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High-pressure and high-temperature vibrational properties and anharmonicity of carbonate minerals up to 6 GPa and 500 °C by Raman spectroscopy

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Abstract

Carbonate minerals play a dominant role in the deep carbon cycle. Determining the high-pressure and high-temperature vibrational properties of carbonates is essential to understand their anharmonicity and their thermodynamic properties under crustal and upper mantle conditions. Building on our previous study on aragonite, calcite (both CaCO₃ polymorphs), dolomite [CaMg(CO₃)₂], magnesite (MgCO₃), rhodochrosite (MnCO₃), and siderite (FeCO₃) (Farsang et al. 2018), we have measured pressure- and temperature-induced frequency shifts of Raman-active vibrational modes up to 6 GPa and 500 °C for all naturally occurring aragonite- and calcite-group carbonate minerals, including cerussite (PbCO₃), strontianite (SrCO₃), witherite (BaCO₃), gaspeite (NiCO₃), otavite (CdCO₃), smithsonite (ZnCO₃), and spherocobaltite (CoCO₃). Our Raman and XRD measurements show that cerussite decomposes to a mixture of...
Pb$_2$O$_3$ and tetragonal PbO between 225 and 250 °C, smithsonite breaks down to hexagonal ZnO between 325 and 400 °C, and gaspeite to NiO between 375 and 400 °C. Spherocobaltite breaks down between 425 and 450 °C and otavite between 375 and 400 °C. Due to their thermal stability, carbonates may serve as potential reservoirs for a number of metals (e.g., Co, Ni, Zn, Cd) in a range of crustal and upper mantle environments (e.g., subduction zones). We have determined the isobaric and isothermal equivalents of the mode Grüneisen parameter and the anharmonic parameter for each Raman mode, and compare trends in vibrational properties as a function of pressure, temperature, and chemical composition with concomitant changes in structural properties. Finally, we use the anharmonic parameter to calculate the thermal contribution to the internal energy and entropy, and isochoric and isobaric heat capacity of certain carbonates.

Keywords

Anharmonicity, cerussite, diamond anvil cell, gaspeite, high pressure, high temperature, otavite, pressure sensor, Raman spectroscopy, smithsonite, spherocobaltite, strontianite, witherite

Introduction

Carbonate minerals play a dominant role in the deep carbon cycle that includes the transport of carbon bearing phases in subducting slabs to deep Earth, their devolatilization, melting, and dissolution in slab fluids, the transport of liberated CO$_2$, followed by volcanic outgassing (e.g., Dasgupta and Hirschmann 2010; Ague and Nicolescu 2014; Manning 2014; Kelemen and
Manning 2015; Plank and Manning 2019). Carbonates transport carbon into deep Earth in three distinct lithologies (oceanic sediments, igneous crust, and lithospheric mantle). Their behavior as a function of pressure ($P$), temperature ($T$), and composition of adjacent phases determines the extent and rate of carbon recycling to the atmosphere and oceans. Modeling the deep carbon cycle therefore requires an understanding of numerous geologic processes involving carbonate minerals, which in turn depend on the thermodynamic properties of carbonates under crustal and upper mantle conditions. In all high-temperature environments (e.g., deep Earth), key thermodynamic properties of phases are dependent upon their anharmonicity. In order to obtain meaningful values for thermodynamic properties, anharmonicity and anharmonic corrections must be quantified.

The vibrational properties of a mineral control a number of its thermodynamic properties. Raman spectroscopy provides a route, therefore, to determine thermodynamic properties at the $P$-$T$ conditions of measurement. As abundant CO$_2$-bearing minerals, the thermodynamic properties of carbonates are of particular importance. A significant number of Raman studies of the high-pressure behavior of carbonate minerals have been reported, including aragonite, calcite, vaterite, and other high-pressure CaCO$_3$ polymorphs (Fong and Nicol 1971; Nicol and Ellenson 1972; Salje and Viswanathan 1976; Liu and Mernagh 1990; Hess et al. 1991; Kraft et al. 1991; Biellmann and Gillet 1992; Gillet et al. 1993; Suito et al. 2001; Shi et al. 2012; Pippinger et al. 2015; Koch-Müller et al. 2016; Liu et al. 2017; Lobanov et al. 2017; Maruyama et al. 2017; Gavryushkin et al. 2017; Bayarjargal et al. 2018; Farsang et al. 2018; Yuan et al. 2019), azurite (Xu et al. 2015), cerussite (Lin and Liu 1997c, 1997b; Minch et al. 2010b; Zhang et al. 2013; Gao et al. 2016), dolomite (Kraft et al. 1991; Biellmann and Gillet 1992; Gillet et al. 1993; Efthimiopoulos et al. 2017, 2018; Farsang et al. 2018; Vennari and Williams 2018), ikaite
Calcite-type carbonates are rhombohedral, space group $R\bar{3}c$, with $Z = 2$ formula units per primitive cell ($N = 10$ atoms per lattice point). The six-fold coordination of the $M^{2+}$ metal cation by $O^{2-}$ means they only accommodate ions with relatively small radius (Table 1). Cation ordering in dolomite-type carbonates lowers the symmetry from $R\bar{3}c$ to $R\bar{3}$. Aragonite-type carbonates are orthorhombic, space group $Pmcn$, and $Z = 4$, $N = 20$. The metal cation is coordinated by nine $O$ atoms and they can accommodate larger divalent ions than the calcite-type carbonates (Table 1).

Here, we report pressure- and temperature-induced frequency shifts of the Raman-active vibrational modes of natural aragonite-type carbonates cerussite, strontianite, and witherite, and calcite-type carbonates gaspeite, otavite, smithsonite, and spherocobaltite up to ~6 GPa and 250-500 °C, respectively. To the best of our knowledge, this is the first report of high-pressure and high temperature Raman data for gaspeite, smithsonite, and spherocobaltite and high-temperature Raman data for otavite. The isobaric and isothermal equivalents of the mode Grüneisen
parameters and the anharmonic parameters have been calculated along with the macroscopic Grüneisen parameter. We discuss and compare the high-pressure and high-temperature vibrational properties of these phases with those of aragonite, calcite, magnesite, rhodochrosite, and siderite presented previously (Farsang et al. 2018).

**Experimental methods**

Samples provided by the Natural History Museum, London were used in all experiments (Table S1). Each was characterized by electron probe microanalysis, X-ray diffraction (XRD), and Raman spectroscopy at the Department of Earth Sciences, University of Cambridge prior to investigation. The calculated chemical formulae and measured unit cell parameters are reported in Table 1.

High-pressure Raman experiments were conducted at room temperature using a membrane diamond anvil cell (Letoullec et al. 1988) equipped with type IIas diamond anvils (Almax easyLab) with culet diameters of 500 μm. A 4:1 methanol-ethanol fluid pressure-transmitting medium, hydrostatic over the full pressure range of our experiments (Klotz et al. 2009), was loaded into steel gaskets, pre-indented from an initial thickness of 240 μm to ~100 μm, then drilled with a 200 μm diameter hole, together with the sample crystal grains. Pressure was increased from ~0 to ~6 GPa in pressure increments of ~0.5 GPa using a PDS 200 pneumatic drive system (BETSA). Pressure was measured from the calibrated shift of the ruby R₁ fluorescence line (Mao et al. 1986) at least 30 minutes after each pressure change (Picard et al. 2006).
High-temperature Raman experiments were performed at room pressure using a DSC600 heating stage (Linkam Scientific Instruments) with the sample held within an aluminum sample pan. The temperature was gradually increased from 25 °C to 250 °C for cerussite, 400 °C for otavite, 375 °C for smithsonite, 450 °C for spherocobaltite, and to 500 °C for the other carbonates in temperature increments of 25 °C. The heating rate was 5 °C.min\(^{-1}\) and the temperature was maintained for five minutes at each step to reach thermal equilibrium prior to data collection.

Raman data were collected from 50 to 1800 cm\(^{-1}\) using a confocal LabRAM 300 (Horiba Jobin Yvon) instrument (300 mm focal length) with spectral resolution ~1 cm\(^{-1}\). The 532.05 nm excitation line was produced by a Ventus 532 laser source (Laser Quantum) focused on the sample using a M Plan Apo SL 50× (Mitutoyo) long working distance objective for the high-pressure experiments and an LMPLFLN 50× (Olympus) long working distance objective for the high-temperature experiments. All spectra were treated by PeakFit™ software. For each, the baseline was subtracted, and peaks fitted using Voigt profiles. Spectra were calibrated against the measured excitation of a Ne light reference (Saloman and Sansonetti 2004).

*In situ* high-temperature (ambient pressure) XRD experiments were conducted to investigate carbonate decomposition products using two Bruker D8 ADVANCE instruments equipped with either an MRI or an Anton Paar HPC900 heating stage (Table S2).

