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UNIVERSITY OF CALIFORNIA
SANTA CRUZ

**Understanding Stability and Cycling of Volatiles in the Mantle with High
Pressure Experiments**

A dissertation submitted in partial satisfaction
of the requirements for the degree

DOCTOR OF PHILOSOPHY

in

EARTH SCIENCES

by

Cara Elizabeth Vennari

June 2019

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Abstract

Understanding Stability and Cycling of Volatiles in the Mantle with High Pressure

Experiments

By

Cara E. Vennari

Our understanding of the chemical and physical structure of the mantle is driven by connections between seismologic observations and experimental results. The mantle, which makes up the largest portion of the planet by volume, is heterogeneous, as suggested by seismic discontinuities. Sources of heterogeneity are largely from the surface of the Earth: both the basalt that forms subducted slabs and the volatiles within (and on) the slab provide chemical and thermal heterogeneity to the deep Earth. Four of the chapters in this dissertation concern volatile stability (carbon and nitrogen) and the last chapter is focused on the physical and chemical differences in slab strength and deformation.

To understand the properties of materials in the deep Earth, we need to simulate high pressure conditions that occur at depth. The technique used to generate ultra-high pressures is a diamond anvil cell (where a sample is placed between two diamonds). These cells operate due to the relation of $\text{pressure} = \text{force}/\text{area}$, such that with a small area (from the tip of the diamonds) large pressures can be generated with relatively little force. Since the diamonds are optically transparent, we are able to probe spectroscopically with light (Raman and infrared spectroscopy) to detect changes in local bonding environments. Additionally, we are able to conduct X-ray diffraction *in*

situ to measure density changes to the crystals and interatomic distances within the high pressure crystal structures. We can reliably generate pressures above transition zone pressures (25 GPa) all the way up to the core mantle boundary pressure (135 GPa).

Nitrogen and carbon are ubiquitous on the surface of the Earth and are essential for life; their cycling on the surface of the Earth is well constrained, however their concentration transport and stability in the mantle are still debated. It is generally accepted that volatiles are transported into the mantle via subducting slabs and expelled at mid ocean ridges and volcanoes. Understanding the amount of nitrogen in the deep Earth and fluxes of nitrogen into and out of can help us understand evolution of the Earth and the formation of a habitable atmosphere. Volatiles, such as carbon dioxide, in the deep Earth affect the Earth by (1) lowering the melting temperature of peridotite (2) having local effects on the elastic moduli, thus lowering v_s and v_p in the mantle (3) lowering the viscosity of the mantle, (4) controlling the amount of CO_2 in the atmosphere, and (5) producing metasomatic fluids and magmas (such as carbonatites). To better understand volatile stability, I studied the high-pressure behavior of these four minerals.

Chapter 1. Buddingtonite ($(\text{NH}_4)\text{AlSi}_3\text{O}_8$) to help understand nitrogen's subduction as ammonium in a silicate framework (in this case, sanidine structure).

Chapter 2. Shortite ($\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$), an alkali carbonate which is commonly found in carbonatite alkali rich eruptions to understand carbonatite magmas at depth.

Chapter 3. Dolomite ($\text{CaMg}(\text{CO}_3)_2$), a carbonate mineral commonly subducted to study carbonate bonding in the lower mantle.

Chapter 4. Bastnäsite ((Ce,Nd,La,Pr)CO₃F), a rare earth fluorocarbonate was studied to understand rare earth elements behavior in a carbonate matrix.

The fifth chapter concerns the silicate material that basalt transforms into after being subducted—a majoritic garnet assemblage. We investigate the deformation of garnet to understand (1) it's strength relative to other mantle phases; (2) it's plastic deformation mechanism; and (3) it's influence on the seismic anisotropy of the upper mantle

Chapter 5. Natural pyrope (Py₂Al₁) was studied to understand the strength of the subducted slab at depth.

Published Content and Contributions

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- Vennari, C. E.** and Williams, Q. (2018) A Novel Carbon Bonding Environment in Deep Mantle High-Pressure Dolomite. *American Mineralogist* 103, 171-174.
- Vennari, C. E.,** O'Bannon, E. F., and Williams, Q. (2017) The ammonium ion in a silicate under compression: infrared spectroscopy and powder X-ray diffraction of $\text{NH}_4\text{AlSi}_3\text{O}_8$ —buddingtonite to 30 GPa. *Physics and Chemistry of Minerals* 44, 149-161.

Chapter 1: The Ammonium Ion in a Silicate under Compression: Infrared Spectroscopy and Powder X-ray diffraction of $\text{NH}_4\text{AlSi}_3\text{O}_8$ —Buddingtonite to 30 GPa

1.1 Abstract

The behavior of the ammoniated feldspar buddingtonite, $\text{NH}_4\text{AlSi}_3\text{O}_8$, has been studied using infrared (IR) spectroscopy up to ~ 30 GPa and using synchrotron powder x-ray diffraction to 10 GPa at room temperature. We examine the bonding of the ammonium ion under pressure, and in particular whether hydrogen bonding is enhanced by compaction, as well as probe how the ammonium ion affects the elasticity and behavior of the aluminosilicate framework at pressure. Powder diffraction data yield a bulk modulus of 49 GPa and a pressure derivative of 3.9, implying that the ammonium ion substitution induces a modest softening of the feldspar lattice relative to the potassium ion. Under compression, the N-H vibrations are remarkably insensitive to pressure throughout the pressure range of these experiments. However, the vibrations of the aluminosilicate framework of buddingtonite undergo changes in their slope at ~ 13 GPa, implying that a change in compressional mechanism occurs near this pressure, but the vibrational modes of the ammonium molecule show little response to this change. These results show that (1) there is little, if any, enhancement of hydrogen bonding between the ammonium ion and the oxygen ions of the silica and aluminum tetrahedral framework under pressure, as manifested by the slight (and mostly positive) shifts in the N-H stretching vibrations of the ammonium ion; (2) ordering of the ammonium ion is not observed under compression, as no changes in

peak width or in the general appearance of the spectra are observed under compression; and (3) structural changes induced by pressure in the aluminosilicate framework do not produce significant changes in the bonding of the ammonium ion. Hence, it appears that the ammonium ion interacts minimally with its surrounding lattice, even at high pressures: its behavior is compatible with it being, aside from Coulombic attraction to the oxygen-dominated matrix, a largely non-interactive guest molecule within the silicate framework. This lack of interaction with the surrounding oxide lattice under compression may impact the stability of ammoniated minerals at high pressures and temperatures, and ultimately likely favors nitrides or fluid phases as the dominant nitrogen carriers within the deeper mantle.

1.2 Introduction

Nitrogen is thought to have degassed over Earth's history through volcanism produced by plate tectonics and hot spots (Marty and Dauphas, 2003), with its initial presence in the planet likely being associated with its retention within a primordial magma ocean. The cycling of nitrogen into, and out of, Earth's mantle and its retention mechanisms within the solid Earth have each been of considerable recent interest. Nitrogen's escape from the mantle can be constrained using $\delta^{15}\text{N}$ values in volcanic outgassings (Sano et al., 2001; Zhang and Zindler, 1993) and within magmatic rocks (Dauphas and Marty, 1999); however, recycling of nitrogen back into the mantle is much more difficult to quantify. Nitrogen analyses of serpentinites and ultramafic assemblages clearly illustrate that nitrogen can be retained during the subduction process (e.g., Halama et al., 2014), and observations of deep xenoliths indicate that

nitrogen is ultimately retained as nitrides at depths of ca. 300 km (Dobrzhinetskaya et al., 2009). Li and Keppler (2014) investigated the speciation and partitioning of nitrogen between fluids and melts, and concluded that cold, reduced conditions favor nitrogen's subduction, relative to hot and oxidized conditions. In addition, they provided evidence that, depending on the redox conditions of the upper mantle, ammonia may be the dominant nitrogen species in upper mantle fluids, rather than N_2 (Li and Keppler, 2014). By the same token, the substitution of the ammonium ion for potassium in minerals (e.g. feldspars, micas, and pyroxenes) is well-known as the dominant means of substitution of nitrogen into metasediments and other metamorphic assemblages, and hence for recycling of nitrogen into Earth's interior (Barker, 1964; Honma and Itihara, 1981; Mingram and Brauer, 2001; Busigny et al., 2003; Palya et al., 2013). Correspondingly, studies of the solubility of nitrogen in upper mantle minerals at high pressures have shown that nitrogen contained within pyroxenes and feldspars (and perhaps other upper mantle minerals) is present as ammonium (Schmidt and Watenphul, 2010; Watenphul et al., 2010; Li et al., 2013).

Here, we investigate the interaction of the ammonium ion with the feldspar aluminosilicate framework under compression. As ammonium-substituted silicates are likely the major means through which nitrogen is brought into subduction zones, results on how ammonium behaves within silicate phases at pressure are relevant to the stability of the ammonium substitution in high-pressure metamorphic and upper mantle environments, and thus for the microscopic means by which nitrogen is recycled into the deep Earth through subduction.

The particular material on which we focus, the end-member ammoniated feldspar buddingtonite ($\text{NH}_4\text{AlSi}_3\text{O}_8$), is a key part of the prograde metamorphic part of the nitrogen cycle, as nitrogen retention shifts from sediments into rocky hosts (Bebout et al., 2016). Indeed, buddingtonite is typically found in hydrothermally altered rock that has been infiltrated with ammonia rich fluids (Loughnan et al., 1983). The crystal structure of buddingtonite is analogous to that of high sanidine, with the K^+ ion being substituted with an NH_4^+ ion (e.g., Harlov et al., 2001). We probe this ammonium-bearing feldspar both because feldspars are the most common mineral on the surface of the Earth and a major constituent of the rocks being subducted back into the mantle. For reference, sanidine has been shown to be stable within the monoclinic crystal system up to 5 GPa at 300 K, and its compaction is predominantly generated by Si-O-(Si,Al) bond bending, rather than decreases in first-neighbor distance (Angel et al., 1988). Spectroscopic experiments conducted on potassium feldspar at room temperature have also shown evidence for compaction via angle-bending, especially up to ~ 12 GPa, with amorphization occurring at pressures near 30 GPa at 300 K (Williams, 1998). Thus, because the high pressure behavior of feldspars has been examined using both X-ray and infrared probes (e.g. Angel et al., 1988; Williams, 1998), we characterize buddingtonite with these techniques to constrain the effect of ammonium on the elasticity and bonding of feldspars under compression.

NH_4^+ has an estimated ionic radius that is likely somewhat larger than that of K^+ (by $\sim 0.16\text{-}0.20$ Å: e.g., Harlov et al., 2001; Watenphul et al., 2009), and there is complete solid solution between the potassic and ammonium feldspar endmembers

(Pöter et al., 2007). The behavior of ammonium in buddingtonite has been probed at low temperatures, with no evidence for an increase in hydrogen bonding or of ordering of the NH_4^+ ion at temperatures down to 20 K (Mookherjee et al., 2005); at high temperatures, the presence of the larger-volume ammonium ion markedly depresses the thermal expansion of buddingtonite relative to other feldspars (Hovis et al., 2008). In terms of prior information on the behavior of the ammonium ion under pressure, considerable effort has been devoted to examining ammonium monohalides at high pressures, with spectroscopic indications of complex interactions between the ammonium ions and their neighboring anions. In particular, non-linear and, at times, positive shifts of the N-H stretching vibrations under pressure are observed (Jeon et al., 1988; Reed and Williams, 2006), indicating that an increase in hydrogen bonding does not occur under compression in these materials (increased hydrogen bonding is typically manifested by negative stretching shifts). Watenphul et al. (2009) synthesized a range of ammonium analogues of high-pressure potassium silicates, and confirmed that the ammonium ion substitution persists in ammonia-rich systems to high pressures (7.8-12.3 GPa) and temperatures of 700-800°C. However, we are aware of no studies that have probed the *in situ* bonding characteristics of the ammonium ion in silicate frameworks at high pressures.

1.3 Experimental Methods

Buddingtonite $(\text{NH}_4,\text{K})\text{AlSi}_3\text{O}_8$ from the well-known Menlo Park locality (e.g., Pameyan, 2010) was used for these experiments: material from this locality was also characterized by Harlov et al. (2001). The identity of buddingtonite was confirmed

using infrared spectroscopy and x-ray powder diffraction (Fig. 1-1a and 1-1b), both of which are in excellent agreement with previous determinations (Harlov et al., 2001). High pressures were generated using a Merrill-Bassett diamond anvil cell, equipped with type IIa diamonds with 350 μm diameter culets. Spring steel was used for the gasket material, which was preindented to 30 μm thickness, and sample chambers were 150 μm in diameter. For infrared samples, about 10 wt% of the sample was mixed with 90 wt% of a pressure medium/infrared window, which was either potassium bromide or cesium iodide: results from the two media were indistinguishable. For some of the highest pressure experiments, a larger ratio of buddingtonite to pressure medium was needed to resolve the ammonium peaks. The mix was powdered using a mortar and pestle and heated to 50°C to remove water as a contaminant.

For the x-ray experiments, a symmetrical type DAC equipped with type Ia diamonds with 350 μm culets was used. Neon gas was used as a quasi-hydrostatic pressure medium, and was loaded using a high-pressure gas-loading apparatus at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. In both the infrared and x-ray experiments, several ruby chips were used for pressure determination, with pressure gradients being monitored (Mao et al., 1986). All experiments were conducted at room temperature. Spectra were collected on a Bruker IFS-70v Fourier Transform Infrared Spectrometer (FTIR), with 4 cm^{-1} resolution using a mercury cadmium telluride (MCT) detector, a globar source, and a KBr beamsplitter. Peak locations were determined by fitting a combination of Gaussian and Lorentzian functions with Bruker OPUS software. Angle-dispersive powder X-ray diffraction

patterns at ambient and high-pressure were collected at Beamline 12.2.2 at the Advanced Light Source at Lawrence Berkeley National Laboratory using an x-ray wavelength of 0.6199 Å (20 keV). Patterns were collected with exposure times of 600 s on a MAR3450 image plate, and the detector distance was calibrated using a LaB₆ standard at the sample position. Powder X-ray diffraction data were analyzed using DIOPTAS (Prescher and Prakapenka, 2014) and GSAS EXPGUI (Toby, 2001), and the bulk modulus was calculated using the EosFit7 GUI (Angel et al., 2014).

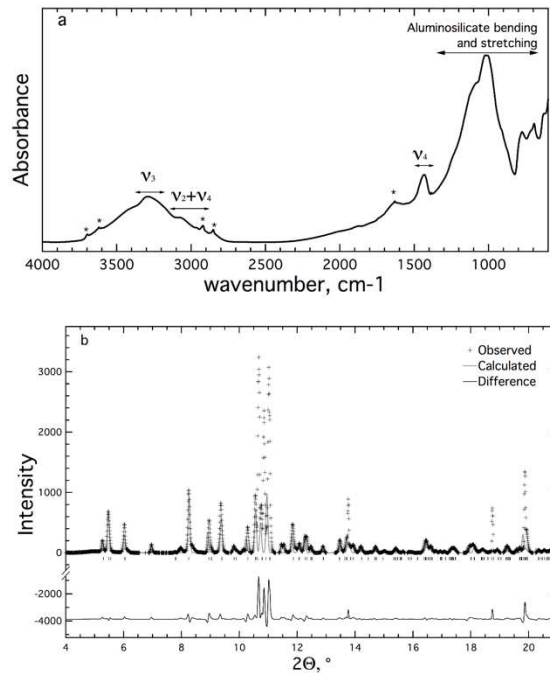


Figure 1-1. Room pressure, room temperature (a) infrared spectrum of buddingtonite; sharp peaks (*) at ~3,650 and ~2800 cm⁻¹ are hydroxyl and hydrocarbon contaminants, respectively (b) Rietveld refinement of buddingtonite's powder diffraction data; (crosses) observed intensities, (grey solid) calculated intensities, (tick marks) positions of calculated diffraction lines, and (lower) difference between the observed and calculated patterns.

1.4 Results

1.4.1 Powder diffraction

To analyze our x-ray data, we used Mookherjee et al.'s (2004) neutron diffraction-derived crystal structure for the monoclinic unit cell of buddingtonite as a starting point (Fig. 1-2).

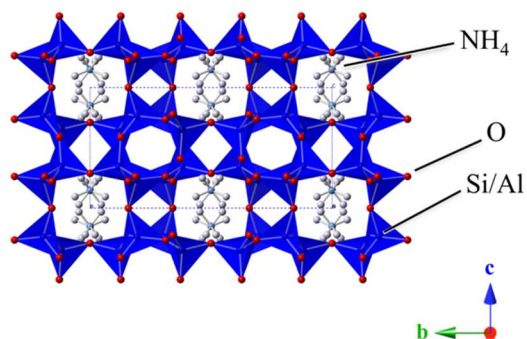


Figure 1-2. Crystal structure of buddingtonite from our Rietveld refinement, based on the structure from Mookherjee et al. (2004); the two possible positions for the hydrogen atoms are both shown.

The room pressure structure was analyzed using Rietveld refinement (Rietveld, 1969), with results shown in Fig. 1-1b. The high pressure unit cells were calculated using the program Unit Cell (Holland and Redfern, 1997), using diffraction from the Miller indices (110), (11-1), (20-1), (130), (131), (22-2), and (13-2). These peaks were selected due to their strong relative intensities, and hence the ability to track them to higher pressures, and their lack of overlap with other peaks at room pressure. Representative diffraction patterns at pressure are shown in Fig. 1-3. Up to 10 GPa, the crystal structure of buddingtonite remained monoclinic. Due to the low symmetry and minor preferred orientation effects, Rietveld refinements were not conducted above room pressure.

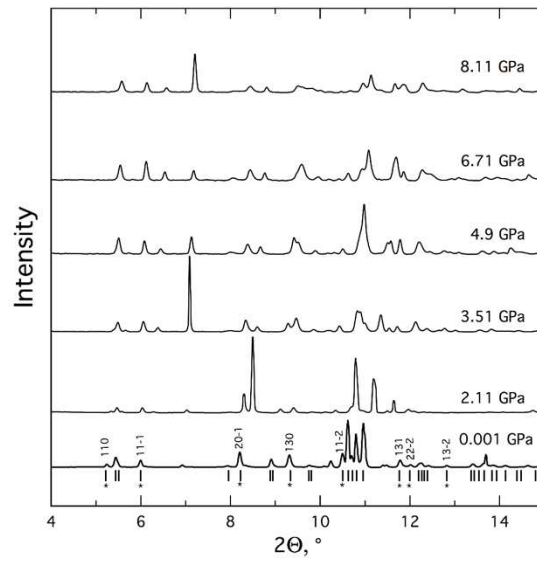


Figure 1-3. Representative powder diffraction patterns of buddingtonite under compression. * indicate peaks used for unit cell calculation. Neon and gasket lines have been removed. Based on anomalous amplitude ratios, preferred orientation is clearly present in several of the patterns.

The pressure-volume relationship for buddingtonite is similar in slope to that of sanidine (Angel et al., 1988): as with sanidine, there is little curvature in the P-V relationship over the pressure range to 9.5 GPa (Fig. 1-4).

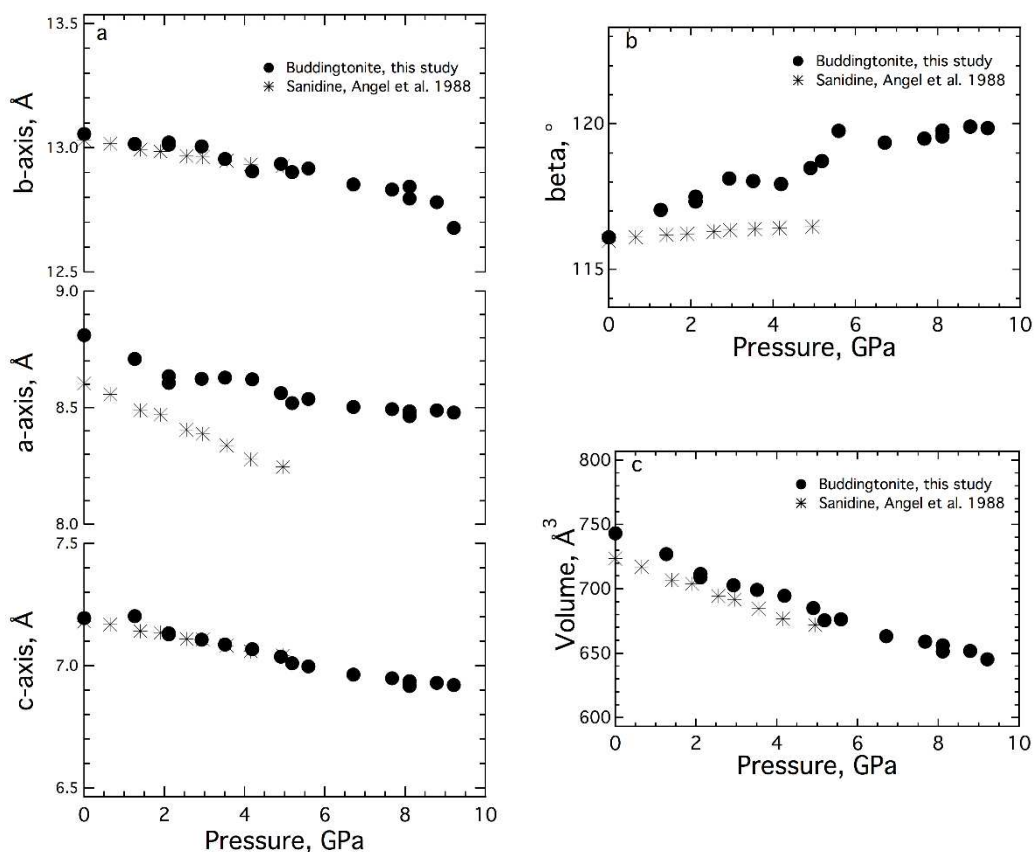


Figure 1-4. Buddingtonite crystallographic parameters under pressure; standard error for data is smaller than the size of the markers. (a) Calculated lattice parameters (b) β angle, and (c) volume. Sanidine values are plotted for comparison (crosses: Angel et al. 1988).

The primary differences between the compression of sanidine and buddingtonite lie in the difference in the compressibility of the a -axis (Angel et al., 1988) between the two phases--the a -axis in buddingtonite is substantially stiffer than that of sanidine, while the b - and c -axes are almost indistinguishable from sanidine in both their absolute values and pressure dependences. The monoclinic β -angle also increases with pressure in buddingtonite at a rate substantially greater than that in sanidine. Compaction along the a -axis is in a direction that contains a mirror plane of the ammonium cation site,

and the compression in this direction is largely controlled by the Si-O-(Si,Al) bond angle. Notably, the *a*-axis is entirely responsible for the thermal contraction on cooling of buddingtonite: both the *b*- and *c*-axes weakly (and anomalously) expand on cooling (Mookherjee et al., 2004). Thus, the role of the larger ammonium cation appears to be to expand the M-site within buddingtonite, and hence it impedes the pressure-induced closing of the Si-O-(Si,Al) angle relative to potassium-bearing feldspar.

From the results of Fig. 1-4, a bulk modulus (K_0) of buddingtonite of $51.0 (\pm 5.8)$ GPa was calculated using a 3rd order Birch-Murnaghan equation of state, with a K_0' of $3.6 (\pm 1.1)$. If a 2nd order Birch Murnaghan equation of state is used, in which K_0' is fixed at 4, the resultant bulk modulus is $49.0 (\pm 1.6)$ GPa. For comparison, there are few analogues that illuminate how the ammonium ion affects the elasticity of materials relative to potassium. Previous elasticity studies on ammonium and potassium halides reported either similar or smaller values for the bulk modulus of the potassium halides relative to ammonium halides (Combes et al., 1951; Garland and Yarnell, 1966). These face centered cubic systems provide a potentially direct comparison for the relative effects of ammonium and potassium ions on elasticity, and may be relevant analogues for the corresponding substitution in feldspar. Combes et al. (1951) reported a bulk modulus for KBr and KCl of 15.1 GPa and 17.4 GPa respectively; the latter value is in close accord with the value of 18.1 GPa reported by Hearmon (1979), and the former with the 17.8 GPa of Yamamoto and Anderson (1987). Garland and Jones (1963) reported a value for NH_4Br 's bulk modulus of 16.6 GPa, and Garland and Yarnell (1966) reported NH_4Cl 's bulk modulus as 17.8 GPa. The uncertainty here, however,

lies in the possible differences in hydrogen bonding between the halides and the silicate system: if hydrogen bonding has an important effect on ammonium bonding in oxides, the interaction of ammonium with an aluminosilicate framework and halide systems may not necessarily be comparable. Nevertheless, these results indicate that the bulk modulus of buddingtonite might be expected to be similar to that of sanidine, with perhaps a weak tendency for the ammoniated compound to be slightly stiffer. In this context, the expansion of the lattice and cation site that accompanies substitution of ammonium for potassium in feldspars (Fig. 1-2) may affect the bending of the Si-O-(Si,Al) angles that are responsible for much of the low-pressure compressibility of these materials. Indeed, the thermal expansion of buddingtonite is notably depressed relative to that of other alkali feldspars (Hovis et al., 2008), which may also reflect the role of the ammonium ion in inhibiting the flexibility of the Si-O-(Si,Al) bond angle.

Angel et al. (1988) presented single crystal x-ray diffraction data up to 5 GPa for sodic, calcic and potassic end-member feldspars, with bulk moduli calculated using a linear fit to the pressure-volume data. Using this linear fit (which implicitly assumes a K_0' of 0), they reported sanidine's bulk modulus as 67 GPa (Angel et al., 1988). Subsequently, Angel (2004) noted that the precision of the earlier data was insufficient to resolve K_0' . In order to directly compare our data with the previous compressional data on sanidine (Angel et al., 1988), we fit our pressure-volume data for buddingtonite linearly. Such a linear fit to our data yields a bulk modulus of 73 GPa which is (as to be expected) significantly larger than that calculated using the more accurate 2nd and 3rd order Birch-Murnaghan equations. The key aspect here is that, as with the

ammonium halides and as is apparent from Fig. 1-4, our static compression results indicate that buddingtonite is slightly stiffer than sanidine.

For comparison, Haussühl (1993) determined elastic constants for a sanidine of $(K_{0.89}Na_{0.11})AlSi_3O_8$ composition using ultrasonic resonance frequency spectroscopy. These constants yielded an upper bound (Voigt average) of 65.2 GPa, a lower bound of 55.6 GPa (Reuss average) and a Voigt-Reuss-Hill (VRH) average of 60.0 GPa (Hill, 1952). We calculate the 300 K isothermal bulk modulus to be 59.8 GPa using the VRH average and the thermal expansion of Hovis et al. (2008). The bulk modulus calculated for sanidine using data reported by Haussühl matches more closely with buddingtonite, but yields a value which is larger than our Birch-Murnaghan fits to the buddingtonite compression data. The origin of the difference between the relative static compression values and the ultrasonic data is unclear, but it might be either of compositional origin, or may reflect that the pressure derivative of the bulk modulus of sanidine is substantially less than 4. Alternatively, if buddingtonite's behavior at high pressures is modulated by a lack of interaction/hydrogen bonding between ammonium and the silicate framework (as discussed in the following section), then ambient pressure elastic results might not fully reflect the complex structural interactions (or lack thereof) occurring at high pressures.

With respect to order/disorder, Downs et al. (1994) determined that the ordering of Al and Si tetrahedra exercises a significant control on the bulk modulus of albite (Na-feldspar). Disorder tends to stiffen the Si-O-(Si,Al) bond angle, and thus decreases compressibility, so buddingtonite, which is disordered, would be anticipated to have a

bulk modulus similar to that of sanidine in accord with our observations, with any difference generated largely by the differing effects on elasticity of ammonium relative to potassium. Downs et al. (1994) reported that the bulk modulus of albite is 54 GPa, in accord with Angel (2004); Angel et al.'s (1988) linear fit to their compressional data on this compound resulted in a value of 70 GPa. Thus, while Angel et al (1988) provide the only available high-pressure compression for sanidine, it appears likely that their reported bulk modulus is overestimated, and a direct comparison of our respective results (Fig. 1-4) indicates that buddingtonite is less compressible than sanidine.

1.4.2 Infrared Spectroscopy: Aluminosilicate framework

Representative mid-infrared spectra of buddingtonite under compression are shown in Figure 1-5. There are two regions in the ~ 700 - 1400 cm^{-1} range of the buddingtonite infrared spectrum that we characterize in which vibrations of the aluminosilicate framework are present. The peaks from ~ 700 to $\sim 800\text{ cm}^{-1}$ at ambient pressure are assigned to Si-O-(Si,Al) bending vibrations, and the peaks from $\sim 800\text{ cm}^{-1}$ to $\sim 1,400\text{ cm}^{-1}$ are assigned to (Si,Al)-O stretching vibrations (e.g., Couty and Velde, 1986). As is typical for a disordered feldspar (e.g., Atkinson et al., 1999), the infrared peaks are broad and, in the case of the silicate stretching vibrations, multiple difficult-to-deconvolve broad components are present.

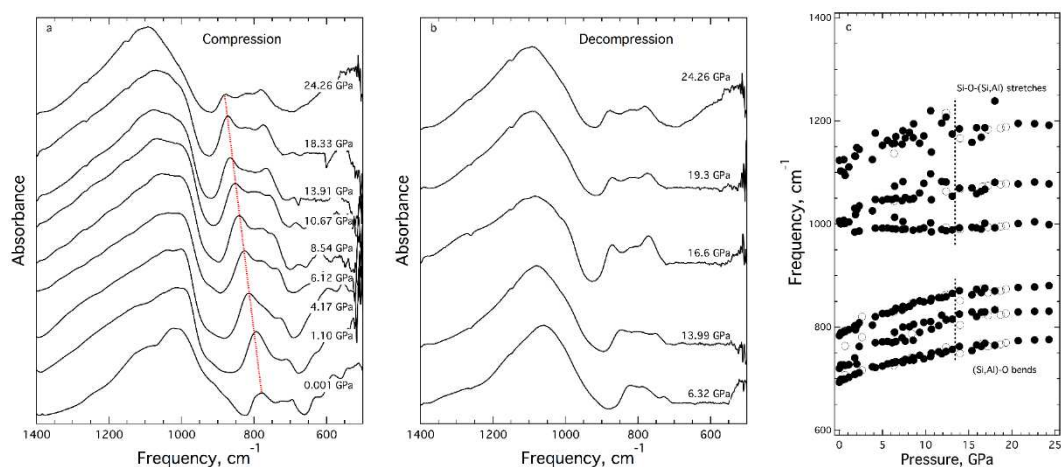


Figure 1-5. (a) Representative infrared spectra of aluminosilicate vibrations in buddingtonite under compression; (b) spectra of the aluminosilicate vibrations in buddingtonite under decompression; (c) peak positions of observed infrared modes as a function of pressure at room temperature: filled circles indicate compression, open circles indicate decompression, and the vertical line indicates the pressure which a transition in compressional mechanism occurs. The scatter in some of the peak locations (and particularly those at high frequency) is generated from the deconvolution of difficult-to-resolve shoulders on broad peaks.

The three Si-O-(Si,Al) bending vibrations initially shift rapidly, which is consistent with the concept that Si-O-(Si,Al) angle closure is the primary initial mechanism of compaction in this material; however, their pressure shifts markedly decrease above ~13 GPa (Table 1-1 and Fig. 1-5c). This change in slope above 13 GPa indicates that the mechanism of deformation of the aluminosilicate framework likely changes. This shift is probably associated with the Si-O-(Si,Al) angles deforming less rapidly with pressure, and (based on the marked decrease in pressure shifts of the two higher frequency shoulders of the (Si,Al)-O stretches) an increase in the stiffness of buddingtonite at this pressure.

However, because no new peaks appear nor do any modes disappear near the pressure at which this change in Si-O-(Si,Al) mode shifts occurs, there is no evidence for a major structural change (such as a phase transition, a shift in the coordination number of Si/Al and/or amorphization of the buddingtonite). The general morphology of these peaks stays consistent, although variations in their intensity do occur: these are particularly apparent in the increase in amplitude of high-frequency shoulders on the Si(Al)O₄-stretching manifold of peaks (Fig. 1-5a). We have no simple explanation for these shifts in intensities, beyond noting that growth of high-frequency components on the stretching peaks may indicate a locally more rigid/incompressible environment surrounding either a subset of the tetrahedra, or a subset of the Si(Al)-O bonds within the tetrahedra. For comparison, in the infrared spectrum of microcline under pressure (Williams, 1998), a new (Si,Al)O₄ tetrahedral peak begins to grow in between the stretching and bending modes near 12 GPa. No comparable change is observed in buddingtonite, indicating that no depolymerization of silicate tetrahedra occurs within this pressure range in buddingtonite under compression.

The (Si,Al)-O peaks also have different mode shifts above 13 GPa. The lowest frequency peak at $\sim 984\text{ cm}^{-1}$, which is the dominant spectral feature up to $\sim 6\text{ GPa}$, has an almost negligible pressure shift. However, the peaks with initial frequencies of 1006 and 1123 cm^{-1} also have dramatically decreased mode shifts above $\sim 13\text{ GPa}$ (Table 1-1). The peaks substantially broaden (which may be partially a consequence of non-hydrostatic stress) and become less intense. Again, at 25 GPa--the highest pressure at which we probed the silicate vibrations--there is no evidence for amorphization or

extensive disordering of the feldspar framework, as is found in some other feldspars (Williams, 1998): the silicate stretching and bending peaks remain discrete (albeit with broadened stretching vibrations) and well-resolved.

The possible change in the response of the feldspar framework to compression at ~13 GPa is at higher pressure than the ~11 GPa pressure at which shifts in the compressional mechanism (as exemplified by markedly decreased mode shifts of the silicate stretching vibrations) initiate in ordered potassium feldspar (Williams, 1998). This higher pressure range for this shift in compressional mechanism could be due to either the difference in ionic radii of the ammonium and potassium cations, and the corresponding amount of compaction that the Si-O-Si(Al) angles can accommodate, or possibly due to differing structural responses for ordered and disordered feldspars. Notably, there is some disagreement on the relative sizes of the ammonium and potassium ions. Mookherjee et al. (2005) propose that ammonium is slightly smaller than potassium, but Harlov et al. (2001) and Watenphul et al. (2009) based on composition-volume relations report ionic radii for ammonium that are larger than that of potassium. A portion of this disagreement is likely semantic: ammonium is clearly a tetrahedral cation, and ionic radii are defined on the basis of spherical ions. Nevertheless, typical ionic radii for potassium within crystalline environments are reported for 6-, 8- and 12-fold coordination as 1.38, 1.51 and 1.64 Å relative to estimated values for ammonium of 1.59, 1.68 and 1.80 Å, respectively (Shannon, 1976; Watenphul et al., 2009). In buddingtonite, the ammonium is in a 9-fold coordinated site, and we accordingly expect that the ionic radius of ammonium in buddingtonite is

larger than that of potassium in sanidine. Therefore, substitution of the ammonium ion into this site is likely to generate a more rigid environment associated with greater resistance to narrowing of the Si-O-Si(Al) angles of the silicate framework. Larger cation sizes have long been invoked to hold open feldspar frameworks, and to explain the higher rigidity of, for example, potassium feldspars relative to sodic feldspars (the sodium ion radii is 1.03 Å) (e.g. Angel et al., 1988).

The broadening of the stretching vibrations of the Si/Al tetrahedra under compression (and to a lesser extent the bending vibrations), imply that the local tetrahedral environments may become more disordered under pressure: the lack of new peaks, however, preclude a transition of the Si and Al cations from 4-fold to 5- or 6-fold with respect to oxygen (e.g., Williams and Jeanloz, 1988; Williams, 1998). On decompression (Fig. 5b), the changes observed in the buddingtonite spectra are largely reversible; the spectrum of the quenched sample is moderately broadened, and the highest frequency shoulder on the Si(Al)-O stretching vibrations is no longer well-defined. However, beyond the change in the shape of the high frequency stretching envelope, no marked changes in peak positions or overall morphology are observed. Hence, the response of buddingtonite to compression to ~30 GPa appears to involve no major reconstructional changes of the aluminosilicate framework, although a shift in compressional mechanism does occur at ~13 GPa.

Grüneisen parameters were calculated to assess how the vibrations of the aluminosilicate framework respond to the changing volume of the crystal. Grüneisen parameters are calculated from $\gamma_i = K_0 / v_{0i} (dv/dP)$, using the bulk modulus (K_0)

calculated from our powder diffraction data, and room pressure frequencies for the aluminosilicate bending and stretching (ν_{0i}), and the pressure dependences of vibrational frequencies up to 13 GPa (Table 1-1). The Grüneisen parameters of the bending vibrations in buddingtonite are similar to those in both albite and microcline; however, the Grüneisen parameters of the stretching bands are, on average, less than those of either microcline or albite (Williams, 1998). The average Grüneisen parameters of the silicate stretching bands shift in the order albite > microcline > buddingtonite, implying that compaction of the tetrahedra may increase as the size of the monovalent cation decreases.

		Up to 13 GPa		Above 13 GPa
Frequency (cm ⁻¹)	Assignment*	Mode Shift (cm ⁻¹ /GPa)	Grüneisen Parameter**	Mode Shift (cm ⁻¹ /GPa)
693	Si-O-(Si,Al) bend	4.4 ± 0.2	0.31	1.8 ± 0.3
720	Si-O-(Si,Al) bend	7.4 ± 0.5	0.50	0.9 ± 0.4
784	Si-O-(Si,Al) bend	6.2 ± 0.2	0.39	1.3 ± 0.3
985	(Si,Al)-O stretch	0.0 ± 0.2	0.00	1.1 ± 0.3
1006	(Si,Al)-O stretch	6.3 ± 0.6	0.31	2.0 ± 0.6
1124	(Si,Al)-O stretch	6.9 ± 0.9	0.20	2.0 ± 0.9

Table 1-1. Infrared modes observed at room pressure and temperature, pressure dependences of peak positions, and calculated mode Grüneisen parameters of aluminosilicate stretching and bending vibrations up to 13 GPa. *From Couty and Velde (1986) **Assuming a bulk modulus of 49 GPa.

