Raman signatures of the distortion and stability of MgCO$_3$ to 75 GPa

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**Abstract**

Knowledge of the stability of carbonate minerals at high pressure is essential to better understand the carbon cycle deep inside the Earth. The evolution of Raman modes of carbonates with increasing pressure can straightforwardly illustrate lattice softening and stiffening. Here, we report Raman modes of natural magnesite MgCO$_3$ up to 75 GPa at room temperature using helium as a pressure-transmitting medium (PTM). Our Raman spectra of MgCO$_3$ show the splitting of $T$ and $v_4$ modes initiated at approximate 30 and 50 GPa, respectively, which may be associated with its lattice distortions. The MgCO$_3$ structure was referred to as MgCO$_3$-Ib at 30–50 GPa and as MgCO$_3$-Ic at 50–75 GPa. Intriguingly, at 75.4 GPa some new vibrational signatures appeared around 250–350 and ~800 cm$^{-1}$. The emergence of these Raman bands in MgCO$_3$ under relatively hydrostatic conditions is consistent with the onset pressure of structural transition to MgCO$_3$-II revealed by theoretical predictions and high-pressure and high-temperature experiments. This study suggests that hydrostatic conditions may significantly affect the structural evolution of MgCO$_3$ with increasing pressure, which shall be considered for modeling the carbon cycle in the Earth’s lower mantle.

**Keywords:** Carbonate, high pressure, Raman spectroscopy, lattice distortion

**Introduction**

Carbonate minerals play a significant role in the deep-carbon cycle of the Earth’s interior (Hazen et al. 2013; Hazen and Schiffris 2013). Geochemical and petrologic evidence indicates that carbon is subducted mainly as carbonates (e.g., Plank and Fiquet 2013). Therefore, there is a consensus on the crystal structure of MgCO$_3$-I (defined as “MgCO$_3$-I”). Santillán et al. (2005) observed evident changes in the vibrational modes of MgCO$_3$-I in infrared spectra at ~30 GPa, together with a remarkable decrease in the pressure dependence of the $v_1$ mode. They used KBr as a pressure-transmitting medium (PTM). However, there were no new Raman signatures observed in the similar pressure range when the methanol-ethanol 4:1 mixture (ME), argon, and KBr were used as PTMs (Gillet et al. 1993; Williams et al. 1992). In addition, no structural transition was evidenced through X-ray diffraction (XRD) experiments using argon or no PTM at pressures up to 83 GPa (Fiquet et al. 2002; Katsura et al. 1991). Interestingly, it was experimentally observed that rhombohedral MgCO$_3$-I transformed into orthorhombic MgCO$_3$-II at 115 GPa and 2100 K using Al$_2$O$_3$ powder as a PTM (Isshiki et al. 2004). These experimental results were later confirmed by theoretical calculations (Skorodumova et al. 2005; Panero and Kabbes 2008), which predict that MgCO$_3$-II becomes stable at ~113 GPa and 0 K. On the contrary, some theoretical calculations suggested that MgCO$_3$-I could transform into the MgCO$_3$-II phase with different structures, including $PT$, $C2/m$, and $P2_1/c$ at 75–85 GPa and 0 K (Li and Stackhouse 2020; Oganov et al. 2008; Pickard and Needs 2015). Similarly, recent high-pressure and high-temperature experiments have not reached a consensus on the crystal structure of MgCO$_3$-II using diamond-anvil cells (DAC) coupled with laser-heating XRD (Boulard et al. 2011; Maeda et al. 2017). Therefore, there is a
large discrepancy in the structural stability of MgCO$_3$ at lower mantle pressures among existing studies, demanding further dedicated investigation.

In the present work, we collected high-pressure Raman spectra of a natural MgCO$_3$ sample up to 75 GPa at room temperature in a DAC with helium (He) as a PTM. Since the deep mantle is under relatively hydrostatic conditions, the use of He as a PTM allowed us to better understand the structural evolution of MgCO$_3$ at high pressure, compared to the results in previous studies under non-hydrostatic conditions (e.g., Fiquet et al. 1994; Williams et al. 1992). The obtained Raman spectra indicate that the two lattice distortions in MgCO$_3$ likely occurred at 30 and 50 GPa, respectively, in the helium pressure medium, while spectroscopic signatures were observed for the transition from MgCO$_3$-I to MgCO$_3$-II at ~75 GPa. The lattice distortions may significantly affect the chemical bonding environments in MgCO$_3$ and its structural stability at elevated pressures. These results shed new light on the stability of carbonates under quasi-hydrostatic conditions, indicating that the effect of hydrostaticity must be taken into account for modeling the deep-carbon cycle (Efthimiopoulos et al. 2018).

