

High-temperature Raman spectroscopy of $\text{K}_2\text{Ca}(\text{CO}_3)_2$ bütschliite and $\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$ shortite

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ABSTRACT

Raman spectra of $\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$ shortite and $\text{K}_2\text{Ca}(\text{CO}_3)_2$ bütschliite were measured to 715 and 740 °C, respectively, under vacuum. The vibrational spectra demonstrate that shortite converts to nyerereite [$\text{Na}_2\text{Ca}(\text{CO}_3)_2$] and calcite at 535 °C. This assemblage remains stable up to ~700 °C, at which point nyerereite begins to decompose. Bütschliite converts to the isochemical phase fairchildite at 570 °C, which is stable to 665 °C, where it decomposes to an assemblage of K_2CO_3 and CaO. The variation of anharmonicity between different vibrational modes of each of the low-temperature phases is assessed, and these yield insights into inter-carbonate group couplings. Both fairchildite and nyerereite exhibit spectral features consistent with extensive disordering.

Keywords: Carbonate, high-temperature, Raman spectroscopy, carbonatite

INTRODUCTION

Bütschliite and shortite are alkali-calcium carbonate minerals with the chemical formulas $\text{K}_2\text{Ca}(\text{CO}_3)_2$ and $\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$, respectively; they each represent structurally different manifestations of double carbonates. Bütschliite crystallizes in the trigonal system (space group: $R\bar{3}m$) with three formula units per unit cell, and shortite crystallizes in the orthorhombic system (space group: $Amm2$) with two formula units per unit cell. The structure of bütschliite is characterized by sheets of planar $[\text{CO}_3]$ units stacked on interstitial Ca^{2+} and K^+ cations (Pabst 1974). The lower symmetry of shortite is in accord with its more complex structure, which is characterized by the presence of three distinct cation sites (one Ca^{2+} and two Na^+ sites) and two distinct $[\text{CO}_3]$ sites (Dickens et al. 1971). While bütschliite and shortite do not form a solid solution, the minerals that they convert to at high temperatures, fairchildite and nyerereite ($\text{Na}_2\text{Ca}(\text{CO}_3)_2$), do. Indeed, nyerereite samples from the natrocarbonatites of Oldoinyo Lengai in Tanzania have been reported to contain between 6–9 wt% K_2O (Zaitsev et al. 2009). Shortite has been observed in the groundmass of magmatic carbonatites (Zaitsev and Chakhmouradian 2002), and both phases have been observed within melt inclusions in olivine and/or diamond (Mernagh et al. 2011; Logvinova et al. 2019; Abersteiner et al. 2022). Notably, bütschliite is the only potassium-bearing carbonate mineral that has been found as an inclusion in mantle phases, and alkali-rich carbonate fluids have been invoked as being the medium within which a subset of diamonds are formed within Earth's mantle (Pal'yanov et al. 2002; Weiss et al. 2015). Hence, while alkaline earth carbonates are viewed as the principal means by which carbon may be transported to depth via the subduction process, alkali-rich carbonate fluids are not only important mantle metasomatic agents (e.g., Gervasoni et al. 2017; Chen et al. 2022), but are also likely critical players in several paths that return carbon from depth to Earth's surface,

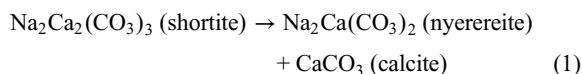
including diamond petrogenesis and the genesis of kimberlites (e.g., Kamenetsky and Yaxley 2015). Thus, as crystalline carbonate hosts for alkalis, the properties of these two phases at extreme conditions of pressure and/or temperature are highly relevant to the behavior of alkali-rich carbonate materials, and hence carbon cycling, within Earth's interior.

Previous studies have documented extensive high-pressure polymorphism in both shortite and bütschliite. In a high-pressure study on shortite, Vennari et al. (2018) reported a transition to a crystalline monoclinic phase, shortite-II (space group: Pm), at 15 GPa, followed by a transition to an amorphous phase above 22 GPa. The $[\text{CO}_3]$ groups of shortite-II are substantially distorted, with carbon adopting a 3+1 coordination with surrounding oxygen atoms. Additionally, they report the existence of a high-temperature/high-pressure crystalline phase, shortite-III, generated at pressures between 12 and 30 GPa and $T > 1300$ °C. Below 12 GPa, shortite-III decomposes into a mixture of shortite, nyerereite, and aragonite. In a high-pressure X-ray diffraction and Raman spectroscopy study of bütschliite, Zeff et al. (2024) documented four phase transitions up to 94 GPa, with single-crystal diffraction showing that a transition at ~6 GPa was associated with conversion to a monoclinic phase (space group: $C2/m$). This lowest-pressure transition was also observed in other Raman experiments (Likhacheva et al. 2024a), and its crystal structure was subsequently confirmed (Likhacheva et al. 2024b). Raman and polycrystalline X-ray measurements of Zeff et al. (2024) indicate the onset of three subsequent phase transitions at 28, 34, and 37 GPa.

High-temperature phase transitions have been previously documented in both bütschliite and shortite. In synthesizing samples of bütschliite for his X-ray diffraction measurements, Pabst (1974) bracketed the isochemical bütschliite-fairchildite transition between 505 and 585 °C at ambient pressure. A novel feature of this transition is that it involves the partial disordering of carbonate ions in the quenched high-temperature phase, fairchildite (Pertlik 1981). At 300 K, one of the two crystallographically distinct carbonate sites, C(2), shows orientational

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disordering of the oxygens around the carbon location. Cooper et al. (1975) studied the K_2CO_3 - CaCO_3 - Na_2CO_3 ternary system and reported a bütschliite-fairchildite transition temperature of 547 °C at 1 kbar. Calorimetric measurements conducted by Navrotsky et al. (1997) determined enthalpy and entropy changes of $\Delta H_{\text{büt} \rightarrow \text{fc}} = 33.6 \pm 4.2$ kJ/mol and $\Delta S_{\text{büt} \rightarrow \text{fc}} = 40.9 \pm 5.1$ J/mol-K. Assuming that bütschliite and fairchildite have similar thermal expansions, this value of the entropy change and the density difference reported by Pabst (1974) yield a Clapeyron slope of $dT/dP \sim 145$ GPa for this transition, implying an enhanced stability field of bütschliite at high pressures relative to fairchildite. This slope generally aligns with the lack of observation of fairchildite stability at 3 GPa (Arefiev et al. 2019). The thermal properties of shortite were measured at the Bureau of Mines, with the decomposition reaction:



being observed at 470 °C. Using differential scanning calorimetry, they determined $\Delta H_{\text{shor} \rightarrow \text{nyer} + \text{cal}} = 28.8$ kJ/mol (Johnson et al. 1974).

To examine the nature of in situ disordering processes within these phases at high temperatures, and to characterize the anharmonic behavior of vibrational modes prior to the transitions to disordered phases, we have conducted high-temperature Raman spectroscopy measurements on bütschliite and shortite under vacuum. We document the spectroscopic signature of two high-temperature phase transitions in each mineral: the previously thermochemically characterized transitions and their subsequent decarbonation reactions. Notably, both shortite and bütschliite convert to disordered phases before undergoing decomposition reactions at higher temperatures. These results shed light not only on the behavior of vibrational modes at high temperatures in these phases but also on the stability of alkali double carbonate minerals at high temperatures.

METHODS AND SAMPLE SYNTHESIS

The shortite sample used in this study is from the FMC Westvaco mine in Sweetwater County, Wyoming, U.S.A. The cation composition of this shortite sample was previously determined by Vennari et al. (2018): $\text{Na}_{1.9}\text{Ca}_{2.1}(\text{CO}_3)_{3.0}$, implying a slight excess of calcium relative to the ideal stoichiometry. Crystals of bütschliite were synthesized via the hydrothermal method (E) described by Pabst (1974). Briefly, small chunks of optical quality calcite were immersed in a saturated solution of K_2CO_3 and held at ~ 70 °C. In this method, crystals of $\text{K}_2\text{Ca}(\text{CO}_3)_2$ begin to grow on the cleavage surfaces of the calcite within a few days. The crystals resulting from this synthesis method were optically transparent and euhedral (e.g., Zeff et al. 2024); occasional crystals that incorporated inclusions were not used in these measurements. No variability in Raman spectra was detected across individual grains, implying that they were spectroscopically homogeneous at the micrometer scale.

Raman spectra were collected using a Labram HR Evolution spectrometer equipped with 633 and 532 nm diode excitation lasers nominally rated at 50 mW. The spectral range of our measurements spanned ~ 60 – 2000 cm^{-1} , and typical spot sizes at the sample were about 2 μm . Although most measurements were conducted with the 532 nm laser, a few redundant spectra were collected with the 633 nm laser either when signals were weak or to probe a slightly lower frequency range than is available with the 532 nm excitation. Typical collection times ranged from 10 to 40 min (12–40 s acquisition times and 50–130 accumulations). A diffraction grating with a grating density of 1200 lines/mm was used for all measurements with a spectral resolution of ~ 1 cm^{-1} . Spectral processing (baseline removal, peak fitting, and peak deconvolution) was carried out with the Horiba

LabSpec6 software. Linear baselines were subtracted from the spectra for plotting and peak fitting. Such peak fitting of well-resolved peaks is well known to produce notably higher precisions of peak positions (by as much as an order of magnitude) relative to the formal single-point spectral resolution (e.g., Cizina et al. 2023). Samples were heated under vacuum ($\sim 10^{-3}$ mbar pressure) in a Linkam TS1500 heating stage, with temperature control provided by a T96 system controller. The typical precision of the temperature control is < 1 °C. All high-temperature data were collected on samples that were initially single crystals. Expanded data, including mode shifts and spectra, are available in the Online Materials¹. Typical heating rates of the samples were 20–40 °C/min, with the samples held at each temperature for 10–60 min while spectra were taken. A thin layer of platinum foil was placed between the sample and the sapphire sample holder to prevent chemical reactions from occurring with the samples at high temperatures.

