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Tetrahedrally coordinated carbonates in Earth's lower mantle

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Carbonates are the main species that bring carbon deep into our planet through subduction. They are an important rock-forming mineral group, fundamentally distinct from silicates in the Earth's crust in that carbon binds to three oxygen atoms, while silicon is bonded to four oxygens. Here we present experimental evidence that under the sufficiently high pressures and high temperatures existing in the lower mantle, ferromagnesian carbonates transform to a phase with tetrahedrally coordinated carbons. Above 80 GPa, *in situ* synchrotron infrared experiments show the unequivocal spectroscopic signature of the high-pressure phase of (Mg,Fe)CO₃. Using *ab-initio* calculations, we assign the new infrared signature to C–O bands associated with tetrahedrally coordinated carbon with asymmetric C–O bonds. Tetrahedrally coordinated carbonates are expected to exhibit substantially different reactivity than low-pressure threefold coordinated carbonates, as well as different chemical properties in the liquid state. Hence, this may have significant implications for carbon reservoirs and fluxes, and the global geodynamic carbon cycle.

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Ferromagnesite ((Mg,Fe)CO₃) minerals are probable candidates for deep-Earth carbon storage and are expected to play a key role in the deep carbon cycle (for example, see refs 1,2). Therefore, the properties of ferromagnesite at lower mantle conditions have been the focus of many theoretical and experimental studies^{2–8}. Results of high-pressure experiments have suggested that the rhombohedral structure of magnesite (MgCO₃) is stable up to 115 GPa at 2,000–3,000 K, and that it transforms to a new structure at higher pressures². On the other hand, first-principles calculations predict that magnesite transforms into a phase containing CO₄ tetrahedral groups at lower pressure (~82 GPa)⁵. Boulard *et al.*⁶ proposed that magnesite and ferromagnesite adopt the theoretically proposed structure above 80 GPa at 2,300 K, based on *in situ* X-ray diffraction (XRD) and *ex situ* spectroscopy analysis on recovered samples (electron energy loss spectroscopy and scanning transmission X-ray microscopy performed at the C–K edge). However, these observations have been controversial for two reasons: (1) only LeBail refinements were performed on the high-pressure, high-temperature XRD data and, hence, determination of the atomic positions within the unit cell was not possible; (2) spectroscopic analyses were performed *ex situ* on recovered samples after temperature quenching and decompression to ambient conditions, where transmission electron microscopic analyses showed amorphization of the sample indicating the high-pressure crystal structure was not preserved.

Here we report the first unequivocal evidence of tetrahedrally coordinated carbon in high-pressure carbonates, obtained by a combined experimental and theoretical study. We perform *in situ* synchrotron infrared spectroscopic studies on ferromagnesite in diamond anvil cells (DAC) and identify a unique vibrational signature present only in the high-pressure phase. We perform *ab initio* calculations of the infrared spectra, which allow us to assign this vibrational signature to asymmetric, sp³-like C–O bonds.

Results

***In situ* infrared spectroscopy characterization.** Magnesite and siderite (FeCO₃) form a solid solution at ambient conditions and adopt the same structure at high pressure and temperature, except that on substitution of Mg by Fe, the volume of the unit cell decreases by about 7% (ref. 6) ($V(\text{MgCO}_3) = 351.7 \text{ \AA}^3$ at 85 GPa and $2,400 \pm 150 \text{ K}$ and $V(\text{Mg}_{0.25}\text{Fe}_{0.75}\text{CO}_3) = 328.9 \text{ \AA}^3$ at 80 GPa and 300 K). We note that only the Fe-bearing phase is temperature quenchable⁶, an important requirement for infrared spectra measurements in the DAC. We thus chose a natural sample of ferromagnesite with a composition (Mg_{0.25}Fe_{0.75})CO₃, which was measured with an electron microprobe. Here we refer to the high-