**EXPERIMENTAL METHODS**

**Starting materials**

The starting material was a naturally occurring magnesite single-crystal sample from Dabieshan Mountain, China. The chemical composition of the magnesite sample was determined to be MgCO$_3$ with trace amounts of Ca, Fe, and Mn (<0.1 mol% in total) using a JEOL JXA-8200 electron microprobe. For simplicity, the sample was referred to as MgCO$_3$ thereafter. Single-crystal X-ray diffraction analyses confirmed the R$3c$ structure of the MgCO$_3$ sample, with lattice parameters $a = 4.6435(17)$ Å and $c = 15.0361(56)$ Å under ambient conditions. These lattice parameters are in good agreement with previous studies (Farsang et al. 2018; Fiquet et al. 1994; Liang et al. 2017).

**High-pressure Raman spectroscopy**

High-pressure Raman spectra of MgCO$_3$ were collected from 120 to 1292 cm$^{-1}$ using a Renishaw RM1000 Raman microscope equipped with a 250 mm spectrometer focal length at the Center for High Pressure Science and Technology Advanced Research (HPSTAR). The Raman signal was excited using an Ar$^+$ laser with a 532 nm wavelength, delivering a maximum power of 20 mW focused onto an ~2 μm spot by a Nikon L Plan EPI 20X, 0.35 objective. The spectral resolution was about 2 cm$^{-1}$ with a holographic diffraction grating of 1800 lines/mm. A symmetric diamond-anvil cell (DAC) was mounted with a pair of diamond anvils with 200 μm flat culets. The sample chamber was drilled in the center of a pre-indent tungsten gasket with diameter of 120 μm and thickness of ~30 μm. A platelet of single-crystal MgCO$_3$ sample with a thickness of 6–8 and ~30 μm in diameter was loaded into the sample chamber with the (101) crystal plane facing the incident laser beam, together with two ruby spheres as the pressure calibrant. The PTM, He, was loaded into the sample chamber using the high-pressure gas loading system at HPSTAR. The use of He still maintains the hydrostatic conditions at 50 GPa (Klotz et al. 2009) and thus can avoid the influence of deviatoric stress. The pressure was determined by multiple measurements of the ruby fluorescence before and after each experimental run (Mao et al. 1986). Raman spectra fitting was carried out using the software PeakFit v4.12 with the Voigt area method.

**RESULTS AND DISCUSSION**

Raman spectra of magnesite MgCO$_3$ were collected up to 75 GPa at room temperature using helium as a PTM (Fig. 1). Rhombohedral carbonates (e.g., calcite, magnesite, siderite, and rhodochrosite) with the space group R$3c$ have two lattice modes ($T$ and $L$ modes) and four internal modes [in-plane bend internal ($v_3$), symmetric stretch internal ($v_4$), the anti-symmetric stretch ($v_5$), and out-of-plane bend ($2v_5$)] modes (Boulard et al. 2012; Rividi et al. 2010). Therein, two Raman-active modes $v_3$ and $2v_5$ are hardly detected at high pressure due to their relatively weak intensity through diamond anvils. Four representative Raman modes at 213, 330, 737, and 1095 cm$^{-1}$ corresponding to $T$, $L$, $v_3$, and $v_5$, respectively, were collected for MgCO$_3$ at ambient conditions. These Raman mode values agree with previously reported literature values (Boulard et al. 2012; Farsang et al. 2018; Liang et al. 2018; Rividi et al. 2010). The $T$ and $L$ lattice modes result from the interactions between Mg$^{2+}$ and CO$_3^{2-}$ ions, while the $v_3$ and $v_5$ modes from the in-plane bending and symmetric stretching of the CO$_3^{2-}$ units, respectively (Farsang et al. 2018).

