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Carbon in the Deep Earth: A Mineral Physics Perspective

A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy
in Geochemistry

by

Sarah Eileen Maloney Palaich

2016

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ABSTRACT OF THE DISSERTATION

Carbon in the Deep Earth: A Mineral Physics Perspective

by

Sarah Eileen Maloney Palaich

Doctor of Philosophy in Geochemistry

University of California, Los Angeles, 2016

Professor Abby Kavner, Co-Chair

Professor Craig E. Manning, Co-Chair

Carbon is an essential component to life on Earth, and plays a role in the carbon cycle at the surface of the Earth. Beyond these surface interactions lies the deep carbon cycle. This cycle controls the flux of carbon subducting into the earth and provides clues as a possible carbon reservoir in the deep earth. The studies included in this dissertation examine various forms of carbonate under high pressure, high temperature conditions found in the deep earth. Carbon is subducted as carbonate in calcite, aragonite and dolomite, as elemental carbon or as CO₂. To achieve these the high pressures experienced by subducting material, diamond anvil cells are

used to expose milligrams of material to extreme conditions. The experiments detailed here were conducted using a wide range of diamond anvil cell techniques and the data was collected at numerous synchrotron and neutron diffraction facilities across the globe including the Advanced Light Source, Lawrence Berkeley National Laboratory, the Spallation Neutron Source, Oak Ridge National Laboratory and the European Synchrotron Radiation Facility, Grenoble France. These experiments are the result of fruitful collaborations that brought scientists from around the globe together to study the thermoelastic properties of carbonate and CO₂. I found important thermoelastic properties for the following minerals: hanksite, tychite, kutnohorite, aragonite and carbon dioxide. Each study yields isothermal bulk modulus data and the studies on aragonite and carbon dioxide also yield thermal expansion data. The equation of state, phase stability and thermoelastic data derived from these experiments will inform models of planetary interiors while giving insight into the evolution of carbon at the high pressures and temperatures of the Earth's interior.

The dissertation of Sarah Eileen Maloney Palaich is approved.

Edwin Arthur Schauble

Mark S. Goorsky

Craig E. Manning, Committee Co-Chair

Abby Kavner, Committee Co-Chair

University of California, Los Angeles

2016

DEDICATION

To my husband and often co-author Rob Heffern, my dear friends Barbara and Gunther Liebhart,
my scientific inspirations Anjali and Stephen Arnold and my ever supportive parents, Greta
Maloney and Bob Palaich.

TABLE OF CONTENTS

Chapter 1: Introduction	1
1.1 Carbon in the earth and planets	2
1.2 Deep Carbon	3
1.3 Overview of the dissertation	5
1.3.1 Changing coordination of carbon at depth	5
1.3.2 CO ₂ , carbon coordination and phase stability	6
1.3.3 Carbonate and CO ₂ experiment summaries	6
1.4 References	8
 Chapter 2: Spectroscopic and X-ray diffraction study of hanksite and tychite at high pressure, and a model for the compressibility of sulfate minerals	 10
2.1 Introduction	11
2.2 Experiment setup	12
2.3 Results and Discussion	15
2.3.1 Raman Spectroscopy	15
2.3.2 X-Ray diffraction	16
2.3.3 Effects of non-hydrostaticity	17
2.3.4 Sulfate systematics	18
2.4 Summary	20
2.6 Tables	21
2.7 Figures	29
2.8 References	40
 Chapter 3: High-pressure compressibility and phase stability of Mn-dolomite (kutnohorite)	 44
3.1 Introduction	45
3.2 Experimental Methods	45
3.3 Results and Discussion	47
3.4 Implications for dolomite structures	50
3.5 Summary	50
3.6 Tables	52
3.7 Figures	53
3.8 References	57
 Chapter 4: High-Pressure Compressibility and Thermal Expansion of Aragonite	 59
4.1 Introduction	60
4.2 Experimental Methods	62
4.3 Results	63
4.3.1 Phase stability and lattice compressibility	63
4.3.2 Axial ratios and polyhedral evolution	65
4.3.3 Atomic evolution and polyhedral distortion	68

4.3.4 Thermal expansion	70
4.4 Implications.....	71
4.5 Summary	73
4.6 Tables	74
4.7 Figures.....	76
4.8 References	86
 Chapter 5: Structure, stability, and thermoelastic properties of CO₂-IV	89
5.1 Introduction.....	90
5.2 Experimental Methods	91
5.3 Results and Discussion.....	95
5.3.1 Phase stability.....	95
5.3.2 Compression and bulk modulus	96
5.3.3 High temperature data	99
5.4 Implications.....	100
5.5 Summary	102
5.6 Tables	104
5.7 Figures.....	106
5.8 References	117
 Chapter 6: Conclusions	119
6.1 Carbon in the deep earth	120
6.2 Future work	121
6.3 References	124

