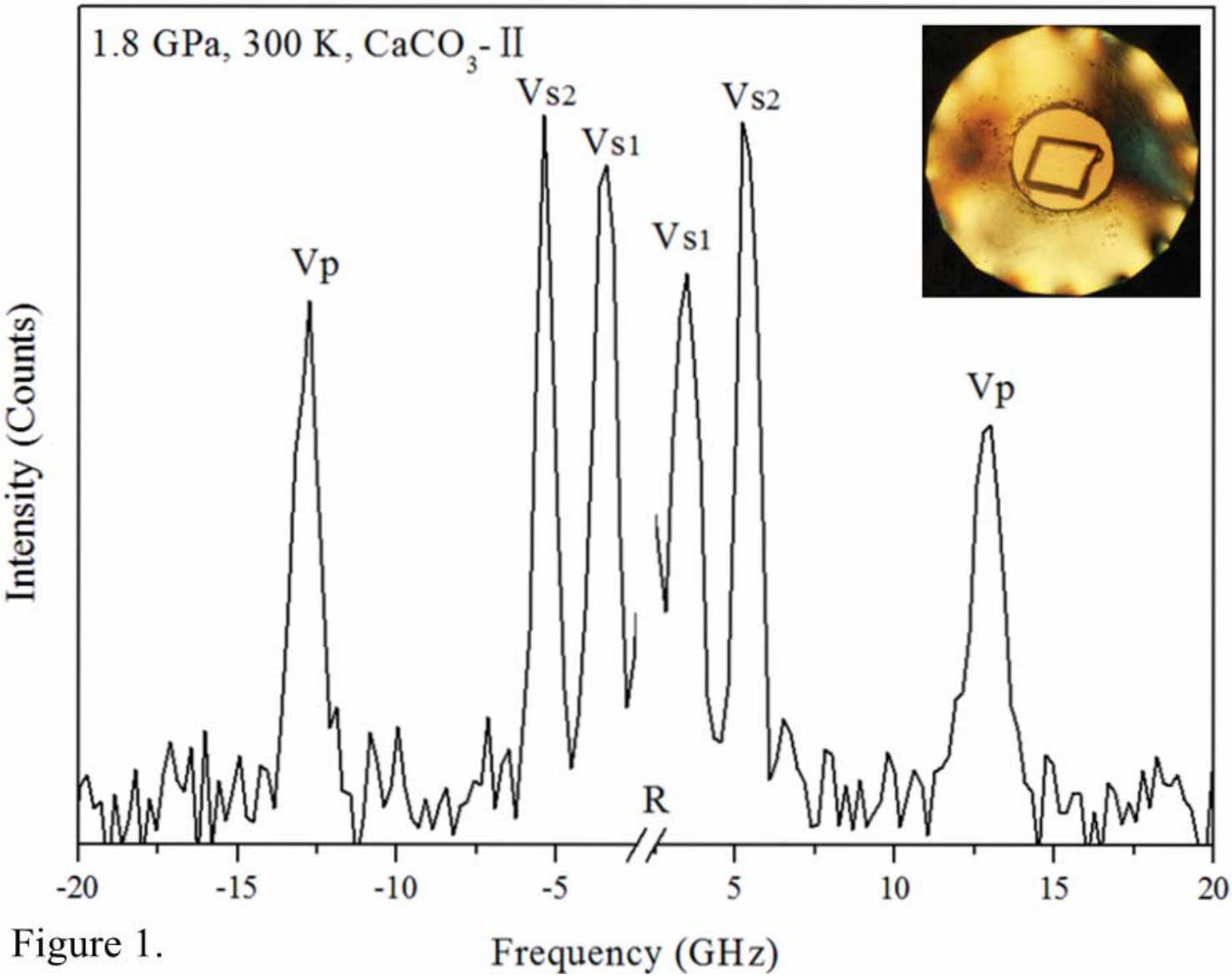

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