**Lattice distortion of MgCO$_3$ at high pressure**

Representative high-pressure Raman spectra of MgCO$_3$ are presented in Figure 1. The splitting of $T$ mode at 307 cm$^{-1}$ was detected at 29.6 GPa and was observed up to at least 75 GPa, the maximum pressure reached in this study. However, it is noted that Williams et al. (1992) did not observe any new Raman bands in magnesite around 30 GPa using the same method, possibly due to the broadening of Raman peaks of magnesite induced by the large deviatoric stress in the sample chamber. They used...
methanol–ethanol 4:1 mixture (ME) and argon as PTMs, both exhibiting non-hydrostaticity above 10 GPa (Klotz et al. 2009). That is, the splitting of $T$ mode observed in this study might be overlapped by the broadening of Raman peaks. In contrast, the use of He here as a PTM improves the hydrostatic conditions inside the sample chamber. The use of a soft PTM may crucially contribute to the splitting of $T$ mode at ~30 GPa. Furthermore, another Raman peak splitting was observed in the $v_4$ mode at ~883 cm$^{-1}$ at 51.1 GPa (Fig. 1). It was previously reported that the $v_4$ mode of dolomite splits into four separate Raman peaks using Ne as a PTM at ~39 GPa, whereas only one peak was observed within the same Raman region when argon was used as a PTM (Efthimiopoulos et al. 2018).

Fiquet et al. (2002) carried out synchrotron XRD experiments on magnesite MgCO$_3$ up to 83 GPa without using any PTMs. They concluded that there was no structural phase transition in the investigated pressure range. The anomalous compression behavior of sharp decreases in the $a$, $c$, and $\nu_4$ modes was reported in magnesite MgCO$_3$ at ~25 GPa, with silicone oil as a PTM by Fiquet et al. (1994). However, Ross (1997) suggested that such anomalies would be artificial and induced by deviatoric stress. Therefore, considering that the magnesite structure is structurally stable over 0–50 GPa, the splittings of $T$ and $v_4$ modes at ~30 and ~50 GPa would not be caused by a crystal structure transition, but rather by local lattice distortions.

By comparison, the splitting of the low-frequency $T$ mode at 175 cm$^{-1}$ around 11 GPa was reported in dolomite CaMg(CO$_3$)$_2$, while there were no significant changes in the remaining Raman-active modes (Efthimiopoulos et al. 2017). They assigned the new mode as a result of the local structural distortion of dolomite and denoted it as the CaMg(CO$_3$)$_2$-Ib phase. Although the splitting of $T$ mode in magnesite MgCO$_3$ occurs at ~20 GPa higher than that in dolomite, both would share the same nature. We thus denote distorted magnesite as the MgCO$_3$-Ib phase (magnesite-Ib) between 30 and 50 GPa. With the emergence of the splitting of $v_4$ mode at about 50 GPa, the MgCO$_3$-Ib phase would undergo further distortion. Consequently, it would be denoted as the MgCO$_3$-Ic phase (magnesite-Ic) between 50–75 GPa based on the similar phenomena observed in dolomite and calcite at high pressures (Binck et al. 2019; Efthimiopoulos et al. 2017; Pippinger et al. 2015).

Both laser Raman and infrared spectroscopy can probe the local structure of neighboring atoms and groups of atoms, and they are therefore sensitive to short-range order features (Cerantola et al. 2015). Santillán et al. (2005) collected infrared spectra of magnesite up to 60 GPa with the use of KBr as a PMT. They found an unexpected negative curvature of the $v_4$ asymmetric-stretch mode between 30 and 50 GPa, without observing any splitting of infrared modes between 0–60 GPa. Moreover, the frequency of the $v_4$ mode rapidly increased above 50 GPa, likely due to the strengthening of the O–O repulsion in the CO$_3^2-$ group as well as the reduction in the distance between the CO$_3^2-$ groups and cations, together with a sharp decrease in the C–O band length at ~50 GPa (Fiquet et al. 2002; Santillán et al. 2005). The splitting of those modes was absent in the infrared spectroscopic measurements on MgCO$_3$. The clue may be the use of different PTMs, He vs. KBr/Ar/ME, in those studies as described above in the Raman spectra of magnesite and dolomite (Efthimiopoulos et al. 2018).