**Results and Discussion**

**Raman-active modes of aragonite-group carbonate minerals**
Aragonite, cerussite, strontianite, and witherite possess $3N - 3 = 57$ optical modes. Based on nuclear site group analysis, the irreducible representations of these modes at the Brillouin Zone center, $\Gamma$, are

$$\Gamma = 9A_g + 6A_u + 6B_{1g} + 8B_{1u} + 9B_{2g} + 5B_{2u} + 6B_{3g} + 8B_{3u}$$

of which the $A_g$, $B_{1g}$, $B_{2g}$, and $B_{3g}$ modes (30 in total) are Raman-active. Due to variations and anisotropy in polarizability, the intensity of certain modes may vary significantly depending on the crystallographic orientation. In certain orientations some bands may be absent. Therefore, ten spectra of crystals in different orientations were collected for each carbonate. However, the assessment of orientation and polarization effects is beyond the scope of this study. Of the 30 expected Raman-active modes, 20 were observed for aragonite at 25 °C (Farsang et al. 2018), and 21, 23, and 17 for strontianite, cerussite, and witherite, respectively (Figure 1).

The low-frequency (< 300 cm$^{-1}$) external modes associated with lattice vibrations include rotations and translations of the $M^{2+}$ ions ($M$ being Ca, Sr, Pb, and Ba, respectively) and $CO_3^{2-}$ groups (Couture 1947). Aragonite shows 13 such external modes, while there are 12 in cerussite and strontianite, and 11 in witherite (Figure 1). At elevated $P$, two additional low-frequency bands were seen for cerussite with extrapolated ambient $P$ frequencies 63 and 67 cm$^{-1}$, respectively.

The high-frequency (> 650 cm$^{-1}$) internal modes of the $CO_3^{2-}$ group include the $\nu_4$ in-plane bendings around ~700 cm$^{-1}$, the $\nu_2$ out-of-plane bending around ~840 cm$^{-1}$, the $\nu_1$ C–O stretching around ~1070 cm$^{-1}$, and the $\nu_3$ C–O stretchings above 1300 cm$^{-1}$ (Couture 1947; Carteret et al. 2013). The frequencies of the $\nu_1$ modes of the three alkali earth orthorhombic carbonates correlate well with ionic radii and $M$–O bond lengths (Figure 2). The $\nu_2$ satellite band at 824 cm$^{-1}$ seen for cerussite and the $\nu_1$ satellite bands at 1059, 1050, 1031, and 1038 cm$^{-1}$ in
aragonite, strontianite, cerussite, and witherite, respectively are assigned to isotopic substitutions of $^{13}$C and $^{18}$O (Cloots 1991; Martens et al. 2004). The frequencies of each of the internal modes decrease in the order of aragonite $>$ strontianite $>$ witherite (although the frequency of the $v_2$ mode is very similar in aragonite and strontianite) as predicted from the relative cation size ($Ca^{2+} < Sr^{2+} < Ba^{2+}$). Despite $Pb^{2+}$ being smaller than $Ba^{2+}$ (1.35 vs. 1.47 Å in nine-fold coordination, Shannon 1976), cerussite has the lowest frequency internal modes of the four aragonite-group carbonates. Our data confirm the general trend of frequency (aragonite $>$ strontianite $>$ witherite $>$ cerussite) noted in earlier works (Wang et al. 2019a and references therein).

Raman-active modes of calcite-group carbonate minerals

Calcite, gaspeite, magnesite, otavite, rhodochrosite, siderite, smithsonite, and spherocobaltite have $3N - 3 = 27$ optical modes. The irreducible representations of these modes at the Brillouin Zone center, $\Gamma$, are

$$\Gamma = A_{1g} + 2A_{1u} + 3A_{2g} + 3A_{2u} + 4E_g + 5E_u$$

of which the $A_{1g}$ and $E_g$ modes (five in total) are Raman-active. All of these were observed in the Raman spectra of calcite-group carbonates at 25 °C, except that one of the $E_g$ modes was absent for siderite (Figure 3 and Table 2).

The translational (T) $E_g$ lattice mode corresponds to translation of the $CO_3$ groups (Bischoff et al. 1985; Liu and Mernagh 1990). T modes frequencies correlate well with ionic radii and M–O bond lengths (Figure 4), with similar values to those previously reported (Dufresne et al. 2018). The librational (L) $E_g$ lattice mode arises from librations of the $CO_3$ groups (Bischoff et al. 1985; Liu and Mernagh 1990). The L mode frequencies correlate...
moderately well with ionic radii (Figure 4), in agreement with the earlier observations of Dufresne et al. (2018).

The high-frequency (700-1500 cm\(^{-1}\)) bands are internal modes of the CO\(_3^{2-}\) group (Couture 1947). They include the \(v_4\) \(E_g\) asymmetric in-plane bending mode, the highest intensity \(v_1\) \(A_{1g}\) symmetric C–O stretching mode, and the \(v_3\) \(E_g\) asymmetric C–O stretching mode. We do not find a strong correlation between \(v_1\) frequencies and ionic radii or M–O bond distances (Figure 4) in contrast to Dufresne et al. (2018).

The highest-frequency (> 1700 cm\(^{-1}\)) band represents either the 2\(v_2\) overtone mode of the IR active \(v_2\) \(A_{2u}\) mode (Krishnan 1945; Couture 1947; Krishnamurti 1957; De La Pierre et al. 2014) or the \(v_1\) \(A_{1g}\) + \(v_4\) \(E_g\) combination mode (Rutt and Nicola 1974; Herman et al. 1987). We prefer the former interpretation based on the simple observation that this band, just like the IR-active \(v_2\) band (Santillán and Williams 2004), shows close to 0 or negative shift with \(P\), in contrast to the other observed Raman-active modes.

An additional broad, low-intensity feature occurs at 507 cm\(^{-1}\) for siderite. This is caused by an Fe\(^{2+}\) electronic excitation (Popkov et al. 1972). We did not observe the broad feature of unknown origin reported by Chariton et al. (2018) at 1970 cm\(^{-1}\) in their study of spherocobaltite.

**High-pressure spectra of aragonite-group carbonates**

In aragonite, strontianite, cerussite, and witherite 15, 16 (including a satellite), 21 (including a satellite), and 14 modes, respectively, could be traced over at least part of the measured pressure range. Their frequency evolutions as a function of pressure (Figure 5 and Figure S1 and
Supplementary Material 1) are, to first degree, linear and $\delta \nu / \delta P$ for all modes are effectively constant over the observed pressure range (Table S3).

For all carbonates studied, the pressure-induced shifts of internal modes are generally smaller than those of the external modes due to the greater incompressibility of the CO$_3$ units (Ross and Reeder 1992; Gillet et al. 1993) (Figure 5). The frequencies of all external modes increase with pressure, except the lowest-frequency bands in aragonite and strontianite. In all carbonates, three $\nu_4$ in-plane bending modes could be traced, with positive $\delta \nu / \delta P$. The site group splitting of $\nu_4$ bands increases with pressure, indicating increasing distortion of the CO$_3$ units (White 1974 and references therein). The inverse relationship between the magnitude of $\nu_4$ band splitting and cation size described by White (1974) is seen in all samples except cerussite, which displays much larger $\nu_4$ band splitting than other carbonates. The $\nu_2$ out-of-plane bending mode and its satellite could only be traced in cerussite and they have similar negative $\delta \nu / \delta P$. The $\nu_1$ C–O stretching mode showed positive $\delta \nu / \delta P$ in all samples. The $\nu_1$ satellite band was only traced (up to ~5 GPa) in strontianite, with $\delta \nu / \delta P$ similar to the $\nu_1$ band. One $\nu_3$ C–O stretching mode could be traced in aragonite, two in strontianite and witherite, and three in cerussite. All $\nu_3$ bands have positive $\delta \nu / \delta P$. Slightly increased splitting of $\nu_3$ bands with pressure was only observed in witherite, indicative of increasing distortion of the CO$_3^{2-}$ units in the CO$_3^{2-}$ plane (Greenaway et al. 1986; Kraft et al. 1991). The splitting of $\nu_3$ bands showed little variation in strontianite and cerussite.

Beyond the simple dependence on instrumental resolution, the linewidth of a Raman peak is inversely dependent upon phonon lifetime. Hence it generally increases with temperature and linewidth may also reflect phonon – point defect scattering associated with either trace element incorporation or other defect accumulation. The $\nu_1$ modes in aragonite-group carbonates have
narrow linewidths, below 4 cm\(^{-1}\) over the studied pressure range (Figure S1). Linewidths of other modes were not determined due to overlaps and/or low-intensity peaks.