pressure structure of ferromagnesite as post magnesite. *In situ* infrared experiments were performed at the National Synchrotron Light Source on the high-pressure infrared beamline U2A. Two experiments were conducted: (1) infrared spectra were collected on compression and decompression of (Mg_{0.25}Fe_{0.75})CO₃ between 0 and 54 GPa at ambient temperature. As the sample was not heated, (Mg_{0.25}Fe_{0.75})CO₃ did not transform into the post-magnesite structure, but only experienced an isostructural electronic spin transition around 50 GPa^{9,10}. (2) In a second set of experiments, powdered (Mg_{0.25}Fe_{0.75})CO₃ was compressed up to 103 GPa and then transformed into the post-magnesite phase when laser heated at ~2,100 K. *In situ* XRD was used to monitor the transformation into the post-magnesite phase (Supplementary Fig. 1). Infrared spectra were recorded at the highest pressure of 103 GPa and during decompression of the post-magnesite phase back to 0 GPa at room temperature.

At low pressure, ferromagnesite is composed of repeating, alternating layers of (CO₃)^{2–} radicals (anions) and layers of divalent, positively charged cations (Fe²⁺ and Mg²⁺) (Fig. 1a). The mid-infrared spectral absorption features result primarily from fundamental internal vibrations of the C–O bonds in the carbonate radical: the out-of-plane bending (ν_2), the asymmetric stretch (ν_3) and in-plane bending (ν_4) modes (for example see, ref. 11). At ambient conditions, we measured these three modes on the polycrystalline carbonate phase (symmetry group: R-3C) at 867, 1,460 and 739 cm^{–1}, respectively (Fig. 2a). Frequency of ν_3 was determined using a thinner sample (*cf.* Supplementary Fig. 2). These frequencies are in good agreement with those reported by previous infrared studies on iron-bearing carbonates^{3,11,12}. Additional modes resulting from the combination of the three fundamental ones are also present: a band at 1,811 cm^{–1}, which stems from the combination of $\nu_1 + \nu_4$, and one at 2,512 cm^{–1}, which corresponds to the combination $2\nu_2 + \nu_3$ (ref. 13). Under compression at room temperature, no additional infrared bands were observed; rather, a shift to higher wave numbers was detected for all infrared bands, except for the transverse-optical (TO) component of the ν_2 band, which exhibited a slight negative pressure shift ($-0.29 \text{ cm}^{-1} \text{ GPa}^{-1}$). Such a shift is in agreement with previous studies on iron-bearing carbonates³ and has been interpreted as stemming from the increased strength of the divalent cation–oxygen bonds under compression. We observed no hysteresis on decompression of the untransformed carbonate.

In the second set of experiments, several new infrared bands were observed after transformation into the post-magnesite phase by laser heating (Fig. 2a). At very high pressure (from 103 to 81 GPa), the most intense infrared bands appeared to be saturated, which made their positions difficult to determine precisely; however, our experiment showed that between 103 and 43 GPa these new infrared modes gradually shift to lower wavenumbers (Fig. 2b). At 0 GPa, the experimental spectrum does not correspond to a carbonate phase and displayed infrared modes at 746, 836, 872, 1,092, 1,480, 1,823, 2,349 and 2,530 cm^{–1}. We note that Boulard *et al.*⁶ reported a redox reaction on laser heating of (Mg_{0.25}Fe_{0.75})CO₃, resulting in the formation of magnetite (Fe₃O₄) together with the post-magnesite phase. However, the new infrared bands observed at ambient pressure after decompression cannot be assigned to magnetite^{14,15}.

First-principles calculations. To interpret the infrared spectrum measured for the post-magnesite phase, we carried out first-principles calculations of the infrared spectra of MgCO₃ at low and high pressure, and we identified specific vibrational modes that are present only in the post-magnesite phase. Calculation were conducted for pure MgCO₃ instead of the solid solution,

Figure 1 | Ball and stick representation of the two structures.

Ferromagnesite at ambient conditions (a) and the post-magnesite phase above 80 GPa (b). Red, grey and blue spheres represent oxygen, carbon and cations (Fe or Mg) atoms, respectively.

Figure 2 | In-situ infrared measurement at high pressure. (a) Experimental infrared spectra collected on compression of the ferromagnesite (black lines) at 0 and 54 GPa, and on decompression of the post-magnesite phase (red lines) at 58 and 0 GPa. The region between 1,900 and 2,300 cm^{-1} is dominated by absorption from the diamond anvils. (b) Experimental infrared spectra collected on the decompression of the post-magnesite phase from 103 to 0 GPa. The scale bars give the absorbance scale for each panel.