The trend of intensity ratio and full-width at half maximum (FWHM) provides another qualitative measure of changes in local structures. They have been successfully applied in detecting lattice distortion and phase transition of materials (e.g., siderite and water ice) using a battery of probes including Mössbauer, Raman, and X-ray absorption fine structure spectroscopy (Cerantola et al. 2015; Hirai et al. 2014; Xu et al. 1996). To further elucidate the evolution of local structures of MgCO$_3$ as a function of pressure, the intensity ratio and FWHM were analyzed here (Figs. 2 and 3). The representative intensity ratios of the $L/v_4$ and $L/v_1$ of MgCO$_3$ with increasing pressure are shown in Figure 2. A clear decrease in the $L/v_1$ and $L/v_4$ ratios of MgCO$_3$ was detected from 0 to ~30 GPa. The $L/v_1$ values change approximately from 1.0 at ambient pressure to 0.2 at 30 GPa while the $L/v_4$ values change approximately from 8.4 at ambient pressure to 0.8 at 30 GPa.

![Figure 2](https://example.com/figure2.png)  
**Figure 2.** The intensity ratios of $L/v_1$ and $L/v_4$ in MgCO$_3$ with increasing pressure. Dashed lines represent the changing trends of the intensity ratios of $L/v_1$ and $L/v_4$. The kinks in the intensity ratio of $L/v_1$ are observed around 30 and 51 GPa, and are likely due to the lattice distortions of MgCO$_3$. (Color online.)

![Figure 3](https://example.com/figure3.png)  
**Figure 3.** The FWHM of $v_1$ and $v_4$ modes as a function of pressure. (Color online.)
owing to the relatively large increase in Raman intensities of the \( v_1 \) and \( v_4 \) modes with increasing pressure. Both the intensity ratios of the \( L/v_1 \) and \( L/v_4 \) of MgCO\(_3\) exhibit a plateau pattern at 0.2 and 0.7, respectively, between 30–50 GPa. A second plateau seems to appear in the \( L/v_1 \) and \( L/v_4 \) ratios approximately at 0.1 and 0.5, respectively, between 50–75 GPa. The changes in the \( L/v_1 \) and \( L/v_4 \) intensity ratios are mainly related to the change of the CO\(_3^2^-\) group. In addition, the internal \( v_1 \) and \( v_4 \) modes rise from the symmetric and asymmetric stretching of CO\(_3^2^-\) group, and the C-O bond in CO\(_3^2^-\) group undergoes pressure-induced shortening with increasing pressure between 0–30 GPa as revealed by infrared and XRD studies (Fiquet et al. 2002; Santillán et al. 2005). Upon compression, the carbonate groups are pushed closer, which changes their chemical bonds relative to the crystallographic axes and thus leads to the sharp increase of the polarizability (Chukanov and Vignasina 2020). Hence, the pressure-induced packing of magnesite structure enhances the intensity of \( v_1 \) and \( v_4 \) modes due to the positive correlation between Raman intensity and polarizability (Larkin 2011). On the contrary, the CO\(_3^2^-\) group undergoes pressure-induced lengthening with increasing pressure from \( \sim 30–40 \) GPa (Fiquet et al. 2002; Lin et al. 2012; Santillán et al. 2005). Santillán et al. (2005) considered the C-O distance might be overestimated due to the large deviatoric stress induced by the absence of PTM in the sample chamber of Fiquet et al. (2002). They suggested a minor increase in the C-O bond length from \( \sim 30–40 \) GPa. The process may lead to a decrease in the polarizability and thus reduce the intensity of \( v_1 \) and \( v_4 \) modes (namely, increase the \( L/v_1 \) and \( L/v_4 \) values) to some extent at \( \sim 30–40 \) GPa. The change is more obvious in the \( v_4 \) mode because it directly relates to the C-O bond. The intensity ratios of the \( L/v_1 \) and \( L/v_4 \) further diminish as the compression of CO\(_3^2^-\) group increases with increasing pressure. A minor deviation from the decreasing intensity trend was observed around 50 GPa, possibly due to increased stiffness of the MgO octahedra and CO\(_3^2^-\) unit (C-O bond) (Fiquet et al. 2002; Santillán et al. 2005). Furthermore, note that the FWHM values of the \( v_1 \) and \( v_4 \) modes decrease from \( \sim 13 \) to 5 cm\(^{-1}\) and from 16 to 7 cm\(^{-1}\), respectively, at pressures up to \( \sim 15 \) GPa (Fig. 3). The reduction in the FWHM with increasing pressure likely results from the enhancement of ordered arrangement of atoms in magnesite as observed in water and deuterated water (D\(_2\)O) at \( \sim 11 \) GPa (Hirai et al. 2014; Pruzan et al. 1990; Xu et al. 1996). The FWHM values of \( A_{1g} \) modes (O-H and O-D stretching mode) in ice-VII and deuterated ice-VII phase significantly decrease with increasing pressure up to \( \sim 11–13 \) GPa and clearly increase thereafter. The minimum of the FWHM of \( A_{1g} \) mode occurs at \( \sim 11–13 \) GPa, corresponding to the highest ordering of ice-VII and deuterated ice-VII (Hirai et al. 2014; Pruzan et al. 1990; Xu et al. 1996). Between 15–28 GPa, the FWHM values of the \( v_1 \) and \( v_4 \) modes marginally increase by \( \sim 1 \) cm\(^{-1}\) prior to lattice distortions occurring in magnesite. At pressure around 30 GPa, both the FWHM values of \( v_4 \) and \( v_1 \) modes sharply increase. Both fluctuate around 12 cm\(^{-1}\) at approximately 35–75 GPa (Fig. 3). It can be attributed to the enhanced positional disorder of magnesite (Bischoff et al. 1985), resulting from the rotation of MgO octahedra around the c axis and the associated change in C-O bond as proposed by Fiquet et al. (2002) and Santillán et al. (2005).

