**Supplementary info**

**Discussion: dolomite-I and -II:**

**Lattice Modes**

As with Efthimiopoulos et al. (2017), we observe that the three lattice modes of dolomite-I migrate to higher frequency up to 15 GPa (Fig.1, 2b, S1). At 15 GPa, the $E_g$ symmetry modes with zero-pressure frequencies of 175 and 297 $cm^{-1}$ broaden and split into 3-4 modes that continue to increase in frequency at higher pressures; the majority of these modes persist to 42 GPa (Fig.1, 2b, S2). At 17 GPa, a new, not previously observed mode becomes resolvable above ~78 $cm^{-1}$. This band initially shifts rapidly (4.84(22) $cm^{-1}$/GPa) up to 30 GPa where it reaches a maximum and shifts slightly negatively (-0.21(4) $cm^{-1}$/GPa) up to 42 GPa, where it can no longer be resolved (S2).

**Carbonate Modes**

The single out-of-plane bending vibration near 882 $cm^{-1}$ shifts monotonically up to 15 GPa (Fig. 1, 2a, S1). At 15 GPa, the mode splits and a higher frequency shoulder appears. The two bands slowly diverge (while both increasing with frequency) as pressure is increased up to 41 GPa (S2), indicating that the distortion of the carbonate group in dolomite-II may weakly increase with pressure. The single in-plane bending vibration decreases in frequency with increasing pressure up to 15 GPa (S1): this negative shift is normal for this vibration in carbonates (Kraft et al. 1991). At 15 GPa, the in-plane bend mirrors the out-of-plane bend vibration by splitting, with a new peak forming at lower frequency; these two modes separate as they continue to shift negatively (Fig. 1, 2a, S2).

The symmetric stretch peak is slightly asymmetric at room pressure; in accord with past studies on dolomite (Kraft et al. 1991; Gillet et al. 1993; Efthimiopoulos et al. 2017), we fit one component to this stretch. This single band shifts up to 15 GPa where it splits into two bands (Fig. 1, 2a, S1). These two bands slowly merge into a single peak by 34 GPa and continue as a single peak up to 41 GPa.

The asymmetric stretch shifts as a single peak up to 15 GPa, where it splits, and a third shoulder becomes resolvable near 32 GPa. Above 42 GPa, the pressure shift of this vibration is complex, with a nearly invariant shift up to 54 GPa, followed by an increase above this pressure.

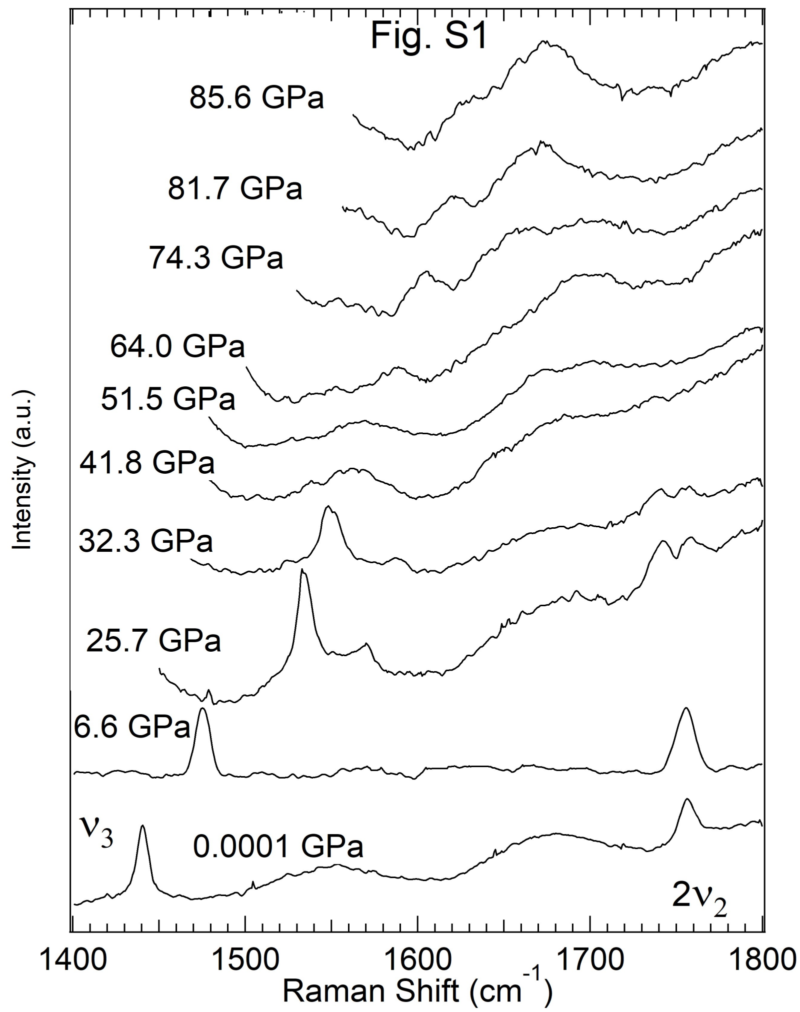
**Discussion: a new low frequency mode and the dolomite to dolomite-II transition**

Our results are in accord with the analysis by Merlini et al.(2012) that the structure of dolomite-II is calcite-II-like. A mode that provides diagnostic information on the nature of the transition to dolomite-II appears at low frequency (~78 $cm^{-1}$): this band has a rapid initial positive pressure shift of nearly 5 $cm^{-1}$/GPa. Based on its low frequency and large pressure shift, this mode likely corresponds to a zone-edge acoustic mode at room pressure, and at 15 GPa, the increase in size of the unit cell across the transition renders this zone edge mode Raman-active. Computational results on the transition from dolomite to dolomite-II indicate that the transition is soft-mode generated via an acoustic vibration becoming unstable at the F point in the Brillouin zone (Zucchini et al. 2017). This transition thus is likely to have a similar mechanism to the transition from calcite to calcite-II (Merrill and Bassett 1975; Hatch and Merrill 1981; Harris et al. 1998). This indicates that this transition may be displacive, and involves an associated expansion of the spectroscopic unit cell (Dove 1997). Our results support the structure proposed by Merlini et al. (2012), with a doubling occurring in the spectroscopic unit cell. Near 32 GPa, the pressure shift of this new mode becomes negative. This negative shift may be associated with an approach towards instability of this specific mode: such phonon instabilities may be associated with the metastability of dolomite-II observed within computations (Solomatova and Asimow 2017).

**Dolomite-III further discussion:**

For comparison, the asymmetric stretch and $\nu_2$ (out-of-plane-bend)-overtone are weak bands that are difficult to consistently observe at high pressures. Above 68 GPa, these vibrations have multiple components with variable pressure shifts (Fig. 2): at these pressures, it is likely that a resonant interaction exists between the asymmetric stretch and the out-of-plane bend overtones (which were not resolvable above 42 GPa: S7). Thus, these bands provide less insight into the structural changes occurring within the carbonate units than the bending and symmetric stretching vibrations.

**Figures**




**Supplementary Figure 1.** Representative Raman spectra of dolomite under compression at room temperature (spectra are vertically offset for clarity). The asymmetric stretch ($\nu_3$) and overtone of the out of plane bend ($2\nu_2$) are shown.

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