High-pressure spectra of calcite-group carbonates

The frequency-evolution of all Raman-active modes in the calcite-group carbonates could be traced over the entire pressure range of our experiments with the exception of those for calcite (Farsang et al. 2018). The ambient pressure and temperature \(R\overline{3}c\) phase of calcite (calcite I) undergoes a ferroelastic symmetry-breaking structural phase transition to calcite II on increasing pressure through \(\sim1.4\) GPa, with a subsequent transition to calcite III at \(\sim1.7\) GPa (Bridgman 1938). The Raman-active modes of calcite I could only be traced up to the pressure corresponding to the first transition, therefore (Farsang et al. 2018). The frequency-evolution of all calcite-group carbonate modes as a function of pressure is reported in Figure 6 and Figure S2 and Supplementary Material 1 and the relative changes in frequency \(\delta \nu / \delta P\) are given along with earlier reported values in Tables 3 and S4. We find \(\delta \nu / \delta P\) for all modes is effectively constant over the observed pressure range, with linear changes in the pressure dependence of mode frequencies. All measured Raman peaks increase in frequency with pressure, with the exception of the Fe\(^{2+}\) electronic excitation feature seen in siderite and the overtone mode in certain calcite-group carbonates. Calcite has the lowest \(\delta \nu / \delta P\) of T mode and the highest \(\delta \nu / \delta P\) of L and \(\nu_1\) modes. The extreme values are likely associated with the structural transition of calcite occurring at and above \(\sim1.4\) GPa. The close to 0 or negative slope of the highest frequency mode supports the interpretation that this is the \(2\nu_2\) overtone of \(\nu_2\) out-of-plane bending mode of the \(\text{CO}_3\) group rather than the \(A_{1g} + E_g\) combination mode. The negative \(\delta \nu / \delta P\) of the \(2\nu_2\) overtone mode has
been related to the distortion of MO$_6$ octahedra (Liang et al. 2018b). Carbonates with large
cations (e.g., Fe$^{2+}$, Mn$^{2+}$, Cd$^{2+}$, Ca$^{2+}$) show a larger negative $\delta\nu/\delta P$ of $2\nu_2$ indicating a more
significant MO$_6$ octahedral distortion.

Due to the large uncertainty arising from peak fitting, it is difficult to discern changes in
linewidth of T and L modes (Figure S2). The linewidth of the $\nu_1$ mode is much broader in
calcite-group carbonates than in the aragonite-group carbonates (Figure S2). It decreases with $P$
in carbonates with small cations (e.g., magnesite, gaspeite), but remains quasi-constant or
increases in carbonates with larger cations. Once again, carbonates with large cations likely
experience greater distortions of MO$_6$ octahedra and CO$_3$ units that connect these polyhedra,
resulting in broader $\nu_1$ peaks.

High-temperature spectra of aragonite-group carbonates

In aragonite, strontianite, cerussite and witherite, 20 (including a satellite), 13 (including a
satellite), 16 (including a satellite), and 15 modes, respectively, could be traced over (at least part
of) the observed temperature range. The temperature-dependence of the frequency of modes in
these aragonite-group carbonates (Figures 7, S3 and Supplementary Material 2) is linear and the
values of $\delta\nu/\delta T$ (Table S3) are, to first approximation, constant over the observed temperature
range. In both aragonite and calcite-group carbonates, the temperature-induced shifts of internal
modes are generally smaller than those of the external modes, due to the rigidity of C–O bonds
in the CO$_3$ units (Markgraf and Reeder 1985; Reeder and Markgraf 1986; Gillet et al. 1993). All
external modes decrease in frequency with temperature. In aragonite, strontianite, and witherite,
some bands appear to cross or merge at elevated temperatures, become indistinguishable from
one another and were therefore further treated as one band. Three \( \nu_4 \) bands could be traced in
aragonite, cerussite, and witherite, but only two were seen in strontianite; all show positive \( \delta \nu / \delta T \)
for all samples. In aragonite and witherite, the highest frequency \( \nu_4 \) band decreases in intensity
on heating, while the two lower frequency \( \nu_4 \) bands merge into one at 250 and 300 °C,
respectively. In contrast to the work of White (1974), we observed \( \nu_4 \) site group splitting in all
aragonite-group carbonates. The converging nature of \( \nu_4 \) bands, i.e. decreasing site group
splitting with increasing temperature, is interpreted as a symmetry change in the local crystal
field surrounding the \( \text{CO}_3 \) group, or as a decrease in distortion of the \( \text{CO}_3 \) group itself (Gillet et
al. 1993). The \( \nu_2 \) band could only be traced in aragonite, strontianite, and cerussite and has a
negative \( \delta \nu / \delta T \) in all carbonates. The \( \nu_1 \) band has negative \( \delta \nu / \delta T \) in all carbonates. Its satellite
band could only be measured for aragonite, strontianite, and cerussite up to 250, 300, and 175
°C, respectively. The \( \delta \nu / \delta T \) of satellite bands are very similar to those of \( \nu_1 \) bands. Two \( \nu_3 \) bands
could be traced over at least part of the observed temperature range and show negative \( \delta \nu / \delta T \) in
all carbonates. Among all samples, only strontianite showed slightly decreasing splitting of \( \nu_3 \)
bands on heating, suggesting decreasing distortion of the \( \text{CO}_3^{2-} \)! units within the \( \text{CO}_3^{2-} \)
plane (Greenaway et al. 1986; Kraft et al. 1991). The splitting of \( \nu_3 \) bands is near-constant in other
aragonite-group carbonates. In general, \( \delta \nu / \delta T \) values of \( \nu_4 \) modes are greater (positive or less
negative) than those of \( \nu_2 \), which are greater (less negative) than those of \( \nu_1 \), which are in turn
greater (less negative) than those of \( \nu_3 \), in agreement with the observations of Wang et al.
(2019a).

At ambient pressure and above 425 °C, aragonite transforms to calcite. The modes of
aragonite could only be traced below this temperature, therefore (Figure S4). The thermal
decomposition of cerussite to Pb-oxide(s) and presumably \( \text{CO}_2 \) was observed between 225 and
At 250 °C, Raman peaks characteristic to cerussite are no longer visible. Instead, new peaks appear at 84, 136, 268, and 367 cm\(^{-1}\), indicative of PbO (Cortez-Valadez et al. 2013). In contrast, \textit{in situ} high-temperature XRD revealed the presence of two decomposition products, Pb\(_2\)O\(_3\) and minor tetragonal PbO (litharge). Both these results are in sharp contrast to the observed melting of cerussite observed at 570 K (297 °C) by Wang et al. (2019a). The widths of \(\nu_1\) modes increase significantly with temperature (Figure S3). Linewidths of other modes were not determined due to overlaps and/or low-intensity peaks.

**High-temperature spectra of calcite-group carbonates**

The frequency evolution of all Raman modes from calcite-group carbonates could be traced over the observed temperature range with the exception of the \(\nu_3\) \(E_g\) mode in spherocobaltite, the Fe\(^{2+}\) electronic excitation feature in siderite, and the \(\nu_4\) \(E_g\) mode in otavite due to the decreasing intensity of these peaks. The frequency of all measured modes decrease or remain constant with increasing temperature (Figure 8 and Figure S6 and Supplementary Material 2) and \(\delta\nu/\delta T\) for all modes is approximately constant over the observed temperature range (Tables 4 and S4). In smithsonite, gaspeite and siderite, \(\delta\nu/\delta T\) for \(\nu_1\) decreases rapidly above 200 °C. In rhodochrosite and otavite, \(\delta\nu/\delta T\) for \(\nu_1\) shows significant fluctuation. Gillet et al. (1993) noted that in calcite and presumably in other calcite-group carbonates too), the changes in frequency of the \(\nu_1\) mode are not primarily due to changes in bond length or polyhedral volume, but rather due to increasing distortion as the O–O distance in the basal plane of the CaO\(_6\) octahedra shortens.

Similar to aragonite-group carbonates, \(\delta\nu/\delta T\) for \(\nu_4\) is greater (positive or less negative) than that
for ν₁ (except in magnesite and siderite). Furthermore, δν₁/δT for ν₁ is greater (less negative),

than that for ν₃.

In general, the linewidths of T, L, and ν₁ modes in the calcite-group carbonates increase

with temperature (Figure S6). In calcite, a nonlinear increase in width of the T mode peak occurs

above 400 °C, as noted by Gillet et al. (1993). They related the quasi-linear increase up to 400 °C

to the simple volume thermal expansion associated with a cubic anharmonicity term (Brehat and

Wyncke 1985) and the anomalous increase above 400 °C to additional anharmonic terms

associated with the relaxational mode, before the onset of rotational order-disorder transition at

higher temperatures (Megaw 1970; Redfern et al. 1989). In gaspeite, the large linewidth of the ν₁

mode may be a consequence of compositional heterogeneity and the existence of Mg-rich

domains in the sample.

The thermal decomposition of gaspeite to NiO (and presumably CO₂) commences above

375 and is complete below 400 °C (Figure S7). The broad peaks at 525 and 1075 cm⁻¹

correspond to one-phonon (1P) TO and LO modes and two-phonon (2P) 2LO modes of NiO,

respectively (Dietz et al. 1971). At room temperature, NiO exhibits its highest intensity two-
magnon (2M) scattering band at ~1500 cm⁻¹ but (being well above the Néel temperature of NiO)

this band becomes unidentifiable in our spectra (Dietz et al. 1971). The gradual thermal

decomposition of smithsonite starts above 325 and is complete below 400 °C (Figure S8). This

temperature range is slightly higher than that reported by Hales and Frost (2008). Our in situ

high-temperature XRD experiments indicate that the decomposition product is hexagonal ZnO

and presumably CO₂. In the spectrum collected at 400 °C bands corresponding to smithsonite are

absent. The high-intensity peaks at 102, 325, 433, and 573 cm⁻¹ indicate the presence of

hexagonal ZnO (Decremps et al. 2002). The thermal decomposition of spherocobaltite was
observed between 425 and 450 °C and the decomposition of otavite between 375 and 400 °C, marked by the disappearance of all its Raman bands. The latter temperature range is slightly higher than the previously suggested range of 330-375 °C (Ballirano 2016), probably due to the trace element content of our otavite. Gaspeite, otavite, and spherocobaltite showed increased sensitivity under the laser beam at higher temperatures and it was necessary to decrease the laser power at temperatures starting at 375, 350, and 200 °C, respectively. The sensitivity of spherocobaltite to laser beam damage has also been reported elsewhere (Rutt and Nicola 1974). For comparison, the decomposition of rhodochrosite takes place between 400 and 425 °C, while the decomposition of siderite occurs between 375 and 400 °C (Farsang et al. 2018).