1.4.3 Ammonium Vibrations

The four fundamental vibrational modes of the isolated tetrahedral ammonium ion are produced by symmetric stretching of N-H bonds ($\nu_1 \sim 3,040$ cm⁻¹), symmetric bending of H-N-H bond angles ($\nu_2 \sim 1,680$ cm⁻¹), asymmetric stretching of N-H bonds ($\nu_3 \sim 3,145$ cm⁻¹), and asymmetric bending of the H-N-H bond angle ($\nu_4 \sim 1,400$ cm⁻¹). Of these, the ν_3 and ν_4 vibrations of the isolated molecule are infrared active, and these are the strongest infrared vibrations of ammonium in the lower symmetry site which it

occupies in buddingtonite (Fig. 1-1a). Additionally, combination bands also appear in the spectrum: in particular, the $\nu_2 + \nu_4$ band occurs as a shoulder on the low frequency side of the ν_3 band, where it may be enhanced in its amplitude through a resonant interaction with the higher amplitude ν_3 band. Thus, we characterize 3 clearly resolved ammonium vibrations under compression: ν_4 (at a zero pressure frequency of $1,441\text{ cm}^{-1}$), a combination band of $\nu_2 + \nu_4$ ($3,053\text{ cm}^{-1}$) and ν_3 ($3,270\text{ cm}^{-1}$); these locations and assignments are consistent with those of Harlov et al. (2001).

The nitrogen of the ammonium ion lies in the M-site, in line with the mirror plane associated with the $C2/m$ space group, and has point symmetry m with the four hydrogens (Mookherjee et al., 2005). Because buddingtonite typically does not form large single crystals, single crystal structural refinements are not available: powder neutron diffraction (using the rigid body approximation) provides the primary constraints on the hydrogen locations in the crystal structure (Mookherjee et al., 2004). The neutron diffraction data show that the hydrogen positions are disordered down to a temperature of 20 K, which is consistent with the broad ammonium vibrational peaks observed in the infrared spectra (Figs. 1-1, 1-6). Ordering of ammonium ions within crystals is well-known to produce marked sharpening of vibrational bands, and we anticipate that our high-pressure infrared measurements will be sensitive to any pressure-induced ordering (as occurs within the ammonium halides: Hamann, 1978; Reed and Williams, 2006).

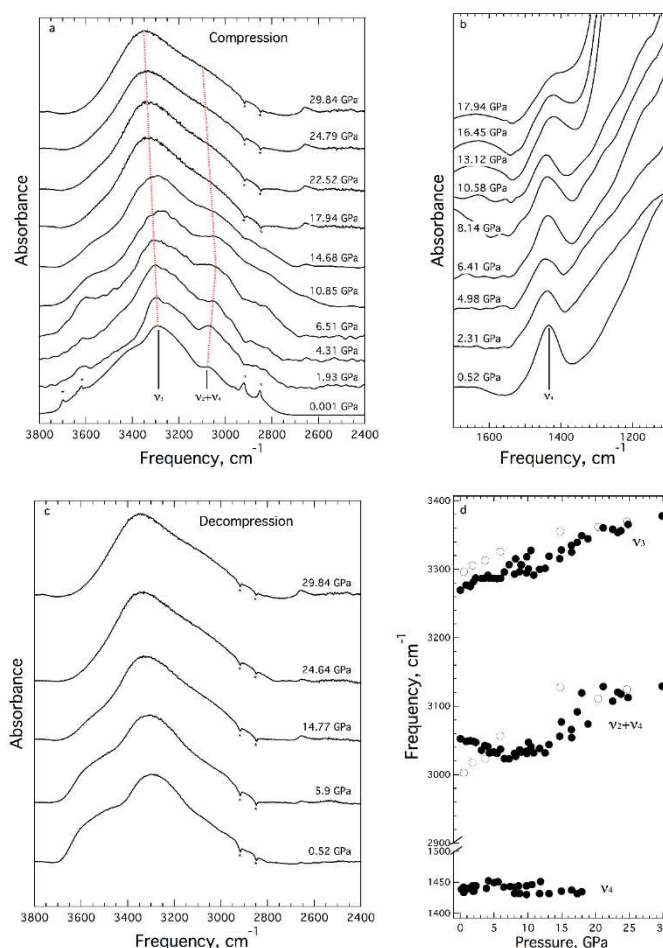


Figure 1-6. (a and b) Representative infrared spectra of the ammonium vibrations in buddingtonite under compression; (c) spectra on decompression (d) peak positions of the observed infrared modes as a function of pressure at room temperature: filled circles indicate compression, open circles indicate decompression, and error bars are smaller than the symbols. Standard error for data is smaller than the size of the markers Asterisks are hydrocarbon contamination.

Pressure-induced increases in frequency in vibrational spectra typically indicate an increase in bond strength generated by compression, while pressure-induced decreases of hydrogen stretching vibrations are associated with increases in hydrogen bonding (and hence weakening of the primary anion-H bond). Thus, the vibrations of the ammonium ions under pressure constrain changes in hydrogen bonding. Hence, the degree to which the ammonium molecule is bonded via hydrogen bonding (in addition

to its Coulombic interaction) to the aluminosilicate framework under pressure can be monitored.

The asymmetric N-H stretch, ν_3 , is an extremely broad peak which increases linearly in frequency up to 30 GPa at a rate of $\sim 3.6 \text{ cm}^{-1}/\text{GPa}$, and shows no evidence for any discontinuities (Fig. 1-6). Its breadth is such that at some pressures it was challenging to fit with two components (the ν_3 band and the lower frequency $\nu_2 + \nu_4$ combination). It is possible that the band itself may be asymmetric due to a frequency-dependent absorption coefficient associated with its extreme breadth ($\sim 400 \text{ cm}^{-1}$ full-width-at-half-max at high pressures). Such frequency-dependent absorption coefficients are well-known in, for example, hydroxyl units in silicate glasses (e.g., Paterson, 1982). Nevertheless, because of both the positive and monotonic shift of ν_3 , there are no indications of enhanced hydrogen bonding with the aluminosilicate framework under compression. Indeed, the positive pressure shift indicates that hydrogen-cation repulsive effects dominate over any compression-enhanced hydrogen bonding. Moreover, the broadening of the vibration under compression indicates that no pressure-induced ordering of the ammonium ions occurs. On decompression, the ν_3 vibration shifts reversibly back to lower frequency, but does show some hysteresis (it lies at 10-15 cm^{-1} higher frequency on decompression: Fig. 1-6). A significant high-frequency shoulder on ν_3 does appear on decompression below 15 GPa (Fig. 1-6c): we have no simple explanation for the appearance of this band (Fig. 1-6), but, as with the hysteresis in band position, its appearance is compatible with a modest irreversible

change in the local environment of the alkali cation site and/or in the orientation of the ammonium molecule occurring under pressure.

The $\nu_2 + \nu_4$ combination band of the symmetric and asymmetric bending vibrations is substantially less distinct and more difficult to track. However, our deconvolutions indicate that it shows substantially more complex behavior than ν_3 . This combination band initially decreases in frequency up to 7 GPa, where the sign changes and the band begins to increase in frequency. For comparison, the asymmetric bend, ν_4 , increases in energy up to 18 GPa, but its pressure shift is small. The shift and broadening of the high frequency tail of the aluminosilicate tetrahedral stretching bands make this ammonium band difficult to resolve above 18 GPa, or upon decompression (Fig. 1-6).

The pressure shift of the ν_2 symmetric stretching vibration can be constrained from the combined shifts of the $\nu_2 + \nu_4$ and ν_4 vibrations (this analysis implicitly assumes that anharmonic coupling between these vibrations is small). Because of the small and monotonic shift of the ν_4 band, the ν_2 band must be responsible for the strong non-linearity of the combination band. Thus, we infer that the symmetric bending vibration shifts negatively to 7 GPa, followed by a change in sign to a significant positive shift. The notable difference between the behaviors of the symmetric and asymmetric bending vibrations implies that, despite the continuous positive shift of the stretching vibration, a complex shift in the interaction between the ammonium molecule and its aluminosilicate surroundings occurs under pressure. Moreover, the $\nu_2 + \nu_4$ band shift is not fully reversible on decompression: on decompression, the band does not appear to

have a negative pressure shift as it does below 7 GPa on compression, and its ultimate position is about 50 cm⁻¹ lower than the starting material (Fig. 1-6d). Taken together, these observations indicate that the ammonium ion may adopt a new orientation in the 9-coordinated site upon compression above 7 GPa: the manifestation of this shift lies primarily within the bending vibrations, and particularly the symmetric bend. Upon decompression, the differing pressure shift and change in location of the $\nu_2 + \nu_4$ combination band indicates that the reorientation of the ion is not fully reversible (Table 1-2): such a shift in orientation may also generate the observed hysteresis of the position of the ν_3 band. Beyond the modest shifts in slope near 7 GPa, and somewhat complex behavior of the combination band, perhaps the most notable aspect of these results is how small the relative changes in frequency of the ammonium vibrations are on compression. This is illustrated by the Grüneisen parameters in Table 1-2, which are roughly half an order-of-magnitude smaller than the aluminosilicate vibrations (Table 1-1). Thus, the bonding within the ammonium ion is only slightly altered by compression (the changes in force constants are quantified in the next section), and it appears that ammonium behaves like a largely non-interactive guest ion within the aluminosilicate framework.

Frequency (cm ⁻¹)	Assignment	Mode Shift Compression (cm ⁻¹ /GPa)	Grüneisen Parameter**	Mode Shift Decompression (cm ⁻¹ /GPa)
1434	H-N-H ν_4 bend	$1.3 \pm 1.0^*$ (up to 18 GPa)	0.04 (up to 18 GPa)	Not measured (see text)
3053	H-N-H $\nu_2+\nu_4$ bends	-4.0 ± 0.5 (below 7 GPa)	-0.06 (below 7 GPa)	5.2 ± 0.9
	H-N-H $\nu_2+\nu_4$ bends	5.6 ± 0.4 (above 7 GPa)	0.09 (above 7 GPa)	
3270	N-H ν_3 stretch	3.7 ± 0.2	0.06	3.0 ± 0.3

Table 1-2. Infrared modes observed at room pressure and temperature, pressure dependences of peak positions for the ammonium ion. *Averaged multiple experiments together to calculate mode shift.

**Assuming a bulk modulus of 49 GPa.

In comparison to simpler, alkali-halide structured ammonium salts, the pressure-induced vibrational mode shifts of the ammonium ion in buddingtonite are complex. In a Raman spectroscopic study of NH_4Cl , NH_4Br , NH_4I , the ν_1 vibration was observed to merge with ν_3 at 22.5, 33.5 and 35 GPa, respectively (Jeon et al., 1988): this was explained by a higher site symmetry induced by pressure. Within the infrared spectrum of NH_4Br under compression (Reed and Williams, 2006), the sign of the shift of the ν_3 peak changes from negative to positive (indicating a shift from enhanced H-bonding to inter-H repulsion at high pressures) at relatively low pressure conditions (~ 5 GPa), but all other peaks shift monotonically.

1.4.4 Ammonium tetrahedral force constants

In order to illuminate the nature of the shift in bonding forces taking place within the ammonium tetrahedra under pressure, tetrahedral force constants were calculated using the assumption of valence forces, first utilized by Bjerrum (1914). Under this assumption, the ammonium tetrahedra are regarded as harmonic oscillators with two force constants. There is a stretching force constant (k), which is associated with a change in the length of the N-H bond and is linked to the restoring force between the individual nitrogen and hydrogens, and a bending force constant (ks/l^2), where l is the distance between N and H), which corresponds to a change in the H-N-H bond angle and incorporates the restoring force for H-N-H angle changes (Herzberg 1945).

At room pressure, the N-H stretching force (k) constant in buddingtonite is calculated to be 5.8×10^5 dyne/cm as compared with that of the idealized free ion of 4.9×10^5 dyne/cm; the H-N-H bending force constant ($k\delta/l^2$) is 0.52×10^5 dyne/cm in buddingtonite, with 0.56×10^5 dyne/cm being the free ion value. For reference, comparable force constants in ammonium bromide are intermediate between the free ion values and those of buddingtonite: a k of 5.6×10^5 dyne/cm and a $k\delta/l^2$ of 0.54×10^5 dyne/cm (Wagner and Hornig, 1950). The stretching force constant in buddingtonite indicates that the N-H bond is slightly stronger than in the free ion or in ammonium bromide. The rationale for the increased strength of the N-H bond in the ammonium ion in crystals is unclear, but is likely associated with cation-hydrogen repulsive forces within the crystals (Si and Al in the case of buddingtonite, and nearby H's/ammonium in ammonium halides). The smaller value of the bending force constant in buddingtonite relative to free ammonium and ammonium bromide is likely due to the geometrically complex relationship of the tetrahedral ammonium ion with the nine-fold coordinate M-site in the feldspar framework.

Pressure-induced changes in the force constants of the ammonium ion were calculated by determining the ν_2 frequency from the difference between the ν_4 location, and the $\nu_2 + \nu_4$ peak. This approach works up to 18 GPa, which is the maximum pressure at which ν_4 is resolved. Fig. 7 shows the pressure dependence of the two force constants. The stretching constant (k) increases up to 7-10 GPa, and then is approximately constant up to 18 GPa. There are hints that it may turn over at the highest pressures, but this is not well-resolved; speculatively, this possible turnover could

represent a hint of a higher-pressure onset of significant hydrogen bonding. The bending force constant markedly weakens to 7 GPa, is nearly constant from ~7-13 GPa (Fig. 1-7), and then increases above ~13 GPa. The tandem shifts in the pressure dependence of both force constants initiating at 7 GPa may be indicative of a change in the orientation of the ammonium ion. The second change in slope around 13 GPa likely reflects the change in the compressional mechanism of the surrounding aluminosilicate framework that is manifested in the shift in pressure dependences of the aluminosilicate vibrations. These observations indicate that two subtle structural shifts take place in buddingtonite under compression. First, a possible reorientation of the ammonium ion takes place near 7 GPa, as manifested by the change in sign of the pressure shift of the ν_2 vibration (from the $\nu_2 + \nu_4$ combination band) and hysteresis in the ammonium vibrations on decompression. Second, a shift in compressional mechanism near 13 GPa occurs, as shown by the shifts in slope of both the pressure dependence of the aluminosilicate vibrations and in the force constants of the ammonium unit.

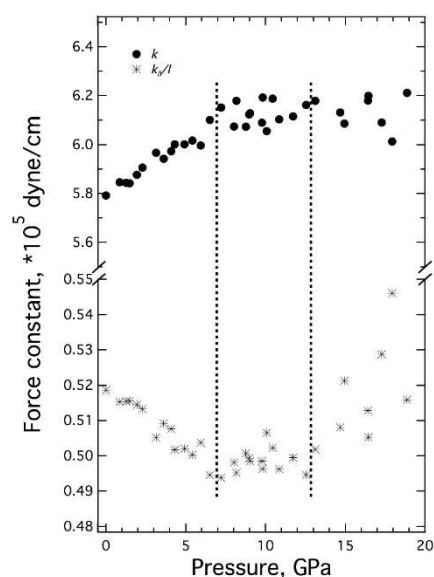


Figure 1-7. Calculated stretching (k) and bending ($k_{\delta}/12$) force constants of the ammonium ion under compression, assuming valence force constants.

1.5 Implications

From the vibrational spectra of buddingtonite under pressure, we conclude that (1) increased hydrogen bonding between the ammonium ion and the feldspar framework does not occur under compression; (2) no ordering of the ammonium ions occurs under compression, and hence ordering is unlikely within bound ammonium at the higher temperatures associated with subduction environments; and (3) the ammonium ion appears to remain largely unaltered by its presence within a compacting aluminosilicate framework. The mode shifts of the ammonium ion are small, and generally consistent with modest compaction of the ammonium ion. Given the lack of hydrogen bonding with the surrounding aluminosilicate framework under pressures up to 30 GPa, the ammonium ion appears to act as a guest molecule, and likely primarily interacts with the aluminosilicate framework through Coulombic interactions. The absence of hydrogen bonding (or, indeed, much shift in bonding at all of the ammonium

ion) indicates that pressure does not play a primary role in enhancing the stability of the ammonium ion within the aluminosilicate lattice. Although no discontinuous changes in the ammonium ion vibrations are resolved, the ion may shift its orientation in the 9-fold coordinated site near 7 GPa, as indicated by markedly non-linear shifts of the bending vibrations: this change appears not to be fully reversible on decompression, and it is not resolved in our polycrystalline diffraction measurements. For comparison, the feldspar framework undergoes largely reversible compaction up to 25 GPa and does not appear to amorphize: in this sense, relative to other feldspars, the ammonium ion may serve to stabilize the aluminosilicate framework. The elasticity of buddingtonite under compression indicates that the ammonium ion induces modest stiffening of the structure relative to sanidine, and this stiffening is likely associated with increased rigidity of the Si-O-(Al,Si) angles produced by the substitution of the larger ammonium ion into the feldspar lattice.

The behavior of the ammonium ion at high pressures within silicates is important in determining how nitrogen is subducted into, and retained within, the mantle. While the larger ammonium ion may structurally stabilize the feldspar framework more than potassium does at high pressures and 300 K (as indicated by an apparent structural transition at high pressures in microcline: Williams, 1998), the lack of bonding interactions between the ammonium ion and the aluminosilicate framework indicates that pressure is unlikely to markedly enhance the stability of the ammonium substitution within silicates. Hence, ammonium may, on primarily structural/bonding grounds, not be a particularly viable retention mechanism for nitrogen within silicates

at high pressures and temperatures. Certainly, we observe no structural indications that the thermal stability of the ammonium substitution would be markedly enhanced at high pressures in silicates. Indeed, the lack of bonding interactions between ammonium and its host lattice may contribute to the likely high-temperature, high pressure presence of nitrogen in nitrides or fluids within Earth's mantle. However, at low temperatures, the ammonium ion can be metastably retained to pressures corresponding to those within the transition zone, indicating that in cold environments the ammonium ion may still play a primary role in the processing of nitrogen into the mantle via subduction.

1.6 Acknowledgements

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Chapter 2: High-Pressure/Temperature Behavior of the Alkali/Calcium

Carbonate Shortite ($\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$): Implications for Carbon Sequestration in Earth's Transition Zone

2.1 Abstract

The behavior of shortite ($\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$) has been probed using synchrotron-based single crystal X-ray diffraction and Raman spectroscopy at high pressures and following laser heating to illuminate carbon retention within the deep earth, and phase equilibria of alkali/calcium carbonate-rich systems. Above 15 GPa, a transition to the shortite-II structure occurs at 300 K. This phase is novel as it involves a large distortion of the carbonates, with an onset of 3+1 coordination and near-dimerization of carbonate groups. Above 22 GPa, shortite-II amorphizes. Samples laser-heated at pressures between 12 and 30 GPa crystallize in a new structure, shortite-III. Below 12 GPa, this phase appears to decompose into a mixture of shortite, nyerereite ($\text{Na}_2\text{Ca}(\text{CO}_3)_2$), and aragonite (CaCO_3) in accord with prior phase equilibria results. The high-pressure behavior of nyerereite using Raman spectroscopy was also investigated to 25 GPa. The structural response of shortite to pressure is modulated by the sodium cations in the structure; hence, the behavior of alkali-rich carbonates within kimberlitic systems at depth is likely dependent on the bonding and local geometry of alkali cations. Our results show that complex, dense high-pressure structures are generated in the shortite system, and phase equilibria of the protoliths of carbonatites and kimberlites at deep upper mantle and transition zone pressures will involve intermediate alkali-calcium carbonate phases, including the high-pressure phases of shortite. Moreover, 3+1 coordination of carbon is observed at far lower pressures than other systems: this

coordination could become important in complex carbonates and possibly liquids at substantially shallower depths than previously anticipated.

2.2 Introduction

The fluxes and storage of carbon in the deep Earth are of great interest, as carbon species have a significant influence on the Earth's chemical and physical properties. In addition to any primordial carbon retained within the deep Earth, carbonate minerals are considered the major source of carbon that is reintroduced into the mantle from the surface (e.g. Piccoli et al. 2016) and, if present within cold slabs, they can be brought down to at least transition zone depths (Kerrick and Connolly 2001). The phases in which carbon is sequestered at depth depend on the local oxygen fugacity of the mantle (Poli et al. 2009). Carbonates are thought to be the dominant species in oxidized regions of the mantle (e.g., Brenker et al., 2007), while graphite or diamond are the dominant species in reduced regions (e.g., Stachel et al., 2005); carbonate may also be formed at depth in upwellings via the reduction of Fe^{3+} (Stagno et al. 2013).

Shortite ($\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$) is observed both in the ground-mass of carbonatites (e.g., Zaitsev & Chakhmouradian, 2002), and as a daughter phase in melt inclusions within forsteritic olivine found within kimberlites (Kamenetsky et al. 2009; Mernagh et al. 2011). The alkaline-/carbon-rich character of kimberlitic magmas implies that shortite may represent a protolith and/or structural model for such magmas. Here, we focus on shortite's high pressure and high temperature behavior, which is relevant to the behavior of alkali-carbonate systems within Earth's upper mantle. Specifically,

kimberlites, lamprophyres and carbonatites are each manifestations of alkali- and carbonate-rich, and silica-poor, low-degree melting processes in the Earth's upper mantle. Sodium/calcium carbonates that include shortite, nyerereite ($\text{Na}_2\text{Ca}(\text{CO}_3)_2$), and natrite (Na_2CO_3) are found as crystallization products of natrocarbonatite magmas in the only actively erupting carbonatite volcano, Oldoinyo Lengai (Dawson 1962; Zaitsev and Chakhmouradian 2002; Zaitsev, Zaitsev et al. 2010). Although the precise origins and transport of carbonatite magmas remain controversial, the lack of significant carbon solubility within silicate phases, and hence the anticipated presence of carbonate phases in carbon-bearing mantle systems (e.g., Grassi & Schmidt, 2011; Shcheka et al., 2006; Thomson et al., 2016), is central to the petrogenesis of carbonatite magmas. Alkali carbonates have been shown to markedly lower the solidus temperature of the mantle (Hirschmann 2000; Brey et al. 2011; Litasov et al. 2013), and to a greater degree than modest concentrations of water lower the solidus of mantle peridotite (Wyllie and Huang 1975). Shatskiy et al. (2016) investigated the melting of calcium/alkali carbonates in the K-Ca-Mg system at 6 GPa to determine the pressure-temperature conditions required for melt generation (Buob et al. 2006; Shatskiy et al. 2015a), and found that the combination of alkalis and carbon resulted in a ~ 1000 K decrease in the melting temperature of mantle material. Hence, alkalic carbonates juxtaposed with silicates at depth have a large impact on the melting relations of the mantle. Here, we use high pressure techniques to probe the high-pressure behavior of $\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$ -shortite, an alkali-calcium carbonate of potential relevance for the phase equilibrium of carbonatite compositions. The motivation is to understand both the

polymorphism and structural changes undergone by this alkali-bearing carbonate, with a goal of understanding its response to compression, its structural environments at extreme conditions, and its possible stability at deep upper mantle and transition zone conditions.

From a structural perspective, Dickens et al. (1971) reported that the crystal structure of shortite is orthorhombic, and in the *Amm2* space group. Shortite has two distinct carbonate sites within its unit cell, which gives rise to splittings of the normal modes of the carbonate ion in its vibrational spectra at ambient conditions (Frost and Dickfos 2008). Alkaline-earth carbonates have been studied extensively under pressure using vibrational spectroscopy to investigate the changes in the bonding environment of carbon with relevance to how carbon is bound under deep Earth pressures (e.g., Boulard et al., 2015; Catalli & Williams, 2005; Gillet et al., 1993; Koch-Müller et al., 2016; Kraft et al., 1991); here, we extend these *in situ* studies to shortite.

Studies on samples quenched from simultaneous high pressures and high temperatures on a range of alkali carbonate systems have been analyzed, as well as a few X-ray experiments conducted at high-pressures and temperatures on $\text{Na}_2\text{Ca}_3(\text{CO}_3)_4$ (Shatskiy et al. 2015b, a, 2016). Within the Na-Ca system, at the sodium endmember, these studies concluded that $\gamma\text{-Na}_2\text{CO}_3$ is unstable at high pressures and temperatures, converting to $\alpha\text{-Na}_2\text{CO}_3$ at higher temperatures ($\sim 500^\circ\text{C}$) and $\beta\text{-Na}_2\text{CO}_3$ at high pressures (~ 2 GPa; Shatskiy, Gavryushkin, et al., 2015). Multi-anvil experiments at 950°C and 6 GPa showed that shortite's presence is confined to low temperature and

pressure conditions, but that a suite of other alkali-calcium carbonates become stable near 6 GPa. Our goal here is to investigate whether shortite undergoes higher pressure polymorphism that could stabilize the equimolar sodium-calcium composition within carbon-rich systems at depth within Earth's mantle. Our in-situ X-ray and Raman spectroscopic measurements not only document the elasticity of this phase and the response of its bonding to pressure, but also demonstrate that shortite does undergo high-pressure (and high pressure/high temperature) phase transitions that likely markedly enhance its petrologic importance at deep upper mantle and transition zone pressures.

2.3 Materials and Methods

Natural shortite $\text{Na}_{1.9}\text{Ca}_{2.1}(\text{CO}_3)_2$ from Westva Co, Wyoming was used for these high-pressure experiments. Its chemical composition was confirmed using a JEOL JXA-8230 electron microprobe at Stanford University. Raman spectroscopy and single crystal X-ray diffraction were in excellent agreement with previous determinations by Frost and Dickfos (2008) and Dickens et al. (1971), respectively.

2.3.1 Raman Experiments

Raman measurements were performed using a Horiba LabRAM HR Evolution spectrometer equipped with a 633 nm excitation laser. The spectrometer focal length was 800 mm, and a grating of 1800 lines/mm was used with a spectral resolution of $\sim 1 \text{ cm}^{-1}$. Spectra were collected to a pressure of $\sim 26 \text{ GPa}$ at $\sim 300 \text{ K}$. Peak positions were calculated from fits that used a combination of Gaussian and Lorentzian peak shapes with Horiba Labspec6 software.

For the high-pressure Raman experiments, pressures were generated using a symmetric diamond anvil cell (DAC) with type IIa diamonds and 350 μm culets. Spring steel was used as the gasket material. The gasket was preindented to ~ 30 μm thickness, and the sample compartment was ~ 150 μm in diameter. For the room temperature measurements, a 4:1 ratio of methanol:ethanol was used as a pressure medium to avoid chemical reactions, while for laser heated Raman spectroscopy experiments, no pressure medium was used. The standard ruby fluorescence technique was used to measure pressure from multiple ruby grains in the high-pressure samples (Mao et al. 1986).

Laser heating experiments were conducted on powdered shortite mixed with ~ 5 wt% platinum black. The sample was brought up to 28 GPa, and heated using a 50 W Nd:YAG laser tuned in TEM00 mode, as described by Chaney et al. (2015). Temperatures are estimated to be between 1600 and 2000 K.

2.3.2 X-Ray Diffraction

Room pressure single crystal X-ray diffraction data were collected at the Advanced Light Source (Beamline 11.3.1). Diffraction images were collected at 298 K with a Bruker D8 diffractometer equipped with a Photon 100 CMOS detector, employing X-rays monochromated by silicon (111) to 0.7749(1) Å (16 keV). The single crystal sample was a clear cube that was free of visible cracks and/or imperfections, with an approximate size of 40x40x40 μm . The sample was mounted in Paratone-N oil on a MiTeGen MicroMount.

High pressure single crystal X-ray diffraction data were conducted at the Advanced Light Source (Beamline 12.2.2). High pressures were generated using either a DESY BX-90 or Merrill-Bassett type diamond anvil cell with Boehler Almax type diamonds (Boehler and De Hantsetters 2004) with 500 μm culets and 80° opening angles. Rhenium was used as the gasket material and, depending on the pressure range, either a 4:1 ratio of methanol:ethanol or neon was used as a pressure medium. Diffraction images were collected with a Perkin Elmer amorphous silicon detector using synchrotron radiation monochromated by silicon (111) to an energy of 25 keV or 30 keV (0.4959(1) Å or 0.4133(1) Å respectively). Calibrations for sample-detector distance and wavelength were done using a NIST single crystal ruby sphere (Wong-Ng et al. 2001).

Ambient single crystal diffraction data and images were collected using APEX II (Bruker 2013a), and high pressure single crystal diffraction data and images were collected using in-house LabView code and analyzed using APEX3 (Bruker 2016a). Images were integrated and cell refinements were computed using SAINT V8.34A (Bruker 2013b) with dynamic masks for the diamond anvil cell created using ECLIPSE (Parsons 2010). The sample symmetry of the ambient structure was determined using XPREP. Crystal absorption was corrected using SADABS-2016/2 (Bruker 2016b). The ambient pressure shortite structure was used as an initial fit, and refined using full-matrix least-squares on F^2 with SHELXL-2018/1 (Sheldrick 2015) using software packages OLEX2 (Dolomanov et al. 2009) and ShelXle Rev 867 (Hübschle et al. 2011). CIFs were completed and checked using enCIFer (Allen et al. 2004) and

checkCIF. Gasket and diamond reflections were omitted. High pressure structures of shortite-I were refined with rigid bond restraints, and the calciums were refined anisotropically. Similarity restraints were used on the carbon-oxygen bonds and on oxygen-oxygen interatomic distances within the separate carbonate ions. The shortite-II refinement had no rigid bond restraints; thermal parameter equivalence restraints were used for carbons and oxygens. A 2-fold rotation twin law $[0\ 0\ -1\ 0\ -1\ 0\ -1\ 0\ 0]$ was identified and used for the high pressure structure.

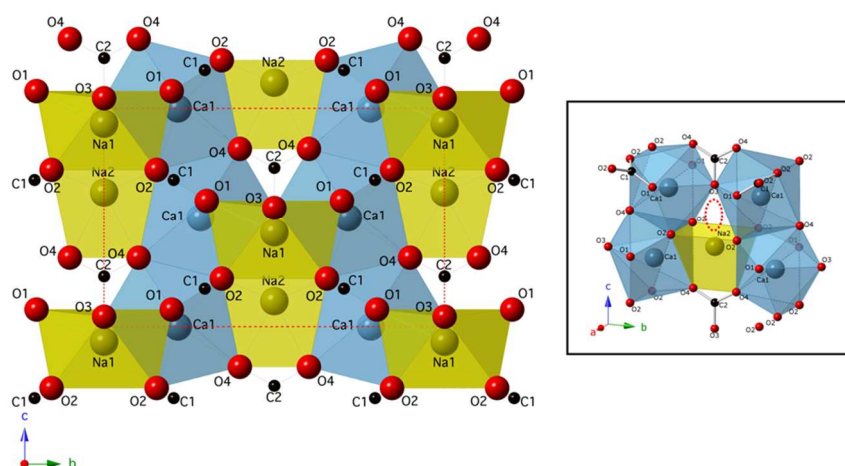


Figure 2-1. Crystal structure of shortite-I looking down the a -axis with the unit cell delineated by the dotted red lines; Na polyhedra are yellow, Ca polyhedra are blue, C atoms are black, and oxygen atoms are red; inset is a view of the partial unit cell showing the void space between Na2 and O1 (red dotted oval).

2.4 Results and Discussion

2.4.1 Room Pressure Single Crystal Refinement

Single crystal analysis of shortite yielded a crystal structure that is in excellent agreement with Dickens et al. (1971) (Fig. 2-1, Table S2-1). Within the orthorhombic structure ($Amm2$ space group), there are two formula units within the unit cell (Table

S2-1). Table S2-2 gives the atomic coordinates within the unit cell. Overall, the structure consists of Na-CO₃ layers centered at $x=0$ and Ca₂Na(CO₃)₂ layers centered at $x=0.5$. There are two sodium sites within the unit cell—both of which have point symmetry $mm2$. Na1 resides within an 8-fold disordered trigonal prismatic site (volume: 26.679 Å³); while Na2 is in a 7-fold site (volume: 18.978 Å³). Dickens et al. (1971) reported a void between the Na2 and O3 sites, with excess electron density between them: we also observe this void and excess density. The single calcium site has 9-fold coordination with a single mirror plane in the b - c plane bifurcating it at $x=0.5$ (volume: 30.328 Å³); the calcium-calcium polyhedra are face sharing. Of the two distinct carbonate ion sites within the unit cell, the carbonate ion containing the C1 site has m symmetry where the carbon ion is mostly in plane with the oxygen plane, however is not constrained by symmetry, so the carbon is 0.0262(182) Å out of the oxygen plane and the O-C-O angle variance is 0.70°. The carbonate ion containing C2 has a point symmetry of $m2$, and the carbonate is constrained to be flat due to symmetry and has an angle variance of 2.02°. Both carbonate ions are approximately aligned with their edges along the calcium site at a regular interval, which causes the calcium site to have close to an equidistant 9-fold coordination, similar to the calcium site in aragonite (Bragg 1924).

2.4.2 Equation of State

The dependence of the volume of shortite at pressures up to 19 GPa is shown in Fig. 2-2a: data up to 14 GPa were fit with 2nd order and 3rd order Birch-Murnaghan and 3rd order Vinet equations of state. Near 15 GPa, as is described below, a first-order

phase transition takes place within shortite. The isothermal bulk modulus (K_0) at room pressure for orthorhombic shortite was calculated as to be 56.6(39) GPa and its pressure derivative, K_0' , is 4.8(11). If a 2nd order Birch-Murnaghan equation is used, $K_0=59.6(12)$ GPa, with K_0' being constrained to 4. A 3rd order Vinet equation of state yields a K_0 of 56.4(39) GPa and K_0' of 5.0(11). If K_0' is fixed at 6.0 (the identical value to that used for the high pressure $\text{Na}_2\text{Ca}_3(\text{CO}_3)_4$ phase by (Shatskiy et al. 2015a) with a Vinet equation of state, the derived K_0 is 53.2(12) GPa. These values are substantially lower than the bulk moduli of aragonite and magnesite, which lie near 73 and 117 GPa, respectively (Ross 1997; Ono et al. 2005). It also is less than that of the high pressure $\text{Na}_2\text{Ca}_3(\text{CO}_3)_4$ phase, which has a K_0 of 70 GPa for a K_0' of 6 (Shatskiy et al. 2015a). Q. Liu et al. (2007) mention a bulk modulus for Na_2CO_3 of 60 GPa calculated with a static lattice simulation; this value is quite close to those for shortite. For mixed alkali-magnesium carbonates, Golubkova et al. (2015) used a 3rd order Birch-Murnaghan equation to derive bulk moduli for $\text{K}_2\text{Mg}(\text{CO}_3)_2$, $(\text{K}_{1.1}\text{Na}_{0.9})_2\text{Mg}(\text{CO}_3)_2$, and $\text{Na}_2\text{Mg}(\text{CO}_3)_2$ of 57.0(10), 54.9(13), and 68.6(13) GPa, respectively; in combination with our results, this indicates that mixed alkali/alkaline-earth carbonates are substantially more compressible than end-member alkaline-earth carbonates. In these crystal structures, the sodium sites tend to have more non uniform Na-O bond distances and O-Na-O angles, and are less compressible than potassium sites (Golubkova et al. 2015).

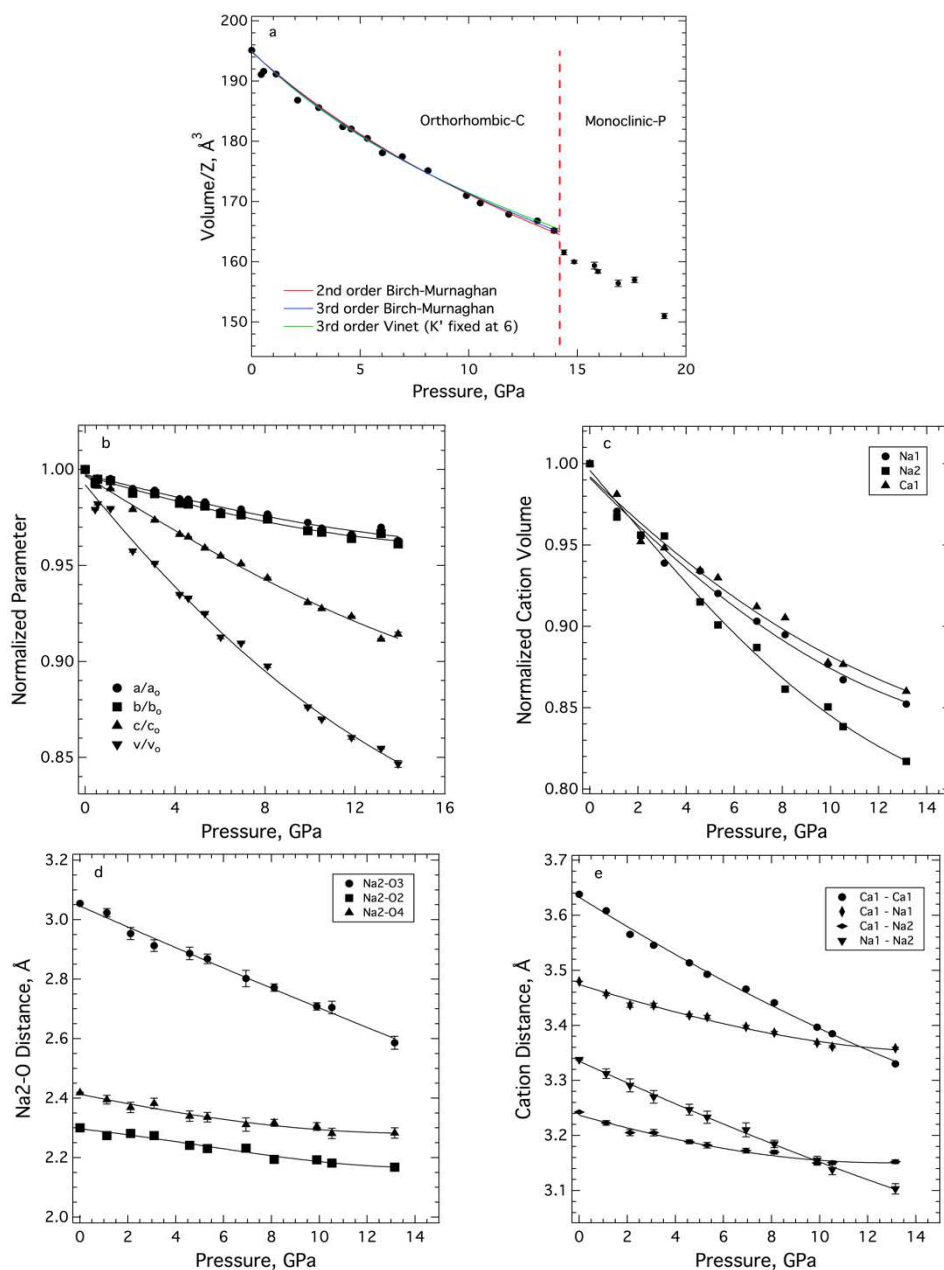


Figure 2-2. Crystallographic parameters of shortite-I under pressure: (a) unit cell volume to 14 GPa; error bars represent one standard deviation, red curve is a 2nd order Birch-Murnaghan fit, blue curve is a 3rd order Birch-Murnaghan fit, and green curve is a 3rd order Vinet fit; (b) normalized unit cell parameters; (c) normalized cation site volume with pressure; (d) Na2-O_{2,3,4} distances with pressure; (e) intercation distances with pressure. Lines in (b-e) are to guide the eye.