The structural transition of MgCO\(_3\) at 75 GPa and room temperature

Interestingly, several new Raman bands appeared in the frequency range of 250–350 and \( \sim 800 \) cm\(^{-1}\) in MgCO\(_3\) at 75 GPa and room temperature in the He pressure medium (Fig. 1). Note that the XRD pattern of MgCO\(_3\) was not collected due to the failure of the diamond anvils at 75 GPa. Recently, Li and Stackhouse (2020) theoretically predicted the phase transition pressure from magnesite-I to magnesite-II (space group: \( PT \)) at 75 GPa and 0 K, which coincides with the pressure at which the new Raman bands of MgCO\(_3\) emerged in the He pressure medium in our experiments. Meanwhile, Pickard and Needs (2015) also reported a comparable transition pressure from \( R3c \) to \( PT \) at 85 GPa from magnesite-I to magnesite-II via theoretical calculations. Hence, the \( R3c \) to \( PT \) phase transition may be responsible for the new Raman bands of MgCO\(_3\) in the frequency range between 250–350 and \( \sim 800 \) cm\(^{-1}\) at 75 GPa. Alternatively, other possible structures (i.e., \( C2/m \), orthorhombic, etc.) could be responsible for those new vibrational modes due to the large uncertainty of phase transition pressure from theoretical calculations (Li and Stackhouse 2020; Oganov et al. 2013; Pickard and Needs 2015). Further high-pressure XRD experiments under hydrostatic environment are required to determine the onset pressure of phase transition and high-pressure crystal structure of magnesite-II.

Vibrational properties of MgCO\(_3\) at high pressure

Raman shifts of MgCO\(_3\) with increasing pressure can be linearly fitted at 0–29, 30–50, and 50–75 GPa, respectively (Fig. 4; Table 1). In the pressure range from 0 to 29 GPa, the pressure-induced Raman shifts of \( T, L, v_3, \) and \( v_1 \) modes are 2.91, 4.20, 1.82, and 2.78 cm\(^{-1}\)/GPa, respectively. The slopes of the external modes (\( T \) and \( L \)) are generally larger than the internal modes (\( v_3 \) and \( v_1 \)) due to the greater compressibility between Mg\(^{2+}\) cation and CO\(_3^2^-\) ions than the CO\(_3^2^-\) unit (C-O bond) (Farsang et al. 2018). Our results using He as the PTM agree well with Liang.

