

In situ Raman vibrational spectra of siderite (FeCO₃) and rhodochrosite (MnCO₃) up to 47 GPa and 1100 K

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ABSTRACT

Siderite (FeCO₃) and rhodochrosite (MnCO₃) are two interesting carbonate minerals, which normally occur in hydrothermal deposits on deep-sea altered oceanic crust. Despite the ubiquity of carbonates in the slab, little is known of the physicochemical behavior of siderite and rhodochrosite at high-pressure (*P*) and high-temperature (*T*) conditions during slab subduction. In this study, we characterized the Raman vibrational spectra of natural siderite and rhodochrosite up to 47 GPa and 1100 K in an externally heated diamond-anvil cell (DAC). Experimental results show that the Raman frequency shifts (ν_i) for siderite and rhodochrosite are a function of both *P* and *T*, and the effect of the *P*-*T* cross derivative term cannot be neglected, especially at high-*P* and high-*T* conditions. Based on the functional relationship of ν_i -*P*-*T*, the *P*-*T* calibrants of siderite and rhodochrosite are developed, respectively. This is significant for studying the water-carbonate interaction at high *P*-*T* conditions in a DAC because the undesired change of the experimental system from traditional pressure sensors (e.g., ruby, quartz) in a reaction chamber can be avoided. Like previous studies, we observed a sharp spin transition at ~45 GPa in siderite and a phase transition from MnCO₃-I to MnCO₃-II at ~46 GPa for rhodochrosite at room temperature. Furthermore, we determined the isobaric and isothermal equivalents of the mode Grüneisen parameter (γ_{iT} , γ_{iP}) and the anharmonic parameter (α_i) for each Raman mode of siderite and rhodochrosite. The $\delta\nu_i/\delta P$, $\delta\nu_i/\delta T$, γ_{iT} , γ_{iP} , and α_i span a much larger value range for the external lattice modes (T, L) than internal modes (ν_4 , ν_1) in both siderite and rhodochrosite. Combining Raman frequency shifts and the first-order Murnaghan equation of state, we also developed a method to calculate the temperature dependence of the bulk modulus (K_T) for siderite and rhodochrosite, respectively.

Keywords: Siderite, rhodochrosite, Raman spectroscopy, high-*P* and high-*T*, *P*-*T* sensor, thermodynamical parameters

INTRODUCTION

Carbonates are the major carbon reservoir on the Earth's surface. Previous studies estimate that more than 6.5×10^8 Gt carbon have been stored in carbonate sediments and carbonated oceanic/continental crusts (DePaolo 2015). These carbonates can be transported into deep mantle through the subduction of oceanic and continental slabs (Javoy 1997; Dasgupta and Hirschmann 2006; Seto et al. 2008). With increasing depth in the Earth's interior, some carbon may return to Earth's surface by decarbonation processes from subducted slabs through the magmatic processes (Stewart et al. 2019). The stability of carbonates at high-*P* and high-*T* conditions controls the extent and rate of carbon recycling to the Earth's surface. Therefore, knowing the physicochemical (e.g., thermodynamic) properties of carbonates at high *P*-*T* conditions relevant to subduction zones is particularly important for understanding the deep carbon cycle process (Dasgupta and Hirschmann 2010; Tao et al. 2013; Plank and Manning 2019; Farsang et al. 2021).

Siderite (FeCO₃) and rhodochrosite (MnCO₃) occur as common carbonate minerals in many hydrothermal deposits in the altered oceanic crust (Robie et al. 1984). Subduction of siderite and rhodochrosite may therefore play an important role in the geochemical cycles of key elements (e.g., Fe, Mn, and C) between Earth's surface and deep interior (Sherman 2009). On the other hand, previous studies have suggested magnesite (MgCO₃) is the most important carbonate mineral in the deep Earth mantle, which could be stable up to the *P*-*T* conditions of core-mantle boundary (Fiquet et al. 2002; Isshiki et al. 2004; Dasgupta and Hirschmann 2010). Considering the average Fe/Mg molar ratio of ~0.12 in the bulk composition of Earth's mantle (McDonough and Sun 1995), and the commonly occurring Fe-Mg exchange between carbonates and Fe-bearing silicates at high-*P* and high-*T* conditions (Boulard et al. 2015), it is believed that siderite (FeCO₃) should be a significant component in solid solution with magnesite in the subducted slab and deep mantle (Anovitz and Essene 1987; Wood et al. 1996; Lin et al. 2012; Tao et al. 2013; Kang et al. 2015). Similarly, divalent Mn has a cation size between that of Mg²⁺ and Ca²⁺, which could make rhodochrosite (MnCO₃) a non-trivial end-member component in aragonite

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(CaCO₃) or dolomite [CaMg(CO₃)₂] at high *P-T*. However, less attention has been paid to the physiochemical behavior of siderite and rhodochrosite in comparison with calcite, dolomite, and magnesite, especially at high-*P* and high-*T* conditions relevant to subduction zones and deep mantle environment.

More interestingly, Fe and Mn are 3d transition metals, which make siderite and rhodochrosite have more complicated phase transitions and special spin states than other carbonates at different chemical and *P-T* environments (Farfan et al. 2013; Litasov et al. 2020). For example, the stability of siderite and rhodochrosite have been determined as a function of pressure, temperature, and oxygen fugacity by previous studies (Robie et al. 1984; Santillán and Williams 2004; Tao et al. 2013; Kang et al. 2015; Litasov et al. 2020). In addition, the spin transition of siderite at room temperature was observed at 43 to 50 GPa, which results in a sharp isostructural volume collapse ranging from 6.5 to 10% (Nagai et al. 2010; Lin et al. 2012; Farfan et al. 2012; Müller et al. 2016). Theoretically, if all thermodynamical data for different FeCO₃ and MnCO₃ phases at high-*P* and high-*T* conditions are derived, the complete phase diagram for FeCO₃ and MnCO₃ systems can be constructed. However, few experimental data are available at simultaneous high *P-T* conditions (>700 K) (e.g., Farsang et al. 2018, 2021). As a result, the accurate thermodynamic properties of siderite and rhodochrosite are not well constrained at high *P-T* conditions. For example, the bulk modulus parameter (*K*_T) of rhodochrosite at high-*T* is not available, and the anharmonicity and anharmonic corrections have yet to be quantified as well.

In this study, we studied the *P*- and *T*-induced frequency shifts of the Raman-active vibrational modes of natural siderite (Fe_{0.95}Mn_{0.046}Mg_{0.004})CO₃ and rhodochrosite (Mn_{0.936}Fe_{0.059}Mg_{0.005})CO₃ in a diamond-anvil cell (DAC) at pressures to 47 GPa and temperatures from 300 to 1100 K. To the best of our knowledge, this is the first systematic report of simultaneous in situ high *P-T* Raman data for siderite and rhodochrosite. Our results show that the frequency shifts of both siderite and rhodochrosite are coupled functions of *P* and *T*. Based on in situ measurements, we calculated the isobaric and isothermal equivalent of the Grüneisen parameter, the anharmonic parameter, and the temperature-dependent bulk modulus for each vibrational mode. Furthermore, we established *P-T* sensors according to their Raman-active modes, which can be used to accurately determine the *P* in DAC at high-*T* and high-*P* conditions (e.g., up to 15 GPa and 1100 K for siderite; up to 13 GPa and 900 K for rhodochrosite). This is very useful for DAC experiments studying water-carbonate interactions (e.g., carbonate solubility in water) at the high *P-T* conditions relevant to subduction zones while avoiding contamination by traditional pressure calibrants (e.g., ruby, SrB₄O₇:Sm²⁺).

EXPERIMENTAL METHODS

The starting materials for the experiments are natural siderite (Ivigtut, Greenland) and rhodochrosite (Wuzhou, China). They were characterized by electron microprobe and Raman spectroscopy at the School of Earth and Space Sciences, Peking University. The measurements yielded the molecular formula (Fe_{0.95}Mn_{0.046}Mg_{0.004})CO₃ and (Mn_{0.936}Fe_{0.059}Mg_{0.005})CO₃ for siderite and rhodochrosite, respectively, indicating that the starting siderite and rhodochrosite are close to the FeCO₃ and MnCO₃ end-members. For simplification, we will refer to them as FeCO₃ and MnCO₃ in the rest of the text. Three kinds of experiments

(atmospheric-*P* high-*T* experiments; room-*T* and high-*P* experiment; and high-*T* and high-*P* experiment) were conducted in this study.

The atmospheric-*P* (1 bar) high-*T* experiments were conducted up to 500 °C using an HRTS1000 heating stage (Shanghai Photographic Instrument Co., Ltd) with the sample held within the center of a heater coil on a sapphire pan. Before the atmospheric-*P* high-*T* experiments, a series of calibrations were carried out to check the temperature distribution in the center of the heater coil. Pure foils (0.5–1 mm in diameter) of 63A solder, tin, zinc, and silver with known melting points of 183, 232, 420, and 961 °C, respectively, were heated in the sapphire pan. The temperature of the sample position in the heater coil was determined by the instantaneous shrinkage of the loaded metal foils at their melting point under a microscope (the shrinkage duration was within 2 s, and the temperature interval was <0.1 °C). The calibration was calculated using a linear fit of the four melting points of each foil between 0 and 1000 °C. Repetition of the calibration procedure shows that the temperatures are reproducible to less than ±1 °C. Following calibration, the formal atmospheric-*P*, high-*T* experiments were conducted by gradually increasing *T* to 400 °C for siderite and to 500 °C for rhodochrosite. A low flow (~50 mL/min) of hydrogen-argon mixture gas (98% Ar–2% H₂) was introduced to prevent the oxidation of divalent iron (Fe²⁺) and manganese (Mn²⁺) in the carbonates by the air at high temperature.