2.4.3 High Pressure Structural Changes

Up to ~15 GPa, the compaction of the unit cell of shortite-I is anisotropic: the *c*-axis contracts about a factor of two more rapidly than the *a*- or *b*-axes with pressure

(Fig. 2-2b). The refined high-pressure structures of shortite help explain the disparity in the contraction. The normalized site volume of each cation with pressure indicates that the Na2 site, which has the smallest volume at ambient pressure, contracts the most of the three cation sites within the unit cell (Fig. 2-2c). As noted by Dickens et al. (1971), a substantial void is present within the structure (Fig. 2-1 inset). Our results are consistent with a seventh oxygen (O3) moving in to fill the void, and into closer proximity (and approaching coordination) to the Na2 ion: the reduction in the Na2-O3 distance is substantially larger than that of the other 6 oxygen ions in the Na2 coordination sphere (Fig. 2-2d). From 0 to 13 GPa (the highest-pressure structure of shortite-I we could refine), the *c*-axis compacts by 0.441(2) Å, while the Na2-O3 distance (which is aligned with the *c*-axis) compacts slightly more: 0.47 (2) Å (Fig. 2-2d). The compaction of the void space is likely the major contributor to this compaction: since both the highly-coordinated sodium ions and the void are located preferentially along the *c*-axis, the high compressibility along the *c*-axis and hence the anisotropy of compaction can be qualitatively well-understood.

The compression of shortite-I is complex: for example, the carbonates associated with C2, lying in the {022} planes likely rotate associated with the rapid *c*-axis compression, rather than simply compressing isotropically. The closest cation-cation distances are shown in Fig. 2-2e. Under compression, the Ca1-Ca1 (which is highly aligned with the *c*-axis) and Na1-Na2 distances shortens almost linearly. The distances between Ca1 and both Na1 and Na2 do not compress linearly with pressure:

above 9 GPa, they begin to flatten out. This change in slope is plausibly a result of increased cation-cation repulsion (Fig. 2-2e).

At 14.4 GPa, shortite-II, which is indexed as a monoclinic-P phase appears: it has space group Pm and one formula unit per unit cell. The phase change is manifested by a decrease in volume of $\sim 2.5\%$, from $165 \text{ \AA}^3$ at 14 GPa to $161 \text{ \AA}^3$ at 14.4 GPa (Fig. 2-2a). The scatter in the pressure-volume curve of shortite-II is due to broadening of the diffraction spots from both being in a quasi-hydrostatic pressure medium (neon) and the presence of diffuse scattering in reciprocal space. The linear pressure dependence of the volume in the monoclinic phase is $-2.03(28) \text{ \AA}^3/\text{GPa}$, which is indistinguishable from a linear fit of the volume of the orthorhombic phase ($-2.06(7) \text{ \AA}^3/\text{GPa}$). The similarity of the pressure dependences of the volume indicates that the high-pressure phase does not access markedly more efficient mechanisms of compression relative to the low-pressure phase.

The synthesized precession images before and after the phase change indicate that the phase change is sluggish (Fig. S2-1a,b). Up to 14 GPa, the diffraction spots are distinct and separate. However, at 15 GPa, the spots in the (h0l) plane are no longer discrete: they have diffuse rods connecting them in the $[101]^*$ direction which corresponds to the $[110]^*$ direction in shortite-I. Ca1, Na1 and Na2 each lie in approximately the same plane along the $[101]$ direction in shortite-II. If an instability in the Ca1, Na1 and Na2 distances is the trigger for the phase change, following the phase change, these cations are expected to be more variably located along the shortite-II $[101]$ direction.

As pressure is increased beyond 15 GPa, the diffuse rods connecting the diffraction peaks lessen (for example, those that indicate the sluggish nature of the transition in the [101] direction, disappear), but the peaks themselves become broader (Fig. S2-1c). The broadness of the diffraction spots in a single direction signifies continued, likely inconsistent, atomic translations in one direction (here, the monoclinic [101] direction). The structure remains monoclinic-P to the highest pressures probed with X-ray diffraction, 19 GPa, and we see no evidence for a decrease in symmetry above 17 GPa.

2.4.4 Shortite-II Structure

The structure of shortite-II was solved at 15 GPa (Fig. 2-3a-c, Appendix A, Table S2-3). The unit cell of shortite-II is in the Pm spacegroup with unit cell parameters: $a = 5.970(3) \text{ \AA}$, $b = 4.816(2) \text{ \AA}$, $c = 6.009(3) \text{ \AA}$, $\beta = 116.01(3)$. Table S2-4 contains the fractional coordinates of shortite-II, and Table S2-5 reports interatomic distances and angles of this structure. The transition results in a loss of the 2-fold rotation axis that is present in the orthorhombic structure. This decrease in symmetry creates a second calcium site and a third carbon site (and three more oxygen sites). The calcium ions remain in chains in the [101] direction in the monoclinic cell. While Ca1A decreases in coordination number (from 9-fold to 7-fold, with a site volume of $18.983 \text{ \AA}^3$), the Ca1B maintains the same coordination number at 9-fold with a site volume of $27.939 \text{ \AA}^3$. And, while the polyhedra change conformation (especially Ca1A, which becomes more topologically elongate) due to the shifting of carbonate ions, the face sharing polyhedra persist through the transition.

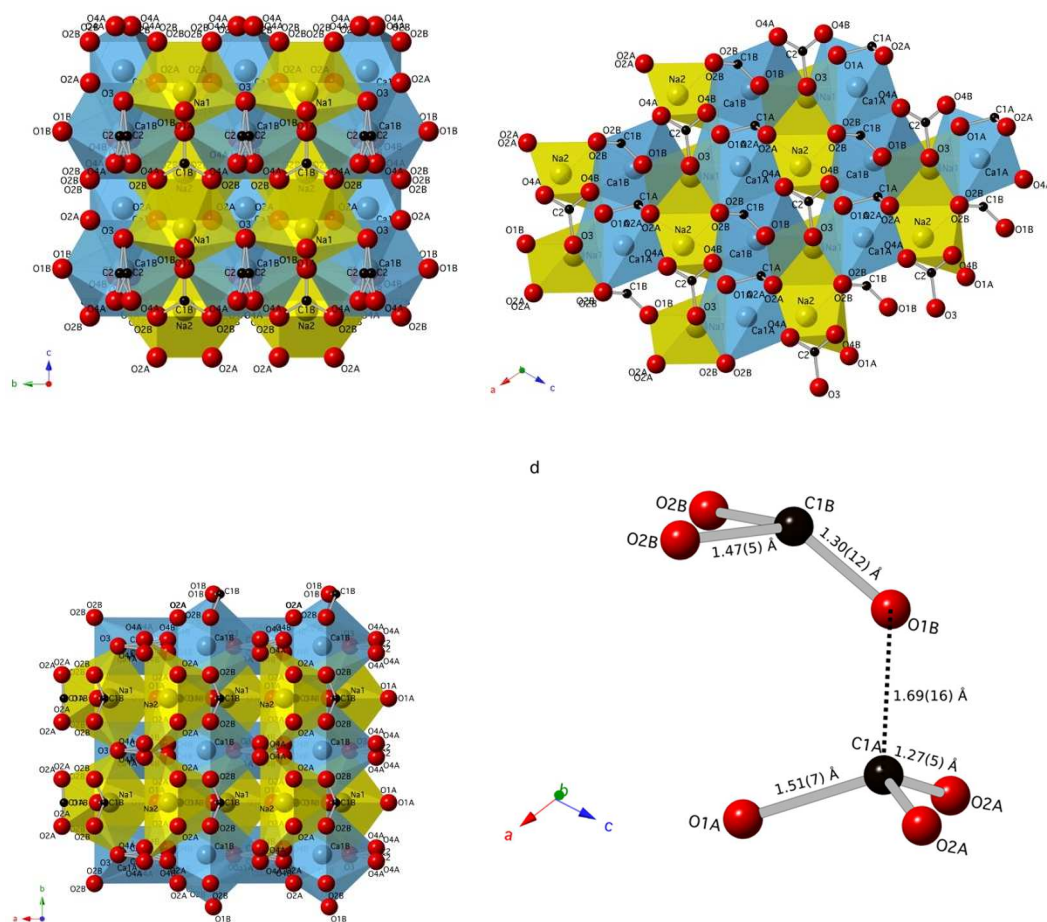


Figure 2-3. Shortite-II crystal structure (a) down the *a*-axis; (b) down the *b*-axis; (c) down the *c*-axis. (d) local carbonate environment of the C1A and C1B carbonate units, showing the onset of 3+1 coordination and dimerization.

The sodium ions change in relative position dramatically. In the shortite-I structure, the sodium ions are offset in the *a*- direction, while in shortite-II, they are no longer offset in the *b*-direction, and are aligned in the $[101]$ direction. This displacement is manifested in a change in polyhedral orientation: in shortite-I the polyhedra are all corner sharing, while in shortite-II, the Na polyhedra are face sharing. The two sites have different coordination numbers and volumes: Na1 is 8-fold coordinated with a site

volume of 21.015 Å³, and Na2 is 9-fold coordinated with an associated volume of 20.170 Å³.

The carbonate ions change dramatically in their bonding characteristics across the phase transition. The three carbonate ions are distorted significantly from planar geometries, and two undergo dimerization with a probable partial change in coordination across the transition. The carbonate ions were not restrained to idealized geometry in the inversion, which allowed us to observe these changes. Refinements with similarity constraints on the C-O bonds and planar restraints on the [CO₃]²⁻ ions resulted in systematically higher R1 and GooF values, so we chose to exclude these constraints and restraints from the final refinement (Table S3-6). This leads to somewhat larger errors in bond lengths than in the constrained/restrained models, but the determined structural information is more rich overall without these constraints. The carbonate ions (C1) that were equivalent in shortite-I (generated by the 2-fold rotation axis) are not equivalent above the transition, as that symmetry is lost. Instead, both carbons now lie on a mirror plane along with two oxygens, and the third oxygen is generated through the mirror plane. C1A lies 0.39(12) Å out of the plane generated from O1A(x2) and O2A. Bond distances between C1A and O1A and O2A are 1.51(7) Å and 1.27(5) Å respectively. C1B is 0.63(7) Å away from the plane generated by O1B and O2B(x2). The bond distances between C1B and O1B is 1.30(12) Å and between C1B and O2B is 1.47(5) Å. A dimer appears to form between these two carbonate ions: the distance between C1A and O1B is 1.69(16) Å (Fig. 2-3d, Table S2-5). This distance is likely marginally too long to be viewed a traditional C-O bond, but it is close enough

to have a major effect on both the C1A and C1B carbonate ions. This distortion, and interaction, is similar to the 3+1 coordination observed at much higher pressures (above ~63 GPa) in dolomite-III (Vennari and Williams 2018), and our results indicate that the dimerization, and partial shift in coordination, of carbonate groups can occur at transition zone pressures depending on the chemistry and local structural environment of carbonate units.

The third carbonate (containing C2) ion is positionally disordered. While O3 lies on the mirror plane, C2, O4A and O4B lie just off the mirror plane in the *b*-direction. The disorder in C2, O4A and O4B occurs along the *b*-axis. Assuming the disorder occurs across the mirror plane, these ions are more planar than the carbonates containing C1A and C1B, with C2 deviating from the O3-O4A-O4B plane by 0.14(6) Å. The distances between C2 and O3, O4A, O4B are 1.49(14), 1.19(15) and 1.31(13) Å, respectively (Table S2-5). Thus, the C2 carbonate group is also substantially distorted from an ideal 3-fold geometry, but it does not undergo the dimerization and partial coordination change of the C1A and C1B carbonate groups.

2.4.5 Shortite: Raman Results

A representative Raman spectrum of shortite at room temperature and room pressure is shown in Fig. 2-4; this agrees with previous results (Frost and Dickfos 2008), but more weak peaks are resolved. Lattice modes are present from ~100 to 300 cm⁻¹, and these are associated with vibrations between the carbonate groups and the sodium and calcium sublattices. As expected, peaks generated by each of the four fundamental vibrations of a free carbonate ion are also clearly present. These are the

symmetric stretches of the carbonate group ($\nu_1 \sim 1,080 \text{ cm}^{-1}$), the out of plane bend ($\nu_2 \sim 870 \text{ cm}^{-1}$), the asymmetric stretches ($\nu_3 \sim 1,415 \text{ cm}^{-1}$), and the in-plane bends ($\nu_4 \sim 700 \text{ cm}^{-1}$). In the unit cell of shortite, there are two distinct carbonate sites giving rise to multiple peaks for each associated normal mode; the C1 carbonate group is substantially distorted, whereas the C2 carbonate group is nearly trigonal (Fig. 2-1).

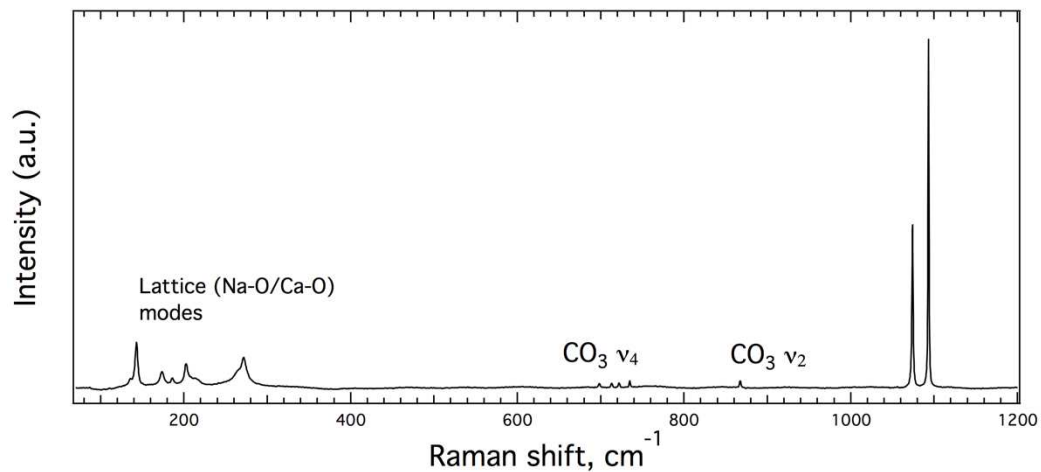


Figure 2-4. Representative room pressure, room temperature Raman spectrum of shortite.

Unlike Frost and Dickfos (2008), we are able to resolve a clear Raman-active ν_2 -associated carbonate mode, which appears as a single peak at 865 cm^{-1} , ν_4 as four peaks between 696 and 732 cm^{-1} , and ν_3 at 1405 cm^{-1} and 1513 cm^{-1} , in addition to the two peaks associated with ν_1 at 1071 and 1091 cm^{-1} . Factor group analysis indicates that of the 69 optically active vibrational modes of shortite, all are Raman active (of either A_1 , A_2 , B_1 or B_2 symmetries): the numbers of expected vibrational modes associated with each carbonate fundamental mode are 4, 5, 9 and 9 for ν_1 , ν_2 , ν_3 , and ν_4 , respectively. However, the number of A_1 and A_2 symmetry modes, which are anticipated to be the

most intense in the spectra, are 2, 1, 3 and 3, respectively. This distribution is in better accord with our observations, implying that most of the peaks we observe are of A_1 or A_2 symmetry.

2.4.6 Shortite: Room-Temperature, High-Pressure Raman

In our high-pressure, ambient-temperature Raman experiments, shortite was compressed at room temperature to ~ 26 GPa, and monitored on both compression and decompression; representative spectra on compression are shown in Fig. 2-5 a,b. Two dramatic phase transitions were observed: the first initiates at ~ 14.9 GPa (in accord with our X-ray observations), and the second is an apparent amorphization which initiates at 22 GPa and approaches completion around ~ 26 GPa. The number of peaks and, in many instances, their locations shift markedly at the first transition (Fig. 2-5a,b), and the number of peaks decreases dramatically at the amorphization transition. Indeed, the symmetric stretches of the carbonate unit shift to markedly lower frequency at the transition to the high-pressure phase (Fig. 2-5b), including a notably low-frequency component (at $\sim 1093 \text{ cm}^{-1}$ at 15 GPa) of the symmetric stretch appearing. Additionally, a lower frequency set of bands associated with the symmetric bending vibrations also appear at this transition. Each of these shifts are indicative of a weakening of a subset of the C-O bonds in the crystal, and are concordant with the Raman signature of the onset of 3+1 coordination of carbon group in dolomite-III (Vennari and Williams, 2018), and with our X-ray observations of carbonate dimerization.

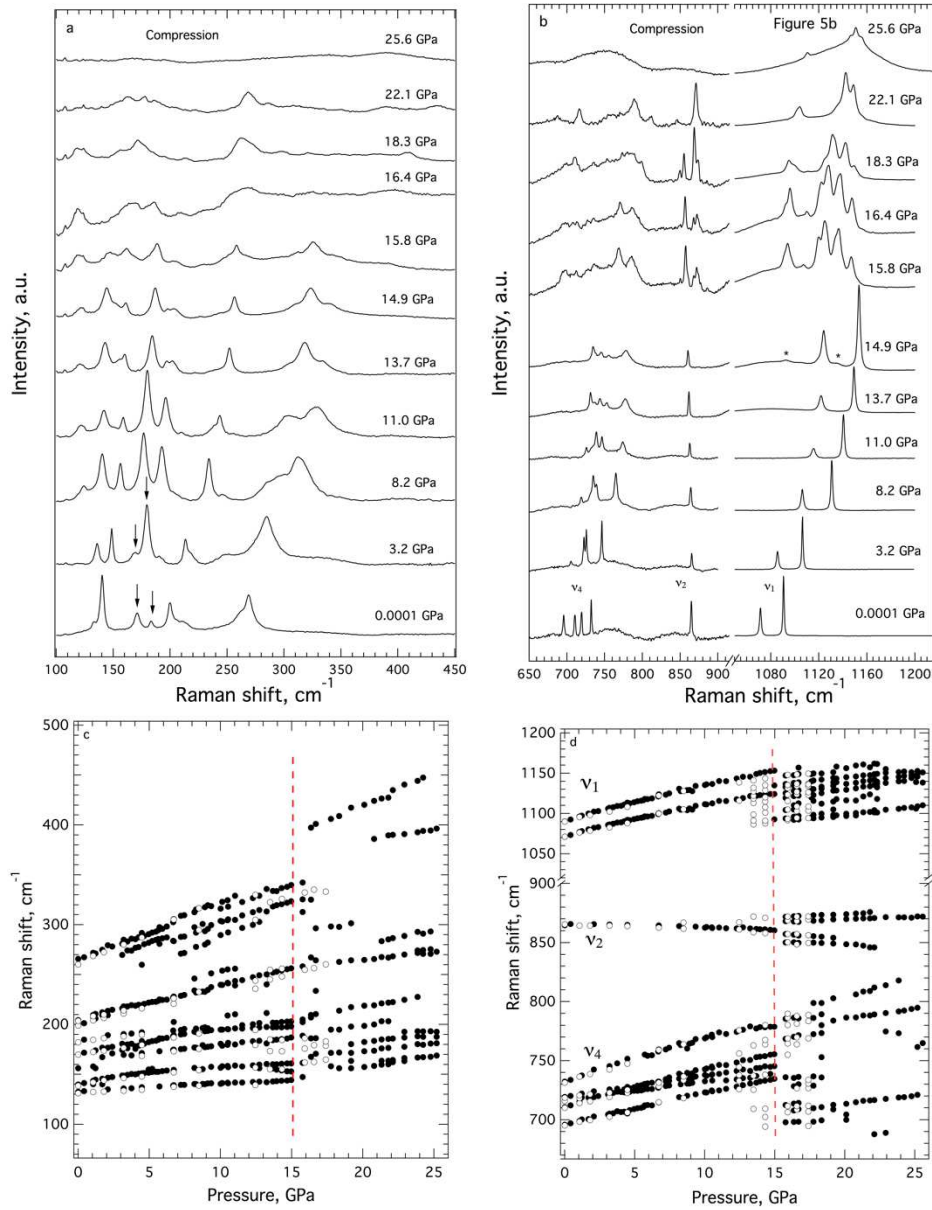


Figure 2-5. (a and b) Representative Raman spectra of the lattice modes and carbonate modes with compression. Arrows indicate the effects on intensity of preferred orientation; this is common within carbonate minerals. Asterisks are added to draw the eye to two small peaks that mark the initiation of the phase transition; (c and d) peak positions of observed Raman modes as a function of pressure at room temperature under (solid) compression and (open) decompression, from 17.5 GPa. Red dotted line indicates the shorttite-I to shorttite-II phase transition.

A less marked spectral change occurs near 17 GPa, as indicated primarily by splitting of the carbonate peaks, and particularly the ν_4 associated peaks (Fig. 2-5b); additional

changes are present in the low frequency region as peaks associated with shortite-I disappear (Fig. 2-5c). We attribute these changes, in accord with our X-ray data, to a completion of the sluggish phase change within the Raman experiments; that the transition is kinetically impeded is confirmed by our results on decompression from ~ 18 GPa (Fig. 2-5d), which show that shortite-II persists to ~ 13 GPa on decompression.

Above 22 GPa, the spectra become simpler as peaks are lost, and a markedly broad feature appears in the symmetric stretching region. By 26 GPa, most of the peaks associated with the carbonate groups have disappeared (although there is some evidence of residual ordering, as manifested by three small, persistent symmetric stretching peaks). The nature of the transition is thus strongly indicative of amorphization: this amorphization is irreversible, with the amorphous phase persisting on decompression.

Up to 14.8 GPa, most of the shortite-II bands shift monotonically under compression (Fig. 2-5a,b). Two lattice modes show somewhat more complex behavior (Table 1). At around 3.5 GPa, a mode that initiates around 275 cm^{-1} splits, and gives rise to another peak at lower frequency. This new peak remains until the transition; we attribute this to possible orientation effects within shortite, which are common in carbonates (such as calcite-II: L.-G. Liu & Mernagh, 1990), possibly coupled with an accidental degeneracy at low pressures. At 12 GPa, a lattice vibration near $\sim 150\text{ cm}^{-1}$ splits, with its lower frequency component decreasing in frequency with pressure up until the transition; it is possible that this mode softening is a precursor to the phase transition.

The bands which are derived from the three carbonate modes (ν_1 , ν_2 , ν_4) also shift monotonically upto 14.8 GPa. The out of plane bend, ν_2 , decreases linearly to 14.9 GPa with a slope of $-0.32 \text{ cm}^{-1}/\text{GPa}$ (Table 2-1). This decrease in frequency with pressure of this band is common in carbonates, and likely reflects the enhanced strength of bonding between the sodium and calcium with the oxygens within the carbonate group—as the Na/Ca-O bonds strengthen, the C-O out-of-plane bend weakens, and decreases in frequency (e.g., Kraft et al., 1991).

Assignment*	$\nu_0 \text{ (cm}^{-1}\text{)}$	$(d\nu_i/dP)$ to 14.9 GPa	γ_i
Na1-lattice	133	0.71(2)	0.31
Na1-lattice	140	1.23(5)	0.50
Ca1-lattice	171	1.88(8)	0.62
Ca1-lattice	199	3.48(5)	0.99
Na2-lattice	269	5.04(1)	1.06
C1: $(\text{CO}_3)^{2-} \nu_4$	696	2.59 (3)	0.21
C1: $(\text{CO}_3)^{2-} \nu_4$	710	1.63(6)	0.13
C1: $(\text{CO}_3)^{2-} \nu_4$	719	1.74(2)	0.14
C2: $(\text{CO}_3)^{2-} \nu_4$	732	3.17(9)	0.25
C1: $(\text{CO}_3)^{2-} \nu_2$	865	-0.32(2)	-0.02
C2: $(\text{CO}_3)^{2-} \nu_1$	1071	3.50(5)	0.19
C1: $(\text{CO}_3)^{2-} \nu_1$	1090	4.12(4)	0.21

Table 2-1. Raman modes observed at room temperature with increasing pressure, and calculated Grüneisen parameters of shortite-I (using a bulk modulus of 56.6 GPa) *Assignments are from the WURM database (Caracas and Bobocioiu 2011).

The in-plane bend initially has four peaks between 696 and 732 cm^{-1} at room pressure. As pressure is increased, a fifth peak is sporadically resolvable: again, this likely is either an orientation-dependent effect, or perhaps a manifestation of accidental degeneracy near room pressure. The slopes of the ν_4 -associated modes with pressure range from 1.63(6) to 3.17(9) $\text{cm}^{-1}/\text{GPa}$. These slopes are intermediate between those of the in-plane bend of the sodium carbonate trona (these values range from 4.14 to

5.66 cm⁻¹/GPa: O'Bannon et al., 2014) and those of the in-plane bend for aragonite (values from 1.4 to 1.8 cm⁻¹/GPa: Kraft et al., 1991).

The two symmetric stretching modes shift almost linearly with pressure up until the transition. The lower frequency peak initiating at 1071 cm⁻¹ shifts at a rate of 3.50(5) cm⁻¹/GPa, while the peak at 1090 cm⁻¹ shifts at a rate of 4.12(4) cm⁻¹/GPa: as such, the separation of these peaks increases weakly with compression. Calculations done by Caracas and Bobocioiu (2011) in the WURM database have calculated the expected Raman spectrum and assignments for shortite, which help identify which carbonate ion generates each peak. The lower frequency peak is associated with the C2 carbonate groups, while the higher frequency peak is produced by the more distorted C1 groups: the weak increase in separation implies that the structural differences between these two groups is enhanced at high pressures. As with the in-plane bends, the mode shifts lie between those of aragonite (2.3 cm⁻¹/GPa; Kraft et al., 1991) and trona (5.3 cm⁻¹/GPa; O'Bannon et al., 2014).

The phase transition to shortite-II initiates at 14.9 GPa in the Raman experiments, and is first detectable in the symmetric stretch of the carbonate ion: this is likely because it is the most intense vibration in the spectrum, and new peaks appear at 1093 cm⁻¹ and at 1135 cm⁻¹ (Fig. 2-5b). By 15.8 GPa, ~7 carbonate symmetric stretching vibrations are resolved, with most of these lying at lower frequency than the carbonate stretching vibrations in the starting material. These lowered frequencies directly indicate that the C-O bonds have, on average, weakened across the transition, and the greater number of peaks indicates that there are both a larger variation in the

carbon-oxygen bonds, and in the crystallographically distinct carbonate groups in the unit cell of shortite-II relative to shortite-I. The ν_2 -associated band undergoes similar splitting, with at least four components clearly visible in the high-pressure phase. The two higher frequency of the ν_2 -peaks each shift positively with pressure in the high-pressure phase, while the lower frequency two behave in accord with that of most carbonates, with clear shifts to lower frequencies with pressure. That a subset of the out-of-plane bends increases in frequency and stiffens under compression in shortite-II is fully consistent with both narrowed, and possible pressure-induced narrowing of, O-C-O angles in the high-pressure phase. Thus, these variable shifts are in accord with the CO_3 groups' deviation from a planar geometry in shortite-II, and the out-of-plane bends that increase in frequency are hence assigned to the C1A and C1B carbonate groups.

The ν_4 -associated peaks significantly broaden across the transition, and it is not straightforward to resolve the number of peaks, although at least 5-7 are present (Fig. 2-5b). What is clear is that, as with the symmetric-stretching peaks, several of the ν_4 -associated peaks lie at lower frequencies than in the low-pressure phase. Thus, both the symmetric stretch and the ν_4 in-plane bending bands drop significantly after the initial phase transition (by an average of 31 and 37 cm^{-1} , respectively). The drop in frequency is again consistent with the C-O bonds being (on average) less strong in the high-pressure phase relative to within shortite, and is fully consistent with lengthening of the C-O bonds. Indeed, the magnitude of the frequency drop associated with the carbonate symmetric stretching bands is substantially larger than those observed in high-pressure

transitions in other alkali- or alkaline-earth CO₃-bearing phases (e.g., Catalli & Williams, 2005; Koch-Müller et al., 2016; O'Bannon et al., 2014).

Above 16-17 GPa (where the high-pressure transition likely is completed), the lattice modes shift in character, with new peaks replacing those of shortite-I. Nevertheless, some modes appear to persist through the transition: these vibrations, with initial frequencies at 171 and 199 cm⁻¹, are associated with the Ca1-lattice vibrations (Table 1; Caracas & Bobocioiu, 2011), and their persistence likely reflects that one of the shortite-II calcium sites is similar to that within shortite-I. The disappearance of other bands (such as those initiating near 269 cm⁻¹, which are associated with the Na2 site: Fig. 2-2c) across the transition likely reflects the tandem distortions of both the sodium sites and the carbonate units, in accord with the single crystal structural data. In particular, the Na2 polyhedron is initially in a six-fold coordinate trigonal prism (e.g., Fig. 2-1 and Dickens et al., 1971) and after the transition, it is 8-fold: a dramatic change. We hypothesize that a portion of the new modes between 160 and 190 cm⁻¹ at 20 GPa represent new Na2-lattice vibrations, and are generated because of the new bonds (and weaker individual bonds in higher coordination) that form between Na2 and oxygen atoms.

With respect to the bonding characteristics of Na, the four to five initial out-of-plane bending (ν_2) modes generated following the high-pressure phase transition gradually decrease in number through the pressure range from 17-24 GPa, with the final resolved peak having a positive pressure shift of 0.45(2) cm⁻¹/GPa (the opposite sign of the pressure shift in shortite-I) which may reflect both the dramatic shift in O-

C-O angles across the transition, and the higher coordination number/weaker cation-oxygen bonds associated with the sodium ion.

Above ~17 GPa, shortite-II remains until amorphization occurs between 22 and 26 GPa. Over this pressure range, the lattice modes increase regularly in frequency with no major changes until 25-26 GPa. At this pressure, the low frequency modes from 150-450 cm^{-1} and the carbonate ion bands between 650-900 cm^{-1} broaden and weaken, and become unresolvable. The three discrete symmetric stretching bands that remain marginally visible on the broad background at the highest pressures (Fig. 2-5b) likely reflect a small percentage of ordered regions within the sample, as the intensity of Raman scattering from fully amorphized material is expected to be markedly weaker than that from ordered zones. The carbonate peaks begin to broaden at 22 GPa, and this is likely the beginning of the amorphization (Fig 2-5a,b). The amorphization is nearly completed at ~26 GPa, where almost all of the modes have become unresolvable.

2.4.7 Nature and causes of the 300 K phase transitions(s) in shortite

Below 15 GPa, the major compaction direction within the shortite structure is along the *c*-axis (Fig. 2-2b). Based on the crystal structure, we believe that this is achieved mostly through compaction of the sodium polyhedra and the void space within the structure (Fig. 2-1, inset). As the sodium ions are initially off-set from one another along the *a*-axis (with a zig zag down the *c* direction), the inter-Na repulsion is not strongly affected by the rapid *c*-axis compaction (Fig 2-2e).

At 15 GPa, several observations bear on the properties of the transition: (1) there is a volume drop (~2.5%) associated with the transition, (2) there is a change in

polyhedral stacking along the *b*-axis of shortite-II, (3) there is a major change in the bonding characteristics of the C1 carbonate groups (the change in the C2 carbonates, a manifested by the change in its associated symmetric stretch, is less severe), and (4) a small subset of the Raman lattice modes appear to persist across the transition, while most bands disappear and new bands initiate. Ultimately, shortite-II becomes unstable with respect to an amorphous phase by 26 GPa: an unusual pressure-induced transition within carbonates that likely reflects a topological frustration with sodium and calcium ion face-sharing becoming unstable.

We hypothesize that cation-cation repulsion between the calcium and sodium ions is the driver of the transition to shortite-II. The rearrangement of the sodium ions across the phase transition causes the Na polyhedra to change from corner sharing in shortite-I to edge sharing in shortite-II, and this shift in packing, coupled with the elimination of the void space within the structure, results in the volume drop of ~2.5%. This is supported by the dramatic change in Raman lattice modes after the phase change to shortite-II, with bands associated with the sodium sites in shortite-I (Table 1) disappearing.

The initiation of dimerization of the carbonate ions in shortite-II (Fig. 2-3) is manifested in both the single crystal diffraction data and the Raman spectra. The approach of the fourth oxygen (O1B) to C1A at ~1.7 Å clearly affects the vibrations associated with both the C1A and C1B carbonate groups: in both cases, the symmetric stretching vibrations and in-plane bends are notably reduced in frequency, while the out-of-plane bend is increased. Given the assignments of the symmetric stretch peaks

of Caracas & Bobocioiu, (2011), the higher frequency symmetric stretching vibration associated with the C1 in shortite-I is replaced above 15 GPa with lower frequency modes. The lowest frequency symmetric stretch in shortite-II is at 1093 cm^{-1} ; a frequency comparable to this carbonate vibration at ambient pressure. At 15 GPa, however, it represents an extremely low-lying symmetric stretching vibration (e.g. Kraft et al., 1991; Gillet et al., 1993; Santillán and Williams, 2004; Vennari and Williams, 2018). This low-lying symmetric stretch is a natural consequence of the 3+1 coordination of the C1-associated carbonate groups (Fig. 2-3d). This general configuration was proposed to be present in dolomite-III based on an extrapolation of single crystal X-ray diffraction results (Merlini et al. 2012) and documented to be present above 63 GPa using Raman spectroscopy (Vennari and Williams 2018). In dolomite, the highest pressure crystal structure reported is at 56 GPa (Merlini et al. 2012), where the interatomic distance between the carbon and the approaching 4th closest oxygen was 2.066 Å. In shortite-II, the interatomic distance between C1A and O1B is 1.69(16) at 15 GPa. In dolomite-III, distances of $\sim 1.7\text{ Å}$ were predicted to occur at $\sim 80\text{ GPa}$. However, the spectral signature of 3+1 coordination initiated at 63 GPa (Vennari and Williams, 2018). In dolomite-III, the in-plane and out-of-plane bends merge together into a multiplet of modes; in contrast, in shortite-II, the in-plane bend develops into a multiplet that is clearly separate from the out of plane bends. This may be due to differing degrees of distortion within carbonate groups: in shortite-II, the carbonate ions are much less planar than those in dolomite are inferred to be under pressure (Merlini et al., 2012).

The amorphization transition is certainly driven by an instability of the monoclinic-P shortite-II phase. The observed diffuse scattering in shortite-II (Fig. S2-1b,c) may be a precursor to the amorphization. It is possible that disordering of the Ca polyhedral chains along the shortite-II [101] direction generates the transition. These are distorted polyhedra that compact anisotropically under compression, and the face-sharing chain could ultimately be destabilized by inter-cation repulsion following the extensive compaction that has occurred along the [101] direction. The shortite-II structure is racked with energetically anomalous features, including from two sets of face sharing polyhedral, markedly distorted carbonate groups, and carbonates approaching 4-fold coordination. It is not surprising that this structure is destabilized as cations approach each other, or as a subset of the carbonates approach tetrahedral coordination.

2.4.8 Nyerereite: Raman Spectra

Nyerereite ($\text{Na}_2\text{Ca}(\text{CO}_3)_2$) is known to be a product of shortite instability at low-pressure and temperature conditions (Shatskiy et al. 2015a). Therefore, understanding its Raman spectra at high-pressures is critical for assessing the high-temperature reversion products of shortite. Accordingly, we measured the high-pressure Raman spectra of nyerereite to pressures of 25 GPa. This complements recent work to 6.4 GPa by Rashchenko et al. (2017). The crystal structure of nyerereite is complex due to the existence of three ambient pressure phases (α, β, γ), its incommensurate modulation (Gavryushkin et al. 2016), and variable elemental concentration (in all natural samples of nyerereite, there is some amount of substitution of sulfur (as SO_4), phosphorus (as

PO₄), and other alkalis or alkaline earths for the sodium or carbonate ions: Gavryushkin et al. (2016). The average unit cell is in the orthorhombic crystal system with space group *Cmc2₁* (McKie and Frankis 1977). The crystal structure is incomplete (lacking two oxygens' positions) due to these complications. This complex structure is reflected in the Raman spectrum (Fig. S2-2), where there are only very broad and low intensity lattice modes, modes associated with the carbonate ion, and a band associated with sulfate defects.

Initially, under pressure, we were able to resolve one in plane bending and two symmetric stretching vibrations of the carbonate group up to 25 GPa (Fig. S2-3a). The peaks are initially reasonably sharp, and no decrease in peak width is observed under pressure, indicating that there is no pressure-induced ordering. As such, we believe nyerereite remains distorted and incommensurate with pressure. Up to 5 GPa, the mode associated with the in-plane bend increases in frequency with pressure at 1.33(32) cm⁻¹/GPa; this shift is similar to the pressure shift of shortite's in plane bend, and with the shift reported by Rashchenko et al. (2017) above 3 GPa. The two modes associated with the symmetric stretch also increase in frequency with pressure at 2.89(35) and 3.20(16) cm⁻¹/GPa (Fig. S2-3a,b, Table S2-7), which are slightly lower than the shifts of Rashchenko et al. (2017). Both these shifts are less than that of shortite, indicating that the symmetric stretches in nyerereite are less affected by compression than the carbonate ions in shortite.