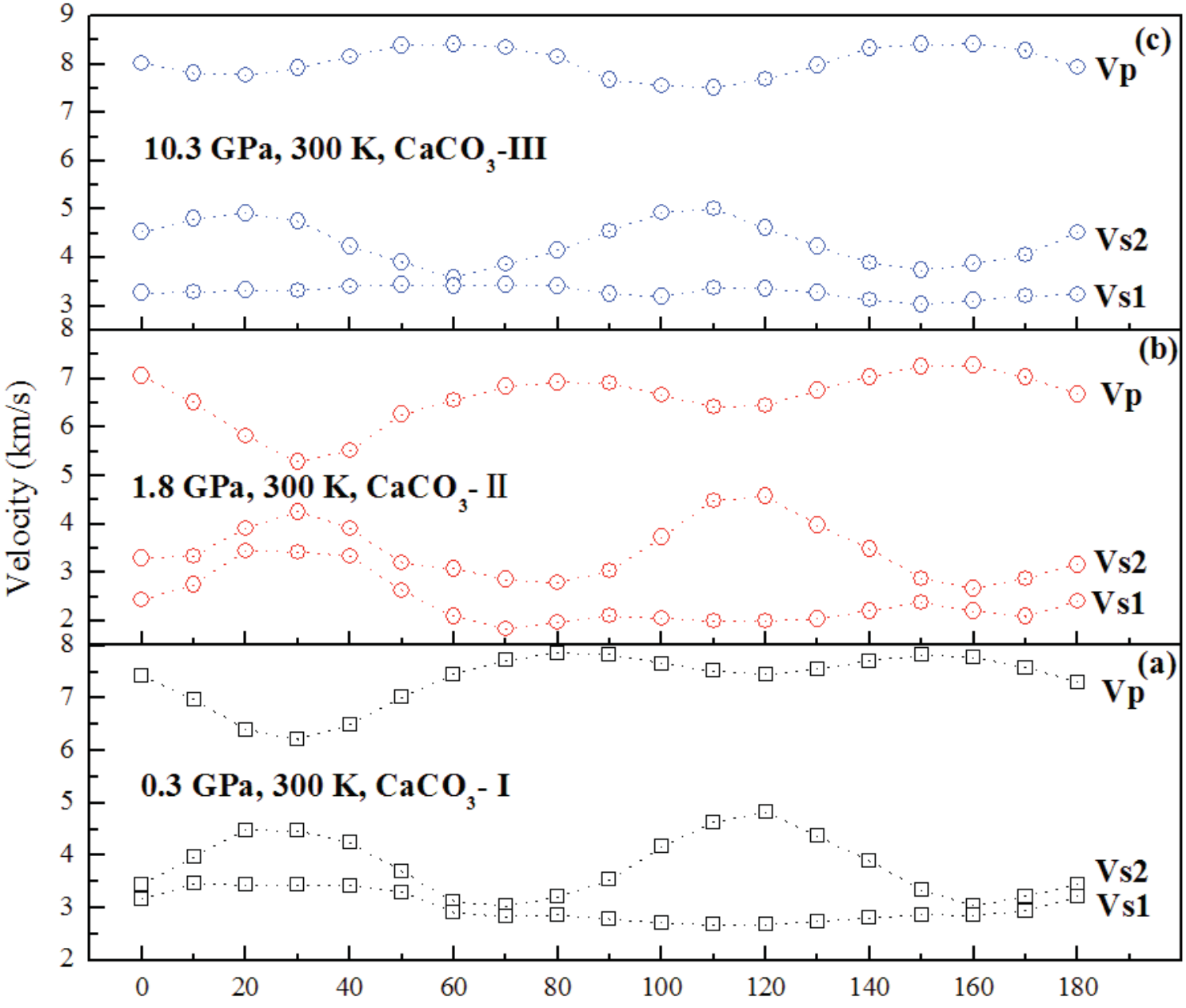

Figure 2.