![Figure 4. Raman shifts of MgCO\(_3\) at high pressures. Raman shifts of each mode as a function of pressure can be well linearly fitted at 0–29, 29–50, and 50–75 GPa. Error bars are not shown for clarity. (Color online.)](image-url)
et al. (2018) using neon (Ne). This indicates that the enhanced hydrostasticy from Ne to He has little influence on the pressure-induced Raman shift of MgCO$_3$. The $dv/dP$ slopes from other studies (see Table 1) mostly range within 20% difference from our result (Farsang et al. 2018; Gillet et al. 1993; Williams et al. 1992). The deviation could be mainly attributed to the dramatic increase of shear stress above 10 GPa for the use of ME and argon as PTMs by Williams et al. (1992) and that of KBr by Gillet et al. (1993). The little discrepancy could be mainly accounted for by the narrow pressure range using ME as the PTM and composition effect of minor iron-bearing magnesite (Mg$_{0.96}$Ca$_{0.04}$Fe$_{0.01}$CO$_3$) from Farsang et al. (2018). In the pressure range from 30 to 50 GPa, the corresponding pressure-induced Raman shifts of $T$, $L$, $v_4$, and $v_1$ modes are 2.09, 3.12, 1.42, and 1.99 cm$^{-1}$/GPa, respectively. Those values further reduce to 1.77, 2.27, 1.26, and 1.86 cm$^{-1}$/GPa between 50 and 75 GPa (Table 2). Compared with the MgCO$_3$-I phase, the $dv/dP$ values drop significantly by 22–28% for MgCO$_3$-Ib and 7–27% for MgCO$_3$-Ic. These results indicate that MgCO$_3$-Ib and MgCO$_3$-Ic have vibrational properties distinct from MgCO$_3$-I, and magnetite becomes stiffer when it undergoes lattice distortions. It is probably due to the large incompressibility of the CO$_2$ and MgO octahedra with increasing pressure, which may contribute to their notable stability (Fiquet et al. 2002; Santillán et al. 2005). Therein, the increase of C-O bond length accompanied by a sharp decrease in the Mg-O bond length at ~30 GPa may contribute to the lattice distortion from MgCO$_3$-I to MgCO$_3$-Ib. On the contrary, the decrease of C-O bond length accompanied by a slow decrease of Mg-O bond length at ~50 GPa may contribute to the lattice distortion from MgCO$_3$-Ib to MgCO$_3$-Ic (Fiquet et al. 2002; Santillán et al. 2005).

Mode Grüneisen parameters provide important information about the relative contributions of each vibration to the thermochemical properties (Williams et al. 1992). Combining XRD and Raman results from previous work and this study, the mode Grüneisen parameters ($\gamma$) can be derived as follows:

$$\gamma_i = -\frac{d \ln \nu_i}{d \ln V} = \frac{K_v}{V} \left(\frac{dv_i}{dP}\right)$$

where $\nu_i$, $V$, $P$, and $K_v$ are the frequency at ambient conditions in cm$^{-1}$, volume in Å$^3$, pressure in GPa and isothermal bulk model in GPa, respectively. The $K_v$ set as 115 GPa from Fiquet and Reynard (1999) with $K_v$ fixed to 4 was used to derive the mode Grüneisen parameters $\gamma_i$ of MgCO$_3$. Based on the Equation 1, the $\gamma_i$ value depends on the values of $1/\nu$ and $dv/dP$ due to the fixed $K_v$ at a giving pressure. It means that the lower-frequency $\nu_i$ and higher slope $dv/dP$ correspond to larger mode Grüneisen parameters $\gamma_i$. As shown in Table 1, the frequencies of internal modes ($T$ and $L$) of MgCO$_3$ at ambient conditions are much lower than those of external modes ($v_4$ and $v_1$) while their slopes $dv/dP$ are much larger than the latter. The $\gamma_i$ for the internal modes ($T$ and $L$) and external modes ($v_4$ and $v_1$) of MgCO$_3$ at ambient conditions are 1.57, 1.46, 0.28, and 0.29, respectively. The values of the internal modes are about five times those of the external modes. In line with other carbonates, the major contribution to the thermodynamic Grüneisen parameters is from the $T$ and $L$ modes (Williams et al. 1992).

Our mode Grüneisen parameters agree with those values reported by Liang et al. (2018) using Ne as the PTM, implying comparable hydrostaticity between He and Ne (Klotz et al. 2009). Moreover, the mode Grüneisen parameter $\gamma$ of the $T$ mode in magnetite is 2.6 (Gillet et al. 1993), which is much higher than the values from this and other studies (Farsang et al. 2018; Liang et al. 2018). The reason is that Gillet et al. (1993) calculated the $\gamma$ values by using the first item (value with 4.6 cm$^{-1}$/GPa) of second-order polynomial fitting to the $dv/dP$ and neglected the second item (Table 1). We analyzed their data and used linear