The room-*T* (~20 °C) and high-*P* experiments were conducted up to 47 GPa in a symmetrical anvil cell, equipped with type IIa diamond anvils with culet diameters of 500 or 250 μm. High-purity nitrogen gas (for experiments below 13 GPa) or helium gas (for experiments above 13 GPa) at 160 MPa was loaded into the reaction chamber as a pressure medium using high-pressure gas loading apparatus at the Center for High Pressure Science and Technology Advanced Research (HPSTAR). Hydrostatic conditions in the reaction chamber are expected to prevail over the full *P* range of our experiments (Klotz et al. 2009). Siderite or rhodochrosite grains were loaded into a pre-indented (80–30 μm thick) steel gasket, drilled with a 200–100 μm diameter hole. A ruby sphere (BETSA) and small amount of SrB₄O₇:Sm²⁺ grains (Zhao et al. 2017) were loaded together with the carbonate samples as pressure sensors (Mao et al. 1986; Datchi et al. 2007). The pressure deviation range given by ruby and SrB₄O₇:Sm²⁺ was consistently kept within ±0.2 GPa in our experimental *P-T* range.

For the high *P-T* experiments, which were conducted up to 15 GPa and 1100 K for siderite and up to 13 GPa and 900 K for rhodochrosite, we used a high-*T* BX-90 DAC. Experiments were performed using ultra low-fluorescence type IIa diamonds with 500 μm culets. Heating was achieved using Ni–Cr wires wrapped around ZrO₂ seats that support the diamond anvils. During operation, the whole cell was flushed with an Ar–H₂ mixture (98% Ar–2% H₂) to prevent the oxidation of the diamonds and Ni–Cr heaters by air. An external cooling system was used to maintain the temperature of <100 °C in the body of the DAC while the sample was at high temperature for tens of hours. The temperature was measured using K-type thermocouples attached to the diamond through the heater wires, allowing the temperature of each diamond to be monitored during the experiment (Fig. 1). Temperatures were calibrated based on the melting point of tin (232 °C), and the deviation was within 3 °C. Rhenium gaskets with 80 μm thickness and 200 μm diameter holes were used to contain the sample, and a few pieces of SrB₄O₇:Sm²⁺ were loaded into the sample chamber as the pressure sensor at high temperature (Datchi et al. 2007). High-purity N₂ gas was used as a pressure medium.

In situ Raman measurements were performed using a confocal RM 1000 (Renishaw) instrument equipped with a 532 nm Nd: YAG laser, a Mitutoyo ×20 long working distance objective, and a grating with a groove density of 2400 grooves/mm at HPSTAR. Each Raman spectrum was acquired between 100 and 1250 cm^{−1} with a spectral resolution of ~1 cm^{−1} and acquisition time of 10 to 60 s. To obtain the steady-state Raman frequency, measurements were carried out for 5 to 10 min following each increase or decrease of *P* or *T*. All spectra were processed by PeakFit software (SeaSolve Software inc., Massachusetts, U.S.A.) and were calibrated against the measured excitation of Si at ~520 cm^{−1}. After the baseline was subtracted with reasonable function, the Raman peaks were fitted using symmetric Gauss + Lorentz function.

EXPERIMENTAL RESULTS

Atmospheric-*P* high-*T* experiments

Both siderite and rhodochrosite crystallize in the space group *R* $\bar{3}c$. The rhombohedral carbonate minerals consist of two basic building blocks, the extremely incompressible CO₃^{2−} groups (with an orientation of nearly planar CO₃^{2−} units, in which the C–O bonds lie, perpendicular to *z*-axis), and the more compressible corner-linked MO₆ octahedra (Redfern 2000; Farsang et al.

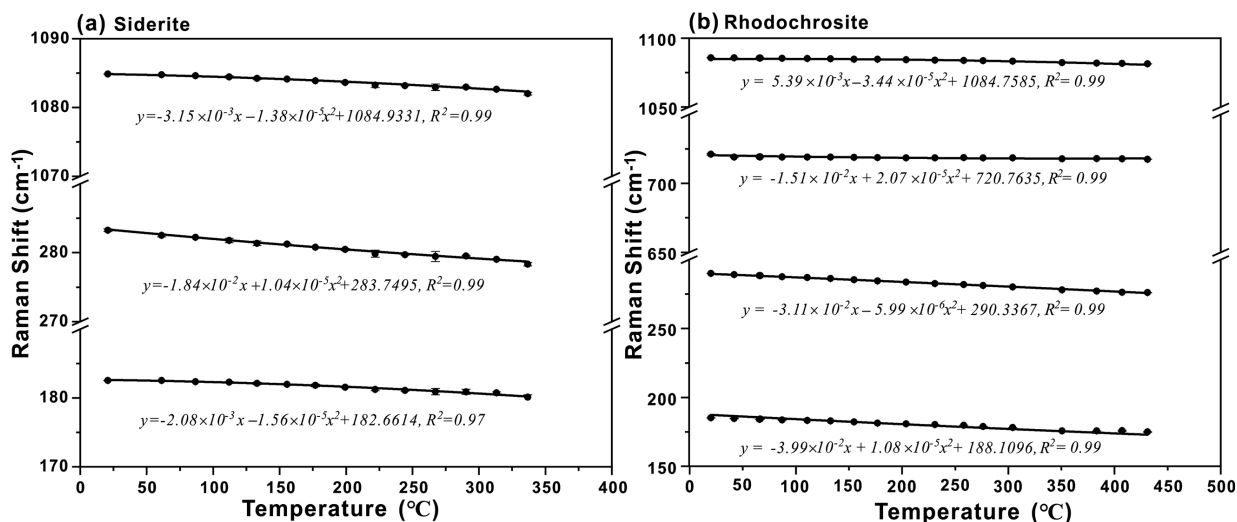


FIGURE 3. Frequency evolution of the traced vibrational modes of siderite (a) and rhodochrosite (b) as a function of *T* at atmospheric *P*. Polynomial fits are shown as described in the text. The experimental uncertainties are given but generally lie within the size of the data marker.

and 400 °C, above which the vibrational modes cannot be detected. Raman analysis and SEM-EDS characterization of the quenched products indicate that magnetite and scaly graphite are produced. The decomposition *T* and products are in good agreement with those in previous studies (Kissinger et al. 1956; Tao et al. 2013). Thermal decomposition of rhodochrosite was observed between 400 and 425 °C, marked by the sudden disappearance of all Raman bands. Only a broad Mn-O vibration (~650 cm⁻¹) can be detected after quenching.

Room-*T* and high-*P* experiments

The Raman mode frequency evolutions of siderite and rhodochrosite as a function of pressure at room *T* are reported in Figures 4a and 4b, respectively. The relative changes in frequency $\delta\nu_i/\delta P$ are listed in Table 1 in comparison with literature values. The frequencies of all traced modes increase monotonously with *P*. Our $\delta\nu_i/\delta P$ values are in good agreement with previous experiments of Farsang et al. (2018) at *P* < 10 GPa, which were conducted under hydrostatic conditions when using a 4:1 methanol-ethanol fluid mixture (*P*_{max} of quasi-hydrostatic limit: < 9.8 GPa) as pressure-transmitting medium (PTM). However, the $\delta\nu_i/\delta P$ values given by linear fitting in other experimental studies (e.g., Farfan et al. 2012, 2013; Cerantola et al. 2015; Liang et al. 2018; Zhao et al. 2018) over a wider *P* range are generally lower than our studies (Table 1). These differences cannot be attributed to compositional effects, as our materials have almost identical compositions to those in other studies. One possible explanation is the development of a non-hydrostatic stress regime in the DAC experiments from previous studies because their experimental pressure more or less exceeds the hydrostatic limits of pressure mediums of the silicon oil, neon, and nitrogen at ~2, ~16, and ~13 GPa, respectively (Klotz et al. 2009). Another possible explanation is that the linear fit is not suitable for data under high pressure. For instance, Liu et al. (2016) used helium as pressure medium, which is considered be able to produce hydrostatic conditions at above 50 GPa, but they calculated a smaller $\delta\nu_i/\delta P$ value for MnCO₃ in comparison with that from our study. A subset of 0–47 GPa high-pressure experi-

ments (see section below) show a linear relationship for carbonate modes between the peak position and pressure at ≤10 GPa, whereas a nonlinear relationship is observed at higher *P* above 10 GPa. Nonlinear $\delta\nu_i/\delta P$ trends are observed for MnCO₃ in comparison with FeCO₃. Based on this, we further explored the relationship between $\delta\nu_i/\delta P$ and the fitting pressure range, as shown in the Online Materials¹ Figure OM1. For FeCO₃, our results show that as the fitting range becomes larger, $\delta\nu_i/\delta P$ systematically decreases. Assuming a linear relationship between the peak position and pressure our $\delta\nu_i/\delta P$ values are very close to Cerantola et al. (2015) (3.80 vs. 3.82 for L mode; 2.13 vs. 2.17 for *v*₁ mode) in the similar fitting range (0–45 GPa vs. 0–40 GPa). For MnCO₃, a larger fitting range also lowers the $\delta\nu_i/\delta P$ values. Assuming a linear relationship between the peak position and pressure, our $\delta\nu_i/\delta P$ values are very close to Liu et al. (2016) (2.95 vs. 2.91 for T mode; 1.38 vs. 1.28 for *v*₄ mode; 2.13 vs. 2.17 for *v*₁ mode) in the same fitting range (0–45 GPa). Farfan et al. (2013) and Zhao et al. (2018) reported a transition of MnCO₃ between 15 and 35 GPa where $\delta\nu_i/\delta P$ values of MnCO₃-I will fluctuate greatly and deviate from the trend. The problem of the incorrect application of linear fitting algorithms may also be compounded if a non-hydrostatic pressure transmitting medium is used, resulting in differential and shear stresses that will also affect the $\delta\nu_i/\delta P$ values.