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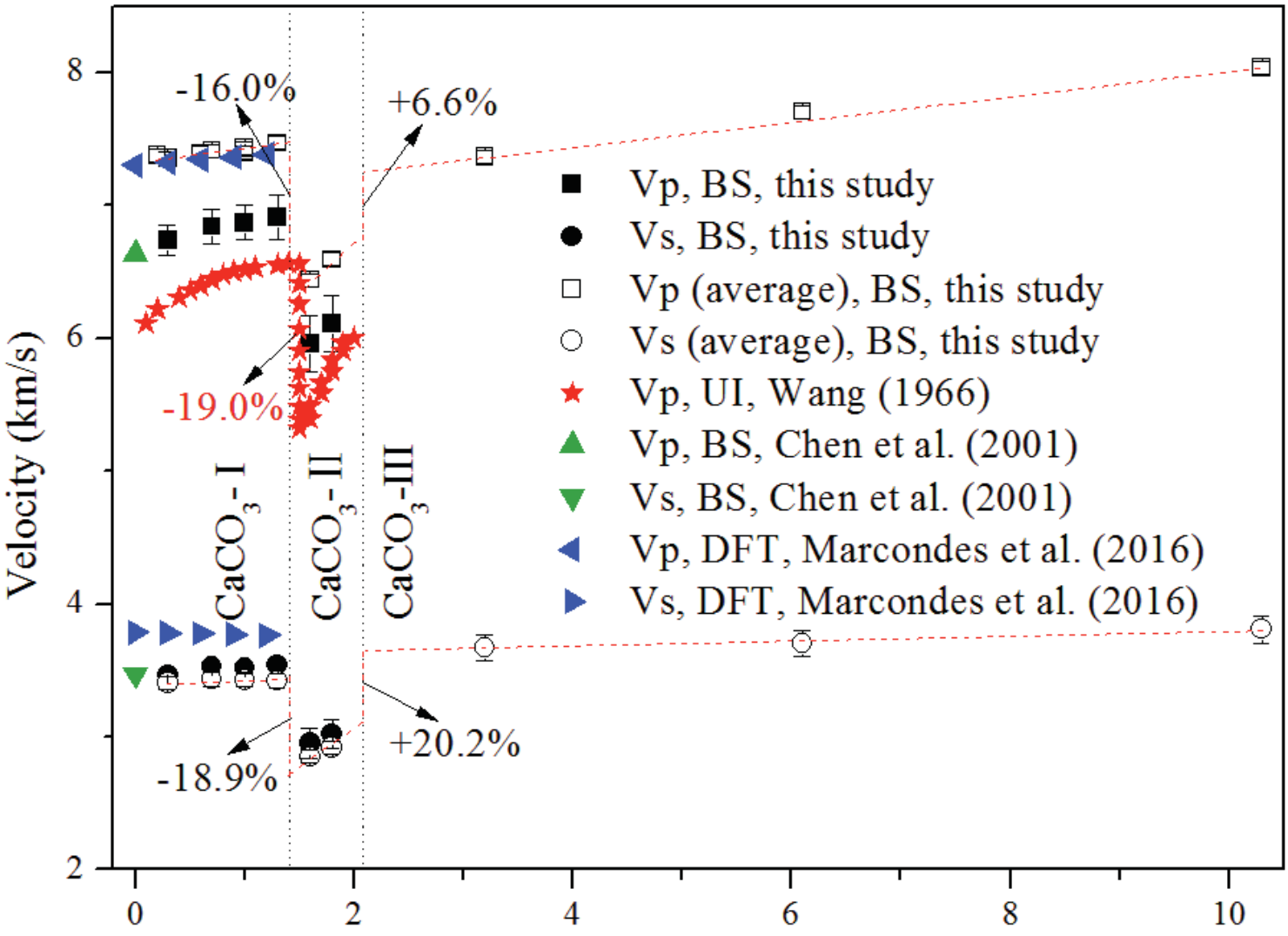