RESULTS AND DISCUSSION

Ambient raman spectra of bütschliite and shortite

The ambient Raman spectra of bütschliite and shortite are shown in Figure 1. The spectra agree well with previous ambient-pressure Raman spectra of these materials (Arefiev et al. 2019; Vennari et al. 2018). Factor group analysis of bütschliite yields:

$$\Gamma_{\text{optic}} = 4A_{1g} + A_{1u} + A_{2g} + 4A_{2u} + 5E_u + 5E_g. \quad (2)$$

Here, the A_{1g} and E_g symmetry modes are Raman active. Similarly, factor group analysis of shortite yields:

$$\Gamma_{\text{optic}} = 14A_1 + 7A_2 + 10B_1 + 14B_2. \quad (3)$$

For the lower-symmetry shortite structure, all modes are Raman active. Notably, the factor group analysis carried out here for shortite proceeds from a primitive unit cell containing 16 atoms ($Z = 1$), while the crystallographic unit cell for shortite contains 32 atoms ($Z = 2$).

High-temperature raman spectra of bütschliite

All of the observed Raman modes of bütschliite shift to lower frequencies upon heating, except for the lowest frequency lattice mode that lies initially at 68 cm^{-1} and the ν_4 in-plane bending vibration (Fig. 2; Table 1). The ν_4 in-plane bending vibration remains essentially constant in frequency during heating. Such near-constant-frequency or positive thermal shifts of vibrations of this type have been observed for aragonite-structured phases (e.g., Gillet et al. 1993; Wang et al. 2019), but not for calcite-related phases or, notably, other double carbonates (e.g., Gillet et al. 1993; Farsang et al. 2018). For comparison, the ν_4 in-plane bending mode of dolomite (space group: $R\bar{3}$), which is structurally similar to bütschliite, exhibits a frequency shift of $-0.0021 - 1.7 (10^{-5} \text{ T})$ (Gillet et al. 1993). The stationary behavior of the in-plane bending mode of bütschliite likely results from a combination of anisotropic expansion of the unit cell along the c -axis, as seen in both aragonite and dolomite (Reeder and Markgraf 1986; Ye et al. 2012), and the orientation of the trigonal planar $[\text{CO}_3]$ units in the unit cell. The $[\text{CO}_3]$ units in aragonite are perfectly aligned (albeit rotated by 180° from their neighboring carbonate) along the c -axis, while the $[\text{CO}_3]$ units in bütschliite are slightly offset, and the $[\text{CO}_3]$ units in dolomite are substantially offset (Fig. 3). The alignment of sheets of $[\text{CO}_3]$ units in the aragonite and bütschliite unit cells hence likely results in stronger vibrational coupling between the $[\text{CO}_3]$ units in adjoining layers. Hence, we attribute the anomalous near-zero shift of the in-plane bend vibration to a decrease in the interlayer coupling

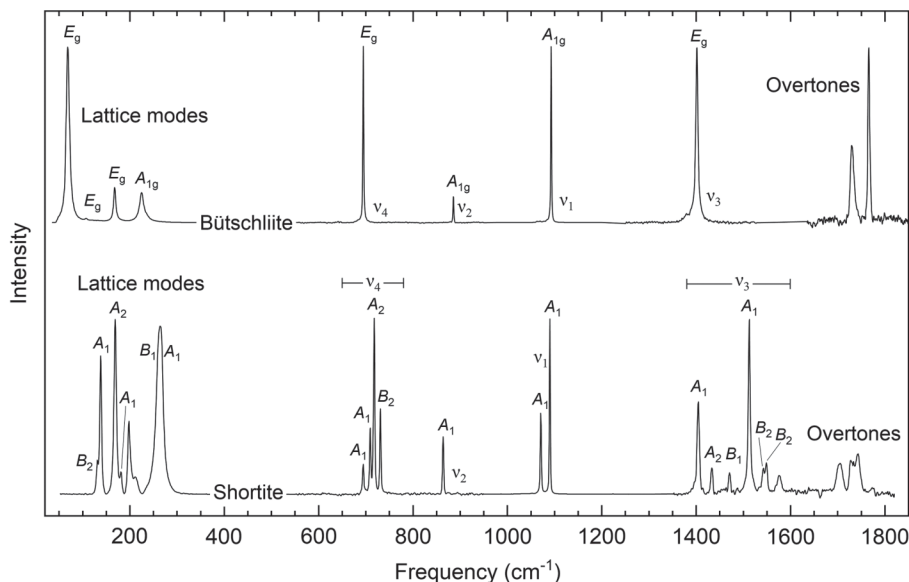


FIGURE 1. Ambient Raman spectra of natural shortite (bottom) and synthetic bütschliite (top).

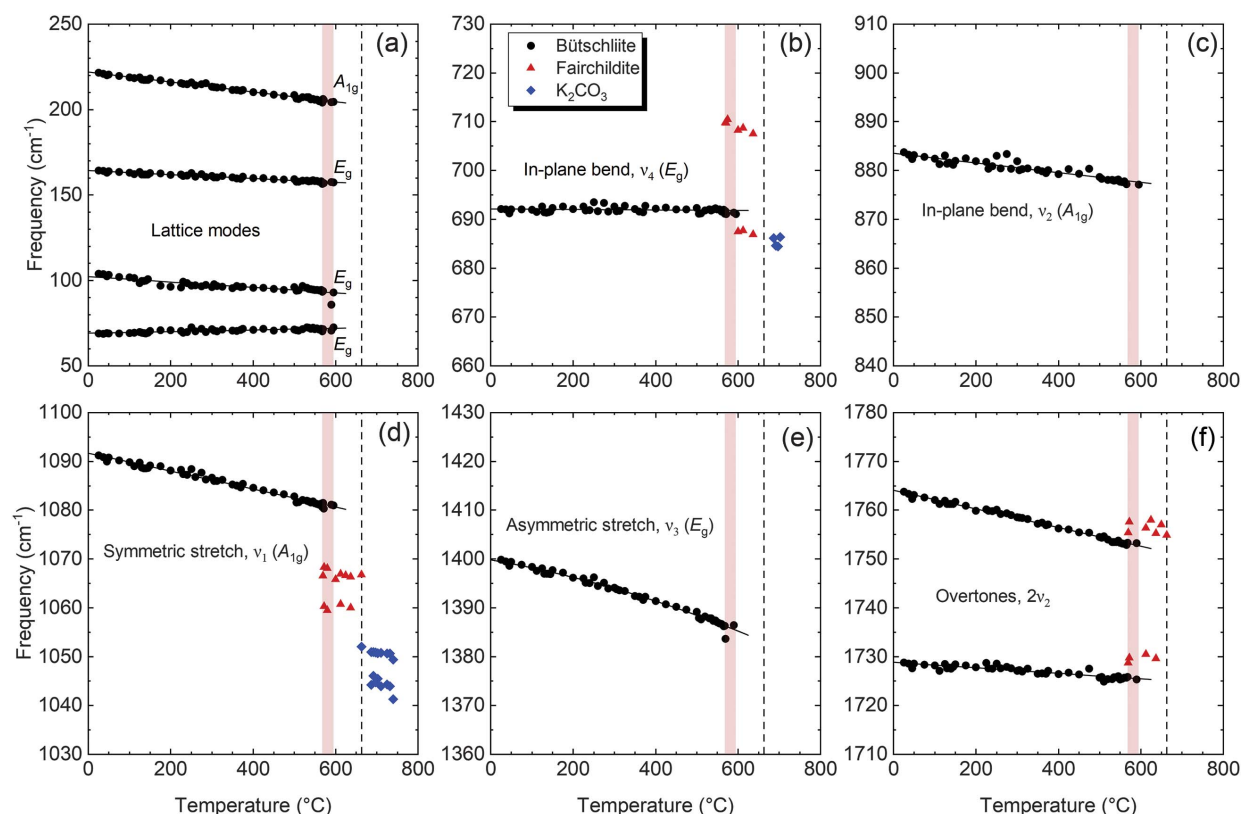


FIGURE 2. High-temperature Raman mode shifts of bütschliite and its associated high-temperature phases. The red shaded region shows the temperature range of the mixed-phase regime. The dashed line marks the decomposition of fairchildite into the assemblage $K_2CO_3 + CaO$.