At 5 GPa, the in-plane bend splits from one peak to three peaks; this splitting persists to the highest pressure, 25 GPa. Rashchenko et al. (2017) report a change in

pressure dependences of the Raman bands of nyerereite near 3 GPa, but do not observe splitting. The three resulting deconvolved in-plane modes increase in frequency at 1.21(3), 1.80(8) and 2.22(16) $\text{cm}^{-1}/\text{GPa}$ (Fig. S2-3a,b, Table S7). The onset of this splitting implies that a phase transition and associated shift in symmetry has taken place in nyerereite at ~ 5 GPa. The symmetric stretches do not undergo a clear splitting at 5 GPa, but the modes do begin to broaden near this pressure, and this trend continues to 25 GPa (Fig. S2-3a). The pressure shifts decrease above 5 GPa, which is typical for vibrational modes as the structure stiffens. Overall, due to the broad peaks associated with both carbonate vibrations, the high-pressure nyerereite structure appears to be both disordered and likely lower symmetry than ambient pressure nyerereite.

2.4.9 A high pressure/high temperature phase in shortite above 12 GPa

In order to assess the nature of the thermodynamically stable phase of shortite at high-pressure and temperature conditions, the amorphous phase (>26 GPa) of shortite was heated at high pressures. In one set of experiments, this phase was laser-heated to temperatures between 1600 and 2000 K at 26 GPa, decompressed, and sequentially re-heated at different pressures on decompression. The sample was quenched to 300 K following each heating episode, and was characterized at pressure using Raman spectroscopy. In another experiment, the sample was heated at high pressures, and then decompressed at room temperature without further heating. A new crystalline high-pressure phase is generated from the high-pressure amorphous phase following heating as illustrated by new, narrower and well defined symmetric stretching peaks (Fig. 2-6). These peaks differ markedly from both the amorphous

high-pressure phase formed at 300 K, and the high-pressure phases observed on compression at 300 K, and we associate them with a shortite-III phase. Indeed, the lowest frequency symmetric stretching vibration that is indicative of the 3+1 carbon coordination in shortite-III, which is near 1110 cm^{-1} at 26 GPa, is clearly not present in the high-pressure, high-temperature phase. As the grain size is small in the laser-heated samples and preferred alignment of the high-pressure phase is possible, the ability to resolve peaks in the thermally-quenched Raman measurements is less than in the 300 K spectroscopic measurements. Therefore, no other peaks were clearly identified at the highest pressures after laser heating. After progressive decompression to below 18 GPa and further laser-annealing, in-plane and out-of-plane bending bands and lattice modes were clearly resolved, suggesting that the sample recrystallized within the high-pressure, high temperature phase.

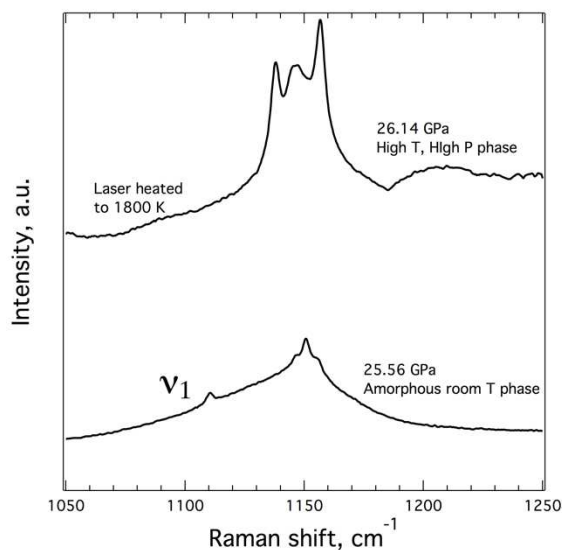


Figure 2-6. Raman spectra of the high-pressure amorphous phase and laser-heated, crystalline shortite-III at high pressure.

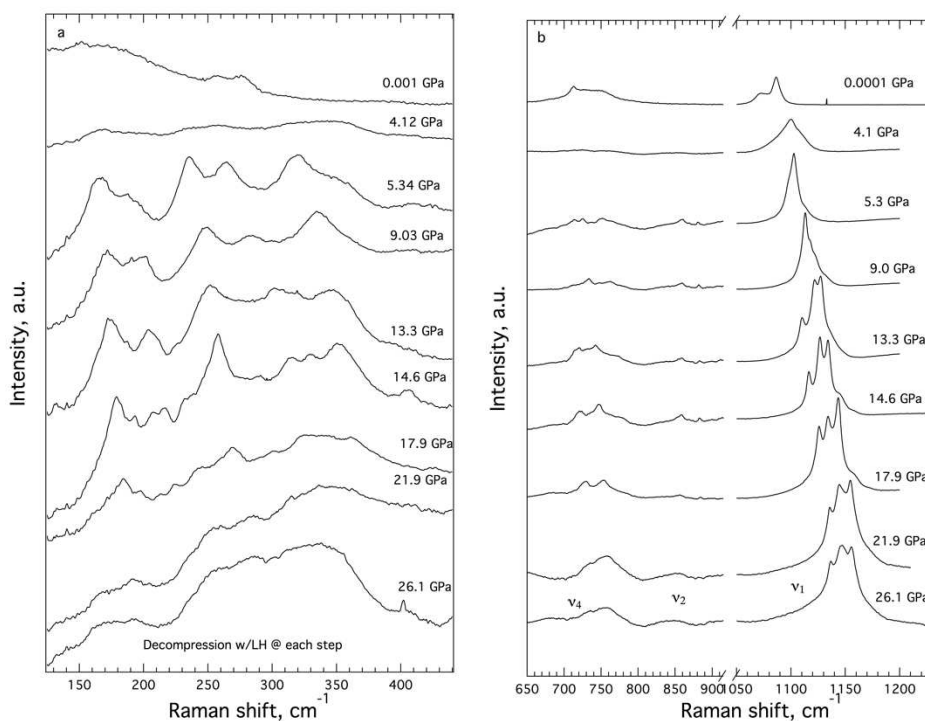


Figure 2-7. (a and b) Representative Raman spectra of shortite during decompression with laser annealing at each pressure step.

During laser heating at each pressure step on decompression, two major additional changes were observed at 12 GPa and 5 GPa (Fig. 2-7a,b, Fig. S2-4a,b). Between 26 GPa and 12 GPa, the symmetric stretch peaks decrease monotonically in frequency. Below 12 GPa, there is a dramatic change in the nature of the symmetric stretching peaks; they shift from three distinct intense peaks to one major peak with high frequency shoulders. This transition at 12 GPa can be explained by decomposition of the high pressure, high temperature phase of shortite to aragonite (CaCO_3) and nyerereite ($\text{Na}_2\text{Ca}(\text{CO}_3)_2$): this disproportionation is in agreement with the phase equilibria observations at 6 GPa of Shatskiy, Gavryushkin, et al. (2015) but bounded from the high-pressure side. Below 5 GPa, lattice modes along with the in-plane bend and out-of-plane bend decrease dramatically in intensity suggesting that there may be

a further shift in phase that takes place within the nyerereite/aragonite assemblage on heating, and probably within the nyerereite. The change at 5 GPa is most plausibly attributed to a change in the phase of nyerereite quenched from high temperature at high pressures. Whether these changes in intensity are connected to the transition we observe in nyerereite at 5 GPa and 300 K (Fig. S2-3a,b) is unclear, but it is possible that this new, high-temperature induced phase is a more stable phase that is kinetically inaccessible via simple compression at 300 K, and that the phase produced at 300 K is metastable. At the lowest pressures, the only lattice modes that are observed are associated with aragonite (Fig. 2-7a,b, Fig. S2-4a,b).

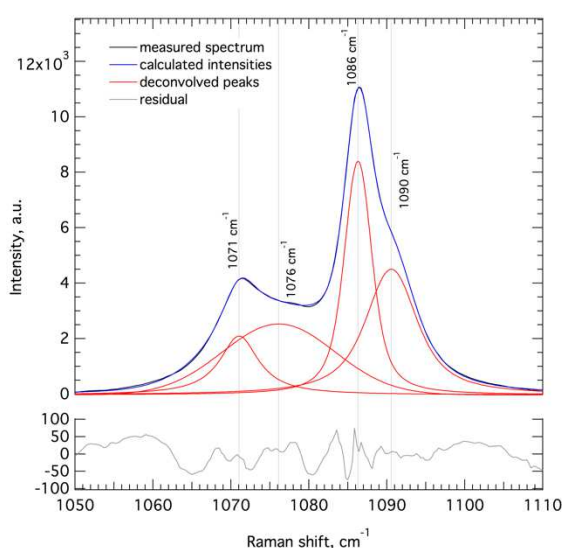


Figure 2-8. Deconvolution of the Raman spectrum of the shortite decomposition product at ambient pressure after laser heating with annealing at each pressure step.

The final product of the sequential heating when fully decompressed is likely a mixed phase assemblage. Due to the complexity of the Na-Ca carbonate system, we propose two possible mixtures that are compatible with the spectra. The most straightforward interpretation of the symmetric stretch region is a combination of

nyerereite (1076, 1086 cm^{-1}), aragonite (1086 cm^{-1}) and shortite-I (1071, 1090 cm^{-1}) as illustrated by the deconvolution of the symmetric stretches of a decompressed sample (Fig. 2-8). The presence of nyerereite at room pressure conditions is supported by Shatskiy, Gavryushkin, et al., (2015) who suggested nyerereite is not stable at mantle relevant conditions, but forms at lower temperatures and pressures. While that interpretation is consistent with the observed spectrum, the decomposition of calcium/sodium carbonates under pressure at elevated temperatures is complex and have not been observed to contain shortite. In heated large volume experiments at 3 and 6 GPa, the observed assemblage of sodium/calcium carbonates consists of CaCO_3 (aragonite and calcite), $\text{Na}_2\text{Ca}(\text{CO}_3)_3$, $\text{Na}_2\text{Ca}_3(\text{CO}_3)_4$ and $\text{Na}_2\text{Ca}_4(\text{CO}_3)_5$ (Shatskiy et al. 2013; Podborodnikov et al. 2018). Thus it is possible that the low-pressure, heated assemblage might consist of a more complicated series of sodium/calcium carbonates: for example, $\text{Na}_2\text{Ca}_3(\text{CO}_3)_4$ (1089, 1085 cm^{-1}) and $\text{Na}_2\text{Ca}(\text{CO}_3)_2$ (1070, 1082 cm^{-1}) (Podborodnikov et al. 2018). One major expected mode in this scenario is not present in our spectrum: the rather strong peak of Podborodnikov et al. (2018) at 1082 cm^{-1} that corresponds to the symmetric stretch in $\text{Na}_2\text{Ca}(\text{CO}_3)_2$. This absence might be explained by preferred orientation effects on the intensity of the mode. However, given our results, we believe it is more likely the two mixed sodium-calcium phases (Podborodnikov et al., 2018) are not present, and that the assemblage we observe shortite, nyerereite and aragonite, which may be a consequence of thermal gradients within our samples.

To confirm the production of a new phase, and determine the (meta)stability of

the high pressure, high temperature phase of shortite at 300 K, we decompressed at room temperature a sample that was laser-heated at 27 GPa. Here, decomposition of the high pressure/high temperature phase of shortite to nyerereite and aragonite was not observed (Fig. 2-9a,b, Fig. S2-5a,b), confirming that the decomposition of the high-pressure/high-temperature phase is thermally activated, and appears to only occur below 12 GPa. During decompression at 300 K of the laser-heated phase, the Raman spectrum becomes progressively better resolved (Fig. 2-9).

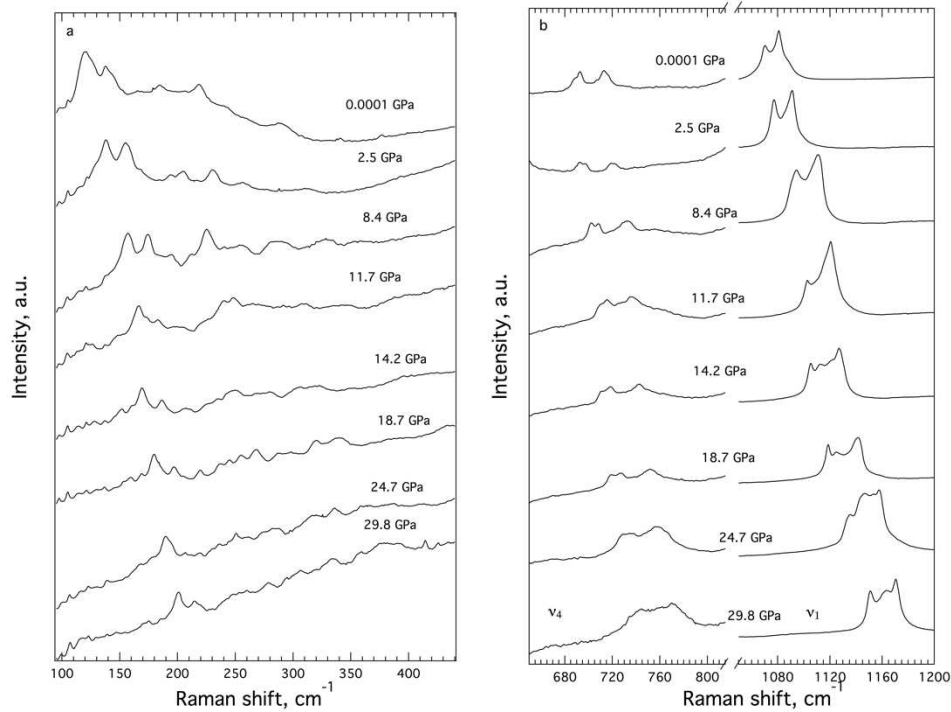


Figure 2-9. (a and b) Representative Raman spectra during decompression at ambient temperature after laser heating at 27 GPa; intensities of the in-plane bend are enhanced not to scale relative to stretching bands in (b).

Between 30 and 12 GPa, there are minor intensity variations between the carbonate symmetric stretches and the in-plane bend: these may be due to preferred orientation effects. However, following deconvolution, the peak positions shift

normally, to lower frequency, with decreases in pressure (Fig. 2-9a,b, Fig. S2-5a,b). The modes associated with the symmetric stretch decrease in frequency at rates between 2.8 and 2.9 $\text{cm}^{-1}/\text{GPa}$.

At around 12 GPa, there is a marked change in intensity of the carbonate symmetric stretches: two peaks become more intense, while the others weaken (Fig. 2-9b). However, there is no change in the number of peaks. We believe that these changes are associated with a subtle change in the symmetry of the high pressure/temperature phase of shortite on decompression. The lattice modes also become better defined at lower pressures (Fig. 2-9a,b, Fig. S2-5a,b).

This phase persists on decompression from 12 GPa to room pressure. It is, however, distinct in its peak locations from the starting shortite material, and we infer that it is a modification of the high pressure/high-temperature phase that is quenchable to ambient pressures. The modes associated with the symmetric stretch decrease in frequency, on average, more rapidly than above 12 GPa, with shifts between 2.7 and 3.3 $\text{cm}^{-1}/\text{GPa}$. The Raman spectrum of the decompressed product (Fig. 2-10) does not match the Raman spectrum of any other sodium calcium carbonate with Na:Ca ratios of 1:0, 4:1, 2:3, 2:4 or 0:1, as observed among carbonate phases synthesized at 6 GPa and 950 °C (Shatskiy et al. 2015a), nor does it match the starting shortite (Fig. 2-3). Hence, the phase synthesized at high pressures and quenched from high temperatures appears to be metastable at ambient conditions, and shortite-III, based on our sequential heating data on decompression, appears to be the stable high-temperature phase of shortite at pressures between 12 and at least 30 GPa. As such, a phase with shortite

stoichiometry could represent a re-entrant phase in alkali-bearing carbonate systems above pressures of 12 GPa, spanning at least to those at the top of the lower mantle.

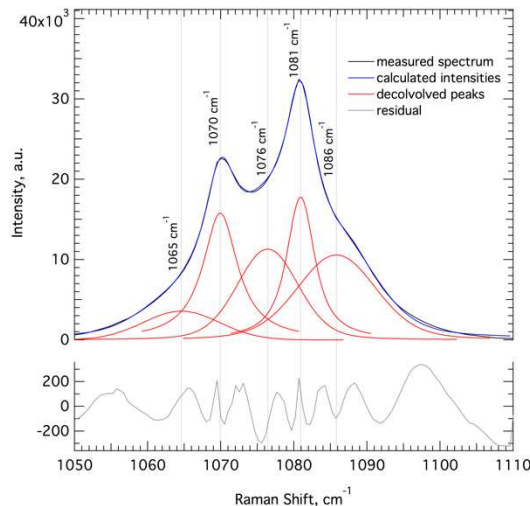


Figure 2-10. Deconvolution of the Raman spectrum of the shortite decompression product after laser heating at 27 GPa and decompressing at 300 K to ambient pressure.

2.5 Conclusions

The isothermal bulk modulus of shortite-I is 56.6(39) GPa, with its pressure derivative being 4.8(11): this is among the more compressible carbonates of potential relevance to Earth's mantle. Up to 14 GPa, the compression is highly anisotropic, with the most compressible axis being the *c*-axis. Two high pressure phase transitions are observed at room temperature: at 15 GPa and 22-26 GPa. The first is a first-order phase transition: shortite-II is in the monoclinic-P system, with a volume drop of ~2.5%, and there are dramatic changes in the bonding strength of the carbonate ions.

This transition is completed by 17 GPa and is associated with changes and increases in the coordination numbers of the Na/Ca sites. Notably, dimerization of carbonate ions and a shift to 3+1 coordination of half of the carbonate groups in shortite

is observed at pressures above 15-17 GPa. This is far lower in pressure than such a bonding configuration has previously been observed, and indicates that carbonate coordination may become less well-defined within complex phases and liquids within Earth's transition zone and shallow lower mantle. Clearly, deep lower mantle pressures are not required to stabilize 3+1 coordination of carbonate groups. This observation is important for carbon retention at depth: enhanced polymerization of carbonate ions under pressure could lead to marked shifts in stabilities, phase equilibria, and melt densities of carbonates at shallower depths than those at which coordination changes of the carbonate unit have previously been inferred to take place.

An amorphization transition also occurs at 300 K in shortite above 22 GPa: such amorphization is uncommon in non-framework materials, and particularly rare in carbonates. We speculate that this amorphization is associated with an onset of irregular coordination of the cations, as suggested by the lack of low frequency vibrations. The associated disordering and more extensive dimerization of the carbonate units within this material are also implicated in the amorphization, as manifested by the extended amplitude towards low frequencies of the carbonate symmetric stretch in the amorphous phase (Fig. 2-5b).

Experiments at high pressures and quenched from high temperatures indicate that a new phase of shortite, shortite-III, is stable between 12 and at least 30 GPa. The high pressure, high temperature structure of this phase has not been solved, but this high-pressure, high-temperature form of shortite appears to be stable relative to the high pressure/high temperature assemblage of nyerereite and aragonite. Therefore, a

phase of shortite stoichiometry could represent a protolith phase for kimberlitic or carbonatitic magmas in Earth's deep upper mantle, transition zone and shallow upper mantle. This high-pressure phase of calcium alkali carbonates appears to convert to a low-pressure nyerereite and aragonite assemblage at lower pressures at high temperature (below 12 GPa). Thus, it appears that a phase of shortite stoichiometry could be a re-entrant phase within the phase diagram of alkali-/alkaline earth carbonates at pressure above 12 GPa. In sum, a key aspect of our high pressure and high temperature results is the demonstration that phases in the alkali-calcium-carbonate systems that have limited stability fields at low pressures and temperatures can show notable polymorphism at both high pressures and high temperatures that could stabilize them at deeper depths: hence, in situ, high-pressure, high-temperature phase equilibria work is of critical importance in characterizing the stabilities of phases within these compositional systems.

2.6 Acknowledgments, Samples, and Data

We thank Earl O'Bannon, Nico Giordano, Simon Teat, and Elise Knittle for helpful discussions. We would like to thank Martin Kunz and Andrew Doran for help with gas loading, and Dale Burns at Stanford University for help with the microprobe measurements. Anton Shatskiy and an anonymous reviewer are thanked for helpful comments. Work supported by NSF-EAR1620423, and with partial support from COMPRES under NSF Cooperative Agreement EAR1606856. We also thank the Advanced Light Source, which is supported by the Director, Office of Science, Office

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2.7 Supporting Information

2.7.1 Supporting Text: Refinement of shortite-II

Refinement of the shortite-II structure originally was done with distance similarity restraints on the carbonate oxygens and carbons, and a soft planarity restraint. All three carbonate anions were treated as identical, and the refinement did not converge in this state. Upon removal of the distance and planarity restraints, the refinement converged to the current model. If distance similarity restraints are placed on the carbonate anions, in the current model, the R1 increases to 12.17%, and the largest two residual density peaks increase to 1.2 and 1.0 e-/Å, from 11.71%, 1.17 and 0.94 e-/Å respectively. This change sounds quite innocuous, but the resulting carbonate bonds are on average 1.36Å, which is much longer than the typical carbonate carbon-oxygen bond (1.3Å), which suggests the distance similarity model is incorrect. Even within the distance similarity model, the C1A and C1B carbonate anions are fairly pyramidalized, with out-of-plane carbon displacements of 0.38(11)Å and 0.36(9)Å respectively. Lastly, the 3+1 coordination is maintained, even with the distance similarity restraints- the C1A-O1B distance contracts to 1.82(16)Å, which is still close enough to represent a significant interaction.

2.7.1 Supporting Figures and tables

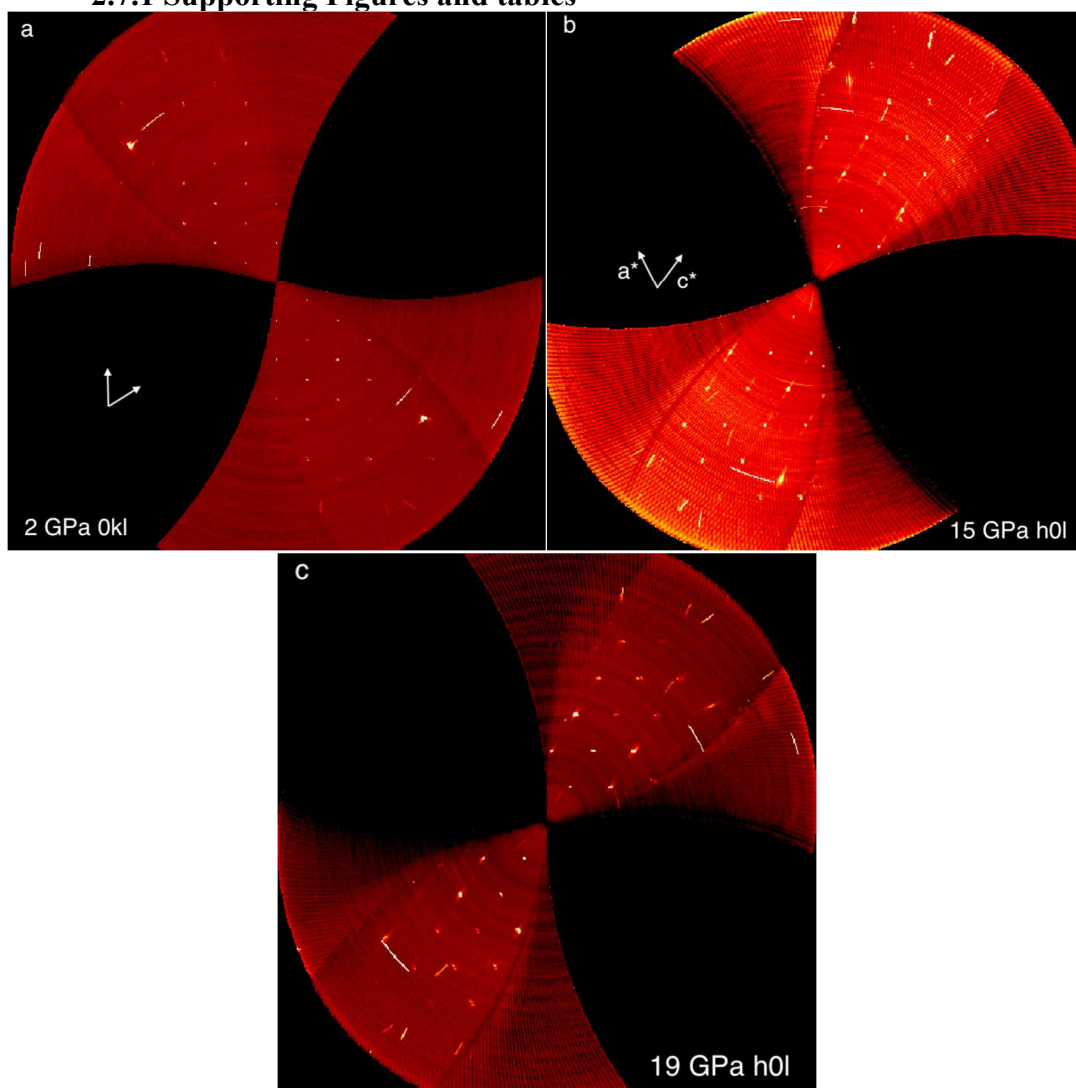


Figure S2-1. Synthesized, precession images of shortite under pressure at (a) 2 GPa, (b) 15 GPa, and (c) 19 GPa.

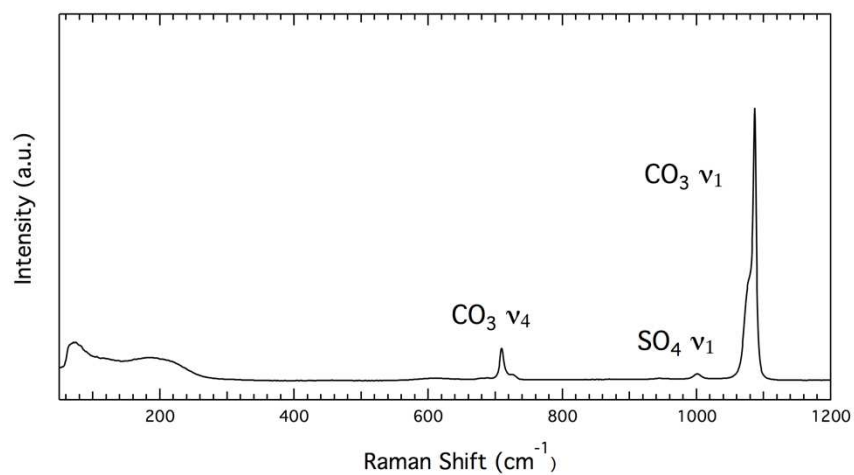


Figure S2-2. Representative room pressure and temperature, Raman spectrum of natural nyerereite.

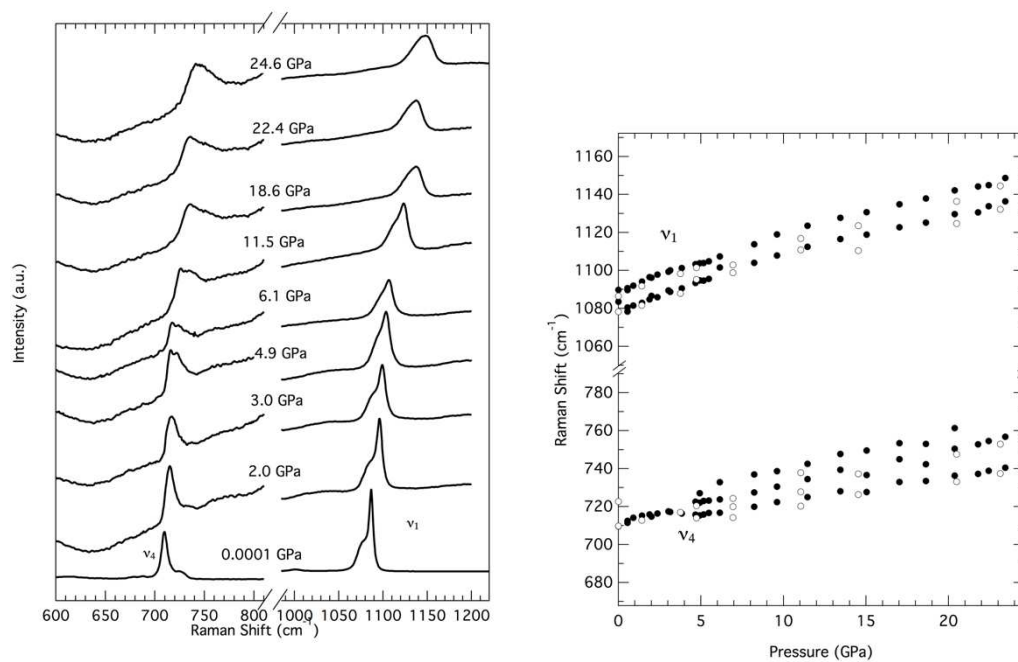


Figure S2-3. (a) Representative Raman spectra of nyerereite at ambient temperature under compression; (b) closed circles are observed Raman peak positions under compression, open circles are observed Raman peak positions under decompression.

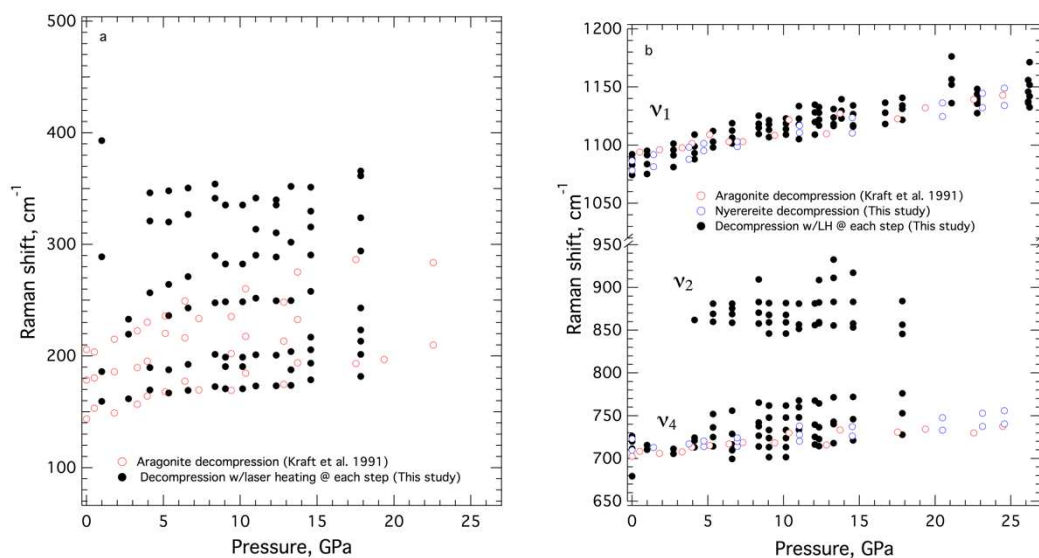


Figure S2-4 (a and b). Black circles are peak positions of observed Raman modes as a function of pressure at room temperature with laser annealing, red open circles are peak positions of the Raman modes of aragonite (Kraft et al. 1991).

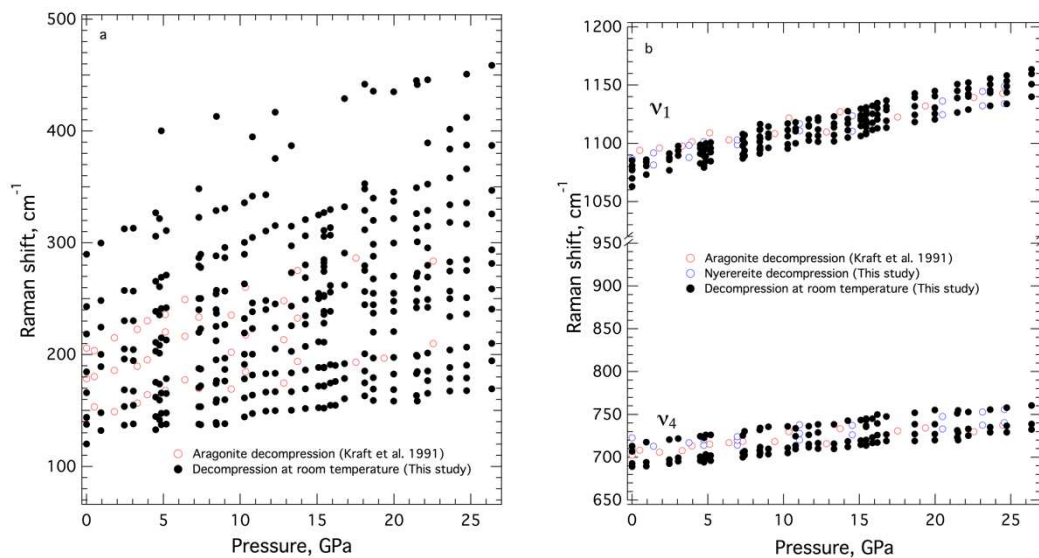


Figure S2-5 (a and b). Black circles are peak positions of observed Raman modes as a function of pressure at room temperature, red open circles are peak positions of Raman modes of aragonite (Kraft et al. 1991), blue open circles are peak positions of Raman modes of nyerereite. No particular correlation is observed between the observed peaks and those of aragonite and nyerereite spectra.

Wavelength (Å)	0.77490
Temperature (K)	298
Crystal system	Orthorhombic
Space group	<i>Amm2</i>
<i>a</i> (Å)	4.9571(3)
<i>b</i> (Å)	11.0514(6)
<i>c</i> (Å)	7.1242(4)
Volume (Å ³)	390.28(4)
<i>Z</i>	2
Nreflections	3098
Nunique	1069
R1 (%)	1.87
wR2(%)	4.45
GooF	1.055

Table S2-1. Unit-cell parameters and experimental details of shortite single crystal refinement at room temperature and room pressure.

Atom	x	y	z
Ca1	0.5000	0.21653(3)	0.00000(4)
Na1	0.0000	0.0000	0.9313(2)
Na2	0.5000	0.0000	0.61742(19)
C1	0.0000	0.29592(17)	0.1747(3)
C2	0.5000	0.0000	0.2301(4)
O1	0.0000	0.19864(15)	0.0792(3)
O2	0.2263(2)	0.34554(9)	0.22031(16)
O3	0.5000	0.0000	0.0462(3)
O4	0.5000	0.10111(13)	0.3164(2)

Table S2-2. Fractional atomic coordinates of shortite at room temperature and room pressure (refined anisotropically).

Empirical formula	C1.50 Ca Na O4.50	
Formula weight	153.08	
Temperature	296(2) K	
Wavelength	0.49594 Å	
Crystal system	Monoclinic	
Space group	Pm	
Unit cell dimensions	a = 5.970(3) Å	$\alpha = 90^\circ$
	b = 4.816(2) Å	$\beta = 116.01(3)^\circ$
	c = 6.009(3) Å	$\gamma = 90^\circ$
Volume	155.28(14) Å ³	
Z	1	
Density (calculated)	3.274 Mg/m ³	
Absorption coefficient	0.731 mm ⁻¹	
F(000)	152	
Crystal size	0.040 x 0.040 x 0.010 mm ³	
Theta range for data collection	2.798 to 18.046°	
Index ranges	-7 ≤ h ≤ 7, -6 ≤ k ≤ 5, -7 ≤ l ≤ 7	
Reflections collected	559	
Independent reflections	293 [R(int) = 0.0423]	
Completeness to theta = 17.311°	54.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7442 and 0.4783	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	293 / 2 / 41	
Goodness-of-fit on F ²	1.427	
Final R indices [I > 2σ(I)]	R1 = 0.1171, wR2 = 0.3037	
R indices (all data)	R1 = 0.1346, wR2 = 0.3285	
Absolute structure parameter	0.3(2)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.166 and -1.623 e.Å ⁻³	

Table S2-3 Crystal data and structural refinement for shortite-II.

	x	y	z	U(eq)
Ca1A	0.3010(60)	0.5000	0.2340(60)	0.038(4)
Ca1B	-0.2650(50)	0.5000	-0.2150(50)	0.032(4)
Na1	-0.4330(60)	0.0	0.0830(60)	0.012(4)
Na2	0.0620(100)	1.0000	0.4950(100)	0.030(6)
O1A	1.1620(150)	1.0000	0.9390(150)	0.023(3)
O2A	0.9810(100)	0.7730(60)	1.1460(100)	0.023(3)
C1A	0.9650(190)	1.0000	1.0330(190)	0.009(6)
O1B	0.6750(170)	1.0000	0.7940(160)	0.023(3)
O2B	0.7000(120)	0.7760(70)	0.4460(110)	0.023(3)
C1B	0.6160(180)	1.0000	0.5600(200)	0.009(6)
O3	0.4950(190)	0.5000	0.0100(200)	0.023(3)
O4A	0.2700(300)	0.4350(90)	-0.4400(300)	0.023(3)
O4B	0.0700(300)	0.5590(110)	-0.2600(200)	0.023(3)
C2	0.2700(200)	0.5290(110)	-0.2400(200)	0.009(6)

Table S2-4. Fractional atomic coordinates of shortite-II at room temperature and 15 GPa (refine isotropically)

Atoms	Distance (Å)	Atoms	Distance (Å) or angles (°)
Ca1A-O3	2.14(5)	Na1-O1B	2.10(5)
Ca1A-O2A	2.18(5)*	Na1-O1A	2.18(8)
Ca1A-O2B	2.53(7)*	Na1-O2B	2.24(6)*
Ca1A-O4B	2.67(14)	Na1-O3	2.45(2)*
Ca1A-O4A	2.38(9)-2.95(8)**	Na1-O2A	2.58(5)*
Ca1B-O4B	2.13(9)	Na2-O2A	2.22(6)*
Ca1B-O3	2.35(5)	Na2-O2B	2.32(7)*
Ca1B-O2B	2.37(5)*	Na2-O1A	2.47(9)
Ca1B-O2A	2.41(6)*	Na2-4A	2.38(9)-2.95(8)**
Ca1B-O1B	2.438(10)*	Na2-4B	2.57(10)-3.06(9)**
Ca1B-O4A	2.37(9)-2.95(8)**		
C1A-O1A	1.51(7)	O1A-C1A-O2A	108(5)
C1A-O2A	1.27(5)	O2A-C1A-O1B	105(5)
C1A-O1B	1.69(16)	O1B-C1A-O1A	111(6)
O1B-C1B	1.30(12)	O1B-C1B-O2B*	121(7)
O2B-C1B	1.47(5)	O2B-C1B-O2B	94(4)
C1B-O2B	1.47(5)		
O3-C2	1.50(14)	O3-C2-O4A	122(7)
O4A-C2	1.31(13)	O4A-C2-O4B	111(10)
O4B-C2	1.19(15)	O4B-C2-O3	123(8)

Table S2-5. Selected bond lengths (Å) and angles (°) for shortite-II. * two equivalent distances/angles generated by symmetry ** positionally disordered oxygens.

