Effects of hydrostaticity on the structural stability of carbonates at lower mantle pressures: the case study of dolomite

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Abstract We have conducted high pressure far-infrared absorbance and Raman spectroscopic investigations on a natural iron-free dolomite sample up to 40 GPa. Comparison between the present observations and literature results unraveled the effect of hydrostatic conditions on the high pressure dolomite polymorph adopted close to 40 GPa, i.e. the triclinic Dol-IIIc modification. In particular, non-hydrostatic conditions impose structural disorder at these pressures, whereas hydrostatic conditions allow the detection of an ordered Dol-IIIc vibrational response. Hence, hydrostatic conditions appear to be a key ingredient for modeling carbon subduction at lower mantle conditions. Our complementary first-principles calculations verified the far-infrared vibrational response of the ambient- and high-pressure dolomite phases.

Introduction

Carbonates constitute the most abundant carbon-bearing minerals on the Earth's crust. Experimental evidence gathered over the past decade strongly indicates that carbonates can be regarded as primary hosts for the carbon cycle in the deep Earth [1–3]. Consequently, the high-pressure and high-temperature behavior of carbonates has attracted worldwide interest in recent years [4–15]. These investigations have established the presence of several different carbonate polymorphs upon high-pressure and/or high-temperature treatment, thus enhancing the idea of carbonates 'surviving' lower mantle conditions [16,17].

One of the most common carbonate minerals is dolomite with chemical formula $CaMg(CO_3)_2$. At ambient conditions, dolomite adopts a rhombohedral structure (space group SG $R\bar{3}$, $Z = 3$) [18]. This phase is composed of alternating layers of CaO_6 and MgO_6 octahedra stacked along the c-axis (in the ordered modification), separated by triangular CO_3 units lying in a nearly planar and parallel arrangement along the ab plane (**Fig. 1**). This phase will be referred to as Dol-I from this point on. We note that partial substitution of Mg^{2+} by Fe^{2+} and/or Mn^{2+} is frequently observed in natural samples [19].

Early high pressure spectroscopic and structural studies conducted at ambient temperature (RT) indicated the stability of the Dol-I structure up to 28 GPa [20–23]. More recent investigations, however, revealed two structural transitions between ambient pressure and 60 GPa [4,8,9]. The first high-pressure phase is adopted near 17 GPa (SG $P\bar{1}$, $Z = 2$, Dol-II). In this Dol-II structure, the coordination of Ca^{2+} increases to eightfold with respect to the oxygen anions, whereas the Mg^{2+} cations retain their sixfold coordination and the CO_3 units remain co-planar as in the Dol-I phase (**Fig. 1**). Despite the Ca^{2+} coordination increase, the Dol-I→Dol-II transformation was shown to be a second-order/displacive transition, reminiscent of the $CaCO_3$ calcite-I→calcite-II transition [24,25].

A second high-pressure polymorph was detected close to 35 GPa (SG $P\bar{1}$, $Z = 8$, Dol-III) [9]. In this phase, both the Ca^{2+} and Mg^{2+} cations exhibit mixed sevenfold and ninefold coordinations. In addition, carbon ions were shown to approach fourfold coordination

between 60-80 GPa [26]. More recent investigations, however, indicate that the exact symmetry of the Dol-III structure is dependent on the Fe^{2+} content of the starting dolomite sample. In particular, a triclinic Dol-IIIc modification ($P1$, $Z = 8$) was found close to 41.5 GPa for a Fe-free dolomite sample, whereas a rhombohedral Dol-IIIb phase ($R3$, $Z = 21$) was adopted above 36 GPa for a Fe-rich $CaFe_{0.4}Mg_{0.6}(CO_3)_2$ dolomite [27]. In **Table 1** we provide a thorough overview of the relevant experimental high-pressure works on dolomite.

Previous high-pressure infrared (IR) and Raman spectroscopic investigations on virtually Fe-free dolomite samples conducted with argon [28] and neon [26] serving as a pressure transmitting media (PTM), recorded the vibrational signature of the Dol-I→Dol-II transition occurring at around 15-17 GPa. Upon further pressure increase, the spectroscopic studies conducted with argon as PTM indicated a structurally disordered Dol-IIIc[1] phase above 38-40 GPa; on the other hand, a recent high-pressure Raman study with neon as PTM recorded clearly an ordered Dol-IIIc Raman spectrum [26], in agreement with the relevant high-pressure XRD experiments [9,27]. Prompted by this discrepancy, we have conducted additional high-pressure Raman spectroscopic investigations with neon as PTM on the same dolomite sample previously probed with argon as PTM [28], in order to understand the PTM effect on the vibrational signature, and consequently the structure of the high-pressure Dol-IIIc modification. Furthermore, we have performed the first high-pressure far-infrared (FIR) absorbance investigations on dolomite, complemented with first-principles calculations, with