**Mode Grüneisen and intrinsic anharmonic parameters**

While pressure-induced frequency shifts of a given vibrational mode arise from the implicit pure volume contribution due to compressibility, temperature-induced frequency shifts of a given vibrational mode arise from two contributions: (1) the implicit, pure volume contribution due to thermal expansion and (2) the explicit, volume independent, phonon-excitation contribution due to phonon-phonon interactions, known as intrinsic anharmonicity (Gervais et al. 1973; Peercy and Morosin 1973; Gillet et al. 1989, 1998). The isobaric and isothermal equivalents of the mode Grüneisen parameter and the intrinsic anharmonic parameter provide the means to quantify these contributions.

The mode Grüneisen parameter, \( \gamma_i \), links the change in frequency of vibrational mode \( i, \nu_i \) (measured at 25 °C in this work), to the change in volume \( V \) (Born and Huang 1954):

\[
\gamma_i = -\frac{d \ln \nu_i}{d \ln V} = -\frac{V d \nu_i}{\nu_i d V}
\]
The isobaric equivalent of mode Grüneisen parameter, $\gamma_{iP}$ (Gillet et al. 1989) describes the temperature dependence of the vibrational mode and can be expressed as:

$$\gamma_{iP} = -\frac{d \ln \nu_i}{d \ln V(T)} = -\frac{d\nu_i}{\alpha\nu_i dT}$$

where $\alpha$ is the thermal expansion coefficient. The isothermal equivalent of mode Grüneisen parameter, $\gamma_{iT}$ (Gillet et al. 1989; Wagner 2000) describes the pressure dependence of the vibrational mode and can be expressed as:

$$\gamma_{iT} = -\frac{d \ln \nu_i}{d \ln V(P)} = \frac{K_T d\nu_i}{\nu_i dP}$$

where $K_T$ is the isothermal bulk modulus. From the difference between $\gamma_{iT}$ and $\gamma_{iP}$, the intrinsic anharmonic parameter, $a_i$, quantifying intrinsic anharmonicity, can be calculated for each mode (Gillet et al. 1989):

$$a_i = \alpha(\gamma_{iT} - \gamma_{iP})$$

The isobaric and isothermal equivalents of the Grüneisen parameter and the anharmonic parameter have been calculated for each measured mode using thermodynamic properties reported in Table 5 and are presented in Table S3 and Figure S9 for aragonite-group carbonate minerals and Table S4 and Figure S10 for calcite-group carbonate minerals. Values of the isobaric and isothermal equivalents of the Grüneisen parameter and the anharmonic parameter span a much larger range for external modes than internal modes in both aragonite and calcite-group carbonate minerals. As a consequence, external modes are expected to contribute significantly more to the intrinsic anharmonicity.

In aragonite-group carbonates, values of $\gamma_{iP}$ of external modes range from 0.14 to 4.10, $\gamma_{iT}$ from -0.69 to 4.75, and $a_i$ from -17.33 to 36.92. The values of $\gamma_{iP}$ of internal modes range from -0.13 to 0.39, $\gamma_{iT}$ from 0.07 to 0.26, and $a_i$ from -1.44 to 1.83. In aragonite-group carbonates, the
values of $\gamma_{IP}$ generally increase with increasing frequency of internal vibrational modes, i.e. they are smaller for the $v_4$ and $v_2$ bending modes than for the $v_1$ and $v_3$ stretching modes of the CO$_3$ groups, a result consistent with earlier observations and implying a lower sensitivity of O–C–O angles to temperature than the C–O bond length (Wang et al. 2019a). At the same time, $a_i$ values generally decrease with increasing frequency of internal modes. In contrast to earlier results, our $\gamma_{IP}$ values for the external vibrational modes of cerussite were not lower than those of other aragonite-group carbonates (Wang et al. 2019a). However, $\gamma_{IT}$ values were higher, in agreement with the same study.

In the calcite-group carbonates, the values of $\gamma_{IP}$ of the external modes range from -0.15 to 12.89, $\gamma_{IT}$ from 1.12 to 2.54, and $a_i$ from -15.29 to 8.03. The values of $\gamma_{IP}$ for the internal modes range from -0.09 to 1.28, $\gamma_{IT}$ from 0.22 to 0.55, and $a_i$ from -1.29 to 0.94. In calcite-group carbonates, $\gamma_{IP}$ values generally increase with increasing frequency of the internal modes, i.e. they are smaller for the $v_4$ bending mode than for $v_1$ and $v_3$ stretching modes of CO$_3$ groups, a result consistent with earlier observations of aragonite-group minerals and implying lower sensitivity of O–C–O angles to temperature than C–O bond length (Wang et al. 2019a). At the same time, $a_i$ values generally decrease with increasing frequency of the internal modes.

Published $\nu_i$, $\delta\nu_i/\delta P$, $\delta\nu_i/\delta T$, $\gamma_{IT}$, $\gamma_{IP}$, and $a_i$ values corresponding to the same Raman-active modes of any particular carbonate mineral show considerable variation. The possible reasons for the variation in measured $\nu_i$, $\delta\nu_i/\delta P$, and $\delta\nu_i/\delta T$ values include trace element content and the use of different pressure transmitting media. Due to differences in the ion size and mass, substitution will change the average inter-atomic distances and bond strengths and, consequently, the frequency of vibrational modes (Krishnamurti 1956; Rutt and Nicola 1974). As large (e.g., CaO$_6$) octahedra are more compressible than small (e.g., MgO$_6$) octahedra (Ross and Reeder...
1992), trace element content will also affect $\delta v/\delta P$ values. The complex effects of temperature on the structure of carbonates with different ions (e.g. Markgraf and Reeder 1985; Reeder and Markgraf 1986), will result in a range of $\delta v/\delta T$ values too. The use of different pressure transmitting media (e.g., Ne, methanol-ethanol, KBr), some of which may not sustain hydrostatic pressure in the pressure range of measurements, may lead to different $\delta v/\delta P$ values as shown by the example of magnesite (Liang et al. 2018a). Differences in $\gamma_T$, $\gamma_P$, and $\alpha_i$ can be further amplified by the use of different literature values of thermodynamic parameters for the calculation.

**Macroscopic Grüneisen parameter**

The macroscopic Grüneisen parameter, $\gamma_{th}$, accounts for all contributions of the mode Grüneisen parameter and can be calculated as:

$$\gamma_{th} = \frac{\alpha K}{\rho C_P} = \frac{\alpha K}{\rho C_V}$$

where $\alpha$ is the thermal expansion coefficient, $K_S$ and $K_T$ are the adiabatic and isothermal bulk moduli, respectively, $\rho$ is the molar density, and $C_P$ and $C_V$ are the heat capacities at constant pressure and volume, respectively. The macroscopic Grüneisen parameters calculated for individual carbonate minerals are reported in Table 5.

**Comparison with structural data**

Previous XRD studies have shown that all four aragonite-group carbonate minerals display anisotropic linear compression (Martinez et al. 1996; Wang et al. 2015; Gao et al. 2016)
and anisotropic thermal expansion (Ye et al. 2012), the compression and thermal expansion
along the $z$ axis being much larger than that along $x$ and $y$ axes. This behavior can be explained
by the much more sensitive M–O bond distance compared to the C–O bond distance, which is
almost constant with pressure (Li et al. 2015) and temperature (Antao and Hassan 2010; Ye et al.
2012), and the orientation of nearly planar CO$_3^{2-}$ groups, in which the C–O bonds lie,
perpendicular to $z$ axis. In isostructural solids, compressional behavior can be explained either by
the size, charge, or electronic configuration of the constituent atoms, in our case limited to the
M$^{2+}$ ion (Zhang and Reeder 1999). The size of M$^{2+}$ ions varies considerably (Table 1), the charge
is the same, and there are two types of electronic configuration present: p$^6$ closed-shell
configuration present in Ca$^{2+}$, Sr$^{2+}$, and Ba$^{2+}$ as opposed to the 6s$^2$ lone pair of Pb$^{2+}$ (Table 1).
Plotting bulk modulus values against unit cell (or molar) volume reveals that compressibility is
directly proportional to the unit cell volume in aragonite-group carbonate minerals having an
alkaline earth element M$^{2+}$ ion, while cerussite has lower compressibility than its unit cell
volume implies (Wang et al. 2015). In addition, the thermal expansion along the $z$ axis is much
larger for cerussite than for the other carbonate minerals and there is also a larger variation
(increase) in $c/c_0$ values with increasing temperature (Ye et al. 2012). The significantly higher
thermal expansion coefficient of cerussite compared to other aragonite-group carbonates (Ye et
al. 2012) indicates that size alone cannot account for the thermal behavior of aragonite-group
carbonates. Instead, a possible reason suggested for the anomalous behavior of cerussite is its
electronic configuration, but no further explanation was given (Minch et al. 2010b). A detailed
account based on the extremely high electronegativity of Pb$^{2+}$ (Table 1) was given by Gao et al.
(2016). According to this, the high electronegativity implies additional metalloid behavior,
adding some covalent character to the Pb–O bond, which, due to its directional nature, may
restrict the movement of CO$_3^{2-}$ groups in the structure. These behave as rigid bodies with only slight changes of O–C–O bond angles with pressure (Li et al. 2015), a result consistent with the distortion of CO$_3^{2-}$ groups reflected in splitting of internal modes as seen in this study and elsewhere (Kraft et al. 1991).