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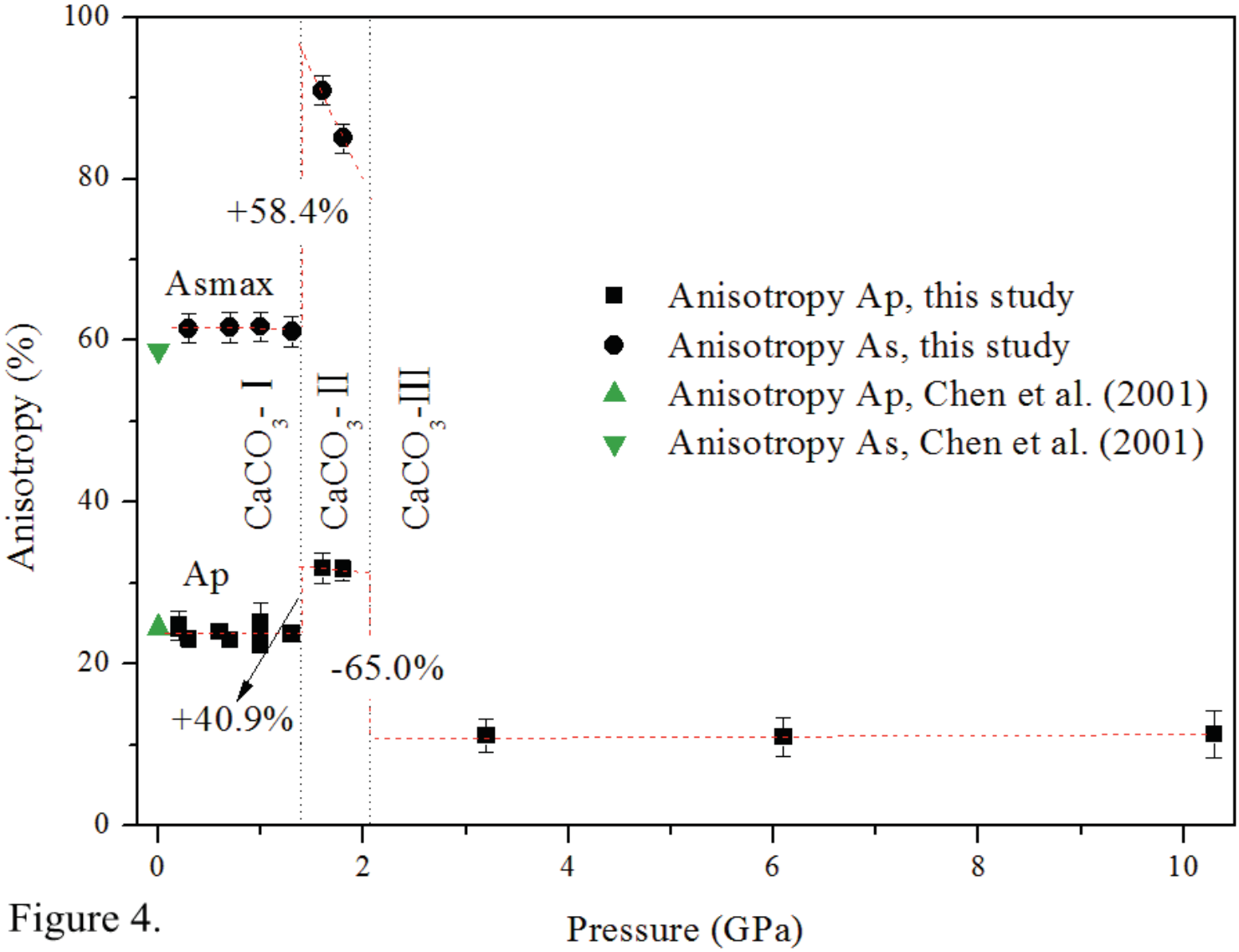

Figure 4.

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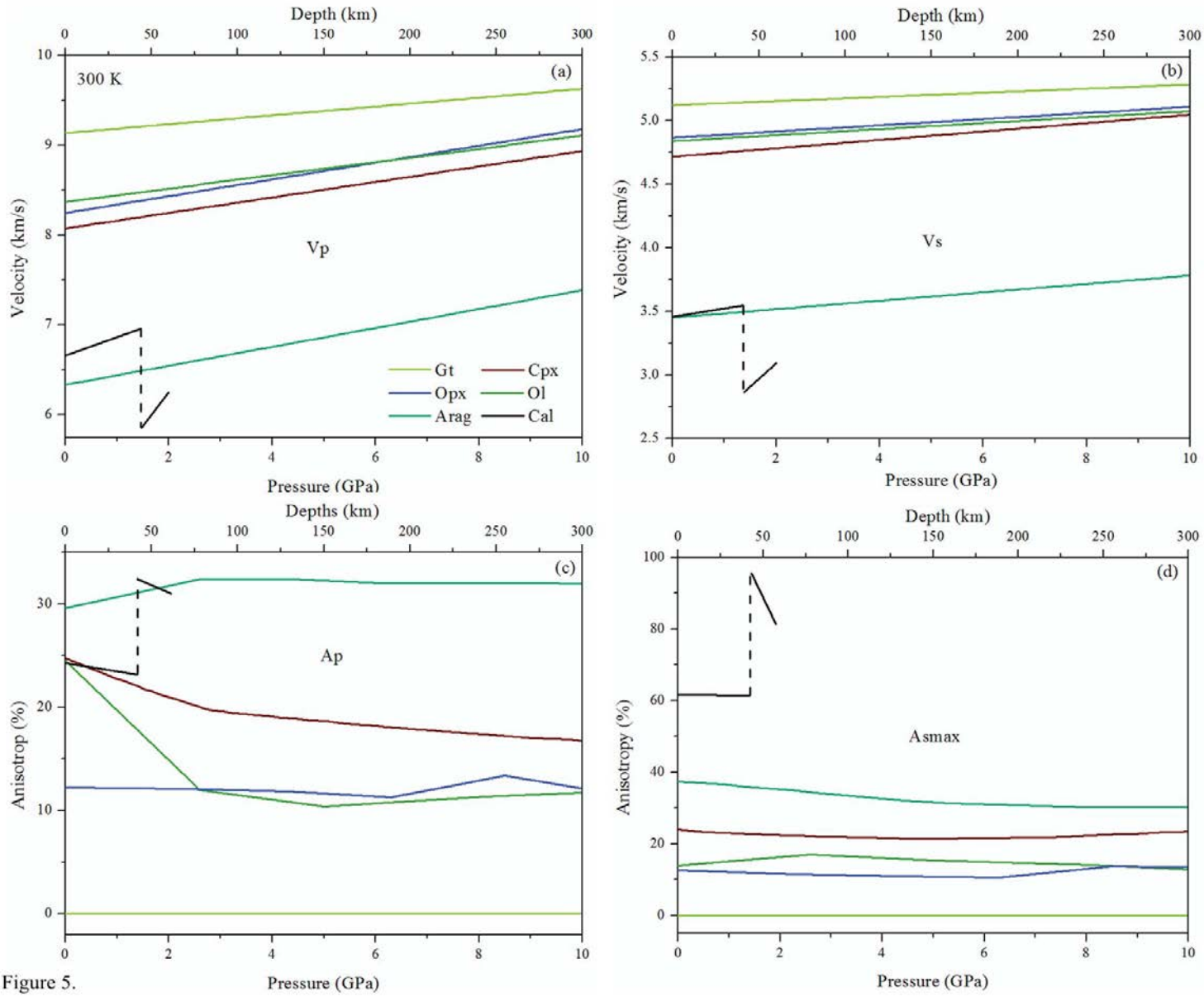