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[1] We remind here that the most recent high-pressure XRD investigation indicated the adoption of a triclinic Dol-IIIc polymorph at 41.5 GPa (neon PTM, RT) for a Fe-free dolomite sample [27], rather than the previously reported (also triclinic) Dol-III structure [9]; since our sample was also a Fe-free dolomite, we will be using the Dol-IIIc nomenclature in the present paper.

a less hydrostatic PTM (i.e. petroleum jelly). Taken together, we unravel the effect of hydrostatic conditions on the pressure-induced structural response of dolomite.

Methods

Experimental Details

Our investigations were conducted on a natural dolomite sample with stoichiometry $CaMg_{0.98}Fe_{0.02}(CO_3)_2$ [29]. The phase-purity of the sample was checked with X-ray diffraction measurements at ambient conditions. Diamond anvil cells (DACs) equipped with low-fluorescence type II diamonds of either 400 μm or 300 μm culet diameters were used for pressure generation. Rhenium gaskets were preindented to a 30-40 μm thickness, with holes of 100-180 μm diameters serving as sample chambers in separate runs. The ruby fluorescence method was used for pressure calibration [30].

The high-pressure FIR absorbance measurements were performed on dolomite powder (ground from single crystals) diluted in petroleum jelly; the latter acted also as PTM as it does not exhibit any IR activity, unlike the neon PTM used in our high-pressure Raman studies [31]. The experiments were conducted with the newly commissioned FIR microscope at the IRIS beamline, BESSY II synchrotron facility, coupled to a Vertex 70v Fourier-transform infrared (FTIR) spectrometer. The spectra were collected in the 50-600 cm^{-1} frequency region with a spectral resolution of 2 cm^{-1}, using a liquid helium-cooled bolometer as detector and a silicon beamsplitter. The microscope was continuously purged with nitrogen gas to avoid contamination of the spectra from the air atmosphere. The measured FIR spectra were averaged over 1024 scans.

The high-pressure Raman measurements at ambient temperature were performed with a Horiba Jobin Yvon LabRAM HR800 UV-VIS spectrometer at GFZ, equipped with a 1800 grooves/mm grating and a CCD detector. The Ar^+ laser line with wavelength $\lambda = 488$ nm and

an average power output of 5 mW was used for excitation. Dolomite single crystals with typical dimensions of 30 x 30 x 20 μm^3 were measured within the 100-1200 cm^{-1} frequency region. Neon served as PTM in the high-pressure Raman spectroscopic experiments.

Computational methods

The FIR vibrational spectra of the Dol-I and Dol-II dolomite polymorphs were derived from electronic structure calculations in the framework of density-functional theory (DFT). All calculations were performed using the ABINIT code [32]. The exchange-correlation functional was treated in the local density approximation (LDA, [33]). The Kohn-Sham orbitals were expanded in plane wave basis sets up to a cutoff energy of 1900 eV. This high cutoff was chosen to ensure convergence of the computed vibrational frequencies. Nuclei and core electrons were represented by Troullier–Martins-type pseudopotentials [34]. The reciprocal space was sampled using suitable Monkhorst-Pack k-point grids [35] generated by ABINIT to ensure convergence of the total energy and its derivatives. In a first step, lattice parameters and atomic positions of the *primitive cells* of the different dolomite polymorphs Dol-I (SG $R\bar{3}$, $Z = 1$) and Dol-II (SG $P\bar{1}$, $Z = 2$) were optimized at different pressures in the athermal limit ($T = 0$ K). Input structures for all phases were taken from the literature [9]. The pressure range of interest extended from ambient pressure to 30 GPa. Geometry optimization was stopped when the maximum force acting on an individual atom was smaller than 2.5 meV/Å and the maximum deviation of a stress tensor component from the desired value was lower than 0.015 GPa.

Starting from the optimized structures of the LDA calculations, phonon frequencies at the Γ point of the Brillouin zone and the Born effective charge tensors were computed using linear response density functional perturbation theory (DFPT [36])] as implemented in the ABINIT code. For comparison of the computed vibrational spectra with the respective experimental FIR spectra, the low-frequency dielectric permittivity tensor was derived from

the response functions using the method of Gonze et al. [37] with a damping factor of 2 cm^{-1}. The imaginary part of this function is a first approximation to the IR spectrum (e.g. [38]).