as temperature is increased and the c -axis expands: such mode interactions often play a strong role in the anharmonic frequency shift and line-broadening in crystals (e.g., Luty and Eckhardt 1985; Lucazeau 2003). This interlayer coupling is expected to be weaker for the dolomite structure, where the $[CO_3]$ units are

misaligned. The thermal expansion within the plane of the $[CO_3]$ groups is small, while the distance to neighboring metal cations increases and the associated in-plane bending vibration is correspondingly temperature-insensitive as the coupled $[CO_3]$ units move away from each other during heating in

TABLE 1. Peak assignments and temperature dependence of Raman modes of bütschliite

Initial frequency, ν_0 [cm^{-1}]	Vibration	Symmetry	$(\partial\nu/\partial T)_P$ [$\text{cm}^{-1}/^\circ\text{C}$]	$-\alpha_{\nu P}$ [$10^4\ ^\circ\text{C}^{-1}$]
68	Lattice mode	E_g	$-0.001\text{--}0.005^a$	-0.29
107	Lattice mode	E_g	$-0.0157(0)$	1.47
167	Lattice mode	E_g	$-0.0115(0)$	0.69
224	Lattice mode	A_{1g}	$-0.0291(0)$	1.30
694	In-plane bend, ν_4	E_g	$-0.0005(0)$	0.01
885	Out-of-plane bend, ν_4	A_{1g}	$-0.0099(0)$	0.11
1092	Symmetric stretch, ν_1	A_{1g}	$-0.0184(0)$	0.17
1401	Asymmetric stretch, ν_3	E_g	$-0.0148(2) - 3.18(0) \cdot 10^{-5}T$	0.11
1730	Overtone, $2\nu_2$ (IR)	—	$-0.0057(0)$	0.03
1766	Overtone, $2\nu_2$ (Raman)	—	$-0.0192(0)$	0.11

^a See text.

bütschliite. Although no thermal expansion measurements have been conducted on bütschliite, under pressure, the *c*-axis is by far the most compressible (Zeff et al. 2024), and the thermal expansion of the material can be anticipated to be highest in the between-layer, *c*-axis direction. Based on the negligible frequency shift and moderate broadening of the peak (Fig. 4), we infer that the in-plane bending mode of bütschliite shows very nearly harmonic behavior during heating, likely due to the competing and compensating effects of the small volumetric expansion (in the *a*-*b*/carbonate unit plane) and decreased intermolecular mode interactions (due to the *c*-axis expansion).

The location of the lowest frequency lattice mode, with an ambient-temperature frequency of 68 cm^{-1} , is the least well resolved of any mode during heating; however, the overarching data are consistent with a shift between $+0.005$ and $-0.001\text{ cm}^{-1}/^\circ\text{C}$. Here, this small shift is compatible with the behavior of this band under pressure (Zeff et al. 2024; Likhacheva et al. 2024a); while not soft, its pressure shift is observed to be anomalously small for a low-frequency lattice mode. This is consistent with its assignment as a mode that solely involves librations of the carbonate group

within the *a*-*b* plane (Caracas and Bobocioiu 2011). This plane is (relative to the *c*-axis) relatively incompressible (Zeff et al. 2024) and likely also has a low thermal expansion relative to the *c*-axis in this layered structure.

The asymmetric stretching ν_3 mode is the only vibration that exhibits any curvature in its frequency-temperature trajectory over the stability range of bütschliite during heating; this peak also broadens substantially more during heating than any of the other internal carbonate vibrations (Figs. 4 and 5). Why this mode, out of the four carbonate internal modes, appears to be the most susceptible to anharmonic effects on its linewidth is not entirely clear. Nevertheless, we speculate that the broadening and nonlinear shift of this band could be associated with its progressively closer proximity to the (unobserved) $2\nu_4$ overtone as higher temperatures are accessed. For reference, twice the frequency of the Raman-active ν_4 peak is 1384 cm^{-1} , or $\sim 2\text{ cm}^{-1}$ below the frequency of the ν_3 mode at the highest temperatures of bütschliite stability (Fig. 4). In this context, Raman linewidths at high temperatures have been shown to vary depending on multi-phonon interactions (e.g., Balkanski et al. 1983), and it is plausible that anharmonic coupling occurs between the ν_3 vibration and the nearly energetically coincident ν_4 overtones.

While the initiation of the transition from bütschliite to fairchildite is tightly constrained in our measurements to between 568 and $571\text{ }^\circ\text{C}$, the transition is characterized by a mixed phase regime that persists until $595\text{ }^\circ\text{C}$. This is roughly $20\text{ }^\circ\text{C}$ hotter than

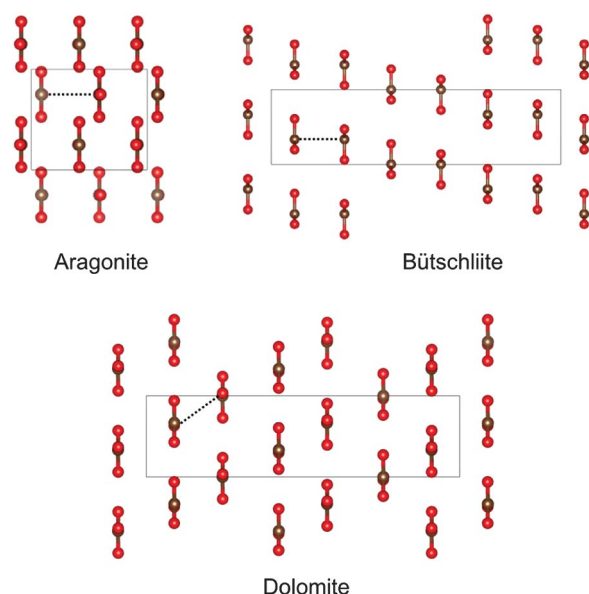


FIGURE 3. Arrangements of the trigonal planar $[\text{CO}_3]$ units in aragonite, bütschliite, and dolomite. Each unit cell is viewed down the *b*-axis. Metal cations are hidden for clarity. Dotted lines emphasize the alignments of nearest-neighbor carbon atoms.

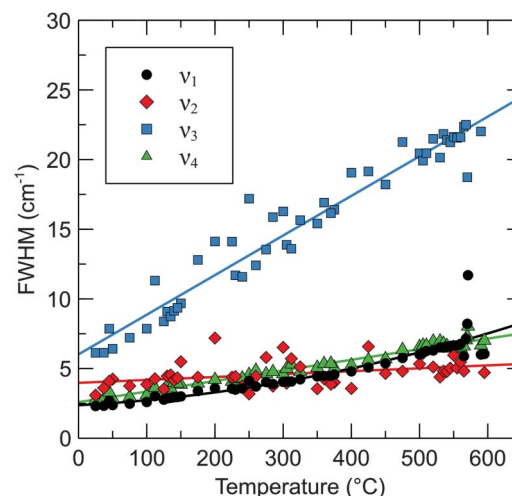


FIGURE 4. Linewidths of the internal carbonate modes of bütschliite.

the temperature reported by Cooper et al. (1975) for this transition at 1 kbar: they conducted experiments at 515, 543, and 550 °C, with the latter two having both bütschliite and fairchildite present. The width that we observe in the transition region generally agrees with that observed in the higher-pressure results (Cooper et al. 1975). Notably, the transition is observed to proceed heterogeneously across the sample in our experiments, with different regions showing fairchildite- and bütschliite-like spectra across this ~25 °C interval. This observation strongly suggests that the transition is kinetically impeded, with nucleation and growth processes controlling the conversion to the high-temperature phase. The first appearance of the new phase is visible in the spectrum at 571 °C (Fig. 5).

The low frequency region of this spectrum appears to be a mixture of the two most intense lattice modes of bütschliite and the broad low-frequency feature associated with the intrinsically disordered structure of fairchildite. The ν_4 in-plane bending vibration of bütschliite is still present in spectra at this temperature, but there is also a high frequency component of lower intensity. For comparison, the ν_2 out-of-plane bending vibration, which is weak in bütschliite but not detectable in fairchildite, is absent (Fig. 5). The ν_1 symmetric stretching vibration is dominated by fairchildite at 571 °C, however a small component of the narrower bütschliite symmetric stretching vibration persists on the high frequency side of the peak. The asymmetric

stretching vibration is absent from this spectrum, in accord with the previous spectra of fairchildite at ambient temperatures (Arefiev et al. 2019). Figure 6 shows the deconvolution of a representative fairchildite spectrum measured at 637 °C. The low frequency feature in Figure 6a can be fit with seven peaks; nevertheless, we do not preclude that a broad asymmetric continuum, cut off by our lower spectral limit may provide a better representation for this low frequency feature. Such low-frequency, disorder-induced quasi-elastic broad continua have long been documented to be present in disordered phases that are structurally similar to carbonates, such as NaNO_3 (Shen et al. 1975; Neumann and Vogt 1978): often, residual peaks from the ordered phase are superimposed on these continua (Fontana et al. 1990). Such a residual signature of ordering could generate the structure on the broad feature in Figure 6b. The ν_4 in-plane bending mode is fit with two peaks: the low and high frequency peaks have widths of 33 and 22 cm^{-1} , respectively. The ν_1 symmetric stretching vibration is also fit with two peaks: the low- and high-frequency peaks have widths of 19 and 22 cm^{-1} . The broad peaks of the internal carbonate vibrations indicate that both carbon sites may be disordered at high temperatures. For reference, at ambient temperature, Pertlik (1981) determined that the oxygens around the C(2) carbon site are orientationally disordered; the comparable peak widths of the two components of each of the carbonate internal vibrations in high-temperature