Figure 5.

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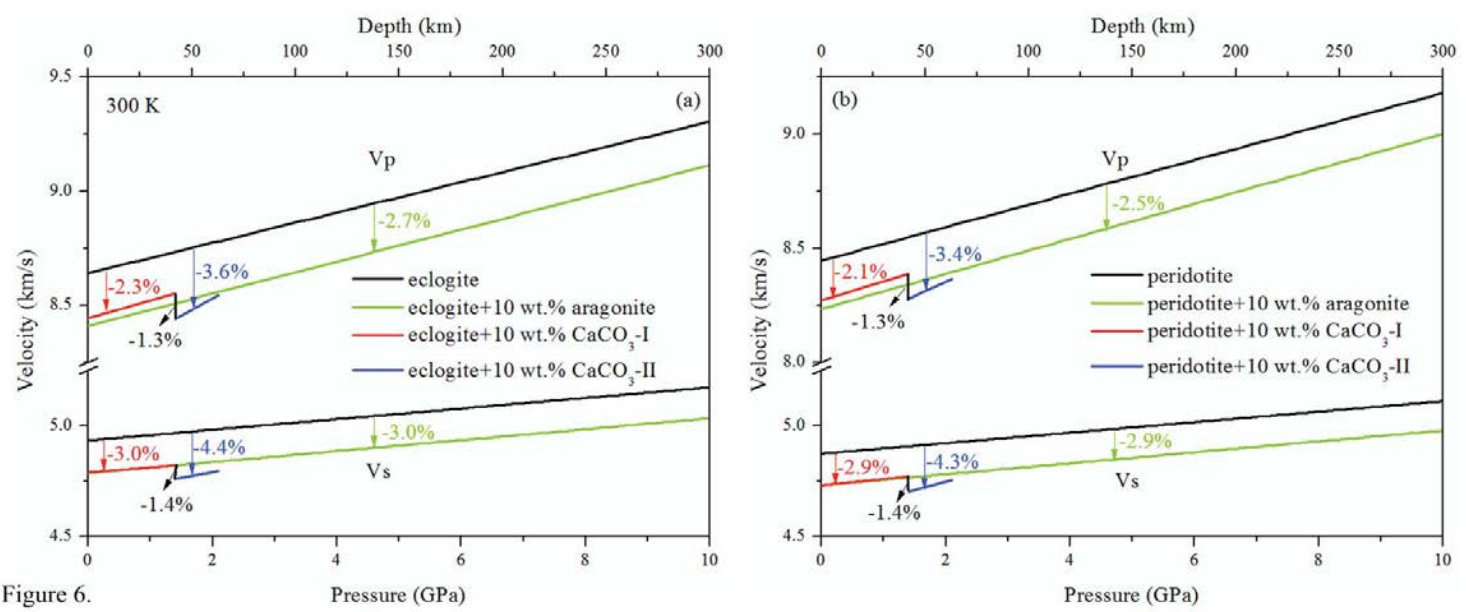

Figure 6.