Results and discussion

Far-infrared studies at room temperature

At ambient conditions, a sum of 8 Raman (R) and 10 infrared (IR)-active vibrational modes are expected for the starting Dol-I phase according to group theory [39]:

$$\Gamma = 4A_g \text{ (R)} + 4E_g \text{ (R)} + 5A_u \text{ (IR)} + 5E_u \text{ (IR)} \qquad (1)$$

Out of the expected 10 IR-active vibrations, six are located in the far-infrared frequency range: three anti-translatory E_u vibrations of the $(CO_3)^{2-}$ units (the CO_3 ions vibrating parallel or perpendicular and in opposite directions to the cations) and three A_u librations of the $(CO_3)^{2-}$ groups [40,41].

The FIR absorbance spectra of the Dol-I phase at ambient conditions exhibit a relatively sharp peak at ~160 cm^{-1} with two adjacent shoulders at lower frequencies, another feature at 260 cm^{-1} with a low-frequency shoulder, and a broad band between 300-500 cm^{-1} composed of three FIR spectral components [**Fig. 2(a)**], consistent with earlier works [41–43]. The respective FIR frequencies and assignments are listed in **Table 2**.

Upon increasing pressure, we can observe that the Dol-I FIR-active modes above 200 cm^{-1} are blueshifted, i.e. shift to higher wavenumbers upon compression as expected; on the other hand, the low-frequency FIR modes below 200 cm^{-1} are redshifted upon increasing pressure. Such pressure-induced softening indicates potential structural instabilities in the Dol-I structure [**Fig. 2(b)** and **Table 2**], as predicted by recent *ab initio* calculations [44]. These Dol-I FIR modes are assigned to anti-translations and librations of the $(CO_3)^{2-}$ units with respect to the Ca^{2+} and Mg^{2+} cations [42]. A similar pressure-induced redshift has been

observed for the internal $(CO_3)^{2-}$ bending mode of dolomite and several relevant carbonates [22,28,45–47], which was attributed to the enhancement of the Ca^{2+}-O^{2-} and Mg^{2+}-O^{2-} bond strength upon compression [22]. In a similar fashion, we tentatively assign the observed Dol-I FIR modes' softening to the pressure-induced enhancement of the Ca^{2+}-O^{2-} and Mg^{2+}-O^{2-} bond strengths of the CaO_6 and MgO_6 octahedra (**Fig. 1**). We note, however, that the negative pressure slope observed in the FIR modes is one order of magnitude larger compared to that reported for the $(CO_3)^{2-}$ bending vibration (**Table 2**). Such prominent frequency redshifts were not detected in any of the previous high-pressure Raman experiments [22,26,28].

Approaching the Dol-I→Dol-II transition close to 17 GPa leads to an overall intensity reduction of the FIR signal [**Fig. 2(a)**]; the reason behind this intensity loss is most likely the non-hydrostatic nature of the petroleum jelly PTM used in the FIR measurements, which in turn results in stress inhomogeneities within the DAC and/or some degree of structural disorder on the sample. Considering previous works [9,28,48], the FIR spectrum at 22 GPa is assigned to the high-pressure Dol-II modification. From group theory, we expect 27 IR- and 30 Raman-active modes for the triclinic Dol-II phase [28]:

$$\Gamma = 27A_u \text{ (IR)} + 30A_g \text{ (R)} \qquad (2)$$

Despite the overall FIR intensity reduction, we can still observe a broad FIR band in the 400-500 cm^{-1} frequency range [**Fig. 2(a)**], which can be assigned to A_u symmetry according to group theory and DFT calculations [28]. The broad Dol-II FIR feature occurs at a lower frequency of ~20 cm^{-1} compared to the respective Dol-I A_u^3 FIR bands constituting the broad 300-500 cm^{-1} Dol-I FIR envelope near the transition point (**Fig. 2**). As we shall see in the following paragraphs, this FIR frequency downshift constitutes the FIR vibrational signature of the Dol-I→Dol-II structural transition.