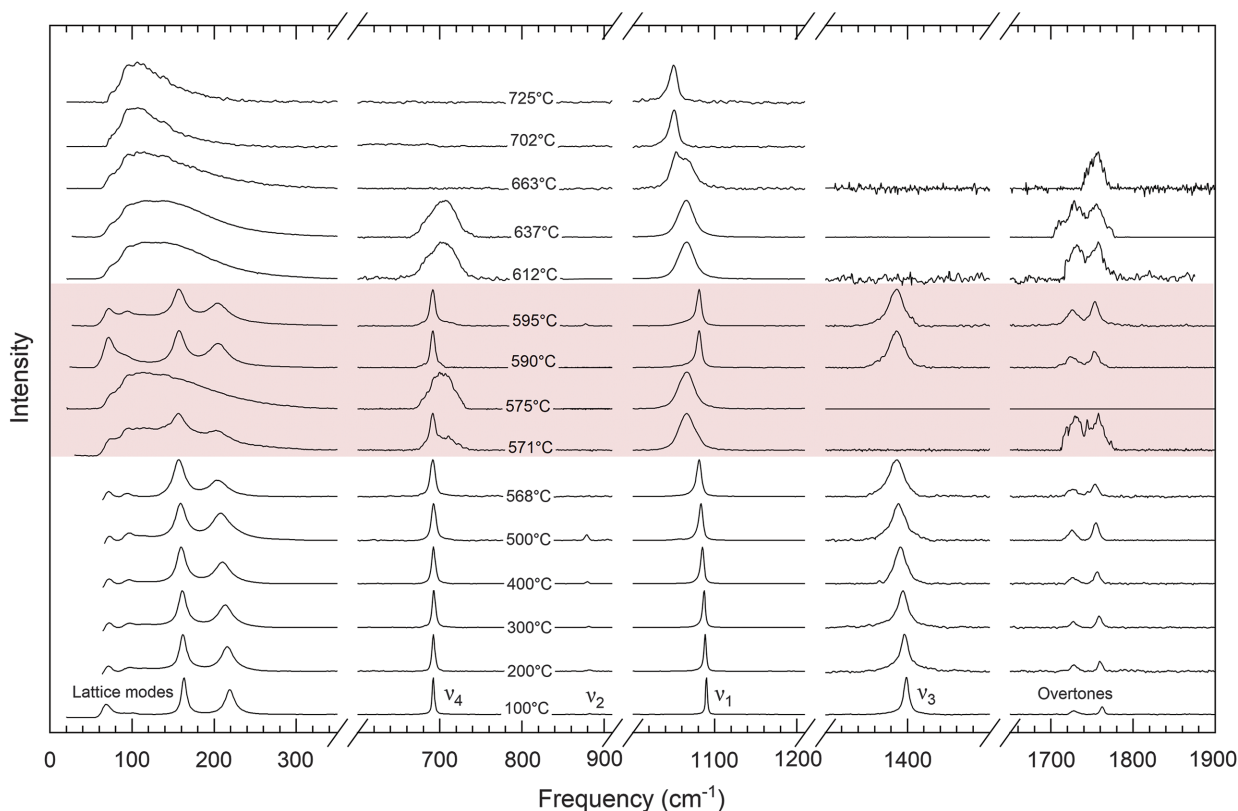


FIGURE 5. High-temperature Raman spectra of bütschliite and its associated high-temperature phases. The spectra between 571 and 595 °C are representative spectra taken in different locations within the sample and show the spatially heterogeneous nature of the bütschliite-fairchildite phase transition. The red region shows spectra corresponding to the mixed phase regime.

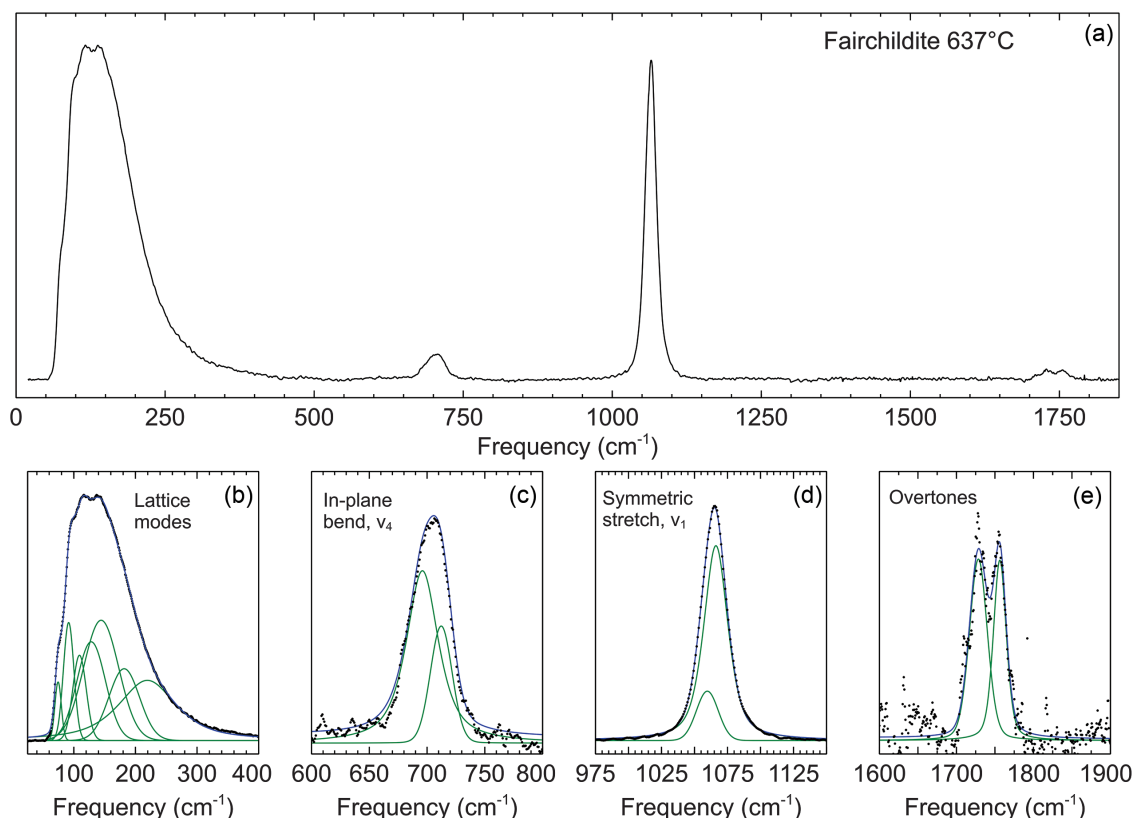


FIGURE 6. Raman spectrum of fairchildite at 637 °C (a). Deconvolution of the fairchildite spectrum (b–e). The measured spectrum is shown as a black dotted line, the deconvoluted peaks are shown in green, and the fitted spectrum is shown in blue.

fairchildite are consistent with disordering, as (for example) each are dramatically larger than the corresponding peak widths in bütschliite (Fig. 4).

Notably, our measurements indicate that the high-temperature/ambient-pressure stability field of fairchildite is limited, as a second phase transition initiates around 663 °C. Based on the previous thermoanalytical work of Winbo et al. (1998), we infer that this transition represents the decomposition of fairchildite into K_2CO_3 and CaO. CaO does not have a first-order Raman spectrum, and we do not resolve any second-order features from this phase (which are expected to be weak) in the spectrum of the quenched sample. Hence, based on our high-temperature measurements conducted in vacuum, we bracket the stability field of fairchildite under evacuated conditions to the temperature range 570–665 °C.

High-temperature raman spectra of shortite

With the exception of a single in-plane bending vibration, all of the vibrational modes of shortite shift to lower frequencies during heating (as anticipated from the volumetric expansion on heating) and shift linearly within the resolution of the data (Fig. 7; Table 2). In contrast to the high-temperature behavior of some other carbonates (e.g., Gillet et al. 1993; Farsang et al. 2018; Wang et al. 2019), the lattice modes of bütschliite and shortite do not systematically shift faster than the internal CO_3 vibrations. The two highest-frequency lattice modes of shortite are closely spaced, with initial ambient temperature frequencies

of 260 and 266 cm^{-1} . By 200 °C, they coalesce to the degree that they can be fitted well with a single peak. This coalescence could be indicative of a slight high-temperature symmetry change, but since no other bands show any signature of such a shift, it appears more likely that this is an instance of temperature-induced accidental degeneracy of these two modes.