Figure 3 | Theoretical infrared results. (a) Calculated infrared intensities (black lines) and spectrum (solid red line) of the post-magnesite phase at 82 GPa. For comparison, the experimental spectrum collected at 81 GPa is shown as a dotted line. The scale bar gives the absorbance scale. (b) The vibrational mode at 1,252 cm^{-1} (marked by the arrow on a) is identified as a unique signature of the high-pressure phase.

(Mg,Fe) CO_3 , for computational simplicity. We used density functional theory (DFT), a semi-local exchange-correlation (xc) functional¹⁶, plane-wave basis sets and pseudopotentials. We first calculated the infrared spectrum of magnesite (symmetry group: R-3C), the phase of MgCO_3 stable at ambient conditions (see Supplementary Fig. 3). We used a rhombohedral cell, with the lattice constant fixed at the experimental value of 5.675 Å and a cell angle of 48.2° (ref. 17; Supplementary Table 1). The computed frequencies of the TO component of the ν_2 , ν_3 and ν_4 modes are 825, 1,411 and 725 cm^{-1} , respectively. The theoretical frequencies computed for a single crystal are lower than the experimental ones by ~4% (refs 11,18). This discrepancy is probably due to the use of the semi-local xc functional Perdew–Burke–Ernzerhof¹⁶. By using the hybrid functional, B3LYP, Valenzano *et al.*¹⁹ found a smaller error of ~0.5% for these three bands compared with the experimental results^{11,18}. The infrared spectrum of the same magnesite structure computed at a pressure of 83 GPa, without allowing for any phase transition (Supplementary Table 1), shows that the TO component of the ν_2 mode is weakly modified (we found a modest blue shift of 5 cm^{-1}), the ν_4 mode (TO) is blue-shifted to 913 cm^{-1} and the ν_3 mode (TO) is blue-shifted to 1,647 cm^{-1} (Supplementary Fig. 4).

Figure 3 shows the calculated infrared spectrum of the post-magnesite phase, compared with the experimental spectrum collected at ~81 GPa. We considered the structure of the post-magnesite (symmetry group: C2/m) previously measured for MgCO_3 at 82 GPa and high temperature (~2,300 K) by Boulard *et al.*⁶, with lattice constants $a = 8.39$ Å, $b = 6.41$ Å, $c = 6.82$ Å and $\beta = 105.49^\circ$ (Supplementary Table 2). This structure is composed of tetrahedrally coordinated carbon atoms (Fig. 1b). In our computed spectrum, the phonon momentum is along the y axis (crystal direction: [010]) to take into account the longitudinal-optical (LO)–TO splitting (infrared spectra obtained by the TO component and the phonon momenta along the z and x directions are shown in Supplementary Fig. 5). We found three bands, at 659, 771 and 1,252 cm^{-1} , slightly red-shifted with respect to experiments (~715, 803 and 1,304 cm^{-1}), again most probably because of the approximation introduced by the semi-local functional used in our calculations (Supplementary Table 3). The two bands measured at 890 and 987 cm^{-1} were well reproduced by our calculations; we found 908 and 987 cm^{-1} , respectively. Overall, the theoretical and experimental spectra were in good agreement and, most importantly, they both exhibit a band at ~1,300 cm^{-1} , which is not present in magnesite at ambient conditions or in the infrared spectrum of the isotropically compressed magnesite phase (Supplementary Fig. 4). The compressed magnesite does not exhibit any extra band between 1,000 and 1,400 cm^{-1} , providing strong evidence that the experimental and theoretical band at ~1,300 cm^{-1} signals the presence of a structural and bonding change.