Increasing pressure further deteriorates the FIR spectra intensity-wise, whereas the Dol-II A_u band broadens more upon reaching the highest pressure achieved in our experiments, i.e. 35.3 GPa (**Fig. 2**). The last FIR spectrum recorded at 35.3 GPa is composed of a low-intensity broad band appearing between 400-500 cm^{-1}, with its center of gravity lying approximately 30 cm^{-1} lower compared to the Dol-II A_u band at 26.6 GPa (**Fig. 2**). Taking into account previous investigations [8,9,28], this FIR mode frequency redshift possibly reflects the Dol-II→Dol-IIIc structural transition. Full decompression leads to the back-transformation of the Dol-I phase; the latter exhibits significantly broader FIR features compared to the ambient-pressure FIR spectrum, indicating some remnant structural disorder in the powder sample [**Fig. 2(a)**].

In order to acquire a better understanding of the Dol-I→Dol-II structural transition in the FIR frequency regions, DFT simulations were performed to support the interpretation of the experimental data. We note that the calculation of the Dol-IIIc FIR theoretical spectra is quite challenging, due to the relatively large unit cell, the low symmetry, and the absence of exact atomic parameters in this structure (SG $P1$, $Z = 8$; [27]). Given also that the corresponding experimental FIR spectra are rather featureless [**Fig. 2(a)**], a comparison does not seem very instructive. Hence, we decided to focus on the Dol-I and Dol-II FIR response.

In **Fig. 3(a)** we plot the experimental and calculated (LO modes) FIR spectra for both the Dol-I and Dol-II phases at ambient pressure and at ~22 GPa, respectively. For the Dol-I phase, we can observe a very good consistency between the calculated and experimental spectra in both the number of observed modes, as well as the relative intensities of the FIR features. On the other hand, a similar comparison for the Dol-II phase is more challenging due to the low intensity and peak broadening, i.e. the overall deterioration of the experimental Dol-II FIR spectrum.

Owing to this shortcoming, we have plotted the calculated FIR spectra of the Dol-I and Dol-II phases at the same pressure of 10 GPa to facilitate direct comparison [**Fig. 3(b)**]. We can immediately observe that upon passing from the Dol-I to the Dol-II phase, several new FIR modes appear in the 150-250 cm^{-1} and the 300-400 cm^{-1} frequency range. Moreover, the sharp Dol-I feature at ~120 cm^{-1} is shifted by 5 cm^{-1} to lower wavenumbers. The appearance of several new FIR features is reminiscent of the Dol-I→Dol-II vibrational signature in Raman spectroscopy [26,28]. The most prominent FIR Dol-I doublet close to 450 cm^{-1} splits now into three modes, two of them located at lower frequencies compared to the Dol-I features, and the third component shifted to higher frequency upon the Dol-I→Dol-II transition. This observation appears to be consistent with the downshift of the Dol-I A_u^3 mode upon passing into the Dol-II phase, as observed experimentally [**Fig. 2(b)**]. The aforementioned softening of both the ~120 cm^{-1} and the ~450 cm^{-1} Dol-I FIR modes is indicative of the displacive character of the Dol-I→Dol-II transition [9,44,48] .

Finally, we need to point out that due to the somewhat different pressures between the experimental and calculated FIR spectra[2], as well as the approximations used in the DFT calculations, the frequencies of the theoretical spectra are shifted with respect to the experimental data [**Fig. 2(a)** and **Fig. 3**]. Nevertheless, the pressure-induced FIR frequency changes for both the Dol-I and Dol-II phases are captured in our calculations [**Fig. 2(b)**].

High-pressure Raman studies at ambient temperature conducted with neon

We now turn to our high-pressure Raman spectroscopic experiments with neon serving as PTM at RT. The measured Raman spectra collected upon compression and decompression are presented in **Figs. 4 (a) & (b)**, respectively. Both the Dol-I and Dol-II Raman response is in

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[2] We note that the DFT calculated Dol-I→Dol-II transition pressure is bracketed between 10-18 GPa, depending on the exact theoretical approximation [28].

excellent agreement with the previously reported Raman spectra [26,28]. We simply remind here that upon the Dol-I→Dol-II structural transition, the high-frequency $(CO_3)^{2-}$ symmetric stretching vibration located at ~1150 cm^{-1} (value at ~15 GPa) splits into two components (**Fig. 5**); several low-intensity Raman features appear also in the Dol-II Raman spectra below 1000 cm^{-1}. These expected changes are clearly documented in the Dol-II Raman spectra recorded here (**Fig. 4**).