For both FeCO₃ and MnCO₃, the lowest $\delta\nu_i/\delta P$ is observed for internal modes (*v*₁ or *v*₄) and the highest $\delta\nu_i/\delta P$ is observed for the T mode, displaying anisotropic compression (Fig. 4; Table 1), because the compressibility along the *z* crystallographic axis (in the hexagonal setting) is much larger than along the *x*-axis (Zhang and Reeder 1999; Redfern 2000; Wang et al. 2018; Farsang et al. 2021). As a result, $\delta\nu_i/\delta P$ values of the external lattice mode (T, L) are more sensitive to pressure in comparison with the internal modes of the CO₃²⁻ unit, where the C-O bonds lie perpendicular to the *z*-axis. Additionally, although MnCO₃ and FeCO₃ are isostructural solids, carbonates with large cations [e.g., Mn²⁺ (0.83 Å) vs. Fe²⁺ (0.78 Å)] exhibit a larger positive $\delta\nu_i/\delta P$ for *v*₁ and *v*₄, indicating a more significant MO₆ octahedral distortion (Farsang et al. 2021).

High-*T* and high-*P* experiments

We report the Raman vibrational behavior of MnCO_3 and FeCO_3 at high-*T* and high-*P*, simultaneously. Several sets of high-*T* and high-*P* experiments were carried out systematically, and the coupled effect of *P* and *T* on Raman shift is presented in Figure 5. A polynomial expression was fitted to the curved surface of Raman frequency shift data across the full experimental *P-T* range and the following equations were derived:

For siderite (FeCO_3):

$$\text{T mode: } \nu(P, T) = 183.163 - 0.00977 \times T + 4.243 \times P + 1.717 \times 10^{-6} \times T^2 - 0.08425 \times P^2 + 8.288 \times 10^{-4} \times P \cdot T \quad (R^2 = 0.998) \quad (1)$$

$$\text{L mode: } \nu(P, T) = 283.535 - 0.01223 \times T + 5.041 \times P - 1.717 \times 10^{-6} \times T^2 - 0.05777 \times P^2 + 2.672 \times 10^{-4} \times P \cdot T \quad (R^2 = 0.998) \quad (2)$$

$$\nu_1 \text{ mode: } \nu(P, T) = 1085.505 - 0.00643 \times T + 3.056 \times P - 2.853 \times 10^{-6} \times T^2 - 0.0734 \times P^2 + 5.998 \times 10^{-4} \times P \cdot T \quad (R^2 = 0.994) \quad (3)$$

For rhodochrosite (MnCO_3):

$$\text{T mode: } \nu(P, T) = 185.6075 - 0.0257 \times T + 3.8149 \times P + 8.1999 \times 10^{-6} \times T^2 - 0.0537 \times P^2 + 9.8688 \times 10^{-4} \times P \cdot T \quad (R^2 = 0.998) \quad (4)$$

$$\text{L mode: } \nu(P, T) = 290.1466 - 0.0321 \times T + 5.6466 \times P + 4.0518 \times 10^{-6} \times T^2 - 0.1092 \times P^2 + 1.63 \times 10^{-3} \times P \cdot T \quad (R^2 = 0.999) \quad (5)$$

$$\nu_4 \text{ mode: } \nu(P, T) = 719.5914 - 0.0059 \times T + 2.3374 \times P + 2.1554 \times 10^{-6} \times T^2 - 0.0585 \times P^2 + 3.92 \times 10^{-4} \times P \cdot T \quad (R^2 = 0.995) \quad (6)$$

TABLE 1. Pressure- and temperature-induced shifts of siderite and rhodochrosite

Observed mode	Symmetry	Pressure medium	ν_i (cm ⁻¹)	$\delta\nu_i/\delta P$ (cm ⁻¹ /GPa)	Pressure range of fit (GPa)	$\delta\nu_i/\delta T$ (cm ⁻¹ /°C)	Temperature range of fit (°C)	Reference	Calculated formula
Siderite									
External	E_g	Neon	182.86	3.58(2)	0–10	$-2.08(98) \times 10^{-3} - 3.12(69) \times 10^{-5(a)} / -6.3(4) \times 10^{-3(b)}$	20–350	This work	$(\text{Fe}_{0.95}\text{Mn}_{0.046}\text{Mg}_{0.004})\text{CO}_3$
		Methanol-ethanol (4:1)	183	3.98(9)	0–6	$1(1) \times 10^{-3}$	25–375	Farsang et al. (2018)	$(\text{Fe}_{0.98}\text{Mn}_{0.01}\text{Mg}_{0.01})\text{CO}_3$
		Neon	176	2.51	0–40	–	–	Cerantola et al. (2015)	Synthesis sample, pure
		Neon	181	2.99(2)	0–30	3.14×10^{-4}	20–300	Liang et al. (2018)	$\text{Fe}_{0.9988}\text{CO}_3$
External	E_g	Neon	283.49	4.50(3)	0–10	$2.82 \times 10^{-5} / -4.3 \times 10^{-3}$ $-1.84(17) \times 10^{-2} + 2.08(97) \times 10^{-5} / -1.47(3) \times 10^{-2}$	20–350	This work	$(\text{Fe}_{0.95}\text{Mn}_{0.046}\text{Mg}_{0.004})\text{CO}_3$
		Methanol-ethanol (4:1)	284	4.52(5)	0–6	$-1.0(1) \times 10^{-2}$	25–375	Farsang et al. (2018)	$(\text{Fe}_{0.98}\text{Mn}_{0.01}\text{Mg}_{0.01})\text{CO}_3$
		Neon	274	3.82	0–40	–	–	Cerantola et al. (2015)	Synthesis sample, pure
		Neon	281	4.01(2)	0–30	$-1.26 \times 10^{-2} - 1.65 \times 10^{-5} / -1.54 \times 10^{-2}$	20–300	Liang et al. (2018)	$\text{Fe}_{0.9988}\text{CO}_3$
Internal ν_1	A_{1g}	silicone oil	299	3.74	0–35	–	–	Farfan et al. (2012)	$(\text{Fe}_{0.76}\text{Mn}_{0.15}\text{Mg}_{0.09}\text{Ca}_{0.01})\text{CO}_3$
		Neon	1085.1	2.51(6)	0–10	$-3.15(63) \times 10^{-3} - 2.76(43) \times 10^{-5} / -7.1(3) \times 10^{-3}$	20–350	This work	$(\text{Fe}_{0.95}\text{Mn}_{0.046}\text{Mg}_{0.004})\text{CO}_3$
		Methanol-ethanol (4:1)	1085	2.60(7)	0–6	$-3(1) \times 10^{-3}$	25–375	Farsang et al. (2018)	$(\text{Fe}_{0.98}\text{Mn}_{0.01}\text{Mg}_{0.01})\text{CO}_3$
		Neon	1077	2.17	0–40	–	–	Cerantola et al. (2015)	Synthesis sample, pure
		Neon	1084	2.46(1)	0–30	$-1.88 \times 10^{-3} - 3.22 \times 10^{-5} / -6.9 \times 10^{-3}$	20–300	Liang et al. (2018)	$\text{Fe}_{0.9988}\text{CO}_3$
		silicone oil	1088	2.20	0–43	–	–	Farfan et al. (2012)	$(\text{Fe}_{0.76}\text{Mn}_{0.15}\text{Mg}_{0.09}\text{Ca}_{0.01})\text{CO}_3$
Rhodochrosite									
External	E_g	Neon	184.41	3.52(3)	0–10	$-3.99(54) \times 10^{-2} - 2.16(96) \times 10^{-5} / -3.63(0) \times 10^{-2}$	20–450	This work	$(\text{Mn}_{0.936}\text{Fe}_{0.059}\text{Mg}_{0.005})\text{CO}_3$
		Methanol-ethanol (4:1)	185	3.38(6)	0–6	$-1.98(6) \times 10^{-2}$	25–400	Farsang et al. (2018)	$(\text{Mn}_{0.99}\text{Fe}_{0.01})\text{CO}_3$
		silicone oil	201	2.69	0–15	–	–	Farfan et al. (2013)	$(\text{Mn}_{0.976}\text{Fe}_{0.012}\text{Mg}_{0.004}\text{Ca}_{0.002})\text{CO}_3$
		Nitrogen	183	2.90(7)	0–16	–	–	Zhao et al. (2018)	$(\text{Mn}_{0.976}\text{Fe}_{0.011}\text{Mg}_{0.001}\text{Ca}_{0.003})\text{CO}_3$
		Neon	184	2.91(5)	0–45	–	–	Liu et al. (2016)	$(\text{Mn}_{0.980}\text{Fe}_{0.009}\text{Mg}_{0.002}\text{Ca}_{0.009})\text{CO}_3$
External	E_g	Neon	289.49	4.94(4)	0–10	$-3.11(0) \times 10^{-2} - 1.20(0) \times 10^{-5} / -3.37(0) \times 10^{-2}$	20–450	This work	$(\text{Mn}_{0.936}\text{Fe}_{0.059}\text{Mg}_{0.005})\text{CO}_3$
		Methanol-ethanol (4:1)	290	4.83(8)	0–6	$-2.93(6) \times 10^{-2}$	25–400	Farsang et al. (2018)	$(\text{Mn}_{0.99}\text{Fe}_{0.01})\text{CO}_3$
		silicone oil	302	4.15	0–15	–	–	Farfan et al. (2013)	$(\text{Mn}_{0.976}\text{Fe}_{0.012}\text{Mg}_{0.004}\text{Ca}_{0.002})\text{CO}_3$
		Nitrogen	288	4.45(10)	0–16	–	–	Zhao et al. (2018)	$(\text{Mn}_{0.976}\text{Fe}_{0.011}\text{Mg}_{0.001}\text{Ca}_{0.003})\text{CO}_3$
		Helium	290	3.68(9)	0–45	–	–	Liu et al. (2016)	$(\text{Mn}_{0.980}\text{Fe}_{0.009}\text{Mg}_{0.002}\text{Ca}_{0.009})\text{CO}_3$
Internal ν_4	E_g	Neon	718.81	2.14(1)	0–10	$-1.51(19) \times 10^{-2} - 4.14(88) \times 10^{-5} / -8.17(0) \times 10^{-3}$	20–450	This work	$(\text{Mn}_{0.936}\text{Fe}_{0.059}\text{Mg}_{0.005})\text{CO}_3$
		Methanol-ethanol (4:1)	718	2.03(4)	0–6	$1.4(8) \times 10^{-3}$	25–400	Farsang et al. (2018)	$(\text{Mn}_{0.99}\text{Fe}_{0.01})\text{CO}_3$
		silicone oil	723	0.95	0–15	–	–	Farfan et al. (2013)	$(\text{Mn}_{0.976}\text{Fe}_{0.012}\text{Mg}_{0.004}\text{Ca}_{0.002})\text{CO}_3$
		Nitrogen	717	1.49(6)	0–16	–	–	Zhao et al. (2018)	$(\text{Mn}_{0.976}\text{Fe}_{0.011}\text{Mg}_{0.001}\text{Ca}_{0.003})\text{CO}_3$
		Helium	719	1.28(6)	0–45	–	–	Liu et al. (2016)	$(\text{Mn}_{0.980}\text{Fe}_{0.009}\text{Mg}_{0.002}\text{Ca}_{0.009})\text{CO}_3$
Internal ν_1	A_{1g}	Neon	1085.5	3.36(3)	0–10	$5.39(90) \times 10^{-3} - 6.88(45) \times 10^{-5} / -1.03(3) \times 10^{-2}$	20–450	This work	$(\text{Mn}_{0.936}\text{Fe}_{0.059}\text{Mg}_{0.005})\text{CO}_3$
		Methanol-ethanol (4:1)	1086	3.34(5)	0–6	$-5.8(7) \times 10^{-3}$	25–400	Farsang et al. (2018)	$(\text{Mn}_{0.99}\text{Fe}_{0.01})\text{CO}_3$
		silicone oil	1100	1.91	0–15	–	–	Farfan et al. (2013)	$(\text{Mn}_{0.976}\text{Fe}_{0.012}\text{Mg}_{0.004}\text{Ca}_{0.002})\text{CO}_3$
		Nitrogen	1084	2.50(9)	0–16	–	–	Zhao et al. (2018)	$(\text{Mn}_{0.976}\text{Fe}_{0.011}\text{Mg}_{0.001}\text{Ca}_{0.003})\text{CO}_3$
		Helium	1086	2.17(7)	0–45	–	–	Liu et al. (2016)	$(\text{Mn}_{0.980}\text{Fe}_{0.009}\text{Mg}_{0.002}\text{Ca}_{0.009})\text{CO}_3$