Our geometry optimization of the tetrahedrally coordinated post-magnesite phase showed that the CO_4 units, with nominal negative charge of four electrons, are asymmetric with both C and O atoms being sp^3 bonded, as shown in Fig. 4, which reports hybrid orbitals (maximally localized Wannier functions²⁰) obtained from linear combinations of the eigenstates of the DFT Hamiltonian used in our calculations²¹. In the primitive cell of the high-pressure phase, carbon atoms have two symmetry non-equivalent positions, C1 and C2 (ref. 5). We found that for the CO_4 units consisting of the C1 atoms, the two longer C–O bonds are 1.427 and 1.375 Å, respectively, and the two shorter ones are 1.256 and 1.287 Å, respectively. For the other type of CO_4 units (C2 atoms), the two longer C–O bonds have the same length of 1.391 Å, while the two shorter ones are 1.285 and 1.276 Å, respectively. However, the bonding structure of these two units is similar and represented in both cases by the hybrid orbitals shown in Fig. 4. The vibrational modes corresponding to the shorter C–O bonds are at frequencies higher than

Figure 4 | Hybrid orbitals in C–O bonds. Threefold (a) and fourfold (b) coordinated carbon atoms in the magnesite and post-magnesite phases, respectively. Grey and red spheres represent C and O atoms, respectively. Green spheres represent the centres of the hybrid orbitals for the CO_3^{2-} anion (a), with 24 valence electrons and 12 doubly occupied hybrids, and for the CO_4^{4-} anion (b) with 32 valence electrons. The white and blue colours denote the positive and negative parts of the wave function, respectively. In magnesite both C and O are sp^2 bonded and three distinct orbitals were identified: σ -like orbitals localized on the C–O bonds (orbital 2), π -like bonds formed by the overlap of p_z orbitals on the O and C atoms (orbital 1) and lone pairs (orbitals 3) on the oxygen atoms; in post magnesite, both C and O are sp^3 bonded and two distinct orbitals were identified: σ -like orbitals localized on the C–O bonds (orbital 5) and lone-pair hybrids (orbitals 4) on the oxygen atoms. Hybrid orbitals were defined using maximally localized Wannier functions, built from linear combinations of single-particle electronic eigenstates (see Methods section).

$1,400\text{ cm}^{-1}$. At 81 GPa (Figs 2b and 3), the band at $1,452\text{ cm}^{-1}$ originates from the stretching mode of the $1.287\text{ \AA}$ C–O bonds and the one at $1,550\text{ cm}^{-1}$ from the stretching mode of the 1.285 and $1.276\text{ \AA}$ C–O bonds. Finally, the modes at $1,631$ and $1,696\text{ cm}^{-1}$ are assigned to the stretching modes of the $1.256\text{ \AA}$ C–O bonds. We note that in the experimental spectra, the bands between $1,400$ and $1,700\text{ cm}^{-1}$ are saturated and individual modes cannot be identified. The vibrational mode at $1,252\text{ cm}^{-1}$ originates from the stretching mode of the 1.375 and $1.391\text{ \AA}$ C–O bonds, with the phonon momentum along the y axis (Fig. 3b). The TO component of this mode is expected at $1,155\text{ cm}^{-1}$. The bands between $1,100$ and $1,300\text{ cm}^{-1}$ may stem from the different LO and TO components of the $1,252\text{ cm}^{-1}$ stretching mode found in the experimental spectrum. As shown in Supplementary Fig. 5, when the phonon momentum is along the x or z directions, the frequency of the stretching mode of the longer C–O bonds is lower than $1,252\text{ cm}^{-1}$. The intensities of the LO and TO components in powder transmission spectra depend on the size and shape of the powder particles. There is an apparent band at $1,304\text{ cm}^{-1}$ in the experimental spectrum, suggesting that the thickness of many sample particles on the y

direction may be much less than the wavelength of exciting radiation ($7.7\text{ }\mu\text{m}$ in air)²².

The modes detected between $1,100$ and $1,300\text{ cm}^{-1}$ are at lower frequencies than the asymmetric stretching mode of the planar carbonate ion ν_3 measured at ambient conditions ($1,401\text{ cm}^{-1}$ in this study). This is consistent with C–O bond lengths of $1.375\sim 1.391\text{ \AA}$ found in the CO_4 units, which are longer than that of the carbonate ion present in magnesite at ambient conditions ($\sim 1.30\text{ \AA}$). As expected, a longer bond length corresponds to a lower vibrational frequency. Such a trend was also found in magnesite by Grzechnik *et al.*²³, who observed a shift of the ν_3 mode to lower frequency by $\sim 114\text{ cm}^{-1}$ when decompressing the sample from 29 GPa to ambient conditions. Consistently, our calculation showed that when releasing the pressure of magnesite, from 58 to 0 GPa, the C–O bonds increase by $0.04\text{ \AA}$, and thus the TO component of the ν_3 mode redshifts by 194 cm^{-1} .