	R1 (%)	Goof
Planar carbonates and similarity restraints to C-O distance	12.87	1.517
Similarity restraints to C-O distance	12.17	1.479
Without planarity or similarity restraints to C-O distance	11.71	1.427

Table S2-6. Summary of refinement results for shortite-II with different constraints and restraints.

Assignment	ν_o (cm ⁻¹)	($d\nu_i/dP$) to 4.9 GPa
------------	-----------------------------	----------------------------

$(\text{CO}_3)^{2-} \nu_4$	709.6	1.33(32)
$(\text{CO}_3)^{2-} \nu_1$	1083.5	2.89(35)
$(\text{CO}_3)^{2-} \nu_1$	1189.68	3.20(16)
Assignment	$\nu_o \text{ (cm}^{-1}\text{)}$	(dv_i/dP) above 4.9 GPa
$(\text{CO}_3)^{2-} \nu_4$	715.3	1.21(3)
$(\text{CO}_3)^{2-} \nu_4$	722.1	1.80(8)
$(\text{CO}_3)^{2-} \nu_4$	727.0	2.22(16)
$(\text{CO}_3)^{2-} \nu_1$	1094.7	2.09(7)
$(\text{CO}_3)^{2-} \nu_1$	1103.8	2.34(7)

Table S2-7. Raman modes observed at room temperature with increasing pressure in nyerereite.

Chapter 3: A Novel Carbon Bonding Environment in Deep Mantle High-Pressure Dolomite

3.1 Abstract

The main source of carbon entering the deep Earth is through subduction of carbonates, including $\text{CaMg}(\text{CO}_3)_2$ -dolomite. We examine the high-pressure structure and stability of dolomite to understand the means through which carbon can be sequestered as it enters the deep Earth carbon cycle. Dolomite is investigated to 86 GPa using Raman spectroscopy at room temperature: this includes spectroscopic characterization of dolomite-III, a phase stable at deep mantle pressures and temperatures. Between 63-86 GPa, within the dolomite-III structure, we observe spectroscopic evidence for the evolution of a subpopulation of carbonate ions characterized by *weaker* C-O bonds, with anomalous pressure shifts: this abnormal bonding change is explained by the onset of a 3+1 coordination of the carbon in some of the carbonate ions in the dolomite-III structure, confirming an earlier prediction of Merlini et al. (2012). The wide suite of carbonate ions (both normal 3-fold and 3+1 coordinate) within this phase at the highest pressures should give rise to a large variety of cation sites: as such, dolomite-III could represent a major host for incompatible elements in the deep mantle, implying that incompatible element distribution may be closely linked to carbon cycling within the deep Earth.

3.2 Introduction

Carbonate minerals have long been accepted as the primary carriers of carbon into the deep Earth. Carbonates are present in and on oceanic plates, and when slabs are subducted, oxidized carbon is brought into the deep Earth (e.g., Alt and Teagle

1999). Carbon can have a strong influence on the chemical and physical properties of the mantle (Duba and Shankland 1982; Dasgupta et al. 2006; Shcheka et al. 2006), so its manner of retention at depth is critical for clarifying its role in deep Earth geophysical and petrologic processes. In higher temperature slabs, carbonates likely decompose and release CO₂, which facilitates melting in the Earth's deep upper mantle (e.g., Rosenthal et al. 2015), and can explain carbon dioxide's ubiquity in back arc volcanoes. However, in high pressure and temperature experiments that mimic cold slab geotherms, carbonate and peridotite phase equilibria indicate that carbonate minerals could persist at least down to the transition zone, and possibly deeper (e.g., Litasov et al. 2013). Moreover, primordial carbon could also be retained within Earth's deep mantle, in addition to recycled carbon from subduction (e.g., Hirschmann and Dasgupta 2009).

Dolomite (CaMg(CO₃)₂) is a common carbonate on the surface of the earth, is found in sedimentary environments and vein deposits, and crystallizes with rhombohedral symmetry in the space group R-3. There have been several previous high pressure experiments on dolomite at room temperature (300 K). Using spectroscopic and X-ray diffraction (XRD) methodology, two well defined transitions of dolomite to dolomite-II and dolomite-III have been identified around 15-20 GPa and 36-38 GPa, respectively (Santillán et al. 2003; Santillán and Williams 2004; Mao et al. 2011; Merlini et al. 2012; Efthimiopoulos et al. 2017). Merlini et al. (2012), using single crystal X-ray diffraction reported a triclinic, calcite-II-like structure for dolomite-II above 17 GPa and a larger triclinic, calcite-III unit cell for dolomite-III

above 35 GPa. Most importantly, Merlini et al. (2012) heated their samples to 2200 K at up to 72 GPa, and Mao et al. (2011) to ~1500 K to 83 GPa, and their results demonstrate that dolomite-III is stable at these extreme conditions. Hence, dolomite-III represents a likely carbon repository at the conditions of Earth's lower mantle. The dolomite-III structure reported by Merlini et al. (2012) is structurally novel, as extrapolated trends of their refinements of interatomic distances to 60 GPa indicate that some of the carbonate ions could adopt a 3+1 coordination with the oxygens at pressures of 60-80 GPa. Experimental and theoretical evidence for the presence of 4-fold coordinate carbon in oxides at high pressures have been previously described (Isshiki et al. 2004; Oganov et al. 2006; Sun et al. 2009; Boulard et al. 2011, 2015; Cerantola et al. 2017; Merlini et al. 2017).

Here, we utilize vibrational spectroscopy to probe the local bonding environment of the carbonate ion (and Ca/Mg cations) within dolomite to 86 GPa: a substantially higher pressure range than previous vibrational studies, and nearly 50 GPa higher than where a previous study (Efthimiopoulos et al. 2017) was unable to resolve any Raman bands from dolomite. Our goals are to evaluate whether dolomite-III undergoes the predicted continuous transition to partial 3+1 coordination of carbon, and to probe the character of the bonding environment of the carbon ion within dolomite-III at these extreme conditions.

3.3 Experimental Methods

Dolomite, $\text{Ca}_{1.00}\text{Mg}_{0.92}\text{Fe}_{0.08}(\text{CO}_3)_2$, from New Almaden, CA (UCSC mineral collection no. 7206) was used for this experiment: this composition was confirmed using a JEOL JXA-8230 electron microprobe. The sample identity was confirmed

using Raman spectroscopy and single crystal XRD, and our results are in excellent agreement with previous studies of nearly endmember dolomite (for example, Nicola et al. 1976). The samples were single crystals with approximate dimensions of 20x20x10 μm . High pressures were generated with a symmetric-type Princeton type diamond anvil cell equipped with type Ia diamonds with 250 μm culets. Neon was used for the pressure medium, and ruby fluorescence was used as the in-situ pressure calibrant (Mao et al. 1986).

Raman measurements were performed using a Horiba LabRAM HR Evolution spectrometer. Both 532 and 633 nm excitation lasers were used for different regions of the spectrum: 532 nm was used to collect spectra from $\sim 1,400$ to $1,800\text{ cm}^{-1}$, and 633 nm was used for 50 - $1,325\text{ cm}^{-1}$. The spectrometer focal length was 800 mm, and it was equipped with a 1,200 lines/mm grating, and a CCD detector. Spectral resolution was $\sim 1\text{ cm}^{-1}$, and spectra were collected from 1-2 micron spots. Spectra were analyzed and peaks deconvolved with a combination of Lorentzian and Gaussian peaks using Horiba Labspec6 software.

Room pressure single crystal analysis was collected at the Advanced Light Source (beamline 11.3.1). Diffraction images were collected with a Bruker D8 diffractometer with a photon 100 SiMOS detector at 298 K. The single crystal sample characterized was a clear cube that was free of visible cracks and/or imperfections. The sample was mounted in oil on a MiTeGen MicroMount. Images were collected using Bruker APEX II software and integrated using the program SAINT.

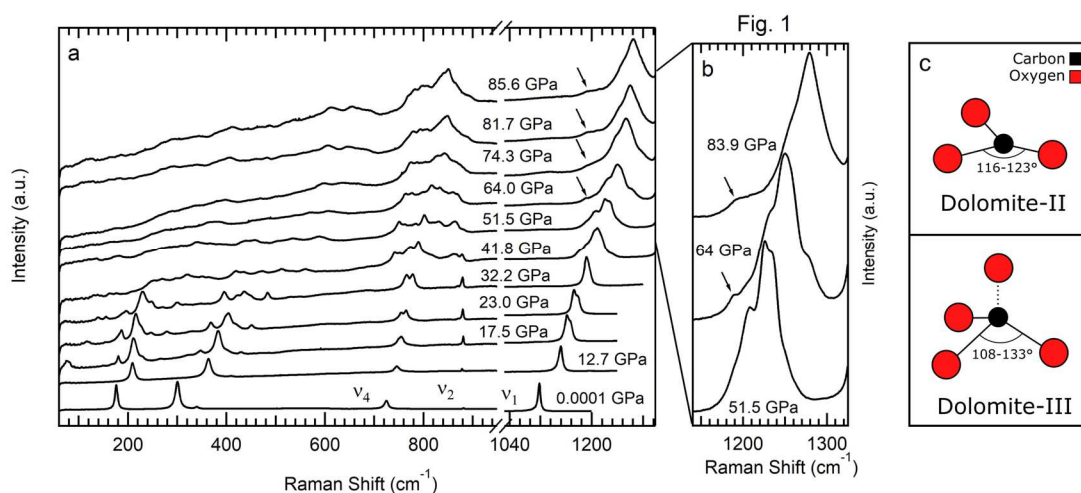


Figure 3-1. Representative Raman spectra of dolomite under compression at room temperature (spectra are vertically offset for clarity). (a) Lattice modes and the carbonate modes associated with the out-of-plane bends, in-plane bends and symmetric stretches are shown. Arrows indicates the peak(s) that is indicative of the onset of 3+1 coordination. Variable relative amplitudes of peaks in some spectra are likely associated with preferred orientation effects. (b) An enlarged view of the carbonate's symmetric stretch at 52, 64 and 84 GPa. Again, arrows indicate the peak that is indicative of the onset of 3+1 coordination. (c) Schematic depiction of the transition of a 3-fold coordinated carbonate ion in dolomite-II to 3+1 coordinated in dolomite-III.

3.4 Results and Discussion

Our lower pressure (up to 38 GPa) Raman results (Figs. 3-1 and 3-2, Table S3-1 and S3-2) are consistent with previous work (Mao et al. 2011; Merlini et al. 2012; Efthimiopoulos et al. 2017) in that we observe two discontinuous, first-order transitions: one at ~15 GPa and another at ~40 GPa respectively. Factor group analysis of the optic modes of dolomite-I, with the space group R-3 (Steinfink and Sans 1959), yields $\Gamma = 4A_g(R) + 4E_g(R) + 5A_u(IR) + 5E_u(IR)$. Dolomite-II, with space group P-1 (Merlini et al. 2012), yields $\Gamma = 30A_g(R) + 27A_u(IR)$. Factor group analysis on dolomite-III, with space group P-1 (Merlini et al. 2012), yields $\Gamma = 120A_g(R)$ and 117 $A_u(IR)$. Previous studies on different starting materials report the transitions to high-

pressure phases of dolomite at modestly higher and lower pressures, respectively (Table S3-3). Results on decompression are not reported; our highest pressure run reconverted to dolomite-I on decompression, with all modes returning to their initial values, with a possible strain-enhanced mode present at 225 cm^{-1} : this involves an increase in amplitude of a weak Raman active mode, with A_g symmetry (Pilati et al. 1998).

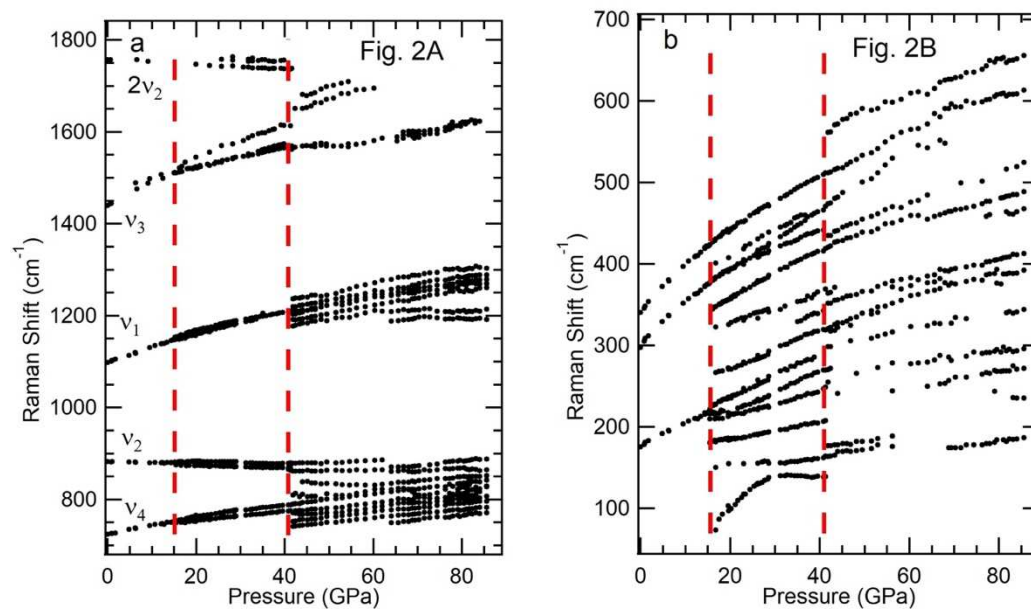


Figure 3-2. Peak positions of observed Raman modes as a function of pressure. (a) Carbonate modes associated with the out-of-plane bend (v_2), in-plane bend (v_4), symmetric stretch (v_1) and asymmetric stretch (v_3). $2v_2$ represents an overtone of the out-of-plane bend. (b) Lattice modes of dolomite. These predominantly involve relative motion between the carbonate groups and the divalent cations. Vertical dashed red lines indicate phase transitions.

3.4.1 Dolomite-III: Lattice modes at high pressure

Above 42 GPa, at least 11 discrete low-frequency vibrational modes can be resolved in the $\sim 200\text{-}600\text{ cm}^{-1}$ range, implying that a broad suite of divalent cation environments and divalent ion/carbonate vibrational interactions are present within the dolomite-III high-pressure phase (Fig. 3-1, 2b, Table S3-4). In short, a broad continuum of bands is present, implying that a range of environments is present, consistent with

the low symmetry of the dolomite-III structure: this diversity of environments appears to be enhanced above 60-70 GPa, as new bands appear near 450 and 660 cm^{-1} , at the lower frequency and higher frequency sides of this manifold.

From a mantle geochemical standpoint, our observation of the markedly enhanced breadth spanned by the low frequency bands (Fig. 3-1) is consistent with dolomite-III having a broad suite of distorted cation environments. This conclusion is consistent with the lower pressure crystal structure results of Merlini et al. (2012), and the suggestion that these distortions are notably enhanced at pressures above 63 GPa. Hence, given both the thermal stability of dolomite-III at these pressures (Mao et al. 2011) and that the major phases comprising the deep mantle have highly symmetric cation sites (e.g. Wicks and Duffy 2016), the prospect exists that the irregular cation sites in dolomite-III could represent a major depository for highly incompatible elements in the deep mantle. In particular, the highly irregular 6-11 coordinated cation sites whose bond distances and angles vary significantly in this phase (Table S5) may represent a primary locus in which rare earths could undergo defect substitutions, similar to those present in calcium perovskites (Corgne and Wood 2005). In this sense, the dolomite-III phase in the deep Earth could mimic the geochemical affinities for incompatible elements of carbonatite melts at shallower depths.

3.4.2 Dolomite-III: Carbonate modes at high pressure

The Raman-active carbonate modes provide bonding environment information at high pressures, including constraining the bonding changes taking place within and dolomite-III under compression. At the higher pressures probed, our results support an increase in coordination number of a subset of the carbonate ions. At 41 GPa, the out-

of-plane and in-plane bends broaden and approach each other in frequency; by 50 GPa, the two types of vibrations merge into a multiplet of energetically similar modes (~9) which span 140 cm^{-1} in width. This coalescence is generated by the small (or negative) pressure shifts of the out-of-plane bends coupled with the positive shifts and increases in width of the in-plane bends. Near 58 GPa, the highest frequency band in this multiplet disappears, and at 68 GPa, a new low frequency band appears near 750 cm^{-1} , and becomes progressively more intense up to the maximum pressure of 86 GPa (Fig. 3-1, 3-2a, Table S3-4).

This appearance of a new lower frequency mode, and disappearance of the highest frequency mode, within the in-plane and out-of-plane bending set of bands, implies that the force constants associated with some O-C-O linkages in the crystal have weakened. This wide breadth of the bending vibrational levels is likely driven by extremely distorted carbonate ions, with both angle variations between the oxygen atoms and the planarity of the ions being variable. The progressive increase in the bending vibrations with pressure in dolomite-III indicates that repulsive forces with neighboring oxygens may play a larger role than cation-oxygen interactions with the carbonate unit.

The behavior of the symmetric stretch provides further confirmation that a subset of the C-O bonds in dolomite-III weakens at the higher pressures of our study. At the onset of the dolomite-III transition, the single strong peak splits into 5-6 separate components at 41 GPa (Fig. 3-1, 3-2a, Table S3-4), with pressure shifts in accord with those of symmetric stretches in a wide range of carbonates (e.g., Kraft et al. 1991; Gillet

et al. 1993; Koch-Müller et al. 2016; Efthimiopoulos et al. 2017). At 64 GPa, two low intensity peaks on the low frequency side of the symmetric stretch emerge from this multiplet. These low-frequency peaks shift at essentially negligible rates between 64 and 86 GPa (Fig. 3-1 (inset), 3-2a, Table S3-4).

As with the in-plane and out-of-plane bends, these new stretching bands at lower frequency than the main group of peaks show that the C-O bonds within a subset of the carbonate ions within the unit cell are dramatically weakened. These bands are anomalous in terms of both their lower frequency (which is consistent with a ~12% decrease in C-O force constant relative to the frequency of the centroid of the symmetric stretching bands), and their negligible pressure shifts (which imply that the force constants of the C-O bonds associated with these vibrations do not increase as the crystal is compacted: this lack of a positive shift, despite compaction, is consistent with a progressive pressure-induced weakening of this subset of C-O bonds).

3.5 3+1 Coordination of the carbonate ion

We attribute these new carbonate bands and their associated mode shifts to a less tightly bound carbon configuration, which we attribute to the 3+1 coordination of carbon (Fig. 3-1c) predicted by Merlini et al. (2012). In the dolomite-III structure proposed by Merlini et al. (2012), there are eight crystallographically distinct carbon sites within the unit cell; we observe six symmetric stretching peaks after deconvolution, in which some vibrations of carbonate ions may be energetically indistinguishable. Merlini et al. (2012) extrapolated their single crystal data and speculated that an uncommon 3+1 coordination of one of the carbonate ions in the unit cell would ultimately arise, with the planar carbonate ion approaching tetrahedral

coordination around 80-90 GPa. In the highest pressure (56 GPa) structure reported by Merlini et al. (2012) the carbonate ion containing the C1 atom is notably distorted (Table S5) in terms of its angular variance from 120° and its torsion angle. This distortion is likely a response to the close approach of its nearest-neighboring, non-bonded oxygen atom, O12. The interatomic distance between C1 and O12 is 2.066 Å at 56 GPa, and strongly decreases with pressure. The C1 carbonate ion the most likely to undergo a coordination change to 3+1 coordination; the carbonate ion that is bonded to O12 is also likely to approach 3+1 coordination. This C7-associated carbonate ion is the most distorted with respect to its angle variance, with O-C-O angles that range from 108° to 133° with an angle variance of 12.6° (Table S3-6). Our Raman spectra appear to record the onset of higher coordination (and hence weaker C-O bonding) through both the appearance of the lowest frequency symmetric stretch peak that appears above 63 GPa, and the onset of a low frequency bend vibration, and disappearance of the highest frequency component of the bends.

The lowest frequency mode associated with the carbonate symmetric stretch at 63 GPa compared to the median of the symmetric stretching band is $\sim 12\%$. this amount approaches the difference between those observed between XY_3 and XY_4 molecular species with the same cations and anions (e.g. boron halides) (Nakamoto 1986). Thus, a partial coordination change involving a progressively increasing interaction with an approaching oxygen anion explains both the decreased frequency of these new bands, and their low-pressure shifts. In tandem with the carbonate stretching and bending modes both having lower frequency components that initiate around 63 GPa, each of

the new features have anomalously low pressure shifts. Such low-pressure shifts indicate that the C-O bond strengths associated with these carbonate vibrations are almost unchanged in strength between 63 and 86 GPa, despite substantial compaction. These minimal shifts are also compatible with a progressively stronger fourth C-O bond forming, with weakening of the C-O bonds of the carbonate group as the additional oxygen becomes progressively more strongly bound to the unit. Furthermore, Mao et al. (2011) (their Supplemental Info) report a slight change in the lattice parameters of dolomite-III near 63 GPa, indicating that a shift in compressional mechanism occurs near this pressure. This shift is consistent with our interpretation that new C-O bonds begin to form at this pressure.

At our highest pressures, the spectra continue to be most readily explained by a 3+1 coordination environment for a subgroup of the carbonate ions. Notably, carbonate vibrations that have normal frequencies (readily extrapolated from lower-pressure conditions) and pressure shifts continue to dominate the spectra, indicating that a mix of 3+1 coordinated carbonate groups and highly compacted, but three-fold carbonate groups, are present within dolomite-III. This interpretation implicitly requires that these vibrations involve carbon environments that are substantially distorted. Thus, the absolute Raman amplitude of these vibrations is expected to underrepresent the true concentration of the more highly coordinated carbon cations within the crystal, since Raman bands are stronger for more symmetric vibrations and environments (for example, Williams 1995). We believe that it is unlikely that full tetrahedral coordination of carbon is achieved in any of the carbonate units in dolomite-III over

this pressure range, since an enhancement in intensity of the bands associated with the weaker C-O bonds would be anticipated if the local environment became more symmetric; it is also possible that the frequency decrement associated with full tetrahedral coordination might be larger than we observe (Sun et al. 2009) .

3.6 Implications

$\text{CaMg}(\text{CO}_3)_2$ evolves a novel bonding environment of carbon above 63 GPa, as manifested by a subset of weaker C-O bonds being present above this pressure in dolomite-III. These weaker C-O bonds are plausibly generated by an additional oxygen progressively approaching one of the carbonate ions, resulting in a 3+1 coordination of the carbonate group, verifying a prediction by Merlini et al. (2012). The broad diversity of distorted structural environments within both the carbonate groups and cation sites (based on the wide range in frequency spanned by the lattice modes) in the dolomite-III structure, indicate that this is a phase in which incompatible elements are likely to substitute. Thus, as dolomite-III is expected to be a stable phase within oxidized zones in the deep mantle (consistent with its observed thermal stability), the low symmetry/distortion of its cation sites likely render it a major host for incompatible elements in the lower mantle. This conclusion provides a potential mineralogic basis for the affinity between carbonate metasomatism and incompatible element signatures in magmas with deep mantle provenances or long-term mantle residence times (Collerson et al. 2010; Castillo 2015; Weiss et al. 2016). Thus, because of its novel structural characteristics and multiple coordination environments, the high-pressure phase of dolomite may be critical in the incompatible element cycling associated with deeply-derived carbon-bearing magmas.

Typically, an increase in coordination number leads to an increase in entropy (e.g. Navrotsky 1980) which implies that dolomite-III's entropy may increase under pressure as the 3+1 coordination is generated. Dolomite-IV, which is characterized by four-coordinate carbon, is a relatively symmetric structure (although it may have divalent cation disorder (Merlini et al. 2017)). The mixed coordination carbon environments and highly distorted carbonate and metal cation sites that we characterize in dolomite-III indicate that this phase is likely to be higher entropy than the symmetric ring structure documented for dolomite-IV synthesized at 120 GPa and 2,500°C (Merlini et al. 2017). Thus, the transition from the highly disordered structure of dolomite-III to higher symmetry dolomite-IV may produce a situation that is reversed from that of the well-known coordination change and transition from γ -spinel to perovskite (Bina and Helffrich 1994). Thus, on structural grounds, we expect that the Clapeyron slope of the dolomite III-IV transition is likely to be positive. Hence, the high temperatures present near the base of Earth's mantle (Anzellini et al. 2013) may result in dolomite-III being stabilized throughout much of Earth's mantle.

3.7 Acknowledgements

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assistance with the electron microprobe analysis. We would like to thank three anonymous reviewers for their helpful comments.

3.8 Supplemental Information

3.8.1 Discussion: dolomite-I and -II:

3.8.1.1 Lattice Modes

As with Efthimiopoulos et al. (2017), we observe that the three lattice modes of dolomite-I migrate to higher frequency up to 15 GPa (Fig. 3-1, 3-2b, Table S3-1). At 15 GPa, the E_g symmetry modes with zero-pressure frequencies of 175 and 297 cm^{-1} broaden and split into 3-4 modes that continue to increase in frequency at higher pressures; the majority of these modes persist to 42 GPa (Fig. 3-1, 3-2b, Table S3-2). At 17 GPa, a new, not previously observed mode becomes resolvable above $\sim 78 \text{ cm}^{-1}$. This band initially shifts rapidly (4.84(22) $\text{cm}^{-1}/\text{GPa}$) up to 30 GPa where it reaches a maximum and shifts slightly negatively (-0.21(4) $\text{cm}^{-1}/\text{GPa}$) up to 42 GPa, where it can no longer be resolved (Table S3-2).

3.8.1.2 Carbonate Modes

The single out-of-plane bending vibration near 882 cm^{-1} shifts monotonically up to 15 GPa (Fig. 3-1, 3-2a, Table S3-1). At 15 GPa, the mode splits and a higher frequency shoulder appears. The two bands slowly diverge (while both increasing with frequency) as pressure is increased up to 41 GPa (Table S3-2), indicating that the distortion of the carbonate group in dolomite-II may weakly increase with pressure. The single in-plane bending vibration decreases in frequency with increasing pressure up to 15 GPa (Table S3-1): this negative shift is normal for this vibration in carbonates (Kraft et al. 1991). At 15 GPa, the in-plane bend mirrors the out-of-plane bend vibration

by splitting, with a new peak forming at lower frequency; these two modes separate as they continue to shift negatively (Fig. 3-1, 3-2a, Table S3-2).

The symmetric stretch peak is slightly asymmetric at room pressure; in accord with past studies on dolomite (Kraft et al. 1991; Gillet et al. 1993; Efthimiopoulos et al. 2017), we fit one component to this stretch. This single band shifts up to 15 GPa where it splits into two bands (Fig. 3-1, 3-2a, Table S3-1). These two bands slowly merge into a single peak by 34 GPa and continue as a single peak up to 41 GPa.

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

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

Our results are in accord with the analysis by Merlini et al.(2012) that the structure of dolomite-II is calcite-II-like. A mode that provides diagnostic information on the nature of the transition to dolomite-II appears at low frequency ($\sim 78 \text{ cm}^{-1}$): this band has a rapid initial positive pressure shift of nearly $5 \text{ cm}^{-1}/\text{GPa}$. Based on its low frequency and large pressure shift, this mode likely corresponds to a zone-edge acoustic mode at room pressure, and at 15 GPa, the increase in size of the unit cell across the transition renders this zone edge mode Raman-active. Computational results on the transition from dolomite to dolomite-II indicate that the transition is soft-mode generated via an acoustic vibration becoming unstable at the F point in the Brillouin

zone (Zucchini et al. 2017). This transition thus is likely to have a similar mechanism to the transition from calcite to calcite-II (Merrill and Bassett 1975; Hatch and Merrill 1981; Harris et al. 1998). This indicates that this transition may be displacive, and involves an associated expansion of the spectroscopic unit cell (Dove 1997). Our results support the structure proposed by Merlini et al. (2012), with a doubling occurring in the spectroscopic unit cell. Near 32 GPa, the pressure shift of this new mode becomes negative. This negative shift may be associated with an approach towards instability of this specific mode: such phonon instabilities may be associated with the metastability of dolomite-II observed within computations (Solomatova and Asimow 2017).

3.8.3 Dolomite-III further discussion:

For comparison, the asymmetric stretch and ν_2 (out-of-plane-bend)-overtone are weak bands that are difficult to consistently observe at high pressures. Above 68 GPa, these vibrations have multiple components with variable pressure shifts (Fig. 3-2): at these pressures, it is likely that a resonant interaction exists between the asymmetric stretch and the out-of-plane bend overtones (which were not resolvable above 42 GPa: S3-1). Thus, these bands provide less insight into the structural changes occurring within the carbonate units than the bending and symmetric stretching vibrations.

3.8.4 Tables and Figures

ν_0 (cm ⁻¹)	Assignment	$d\nu_i/dP$ (cm ⁻¹ /GPa)	γ_i^*
175	LO (E_g)	2.66(5)	1.43
297	TO (E_g)	4.91(96)	1.55
341	Lattice (A_g)	5.33(10)	1.47
725	CO ₃ ²⁻ ν_4 (E_g)	1.82(4)	0.24
882	CO ₃ ²⁻ ν_2 (A_g)	-0.11(4)	-0.01
1096	CO ₃ ²⁻ ν_1 (A_g)	3.28(3)	0.28

1440	$\text{CO}_3^{2-} \nu_3 (\text{E}_g)$	4.47(43)	0.29
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Table S3-1. Pressure shifts of the Raman modes of dolomite-I up to 15 GPa with associated Grüneisen parameters. *Assuming a bulk modulus of 94 GPa(Ross and Reeder 1992; Zucchini et al. 2014)

$\nu_0 (\text{cm}^{-1})$ (at 15 GPa)	Assignment	$d\nu_i/dP$ ($\text{cm}^{-1}/\text{GPa}$)	Notes
73.1	lattice	4.84(22)	17-30 GPa
140.0	lattice	-0.21(4)	above 30 GPa
149.8	lattice	0.40(4)	above 17 GPa
180.1	lattice	1.00(2)	
209.5	lattice	1.47(3)	
215.5	lattice	2.23(5)	
221.5	lattice	2.66(3)	
266.4	lattice	2.36(4)	above 17 GPa
329.3	lattice	2.34(21)	above 35 GPa
322.2	lattice	1.81(6)	above 17 GPa
344.4	lattice	2.99(3)	
399.2	lattice	2.39(2)	Above 23 GPa
376.8	lattice	3.57(2)	
400.7	lattice	3.08(6)	above 17 GPa
423.6	lattice	3.37(3)	
749.3	$\text{CO}_3^{2-} \nu_4$	1.00(1)	
751.5	$\text{CO}_3^{2-} \nu_4$	1.35(3)	
875.1	$\text{CO}_3^{2-} \nu_2$	-0.27(1)	
881.5	$\text{CO}_3^{2-} \nu_2$	-0.17(2)	
1148.0	$\text{CO}_3^{2-} \nu_1$	2.48(2)	
1152.9	$\text{CO}_3^{2-} \nu_1$	2.43(4)	up to 34 GPa

Table S3-2. Pressure shifts of the Raman modes of dolomite-II from 15 GPa to 41 GPa.

Study/ Composition	Dolomite II	Dolomite III	Type of study	Note
Kraft et al. (1991)/ N/A	N/A	N/A	R	
Ross and Reeder (1992)/ $\text{CaMg}_{0.987}\text{Fe}_{0.01}\text{Mn}_{0.02}$ $(\text{CO}_3)^2$	N/A	N/A	scXRD	
Gillet et al. (1993)/ N/A	N/A	N/A	R	

Santillán et al. (2004)/ N/A	20-30 GPa calcite-III (triclinic)		IR	
Mao et al. (2011)/ $\text{Ca}_{0.988}\text{Mg}_{0.918}\text{Fe}_{0.078}\text{Mn}_{0.016}(\text{CO}_3)_2$	17 GPa, 300K orthorhombic	36 GPa, 1500K monoclinic	pXRD	
Merlini et al. (2012)/ $\text{CaMg}_{0.6}\text{Fe}_{0.4}(\text{CO}_3)_2$	17 GPa, 300 K Calcite-II like triclinic, <i>P</i> -1	35 GPa, 300 K Calcite-III like Triclinic, <i>P</i> -1	xcXRD	
Efthimiopoulos et al. (2017)/ $\text{CaMg}_{0.98}\text{Fe}_{0.02}(\text{CO}_3)_2$	16 GPa, calcite-II like	36 GPa Calcite- III like	R & IR	Observed dolomite-Ib above 11 GPa
Merlini et al. (2017)/ $\text{CaMg}_{0.6}\text{Fe}_{0.4}(\text{CO}_3)_2$ and $\text{CaMg}(\text{CO}_3)_2$	17 GPa, calcite-II like	36 GPa (IIIb is <i>R</i> 3 41 GPa (IIIc possibly <i>P</i> 1)	scXRD	Observation of dolomite-IV above 120 GPa and 2,500°C (orthorhombic)
This Study $\text{Ca}_{1.098}\text{Mg}_{0.89}\text{Fe}_{0.012}(\text{CO}_3)_2$	15 GPa Calcite-II like	41 GPa Calcite-III like	R	

Table S3-3. Summary of previous high pressure experiments on dolomite (R = Raman spectroscopy, scXRD = single crystal X-ray diffraction; IR = infrared spectroscopy, pXRD = powder X-ray diffraction)

ν_0 (cm ⁻¹) (at 41 GPa)	Assignment	$d\nu_i/dP$ (cm ⁻¹ /GPa)	Notes
163.2	Lattice	0.38(3)	
176.9	Lattice	0.81(7)	Up to 56 GPa
240.6	Lattice	0.90(4)	
270.0	Lattice	0.67(4)	
298.6	Lattice	1.02(4)	
320.5	Lattice	1.66(4)	
351.5	Lattice	1.36(2)	

458.1	Lattice	0.85(25)	Above 78 GPa
420.2	Lattice	1.44(3)	
435.0	Lattice	1.98(4)	
473.8	Lattice	3.07(14)	Up to 68 GPa
511.9	Lattice	2.44(7)	
561.4	Lattice	2.08(4)	
662.6	Lattice	1.57(19)	Above 71 GPa
163.2	Lattice	0.38(3)	
176.9	Lattice	0.81(7)	Up to 56 GPa
749.1	CO ₃ ²⁻ ν_2/ν_4	1.04(4)	Above 64 GPa
741.6	CO ₃ ²⁻ ν_2/ν_4	0.95(1)	
752.0	CO ₃ ²⁻ ν_2/ν_4	1.00(1)	
771.3	CO ₃ ²⁻ ν_2/ν_4	0.94(3)	
790.2	CO ₃ ²⁻ ν_2/ν_4	1.16(1)	
838.9	CO ₃ ²⁻ ν_2/ν_4	-0.53(7)	Up to 60 GPa
	CO ₃ ²⁻ ν_2/ν_4	-0.82(2)	Above 60 GPa
	CO ₃ ²⁻ ν_2/ν_4	0.09(2)	
862.3	CO ₃ ²⁻ ν_2/ν_4	0.98(5)	Above 64 GPa
878.8	CO ₃ ²⁻ ν_2/ν_4	0.34(4)	
1187.8	CO ₍₃₊₁₎ ²⁻ ν_1	0.09(8)	Above 64 GPa
1209.9	CO ₍₃₊₁₎ ²⁻ ν_1	-0.06(7)	Above 62 GPa
1177.2	CO ₃ ²⁻ ν_1	1.64(8)	Up to 62 GPa
1191.4	CO ₃ ²⁻ ν_1	1.65(2)	
1203.6	CO ₃ ²⁻ ν_1	1.56(3)	
1211.7	CO ₃ ²⁻ ν_1	1.62(3)	

Table S3-4. Pressure shifts of the Raman modes of dolomite-III from 41 GPa to 86 GPa.

	C.N.	Average M-O (Å)	Quad. Elong. comp to average
Ca1-O	10	2.339(241)	0.996
Ca2-O	10	2.331(143)	0.983
Ca3-O	11	2.360(262)	0.913
Ca4-O	11	2.391(225)	0.933
Mg/Fe1-O	6	1.976(62)	0.986
Mg/Fe2-O	6	1.978(125)	0.991

Mg/Fe3-O	6	2.011(58)	1.021
Mg/Fe4-O	7	1.998(107)	1.009

Table S3-5. Metal cation environments in dolomite-III at 56 GPa, from Merlini et al. (2012)

	Average C-O (Å)	Quadratic Elongation (Å)	Torsion Angle (°)	Angle variance (°) compared to 120°	Closest 4th oxygen	
					assignment	distance (Å)
C1- O2,7,19	1.262(80)	0.996	14.86	8.408	C1-O12	2.066
C2- O6,10,23	1.278(42)	1.020	7.17	3.504	C2-O21	2.449
C3- O4,9,13	1.272(39)	1.010	2.25	6.162	C3-O5	2.309
C4- O1,5,17	1.247(29)	0.971	0.44	6.039	C4-O11	2.212
C5- O16,18,20	1.250(21)	0.976	1.17	1.119	C5-O20	2.454
C6- O15,21,22	1.293(41)	1.043	0.85	6.090	C6-O19	2.327
C7- O12,14,24	1.274(130)	1.020	6	12.607	C7-O10	2.234
C8- O3,8,11	1.252(68)	0.980	2.78	3.471	C8-O16	2.244

Table S3-6. Carbon environments in dolomite-III at 56 GPa, from Merlini et al. (2012)

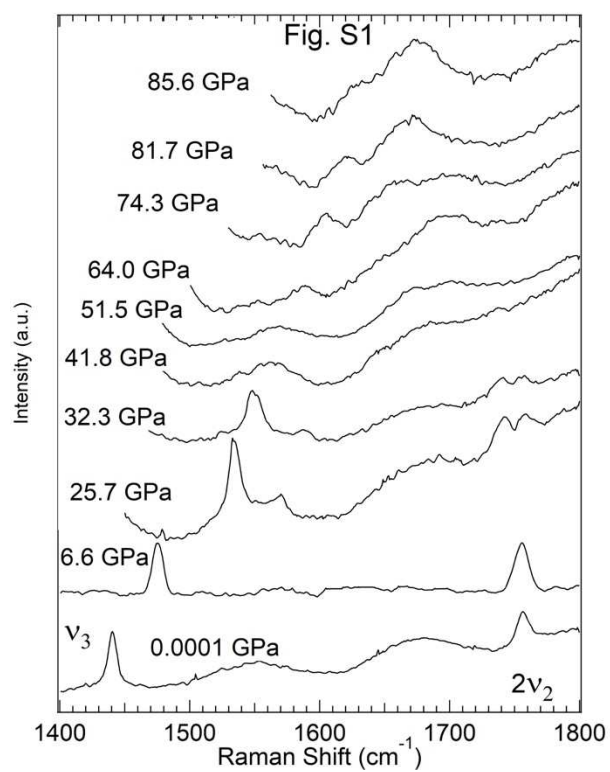


Figure S3-1. Representative Raman spectra of dolomite under compression at room temperature (spectra are vertically offset for clarity). The asymmetric stretch (v_3) and overtone of the out of plane bend ($2v_2$) are shown.