Note: The result by ^(a) polynomial fitting and ^(b) linear fitting.

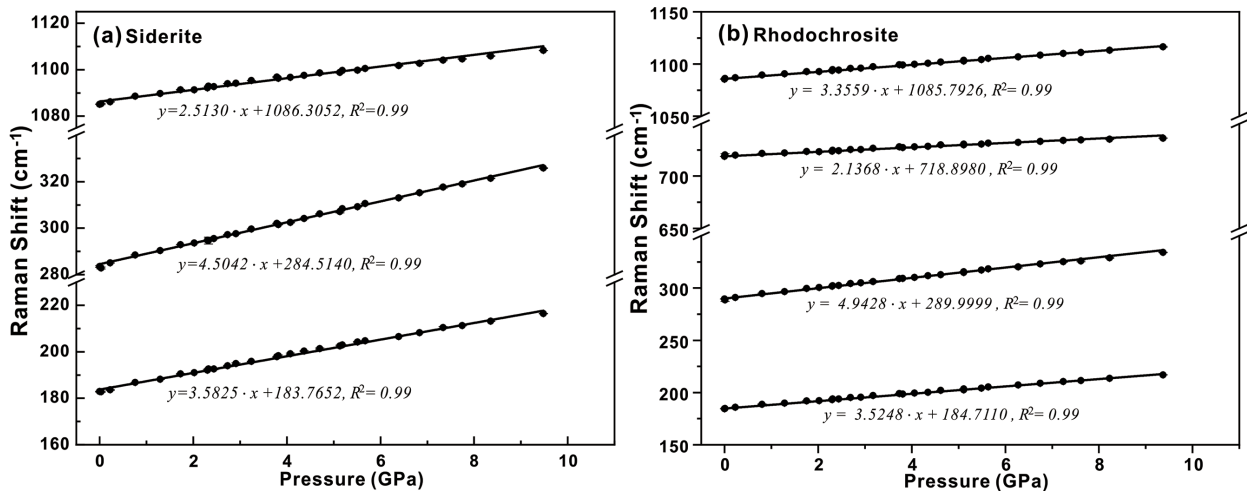


FIGURE 4. Frequency evolution of the traced vibrational modes of siderite (a) and rhodochrosite (b) as a function of *P* at room *T*. Linear fits are shown as described in the text. The experimental uncertainties are given, but generally lie within the size of the data marker.

$$v_1 \text{ mode: } v(P, T) = 1085.9578 - 0.0082 \times T + 3.8162 \times P - 2.7963 \times 10^{-6} \times T^2 - 0.0726 \times P^2 + 6.8004 \times 10^{-4} \times P \cdot T \quad (R^2 = 0.999) \quad (7)$$

Equations (1–7) show that the frequency shifts of the different carbonate modes are a coupled function of both *P* and *T*. The shifts obtained by summing expressions for $(\partial v_i / \partial T)_P$ (equations in Fig. 3) and $(\partial v_i / \partial P)_T$ (equations in Fig. 4) increasingly deviate from the measured data: The predicted frequency shift of the L mode is off by 4.5 and 5.5 cm^{-1} at the highest *P-T* conditions for siderite and rhodochrosite, respectively, and are outside the analytical uncertainty. Therefore, the *P-T* cross derivative term cannot be neglected at high *P-T* conditions, which has been done in previous studies (e.g., Facq et al. 2014, 2016; Farsang et al. 2018; see more detail in section below).

DISCUSSION

Calculation of the mode Grüneisen and intrinsic anharmonic parameters

Pressure-induced frequency shifts of a vibrational mode are the result of the volume change due to compressibility, whereas *T*-induced frequency shifts arise from both volume changes due to thermal expansion and phonon-phonon interactions (Gillet et al. 1989, 1998; Farsang et al. 2021). The mode Grüneisen parameter (γ_i) describes the relative contributions of each vibration to the thermochemical properties (Anderson 2000; Liang et al. 2018). The deviation of vibrational frequency (v_i) as a function of volume (*V*) represents the mode Grüneisen parameter for a phonon mode following the relation (Born and Huang 1954):

$$\gamma_i = - \frac{\partial \ln v_i}{\partial \ln V} \quad (8)$$

The mode Grüneisen parameters (γ_{iT} , γ_{iP}) describe the *P* and *T* dependence at the isothermal and isobaric conditions of the vibrational mode, respectively, and are expressed as:

$$\gamma_{iT} = - \frac{K_T \partial v_i}{v_{i0} \partial P}; \quad (9a)$$

$$\gamma_{iP} = - \frac{\partial v_i}{\alpha_T v_{i0} \partial T} \quad (9b)$$

where K_T is the isothermal bulk modulus, α_T is the isobaric thermal expansion coefficient, v_{i0} is each vibration frequency at corresponding isothermal or isobaric conditions, and $\partial v_i / \partial P$ or $\partial v_i / \partial T$ is the partial derivatives of the frequency shift as a function of *P* and fixed *T*, or *T* and fixed *P*.

Gillet et al. (1989) have used a mode anharmonic parameter (a_i) for considering crystal anharmonicity, which expresses the change in frequency due to *T* at constant volume:

$$a_i = (\partial \ln v_i / \partial T)_V = \alpha (\gamma_{iT} - \gamma_{iP}) \quad (10)$$

In the pure harmonic approximation $a_i = \gamma_{iT} = \gamma_{iP} = 0$. Here, we calculated the isobaric and isothermal equivalents of the Grüneisen parameter and the anharmonic parameter for siderite and rhodochrosite (Tables 2 and 3). We used K_0 and α_0 to calculate γ_{iT} and γ_{iP} at 20 °C, 1 bar respectively. The values of the γ_{iT} , γ_{iP} , and a_i span a much larger range for the external lattice modes (T, L) than the internal modes (v_4 , v_1) in both FeCO_3 and MnCO_3 . Therefore, anisotropic compression (Zhang and Reeder 1999; Redfern 2000; Liang et al. 2018; Farsang et al. 2018, 2021) and anisotropic thermal expansion (Wang et al. 2018; Farsang et al. 2018, 2021) exist. The external modes are expected to contribute significantly more to the intrinsic anharmonicity, and may also be reflected in the $\partial v_i / \partial T$ and $\partial v_i / \partial P$ values discussed above. Both the thermal expansion and compression of FeCO_3 and MnCO_3 along the *z* crystallographic axis are much larger than that along the *x* axis (Zhang and Reeder 1999; Redfern 2000; Wang et al. 2018; Farsang et al. 2021). For FeCO_3 , our γ_{iT} values are very close to the results in Farsang et al. (2018), but larger than those reported by Cerantola et al. (2015) and Liang et al.