Discussion

In summary, we report the first *in situ* characterization of C–O bonds of the post-magnesite phase. We found that at high pressure, on transformation into the post-magnesite phase, the infrared spectrum of $(\text{Mg,Fe})\text{CO}_3$ exhibits novel, unique features not present in the low-pressure spectrum, which we assigned to a fundamentally different bonding configurations of carbon. Carbon bonds transform from sp^2 (in the trigonal, doubly charged carbonate anions) to sp^3 hybridized configurations (in the tetrahedral tetra-charged carbonate anions), which we characterized using *ab initio* calculations within DFT. Hence, our study provides the identification of a mode at $1,304\text{ cm}^{-1}$, which may be used as a fingerprint of tetrahedrally bonded carbon in high-pressure mineral phases. Carbon tetrahedrally bonded to oxygen has also been proposed to be present in high-pressure phase-V of CO_2 (refs 24,25). However, in this phase, tetrahedral CO_4 groups are symmetric with a C–O distance of $1.35\text{ \AA}$, similar to the longer C–O distances observed here. Measured infrared spectra showed the presence of a mode in the same frequency range at $1,126\text{ cm}^{-1}$; however, all modes were reported to involve simultaneous stretching and bending, unlike the pure stretching mode²⁴ identified here.

The dramatic change we found in the carbon environment in ferromagnesite may have significant implications on carbon reservoirs and fluxes in the lower mantle and, therefore, on the deep carbon cycle. For example, the new bonding configuration, identified here in the high-pressure carbonate structure, is dramatically different from trigonal planar group in the ambient conditions structure. This will probably influence its chemical and physical properties such as its reactivity. Moreover, one would expect dramatic changes in the behaviour of carbonate melts with increases in coordination of carbon, owing to the ability of CO_4 to form polymerizable networks while CO_3 trigonal groups can not²⁶. At upper mantle conditions, carbonate melts differ from silicate melts. They exhibit ultra-low viscosity potentially resulting in high mobilities²⁷. Preliminary theoretical studies predict that carbonate melt viscosity increases at high pressures²⁸, which would inhibit mobility of carbonate melts in the lower mantle and might lead to the presence of deep carbon reservoirs.

Methods

In situ high-pressure infrared spectroscopy. The infrared absorbance was measured in the $500\text{--}4,000\text{ cm}^{-1}$ range through a symmetric Mao-type DAC mounted with type-IIa diamond anvils. Measurements were conducted with a Bruker Vertex 80/v spectrometer at the side station of the high-pressure infrared beamline U2A of the National Synchrotron Light Source. The spectral resolution was 4 cm^{-1} and the beam size under the microscope was $\sim 20 \times 20\text{ }\mu\text{m}$. Absorption infrared spectra were obtained after normalization against a background spectrum collected on an area with KBr pressure medium only (set 1) at

each pressure or in the empty DAC (set 2) at ambient pressure. A natural sample of ($\text{Mg}_{0.25}\text{Fe}_{0.75}\text{CO}_3$) siderite, provided by the mineralogical collection of University of Pierre et Marie Curie, was used in this experiment. For both sets of experiments, powdered ($\text{Mg}_{0.25}\text{Fe}_{0.75}\text{CO}_3$) was loaded together with a ruby ball and the pressure was determined before and after infrared absorbance data collection from the shift of the ruby fluorescence line²². In the first set of experiments, KBr was added as a pressure-transmitting medium in a DAC with 400 μm culets. One run was performed with a sufficiently thin sample, to obtain good quality of the high-intensity band ν_3 , and a second run with a thicker sample, to get good data quality of the lower-intensity bands. In the second set of experiments, the sample was loaded without pressure medium in a DAC with 70 μm culets and compressed up to 103 GPa. The sample was then transformed into the post-magnesite phase by laser heating at $\sim 2,100$ K at HPCAT, Argonne National Laboratory. We used *in-situ* XRD to monitor the transformation into the post-magnesite phase.