Chapter 4: High Pressure Raman and Nd³⁺ Luminescence Spectroscopy of Bastnäsite-(REE)CO₃F

4.1 Abstract

Bastnäsite-(Ce), a rare earth element (REE) bearing carbonate (Ce,La,Y,Nd,Pr)CO₃F, is one of the most common REE-bearing minerals, and has importance from both economic and geologic perspectives due to its large REE concentration. It also provides an example of the structural interplay between carbonate groups and fluorine ions, as well as the complex bonding properties of rare earth elements. We report Raman vibrational and Nd³⁺ luminescence ($^4F_{3/2} \rightarrow ^4I_{9/2}$, $^4F_{3/2} \rightarrow ^4I_{11/2}$ and $^4F_{5/2} + ^2H_{9/2} \rightarrow ^4I_{9/2}$) spectra of natural bastnäsite-(Ce) to 50 GPa at 300 K. Two phase transitions are observed under compression. Bastnäsite-I remains the stable phase up to 25 GPa, where it undergoes a subtle phase transition to bastnäsite-II: this is likely produced by a change in symmetry of the carbonate ion. Bastnäsite-II transforms to bastnäsite-III at ~38 GPa, as demonstrated by changes in the luminescence spectra. This second transition is particularly manifested within the $^4F_{3/2} \rightarrow ^4I_{9/2}$ luminescence, and it appears that a new rare earth element site is generated at this phase change. This transition is also accompanied by modest changes in both the Raman spectra and the other two sets of luminescent transitions. Despite these transformations, the carbonate unit remains as a stable, three-fold coordinate unit throughout this pressure range, with a possible increase in its distortion. Correspondingly, the rare-earth element site(s) appears to persist in quasi-9-fold coordination as well, implying that the general bonding configuration in bastnäsite is at least metastable over a ~30% compression range. All pressure-induced transitions

are reversible (with some hysteresis), with the material reverting to its ambient pressure phase on decompression.

4.2 Introduction

Bastnäsite-(Ce) is a REE bearing fluorocarbonate ($(\text{Ce,La,Y,Nd,Pr})\text{CO}_3(\text{F,OH})$) that is typically found associated with carbonatite deposits, and is economically important due to its high content of REEs. Indeed, bastnäsite is one of the two major mineral ores for REEs, with its chief competition being monazite. Geochemically, REEs are typically incompatible in silicate minerals; their concentration in carbonatite melts (often with bastnäsite as their crystallization product) is generally more than 3 orders of magnitude higher than the bulk Earth content (Jones et al. 2013), and greater than 4 orders of magnitude higher than within chondrites (Holtstam and Andersson 2007). Indeed, carbonate-bearing liquids and solids likely play a primary role in transporting and retaining rare earth elements within the Earth's mantle (e.g., Collerson et al. 2010). In addition, light REE have long been used to determine the ages of continental rocks, particularly via the samarium-neodymium dating method (McCulloch and Wasserburg 1978), and the evolution of the depleted mantle has been probed using the distinct $^{143}\text{Nd}/^{144}\text{Nd}$ variation in the mantle compared to chondrites and crustal rocks (DePaolo and Wasserburg 1976). Bastnäsite has significance beyond its REE content: as carbonates are thought to be the dominant species containing carbon within oxidized regions of the mantle (e.g., Brenker et al. 2007), the properties of bastnäsite can provide insight into the bonding of carbon at depth. Specifically, bastnäsite, has importance for understanding the potential behavior of REE at depth

within carbon (and halogen) rich zones of the mantle, and within carbonatite melts (which are frequently halogen-enriched: e.g., Jago and Gittins 1991; Williams and Knittle 2003). Additionally, the optical and magnetic properties of rare-earth carbonate fluorides have attracted interest within the materials science community (e.g., Grice et al. 2007).

Bastnäs site virtually never occurs as an endmember in terms of its REE content, as it commonly contains a mixture of REEs (e.g. Ce, Nd, Eu, Y, etc.). Visible and infrared reflectance spectroscopy have been used to probe the absorption bands of bastnäs site, which can constrain the REE content (Turner et al. 2015); however, assignments to the absorptions and energy levels of different REEs have generally not been made to the observed absorption peaks. In addition, the rare earths in bastnäs site luminesce strongly; as discussed below, it appears that this fluorescence has at times been associated with hydroxyl stretching vibrations in Raman spectroscopic experiments (Frost and Dickfos 2007). In this study, we are able to assign the luminescence peaks to transitions of the neodymium ion, and probe changes to the REE site with pressure by using this Nd^{3+} luminescence.

Luminescence has been employed extensively as a probe for pressure-induced changes in crystal structure or in electronic configuration (e.g., Dolan et al. 1986; Freire et al. 1994; Bray 2001; O'Bannon and Williams 2016). Neodymium luminescence has been investigated for use as a pressure calibrant due to its high fluorescence intensity and insensitivity to changes in temperature (e.g., Hua et al. 1996), with YAlO_3 being typically viewed as the most promising Nd-bearing sensor due to its lack of phase

change or amorphization up to 80 GPa (Hua and Vohra 1997; Hernández-Rodríguez et al. 2018a, 2018b). Other high pressure studies using Nd^{3+} luminescence have investigated the pressure-shifts of different energy levels and their associated crystal field parameters (e.g., Santiuste et al. 2017; Hernández-Rodríguez et al. 2018a). Thus, Nd^{3+} luminescence has been investigated under pressure in a range of oxide crystals to derive insights into the electronic properties of crystals used for solid state lasers under compression, and at ambient pressure within minerals (e.g., Lenz et al. 2013). However, to our knowledge, high-pressure Nd^{3+} luminescence spectroscopy has not been previously utilized to probe the electronic and structural changes within a geologically relevant mineral. Here, we employ both Raman and Nd^{3+} luminescence spectroscopy to constrain changes in the bonding environments of both the carbonate and neodymium ions in bastnäsite; this is the first high pressure study of bastnäsite using these complementary techniques.

4.3 Experimental Methods

Natural bastnäsite ($\text{Ce}_{0.49}\text{La}_{0.25}\text{Nd}_{0.21}\text{Pr}_{0.04}\text{CO}_3(\text{F}_{0.95}\text{OH}_{0.05})$) from Northern Pakistan was used for these experiments. The chemical composition of the sample was confirmed with four grains of bastnäsite using a Thermoscientific Apreo scanning electron microscope equipped with an Oxford Instruments Ultim Max 100 mm energy dispersive X-ray spectrometer (0.8 nA and 15kV beam); SEM results are shown in Table S4-1 and Fig. S4-1. Raman spectroscopy and single crystal X-ray diffraction of this sample were in excellent agreement with previous determinations (Table S4-2; Ni et al. 1993; Frost and Dickfos 2007).

The ambient pressure crystal structure was measured at beamline 12.2.1 at the Advanced Light Source. Diffraction images were collected at 298 K with a Bruker D8 diffractometer equipped with a Photon II CPAD detector, and X-rays monochromated by silicon (111) to 17 keV (0.7288 Å). The single crystal was a clear block that was free of visible cracks and/or imperfections, with an approximate size of 40 x 10 x 10 μm. The sample was mounted in Paratone-N oil on a MiTeGen Micromount. Diffraction images were collected using the APEX3 program (Bruker 2016a). Images were integrated and cell refinements were computed using SAINT V8.34A (Bruker 2013b). The sample symmetry of the ambient structure was determined using XPREP, and crystal absorption was corrected using the algorithms of SADABS-2016/2 (Bruker 2016b). The crystal structure from Ni et al. (1993) was used as an initial fit, and refined using full-matrix least-squares on F^2 via SHELXL-2018/1 (Sheldrick 2015), using the software package ShelXle Rev 806 (Hübschle et al. 2011).

Raman and luminescence spectra were collected using a Horiba LabRam HR Evolution spectrometer equipped with either a 633 or 532 nm excitation laser, depending on the experiment being conducted. The spectrometer focal length was 800 mm, and a grating of 1800 lines/mm was used with a spectral resolution of $\sim 1 \text{ cm}^{-1}$. Spectra were collected up to a pressure of $\sim 50 \text{ GPa}$ at $\sim 300 \text{ K}$. Peak positions were calculated from fits that used a combination of Gaussian and Lorentzian peak shapes with Horiba LabSpec6 software.

High pressures were generated using a Princeton type symmetric diamond anvil cell equipped with type IIa diamonds with 250 μm culets. Rhenium was used as the gasket material. Gaskets were preindented to ~ 30 μm thickness, and the sample compartments were ~ 125 μm in diameter. A pressure medium of neon was used; neon remains hydrostatic to higher pressures than other liquid pressure media (e.g., 4:1 methanol:ethanol; Klotz et al. 2009), so it was used for this study. Ruby fluorescence from multiple ruby grains within the sample compartment was used to both determine pressures, and pressure variations within the chamber (Dewaele et al. 2008).

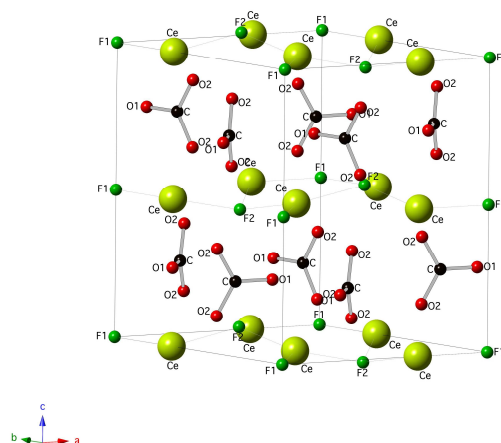


Figure 4-1. The ambient crystal structure of bastnäsite with the unit cell delineated by black lines; as per the labels, dark green spheres are fluorine, lime green is the REE, black is carbon, and red is oxygen.

4.4 Results

The ambient pressure and temperature crystal structure (Fig. 4-1) of our sample agrees with the previously reported structure by Ni et al. (1993), rather than with the structure inferred by Donnay and Donnay (1953). Bastnäsite is in the space group $P-62c$, with $a = 7.1206(4)$ Å, $c = 9.7681(5)$ Å, and 6 formula units in the unit cell. Its

structure has alternating layers comprised of $(\text{CO}_3)^{2-}$ units and Ce ions juxtaposed with F ions in the c -axis direction (Fig. 4-1). The Ce atom is in a 9-coordinate site (with a volume of $31.898 \text{ \AA}^3$), with a point symmetry of C_2 . The atoms comprising the Ce polyhedra are 3 fluorine atoms and 6 oxygen atoms. There is one carbonate group within the unit cell; the carbon and one of its coordinating oxygens (O1) lie on a mirror plane, and the other oxygens (O2) in the carbonate group are related by symmetry. The C-O1 distance is $1.273(11) \text{ \AA}$ and C-O2(x2) are $1.285(7) \text{ \AA}$; the carbon atom lies (within error) in a plane with the three oxygen atoms ($0.0027(76) \text{ \AA}$ out of the plane generated by the three oxygen atoms). There are two fluorine atom sites within the unit cell; F1 lies (roughly) in a plane with the Ce atoms that generate a plane at $x \sim 0.66$. F2 lies out of this plane, causing a distortion of the Ce polyhedra.

At ambient pressure and temperature, thirteen lattice modes and seven modes associated with the carbonate ion are resolved in the Raman spectrum (Fig. 4-2a). There are a large number of modes in the lattice region of the ambient spectrum, reflecting the relatively low symmetry of the polyhedra of the cerium ions, with bonding to both oxygen and fluorine. The modes associated with the carbonate ions are easily assigned: the symmetric stretch (ν_1) is at $1,096 \text{ cm}^{-1}$, one mode associated with the out of plane bend (ν_2) is at 870 cm^{-1} , an asymmetric stretch (ν_3) is at 1432 cm^{-1} , and the in-plane bend (ν_4) has components at $664, 686, 729, \text{ and } 737 \text{ cm}^{-1}$. The increased number of carbonate modes compared to the isolated ion is due to the distortion of the carbonate ion coupled with its low symmetry site within the crystal structure. Factor group analysis of the optic modes of bastnäsité with the space group $P-62c$, yields:

$$\Gamma_{\text{optic}} = 9A'_1(\text{R}) + 7A''_1(\text{Inactive}) + 11A'_2(\text{Inactive}) + 8A''_2(\text{IR}) + 19E'(\text{R,IR}) + 16E''(\text{R}).$$

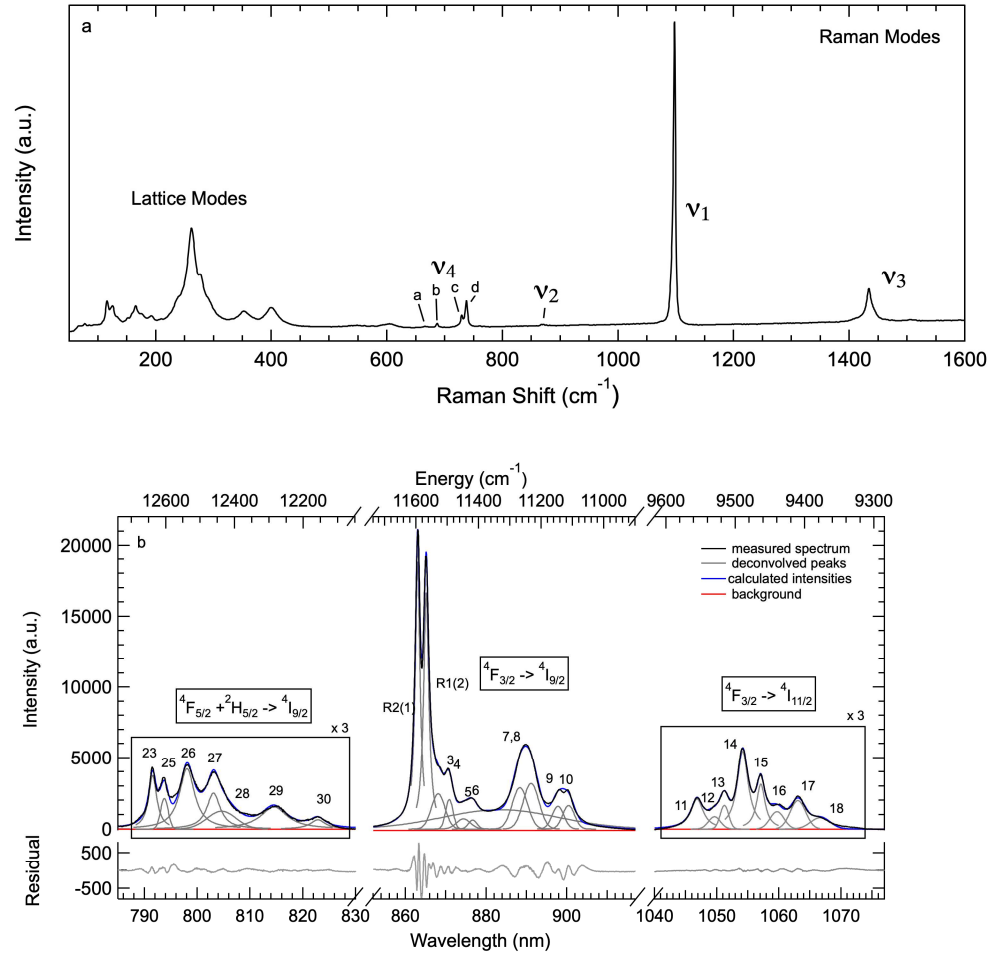


Figure 4-2. Ambient pressure and temperature (a) Raman spectrum and (b) luminescence spectrum of bastnäsité; (black) is the measured spectrum, (gray) is the deconvolved peaks, (blue) is the calculated intensities, and (red) is the background. The intensities for $4F_{5/2} + 2H_{5/2} \rightarrow 4I_{9/2}$ is increased by 3x, and the $4F_{3/2} \rightarrow 4I_{9/2}$ section was collected for 6x longer than the other two luminescence regions.

Thus, there are 44 Raman active vibrations and 27 infrared active vibrations; accordingly, the numbers of anticipated Raman active modes and carbonate modes are substantially greater than we observe, which is not unusual given that both weak modes

and accidental degeneracies are typically present in complex, low-symmetry molecular crystals.

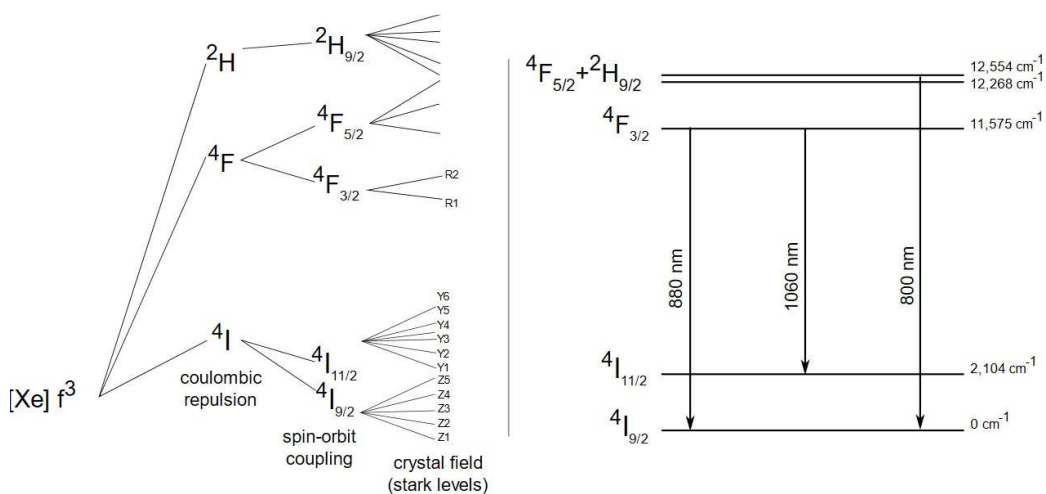


Figure 4-3. (left) Schematic representation of the f-electron energy levels of Nd^{3+} in bastnäsite showing the effects of Coulombic repulsion, spin-orbit coupling, and crystal-field interactions. (right) Partial energy level diagram of Nd^{3+} in bastnäsite showing the major spin-orbit coupling induced energy levels.

Bastnäsite does not naturally occur as the pure endmember with a given rare earth element, so multi-element occupancy of the rare earth element site is expected. In our bastnäsite sample, neodymium substitutes at the 24% level into the cerium site. As such, we probe the Nd^{3+} luminescence within the structural environment of the cerium site (Fig. 4-2b). Within the bastnäsite crystal structure, neodymium's electronic energy levels are split by three principal effects: first, by electrostatic interactions, then spin orbit coupling, and finally by the local electric field that generates 2 to 6 Stark components (depending on the energy level), as imposed by the crystal field surrounding the ion (Fig. 4-3). The observed Nd^{3+} luminescence is entirely consistent with that of a Nd^{3+} ion in a site with low symmetry (e.g., Table 4.3 of Kaminskii 1981).

We observe luminescence associated with energy transitions between these electronic states: ${}^4F_{5/2}+{}^2H_{9/2} \rightarrow {}^4I_{9/2}$ at $\sim 790\text{-}822$ nm, ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ at $\sim 862\text{-}900$ nm, and ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ at $\sim 1046\text{-}1066$ nm (Fig. 4-3). We are able to deconvolve the peaks and assign the energy levels of each Stark-split level (${}^4I_{9/2}$, ${}^4I_{11/2}$, $F_{3/2}$, ${}^4F_{5/2}$, ${}^2H_{9/2}$) of the spin orbit coupled energy levels (Fig. 4-2b).

We collected Raman and Nd^{3+} luminescence spectra to 50 GPa at ambient temperature: two discontinuous, reversible, phase changes were observed: one at ~ 25 GPa, and the second at ~ 38 GPa. Systematic changes in site distortion are monitored via the luminescence spectra, while splittings and mode discontinuities in the Raman data provide *prima facie* evidence for the phase transitions.

4.5 High Pressure Raman Results and Discussion

4.5.1 Bastnäs site-I: Raman spectroscopy under pressure

We resolve mode shifts for both lattice and carbonate modes of the ambient pressure phase of bastnäs site up to 25 GPa (Fig. 4-4). Mode assignments and their pressure shifts are reported with associated mode Grüneisen parameters in Table 4-1, calculated using the bulk modulus of 105 GPa from Rowland (2017). Below 25 GPa, the lattice modes all increase in frequency with pressure, with no major changes in their number or peak shape morphology (Fig. 4-4a, d). Some apparent changes in intensity are observed in this pressure range, but these changes are likely due to a combination of pressure-induced relaxation of accidental degeneracies and possible effects of changes in crystal orientation between different spectra.

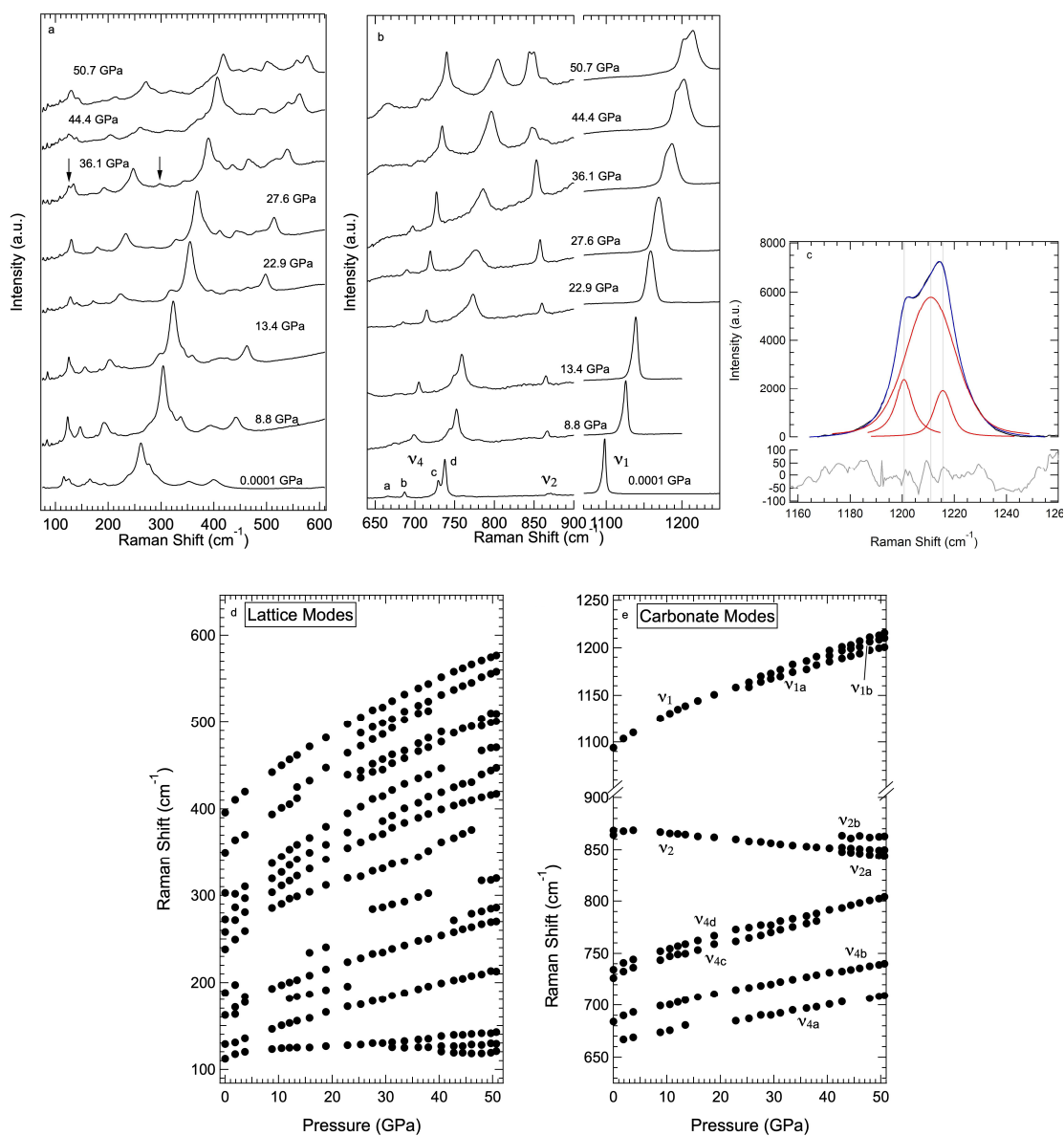


Figure 4-4. (a and b) Representative Raman spectra of the lattice and carbonate spectral regions under compression, arrows indicate new peaks in Raman spectrum; (c) deconvolution of the symmetric stretch of the Raman spectrum of bastnäsite at 50.6 GPa, the highest pressure probed; (d and e) peak positions of observed Raman modes as a function of pressure at room temperature under compression.

ν_0 (cm ⁻¹)	Assignment	$d\nu/dP$ (cm ⁻¹ /GPa)	Grüneisen parameter*
112	Lattice mode	0.59(9)	0.53

129	Lattice mode	1.95(4)	1.59
162	Lattice mode	2.53(16)	1.64
188	Lattice mode	2.74(14)	1.54
238	Lattice mode	3.63(28)	1.60
258	Lattice mode	4.19(16)	1.70
272	Lattice mode	4.36(18)	1.68
303	Lattice mode	4.33(14)	1.50
350	Lattice mode	3.90 (24)	1.17
396	Lattice mode	4.35(14)	1.15
-	(CO ₃) ²⁻ in-plane bend (ν_{4a})	0.89(10)	-
684	(CO ₃) ²⁻ in-plane bend (ν_{4b})	1.28(6)	0.20
726	(CO ₃) ²⁻ in-plane bend (ν_{4c})	1.51(8)	0.22
734	(CO ₃) ²⁻ in-plane bend (ν_{4d})	1.60(6)	0.23
864	(CO ₃) ²⁻ out-of-plane bend (ν_2)	-	-
868	(CO ₃) ²⁻ out-of-plane bend (ν_2)	-0.29(8)	-0.04
1094	(CO ₃) ²⁻ symmetric stretch (ν_1)	2.79(13)	0.30
1434	(CO ₃) ²⁻ asymmetric stretch (ν_3)	-	-

Table 4-1. Raman modes as a function of pressure and calculated mode Grüneisen parameters of bastnäsite-I up to 25 GPa. *Bulk modulus of 105 GPa used from the La/F bastnäsite endmember (Rowland 2017).

The Raman active modes of the carbonate ion shift monotonically up to 25 GPa, indicating that no phase change occurs up to this pressure. The symmetric stretching mode (ν_1) shifts approximately linearly up to 25 GPa at a rate of 2.79 cm⁻¹/GPa. Interestingly, at ambient pressure, this peak is more asymmetric than at 23 GPa. The carbonate out of plane bend (ν_2) shifts negatively at -0.29(8) cm⁻¹/GPa; such a modest negative shift is typical for carbonate minerals (e.g. aragonite and dolomite; Kraft et al. 1991; Vennari and Williams 2018). This mode grows in intensity on compression compared to the in-plane bend, and at 25 GPa, the mode has twice the relative amplitude as at lower pressures. This shift in intensity is plausibly associated with a Fermi resonance between higher-lying components of the ν_4 in plane bend and the ν_2

out of plane bend, as these bands approach one another under pressure (their separation changes from $\sim 130\text{ cm}^{-1}$ to near 75 cm^{-1} at 25 GPa: Fig. 4b).

The four carbonate in-plane bends all shift positively with pressure (Fig. 4-4b,d, Table 4-1), and their relative intensities also shift with pressure. The highest frequency band remains the most intense up to 25 GPa. The second highest frequency mode, which initially is present as a shoulder, merges into the highest frequency band under pressure, and may decrease in relative amplitude: we believe this decrease may be from a combination of a compression-induced loss of Fermi resonance, coupled with a peak broadening of the most intense peak. There appears to be a general increase in relative intensity of the third-highest frequency in-plane bending mode with pressure, although the intensities of the two lowest frequency in-plane bending modes relative to one another appear largely unchanged under compression. The pressure shifts of the two lower frequency bending modes are such that they diverge from the two highest frequency in-plane bending modes, implying that the distortion of the carbonate group may increase under compression in bastnäsite.

4.5.2 Bastnäsite-II: Raman spectroscopy under pressure

The phase change that occurs at 25 GPa is primarily manifested by changes of the carbonate vibrations, although there are some shifts in the lattice region, as well (Fig. 4-4). Most lattice modes appear to persist through this phase change: however, three new low intensity modes appear at 284, 430 and 480 cm^{-1} . Within the carbonate region, the symmetric stretch splits (Fig. S4-3), with a second peak appearing on its lower frequency side. The two highest frequency in-plane bends, which below 25 GPa

are progressively merging into a single peak, become a single, asymmetric peak. The other two in-plane bend modes and the out of plane bend mode each increase in intensity across the transition (Fig. 4-4). Taken together, these changes are consistent with a change in symmetry of the carbonate group, probably from *m* to lower symmetry.

ν_0 (cm ⁻¹)*	Assignment	$d\nu/dP$ (cm ⁻¹ /GPa)
128	Lattice mode	0.52(3)
175	Lattice mode	1.66(4)
228	Lattice mode	1.77(6)
284	Lattice mode	1.76(8)
322	Lattice mode	2.20(11)
362	Lattice mode	2.61(9)
403	Lattice mode	2.92(11)
436	Lattice mode	2.82(9)
444	Lattice mode	2.88(8)
473	Lattice mode	3.35(15)
488	Lattice mode	2.92(8)
506	Lattice mode	3.06(1)
687	(CO ₃) ²⁻ in-plane bend (ν_{4a})	0.87(6)
717	(CO ₃) ²⁻ in-plane bend (ν_{4b})	0.98(2)
765	(CO ₃) ²⁻ in-plane bend (ν_{4c})	1.39(3)
775	(CO ₃) ²⁻ in-plane bend (ν_{4d})	1.09(7)
858	(CO ₃) ²⁻ out-of-plane bend (ν_2)	-0.49(2)
1158	(CO ₃) ²⁻ symmetric stretch (ν_{1a})	1.66(7)
1164	(CO ₃) ²⁻ symmetric stretch (ν_1)	2.09(7)

Table 4-2. Raman modes as a function of pressure of bastnäsité-II from 25 to 38 GPa. * ν_0 is at 25 GPa.

The pressure shifts of the lattice modes in bastnäsité-II are listed in Table 4-2, and shown in Fig. 4-4a,c. In addition to the modes that first are resolved at 25 GPa, there are two weak modes that become unresolvable at this pressure (those with zero pressure frequencies of 140 and 185 cm⁻¹). Relative to the carbonate region, these are relatively subtle changes in the lattice region of the Raman spectrum. Accordingly, the REE site within bastnäsité-II has likely only changed modestly compared to bastnäsité-

I; certainly, no shift in coordination of the REE site occurs. The lowest frequency lattice mode splits at 30 GPa—we believe that this may be due to pressure-induced elimination of an accidental degeneracy rather than the phase change itself, as no other lattice modes split at the same pressure. The new intermediate frequency mode (at 284 cm^{-1} at the transition) is only readily tracked until the transition to bastnäsite-III at 38 GPa. Overall, the lattice modes remain remarkably lightly altered under pressure; the two higher frequency lattice modes that appear at 25 GPa are resolvable to the highest pressure probed. This persistence of many of the lattice modes suggests that the topological changes that occur at the two phase transitions do not profoundly affect the lattice vibrations (which are likely more associated with the CeF layer within the structure and vibrations of the rare earth elements against the carbonate framework). It is possible that a coexistence of multiple REE sites, with different distortions but similar coordination, occurs in the pressure range from 25 GPa to 38 GPa.

The pressure shifts of the modes (ν_1 , ν_{1a}) associated with the symmetric stretch of the carbonate ion decrease above 25 GPa, and, as pressure is increased, the two modes associated with the symmetric stretch in the high-pressure phase separate in frequency. Notably, the lower frequency in-plane bend (ν_{2b}) and the out of plane bending (ν_2) vibrations become sharper after the transition at 25 GPa to bastnäsite-II up until 38 GPa: this may be a consequence of the transition relieving internal stress within the crystal. Nevertheless, even though there is a change in intensity and shape of a subset of the carbonate bending modes across the transition, there is no change in the observed number of peaks, nor a discontinuous change in their frequencies.

Bastnäsite-II may have more distorted cation sites (due to the larger number of lattice peaks observed), but does not have major changes associated with its bonding, nor an apparent doubling of sites within the unit cell. The most marked effect of the transition is the splitting of the symmetric stretching vibration (ν_1 , ν_{1a}) of the carbonate group, implying that the local symmetry of the carbonate group may have shifted.

4.5.3 Bastnäsite-III: Raman spectroscopy under pressure

The transition from bastnäsite-II to -III is marked by further splitting of the carbonate modes and modest changes in the lattice modes near 38 GPa. Again, additional modes split at this transition, and there are significant changes in band intensities: for example, the most intense lattice mode at $\sim 390\text{ cm}^{-1}$ at 38 GPa becomes markedly less intense compared to the other modes. It is unclear whether this transition, which clearly initiates at 38 GPa, is complete near this pressure, or whether it is kinetically impeded, and occurs gradually across a wide pressure range. The net decline in intensity of a number of the vibrational modes of bastnäsite-II between 38 and 51 GPa, and apparent growth of new, or weak, bands is compatible with the latter interpretation. If, however, this is a transition that is complete near 38 GPa, the new modes (at 120, 271 cm^{-1}) that appear at the transition indicate that either the REE site is further distorted, and/or there has been a doubling of the REE sites within the unit cell. We believe, in conjunction with the luminescence data described below, that a new REE site is produced associated with the transition to bastnäsite-III.

$\nu_0\text{ (cm}^{-1}\text{)*}$	Assignment	$d\nu/dP\text{ (cm}^{-1}\text{/GPa)}$
119	Lattice mode	0.007(116)
127	Lattice mode	0.32(8)

139	Lattice mode	0.40(4)
203	Lattice mode	1.39(8)
258	Lattice mode	1.59(5)
271	Lattice mode	1.84(12)
367	Lattice mode	2.50(17)
404	Lattice mode	1.74(4)
425	Lattice mode	2.75(17)
488	Lattice mode	2.07(29)
537	Lattice mode	2.65(6)
558	Lattice mode	2.43(5)
703	(CO ₃) ²⁻ in-plane bend (ν_{4a})	0.78(4)
733	(CO ₃) ²⁻ in-plane bend (ν_{4b})	0.85(4)
794	(CO ₃) ²⁻ in-plane bend (ν_{4d})	1.23(5)
848	(CO ₃) ²⁻ out-of-plane bend (ν_{2a})	-0.68(9)
852	(CO ₃) ²⁻ out-of-plane bend (ν_2)	-0.31(4)
864	(CO ₃) ²⁻ out-of-plane bend (ν_{2b})	-0.007(162)
1186	(CO ₃) ²⁻ symmetric stretch (ν_{1a})	1.54(5)
1192	(CO ₃) ²⁻ symmetric stretch (ν_{1b})	1.79(8)
1197	(CO ₃) ²⁻ symmetric stretch (ν_1)	1.81(7)

Table 4-3. Raman modes as a function of pressure of bastnäsite-III from 38 to 50 GPa. * ν_0 is at 38 GPa.

The changes of the carbonate vibrations at the transition to bastnäsite-III are more dramatic than those associated with the bastnäsite-I to –II transition (Table 4-3). The symmetric stretch, which split into two deconvolvable modes (ν_1 , ν_{1a}) above 25 GPa, requires a new component (ν_{1b}) to fit its band shape above 38 GPa (Fig. 4-4c). The out of plane bend begins to become asymmetric at 36 GPa, and splits from one band to three distinct modes (ν_2 , ν_{2a} , ν_{2b}) above 38 GPa. The highest frequency in-plane bending peak (ν_{4d}) sharpens across the transition to bastnäsite-III; the two components (ν_{4c} , ν_{4d}) of this peak become difficult to deconvolve above 38 GPa. The next highest frequency in-plane bending peak (ν_{4b}) remains sharp and distinct across the transition, but a change in its peak shape is apparent: the top of the peak remains sharp, but the

bottom broadens, and there may be additional, not-readily-resolved modes on its high and low frequency sides. Accordingly, two of the three (and possibly all three) of the different types of carbonate vibrations monitored have additional bands that appear following the transition at 38 GPa.

The Raman spectrum of bastnäsite-III reflects both distorted carbonate ions and potentially multiple REE sites that persist to the highest pressures probed (52 GPa). While Raman spectroscopy is an excellent probe for characterizing changes in local bonding environments, we supplement these results with Nd³⁺ luminescence results to characterize the electronic transitions of Nd in the REE site in order to better constrain structural changes that specifically involve the REE ion.

4.6 High Pressure Nd³⁺ Luminescence Results and Discussion

Figures 4-5,6,7 show both our luminescence results within different spectral regions, and the ambient pressure energy level diagrams for the associated transitions. In each instance, we use the peak nomenclature of Dieke (1969). The majority of the transitions have red shifts of their respective luminescence with pressure – such an approach of long-lived luminescing electronic states towards the ground state under compression is common, such as for Nd³⁺ in garnets (Hua et al. 1996) and Cr³⁺ in ruby (Mao et al. 1986), although exceptions exist (e.g., Hua and Vohra 1997; Hernández-Rodríguez et al. 2018a). The most intense and highest energy bands associated with the transition between the ⁴F_{3/2} state and the ⁴I_{9/2} ground state (which are, by convention, named R1 and R2: Dieke 1969), do not redshift or blueshift notably; while they may have a small and non-linear pressure dependence, they shift little with pressure up to

50 GPa (Fig. 4-5; Fig. 4-4). Thus, the pressure-induced shifts of the $^4F_{3/2}$ states are similar to that of the lowest energy $^4I_{9/2}$ state.