The frequency of the most intense $\nu_1$ band decreases with increasing unit cell volume in alkaline earth aragonite-group carbonates, while the frequency of the $\nu_1$ band of cerussite is lower than expected (Figure 9a). The pressure-induced shift of the $\nu_1$ band decreases with increasing unit cell volume in the three alkaline earth aragonite-group carbonates (Figure 9b). Once again, the pressure-induced shift of $\nu_1$ band of cerussite is slightly lower than implied by the general trend. The pressure-induced shift of the $\nu_1$ band decreases with compressibility too (Figure 9c). Cerussite is once more an outlier indicating that the electron configuration and electronegativity of Pb$^{2+}$ affects both structural and vibrational properties. The three alkaline earth aragonite-group carbonate minerals show no systematic trend between thermal expansion coefficient and unit cell volume. Similarly, no trends were observed between the $\delta \nu_1 / \delta T$ of $\nu_1$ band and unit cell volume and between the $\delta \nu_1 / \delta T$ of $\nu_1$ band and thermal expansion coefficient.

Calcite-group carbonate minerals also display anisotropic compression (Redfern et al. 1993; Redfern and Angel 1999; Zhang and Reeder 1999; Redfern 2000; Liang et al. 2018b) and anisotropic thermal expansion (Wang et al. 2018), the compression and thermal expansion along $z$ axis (in the hexagonal setting) being much larger than that along $x$ axis. While the compressibility along $z$ axis is nearly linear with M–O bond length in calcite-group carbonate minerals, compressibility along the $x$ axis shows large differences depending on the cation type (Zhang and Reeder 1999). Systematic compressibility behavior, expressed as bulk modulus versus unit cell volume, is limited to subsets of carbonate minerals sharing metal ions of similar
valence state: alkaline earth elements with $p^6$ closed-shell configuration, 3d transition metals, and a 4d transition metal (Zhang and Reeder 1999, Table 1). Systematic trends in thermal expansion across calcite-group carbonate minerals are unclear. There is no clear relationship between unit cell volume and thermal expansion along the $z$ axis (Wang et al. 2018). Markgraf and Reeder (1985) reported a positive thermal expansion along $x$ for magnesite and a negative one for calcite, in agreement with Wang et al. (2018), who reported a positive thermal expansion along the $x$ axis for magnesite, rhodochrosite, and smithsonite, a positive thermal expansion along the $x$ axis for otavite over the range 123 – 223 K (-150 – -50 °C), followed by a negative one between 223 and 593 K (-50 – 320 °C), and a negative thermal expansion along the $x$ axis for calcite between 123 and 618 K (-150 – 345 °C). The negative thermal expansion along the $x$ axis for calcite was explained in terms of the shortening of the C–O bond and the basal edge O$_1$–O$_2$ bond distances due to the large libration of the CO$_3^{2-}$ unit (Markgraf and Reeder 1985). The libration of the CO$_3^{2-}$ unit is expected to increase with ion size, explaining why only carbonates with large ions (e.g., Ca$^{2+}$ and Cd$^{2+}$) show negative thermal expansion along the $x$ axis (Wang et al. 2018). An inverse correlation between thermal expansion along the $x$ axis and the M$^{2+}$ cation radius was found by Wang et al. (2018).

In contrast to aragonite-group carbonate minerals, systematic trends in the subgroups of calcite-group carbonate minerals having cations of similar electronic configuration (i.e., alkali earth elements, 3d and 4d transition metals) are difficult to observe for a number of reasons. There are only two alkaline earth calcite-group minerals (calcite and magnesite) and only one 4d transition metal calcite-group carbonate (otavite) and although there are five 3d transition metal calcite-group carbonates, they have different numbers of electrons (and paired electrons) in their outer shell, which may complicate general trends in their behavior.
Regardless of the electronic configuration of the $M^{2+}$ ion, systematic trends can be observed in the behavior of calcite-group minerals. The frequencies of all bands decrease with increasing unit cell volume (Figure 10a,d,g). However, the external translational and $2\nu_2$ overtone modes respond to pressure in the opposite way to external librational and internal $\nu_4$, $\nu_1$, and $\nu_3$ modes. The pressure-induced shift of the external translational and $2\nu_2$ overtone bands decreases with increasing unit cell volume and compressibility (Figure 10b,c), while the pressure-induced shift of the external librational and internal $\nu_4$, $\nu_1$, and $\nu_3$ bands increases with increasing unit cell volume and compressibility (Figure 10e,f,h,i). These contrasting trends can be explained by the differences in displacement vectors of atoms associated with these vibrations. For the external translational and $\nu_2$ bands this displacement has a significantly larger component parallel to $z$ axis (Caracas and Bobociou 2011). The opposite trends in pressure-induced behavior of the two external modes become apparent when plotting their pressure-induced shifts against each other (Figure 11a). When considering calcite-group carbonates with $M^{2+}$ ions of different kinds separately, clear correlations between the pressure-induced frequency shifts of external L band and axial compressibility along $x$ crystallographic axis can be seen (Figure 11b). These trends limited to subgroups of carbonates with cations of similar configuration suggest that besides size, differences in electronegativity and bonding type are important controls on the pressure response of carbonates. Whereas bonds between alkali earth metals (having low electronegativity, Table 1) and oxygen are strongly ionic, those between transition metals (having moderate electronegativity, Table 1) often possess some covalent character. Understanding the exact mechanism underlying high-pressure vibrational and structural behavior requires quantitative data on electron density distribution in different carbonates (Zhang and Reeder 1999). Similarly to aragonite-group carbonate minerals, those
belonging to the calcite group show no systematic trends between the thermal expansion
coefficient and unit cell volume or the temperature-induced shift of any band and unit cell
volume. The only moderate correlation can be seen between the temperature-induced shift of the
external T and L bands possibly indicating an opposite response of these bands to temperature
(Figure 11c).

An additional enigmatic feature is the pressure response of the most intense internal $\nu_1$
symmetric C–O stretching mode in aragonite versus calcite-group carbonate minerals. The
pressure-induced shift decreases with increasing unit cell volume and compressibility in
aragonite-group carbonate minerals, while it increases with increasing unit cell volume and
compressibility in calcite-group carbonates.

Anharmonic contribution to thermodynamic properties

The anharmonicity of vibrational modes has considerable effect on the thermodynamic
properties of these phases at high-temperature conditions. The anharmonic parameter can be
used for the correction and calculation of numerous thermodynamic properties, including the
thermal contributions to the internal energy, the isochoric heat capacity, which is responsible for
the departure from the Dulong-Petit limit at high temperature, the isobaric heat capacity, and the
thermal contribution to the entropy (Gillet et al. 1989; Gillet 1996; Matas et al. 2000; Oganov
and Dorogokupets 2004).

Harmonic expressions for the thermal contributions to the internal energy, $\epsilon_T-\epsilon_0$, isochoric
(constant-volume) specific heat, $C_V$, isobaric (constant-pressure) specific heat, $C_P$, and thermal
contribution to the entropy, $S_T-S_0$, are (Erba et al. 2015; Wang et al. 2019b):
\[ \varepsilon_T - \varepsilon_0 = \sum_{i=1}^{3N} \hbar \nu_i \left( \frac{1}{2} + \frac{1}{e^{\hbar \nu_i / kT} - 1} \right) \]

\[ C_V = \sum_{i=1}^{3N} \left( \frac{(\hbar \nu_i)^2}{kT^2} \frac{\hbar \nu_i}{e^{\hbar \nu_i / kT} - 1} \right)^2 \]

\[ C_p = C_V + \alpha^2 K_T K V T T \]

\[ S_T - S_0 = \int_0^T \frac{C_p}{T} dT \]

where \( k \) is the Boltzmann constant, \( \hbar \) is Planck's constant, and \( V_T \) is the equilibrium volume at temperature \( T \).