### Table 1. Vibrational parameters of MgCO$_3$-I at high pressures from this and previous studies

<table>
<thead>
<tr>
<th>Raman mode</th>
<th>Mag100$^1$(He)</th>
<th>Mag96$^2$(ME)</th>
<th>Mag100$^1$(Ne)</th>
<th>Mag100$^2$(KBr)</th>
<th>Mag$^2$(ME)</th>
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<tbody>
<tr>
<td>$dv/dP$ $\gamma_i$</td>
<td>$dv/dP$ $\gamma_i$</td>
<td>$dv/dP$ $\gamma_i$</td>
<td>$dv/dP$ $\gamma_i$</td>
<td>$dv/dP$ $\gamma_i$</td>
<td>$dv/dP$ $\gamma_i$</td>
</tr>
<tr>
<td>$T$</td>
<td>2.91(10) 1.57(7)</td>
<td>3.52(3) 1.76</td>
<td>3.08(5) 1.49(2)</td>
<td>4.6(4) -4.4(3) $10^{-1}$ 2.6</td>
<td>2.6(2) 1.4(1)</td>
</tr>
<tr>
<td>$L$</td>
<td>4.20(10) 1.46(5)</td>
<td>4.89(3) 1.59</td>
<td>4.49(5) 1.40(2)</td>
<td>4.5(3) 1.7</td>
<td>4.7(1) 1.67(4)</td>
</tr>
<tr>
<td>$v_4$</td>
<td>1.82(2) 0.28(1)</td>
<td>1.52(4) 0.22</td>
<td>1.83(2) 0.26(1)</td>
<td>1.42(2) 0.23</td>
<td>1.52(5) 0.24(3)</td>
</tr>
<tr>
<td>$v_1$</td>
<td>2.78(3) 0.29(1)</td>
<td>2.87(4) 0.28</td>
<td>2.87(2) 0.27(1)</td>
<td>2.5(3) 0.28</td>
<td>2.3(1) 0.24(2)</td>
</tr>
</tbody>
</table>

Notes: $dv/dP$ in the unit of cm$^{-1}$/GPa. $\gamma_i$ = Mode Grüneisen parameters. ME = Methanol and ethanol (4:1).

$^1$Mag100 = Mg$_{0.99}$Mn$_{0.01}$Fe$_{0.01}$CO$_3$ from this study. The measured initial frequencies of Raman modes for MgCO$_3$-I at 0 GPa are chosen to calculate the mode Grüneisen parameters $\gamma_i$.

$^2$Mag96 = Mg$_{0.96}$Ca$_{0.04}$Fe$_{0.01}$CO$_3$ from Farsang et al. (2018).

$^3$Mag100 = Mg$_{0.999}$Mn$_{0.001}$Fe$_{0.01}$CO$_3$ Liang et al. (2018).

$^4$Mag100 = MgCO$_3$ Gillet et al. (1993).

$^5$Mag = Unknown composition, Williams et al. (1992).

### Table 2. Vibrational parameters of MgCO$_3$-Ib, MgCO$_3$-Ib, and MgCO$_3$-Ic at high pressures

<table>
<thead>
<tr>
<th>Raman mode</th>
<th>Mag100-1b (28–50 GPa)</th>
<th>Mag100-1c (50–75 GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_4$ (cm$^{-1}$)</td>
<td>$dv/dP$ $\gamma_i$</td>
<td>$v_4$ (cm$^{-1}$)</td>
</tr>
<tr>
<td>$T$</td>
<td>213 2.91(10) 1.57(7)</td>
<td>297 2.09(1) 0.81(5)</td>
</tr>
<tr>
<td>$L$</td>
<td>330 4.20(10) 1.46(5)</td>
<td>455 3.12(17) 0.79(5)</td>
</tr>
<tr>
<td>$v_4$</td>
<td>737 1.82(2) 0.28(1)</td>
<td>790 1.42(10) 0.21(2)</td>
</tr>
<tr>
<td>$v_1$</td>
<td>1095 2.78(3) 0.29(1)</td>
<td>1177 1.99(13) 0.19(1)</td>
</tr>
</tbody>
</table>