Despite the reproducibility of the Dol-I and Dol-II Raman signatures, the most noteworthy observation is the Raman response of the Dol-IIIc modification (**Figs. 4 & 5**). The latter is adopted clearly at 39.4 GPa, almost 2 GPa higher compared to the previous Raman study conducted with argon as PTM [28], yet consistent with the most recent high-pressure Raman and XRD investigations conducted with neon as PTM (**Table 1**, [26,27]). As we explain in more detail in the next *Section*, the Dol-IIIc structure was shown to exhibit rather featureless Raman and broad mid-IR spectra in the earlier investigation with argon as PTM [28]. Owing to the use of the more hydrostatic neon as PTM, however, we are able to monitor the Raman signature of the Dol-IIIc phase clearly (**Figs. 4 & 5**). The spectra are characterized by several low-intensity Raman features below 1000 cm^{-1} (for a detailed discussion see [26]), whereas the most intense part of the Raman spectrum is the $(CO_3)^{2-}$ stretching vibration frequency region between 1150-1270 cm^{-1} (**Fig. 5**). In the following paragraphs we focus on the latter.

Careful analysis of this $(CO_3)^{2-}$ stretching vibration frequency region reveals the presence of at least six Raman components (**Fig. 6**), in agreement with a recent study [26]. The resolved number of Raman features in this frequency range implies that there are at least six distinct carbon-oxygen bond distances in the Dol-IIIc phase, assuming that the observed Raman features consist only of symmetric C-O stretching vibrations. Due to the low symmetry of the Dol-IIIc structure (triclinic, **Table 1**), as well as its relatively large unit cell containing 80 atoms ($Z = 8$; [27]), the existence of several distinct C-O bonds appears

11

plausible. Hence, our Raman observations are consistent with the proposed Dol-IIIc structural model.

Finally, decompression leads to the recovery of the Dol-II phase at 31 GPa, whereas the Dol-I structure appears at 9 GPa [**Fig. 4(a)**]; the back-transformation of the two dolomite polymorphs exhibits clear hysteresis, resulting (partially) from the first-order character of the Dol-II→ Dol-IIIc transition. On the other hand, the exact Dol-II→Dol-I back-transformation pressure was most likely overstepped upon decompression, as one would not expect any hysteresis effects due to the second-order nature of this transition [9,27,44,48].

Effect of hydrostatic conditions on the Dol-IIIc modification

As we mentioned earlier, previous high-pressure Raman spectroscopic experiments on the same Fe-free dolomite sample conducted with argon as PTM, showed that the Dol-IIIc Raman spectra were essentially featureless [28]. The latter was interpreted as a sign of Dol-IIIc structural disorder, at least on a local scale. This disorder was also visible in the fully recovered spectra of the Dol-I phase, which showed substantially broader Raman features compared to the starting Dol-I Raman response (**Fig. 7**). The Dol-IIIc IR spectra on the other hand were not completely featureless, yet exhibited significantly broad bands, in line with the disordered Dol-IIIc scenario [28]. Adding to that, structural disorder was also observed in high-pressure powder XRD experiments of dolomite upon approaching the Dol-IIIc phase, as demonstrated by the significant Bragg peak broadening and the overall intensity reduction in the respective XRD patterns (see **Fig. 1** in [4]). These observations were quite puzzling, as later single-crystal XRD investigations showed that the Dol-IIIc phase is 'ordered' [27].

Since the single-crystal XRD studies were conducted with neon as PTM [27], whereas the high-pressure Raman and IR experiments with argon [28] and the high-pressure powder XRD investigation with a mixture of methanol-ethanol-water 16:3:1 as PTM [4], another plausible

reason behind the featureless Dol-IIIc vibrational spectra might be the effect of the PTM hydrostaticity. From the two PTM used, argon is known to become solid at 1.4 GPa at ambient temperature and exhibits stress heterogeneities of less than 0.1 GPa up to 10 GPa (increasing more rapidly above ~20 GPa); a similar hydrostatic limit applies also in the case of the methanol-ethanol-water 16:3:1 mixture PTM [49] On the other hand, neon solidifies at 4.8 GPa at ambient temperature, whereas the pressure gradient within the DAC remains small, i.e. less than 1% up to ~50 GPa [49]. Given the reconstructive character of the Dol-II→Dol-IIIc transition [9], it seems possible that the non-hydrostatic conditions imposed by the argon PTM may prevent the direct transformation towards an ordered crystalline phase at these pressures [see e.g. [50–52] for relevant examples]. A very recent high-pressure Raman spectroscopic investigation verified this scenario, that by using the more hydrostatic neon as PTM, one could observe an ordered Dol-IIIc Raman spectrum [26].