The anharmonic corrections for the internal energy and isochoric specific heat are given by (Gillet et al. 1989; Matas et al. 2000):

\[ \varepsilon(\text{anh}) = \varepsilon(1 - a_i T) \]

\[ C_V(\text{anh}) = C_V(1 - a_i T) \]

The measurement of frequencies and anharmonic parameters of individual vibrational modes therefore allows a robust evaluation of importance of any anharmonic thermodynamic properties. The availability of such data is limited to the geologically most relevant carbonate phases only, namely calcite, dolomite, and magnesite (Wang et al. 2019b). Thermodynamic properties for these three phases calculated based on the harmonic and anharmonic approximation and the difference between the two are reported in Figure 12. We find that anharmonic effects are most pronounced for calcite, whereas the properties of magnesite are influenced the least, in agreement with earlier reports (Wang et al. 2019b). Values for the thermal contribution to the internal energy are comparable to those reported previously (Wang et al. 2019b). Small differences arise from the use of recently measured values of frequency and anharmonic
parameters of Raman-active modes (Farsang et al. 2018). Anharmonic corrections for other
thermodynamic properties differ approximately by a factor of two. This is due to the fact that
Wang et al. (2019b) adopted the widely used incorrect factor of $2a_i T$ rather than $a_i T$ to calculate
the anharmonic contribution to thermodynamic properties (Matas et al. 2000).

Implications

At ambient pressure, the stability (in air) of many of the studied carbonate minerals
approaches or even extends beyond 500 °C. At high-pressure, their stability likely increases to
even higher temperatures and carbonates may serve as potential reservoirs for a number of
metals (e.g., Co, Ni, Zn, Cd) in a range of crustal and upper mantle environments (e.g.,
subduction zones). Further experiments are needed to test the simultaneous high-pressure and
high-temperature stability of these carbonate phases, including their solubility behavior in
aqueous fluids resembling those present in subduction zones.

A significant anharmonic contribution to thermodynamic properties has been
demonstrated for calcite, magnesite, and dolomite. To quantify these properties for the remaining
carbonates, complimentary spectroscopic experiments addressing the high-pressure and high-
temperature vibrational behavior of their acoustic and IR-active modes are necessary. The
calculated anharmonic thermodynamic properties allow the refinement of phase equilibria at
high-pressure and high-temperature conditions and should be implemented in any calculation
addressing phase behavior in high-temperature environments. This is necessary for
understanding a range of subduction zone geologic processes involving carbonate minerals (e.g.,
devolatilization, melting, dissolution in slab fluids) and modeling the deep carbon cycle.
Isotope fractionation is also controlled by the thermodynamic properties (e.g., Gibbs free energy) of respective phases. Thermodynamic properties corrected for anharmonicity should therefore be used for calculating isotope fractionation factors at the high-pressure and high-temperature environments of deep Earth (Gillet et al. 1996; Polyakov 1998).

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Figure 1. Raman spectra of aragonite-group carbonate minerals aragonite, strontianite, cerussite, and witherite collected at ambient pressure (1 bar) and temperature (25 °C). Ionic radii are from Shannon (1976). The spectrum of aragonite is from Farsang et al. (2018). Bands marked with * are due to isotopic effects.

Figure 2. The correlation of frequencies of $v_1$ internal vibrational mode with ionic radii and M–O bond lengths in aragonite-group carbonate minerals. Ionic radii are from Shannon (1976). M–O bond lengths are from Ye et al. (2012). Data for aragonite are from Farsang et al. (2018).

Figure 3a. Raman spectra of calcite-group carbonate minerals gaspeite, magnesite, smithsonite, and spherocobaltite collected at ambient pressure (1 bar) and temperature (25 °C). Ionic radii are from Shannon (1976). The spectrum of magnesite is from Farsang et al. (2018). The symmetry of calcite-group carbonate modes is from Rutt and Nicola (1974). Due to submicron size magnesite domains present in gaspeite, the spectrum of gaspeite contains additional bands of magnesite.

Figure 3b. Raman spectra of calcite-group carbonate siderite, rhodochrosite, otavite, and calcite collected at ambient pressure (1 bar) and temperature (25 °C). Ionic radii are from Shannon (1976). The spectra of siderite, rhodochrosite, and calcite are from Farsang et al. (2018). The symmetry of calcite-group carbonate modes is from Rutt and Nicola (1974).

Figure 4. The correlation of frequencies of $T$ (a) and $L$ (b) external vibrational modes and $v_1$ (c) internal vibrational mode with ionic radii and M–O bond lengths in calcite-group carbonate minerals. Ionic radii are from Shannon (1976). M–O bond lengths are calculated by Rutt and

Figure 5. Frequency evolution of the traced vibrational modes in aragonite-group carbonate minerals as a function of pressure. The experimental uncertainty lies within the size of the symbol. Ionic radii are from Shannon (1976). Data for magnesite, siderite, rhodochrosite, and calcite are from Farsang et al. (2018).

Figure 6. Frequency evolution of the traced vibrational modes in calcite-group carbonate minerals as a function of pressure. The experimental uncertainty lies within the size of the symbol. Ionic radii are from Shannon (1976). Data for magnesite, siderite, rhodochrosite, and calcite are from Farsang et al. (2018). The Fe$^{2+}$ electronic excitation feature of siderite is not shown and can be found in Farsang et al. (2018).

Figure 7. Frequency evolution of the traced vibrational modes in aragonite-group carbonate minerals as a function of temperature. The experimental uncertainty lies within the size of the symbol. Ionic radii are from Shannon (1976). Data for magnesite, siderite, rhodochrosite, and calcite are from Farsang et al. (2018).

Figure 8. Frequency evolution of the traced vibrational modes in calcite-group carbonate minerals as a function of temperature. The experimental uncertainty lies within the size of the symbol. Ionic radii are from Shannon (1976). Data for magnesite, siderite, rhodochrosite, and calcite are from Farsang et al. (2018). The Fe$^{2+}$ electronic excitation feature of siderite is not shown and can be found in Farsang et al. (2018).
Figure 9. a) Relationship between the frequency of the internal $\nu_1$ band and unit cell volumes of aragonite-group carbonate minerals, b) Relationship between the pressure-induced frequency shift of $\nu_1$ band and unit cell volumes of aragonite-group carbonate minerals, and c) Relationship between the pressure-induced frequency shift of $\nu_1$ band and isothermal bulk moduli of aragonite group carbonate minerals. Linear correlations indicated by trend lines exist only for aragonite-group carbonate minerals having an alkaline earth element $M^{2+}$ ion. Values of the frequency of the $\nu_1$ band can be found in Table S3, values of unit cell parameters in Table 1, values of pressure-induced frequency shift of $\nu_1$ band in Table S3, and values of isothermal bulk moduli in Table 5.

Figure 10. Relationships between the frequency of different bands and unit cell volumes, the pressure-induced frequency shift ($\delta\nu_i/\delta P$) and unit cell volumes, and pressure-induced frequency shift ($\delta\nu_i/\delta P$) and isothermal bulk moduli ($K_T$) in calcite-group carbonate minerals: a-c) external translational band, d-f) external librational band, and g-i) internal $\nu_1$ band. Values of the frequency of different bands can be found in Table S4, values of unit cell parameters in Table 1, values of pressure-induced frequency shift of different bands in Table S4, and values of isothermal bulk moduli in Table 5.

Figure 11. a) Relationship between the pressure-induced frequency shifts ($\delta\nu_i/\delta P$) of external T and L bands, b) Relationship between the pressure-induced frequency shifts ($\delta\nu_i/\delta P$) of external L band and axial compressibility along x ($\beta_x$), and c) Relationship between the temperature-induced frequency shifts ($\delta\nu_i/\delta T$) of external T and L bands. Values of pressure and temperature-
induced frequency shift of different bands can be found in Table S4 and axial compressibility values are from Zhang and Reeder (1999).

Figure 12. Thermodynamic properties as a function of temperature calculated based on the harmonic and anharmonic approximation and the difference between the two: a) thermal contribution to internal energy ($\varepsilon_T - \varepsilon_0$), b) isochoric heat capacity ($C_V$), c) isobaric heat capacity ($C_P$), and d) thermal contribution to entropy ($S_T - S_0$). Values are normalized to one mole of CO$_3$ groups.
<table>
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<tr>
<th>Mineral</th>
<th>Ideal formula</th>
<th>Calculated formula</th>
<th>Ionic radius of M(^{2+}) (Å)</th>
<th>M–O bond distance (Å)</th>
<th>Outer electron configuration of M(^{2+})</th>
<th>Electro negativity</th>
<th>Space Group</th>
<th>Unit cell parameters (Å)</th>
<th>Unit cell volume (Å(^3))</th>
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<td>Pb(<em>{10})Mg(</em>{3})CO(_3)</td>
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<td>Sn(_{10})CO(_3)</td>
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<td>4e(^{3d}), 5e(^{3d})</td>
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<td>R3c</td>
<td>4.69(1)</td>
<td>293.16(0)</td>
</tr>
<tr>
<td>Smithsonite</td>
<td>Zn(_{10})CO(_3)</td>
<td>Zn(_{10})CO(_3)</td>
<td>0.74</td>
<td>2.11</td>
<td>M(^{2+})</td>
<td>1.65</td>
<td>R3c</td>
<td>4.65(5)</td>
<td>282.44(1)</td>
</tr>
<tr>
<td>Spherocobaltite</td>
<td>Co(_{10})</td>
<td>Co(_{10})</td>
<td>0.745</td>
<td>2.109</td>
<td>M(^{2+})</td>
<td>1.88</td>
<td>R3c</td>
<td>4.65(5)</td>
<td>281.81(3)</td>
</tr>
<tr>
<td>Dolomite</td>
<td>CaMg(_{10})CO(_3)</td>
<td>CaMg(_{10})CO(_3)</td>
<td>0.74</td>
<td>2.10(1)</td>
<td>M(^{2+})</td>
<td>1.88</td>
<td>R3c</td>
<td>4.80(6)</td>
<td>320.42(6)</td>
</tr>
</tbody>
</table>

Table 1. Parameters of carbonate minerals. Chemical formulas are calculated from our EPMA measurements; ionic radii are from Shannon (1976); M–O bond distances for aragonite-group carbonates are from Ye et al. (2012); M–O bond distances for calcite-group carbonates are from Rut and Nicola (1974); electronegativity values are from Haynes (2016); and unit cell parameters are from our XRD measurements. Measured data for aragonite, calcite, magnesite, rhodochrosite, siderite, and dolomite are from Farsang et al. (2018).