DFT calculations. DFT calculations were performed with the Quantum ESPRESSO package³⁰ and maximally localized Wannier functions were computed with the Qbox code (v.1.56.2, <http://eslab.ucdavis.edu/software/qbox/>)³¹ and the algorithm of reference²¹. We used the Perdew–Burke–Ernzerhof xc functional¹⁶, plane-wave basis sets and ultrasoft pseudopotentials³². We used a kinetic energy cutoff of 40 Ry for wavefunctions and 360 Ry for charge densities. Our structural optimizations were performed by fully relaxing all atomic coordinates within the primitive cell until the force on each atom was smaller than 10^{-4} Ry Bohr⁻¹. We used $3 \times 3 \times 3$ k -point mesh for the primitive cell of magnesite and $2 \times 2 \times 2$ k -point mesh for the post-magnesite phase. We used the unit cell and atomic positions of the postmagnesite reported in Boulard *et al.*⁶ in which the space group is P21/c after transferring the atomic positions from C2/m as reported in Oganov *et al.*⁵ to P21/c. In the DFT calculations, the point group $2/m$ was used.

We carried out phonon calculations using density functional perturbation theory³³ to obtain the infrared spectra. The intensity of the m th infrared mode is defined as³⁴:

$$I_m = \sum_{\alpha} \left| \sum_{\beta} Z_{\alpha\beta}^*(s) e_m(s, \beta) \right|^2$$

where α and β are Cartesian components, $Z_{\alpha\beta}^*(s)$ is the Born effective charge tensor of the s th atom and $e_m(s, \beta)$ is the normal mode eigenvector³⁴. The calculated intensities were broadened by a Gaussian function with the full width of 50 cm^{-1} at half maximum.