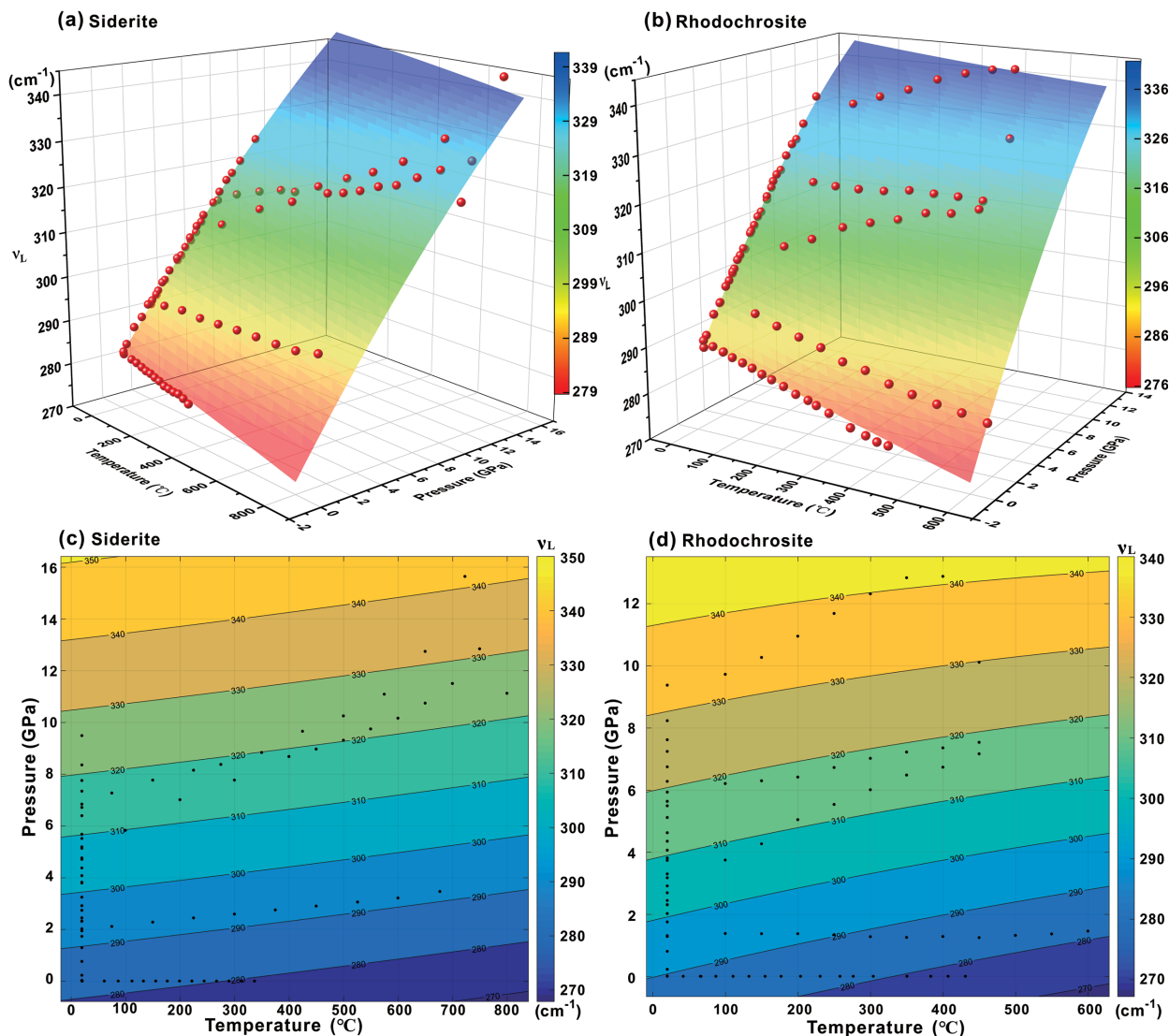


FIGURE 5. (a–b) Frequency shift of the traced L mode of siderite (a) and rhodochrosite (b) as a coupled function of P and T and their polynomial fitting surface. (c–d) P - T diagrams showing contours of the L mode Raman band of siderite (c) and rhodochrosite (d). (Color online.)

(2018) (Table 2), which may underestimate the value of $\delta v_i/\delta P$ due to the non-hydrostatic effect or inappropriate use of a linear fit over a wide pressure range. The γ_{IP} values reported by Farsang et al. (2018) for FeCO_3 are significantly different with that from our study. However, these differences are the result of poorly resolved $\delta v_i/\delta T$ data in Farsang et al. (2018), so that a_i also has a deviation. For MnCO_3 , our γ_{IT} values and those of Farsang et al. (2018) and Liu et al. (2016) are in close agreement, consistent with the hydrostatic conditions in these experiments. However, the data of Zhao et al. (2018) are not in agreement (Table 3). The γ_{IP} is different due to the selection of α_0 values, but overall, our results are more similar to Zhao et al. (2018), at least we report γ_{IP} values with the same (positive) sign.

The a_i , γ_{IT} , and γ_{IP} parameters are T -dependent because K_T , α , and v_i are known functions of temperature (except for K_T of MnCO_3). Thus, we can examine the variation of a_i with temperature and calculate the propagated uncertainty in a_i (Gillet et al.

1990). Here, $\gamma_{\text{IT}(300)}$, $\gamma_{\text{IP}(300)}$, and $a_{\text{i}(300)}$ for siderite are calculated using values of v_i , K_T , and α_T at 300 $^{\circ}\text{C}$ by assuming $\delta v_i/\delta P$ to be independent of T (Tables 2 and 3). For FeCO_3 , the γ_{IT} and γ_{IP} of all modes decrease with T , and the a_i parameter increases between 20 and 300 $^{\circ}\text{C}$. For MnCO_3 , the γ_{IT} and γ_{IP} of external lattice modes (T , L) increase slightly with increasing T , whereas the internal modes (v_4 , v_1) are relatively constant from 20 to 250 $^{\circ}\text{C}$. Overall, the P - T cross term becomes important for mineral behavior if both P and T are elevated.

Calculation of the bulk modulus parameters

To date, there is no treatment of the temperature dependence of the bulk modulus for MnCO_3 . We developed a method of using high P - T Raman scattering data to calculate the mode (macroscopic) Grüneisen parameters (γ_i) and the bulk modulus parameter (K_T), as long as K_0 is known from a fit of isothermal (room- T condition) compression XRD data. In situ high- P and

TABLE 2. Mode Grüneisen and anharmonic parameters of siderite

Raman mode	ν_i (cm ⁻¹)	K_0 (GPa)	K_T (GPa)	α_0 ($\times 10^{-5}$ K ⁻¹)	α (K ⁻¹)	γ_{IT}	γ_{IP}	α_i ($\times 10^{-5}$ K ⁻¹)	$\gamma_{IT(300)}^b$	$\gamma_{IP(300)}^c$	$\alpha_{i(300)}$ ($\times 10^{-5}$ K ⁻¹) ^d	Reference
T	183	117 ^a	117–0.031 $\times (T-300)^a$	2.98 ^a	$1.76 \times 10^{-5} + 3.46 \times 10^{-8} T^a$	2.29	1.2	3.38	2.15	0.93	4.56	This work
	183	117		2.98		2.54	–0.2	8.03				Farsang et al. (2018)
	176	117				1.18						Cerantola et al. (2015)
	181	97.5				1.61						Liang et al. (2018)
L	283	117	117–0.031 $\times (T-300)$	2.98	$1.76 \times 10^{-5} + 3.46 \times 10^{-8} T$	1.86	1.7	0.35	1.75	1.41	1.28	This work
	284	117		2.98		1.86	1.2	2.03				Farsang et al. (2018)
	274	117				1.16						Cerantola et al. (2015)
	282	97.5				1.39						Liang et al. (2018)
ν_i	1085	117	117–0.031 $\times (T-300)$	2.98	$1.76 \times 10^{-5} + 3.46 \times 10^{-8} T$	0.27	0.2	0.15	0.25	0.17	0.29	This work
	1085	117		2.98		0.28	0.1	0.56				Farsang et al. (2018)
	1077	117				0.22						Cerantola et al. (2015)
	1084	97.5				0.22						Liang et al. (2018) ^a

^a From Zhang et al. (1998).^b The isothermal equivalent of mode Grüneisen parameter.^c The isobaric equivalent of mode Grüneisen parameter.^d The intrinsic anharmonic parameter calculated at 300 °C with the actual values of ν_i at 300 °C.**TABLE 3.** Mode Grüneisen and anharmonic parameters of rhodochrosite

Raman Mode	ν_i (cm ⁻¹)	K_0 (GPa)	K_T (GPa)	α_0 ($\times 10^{-5}$ K ⁻¹)	α (K ⁻¹)	γ_{IT}	γ_{IP}	α_i ($\times 10^{-5}$ K ⁻¹)	$\gamma_{IT(250)}^c$	$\gamma_{IP(250)}^d$	$\alpha_{i(250)}$ ($\times 10^{-5}$ K ⁻¹) ^e	Reference
T	184	110 ^a	Not found	2.28 ^b	$2.29 \times 10^{-5} - 5.56 \times 10^{-8} T + 3.36 \times 10^{-10} T^2$	2.1	8.63	–14.89	2.17	9.26	–15.55	This work
	185	110		2.09		2.01	5.12	–6.51				Farsang et al. (2018)
	184	113				2.37						Liu et al. (2016)
	183	110		2.28		1.74	5.33					Zhao et al. (2018)
L	289	110	Not found	2.28	$2.29 \times 10^{-5} - 5.56 \times 10^{-8} T + 3.36 \times 10^{-10} T^2$	1.88	5.1	–7.34	1.93	5.44	–7.7	This work
	290	110		2.09		1.83	4.84	–6.29				Farsang et al. (2018)
	290	113				1.99						Liu et al. (2016)
	288	110		2.28		1.7	5.01					Zhao et al. (2018)
ν_4	719	110	Not found	2.28	$2.29 \times 10^{-5} - 5.56 \times 10^{-8} T + 3.36 \times 10^{-10} T^2$	0.33	0.5	–0.39	0.33	0.52	–0.42	This work
	718	110		2.09		0.31	–0.09	0.85				Farsang et al. (2018)
	719	113				0.33						Liu et al. (2016)
	717	110		2.28		0.23	0.13					Zhao et al. (2018)
ν_i	1086	110	Not found	2.28	$2.29 \times 10^{-5} - 5.56 \times 10^{-8} T + 3.36 \times 10^{-10} T^2$	0.34	0.42	–0.18	0.34	0.44	–0.21	This work
	1086	110		2.09		0.34	0.25	0.17				Farsang et al. (2018)
	1086	113				0.38						Liu et al. (2016)
	1084	110		2.28		0.25	0.3					Zhao et al. (2018)

^a From Boulard et al. (2015).^b From Rao and Murthy (1970).^c The isothermal equivalent of mode Grüneisen parameter.^d The isobaric equivalent of mode Grüneisen parameter.^e The intrinsic anharmonic parameter calculated at 250 °C with the actual values of ν_i at 250 °C, the temperature dependence of the bulk modulus (K_T) is not found, So K_0 is used in this approximate calculation.