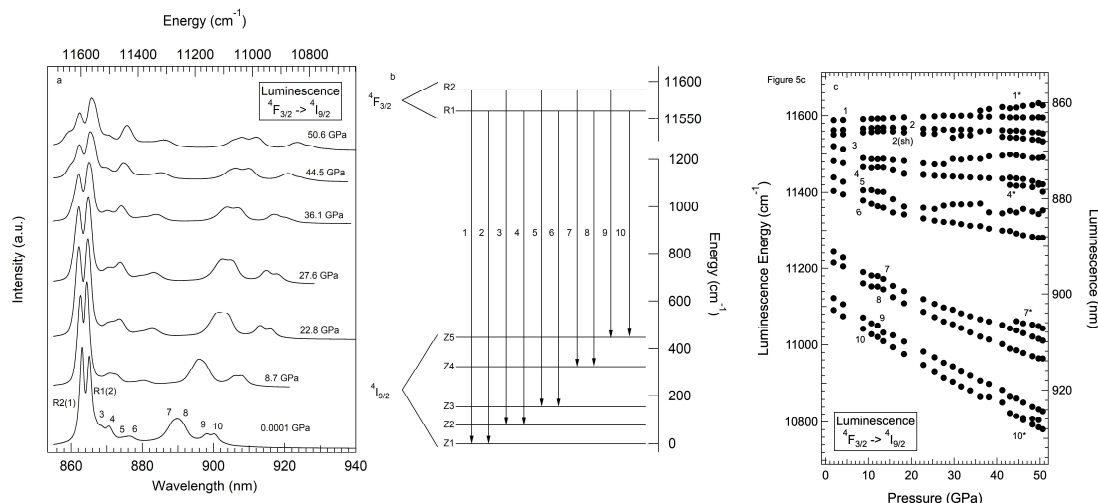


Figure 4-5. (a) Luminescence spectra of the $^4F_{3/2} \rightarrow ^4I_{9/2}$ transition in Nd^{3+} under pressure (left), partial energy level diagram (right). (b) Peak positions of observed luminescence modes with pressure.

Assignment	λ_0 (nm)	ν_0 (cm ⁻¹)	Bastnäsité-I to 25 GPa (cm ⁻¹ /GPa)	Bastnäsité-II 25 to 40 GPa (cm ⁻¹ /GPa)	Bastnäsité-II 40 to 50 GPa (cm ⁻¹ /GPa)
1*					1.05(33)
1	862.91	11,588.7	0.42(2)	-0.27(11)	-0.12(7)
2	864.96	11,561.2	0.20(9)	-0.31(16)	-0.83(11)
3	868.47	11,514.5	-1.84(24)	1.43(48)	-1.13(13)
4	870.63	11,485.9	-1.67(10)	-0.48(2)	-0.87(29)
4*					-1.76(37)
5	874.51	11,435.0	-3.51(26)	-1.14(94)	-1.37(88)
6	876.80	11,405.1	-3.35(13)	-1.61(15)	0.16(62)
7*					-2.76(36)
7	887.95	11,261.9	-5.99(23)	-3.57(14)	-4.28(7)
8	889.68	11,240.0	-6.40(26)	-4.63(15)	-4.08(24)
9	897.84	11,137.8	-6.73(19)	-5.26(10)	-5.62(25)
10	900.23	11,108.3	-6.95(8)	-4.93(40)	-4.75(134)
10*					-5.16(2)

Table 4-4. $^4F_{3/2} \rightarrow ^4I_{9/2}$ luminescence as a function of pressure in bastnäsité.

Overall, the luminescence changes subtly at the transition between bastnäsité-I and -II compared to the changes that occur across the bastnäsité-II to -III transition; this is likely due to the subtle nature of the first transition, and a more dramatic change

in the REE site in the second transition (possibly involving a doubling of the number of cerium sites in the cell). We discuss each of the major transition manifolds in sequence, since each show somewhat different behavior under compression.

4.6.1 $^4F_{3/2} \rightarrow ^4I_{9/2}$ luminescence under pressure

We observe all 10 peaks associated with the transitions between the Stark levels for the $^4F_{3/2}$ and $^4I_{9/2}$ states. The R1 and R2 bands provide a direct measure of the excited state ($^4F_{3/2}$) energy above the ground state. Under pressure, up until ~15 GPa, we see a decrease in their peak separation (Fig. 4-500). However, near 15 GPa this trend reverses, and the peaks begin to separate. Because the Stark splitting is produced by the local electric field at the Nd ion, this turnover is associated with an initial decrease in the electric field gradient, followed by an increase, or an onset of a more anisotropic local bonding environment. Such a change may be indicative of a change in local bonding, and hence a shift in compressional behavior within the REE site, but does not necessarily indicate any change in crystal symmetry. The relative intensities of these bands remains relatively unchanged to 25 GPa.

From 25 to 38 GPa, most of the luminescence peak positions continue to decrease in energy at rates similar to those prior to the transition to bastnäsite-II; representative spectrum at 31.2 GPa is peakfit in Fig. S4-4a. Interestingly, only one transition clearly increases in energy above 25 GPa: R2 $\rightarrow$ Z2(3). This anomalous shift indicates that the splitting of the $^4I_{9/2}$ state is complex under compression, and that the electric field that is impacting the f-orbitals is anisotropic in its shape.

Above 38 GPa, many of the pairs of luminescence bands induced by the two $^4F_{3/2}$ states split from two to three or four peaks: this splitting strongly suggests that an additional rare earth element site is present within the unit cell of bastnäsite-III, consistent with our Raman spectra, with the new site having a modestly different set of Stark splittings. The number of Stark levels is capped by the low symmetry of the REE site—so any decrease in symmetry of the single REE site would not increase the number of peaks observed (Kaminskii 1981). Thus, the most plausible mechanism for producing additional bands is via the onset of a new REE site within the structure. Above 38 GPa, deconvolution of the luminescence bands and the presence of the new bands provides primary evidence for a new electronic environment within the structure; representative spectrum deconvolved in Fig. S4-5a. While we are able to determine the new R1 and R2 energy levels of the new site, we are unable to identify the new site's Z3 level. We believe this is due to the low intensity of the transitions from R1 and R2 to Z3 before the phase transition; thus, after the transition it remains difficult to determine the full suite of peak locations associated with the new site.

Interestingly, a new band begins to appear at the highest energies of this suite of transitions (associated with an additional transition for $R2 \rightarrow Z1$) near 36 GPa—this is likely either a precursor to, or the first indication of the phase change that we observe in the Raman spectra at 38 GPa. The intensity of the peak associated with $R1 \rightarrow Z2(4)$ becomes more intense in bastnäsite-III. The change in intensity indicates that the excitation and/or emission cross sections for those transitions have changed: since we

have not measured excitation spectra, we cannot distinguish which (or both) of these alternatives is the case.

4.6.2 $^4F_{3/2} \rightarrow ^4I_{11/2}$ luminescence under pressure

At room pressure and temperature using 532 nm excitation wavelength, we are able to also observe all 12 peaks associated with the transitions from the $^4F_{3/2}$ to $^4I_{11/2}$ states (Fig. 4-6; Table 4-5). At ambient pressure, the most intense peak is associated with the transition from R1 $\rightarrow$ Y2 (14). The relative intensities of the respective peaks associated with transitions between these states is similar to that of Nd^{3+} in yttrium aluminum garnet, with the most intense being peak #14, with generally comparable intensities of the nearby lower amplitude peaks (e.g., Pokhrel et al. 2012). Fig. 4-6 shows the changes produced by pressure, and Table 5 contains the pressure shifts of the peaks. Interestingly, the highest wavelength peaks (lowest energy transitions) associated with R1 and R2 $\rightarrow$ Y5 and Y6 are not observable with 633 nm excitation—they were only observable with 532 nm excitation (Fig. S4-2). We attribute this to the existence of either rapid non-radiative decay pathways associated with the absorptions that are pumped by the lower energy excitation, or those lower energy transitions being accessible when the higher energy transitions are overpopulated.

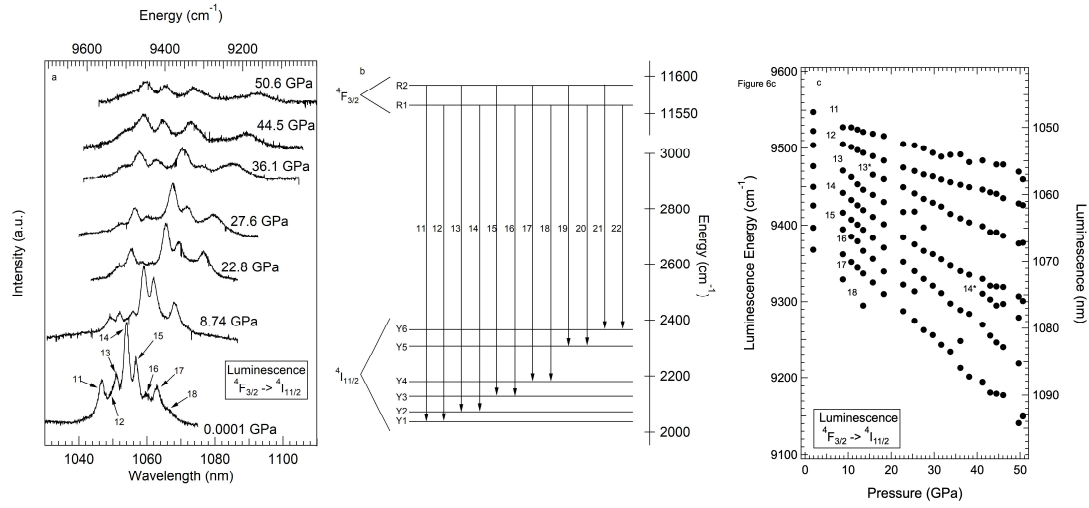


Figure 4-6. (a) Luminescence spectra of the $^4F_{3/2} \rightarrow ^4I_{11/2}$ transition in Nd^{3+} as a function of pressure. Luminescence spectra are produced by 633 nm excitation. (b) Peak positions of the observed luminescence bands with pressure.

Assignment	λ_0 (nm)	ν_0 (cm $^{-1}$)	Bastnäsité-I to 25 GPa (cm $^{-1}$ /GPa)	Bastnäsité-II 25 to 40 GPa (cm $^{-1}$ /GPa)	Bastnäsité-II 40 to 50 GPa (cm $^{-1}$ /GPa)
11	1046.83	9,552.7	-1.91(11)	-1.26(40)	-2.35(51)
12	1049.86	9,525.1	-2.21(4)	-1.59(5)	-2.19(10)
13*			-2.47(12)	-2.99(14)	-2.33(22)
13	1051.0	9,514.7	-4.00(27)		
14	1054.01	9,487.6	-4.42(14)	-3.08(13)	-2.78(33)
14*					-3.54(50)
15	1056.82	9,462.3	-4.77(7)	-4.57(27)	-5.84(37)
16	1060.09	9,433.2	-4.91(13)		
17	1062.86	9,408.6	-5.26(4)	-6.00(39)	-5.35(86)
18	1065.77	9,382.9	-6.35(27)		

Table 4-5. $^4F_{3/2} \rightarrow ^4I_{11/2}$ luminescence as a function of pressure in bastnäsité.

Under compression, all modes shift to lower energy with pressure at varying rates: as with the $^4I_{9/2}$ transitions, the most rapidly shifting are those at the lowest energy. The lowest energy mode (18) becomes unresolvable above 15 GPa. Around this pressure, an additional peak (13*) is observed at slightly lower energy than (13). These changes in peak position and intensity may be associated with the change in the sign of the trend of electric field near this pressure that is observed in the R2-R1 separation (Fig. 4-8). At 25 GPa, the peak (13) becomes unresolvable, and this shift

may be associated with the transition from bastnäsite-I to -II. Overall, across the bastnäsite-I to -II transition, there are no major changes in either the number of luminescence peaks or their intensities, thus confirming our inference from the Raman spectra that this transition likely involves (at most) a subtle change to the REE site. Moreover, the pressures shifts of all bands are consistent in their migration to lower energy, indicating that these transitions may be less sensitive to changes in the detailed electric field gradient.

Above 25 GPa, the peaks associated with bastnäsite-II continue to broaden and decrease in intensity. As pressure is increased, peak (14) decreases particularly in intensity relative to the other bands in this multiplet. All peaks, except (16) (which becomes unresolvable) persist to 38 GPa; representative spectrum at 31.2 GPa is peakfit in Fig. S4-4b.

Above 38 GPa, the relative intensities of individual peaks continue to change. As pressure is increased, the lower energy transitions become less intense relative to the higher energy transitions; specifically, peak (14), which at ambient pressure is the most intense, becomes the third most intense, following peaks (12) and (13). These intensity changes may be due to a splitting of peak (14). At 38 GPa, a lower energy peak branches off of peak (14). This splitting, coupled with the overall drop in intensity of the multiplet of peaks, further indicates that there is likely an additional, distinct REE site in the unit cell above 38 GPa; representative spectrum at 50.6 GPa is peakfit in Fig. S4-5b.

4.6.3 ${}^4F_{5/2}+{}^2H_{9/2}\rightarrow{}^4I_{9/2}$ luminescence under pressure

At ambient pressure and temperature, we observe 7 peaks associated with the transition from ${}^4F_{5/2}+{}^4H_{9/2}\rightarrow{}^4I_{9/2}$. There is well documented overlap between the energy levels of ${}^4F_{5/2}$ and ${}^4H_{9/2}$ (5 in ${}^4H_{9/2}$ and 3 in ${}^4F_{5/2}$), and identification of the individual Stark levels of the ${}^4F_{5/2}+{}^4H_{9/2}$ transitions to ${}^4I_{9/2}$ is helped by the fact that these transitions happen solely to the lowest energy state in ${}^4I_{9/2}$ (e.g., Muñoz Santiuste et al. 2017). Additionally, we are able to separate and identify the majority of the individual Stark levels due to differences in intensity, line shape and line width in both sets of transitions (Henderson et al. 1967). Once compressed above ~ 1 GPa, a fifth band associated with the transition from ${}^4H_{9/2}\rightarrow{}^4I_{9/2}$ is observed (Fig. 4-7; Table 4-6). As an aside, we note that the appearance of this sequence of luminescence bands is essentially indistinguishable in both amplitude and absolute position (laser frequency minus reported Raman frequency) from bands that have been attributed to Raman-active hydroxyl stretching vibrations observed under 633 nm excitation in bastnäsité from Pakistan (Frost and Dickfos 2007).

Around 2 GPa, the pressure-induced removal of accidental degeneracies in the higher energy transitions becomes apparent, and the appearance of new bands continues as pressure is increased in bastnäsité-I. For example, the intensity of peak (25) decreases once pressure is applied: this is likely also from the loss of degeneracy. As with most other emission bands in this system, the nine bands associated with these transitions all shift to lower energy with pressure up to 25 GPa (Fig. 4-7; Table 4-6).

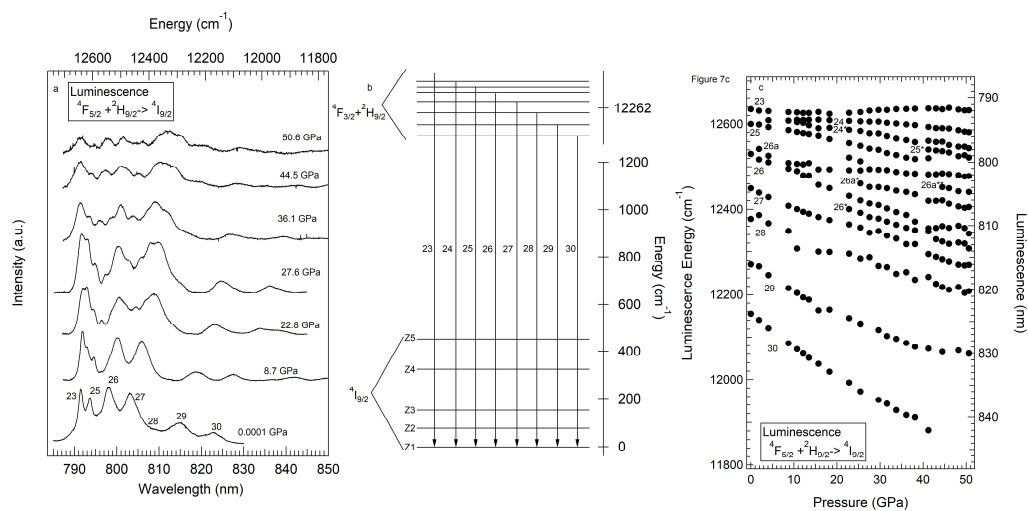


Figure 4-7. Luminescence spectra of the ${}^4F_{5/2} + {}^2H_{9/2} \rightarrow {}^4I_{9/2}$ transition in Nd^{3+} as a function of pressure. Luminescence spectra are produced by 633 nm excitation. (b) Peak positions of observed luminescence bands with pressure.

Assignment	λ_0 (nm)	ν_0 (cm $^{-1}$)	Bastnäsité-I to 25 GPa (cm $^{-1}$ /GPa)	Bastnäsité-II 25 to 40 GPa (cm $^{-1}$ /GPa)	Bastnäsité-II 40 to 50 GPa (cm $^{-1}$ /GPa)
23 (${}^2H_{9/2}$)	791.46	12,634.9	-0.37(8)	0.57(9)	-0.49(18)
24 (${}^2H_{9/2}$)			-0.04(7)	-0.73(7)	-1.30(13)
24* (${}^2H_{9/2}$)			-1.52(33)	-2.01(12)	-1.90(21)
25* (${}^2H_{9/2}$)					-2.00(24)
25 (${}^2H_{9/2}$)	793.65	12,600.0	-1.94(6)	-2.51(11)	
26a (${}^2H_{9/2}$)			-2.30(25)	-0.80(19)	-0.60(23)
26a* (${}^2H_{9/2}$)				-1.83(15)	-2.04(33)
26a**					-2.00(37)
26* (${}^2H_{9/2}$)				-3.72(29)	-0.73(70)
26 (${}^2H_{9/2}$)	798.04	12,530.7	-5.05(47)	-3.20(11)	-3.08(75)
27 (${}^2H_{9/2}$)	803.34	12,448.0	-3.82(18)	-3.19(37)	2.79(28)
28 (${}^4F_{5/2}$)	807.94	12,377.2	-4.41(68)	-3.93(54)	-3.16(76)
29 (${}^4F_{5/2}$)	814.90	12,271.4	-5.98(32)	-4.36(21)	-0.93(43)
30 (${}^4F_{5/2}$)	822.71	12,155.0	-7.22(14)	-4.99(22)	

Table 4-6. $4F_{5/2} + 2H_{9/2} \rightarrow 4I_{9/2}$ luminescence as a function of pressure in bastnäsité.

Above 25 GPa, two new bands emerge, and the highest energy mode (23) undergoes an anomalous shift to higher energy with pressure from 25 to 38 GPa. This shift is consistent with the changes in the highest-lying bands associated with the

$^4F_{3/2} \rightarrow ^4I_{9/2}$ transitions. All other peaks shift to lower energy with pressure until 38 GPa; representative spectrum at 31.2 GPa is peakfit in Fig. S4-4c.

Bastnäsite-III has broader and lower intensity luminescence peaks for this set of transitions (Fig. 4-7). This drop in intensity and increase in breadth is consistent with there being an additional REE site within the unit cell of this phase, but resolution of a separate full manifold of bands associated with the new site is not feasible. In addition to the intensity changes, there are discontinuous changes in some of the bands. For example, the lowest energy peak (30) becomes unresolvable above the transition; (25) shifts discontinuously to a higher energy, and a new band, (26a**), branches out from between (26a) and (26a*) (Fig. 4-7, Table 6); the highest pressure spectrum is peakfit in Fig. S4-5c. As with the other luminescent sets of transitions, the higher pressure phase change involves more marked changes in the spectra than the lower pressure transition from bastnäsite-I to -II.

4.6.4 R1-R2 separation

The energy differences between the R1 and R2 bands are perhaps most readily associated with structural changes in the REE site under pressure (Fig. 4-8). While the absolute shift of each energy level with pressure is quite small (Fig. 4-5), the separation in energy between these two bands does change. An increase in energy separation is characteristic of a REE site that is decreasing in symmetry/increasing in distortion, and a decrease indicates the converse: a transition towards higher symmetry/lower distortion (e.g., Hua et al. 1996).

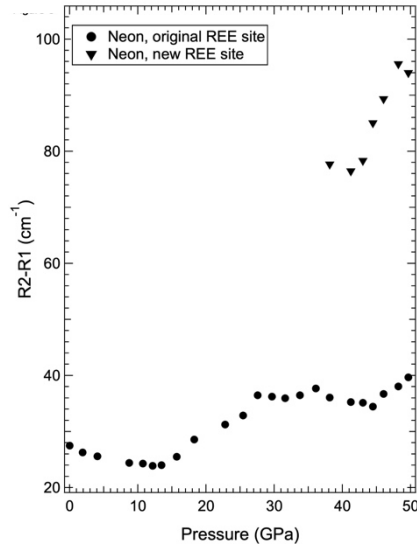


Figure 4-8. R-line separation of Nd^{3+} (R1 and R2) in the original REE site (closed circles), and associated with the new high-pressure site in bastnäsite-III (closed triangles), as a function of pressure. From 0 to 15 GPa, the difference between these two modes initially decreases indicating a REE site that is becoming more symmetric or, in other words, R1 and R2 are becoming closer to degenerate (Fig. 8). At 15 GPa, the difference between these two energy levels increases with pressure until 25 GPa, thus indicating that the REE site is becoming more distorted. Above 25 GPa, the change in energy level separation is negligible until 38 GPa, where the onset of a new REE site occurs. The energy level splitting of the new and old REE site differ dramatically. The most striking change is the energy difference between R1 and R2: at 50 GPa, the difference between R1 and R2 in the original REE site is $\sim 42 \text{ cm}^{-1}$, and in the new site, the difference is $\sim 96 \text{ cm}^{-1}$. While this difference is large, an energy difference between R1 and R2 of above 100 cm^{-1} is common within ambient pressure, highly distorted Nd^{3+} sites. For example, the R2-R1 separation is 123 cm^{-1} in CAZGAR ($\text{CaZn}_2\text{Y}_2\text{Ge}_3\text{O}_{12}$; Sardar and Yow 1998) and 116 cm^{-1} in $\text{CaY}_2\text{MgGe}_3\text{O}_{12}$ (Sharp et al. 1974). In addition, if site distortion

increases under pressure, increased separation is expected, so this doubling of the R2-R1 separation in the new site to nearly 100 cm^{-1} is not outside the bounds of sites observed at ambient pressure in other phases.

4.6.5 Separation of energy levels with pressure

Over most of the pressure range (15-50 GPa) of this experiment, the luminescence bands within each set of transitions separate under compression, indicating a progressive increase in the crystal field splitting, which is likely associated with a pressure-induced increase in distortion of the REE site. The change in the separation energy of $^4\text{I}_{9/2}$ (Z1-Z5) is $+6.03 \text{ cm}^{-1}/\text{GPa}$, $^4\text{I}_{11/2}$ (Y1-Y4), is $3.61 \text{ cm}^{-1}/\text{GPa}$, $^4\text{F}_{3/2}$ (R1-R2) is $+0.32 \text{ cm}^{-1}/\text{GPa}$, $^4\text{F}_{5/2}$ is $2.81 \text{ cm}^{-1}/\text{GPa}$, and $^2\text{H}_{9/2}$ is $3.63 \text{ cm}^{-1}/\text{GPa}$. Fig. 4-9 displays the overall splitting of the spin orbit coupling energy levels, with the barycenters (the arithmetic means) shown as the energy levels (for all but the ground state). Similar rates of changes in the separation of the energy levels $^4\text{I}_{9/2}$, $^4\text{I}_{11/2}$, and $^4\text{F}_{3/2}$ have been observed previously in $\text{YAlO}_3\text{:Nd}$ at high pressures (Hernández-Rodríguez et al. 2018a). Several distinct and separable effects are present in Fig. 4-9. First, the net separation between the Stark levels of the ^2H , ^4F and ^4I levels decreases under compression. As shown in Fig. 4-3, this indicates that the splitting of the f-levels induced by Coulombic splitting is reduced under compression. This implies that the interaction between f-orbitals is lessened, indicating that covalency of the REE site in bastnäsite increases under compression (this is a manifestation of an increased nephelauxetic effect). The shift in Coulombic splitting can be semi-quantitatively assessed from Fig. 4-9: the separations of the averages of the H, F, and I levels decrease

by $\sim 2\%$ for both the H to I level differences and the F to I level differences between 0 and 40 GPa. The relative tradeoffs between a pressure-induced contraction in the size of the f-orbitals relative to decreased electron localization in these levels induced by increased covalency in generating this change in splitting by Coulombic repulsion is unclear. If, as an endmember upper bound on the maximum shift in electron occupancy, the entire shift in Coulombic splitting is attributed to a change in occupancy, then a decrease of $\sim 1\%$ in electron occupancy in the f-orbitals is indicated by the results of Fig. 4-9: a relatively small, but spectroscopically significant, shift relative to the magnitude of the change in volume of the system (which is of order $\sim 19\%$ at 40 GPa using Rowland's (2017) bulk modulus value). In passing, we note that this semi-quantitative estimate, derived from luminescence spectra, could be rigorously tested via single-crystal diffraction constraints on the pressure-dependence of electron density distributions.

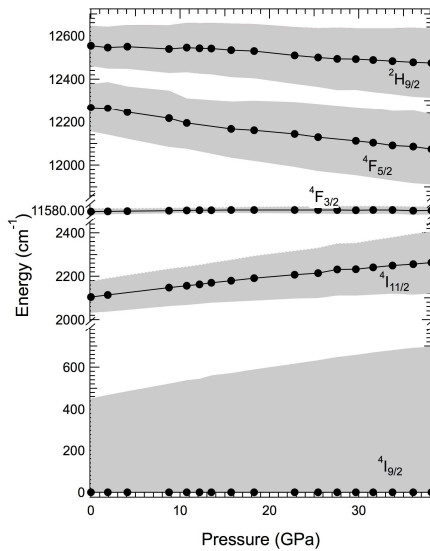


Figure 4-9. Energy levels of Nd^{3+} with pressure; shaded regions designate the observed spread in energy levels, and lines represent the barycenters (or groundstate) of the Stark levels.

In terms of the spin-orbit splittings (Fig. 4-3), the separation between the spin-orbit split levels decreases for the 4F levels, but may increase modestly for the 4I levels (Fig. 4-9). A decreased electron density induced by enhanced covalency would be generally anticipated to decrease spin-orbit coupling, as is clearly the case for the 4F level. We have no simple explanation for the enhanced spin-orbit coupling of the 4I level. Lastly, the splittings of the Stark levels are expected to be enhanced by both increased distortion and enhanced crystal field strength (e.g., Tröster 2003). This is clearly observed over the pressure range of our experiments, with the spread between levels (the shaded regions in Fig. 4-9) clearly expanding under pressure. Indeed, the maximum value of Stark splitting has been shown to scale with the crystal field strength at the site (Auzel and Malta 1983).

4.6.6 Anomalous pressure shifts in Nd^{3+} luminescence

Overall, the general expectation is that luminescence lines will shift to lower energy with pressure; as pressure is increased, the ligands bound to the Nd^{3+} ion are brought closer to the Nd^{3+} ion, and all electronic levels move to higher energy, but the overarching trend is that higher lying levels tend to shift less quickly to higher energies than lower levels. Thus, the effect of the change in spatial distance between the REE and ligands causes the energy difference between the ground state and the excited states to become lessened with compaction. Previously, anomalous behavior has been observed in the perovskite structured Nd^{3+} doped $YAlO_3$: blueshifts of a subset of peaks associated with the transition from $^4F_{3/2}$ to $^4I_{9/2}$ have been observed (Barnett et al. 1973; Hua and Vohra 1997; Hernández-Rodríguez et al. 2018a). These anomalous shifts have

been attributed to a combination of increasing crystal field strength (and hence splitting) and hybridization of the f-orbitals (Hernández-Rodríguez et al. 2018a). The vast majority of the luminescence bands shift to lower energy with pressure in bastnäsite. However, two luminescence bands have pressure shifts that involve an increase in energy in bastnäsite-II ($^2H_{9/2} \rightarrow ^4I_{9/2}$, #23; and $^4F_{3/2} \rightarrow ^4I_{9/2}$, #3), and two increase in bastnäsite-III: the new mode associated with R2 (#1) and (#6) in $^4F_{3/2} \rightarrow ^4I_{9/2}$. Notably, these bands are among the higher energy lines associated with each of their respective transitions; hence, the role of enhanced Stark splitting counterbalances the general decrease in energy of the barycenter of their respective transitions. Thus, these atypical shifts can be attributed to complex crystal field interactions between the Nd^{3+} ion and O/F ligands induced by an enhanced site distortion, and hence anisotropic compression within the REE site.

4.7 Implications

The bonding of both the carbonate units and neodymium ions under pressure is constrained in this critically important ore mineral. Notably, bastnäsite undergoes two apparently distortional phase transitions under compression: the first, near 25 GPa, appears to involve primarily a shift in the symmetry of the carbonate ion, while the second, which initiates at 38 GPa, generates a second REE site in this material. From an overarching perspective, the overall layered bonding of the bastnäsite structure, with Ce-F layers and carbonate layers, appears remarkably stable under compression: no indication is seen within this pressure range of any weakening of C-O bonds that would indicate an incipient increase in coordination, or onset of dimerization associated with

the carbonate group (e.g., Vennari et al. 2018). The general structural stability of this phase indicates that REE retention in the Earth's mantle may continue to involve bonding within phases containing both halogens and carbonate ions. Hence, REE element cycling, which has been used to constrain mantle differentiation, may critically depend on the presence of trace carbonate- and/or halogen-bearing phases at depth. Thus, the affinity of REE for carbonatite-associated lithologies in the near surface may persist to depth within the planet.

From a high-pressure science perspective, bastnäsite (which is quite stable under compression at 300 K) could represent a candidate for a high pressure luminescent calibrant in the near IR region from 0 to ~38 GPa: the transition from R1 to Y2 (Band 14), which is an intense mode in the NIR region does not split under pressure and shifts robustly and continuously through the transition from bastnäsite-I and -II. Furthermore, the splitting between two of the other intense peaks (R1 and R2) may provide a sensitive probe of the degree of distortion of REE sites within a range of REE-bearing oxides and halides under compression.

4.8 Acknowledgments

We thank Simon Teat, Laura McCormick, Nico Giordano, Christine Beavers, Myriam Telus, Earl O'Bannon and Ben Dejarnatt for discussions and assistance with the sample analyses. We would like to thank Andrew Doran for help with gas loading. This work was supported by the US NSF (EAR-1620423) and with partial support from COMPRES under the National Science Foundation Cooperative Agreement (EAR-1606856).

4.9 Supplementary Information

	C	O	F	La	Ce	Pr	Nd
Grain 1	-	-	0.819(38)	0.231(12)	0.482(8)	0.049(10)	0.238(15)
Grain 2	-	-	0.929(4)	0.305(1)	0.526(0)	0.040(1)	0.129(1)
Grain 3	-	-	0.996(130)	0.301(34)	0.516(23)	0.040(23)	0.144(39)
Grain 4	-	-	1.068(123)	0.179(25)	0.453(25)	0.047(24)	0.322(28)
Average	1	3.047	0.953(211)	0.254(44)	.494(35)	0.044(35)	0.208(50)

Table S4-1. SEM summary of the rare earth element content in bastnäsite. Carbon and oxygen contents inferred to be CO_3 plus $\text{O}=3+(1-[\text{Fcontent}])$.

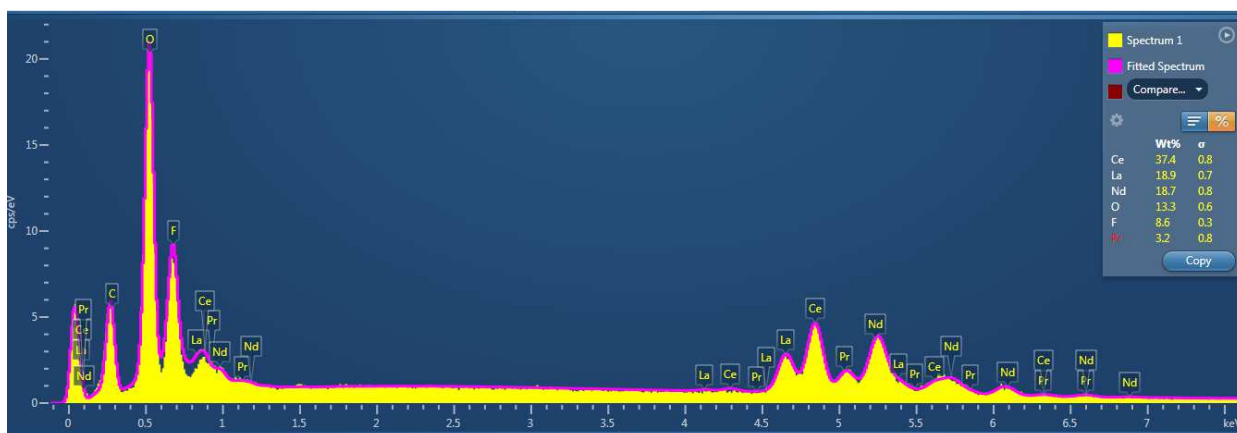


Figure S4-1. Example SEM results from bastnäsite.

Wavelength (Å)	0.7288
Temperature	297 K
Crystal system	Hexagonal
Space group	P-62c
a (Å)	7.1206(4)
b (Å)	7.1206(4)
c (Å)	9.7681(5)
γ (°)	120
Volume (Å ³)	428.92(5)
Z	4
N _{reflections}	8450
R1 (%)	0.0675
wR2 (%)	0.1531
GooF	1.130

Table S4-2. Unit cell parameters and experimental details of bastnäsite single crystal refinement at room temperature and room pressure.

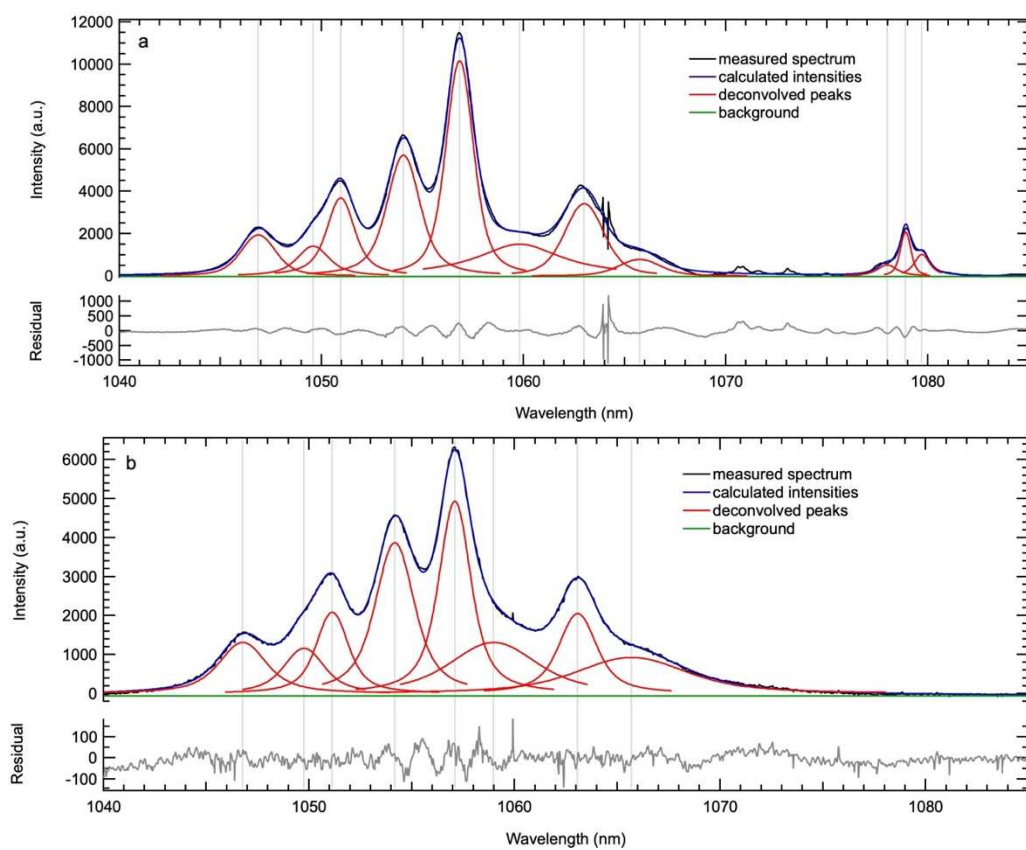


Figure S4-2. Nd³⁺ luminescence spectra of the $^4F_{3/2} \rightarrow ^4I_{11/2}$ transition with (a) 532 nm and (b) 633 nm.

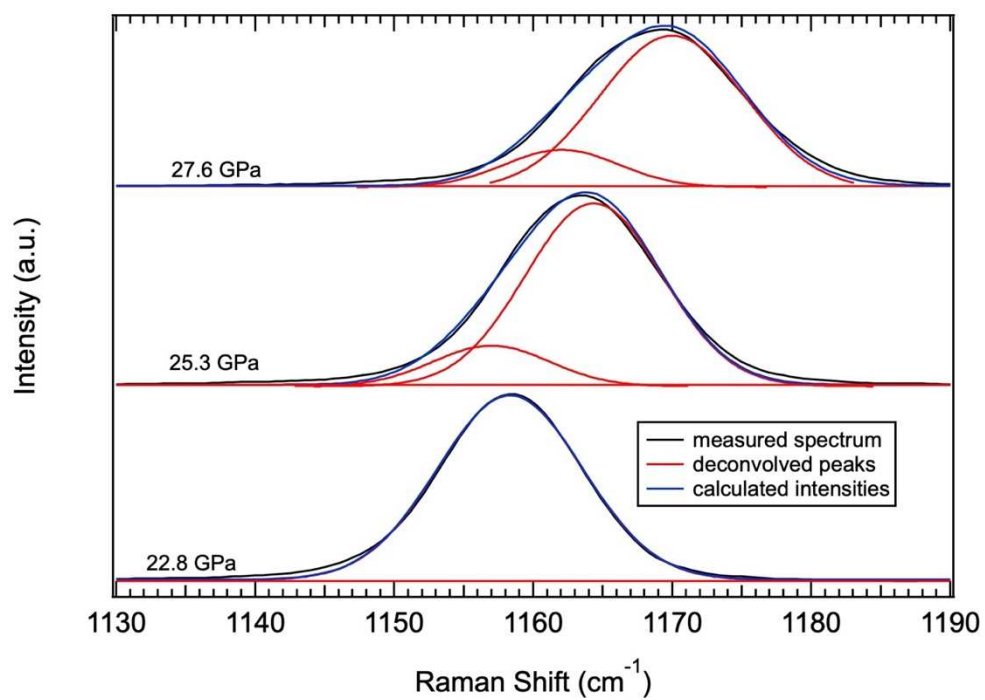


Figure S4-3. Representative spectra of the symmetric stretch under pressure of bastnäsite-I and -II peakfit to show new low frequency peak in bastnäsite-II.