Unlike bütschliite, the ν_4 in-plane bending modes of shortite (labeled ν_{4a-d} from low to high frequency) all shift significantly during heating. Three of the in-plane bending modes, ν_{4a} , ν_{4b} , and ν_{4d} , shift to lower frequencies, while ν_{4c} shifts to a higher frequency. Due to both the comparative complexity of the shortite structure and the spectral region, correlating these shifts with possible anisotropy in expansion (or compression) is challenging. The two ν_1 symmetric stretching vibrations, both with A_1 symmetry, shift at modestly different rates. The lower frequency ν_{1a} peak shifts about 27% faster than the higher frequency ν_{1b} peak: this lower frequency peak is associated with the C(2) carbon environments, which lie within the b - c plane in this structure (Vennari et al. 2018), while the more distorted C(1) environment (the highest frequency band) is sensitive to expansion along each crystallographic direction. Within shortite, the c -axis is also the most compressible (Vennari et al. 2018), and hence is likely to undergo the largest thermal expansion among the axes. In contrast, the ν_3 asymmetric stretching vibrations, which do not share the same symmetry, exhibit considerably more variation in their thermal shifts. The four lowest-frequency asymmetric stretching vibrations (i.e., ν_{3a-d}), with respective symmetries of A_1 , A_2 , B_1 ,

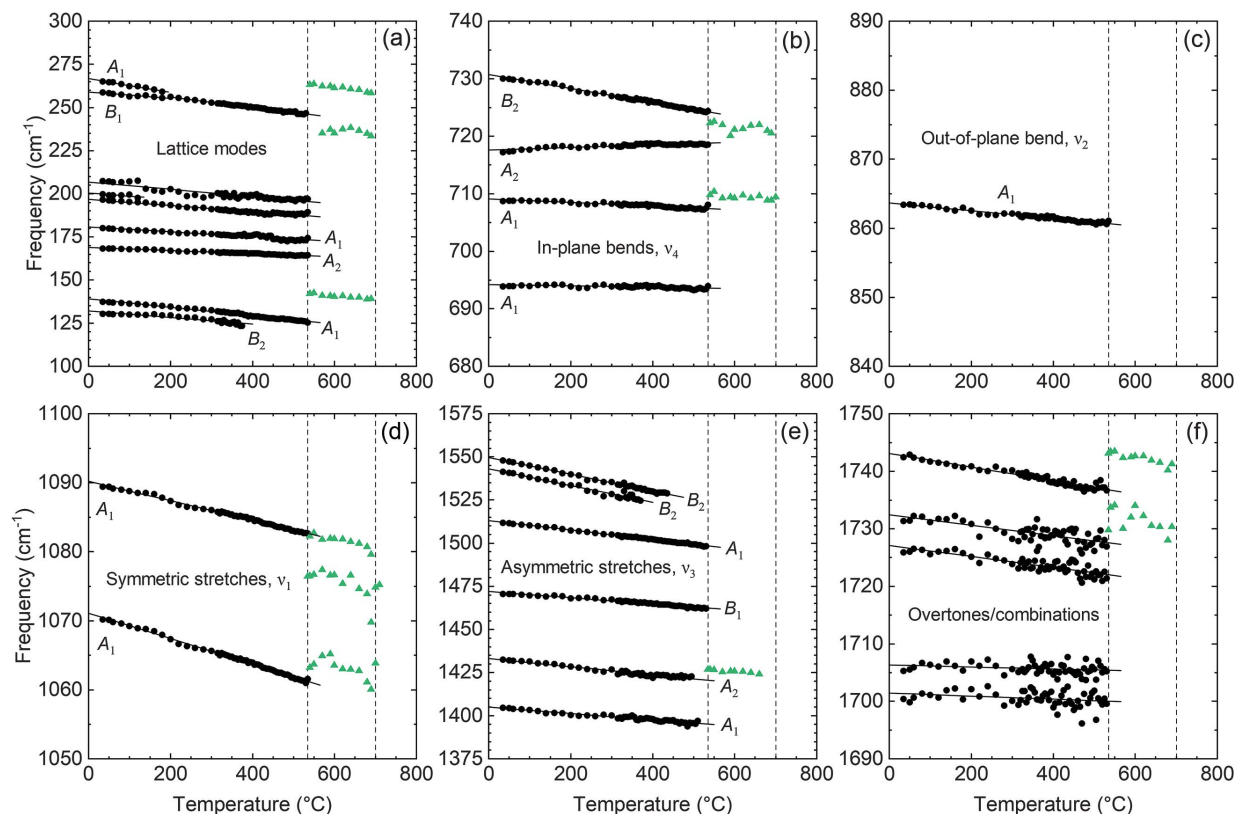


FIGURE 7. Raman mode shifts of shortite and its associated high-temperature phases. The Raman modes of nyerereite are plotted as green triangles. The dotted lines show the stability field of nyerereite.

TABLE 2. Peak assignments, fit range, and temperature dependence of the Raman modes of shortite

Initial frequency, ν_0 [cm^{-1}]	Vibration	Symmetry	Fit range [$^{\circ}\text{C}$]	$(\partial\nu/\partial T)$ [$\text{cm}^{-1}/^{\circ}\text{C}$]	$-\alpha_{\nu}/P$ [$10^4\ ^{\circ}\text{C}^{-1}$]
131	Lattice mode	B_2	$T \leq 375$	-0.0195(1)	1.49
138	Lattice mode	A_1	$T \leq 530$	-0.0244(0)	1.77
169	Lattice mode	A_2	$T \leq 530$	-0.0088(0)	0.52
181	Lattice mode	A_1	$T \leq 530$	-0.0141(0)	0.78
198	Lattice mode	—	$T \leq 530$	-0.0181(0)	0.91
203	Lattice mode	—	$T \leq 120$	-0.0180(7)	0.89
211	Lattice mode	—	$T \leq 375$	-0.0213(0)	1.01
256	Lattice mode	—	$200 \leq T \leq 530$	-0.0297(1)	1.16
260	Lattice mode	B_1	$T \leq 180$	-0.0185(3)	0.71
266	Lattice mode	A_1	$T \leq 180$	-0.0394(3)	1.48
694	In-plane bend, ν_{4a}	A_1	$T \leq 530$	-0.0012(0)	0.02
709	In-plane bend, ν_{4b}	A_1	$T \leq 530$	-0.0032(0)	0.05
717	In-plane bend, ν_{4c}	A_2	$T \leq 530$	0.0023(0)	-0.03
731	In-plane bend, ν_{4d}	B_2	$T \leq 530$	-0.0121(0)	0.17
864	Out-of-plane bend, ν_2	A_1	$T \leq 530$	-0.0056(0)	0.07
1071	Symmetric stretch, ν_{1a}	A_1	$T \leq 530$	-0.0185(0)	0.17
1090	Symmetric stretch, ν_{1b}	A_1	$T \leq 530$	-0.0141(0)	0.13
1404	Asymmetric stretch, ν_{3a}	A_1	$T \leq 510$	-0.0183(1)	0.13
1433	Asymmetric stretch, ν_{3b}	A_2	$T \leq 495$	-0.0235(1)	0.16
1470	Asymmetric stretch, ν_{3c}	B_1	$T \leq 530$	-0.0179(0)	0.12
1512	Asymmetric stretch, ν_{3d}	A_1	$T \leq 530$	-0.0275(0)	0.18
1542	Asymmetric stretch, ν_{3e}	B_2	$T \leq 370$	-0.0485(1)	0.32
1549	Asymmetric stretch, ν_{3f}	B_2	$T \leq 435$	-0.0488(1)	0.32
1699	Overtone/combination	—	$T \leq 530$	-0.0026(0)	0.02
1706	Overtone/combination	—	$T \leq 530$	-0.0017(0)	0.01
1727	Overtone/combination	—	$T \leq 530$	-0.0095(0)	0.06
1732	Overtone/combination	—	$T \leq 530$	-0.0091(0)	0.05
1742	Overtone/combination	—	$T \leq 530$	-0.0119(0)	0.07

and A_1 , shift at rates between -0.0179 and -0.0275 $\text{cm}^{-1}/^\circ\text{C}$. The higher frequency ν_{3e} and ν_{3f} vibrations, with B_2 symmetry, shift at a rate of -0.049 $\text{cm}^{-1}/^\circ\text{C}$. The five combinations/overtone we observe in the shortite spectrum fall into two clusters (Fig. 7f). The first cluster contains the combinations with initial frequencies of 1699 and 1706 cm^{-1} . These vibrations exhibit very small and nearly parallel frequency shifts during heating. The second cluster of combinations/overtone contains the modes initially at frequencies of 1727 , 1732 , and 1742 cm^{-1} . The frequency shifts of these three combinations/overtone are also nearly parallel, but exhibit a much stronger temperature dependence than the modes in the lower frequency cluster. A possible explanation for these two clusters lies in the possible nature of these combination bands: the higher frequency cluster's shifts lie close to twice that of the single ν_2 Raman band (at 864 cm^{-1}) for which we document the temperature dependence (Fig. 7c). However, three Raman-active ν_2 bands are predicted from factor group analysis: these bands are also infrared-active (shortite is non-centrosymmetric), and we infer that the band that we observe in the Raman spectrum is the single A_1 symmetry band, which is predicted to be by far the most intense (Caracas and Bobocioiu 2011). A constraint on the other two vibrations may be derived from the infrared spectra of shortite. Adler and Kerr (1963) reported ν_2 peaks in their infrared spectrum of shortite at 873 , 867 , and 851 cm^{-1} ; Estep et al. (1970) observed peaks at 868 , 862 , and 847 cm^{-1} [apparently systematically offset by 4 – 5 cm^{-1} relative to those of Adler and Kerr

(1963)]; and Frost and Dickfos (2008) reported two peaks at 865 and 849 cm^{-1} . Accordingly, assuming roughly equal anharmonicities of the different ν_2 bands, the first set of combinations and overtones of ν_2 -related bands would be expected to span a ~ 42 cm^{-1} wide range. This is in excellent agreement with the 43 cm^{-1} spread observed among the combination bands in the Raman spectrum (1699 to 1742 cm^{-1}). Moreover, the lowest lying ν_2 shortite infrared vibration lies at 847 – 851 cm^{-1} , or almost precisely half the frequencies associated with the lower overtone cluster. Therefore, the lower-frequency cluster likely involves combinations with vibrations that are strong in the infrared spectrum, and the smaller temperature shifts of this set of combination bands indicate that these lower-lying ν_2 vibrations may have markedly smaller thermal shifts than the corresponding higher-frequency Raman vibration.