\(^{a}\) Due to submicron size magnesite domains present in gaspeite, its formula shows a significant Mg content. However, Mg and Ni do not form solid solution in the mineral phase and gaspeite and magnesite peaks can be clearly distinguished in the Raman spectrum of the sample (Figure 3a). These two phases could also be distinguished by powder XRD and the unit cell parameters reported correspond to those of gaspeite only.
Table 2. Frequencies of Raman-active modes of calcite-group carbonate minerals at ambient pressure (1 bar) and temperature (25 °C). Data for calcite, magnesite, rhodochrosite, and siderite are from Farsang et al. (2018).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ideal formula</th>
<th>Raman-active mode frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>External T</td>
<td>External L</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO₃</td>
<td>158</td>
</tr>
<tr>
<td>Gaspeite</td>
<td>NiCO₃</td>
<td>230</td>
</tr>
<tr>
<td>Magnesite</td>
<td>MgCO₃</td>
<td>214</td>
</tr>
<tr>
<td>Otavite</td>
<td>CdCO₃</td>
<td>161</td>
</tr>
<tr>
<td>Rhodochrosite</td>
<td>MnCO₃</td>
<td>185</td>
</tr>
<tr>
<td>Siderite</td>
<td>FeCO₃</td>
<td>183</td>
</tr>
<tr>
<td>Smithsonite</td>
<td>ZnCO₃</td>
<td>198</td>
</tr>
<tr>
<td>Spherocobaltite</td>
<td>CoCO₃</td>
<td>206</td>
</tr>
<tr>
<td>Mineral</td>
<td>Ideal formula</td>
<td>Pressure range of fit (GPa)</td>
</tr>
<tr>
<td>--------------</td>
<td>---------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO$_3$</td>
<td>0-5.9</td>
</tr>
<tr>
<td>Gaspeite</td>
<td>NiCO$_3$</td>
<td>0-6.2</td>
</tr>
<tr>
<td>Magnesite</td>
<td>MgCO$_3$</td>
<td>0-5.9</td>
</tr>
<tr>
<td>Otavite</td>
<td>CdCO$_3$</td>
<td>0-6.2</td>
</tr>
<tr>
<td>Rhodochrosite</td>
<td>MnCO$_3$</td>
<td>0-6.3</td>
</tr>
<tr>
<td>Siderite</td>
<td>FeCO$_3$</td>
<td>0-6.2</td>
</tr>
<tr>
<td>Smithsonite</td>
<td>ZnCO$_3$</td>
<td>0-6.3</td>
</tr>
<tr>
<td>Spherocobaltite</td>
<td>CoCO$_3$</td>
<td>0-6.2</td>
</tr>
</tbody>
</table>

Table 3. Pressure-induced shifts of Raman-active vibrational modes of calcite-group carbonate minerals. Data for calcite, magnesite, rhodochrosite, and siderite are from Farsang et al. (2018).
<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ideal formula</th>
<th>Temperature range of fit (°C)</th>
<th>Temperature-induced shifts of Raman-active vibrational modes, $\delta\nu/\delta T$ (cm$^{-1}$/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>External T</td>
<td>External L</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO$_3$</td>
<td>25-500</td>
<td>-2.65(2)$\times10^{-2}$</td>
</tr>
<tr>
<td>Gaspeite</td>
<td>NiCO$_3$</td>
<td>25-350</td>
<td>-1.3(1)$\times10^{-2}$</td>
</tr>
<tr>
<td>Magnesite</td>
<td>MgCO$_3$</td>
<td>25-350</td>
<td>-2.05(5)$\times10^{-2}$</td>
</tr>
<tr>
<td>Otavite</td>
<td>CdCO$_3$</td>
<td>25-375</td>
<td>-2.1(2)$\times10^{-2}$</td>
</tr>
<tr>
<td>Rhodochrosite</td>
<td>MnCO$_3$</td>
<td>25-400</td>
<td>-1.98(6)$\times10^{-2}$</td>
</tr>
<tr>
<td>Siderite</td>
<td>FeCO$_3$</td>
<td>25-375</td>
<td>1(1)$\times10^{-1}$</td>
</tr>
<tr>
<td>Smithsonite</td>
<td>ZnCO$_3$</td>
<td>25-350</td>
<td>-3.21(7)$\times10^{-2}$</td>
</tr>
<tr>
<td>Spherocobaltite</td>
<td>CoCO$_3$</td>
<td>25-425</td>
<td>-1.76(6)$\times10^{-2}$</td>
</tr>
</tbody>
</table>

Table 4. Temperature-induced shifts of Raman-active vibrational modes of calcite-group carbonate minerals. Data for calcite, magnesite, rhodochrosite, and siderite are from Farsang et al. (2018).
Table 5. Thermodynamic properties and macroscopic Grüneisen parameters of carbonate minerals. Isothermal bulk moduli ($K_T$) are from: a (Litasov et al. 2017), b (Gao et al. 2016), c (Wang et al. 2015), d (Redfern and Angel 1999), e (Zhang and Reeder 1999), f (Minch et al. 2010a), g (Boulard et al. 2015), h (Gao et al. 2014), i (Chariton et al. 2018), j (Ross and Reeder 1992). Adiabatic bulk moduli ($K_S$) are from: k (Liu et al. 2005), l (Biedermann et al. 2017b), m (Chen et al. 2001), n (Sanchez-Valle et al. 2011), o (Zhao et al. 2018), p (Humbert and Plicque 1972). Thermal expansion coefficients ($\alpha$) are from: q (Ye et al. 2012), r (Wang et al. 2019a), s (Zhang et al. 1998), s (Reeder and Markgraf 1986). Heat capacities at constant pressure ($C_P$) are from: t (Ungureanu et al. 2010), u (Bissengaliyeva et al. 2012), v (Gurevich et al. 2001a), w (Gurevich et al. 2001b), x (Staveley and Linford 1969), y (Hemingway et al. 1977), z (Robie et al. 1984), aa (Bénézeth et al. 2009), ab (Haselton and Goldsmith 1987), ac (Stout and Robie 1963). Molar densities ($\rho$) are calculated from measured unit cell parameters (Table 1).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>$K_T$ (GPa)</th>
<th>$K_S$ (GPa)</th>
<th>$\alpha$ ($\times 10^{-5}$ K$^{-1}$)</th>
<th>$C_P$ (Jmol$^{-1}$K$^{-1}$)</th>
<th>$\rho$ (molm$^{-3}$)</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aragonite</td>
<td>65.7±0.8$^a$</td>
<td>68.9±1.4$^a$</td>
<td>6.5±1$^a$</td>
<td>83.1$^i$</td>
<td>29254</td>
<td>1.84</td>
</tr>
<tr>
<td>Cerussite</td>
<td>63±2$^b$</td>
<td>72.4$^a$</td>
<td>8.0±3$^b$</td>
<td>87.0±0.09$^b$</td>
<td>24543</td>
<td>2.71</td>
</tr>
<tr>
<td>Strontianite</td>
<td>62±1$^c$</td>
<td>64±4$^c$</td>
<td>6.8±1$^c$</td>
<td>86.52±0.15$^c$</td>
<td>25894</td>
<td>1.94</td>
</tr>
<tr>
<td>Witherite</td>
<td>48±1$^d$</td>
<td>58.7$^a$</td>
<td>6.5±2$^d$</td>
<td>93.24±0.17$^d$</td>
<td>21871</td>
<td>1.87</td>
</tr>
<tr>
<td>Calcite</td>
<td>73.46±0.27$^e$</td>
<td>76.1$^a$</td>
<td>1.30±0.12$^e$</td>
<td>83.4708$^e$</td>
<td>27138</td>
<td>0.44</td>
</tr>
<tr>
<td>Gaspeite</td>
<td>131±1$^f$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnesite</td>
<td>107±1$^g$</td>
<td>115.7±1.0$^g$</td>
<td>3.81±0.38$^g$</td>
<td>76.09$^j$</td>
<td>35581</td>
<td>1.63</td>
</tr>
<tr>
<td>Otavite</td>
<td>101±2$^h$</td>
<td></td>
<td>1.80±4$^h$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rhodochrosite</td>
<td>110±11$^i$</td>
<td>108.5±1.8$^i$</td>
<td>2.09±0.19$^i$</td>
<td>80.62±0.10$^i$</td>
<td>32193</td>
<td>0.87</td>
</tr>
<tr>
<td>Siderite</td>
<td>117±1$^j$</td>
<td>115.5±1.5$^j$</td>
<td>2.98$^j$</td>
<td>83.26±2$^j$</td>
<td>33993</td>
<td>1.23</td>
</tr>
<tr>
<td>Smithsonite</td>
<td>126.8±0.6$^k$</td>
<td>3.66±0.13$^k$</td>
<td>80.05$^k$</td>
<td>35276</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spherocobaltite</td>
<td>128±2$^l$</td>
<td>94.8$^a$</td>
<td>2.41$^l$</td>
<td>157.5±0.4$^l$</td>
<td>15547</td>
<td>0.93</td>
</tr>
<tr>
<td>Dolomite</td>
<td>94.1±0.7$^m$</td>
<td>94.8$^a$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dolomite</td>
<td></td>
<td></td>
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</tbody>
</table>