high-*T* Raman experiments are relatively simple to implement in comparison with XRD measurements under the same conditions, and our approach may thus have broad use to the community. Here, we highlight our approach and evaluate its effectiveness. We use a first-order Murnaghan equation of state (Murnaghan 1937) expressed in terms of the Raman frequency (Datchi and Canny 2004):

$$\nu_i(P, 20^\circ\text{C}) = \nu_i(1 \text{ bar}, 20^\circ\text{C})(1 = K'/K_0 P)^{1/K'} \quad (11)$$

Using the bulk modulus K_0 (117 GPa for siderite; 110 GPa for rhodochrosite) and fixed its first derivative $K'_0 = 4$, a least-squares fit of Equation 11 to our high-*P* Raman data at ambient temperature allows us to determine ν_i (1 bar, 20 °C) and γ_{IT} (Table 4) (Zhang et al. 1998; Boulard et al. 2015). The fits to our data produce R^2 values close to 1, and the derived parameters (ν_i , γ_{IT}) are consistent with the measured/calculated values presented in earlier sections. To extract values for K_T from the present simultaneously high *P-T* measurements, we assumed that the

change in K'_0 with temperature is negligible and that K_T can be approximated by a linear function. Therefore, Equation 11 can be generalized in the form

$$\nu_i(P, T) = \nu_i(1 \text{ bar}, T)(1 = K'/K_T P)^{1/K'} \quad (12)$$

where $\nu_i(1 \text{ bar}, T)$ is shown in Figure 3. By fitting K_T to the whole Raman data set (0–15 GPa, 20–800 °C for siderite; 0–13 GPa, 20–600 °C for rhodochrosite) of the highest intensity $\nu_i A_{1g}$ symmetric C–O stretching mode, we obtained:

$$K_T(\text{FeCO}_3) = 117 - 0.02961 \times (T - 20); \quad (13a)$$

$$K_T(\text{MnCO}_3) = 110 - 0.01735 \times (T - 20); \quad (13b)$$

where *T* is in °C, and the derived mode macroscopic Grüneisen parameters (γ_i) and fitting R^2 are reported in Table 4. While we observed that the macroscopic γ_i exhibits some scattering at high *P-T* conditions relative to ambient conditions, these variations do not propagate to significant uncertainties in our fitting

results. Zhang et al. (1998) obtained the *T*-dependence of the bulk modulus K_T of siderite ($\text{Fe}_{0.998}\text{Mn}_{0.002}\text{CO}_3$) by in situ X-ray diffraction at conditions up to 8.9 GPa and 800 °C. We evaluated the difference between our derived K_T and Zhang et al. (1998) (Table 4), and the results show that even at temperatures as high as 773 K, the deviation of the prediction is only 0.5 GPa. This comparison demonstrates the accuracy and reasonability of our prediction model (Eqs. 11 to 13) based on the Murnaghan equation of state. Therefore, it is likely that there are no large systematic errors associated with our estimate of K_T for rhodochrosite, and Equation 13b may be applied accurately within the *T* range of 20 to 600 °C.

Development of a *P-T* calibrant

Subduction of carbonates is a key process for the Earth's long-term deep carbon cycle high-pressure experiments based on DAC technology and in situ Raman spectroscopy measurements have been applied to studying the solubility of carbonate in aqueous fluids (e.g., Facq et al. 2014, 2016), water-rock reaction (e.g., Scott et al. 2004; Chen et al. 2008), and in other areas. However, accurate determination of in situ pressure in the reaction chamber of DAC in high-*T* (>400 °C) aqueous systems has been hampered in this area. Pressure sensors commonly used for calibration are known to result in contamination of the studied aqueous system. For example, ruby, a Cr^{3+} -containing $\alpha\text{-Al}_2\text{O}_3$ phase, gradually dissolves in aqueous fluids during heating (Tropper and Manning 2007; Andreani et al. 2013). Additionally, the broadening of the ruby R_1 and R_2 fluorescence peaks at high-*T* decreases the signal-to-background ratio of the Raman bands and results in uncertainties for pressure determination (Goncharov et al. 2005; Datchi et al. 2007; Farsang et al. 2018). Other pressure sensors, such as $\text{SrB}_4\text{O}_7\text{:Sm}^{2+}$, quartz, and zircon, also exhibited increased solubility at high-*T* (Manning 1994; Datchi et al. 2007; Bernini et al. 2013). Although ^{13}C diamond is a potential candidate material for the study of C-H-O aqueous systems, the Raman shift is relatively *P*-insensitive ($2.83\text{ cm}^{-1}/\text{GPa}$, Schiferl et al. 1997). Here, we used our Raman data to develop *P-T* calibrants for siderite and rhodochrosite. These calibrants will be particularly useful for carbonate solubility and water-carbonate reaction for DAC experiments as no adverse chemical interactions between the sample and the pressure sensor or pressure-transmitting medium (PTM) are expected. Facq et al. (2014, 2016) and Farsang et al.

(2018) first attempted to establish carbonate pressure sensors using linearly superimposed independent *P*- and *T*-induced shifts of carbonate modes but ignored the *P-T* cross derivative term of the frequency. Here, we considered the cross-derivative term in our treatment of *P* estimation by inverting Equations 1 to 7:

$$P = \frac{-B(T) + \sqrt{B(T)^2 - 4A \cdot [C(T) - v_1(P, T)]}}{2A} \quad (14)$$

where A, B, and C are calculated as for siderite (FeCO_3):

$$\begin{aligned} \text{T mode: } A &= -0.08425; B(T) = 4.243 + 8.288 \times 10^{-4} \times T; \\ C(T) &= 183.163 - 0.00977 \times T + 4.172 \times 10^{-6} \times T^2 \end{aligned} \quad (15)$$

$$\begin{aligned} \text{L mode: } A &= -0.05777; B(T) = 5.041 + 2.672 \times 10^{-4} \times T; \\ C(T) &= 283.535 - 0.01223 \times T + 1.717 \times 10^{-6} \times T^2 \end{aligned} \quad (16)$$

$$\begin{aligned} v_1 \text{ mode: } A &= -0.0734; B(T) = 3.056 + 5.998 \times 10^{-4} \times T; \\ C(T) &= 1085.505 - 0.00643 \times T + 2.853 \times 10^{-6} \times T^2 \end{aligned} \quad (17)$$

And for rhodochrosite (MnCO_3):

$$\begin{aligned} \text{T mode: } A &= -0.0537; B(T) = 3.8149 + 9.8688 \times 10^{-4} \times T; \\ C(T) &= 185.6075 - 0.0257 \times T + 8.199 \times 10^{-6} \times T^2 \end{aligned} \quad (18)$$

$$\begin{aligned} \text{L mode: } A &= -0.1092; B(T) = 5.6446 + 1.63 \times 10^{-3} \times T; \\ C(T) &= 290.1466 - 0.0321 \times T + 4.0518 \times 10^{-6} \times T^2 \end{aligned} \quad (19)$$

$$\begin{aligned} v_4 \text{ mode: } A &= -0.0585; B(T) = 2.3374 + 3.92 \times 10^{-4} \times T; \\ C(T) &= 719.5914 - 0.0059 \times T + 2.1554 \times 10^{-6} \times T^2 \end{aligned} \quad (20)$$

$$\begin{aligned} v_1 \text{ mode: } A &= -0.0726; B(T) = 3.8162 + 6.8004 \times 10^{-4} \times T; \\ C(T) &= 1085.9578 - 0.0082 \times T + 2.7963 \times 10^{-6} \times T^2 \end{aligned} \quad (21)$$

The above equations can be used to determine the in situ *P* based on the Raman shift and *T* measured by the thermocouple during high-temperature DAC experiments (e.g., Figs. 5c and 5d). In Figure 6, we compared the difference in predicted pressures with and without accounting for the *P-T* cross-term effects. Without considering the cross term, the calculated *P* may deviate from the real pressure by as much as ~0.5 GPa for FeCO_3 and ~2 GPa for MnCO_3 . For FeCO_3 , the largest deviations occur at low-*T* and high-*P*, whereas the largest deviations for MnCO_3 are at high-*T*. These data demonstrate that the influence of the *P-T* cross term on the predicted *P* is significantly greater for MnCO_3 compared to FeCO_3 .

TABLE 4. Mode Grüneisen and bulk modulus parameters derived from Raman data by fitting the first-order Murnaghan equation of state

Mineral		Siderite			Rhodochrosite			
Raman mode		T	L	v_1	T	L	v_4	v_1
v_1 (cm^{-1})	measured value	183	283	1085	184	289	719	1086
	by fitting	184	284	1086	185	290	720	1086
	by calculation	2.29	1.86	0.27	2.10	1.88	0.33	0.34
γ_T	by fitting	2.41	1.98	0.29	2.30	2.05	0.35	0.39
	R^2 of fitting	0.9965	0.9985	0.9915	0.9976	0.9981	0.9847	0.9975
	K_T (GPa)	$117 - 0.031 \times (T-300)^a$			Not Found			
γ_L derived from the fitting			2.05	0.31	1.94	1.95	0.31	0.38
	K_T (GPa) derived from the fitting		$117 - 0.02961 \times (T-20)^b$					$110 - 0.01735 \times (T-20)^b$
	R^2 of fitting			0.9867	0.9871	0.9949	0.9882	0.9907
Evaluation	Temperature given (K)	373	573	773				
	K_T calculated by (a)	114.7	108.5	102.3				
	K_T calculated by (b)	114.6	108.7	102.8				

^a From Zhang et al. (1998).

^b The unit of *T* is in Celsius.