We observe the onset of the shortite-nyerereite transition at 535 $^\circ\text{C}$ (Fig. 8), a substantially higher temperature than the values of 335 and 400 $^\circ\text{C}$ reported by Cooper et al. (1975) at 1 kbar and 470 $^\circ\text{C}$ reported by Johnson et al. (1974) at near ambient pressure. These results suggest that either very modest increases in pressure substantially reduce the stability field of shortite at high temperatures, and/or (as with bütschliite) kinetics play a major role in this transition. The decomposition of shortite forms calcite and nyerereite at low pressures (Cooper et al. 1975), and at higher pressures the decomposition reaction yields aragonite and $\text{Na}_2\text{Ca}_3(\text{CO}_3)_4$ (Podborodnikov et al. 2018) or aragonite and $\text{Na}_2\text{Ca}_4(\text{CO}_3)_5$ (Shatskiy et al. 2013).

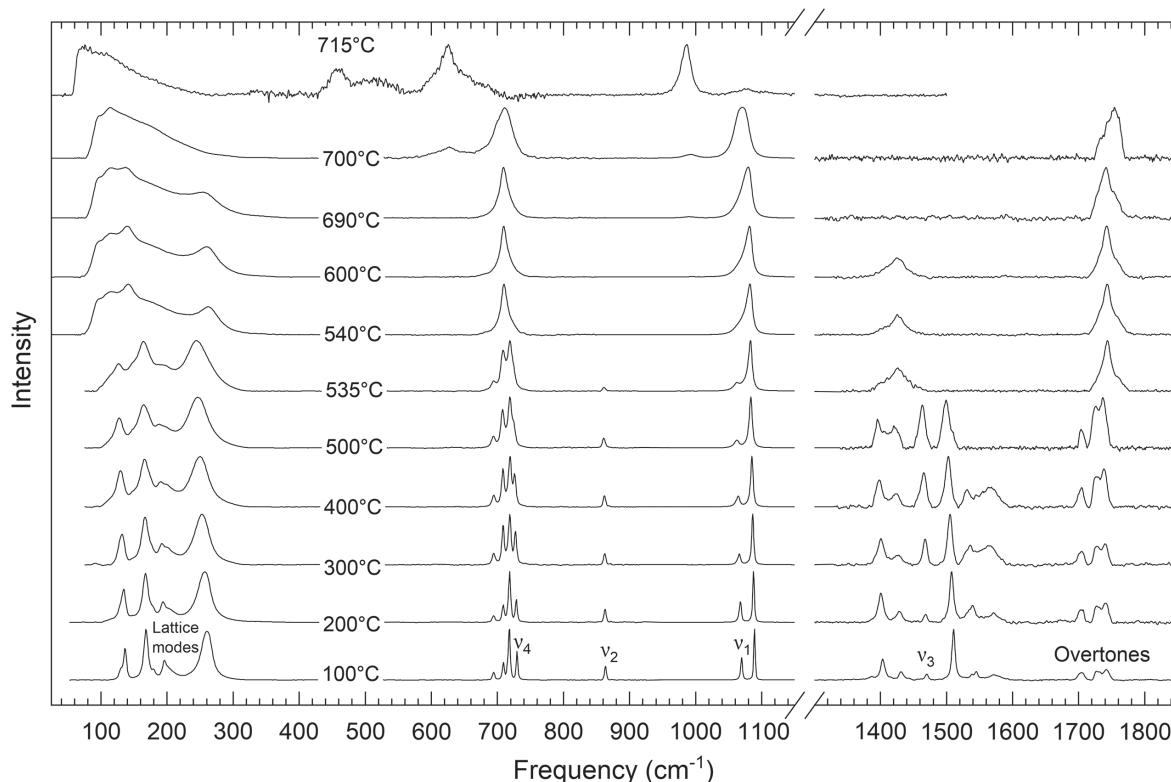


FIGURE 8. High-temperature Raman spectra of shortite and its associated high-temperature phases. The 715 $^\circ\text{C}$ spectrum was collected with a 633 nm excitation laser.

As indicated in the Raman spectra, shortite does not uniformly convert to nyerereite at 535 °C. The baseline underlying the low-frequency region and the lattice modes of shortite increase and broaden smoothly and continuously up to the onset of the nyerereite transition at 535 °C. A further temperature increase of 5 °C results in a dramatically different spectrum at 540 °C, with a low-frequency region that is in accord with a strongly disordered nyerereite phase. Similarly, the amplitude of the ν_{1a} symmetric stretching mode gradually decreases up to 535 °C, and the space between the two symmetric stretching vibrations is uplifted. At 540 °C, the ν_1 symmetric stretching vibration is in a new regime that requires three components to fit. Unlike the ν_1 symmetric stretching and lattice modes, the ν_4 in-plane bending vibrations and ν_3 asymmetric stretches do not smoothly transition into the new phase at 540 °C. The ν_4 in-plane bending vibrations broaden and merge up until 535 °C, at which point they do not show any indications of a new phase. Then, at 540 °C, an asymmetric ν_4 in-plane bending peak, which can be fitted with two components, becomes the dominant feature. At higher frequencies, we track six asymmetric stretching ν_3 modes and five combination/overtone bands up to 530 °C. At 535 °C, these 11 peaks are abruptly replaced by two peaks that roughly correspond to the asymmetric stretching and overtone/combination regions.

A second phase transition initiates at 700 °C. This transition is marked by the broadening of ν_1 symmetric stretching and ν_4 in-plane bending vibrations, and the appearance of two new peaks around 630 and 990 cm^{-1} . The latter peak location is at an anomalously low frequency for a typical resonance-stabilized carbonate group, and if associated with C-O bonding, it appears likely to be associated with the destabilization of the carbonate group. By 715 °C, no spectral features associated with nyerereite remain. This transition likely represents the decomposition of nyerereite into $\alpha\text{-Na}_2\text{CO}_3$ (a high-temperature polymorph of natrite) or possibly to an adsorbed transient species such as NaCO_3^- (Ballirano 2011; Carper et al. 2012) that is a close precursor of decarbonation. In computational studies, Zhao et al. (2013, 2015) modeled decarbonation pathways of CaCO_3 and MgCO_3 and identified a suite of possible transient species that could form just prior to decarbonation. While these species have been challenging to observe experimentally, highly localized

bonding effects associated with heterogeneous decarbonation and the metastable retention of carbonate could be conducive to preserving transient species that are in accord with our highest temperature measured spectra (Fig. 8).

Anharmonic properties of bütschliite and shortite

The isothermal and isobaric mode Grüneisen parameters, γ_{iT} and γ_{iP} , are commonly used to quantify the frequency-dependent contributions to anharmonicity of a crystalline solid during compression and heating. In the idealized case of a crystal with a fully harmonic bonding environment, peaks would remain stationary during heating and compression, and both quantities would be equal to zero. For the special case in which frequency shifts depend only on changes in volume, the isothermal and isobaric Grüneisen parameters are equivalent, and the bonding environment is said to be *quasi-harmonic*. In the absence of experimental thermal expansion data for bütschliite and shortite, we use the quantity $-\alpha\gamma_{iP}$ as a proxy for the isobaric mode Grüneisen parameter, where α is the coefficient of thermal expansion. Figure 9 shows that the major contributions to anharmonicity (and hence the bulk thermodynamic Grüneisen parameter) for bütschliite and shortite come from the lattice modes. This is in agreement with high-pressure experiments, in which the largest values of γ_{iT} also originate from the lattice modes of these phases (Vennari et al. 2018; Zeff et al. 2024).

The shift of the ν_4 in-plane bending mode of bütschliite under isothermal compression is small but nonzero: $(\partial\nu/\partial P)_T = 2.48 \text{ cm}^{-1}/\text{GPa}$ (Zeff et al. 2024). In contrast, this mode neither shifts nor broadens significantly during heating, indicating near-harmonic behavior at high temperatures. The ν_3 asymmetric stretching mode of bütschliite shifts the fastest of the internal carbonate modes during both heating and compression, and broadens dramatically during heating, but has a relatively small value of γ_{iT} due to its high frequency. The ν_1 and ν_2 modes are clearly anharmonic, but they only make small contributions to the overall crystal anharmonicity (Fig. 9).