Notes: The measured initial frequencies of Raman modes for MgCO$_3$-Ib, MgCO$_3$-Ib, and MgCO$_3$-Ic at 0, 29.6, and 51.1 GPa, respectively, are chosen to calculate their mode Grüneisen parameters $\gamma_i$. The bulk moduli $K_v$ set as 115 GPa from Fiquet and Reynard (1999) with $K_v$ fixed to 4 was used to derive the mode Grüneisen parameters $\gamma_i$ of MgCO$_3$. $dv/dP$ in the unit of cm$^{-1}$/GPa. $\gamma_i = $ Mode Grüneisen parameters.
fitting to derive the slope. We obtained a value of 2.9 cm$^{-1}$/GPa, which is similar to the values reported in this study and previous literature (Liang et al. 2018; Williams et al. 1992), thereby further confirming our assumption. The mode Grüniesen parameters $\gamma$ of the MgCO$_3$-Ib and MgCO$_3$-Ic phases further decrease compared to the MgCO$_3$-I phase. The corresponding mode Grüniesen parameters $\gamma$ are listed in Table 2. Compared with the results of the high-pressure MgCO$_3$ Ib and Ic phases, the $\gamma$ values drop significantly by 27–48% for MgCO$_3$-I to MgCO$_3$-Ib and 10–36% for MgCO$_3$-Ib to MgCO$_3$-Ic.

**Implications**

Raman-active modes provide bonding environment information about structures of high-pressure phases (Boulard et al. 2020; Vennari and Williams 2018). In this study, we have detected a lower-frequency $T$ mode at 29.6 GPa corresponding to a distance increasing between the CO$_2$-groups and cations and a higher-$\nu_c$ mode at 51.1 GPa corresponding to a strengthening of the O-O repulsion in the CO$_2$' group by Raman spectroscopy. The phenomena are due to the formation of MgCO$_3$-Ib and MgCO$_3$-Ic via rotation of MgO, octahedra (Santillán et al. 2005). Interestingly, the stability of magnesite is improved through increasing the bond-length of CO$_3$ units with pressure at the expense of a weaker MgO, octahedra. The distorted environment of the chemical bond would greatly improve the stability of magnesite over a large pressure and temperature range and thus prevent it from melting or decomposition (Boulard et al. 2020; Fiquet et al. 2002; Santillán et al. 2005). A similar lattice distortion was also reported in calcite (e.g., Calcite-Iii-b) and dolomite (e.g., Dolomite-Ib, Dolomite-Iiib, Dolomite-IIIc) due to the distorted CaO$_2$ and/or MgO, octahedra (Bincik et al. 2019; Efthimiopoulos et al. 2017; Merlini et al. 2014; Pippinger et al. 2015). More interestingly, the occurrence of the distortion phase Calcite-Iii-b was shown in sediments in nature from the surface in quaternary loess deposits in Central Asia (Schaebertz et al. 2015). The MgCO$_3$-Ib and MgCO$_3$-Ic phases might be preserved in superdeep diamond inclusions.

Interestingly, five new Raman modes were observed at 75 GPa, which may be assigned to the magnesite-II phase with possible structures of $PT$, $C2/m$, orthorhombic, etc. (Li and Stackhouse 2020; Maeda et al. 2017; Oganov et al. 2008; Pickard and Needs 2015). Both experimental and theoretical evidence indicates that magnesite-II represents a diversity of distorted structural environments, where corner-sharing CO$_3$ tetrahedra form C$_4$O$_3$ three-membered rings within the carbonate groups and cation sites (Boulard et al. 2011; Li and Stackhouse 2020; Oganov et al. 2008). Compared to the low-pressure threefold coordinated carbonates (CO$_3$)$^{2-}$ triangles in the $R3c$ structure, the tetrahedrally coordinated carbonates are expected to exhibit substantially different reactivity and different chemical properties in the liquid state (Boulard et al. 2015). These crystallographic characteristics in carbonates may play an important role in deep carbon reservoirs and fluxes in the deep Earth (Boulard et al. 2020). Furthermore, since isotopic fractionation intrinsically reflects different chemical bonding environments among different phases, the bonding strength changes in MgCO$_3$ through lattice distortion and structural transition likely impact the distribution of carbon and magnesium isotopes in the deep mantle (Li et al. 2017).

**Acknowledgments and Funding**

We appreciate two anonymous reviewers for their constructive suggestions and comments, which helped improve the manuscript significantly. We also acknowledge D. Tröger and P. Dera for thoughtful discussions. This work was funded by the National Key Research and Development Program of China (2019YFA0708502). J. Liu acknowledges support from the National Natural Science Foundation of China (NSFC Grant no. U1930401).

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MANUSCRIPT RECEIVED FEBRUARY 24, 2020

MANUSCRIPT ACCEPTED JULY 1, 2020

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