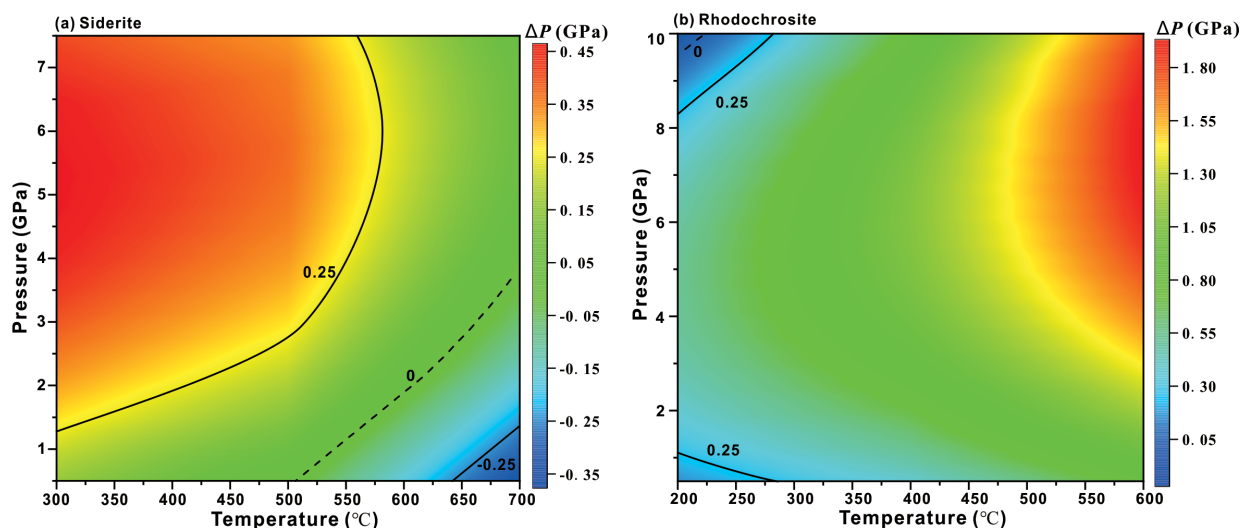


FIGURE 6. Difference in predicted pressures by considering *P-T* cross effects and without considering the impacts of siderite (a) and rhodochrosite (b). $\Delta P = P$ (without cross effects) – P (with cross effects). (Color online.)

It is well known that empirical polynomial fits, like Equation 14, result in poor extrapolations outside of their calibration range. Instead, Equation 12 is grounded in the physical relationship between the bulk modulus and pressure and is likely to be more accurate outside of the calibrated *P-T* range. We inverted Equation 12 to solve for *P* as a function of *T* and the measured Raman frequency:

$$P_{\text{FeCO}_3} = [29.25 - 7.4 \times 10^{-3} \cdot (T - 20)] \cdot \left\{ \left[\frac{v_1(P, T)}{v_1(0, T)} \right]^{12.90} - 1 \right\}; \quad (22a)$$

$$P_{\text{MnCO}_3} = [27.50 - 4.35 \times 10^{-3} \cdot (T - 20)] \cdot \left\{ \left[\frac{v_1(P, T)}{v_1(0, T)} \right]^{10.53} - 1 \right\} \quad (22b)$$

To use Equations 14 and 22, it is necessary to evaluate: (1) the most suitable modes for *P-T* determination and (2) the range of *P-T* conditions over which these equations may be applied accurately. The difference between the measured real pressures and pressures calculated with various modes using Equation 14 or 22 is shown in Online Materials¹ Figures OM2 and OM3. We find that predictions based on L and v_1 modes with Equation 14 are nearly identical and match the known *P* of the experiments within ± 0.25 GPa (or even smaller). However, the pressure calculated by Equation 22 has a large deviation from the actual value at low pressure, and gradually drops back under high pressure, which means that the Equation 22 derived from Murnaghan equation of state may have better high-pressure accuracy for both siderite and rhodochrosite (Online Materials¹ Figs. OM2a, OM2d, OM3a, and OM3d). Therefore, we recommend the use of Equation 14 for calculations of *P* within our *P-T* calibration range from in situ Raman spectral measurements of FeCO₃ and MnCO₃, whereas Equation 22 may be suitable for calculations at >15 GPa (outside our calibration range). Additionally, we find that the different Raman-active vibrational modes exhibit different degrees of intensity and *P-T* sensitivity, affecting their predictive power (Online Materials¹ Figs. OM2b, OM2c, OM3b, OM3c, OM3d, and OM3e). We find that

the L mode, v_1 mode, T mode, and v_4 mode (in decreasing order) are the most suitable for *P* determination (see Table 1). The signal intensity at low wavenumbers (less than 150 cm⁻¹) for the Raman instrument used in this study is relatively low, which significantly limits our ability to consistently fit the T mode data. In addition, the peak intensity of v_4 is much lower than that of the L and v_1 modes, resulting in poor fitting statistics. While the v_1 and L modes are both at high intensities, we find that the peak position of the L mode is more sensitive to changes in *P-T*. Taken together, we recommend the above sequence.

Phase transitions of siderite and rhodochrosite at high *P* and room *T*

We also examined the potential phase changes, spin transitions, and structural changes in FeCO₃ and MnCO₃ as a function of *P* up to 47 GPa at room *T* to explore the applicable scope of the thermodynamic parameters/behaviors obtained above. The Raman spectra of FeCO₃ demonstrate that it is stable up to ~ 44 GPa at ambient temperature (Fig. 7a). However, we observed that the intensities of T, L, and v_4 modes gradually decrease (Online Materials¹ Fig. OM4a). Between 43.6 and 46.6 GPa, we observed an obvious frequency change in all modes, which is a consequence of the spin transition. Both of the external lattice modes (L and T modes) and the internal mode (v_4) jump to higher wavenumbers as the distance between the CO₃²⁻ groups and the cations, as well as the O-O bond lengths, decrease, respectively (Farfan et al. 2012; Lin et al. 2012; Cerantola et al. 2015; Müller et al. 2016). Contrary to the other modes, the v_1 mode is shifted to lower wavenumbers as the result of an increase of C-O bond lengths after the spin transition (Lavina et al. 2010). The color of the crystal also changes from transparent to green at the same time as the phase changes (Fig. 7a). The *P*-induced, isostructural high-spin (HS) to low-spin (LS) transition is caused by the increase in the crystal field splitting energy of the 3d electrons of Fe²⁺ in its octahedrally coordinated site under compression (Farfan et al. 2012). The transition results in a decrease in vol-

ume and octahedral bond distance, an increase in bulk modulus, and a slight increase in the C-O bond length of the CO_3^{2-} groups (Lavina et al. 2009, 2010; Nagai et al. 2010). The *P* of the HS to LS transitions reported in previous literature are summarized in Table 5. Depending on the experimental methods, a general inconsistency about the pressure range of the spin transition exists. Our results support the viewpoint of a sharp spin transition (a range of ≤ 3 GPa), whereas some studies (e.g., Spivak et al. 2014; Cerantola et al. 2015) place the spin transition over a sizeable pressure range (≥ 5 GPa). Interestingly, even when more magnesium-rich siderite is used [e.g., $\text{Fe}/(\text{Fe}+\text{Mg}) = 0.65$], the transition pressure still occurs in the vicinity of 45 GPa. The negligible compositional effect on the transition pressure in the (Mg, Fe) CO_3 system can be explained by the much longer Fe^{2+} - Fe^{2+} distances in the structure that are separated by the CO_3^{2-} units (Lin et al. 2012).

The Raman frequency shift of MnCO_3 as a function of *P* at room *T* is shown in Figure 7b and Online Materials¹ Figure OM4b. Like siderite, the intensities of T, L, and ν_4 modes of rhodochrosite gradually decrease with increasing *P*. In the compression data, we observed an abrupt step in the Raman shift of the ν_1 mode at 46.6 GPa, where a new, higher frequency peak forms and the intensity of the original peak is diminished (Online Materials¹ Fig. OM4b), which we assign to the change from MnCO_3 -I (CaCO_3 -I type structure) to MnCO_3 -II (CaCO_3 -VI type structure) (Merlini et al. 2015; Liu et al. 2016). The L, T, and ν_4 modes are split, and the splitting of the ν_4 modes occurs at a higher wavenumber than the initial peak. Other new peaks may exist but are difficult to identify due to the weak intensity or overlap. Our results closely resemble those of Liu et al. (2016) and Merlini et al. (2015) on the MnCO_3 -I to MnCO_3 -II transition (Table 5), where the structural state of MnCO_3 was measured by XRD and Raman spectroscopy and helium

was used as a PTM. However, our results differ from those of other studies. For example, Farfan et al. (2013), Boulard et al. (2015), and Zhao et al. (2018) reported a transition of MnCO_3 between 15 and 35 GPa using NaCl, silicon oil, or N_2 as the PTM and that this transition may be related to a distortion of the CaCO_3 -I structure due to nonhydrostatic conditions, especially when NaCl undergoes a B1 to B2 phase transition at about 25–30 GPa, which involves a fairly large volume change (Liu et al. 2016). Meanwhile, Ono (2007) did not observe this distorted phase after laser heating, which removed the non-hydrostatic effect and whose experiments could be considered as having a hydrostatic pressure environment. But this study lacks experiments between 44 and 54 GPa and only roughly estimated that MnCO_3 would undergo a phase transition at ~ 50 GPa. Santillán and Williams (2004) did not observe any phase transition up to 50 GPa, which may be related to the relatively impure composition of their sample ($\text{Mn}_{0.77}\text{Fe}_{0.09}\text{Ca}_{0.07}\text{Mg}_{0.07}\text{CO}_3$). The incorporation of Fe^{2+} and Mg^{2+} in MnCO_3 sample may enlarge the stability field of the CaCO_3 -I structure of MnCO_3 (Shi et al. 2012; Boulard et al. 2015; Liu et al. 2016). In short, we find that the transition pressures obtained by XRD and Raman using helium as the PTM are consistent (Table 5). Helium is considered the best hydrostatic pressure media, with a pressure difference of <0.5 GPa at 50 GPa (Klotz et al. 2009). Furthermore, no coexisting MnCO_3 -I and MnCO_3 -II phases (the distorted phase of the CaCO_3 -I structure) are observed between 15 and 35 GPa. As emphasized previously, the choice of PTM is crucial to maintaining hydrostatic conditions in DAC experiments. In addition, the large difference of phase transition pressure for MnCO_3 under non-hydrostatic and hydrostatic conditions indicates that it may be different from other carbonates, which seem sensitive to the stress field in the sample chambers (Liu et al. 2016; Zhao et al. 2018).