The ν_4 in-plane bending mode and ν_2 out-of-plane bending mode of shortite also exhibit anomalous behavior. Vennari et al. (2018) reported that all four ν_4 in-plane bending modes shifted to higher frequencies and identified the ν_2 out-of-plane bending mode as a soft mode during compression. The behavior of the

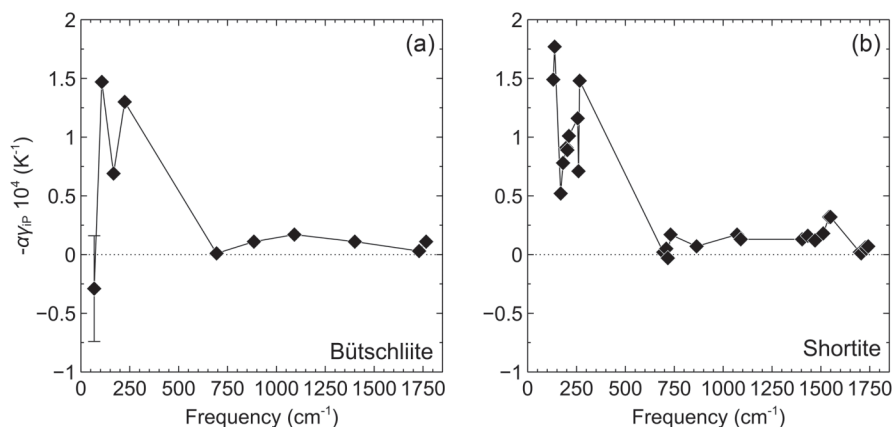


FIGURE 9. Scaled mode Grüneisen parameters of bütschliite and shortite: since no thermal expansion data exist for these phases, these are reported as the product of the thermal expansion coefficients and the isobaric mode Grüneisen parameters. The error bars on the lowest frequency lattice mode of bütschliite correspond to the range reported in Table 1. The dotted line corresponds to ideal harmonic behavior. The solid lines serve as guides to the eye.

ν_4 vibration is consistent with increasing force constants and shortening bond lengths in the carbonate unit, while the anomalous behavior of the ν_2 vibration was explained as associated with the simultaneous strengthening of Ca/Na-O bonds and weakening of C-O bonds. Figure 7 shows that ν_{4a} , ν_{4b} , ν_{4d} , and ν_2 shift to lower frequencies during heating, consistent with weakening of the force constants and lengthening of the bonds in the carbonate unit. The ν_{4c} vibration, however, shifts to higher frequency during heating. The shift of the ν_2 vibration to a lower frequency and the ν_{4c} vibration to a higher frequency during heating and compression is indicative of a substantial isochoric or explicit contribution to anharmonicity. This contribution, $[\partial \nu_i(P, T)/\partial T]_V$, can be approximated as:

$$\left(\frac{\partial \ln \nu_i(P, T)}{\partial T}\right)_V = -\alpha(\gamma_{iP} - \gamma_{iT}) \quad (4)$$

where $\alpha = (1/V)(\partial V/\partial T)$, and this parameter is governed by the thermal population of vibrational levels (Lucazeau 2003). This expression is exact for isotropic materials, but the effect of anisotropic expansion or compression on phonon frequencies is not reflected in Equation 4. However, the isotropic approximation has been proposed to be accurate to better than 10% for anisotropic materials that have been probed (Peercy 1973). Hence, using Equation 4, it appears that this single, positively shifting in-plane bending vibration (ν_{4c}), which likely involves entirely in-phase, in-plane bending between adjoining carbonate groups (e.g., Caracas and Bobocioiu 2011), is particularly sensitive to intermolecular coupling and/or phonon occupancy effects.

IMPLICATIONS

The identification of alkali-alkaline earth carbonate minerals and quenched melts in a compositionally and geographically diverse suite of mantle-derived rocks has fueled interest in the stability and thermodynamic properties of many of the “double carbonate” minerals. Particular interest has been paid to the Na-, Mg-, K-, and Ca-bearing phases. In this study, the Raman spectra of bütschliite and shortite were collected under vacuum at temperatures up to 725 and 715 °C, respectively. In terms of phase equilibria, bütschliite begins to convert to the isochemical disordered phase, fairchildite, at 570 °C. We document a mixed-phase regime consisting of bütschliite and fairchildite up to 595 °C. Upon further heating, fairchildite decomposes to an assemblage of K_2CO_3 and CaO at 663 °C. Shortite also converts to a largely disordered assemblage, composed of nyerereite and disordered $CaCO_3$ at 535 °C, followed by a subsequent decomposition reaction that initiates at 700 °C: this latter reaction involves a phase with particularly weak C-O bonding, which may represent a transitional phase at the onset of decarbonation. From a vibrational perspective, anomalous temperature-dependent behavior of individual bands (involving either positive thermal shifts or anomalous line broadening) appears to be attributable in each of these phases to either multi-phonon interactions or shifts in inter-molecular coupling between carbonate units.

The limited stability of fairchildite at high temperatures and ambient pressure is particularly notable: our results suggest that fairchildite is stable between 570 and 660 °C under vacuum. The

high-pressure phase boundary of fairchildite has been suggested to lie between 0.1 and 3 GPa, with pressure slightly expanding the high-temperature stability (Arefiev et al. 2019). When fairchildite is preserved as an inclusion, the mineral could serve as a useful geothermometer for shallow silicic and carbonatitic melting and crystallization processes.

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REFERENCES CITED

- Abersteiner, A., Golovin, A., Chayka, I., Kamenetsky, V.S., Goemann, K., Rodemann, T., and Ehrig, K. (2022) Carbon compounds in the West Kimberley lamproites (Australia): Insights from melt and fluid inclusions. *Gondwana Research*, 109, 536–557, <https://doi.org/10.1016/j.gr.2022.06.005>.
- Adler, H.H. and Kerr, P.F. (1963) Infrared spectra, symmetry and structure relations of some carbonate minerals. *American Mineralogist. Journal of Earth and Planetary Materials*, 48, 839–853.
- Arefiev, A.V., Shatskiy, A., Podborodnikov, I.V., Rashchenko, S.V., Chanyshiev, A.D., and Litasov, K.D. (2019) The system K_2CO_3 - $CaCO_3$ at 3 GPa: Link between phase relations and variety of K-Ca double carbonates at ≤ 0.1 and 6 GPa. *Physics and Chemistry of Minerals*, 46, 229–244, <https://doi.org/10.1007/s00269-018-1000-z>.
- Balkanski, M., Wallis, R.F., and Haro, E. (1983) Anharmonic effects in light scattering due to optical phonons in silicon. *Physical Review B*, 28, 1928–1934, <https://doi.org/10.1103/PhysRevB.28.1928>.
- Ballirano, P. (2011) Thermal behaviour of natrite Na_2CO_3 in the 303–1013 K thermal range. *Phase Transitions*, 84, 357–379, <https://doi.org/10.1080/01411594.2010.541856>.
- Caracas, R. and Bobocioiu, E. (2011) The WURM project—A freely available web-based repository of computed physical data for minerals. *American Mineralogist*, 96, 437–443, <https://doi.org/10.2138/am.2011.3532>.
- Carper, W.R., Wahlbeck, P.G., and Griffiths, T.R. (2012) DFT models of molecular species in carbonate molten salts. *The Journal of Physical Chemistry B*, 116, 5559–5567, <https://doi.org/10.1021/jp3016694>.
- Chen, X., Wang, M., Inoue, T., Liu, Q., Zhang, L., and Bader, T. (2022) Melting of carbonated pelite at 5.5–15.5 GPa: Implications for the origin of alkali-rich carbonatites and the deep water and carbon cycles. *Contributions to Mineralogy and Petrology*, 177, 2.
- Cizina, M.F., Mikesell, T.D., and Kohn, M.J. (2023) Optimizing Raman spectral collection for quartz and zircon crystals for elastic thermobarometry. *American Mineralogist*, 108, 915–927, <https://doi.org/10.2475/ajs.275.5.534>.
- Cooper, A.F., Gittins, J., and Tuttle, O.F. (1975) The system Na_2CO_3 - K_2CO_3 - $CaCO_3$ at 1 kilobar and its significance in carbonatite petrogenesis. *American Journal of Science*, 275, 534–560, <https://doi.org/10.2475/ajs.275.5.534>.
- Dickens, B., Hyman, A., and Brown, W.E. (1971) Crystal structure of $Ca_2Na_2(CO_3)_3$ (shortite). *Journal of Research of the National Bureau of Standards – A, Physics and Chemistry*, 75A, 129–135, <https://doi.org/10.6028/jres.075A.013>.
- Estep, P.A., Kovach, J.J., Hiser, A.L., and Karr, C. (1970) Characterization of carbonate minerals in oil shales and coals by infrared spectroscopy. In R.A. Friedel, Ed., *Spectrometry of Fuels*, p. 228–247. Springer.
- Farsang, S., Facq, S., and Redfern, S. (2018) Raman modes of carbonate minerals as pressure and temperature gauges up to 6 GPa and 500 °C. *American Mineralogist*, 103, 1988–1998.
- Fontana, M.D., Brehat, F., and Wymcke, B. (1990) A central peaks as a pre-melting feature in $NaNO_3$ spectra. *Journal of Physics: Condensed Matter*, 2, 9125–9131, <https://doi.org/10.1088/0953-8984/2/46/012>.
- Frost, R.L. and Dickfos, M.J. (2008) Raman and infrared spectroscopic study of the anhydrous carbonate minerals shortite and barytoalcite. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 71, 143–146, <https://doi.org/10.1016/j.saa.2007.11.021>.
- Gervasoni, F., Klemme, S., Rohrbach, A., Grützner, T., and Berndt, J. (2017) Experimental constraints on mantle metasomatism caused by silicate and carbonate melts. *Lithos*, 282–283, 173–186, <https://doi.org/10.1016/j.lithos.2017.03.004>.
- Gillet, P., Biellmann, C., Reynard, B., and McMillan, P. (1993) Raman spectroscopic studies of carbonates part I: High-pressure and high-temperature behaviour of calcite, magnesite, dolomite and aragonite. *Physics and Chemistry of Minerals*, 20, 1–18, <https://doi.org/10.1007/BF00202245>.
- Johnson, D., Smith, J.W., and Robb, W.A. (1974) Thermal characteristics of shortite, Volume 7862, U.S. Department of the Interior, Bureau of Mines.