References

- Wood, B. J., Pawley, A. & Frost, D. R. Water and carbon in the Earth's mantle. *Philos. Trans. R. Soc. London* **354**, 1495–1511 (1996).
- Isshiki, M. *et al.* Stability of magnesite and its high-pressure form in the lowermost mantle. *Nature* **427**, 60–63 (2004).
- Santillán, J. & Williams, Q. A high-pressure infrared and X-ray study of FeCO_3 and MnCO_3 : comparison with $\text{CaMg}(\text{CO}_3)_2$ -dolomite. *Phys. Earth Planet. Inter* **143–144**, 291–304 (2004).
- Oganov, A. R., Glass, C. W. & Ono, S. High-pressure phases of CaCO_3 : Crystal structure prediction and experiment. *Earth Planet. Sci. Lett.* **241**, 95–103 (2006).
- Oganov, A. R., Ono, S., Ma, Y., Glass, C. W. & García, A. Novel high-pressure structures of MgCO_3 , CaCO_3 and CO_2 and their role in Earth's lower mantle. *Earth Planet. Sci. Lett.* **273**, 38–47 (2008).
- Boulard, E. *et al.* New host for carbon in the deep Earth. *Proc. Natl Acad. Sci. USA* **108**, 5184–5187 (2011).
- Boulard, E. *et al.* Experimental investigation of the stability of Fe-rich carbonates in the lower mantle. *J. Geophys. Res.* **117**, B02208 (2012).
- Tao, R., Fei, Y. & Zhang, L. Experimental determination of siderite stability at high pressure. *Am. Mineral.* **98**, 1565–1572 (2013).
- Lavina, B. *et al.* Siderite at lower mantle conditions and the effects of the pressure-induced spin-pairing transition. *Geophys. Res. Lett.* **36**, L23306 (2009).
- Farfan, G. *et al.* Bonding and structural changes in siderite at high pressure. *Am. Mineral.* **97**, 1421–1426 (2012).
- Huang, C. K. & Kerr, P. F. Infrared study of the carbonate minerals. *Am. Mineral.* **45**, 311–324 (1960).
- Lane, M. D. & Christensen, P. R. Thermal infrared emission spectroscopy of anhydrous carbonates. *J. Geophys. Res.* **102**, 25,581–25,592 (1997).
- Gunasekaran, S., Anbalagan, G. & Pandi, S. Raman and infrared spectra of carbonates of calcite structure. *J. Raman Spectrosc.* **37**, 892–899 (2006).
- Chamritski, I. & Burns, G. Infrared- and Raman-active phonons of magnetite, maghemite, and hematite: a computer simulation and spectroscopic study. *J. Phys. Chem. B* **109**, 4965–4968 (2005).
- Gasparov, L. *et al.* Infrared and Raman studies of the Verwey transition in magnetite. *Phys. Rev. B* **62**, 7939–7944 (2000).
- Perdew, J., Burke, K. & Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
- Graf, D. L. Crystallographic tables for the rhombohedral carbonates. *Am. Mineral.* **46**, 1283–1316 (1961).
- Hellwege, K. H., Lesche, W., Plühal, M. & Schaack, G. Zwei-phononen-absorptionsspektren und dispersion der schwingungszweige in kristallen der kalkspatstruktur. *Zeitschrift Phys.* **232**, 61–86 (1970).
- Valenzano, L. *et al.* *Ab initio* vibrational spectra and dielectric properties of carbonates: magnesite, calcite and dolomite. *Theor. Chem. Acc.* **117**, 991–1000 (2007).
- Marzari, N., Mostofi, A. a., Yates, J. R., Souza, I. & Vanderbilt, D. Maximally localized Wannier functions: theory and applications. *Rev. Mod. Phys.* **84**, 1419–1475 (2012).
- Gygi, F., Fattetbert, J.-L. & Schwegler, E. Computation of maximally localized Wannier functions using a simultaneous diagonalization algorithm. *Comput. Phys. Commun.* **155**, 1–6 (2003).
- Farmer, V. C. Differing effects of particle size and shape in the infrared and Raman spectra of kaolinite. *Clay Miner.* **33**, 601–604 (1998).
- Grzechnik, A., Simon, P., Gillet, P. & McMillan, P. An infrared study of MgCO_3 at high pressure. *Phys. B* **262**, 67–73 (1999).
- Santoro, M. *et al.* Partially collapsed cristobalite structure in the non molecular phase V in CO_2 . *Proc. Natl Acad. Sci. USA* **109**, 5176–5179 (2012).
- Datchi, F., Mallick, B., Salamat, A. & Ninet, S. Structure of polymeric carbon dioxide CO_2 -V. *Phys. Rev. Lett.* **108**, 125701 (2012).
- Jones, A. P., Genge, M. & Carmody, L. Carbonate melts and carbonatites. *Rev. Mineral. Geochem.* **75**, 289–322 (2013).
- Kono, Y. *et al.* Ultralow viscosity of carbonate melts at high pressures. *Nat. Commun.* **5**, 5091 (2014).
- Jones, A. P., Genge, M. & Carmody, L. Carbonate Melts and Carbonatites. *Rev. Mineral. Geochem.* **75**, 289–322 (2013).
- Mao, H. K., Xu, J. & Bell, P. M. Calibration of the Ruby pressure gauge to 800 kbar under quasi-hydrostatic conditions. *J. Geophys. Res.* **91**, 4673–4676 (1986).
- Giannozzi, P. *et al.* QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *J. Phys. Condens. Matter* **21**, 395502 (2009).
- Gygi, F. Architecture of Qbox: a scalable molecular dynamics code. *IBM J. Res. Dev.* **52**, 1–8 (2008).
- Vanderbilt, D. Soft self-consistent pseudopotentials in generalized eigenvalue formalism. *Phys. Rev. B* **41**, 7892–7895 (1990).
- Baroni, S., de Gironcoli, S., dal Corso, A. & Giannozzi, P. Phonons and related crystal properties from density-functional perturbation theory. *Rev. Mod. Phys.* **73**, 515–562 (2001).
- Giannozzi, P. & Baroni, S. Vibrational and dielectric properties of C60 from density-functional perturbation theory. *J. Chem. Phys.* **100**, 8537 (1994).

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Author contributions

E.B. designed the study. E.B. and Z.L. conducted the experiments. E.B. analysed the data. D.P. performed the theoretical calculations. E.B. and D.P. wrote the manuscript. All authors discussed the results and commented on the manuscript.

Additional information

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