Based on the aforementioned discussion, we believe that the apparent pressure-induced Dol-IIIc structural disorder observed in our previous high-pressure Raman study was imposed by non-hydrostatic stresses acting on the single-crystalline sample arising from the argon PTM (**Fig. 7**). By using the more hydrostatic neon PTM, we could clearly record the Raman spectrum of an ordered Dol-IIIc structure (**Figs. 4-6**), in very good agreement with the recent high-pressure Raman [26] and XRD studies [27]. Considering the (fully) decompressed Dol-I Raman spectrum with broader Raman features reported earlier [28], we can additionally observe that the recovered Dol-I Raman spectrum recorded here does not show any signs of structural disorder, i.e. the recovered Raman features are rather sharp, attributed again to the use of the more hydrostatic neon PTM (**Fig. 7**) .

Finally, we note that the Dol-II→Dol-IIIc structural transition in our Fe-free dolomite sample takes place at 39.4 GPa (**Figs. 4 & 5**). For the sake of comparison, we mention that the Dol-II→Dol-IIIb transition for a Fe-rich dolomite sample [$CaMg_{0.6}Fe_{0.4}(CO_3)_2$] takes place

at ~37 GPa [27], i.e. almost 2 GPa lower compared to the Fe-free Dol-II→Dol-IIIc transition pressure. Since single-crystalline samples and neon as PTM were used in both experiments, the main difference is the Fe^{2+}-content of the starting dolomite sample. Despite the fact that the Dol-I→Dol-II transition does not seem to be affected by the dolomite composition, which may stem from the displacive character of the transition [9,28,48], it might be that the transition pressure of the Dol-II→Dol-IIIb/Dol-IIIc first-order transformation is more 'sensitive' to the Fe^{2+}-content [9,27].

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FIGURE 1. Structural representations of the ambient-pressure ordered dolomite CaMg(CO$_3$)$_2$ phase (SG $R\overline{3}$, Z = 3, Dol-I, left) and the high-pressure Dol-II modification adopted near 17 GPa (SG $P\overline{1}$, Z = 2, right). The gray, purple, black, and red spheres correspond to the Ca^{2+}, Mg^{2+}, C^{4+}, and O^{2-} ions, respectively.

FIGURE 2. (a) Room temperature FIR absorbance spectra of dolomite at selected pressures. The black, red, and blue spectra correspond to the Dol-I, Dol-II, and Dol-IIIc phases, respectively. The spectra have been shifted for clarity. (b) Evolution of the FIR mode frequencies as a function of pressure. The open symbols correspond to DFT-calculated FIR-active modes for the Dol-I (open black circles for LO modes, open star symbols for TO modes) and Dol-II phases (open red squares, data from [28]). The vertical dashed lines represent the onsets of the various pressure-induced transitions, as determined from earlier vibrational spectroscopy studies [28].

FIGURE 3. (a) Experimental and calculated (LO modes) FIR spectra for the Dol-I (black) and Dol-II (red) dolomite polymorphs at ambient pressure (bottom) and at 22 GPa (calculated spectrum at 20 GPa). (b) Calculated FIR spectra for the Dol-I (black) and Dol-II (red) dolomite polymorphs at 10 GPa. The intensities have been scaled to facilitate direct comparison.

FIGURE 4. Raman spectra of dolomite with neon as PTM, recorded upon (a) increasing and (b) decreasing pressure (λ = 488 nm, T = 300 K). The black, red, and blue spectra correspond to the Dol-I, Dol-II, and Dol-IIIc phases, respectively. Background has been subtracted for clarity. The dashed arrow in (b) indicates the decompression cycle.

FIGURE 5. Expanded view of the $(CO_3)^{2-}$ stretching Raman mode frequency region upon increasing pressure with neon as PTM ($\lambda = 488$ nm, $T = 300$ K). The red and blue spectra correspond to the Dol-II and Dol-IIIc phases, respectively. Background has been subtracted for clarity.

FIGURE 6. Lorentzian fitting of the Dol-IIIc Raman spectrum at 40.6 GPa within the 1150-1250 cm^{-1} frequency range, measured with neon PTM.

FIGURE 7. Comparison of the Dol-IIIc Raman spectra (blue) at (a) 38-39 GPa and (b) 40.6-43 GPa, and the (c) Dol-I Raman spectra (black) obtained upon decompression (R stands for recovered) in the two high-pressure experiments with neon (bottom spectra) and argon PTM (top spectra from [28]). We show only the $(CO_3)^{2-}$ stretching frequency region for clarity.