- Kamenetsky, V.S. and Yaxley, G.M. (2015) Carbonate–silicate liquid immiscibility in the mantle propels kimberlite magma ascent. *Geochimica et Cosmochimica Acta*, 158, 48–56, <https://doi.org/10.1016/j.gca.2015.03.004>.
- Likhacheva, A.Y., Miloš, S., Romanenko, A.V., Goryainov, S.V., Semerikova, A.I., Rashchenko, S.V., Miletich, R., and Shatskiy, A. (2024a) High-pressure behavior and stability of synthetic bütschliite $K_2Ca(CO_3)_2$ up to 19 GPa and 300 °C. *Journal of Raman Spectroscopy*, 55, 517–524, <https://doi.org/10.1002/jrs.6654>.
- Likhacheva, A.Yu., Romanenko, A.V., Rashchenko, S.V., Miloš, S., Lotti, P., Miletich, R., and Shatskiy, A. (2024b) Crystallographic mechanism of the elastic behaviour of synthetic bütschliite $K_2Ca(CO_3)_2$ on compression to 20 GPa. *Physics and Chemistry of Minerals*, 51, 29, <https://doi.org/10.1007/s00269-024-01291-8>.
- Logvinova, A.M., Shatskiy, A., Wirth, R., Tomilenko, A.A., Ugap'eva, S.S., and Sobolev, N.V. (2019) Carbonatite melt in type Ia gem diamond. *Lithos*, 342–343, 463–467, <https://doi.org/10.1016/j.lithos.2019.06.010>.
- Lucazeau, G. (2003) Effect of pressure and temperature on Raman spectra of solids: Anharmonicity. *Journal of Raman Spectroscopy*, 34, 478–496, <https://doi.org/10.1002/jrs.1027>.
- Luty, T. and Eckhardt, C.J. (1985) Piezomodulated Raman spectroscopy of molecular crystals: An experimental method for study of the anharmonic properties of solids. *The Journal of Chemical Physics*, 82, 1515–1521, <https://doi.org/10.1063/1.448426>.
- Memagh, T.P., Kamenetsky, V.S., and Kamenetsky, M.B. (2011) A Raman microprobe study of melt inclusions in kimberlites from Siberia, Canada, SW Greenland and South Africa. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 80, 82–87, <https://doi.org/10.1016/j.saa.2011.01.034>.
- Navrotsky, A., Putnam, R.L., Winbo, C., and Rosen, E. (1997) Thermochemistry of double carbonates in the K_2CO_3 – $CaCO_3$ system. *American Mineralogist*, 82, 546–548, <https://doi.org/10.2138/am-1997-5-614>.
- Neumann, G. and Vogt, H. (1978) Rayleigh wing scattering in disordered sodium nitrate. *Physica Status Solidi B: Basic Research*, 85, 179–184, <https://doi.org/10.1002/pssb.2220850119>.
- Pabst, A. (1974) Synthesis, properties, and structure of $K_2Ca(CO_3)_2$, bütschliite. *American Mineralogist*, 59, 6.
- Pal'yanov, N., Sokol, A.G., Borzdov, M., and Khokhryakov, A.F. (2002) Fluid-bearing alkaline carbonate melts as the medium for the formation of diamonds in the Earth's mantle: An experimental study. *Lithos*, 60, 145–159, [https://doi.org/10.1016/S0024-4937\(01\)00079-2](https://doi.org/10.1016/S0024-4937(01)00079-2).
- Peercy, P.S. (1973) Uniaxial-stress dependence of the Raman-active phonons in TiO_2 . *Physical Review B*, 8, 6018–6020, <https://doi.org/10.1103/PhysRevB.8.6018>.
- Pertlik, F., Ed. (1981) Structural investigations of synthetic fairchildite, $K_2Ca(CO_3)_2$. *Zeitschrift für Kristallographie. Crystalline Materials*, 157, 199–205, <https://doi.org/10.1524/zkri.1981.157.3-4.199>.
- Podborodnikov, I.V., Shatskiy, A., Arefiev, A.V., Rashchenko, S.V., Chanyshev, A.D., and Litasov, K.D. (2018) The system Na_2CO_3 – $CaCO_3$ at 3 GPa. *Physics and Chemistry of Minerals*, 45, 773–787, <https://doi.org/10.1007/s00269-018-0961-2>.
- Reeder, R. and Markgraf, S. (1986) High-temperature crystal chemistry of dolomite. *American Mineralogist*, 71, 795–804.
- Shatskiy, A., Sharygin, I.S., Litasov, K.D., Borzdov, Y.M., Palyanov, Y.N., and Ohtani, E. (2013) New experimental data on phase relations for the system Na_2CO_3 – $CaCO_3$ at 6 GPa and 900–1400 °C. *American Mineralogist*, 98, 2164–2171, <https://doi.org/10.2138/am.2013.4436>.
- Shen, T.Y., Mitra, S.S., Prask, H., and Trevino, S.F. (1975) Order-disorder phenomenon in sodium nitrate studied by low-frequency Raman scattering. *Physical Review B*, 12, 4530–4533, <https://doi.org/10.1103/PhysRevB.12.4530>.
- Vennari, C.E., Beavers, C.M., and Williams, Q. (2018) High-pressure/temperature behavior of the alkali/calcium carbonate shortite ($Na_2Ca_2(CO_3)_3$): Implications for carbon sequestration in Earth's transition zone. *Journal of Geophysical Research: Solid Earth*, 123, 6574–6591, <https://doi.org/10.1029/2018JB015846>.
- Wang, X., Ye, Y., Wu, X., Smyth, J.R., Yang, Y., Zhang, Z., and Wang, Z. (2019) High-temperature Raman and FTIR study of aragonite-group carbonates. *Physics and Chemistry of Minerals*, 46, 51–62, <https://doi.org/10.1007/s00269-018-0986-6>.
- Weiss, Y., McNeill, J., Pearson, D.G., Nowell, G.M., and Ottley, C.J. (2015) Highly saline fluids from a subducting slab as the source for fluid-rich diamonds. *Nature*, 524, 339–342, <https://doi.org/10.1038/nature14857>.
- Winbo, C., Rosen, E., Heim, M., Garcia, F., Barré, L., Hammerich, O., Sotofte, I., and Långström, B. (1998) Thermal analytical study of the decomposition of $K_2Ca(CO_3)_2$. *Acta Chemica Scandinavica*, 52, 431–434, <https://doi.org/10.3891/acta.chem.scand.52-0431>.
- Ye, Y., Smyth, J.R., and Boni, P. (2012) Crystal structure and thermal expansion of aragonite-group carbonates by single-crystal X-ray diffraction. *American Mineralogist*, 97, 707–712, <https://doi.org/10.2138/am.2012.3923>.
- Zaitsev, A.N. and Chakhmouradian, A.R. (2002) Calcite amphibole clinopyroxene rock from the Afrikanda Complex, Kola Peninsula, Russia: Mineralogy and a possible link to carbonatites. II. Oxsalt minerals. *Canadian Mineralogist*, 40, 103–120, <https://doi.org/10.2113/gscanmin.40.1.103>.
- Zaitsev, A.N., Keller, J., Spratt, J., Jeffries, T.E., and Sharygin, V.V. (2009) Chemical composition of nyerereite and gregoryite from natrocarbonatites of Oldoinyo Lengai volcano, Tanzania. *Geology of Ore Deposits*, 51, 608–616, <https://doi.org/10.1134/S1075701509070095>.
- Zeff, G., Kalkan, B., Armstrong, K., Kunz, M., and Williams, Q. (2024) High pressure Raman spectroscopy and X-ray diffraction of $K_2Ca(CO_3)_2$ bütschliite: Multiple pressure-induced phase transitions in a double carbonate. *Physics and Chemistry of Minerals*, 51, 2, <https://doi.org/10.1007/s00269-023-01262-5>.
- Zhao, Z., Wang, D., Wang, Q., Li, Z., and Fang, Z. (2013) Quantum chemical study on thermal decomposition mechanism of calcium carbonate. *Journal of Theoretical and Computational Chemistry*, 12, 1350049, <https://doi.org/10.1142/S0219633613500491>.
- Zhao, Z., Li, Z., Wang, Q., and Wang, Y. (2015) Quantum chemical study of thermal decomposition mechanism and polymorph predict phase transitions of magnesite. *Research on Chemical Intermediates*, 41, 8471–8482, <https://doi.org/10.1007/s11164-014-1904-2>.

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