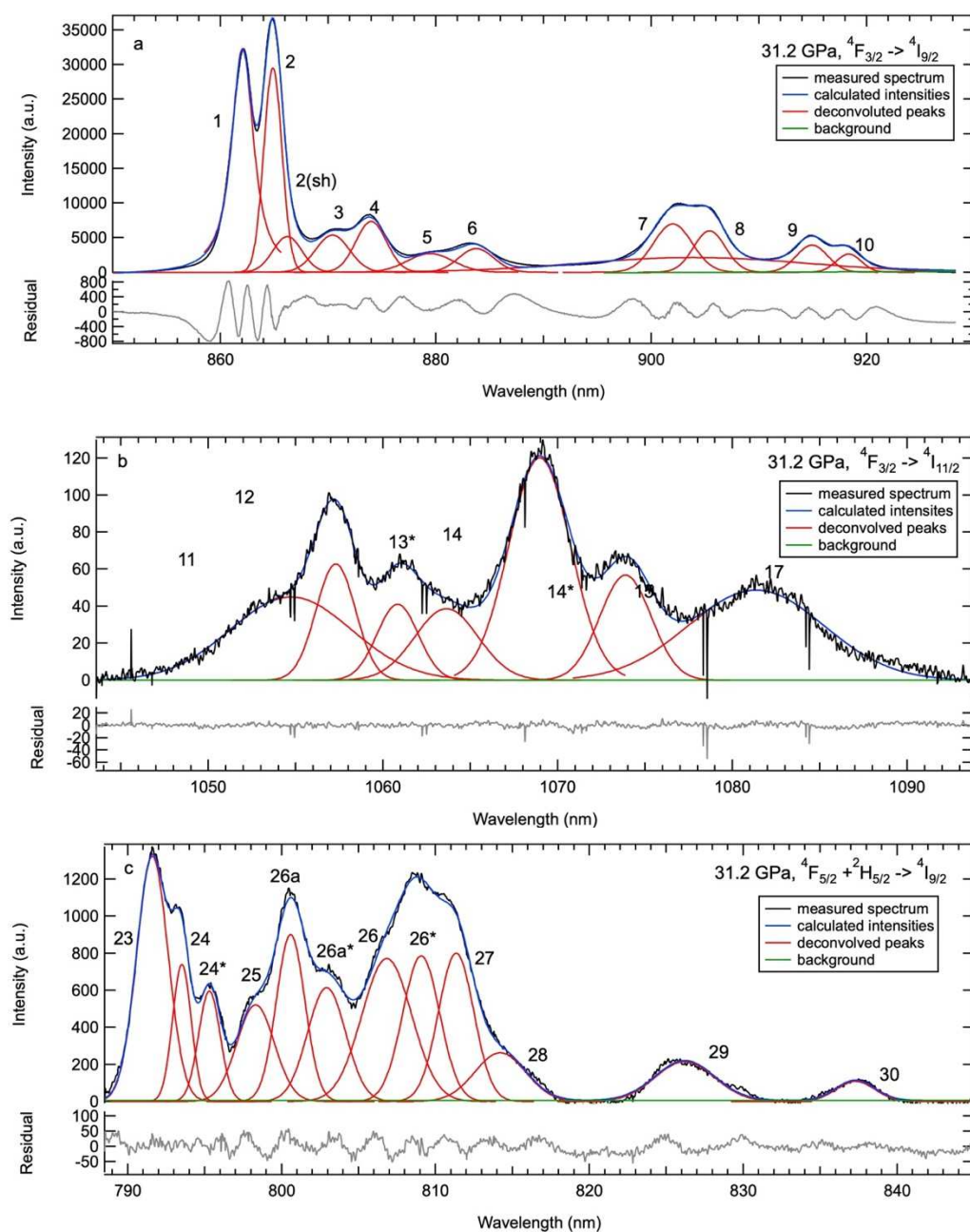


Figure S4-4. Representative luminescence spectra, at 31.2 GPa, of (a) $4F_{3/2} \rightarrow 4I_{9/2}$, (b) $4F_{3/2} \rightarrow 4I_{11/2}$, and (c) $4F_{5/2} + 2H_{9/2} \rightarrow 4I_{9/2}$. Spectra are deconvolved with Gaussian and Lorentzian peaks; (black) is the measured spectrum, (red) is the deconvolved peaks, (blue) is the calculated intensities, (green) is the background, and (grey) is the residual between the fit and the observed intensities

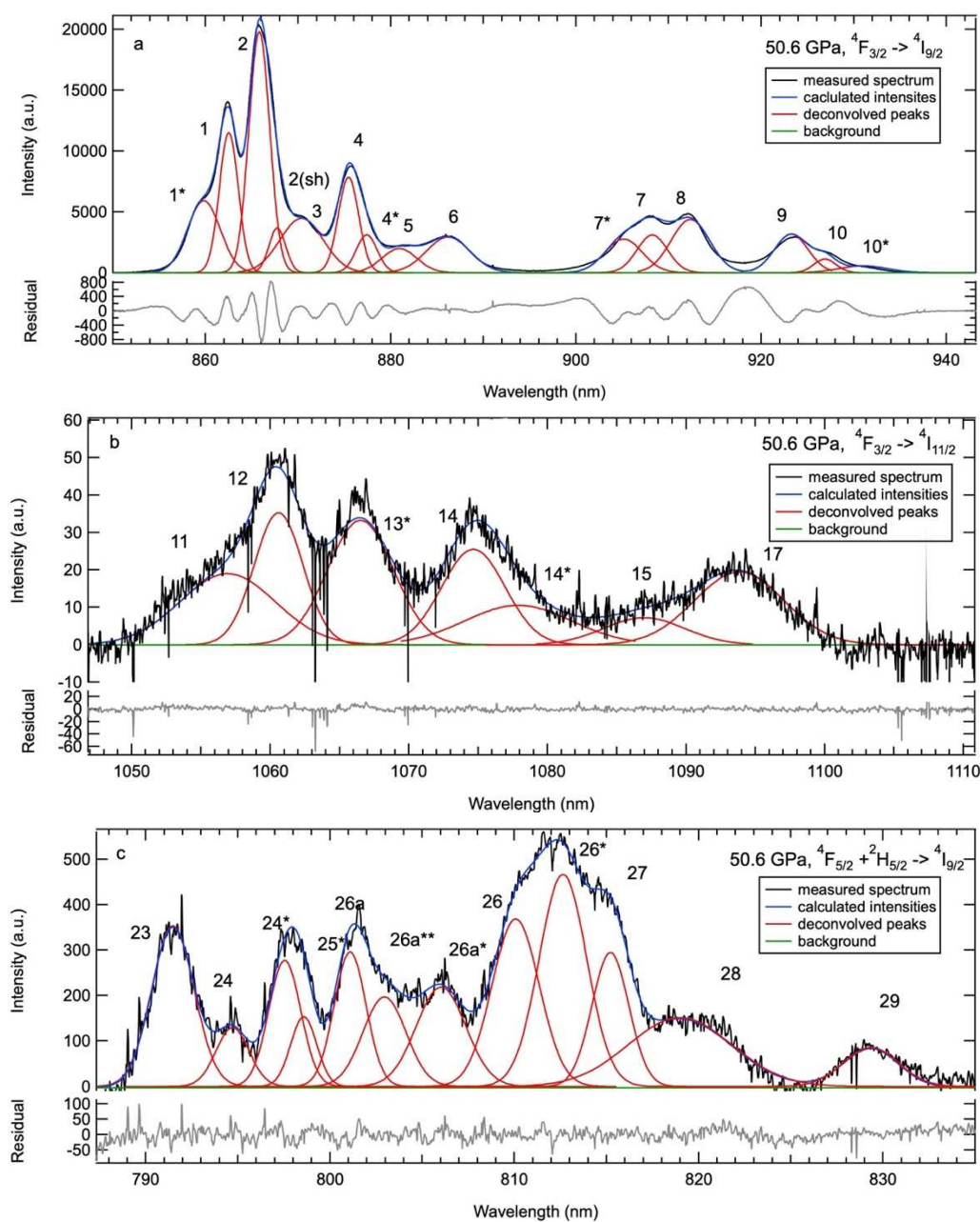


Figure S4-5. Representative luminescence spectra, at 50.6 GPa, of (a) ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$, (b) ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$, and (c) ${}^4F_{5/2} + {}^2H_{9/2} \rightarrow {}^4I_{9/2}$. Spectra are deconvolved with Gaussian and Lorentzian peaks; (black) is the measured spectrum, (red) is the deconvolved peaks, (blue) is the calculated intensities, (green) is the background, and (grey) is the residual between the fit and the observed intensities.

Chapter 5. Slip Systems and Strength of Natural Pyrope Garnet

$((\text{Mg,Fe})_3\text{Al}_2(\text{SiO}_4)_3)$ at High Pressures

5.1 Introduction

Our understanding of mantle heterogeneity and circulation is largely from observations of discontinuities and anisotropy in seismic wave velocity at depth. Small scale heterogeneities have been observed via seismology (e.g., Hedlin et al. 1997), and some of those heterogeneities have been explained as subducted basaltic lithosphere via geochemical and geophysical observations (Davies 1984) and minor seismic reflections (Williams and Revenaugh 2005). By the same token, shape-preferred orientation of (likely basaltic) heterogeneities has been invoked as one of the possible origins for mantle anisotropy. Previously subducted or delaminated basalt is likely prevalent within the mantle, and it was estimated that the mantle could be made up of a roughly 3:1 ratio of dunite:subducted basalt (Ringwood 1962). Subsequent studies have provided variable tests of, and constraints on, the abundance of basalt at depth (e.g., Allègre and Turcotte 1986; Williams and Revenaugh 2005; Xu et al. 2008; Schmerr et al. 2013). The significant anisotropy that has been observed associated with seismic velocities within the Earth's mantle (especially in the transition zone) is likely due to the shearing and stretching of the rock within the mantle, including subducted basaltic slabs and depleted mantle dunite (McNamara et al. 2001). Direct observations of subducted slab anisotropy is limited due to the lack of ray paths through subducted slabs and because the mantle wedge and sub slab anisotropy obscure slab anisotropy through the whole upper mantle anisotropy; however, there have been observations of

anisotropy within slabs (e.g., Tian and Zhao 2012). On the microscopic scale, this deformation of the mantle rock gives rise to crystallographic preferred orientation (texture) within the rock. As oceanic lithosphere is subducted, it converts to a garnet dominated assemblage; the deformation of garnet has not been fully examined at transition zone pressures thus far.

Pyrope garnet is also relevant to the mantle due to its presence in ultra-mafic and high-pressure metamorphic assemblages. Our understanding of the strength of garnets under pressure is derived largely from naturally deformed eclogites which are resistant to plastic deformation, especially in the presence of weaker minerals like omphacite and quartz that accommodate strain (e.g., Bascou et al. 2001). In low pressure metamorphic facies, garnet is thought to deform via grain boundary sliding, (however high pressure likely suppresses grain boundary sliding) rather than intracrystalline deformation (e.g., Zhang and Green 2007). However, in garnet dominated facies, like at the top of subducted slabs within the transition zone, 90% of the volume of the crustal material is expected to be garnet; hence, understanding the deformation of single phase garnet is highly relevant. Garnet has been shown to be plastically strong compared to other mantle materials, indicating that the garnet rich zones (i.e. subducted oceanic crust) are stronger than the surrounding mantle (Karato et al. 1995). Previous in situ high pressure studies on the high pressure behavior of pyrope have focused on the equation of state (e.g., Sato et al. 1978; Zhang et al. 1999), elastic constants and sound velocities (e.g., Gwanmesia et al. 1998; Conrad et al. 1999) which are helpful for understanding their bulk properties in the mantle; however, they

do not constrain the strength and deformation mechanisms of garnet at mantle pressures and temperatures.

Pyrope garnet crystalizes in the $Ia3d$ space group, and has a structure based on a bcc lattice. Work on the deformation of pyrope garnets has been conducted using electron backscatter diffraction on naturally deformed eclogite assemblages; these have found that the $\{110\} \langle 1-11 \rangle$ slip system provides over 86% of the slip with the $\langle 100 \rangle$ direction aligning with the compression direction (Mainprice et al. 2004). The dominant Burgers vector for naturally deformed silicate garnets in a range of temperature regimes is $\frac{1}{2} \langle 1-11 \rangle$, which most commonly operates on the $\{110\}$ plane (Voegelé et al. 1998b). This supports the results of an experimental deformation study where the dominant slip systems are $\frac{1}{2} \langle 111 \rangle$ on $\{1-10\}$, $\{11-2\}$ or $\{12-3\}$, or $\langle 100 \rangle$ on $\{010\}$ or $\{011\}$ (Voegelé et al. 1998a). Other deformation experiments on garnets with ex situ slip analysis indicate Burgers vectors of $\langle 100 \rangle$ and $\frac{1}{2} \langle 111 \rangle$ at high pressures and temperatures (Couvry et al. 2011). One study has been conducted using high-pressure in situ X-ray diffraction in radial geometry on a natural grossular-rich garnet (Kavner 2007); however, while the strength of this garnets was studied, the resulting textures that developed (with assigned slip systems) were not investigated. Hence, we study the high pressure strength and deformation of pyrope-rich garnet and report the active slip systems up to 30 GPa using radial diffraction in the diamond anvil cell.

5.2 Methodology

Experiments were conducted on pyrope (var. rhodolite) from Franklin Macon Co., North Carolina (UCSC #3248). Gold (5 wt%) was used as the pressure standard (Anderson et al. 1989) with a grain size of 5.5 – 9.0 μm . Pyrope was ground for 1.5 hours with acetone in an agate mortar and pestle, then an additional 30 minutes with the gold to ensure even dispersal. A BX90 style diamond anvil cell was used for diffraction with a radial geometry at 300 K. Diamonds with culets of 300 μm were used. Gasket material was comprised of a kapton gasket with a boron-epoxy insert; the sample diameter was 60 μm .

Diffraction images were collected at the Advanced Light Source, beamline 12.2.2 using a MAR3450 image plate with X-rays monochromated to 25 keV (wavelength 0.4978 Å) and a sample to detector distance of ~330 mm. Wavelength, sample to detector distance, instrument broadening, peak shape, crystallite size, microstructure and texture were calibrated using the NIST standard CeO_2 , and initial fits to the instruments calibration were completed using DIOPTAS (Prescher and Prakapenka 2015), with refinements completed with the MAUD software.

Diffraction images were processed using Fit2D (Hammersley 2016) coupled with fit2D2maud: images were unrolled with diffraction intensity integrated over 5° azimuthal arcs, for a total of 72 spectra per diffraction image. Rietveld analysis was implemented in the MAUD software (Lutterotti et al. 1997) to extract information constraining the lattice preferred orientation generally following the procedure for DAC data outlined in (Wenk et al. 2014) Texture was calculated using E-WIMV with

10° resolution for the ODF and fiber symmetry was imposed. Pole figures and inverse pole figures were smoothed and produced using BEARTEX.

Lattice strain and texture development are modeled together using elasto-viscoplastic self-consistent method (EVPSC) (Wang et al. 2010). EVPSC is an effective medium method, which treats single grains in an aggregate as inclusion in a homogeneous but anisotropic medium. Plastic strain rate is described by a rate-sensitive constitutive law for each slip system. The properties of the medium are determined by the average of all the inclusions. At each deformation step, the inclusions interact with the medium and the medium is updated when the average strain and stress of all inclusions equal the macroscopic stress and strain. In order simulate high pressure experiment data, a pressure dependence of elastic moduli and CRSS are used. The details for using EVPSC to simulate high pressure data can be found in Lin et al. (2017).

5.3 Background

We assume that linear elastic theory holds for small lattice strains experienced due to deviatoric stress (e.g., Singh and Balasingh 1993, 1994; Singh et al. 1998). For a sample deformed under axial compression, the stress state is described by the following:

$$\sigma_{ij} = \begin{bmatrix} \sigma_1 & 0 & 0 \\ 0 & \sigma_1 & 0 \\ 0 & 0 & \sigma_3 \end{bmatrix} = \begin{bmatrix} \sigma_P & 0 & 0 \\ 0 & \sigma_P & 0 \\ 0 & 0 & \sigma_P \end{bmatrix} + \begin{bmatrix} -t/3 & 0 & 0 \\ 0 & -t/3 & 0 \\ 0 & 0 & 2t/3 \end{bmatrix}$$

$$= \sigma_P + D_{ij}$$

Where σ_{ij} is the stress state of the sample, σ_P is the hydrostatic stress component, t is the axial stress component, and D_{ij} is the deviatoric stress. As we probe the sample

perpendicular to the compression direction, we are able to measure variations in lattice spacing with respect to the compression direction i.e. the lattice strain.

For radial diffraction geometry, diffraction patterns have variations in d-spacing and intensities with azimuth. The measured d-spacings (d_m) are fit using a hydrostatic component (d_p) and the azimuthal angle (ψ):

$$d_m(hkl, \psi) = d_p(hkl)[1 + Q(hkl)(1 - 3 \cos^2 \psi)]$$

From this, we fit a value for Q which is a measure of the elastic strain on an individual lattice plane. Systematic intensity variations around Debye rings are due to texture.

5.4 Results

5.4.1 Differential Stress and Elasticity

X-ray diffraction data were collected up to 30 GPa. Representative experimental and calculated diffraction images are shown in Fig. 5-1. We are able to track the (400), (420), (422), (521), (611) (444), (640) and (642) diffraction lines of pyrope and gold. Overall, with compression, the peaks broaden. This is due to microstrain (defect structure and strain heterogeneity) within the lattice and likely grain size reduction. Using the four diffraction lines (400), (420), (640), and (321), which are strong and do not overlap with other diffraction lines, we are able to measure accurate values of $Q(hkl)$.

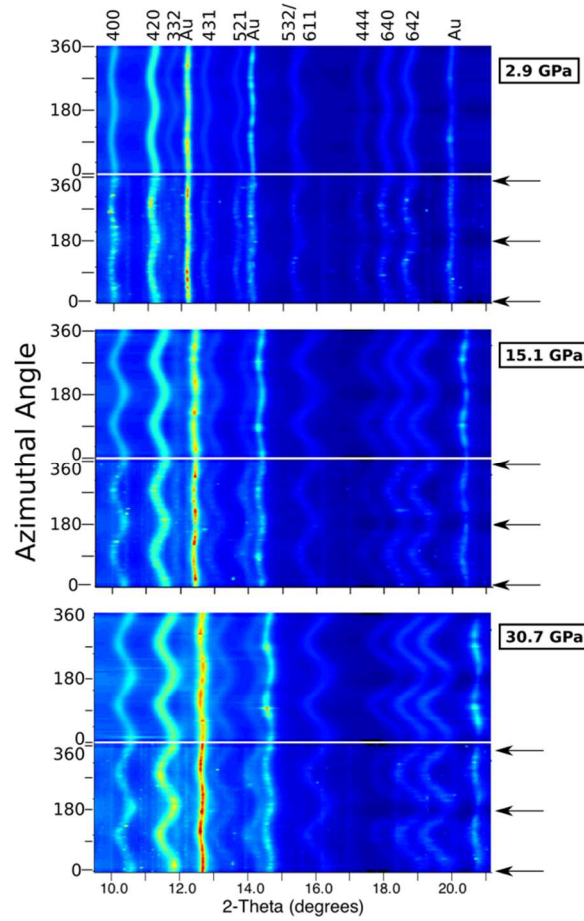


Figure 5-1. Representative unrolled diffraction images of pyrope with gold at high pressures; calculated diffraction patterns are on top, and experimental diffraction patterns on the bottom. Compression direction indicated by arrows.

The Q-values for these four lines increase at similar rates up to 30 GPa (Fig. 5-2a). Using the approximation for the uniaxial stress component,

$$t = 6G \langle Q(hkl) \rangle \quad (= \sigma_3 - \sigma_1 = \sigma_Y)$$

we are able to estimate the flow strength and measure the elastic limit of pyrope. We utilize a shear modulus of 94.7 GPa from Chai et al. (1997) and find that pyrope likely has a flow stress between 6 and 10 GPa. As pressure is increased, the flow strength increases (Fig. 5-2b).

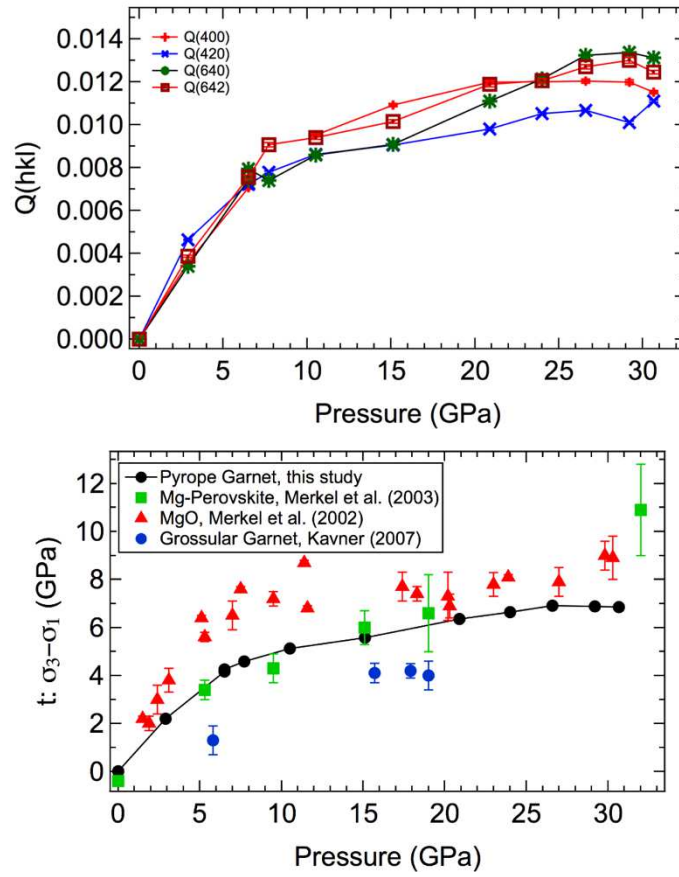


Figure 5-2. (top) $Q(hkl)$ with increased pressure of the (400), (420), (640), and (321) diffraction lines; (bottom) strength with pressure compared to magnesium perovskite (Merkel et al. 2003), MgO (Merkel 2002), and grossular garnet (Kavner 2007). Error bars for this study are smaller than the symbols.

Pressure (GPa)	$Q(hkl)$	t (GPa)
0.0	0.0000	0.00
2.9	0.0038	2.20
6.5	0.0073	4.17
6.5	0.0075	4.26
7.7	0.0081	4.59
10.5	0.0092	5.13
15.1	0.0101	5.57
20.9	0.0117	6.36
24.0	0.0124	6.63
26.6	0.0129	6.91
29.2	0.0128	6.88
30.7	0.0127	6.84

Table 5-1. $Q(hkl)$ and uniaxial stress component of pyrope under pressure.

The strength of pyrope that we obtain is comparable to other mantle phases (Fig. 5-2b). Bridgmanite has a comparable flow strength and can accommodate similar differential stress up to ~20 GPa (Merkel et al., 2003). Periclase is stronger than pyrope at all pressures probed (Merkel, 2002). We find that pyrope is stronger than grossular garnet, as reported by Kavner (2007). We have four possible explanations for this difference: (1) There are likely grain size differences between the two samples, (2) there may be an intrinsic strength difference associated with Ca substitution in the garnet lattice; (2) there may be a higher water content/defect concentration in the grossular samples; or (3) the azimuthal coverage may not have allowed for full characterization of the strength of the grossular garnet. While we probe from 0-360° with 5° arcs, Kavner (2007) utilized 8 discrete angles spanning 180° and fit Q-values from those angles.

5.4.2 Texture and Plasticity

With increasing pressure, modest texturing (plastic deformation) is observed as demonstrated by the development of intensity variations along the Debye rings. As pressure is increased, a (100) maximum develops in the compression direction. With compression to at 30 GPa the pole density increases to a maximum of 1.88 times a random distribution (m.r.d: multiples of random distribution)), with a minimum of 0.70 mrd in (111) (Fig. 5-3). The (100) plane aligning at high angles to the compression direction has been observed in other garnets by Mainprice et al. (2004); however, they also found that there was a maximum of {110} poles in the compression direction. These differences indicate that the slip systems described by Mainprice et al. (2004)

may not be sufficient to fully model the texture we observe. The pole figure densities (m.r.d.) are low compared to other mantle material at similar pressures (e.g., MgO and Mg-perovskite; Merkel 2002; Merkel et al. 2003). This has been attributed to the large number (66) of possible slip systems within the garnets structure or a change in deformation mechanism to diffusion creep (Mainprice et al. 2004). In our experiments at room temperature low m.r.d. is most likely do to the high number of symmetric variants for slip systems and relatively low strain (~20%). the previous in situ study of strength of grossular garnet alluded to plastic deformation, but did not characterize textures of deformation mechanisms (Kavner 2007).

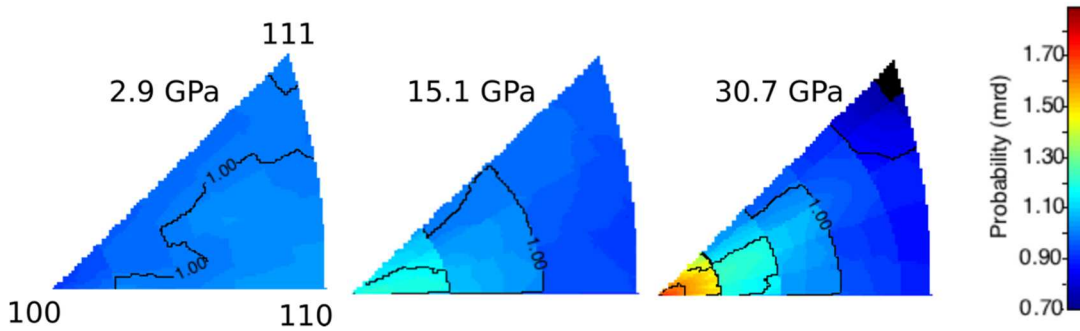


Figure 5-3. Inverse pole figures of pyrope at 2.9, 15.1 and 30.7 GPa.

5.4.3 Active slip systems

Texture and lattice strain evolution was modeled as a function of slip system activities using the EVPSC code; seven slip systems were tested: $\{110\}\langle 1\text{-}11\rangle$, $\{112\}\langle 11\text{-}1\rangle$, $\{123\}\langle 11\text{-}1\rangle$, $\{001\}\langle 110\rangle$, $\{011\}\langle 100\rangle$, $\{010\}\langle 100\rangle$, and $\{110\}\langle 1\text{-}10\rangle$ (Fig. 5-4). Based on the $Q(hkl)$ and the texture development with pressure, no single slip system can explain the deformation of pyrope at high pressures. Only with

the activation of two slip systems ($\{110\}\langle 1-11 \rangle$ and $\{001\}\langle 110 \rangle$; Fig. 5-5, Table 5-2) can we generate the observed textures and lattice strain development.

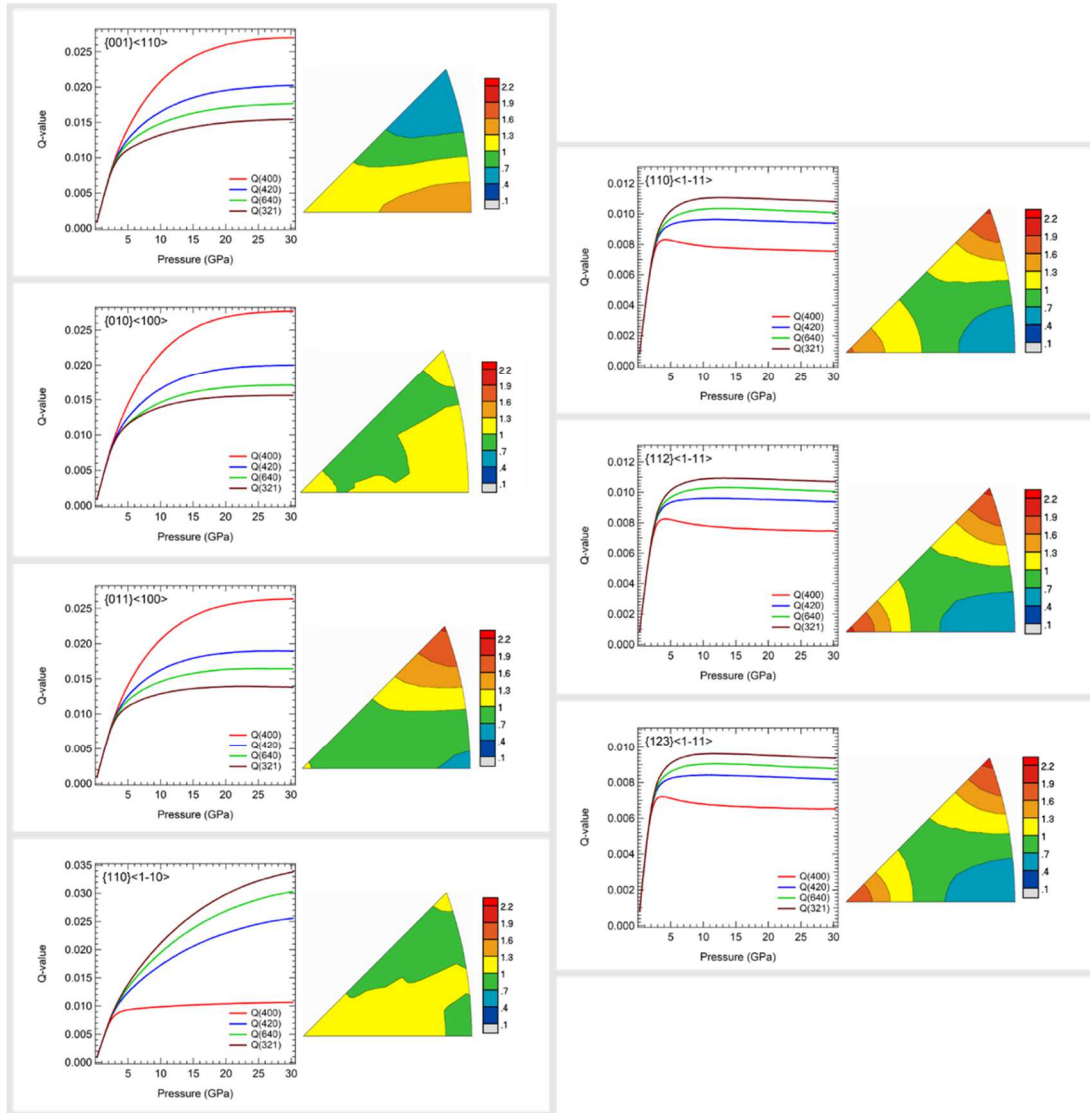


Figure 5-4. Single slip systems tested for pyrope with the resulting Q-factors and texture development.

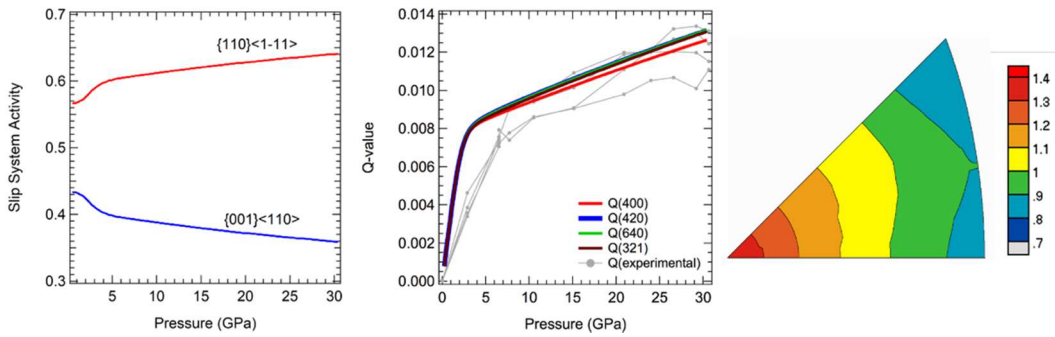


Figure 5-5. (left) Active slip systems with pressure; (right) resulting Q-factors with pressure and texture at 30 GPa.

Slip System	τ_0	$d\tau/dP$	n
$\{110\}\langle 1-11 \rangle$	3.7	0.11	5
$\{001\}\langle 110 \rangle$	3.4	0.11	5

Table 5-2. Parameters used in modeling slip systems including active slip systems with associated (initial and pressure derivative) critical resolved shear stress, and stress exponent.

The two slip systems that are active in pyrope at high pressures have been observed in ex situ analysis of deformed garnets with the two most common Burgers vectors being $\{110\}$ and $\frac{1}{2}\{1-11\}$. For example, deformed eclogite garnets deform such that the $\{100\}$ aligns with the compression direction and slip occurs on the $\{110\}\langle 1-11 \rangle$ system (Mainprice et al. 2004). Over our experimental pressure range, the majority of the strain in pyrope is accommodated by this slip system. This Burgers vector is also consistent with the slip observed by (Voegelé et al. 1998a) on $\frac{1}{2}\langle 111 \rangle$ and by Couvy et al. (2011). While Voegelé et al. (1998b) reported equivalent slips in the $\frac{1}{2}\langle 1-11 \rangle$ direction on the $\{110\}$, $\{112\}$, and $\{123\}$ planes, Mainprice et al. (2004) reported 86% of the slip in garnets in naturally deformed eclogites occur with the $\{110\}\langle 1-11 \rangle$ slip system. It should be noted, it is difficult to distinguish between the three slip planes $\{110\}$, $\{112\}$, and $\{123\}$ due to the similarity of the texture and development of Q-values. This is likely because the three planes are almost parallel.

Thus, our selection of the $\{110\}$ plane is partially constrained from the observation from Mainprice et al. (2004), slip in other non-silicate garnets like GGG (Garem et al. 1982) and also from the knowledge of the dominant slip systems observed in bcc metals (e.g., Kocks et al. 1998).

The other ~40% of the strain is accommodated via the $\{001\}\langle 110 \rangle$ system. This slip system has not been observed in garnets in high pressure/temperature deformation experiments (Voegelé et al. 1998a), nor in most deformed eclogites (Mainprice et al. 2004). However the resulting texture has been observed in other cubic materials. For example, this slip system has been observed in ferropericlase at high pressures and temperatures (Immoor et al. 2018) and is common in halite (Wenk et al. 1989).

Differences between this experiment and the observed slip systems in the garnets probed via TEM are likely at least partially due to a difference in temperature between the high temperatures that the garnets experienced during either the experiments or metamorphism, and the 300 K experiments we conducted. Garnets analyzed in Mainprice et al. (2004) experienced pressures over 2.1 GPa and temperatures ranging from 480 °C to >700 °C. It is well known that slip system activities can change with temperature, for example in ferropericlase (Heidelbach et al. 2003; Immoor et al. 2018). Alternatively, there may be a difference in slip systems due to the higher pressures probed compared to the TEM studies: ferropericlase, for example, activates different slip systems below 20-30 GPa and above 60 GPa (Amodeo et al. 2012; Marquardt and Miyagi 2015).

5.5 Seismic signature

Shear wave splitting is generated by both the single crystal elastic anisotropy and the texturing. Brillouin spectroscopic studies of garnets have demonstrated they remain elastically isotropic to high pressures. Anisotropy of pyrope ($2C_{44}/(C_{11}-C_{12})$) was observed to be 0.98 at ambient conditions, 1.01 at 14 GPa (Sinogeikin and Bass 2000), with a linear extrapolation out to 30 GPa, the anisotropy would be 1.04. P- and s- wave velocities were calculated at 30 GPa with simple shear applied (100% shear strain), and using the extrapolated elastic constants from *Sinogeikin and Bass* [2000] and the observed texture in pyrope. Overall, the s-wave shear splitting of a polycrystalline aggregate has a maximum of 0.28% in the (100) direction. Since the shear splitting of a rock assemblage depends on the shear splitting each materials' contribution to the shear splitting, we expect that pyrope garnet does not play a large role in anisotropy in slabs in the upper mantle.

5.6 Conclusions

We provide the first in situ analysis of the plastic deformation and flow strength of pyrope to 30 GPa at 300 K. Overall, pyrope is relatively strong, in comparison to other mantle phases (e.g. bridgmanite). Pyrope exhibits a flow strength, 4.5 GPa at 7 GPa, and pyrope can accommodate ~6 GPa differential stress above 15 GPa at 300 K. This differs markedly with the previously reported strength of grossular garnet (Kavner 2007)—we attribute the differences to either a strong chemical dependency of garnet strength, variations in grain size, different defect contents or a difference in data coverage. These ambient temperature experiments imply that garnet-rich crustal layers

on subducted slabs likely behave as comparatively rigid layers compared to other rocks in the mantle (particularly if the crustal layer remains relatively cold at depth).

Using the elasto-visco plastic self-consistent method, we identify two active slip systems: $\{110\}\langle 1-11 \rangle$ and $\{001\}\langle 110 \rangle$. Both slip systems are needed to simultaneously match the observed lattice strain and texture development. Slip systems obtained in this study are consistent with previous ex situ analysis of deformed garnets. Overall, seismic anisotropy observed in subducted slabs is likely not due to pyrope garnet; however, majorite (e.g., Gerald Pacalo and Weidner 1997) and andradite (Jiang et al. 2004) garnet are less isotropic, and may contribute to seismic anisotropy in the upper mantle.

6. References

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