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Fig. 1

**Aragonite-group carbonates**

Aragonite, CaCO$_3$

$r_{\text{Ca}^{2+}} = 1.18$ Å

---

**Strontianite, SrCO$_3$**

$r_{\text{Sr}^{2+}} = 1.31$ Å

---

**Cerussite, PbCO$_3$**

$r_{\text{Pb}^{2+}} = 1.35$ Å

---

**Witherite, BaCO$_3$**

$r_{\text{Ba}^{2+}} = 1.47$ Å
Fig. 2

(a) Raman Shift (cm$^{-1}$) vs. Ionic radius (Å)

$v = -90(2) \times r_{ion} + 1192(2)$

$r^2 = 0.99$

(b) Raman Shift (cm$^{-1}$) vs. M–O Bond Length (Å)

$v = -92(9) \times r_{M-O} + 1320(20)$

$r^2 = 0.99$
Calcite-group carbonates

Gaspeite, NiCO$_3$
$r_{Ni^{2+}} = 0.69$ Å

Magnesite, MgCO$_3$
$r_{Mg^{2+}} = 0.72$ Å

Smithsonite, ZnCO$_3$
$r_{Zn^{2+}} = 0.74$ Å

Spherocobaltite, CoCO$_3$
$r_{Co^{2+}} = 0.745$ Å

Raman Shift (cm$^{-1}$)
### Calcite-group carbonates

**Siderite, FeCO₃**
- $r_{Fe^{2+}} = 0.78 \text{ Å}$
- Peak at 1085 cm$^{-1}$

**Rhodochrosite, MnCO₃**
- $r_{Mn^{2+}} = 0.83 \text{ Å}$
- Peak at 1086 cm$^{-1}$

**Otavite, CdCO₃**
- $r_{Cd^{2+}} = 0.95 \text{ Å}$
- Peak at 1086 cm$^{-1}$

**Calcite, CaCO₃**
- $r_{Ca^{2+}} = 1.00 \text{ Å}$
- Peak at 1088 cm$^{-1}$

---

**Raman Shift (cm$^{-1}$)**

- 200
- 400
- 600
- 800
- 1000
- 1200
- 1400
- 1600
- 1800

**Intensity (a.u.)**

- 0
- 1
- 2
- 3
Aragonite-group carbonates

- **Aragonite**: $r_{\text{Ca}^{2+}} = 1.18$ Å
- **Strontianite**: $r_{\text{Sr}^{2+}} = 1.31$ Å
- **Cerussite**: $r_{\text{Pb}^{2+}} = 1.35$ Å
- **Witherite**: $r_{\text{Ba}^{2+}} = 1.47$ Å

Raman Shift (cm$^{-1}$) vs. Pressure (GPa) for each mineral:

- **Aragonite**: $v_1$, $v_2$, $v_3$, $v_4$
- **Strontianite**: $v_3$
- **Cerussite**: $A_g$
- **Witherite**: $v_2$, $v_3$, $v_4$
Calcite-group carbonates

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Cation</th>
<th>Coordination</th>
<th>Raman Shift (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaspeite</td>
<td>Ni²⁺</td>
<td>0.69 Å</td>
<td>1760</td>
</tr>
<tr>
<td>Magnesite</td>
<td>Mg²⁺</td>
<td>0.72 Å</td>
<td>1740</td>
</tr>
<tr>
<td>Smithsonite</td>
<td>Zn²⁺</td>
<td>0.74 Å</td>
<td>1720</td>
</tr>
<tr>
<td>Spherocobaltite</td>
<td>Co²⁺</td>
<td>0.745 Å</td>
<td>1700</td>
</tr>
<tr>
<td>Siderite</td>
<td>Fe²⁺</td>
<td>0.78 Å</td>
<td>1680</td>
</tr>
<tr>
<td>Rhodochrosite</td>
<td>Mn²⁺</td>
<td>0.83 Å</td>
<td>1660</td>
</tr>
<tr>
<td>Otavite</td>
<td>Cd²⁺</td>
<td>0.95 Å</td>
<td>1640</td>
</tr>
<tr>
<td>Calcite</td>
<td>Ca²⁺</td>
<td>1.00 Å</td>
<td>1620</td>
</tr>
</tbody>
</table>

Raman Shift (cm⁻¹) vs Pressure (GPa)
Aragonite-group carbonates

Aragonite
$r_{\text{Ca}^{2+}} = 1.18 \, \text{Å}$

Strontianite
$r_{\text{Sr}^{2+}} = 1.31 \, \text{Å}$

Cerussite
$r_{\text{Pb}^{2+}} = 1.35 \, \text{Å}$

Witherite
$r_{\text{Ba}^{2+}} = 1.47 \, \text{Å}$

Raman Shift (cm$^{-1}$) vs. Temperature (°C)
Calcite-group carbonates

Gaspeite $r_{\text{Ni}^{2+}} = 0.69$ Å

Magnesite $r_{\text{Mg}^{2+}} = 0.72$ Å

Smithsonite $r_{\text{Zn}^{2+}} = 0.74$ Å

Spherocobaltite $r_{\text{Co}^{2+}} = 0.745$ Å

Siderite $r_{\text{Fe}^{2+}} = 0.78$ Å

Rhodochrosite $r_{\text{Mn}^{2+}} = 0.83$ Å

Otavite $r_{\text{Cd}^{2+}} = 0.95$ Å

Calcite $r_{\text{Ca}^{2+}} = 1.00$ Å

Raman Shift (cm$^{-1}$)

Temperature (°C)
Fig. 9

(a) $v = -0.34(3) \, V_{uc} + 1161(8)$

$\Delta v / \Delta P = 0.0114(8) \, V_{uc} + 5.7(2)$

$\Delta v / \Delta P = 0.047(6) \, K_T - 0.04(4)$

$r^2 = 0.99$

$r^2 = 0.99$

$r^2 = 0.98$
Fig. 10a-c

(a) 
\[ v = -0.71(1) V_{uc} + 400(40) \]
\[ r^2 = 0.82 \]

(b) 
\[ \frac{\delta v}{\delta P} = -0.011(4) V_{uc} + 7(1) \]
\[ r^2 = 0.57 \]

(c) 
\[ \frac{\delta v}{\delta P} = 0.022(6) K_T + 1.1(7) \]
\[ r^2 = 0.71 \]
Fig. 10d-f

**d**

![Diagram showing the relationship between Raman shift and unit cell volume.](Image)

\[ \nu = -0.52(2) V_{UC} + 460(60) \]

\[ r^2 = 0.57 \]

**e**

![Diagram showing the relationship between Raman shift and unit cell volume with a legend of mineral symbols.](Image)

\[ \delta \nu/\delta P = 0.014 V_{UC} + 0(1) \]

\[ r^2 = 0.70 \]

**f**

![Diagram showing the relationship between Raman shift and unit cell volume.](Image)

\[ \delta \nu/\delta P = -0.026(5) K_T + 7.9(6) \]

\[ r^2 = 0.79 \]
Fig. 11

(a) $\delta v/\delta P = -1.0(2) \delta v/\delta P + 8.4(8)$

$\bar{r}^2 = 0.78$

(b) $\delta v/\delta P = 4.0(4) \beta_a - 2.2(7)$

$\bar{r}^2 = 0.97$

(c) $v = 0.7(3) v - 0.013(5)$

$\bar{r}^2 = 0.56$
Fig. 12

Harmonic

Anharmonic

Difference

\( \varepsilon - \varepsilon_0 \) (kJ/mol)

\( \varepsilon - \varepsilon_0 \) (kJ/mol)

\( \Delta \varepsilon \) (kJ/mol)

Temperature (K)

Temperature (K)

Temperature (K)
Fig. 12

C

![Graphs showing thermodynamic properties as functions of temperature.](image-url)