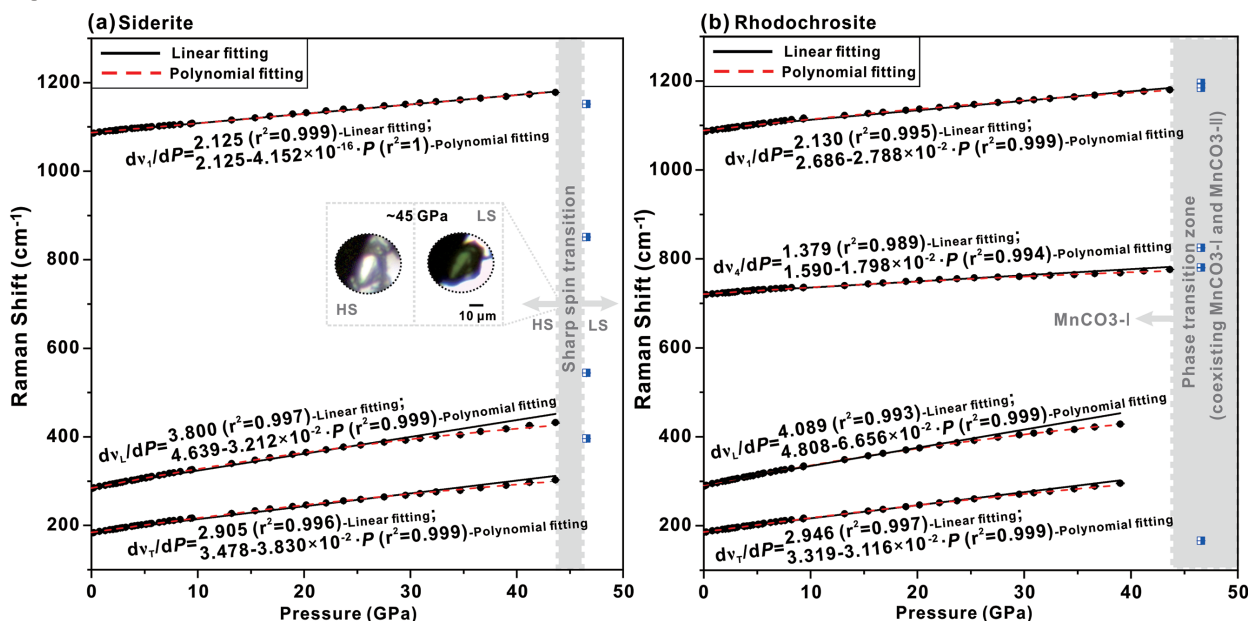


FIGURE 7. Raman shifts of siderite (a) and rhodochrosite (b) as a function of pressure at ambient temperature up to 47 GPa to show a nonlinear migration at higher pressure and peak splitting. The shaded area indicates the approximate phase transition pressures. The color change of HS state (clear) to LS state (green) of siderite is also attached to a. (Color online.)

TABLE 5. Literature review including methods, composition, and transition pressure for siderite and rhodochrosite

Reference	Method	Pressure-transmitting medium	Composition	Transition <i>P</i> (GPa)
Siderite				
(Ionic radius: 0.78 Å; M-O bond distance: 2.142 Å; Outer electron configuration: 3d ⁶)				
This work	Raman	Helium	(Fe _{0.95} Mn _{0.046} Mg _{0.004})CO ₃	43.6–46.6
Müller et al. (2016)	Raman	Neon	(Fe _{0.89} Mn _{0.07} Mg _{0.03} Ca _{0.01})CO ₃	43.3–45.5
Cerantola et al. (2015)	Raman	Neon	FeCO ₃	40–47
Lobanov et al. (2015)	UV-VIS	Neon	(Fe _{0.95} Mn _{0.05})CO ₃	43–45
Spivak et al. (2014)	Raman	Neon	FeCO ₃	40–47
Liu et al. (2014)	Powder + single-crystal XRD	Neon	(Fe _{0.65} Mg _{0.33} Mn _{0.02})CO ₃	43–47 (single-crystal XRD)
Farfan et al. (2012)	Powder XRD + Raman	None (XRD); silicone oil (Raman)	(Fe _{0.76} Mn _{0.15} Mg _{0.09} Ca _{0.01})CO ₃	46 (XRD); 46–50 (Raman)
Lin et al. (2012)	Powder + single-crystal XRD + Raman	Neon	(Fe _{0.65} Mg _{0.33} Mn _{0.02})CO ₃	45
Nagai et al. (2010)	Powder XRD	Argon	N/A	47–50
Lavina et al. (2010)	Single-crystal XRD	Neon	Near end-member	44–45
Mattilla et al. (2007)	XES	Argon; None above 40 GPa	(Fe _{0.96} Mn _{0.04})CO ₃	~50
Rhodochrosite				
(Ionic radius: 0.83 Å; M-O bond distance: 2.195 Å; Outer electron configuration: 3d ⁵)				
This work	Raman	Helium	(Mn _{0.936} Fe _{0.059} Mg _{0.005})CO ₃	from 44 GPa
Zhao et al. (2018)	Raman	Nitrogen	(Mn _{0.976} Fe _{0.011} Ca _{0.003} Mg _{0.001})CO ₃	16–32
Liu et al. (2016)	Single-crystal XRD + Raman	Neon (XRD); Helium (Raman)	(Mn _{0.980} Fe _{0.009} Ca _{0.009} Mg _{0.002})CO ₃	45–48 (XRD); 44–47 (Raman)
Merlini et al. (2015)	Single-crystal XRD	Helium	(Mn _{0.96} Ca _{0.04})CO ₃	44
Boulard et al. (2015)	Infrared + Powder XRD	KBr (Infrared); NaCl (XRD)	(Mn _{0.976} Fe _{0.012} Ca _{0.002} Mg _{0.004})CO ₃	39 (Infrared); 15–34 (XRD)
Farfan et al. (2013)	XES + Powder XRD + Raman	NaCl (XRD); Silicone oil (Raman); None (XES)	(Mn _{0.976} Fe _{0.012} Ca _{0.002} Mg _{0.004})CO ₃	15–30 (XRD); 15–30, 48 (Raman); No (XES)
Ono (2007)	Powder XRD	None	Mn _{0.999} CO ₃	~50
Santillán and Williams (2004)	Infrared + Powder XRD	KBr (Infrared); None (XRD)	(Mn _{0.77} Fe _{0.09} Ca _{0.07} Mg _{0.07})CO ₃	No

Note: M-O bond distances are from Rutt and Nicola (1974).

Previous studies have concluded that the observed jumps in the Raman spectra for MnCO₃ are the result of changes in the crystal structure itself, with no contribution of an electronic spin transition of Mn²⁺ (Farfan et al. 2013; Boulard et al. 2015). As a result, the bulk modulus and density of MnCO₃ increase by ~12 and 5.5% across the phase transition from I to II (Liu et al. 2016). These data suggest that although the Ca, Mg, Fe, and Mn carbonate group minerals all have the same structure at ambient conditions (rhombohedral, space group $\bar{R}3c$), their high-pressure behavior is markedly different due to the size, charge, or electronic configuration of their constituent atoms (Zhang and Reeder 1999).

IMPLICATIONS

To date, little is known about the fate of the FeCO₃ and MnCO₃ carbonates in the subduction zones and Earth's deep interior. These components may be significant: MnCO₃ is found as a vein-filling phase in seafloor hydrothermal ore deposits (Hazen et al. 2013), and the FeCO₃ component is present as a solid solution of magnesite and dolomite in metamorphosed iron formations (Klein 1978, 2005), altered igneous rocks (Buckley and Woolley 1990; Laverne 1993), and so on. To address this knowledge gap, we systematically quantified the effects of temperature, pressure, and the *P-T* cross derivative on the Raman frequency shifts of siderite and rhodochrosite. Additionally, we report the first (to our knowledge) measurements of the Raman spectra of these phases at simultaneously high-*P* and high-*T* conditions, which we analyzed over the range 0 to 15 GPa and 300 to 1100 K. Importantly, we used these data to develop Raman shift pressure sensors of siderite and rhodochrosite. This was done because other commonly used pressure calibrants (e.g., ruby, SrB₄O₇:Sm²⁺, quartz) in the sample

chamber are known to change the reaction system due to their instability at high *P-T* conditions, especially involving aqueous systems. The derived temperature from 300 to 1100 K at high pressure up to 15 GPa in our study covers a significant portion of the *P-T* range for the subduction zones. The *v_i-P-T* relationships of siderite and rhodochrosite established in our study can be used specifically to calibrate pressure of the reaction chamber while studying the solubility of FeCO₃ and MnCO₃ in water or the water-carbonate interaction progress (e.g., in Fe-C-O-H or Mn-C-O-H system) under the conditions of the deep Earth, so as to derive important physical and chemical properties. More research is needed to reveal carbon behavior in aqueous-bearing systems in the subduction zones.

Additionally, the measured *P*-, *T*-, and *P-T* cross induced Raman frequency shifts were used to calculate the mode Grüneisen, intrinsic anharmonic and bulk modulus parameters. We developed a method based on a first-order Murnaghan equation of state to calculate the temperature dependence of the bulk modulus (*K_T*), which is more convenient than *in situ* high-*P* and high-*T* XRD measurements. The derived anharmonic thermodynamic properties allow us to refine the phase diagram for FeCO₃ and MnCO₃ systems at high *P-T* conditions.

Finally, we re-examined the high-*P* phase transition behavior of siderite and rhodochrosite at room temperature. A sharp spin transition in FeCO₃ is observed at ~45 GPa, and the transition of MnCO₃-I to MnCO₃-II occurs at ≥46 GPa. Further simultaneous high-*P* and high-*T* experiments relevant to subduction zones will be needed to quantify the phase transition boundaries for divalent carbonates. Such data are vital to constrain the fate of carbonates in subduction zones and the deep carbon cycle behaviors.

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