LIST OF FIGURES

2-1	Hanksite unit cell from three perspectives	29
2-2	Diffraction pattern of hanksite at 2.8 GPa.....	30
2-3	Ambient pressure Raman spectra of hanksite	31
2-4	Raman spectra of hanksite as a function of pressure.....	32
2-5	Raman shift versus pressure	33
2-6	Volume as a function of pressure for hanksite	34
2-7	Normalized volume as a function of pressure for sulfate minerals	35
2-8	Ratio of sulfate ν_1 modes and normalized compressibilities of a and c axes	36
2-9	Isothermal bulk modulus and average SO_4 - SO_4 distance	37
2-10	Selected hanksite diffraction patterns.....	38
2-11	Selected tychite diffraction patterns	39
3-1	Diffraction patterns of kutnohorite to 19 GPa.....	53
3-2	Unit cell volume of kutnohorite as a function of pressure	54
3-3	Calcite-type carbonate data and dolomite data (bulk modulus vs. unit cell volume)	55
3-4	Single crystal diffraction data (volume vs. pressure)	56
4-1	Structure of aragonite at ambient pressure and temperature	76
4-2	Aragonite unit cell volume versus pressure	77
4-3	Compressibility of a , b , and c crystallographic axes of aragonite	78
4-4	c/b , b/a and b/c ratios of aragonite.	79
4-5	Unit cell comparison at ambient and 31.5 GPa	80
4-6	b/c ratio from unit cell parameters and CO_3 - CO_3 distances	81
4-7	Pressure-dependent atomic positions	82
4-8	C-O bond lengths and O-C-O bond angles.	83
4-9	Evolution of carbonate groups	84
4-10	Thermal expansion of aragonite	85
5-1	DAC assembly in the membrane press.....	106
5-2	Stability diagram of CO_2	107
5-3	Comparison of Reitveld refinements of CO_2 -IV	108
5-4	CO_2 -IV data fit to the Birch-Murnaghan equation of state	109
5-5	Ambient temperature CO_2 data from various studies.....	110
5-6	CO_2 -IV data and equation of state in comparison to previous CO_2 -IV studies	111
5-7	Neutron diffraction data from thermal expansion experiment	112
5-8	Linear thermal expansion fit.....	113
5-9	Thermal data in P, V space.....	114
5-10	Normalized CO_2 patterns at ~ 18 GPa from both DAC experiments.....	115
5-11	Neutron diffraction data from compressional experiment	116

LIST OF TABLES

2-1	Hanksite lattice parameters	21
2-2	Tychite lattice parameters	22
2-3	Pseudopotentials used in the first principles tychite model.	23
2-4	Raman frequencies of various sulfate minerals.....	24
2-5	Sulfate ν_1 and ν_3 and carbonate ν_1 vs. pressure and mode Grüneisen parameters.....	25
2-6	Tychite d -spacings and standard deviations.....	26
2-7	Hanksite d -spacings and standard deviations.....	27
2-8	Ambient hanksite d -spacings and standard deviations.....	28
3-1	Ambient temperature kutnohorite and Au unit cell parameters to 20 GPa	52
4-1	Unit cell parameters of aragonite from ambient to 34.8(3) GPa.	74
4-2	Thermal expansion of aragonite unit cell parameters from 298 to 673 K.....	75
5-1	Rietveld Refinement results for CO ₂ -IV and CO ₂ -I.....	104
5-2	Bulk modulus, pressure derivative and initial volume for several CO ₂ phases	105

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A version of the material in Chapter 3 was published as “High-pressure compressibility and phase stability of Mn-dolomite (kutnohorite)” by S. E. M. Palaich, R. A. Heffern, A. Watenphul, J. Knight, and A. Kavner, *Am. Min.*, **100**, 2242-2245 (2015).

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The work in Chapter 5 is being prepared for submission to Physical Review Letters and will appear in publication in either 2016 or 2017.

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VITA

2011-2016	Graduate Research Assistant Department of Earth, Planetary and Space Sciences University of California, Los Angeles
2013-2016	Department of Energy Stewardship Science Graduate Fellow National Nuclear Security Administration University of California, Los Angeles
2015	Summer Research Assistant Radiogeochemistry Team Los Alamos National Laboratory, Los Alamos, NM
2011	Laboratory Assistant Geology Department University of Colorado, Boulder, CO
2009	B.A., Physics and Astronomy, Departmental Honors Vassar College Poughkeepsie, NY
2007-2008	Undergraduate Research Assistant Department of Physics and Astronomy Vassar College, Poughkeepsie, NY

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Chapter 1: Introduction

1.1 Carbon in the earth and planets

The influence of carbon on the Earth is clear at the surface. The life we interact with everyday evolved through the bonding of element six, carbon, to its near neighbor oxygen and the simplest element of all, hydrogen. Carbon also possesses the ability to form covalent bonds that are sufficiently strong to achieve arbitrarily long chains of carbon atoms, which is the basis of organic chemistry, the chemical dictionary of life. The cornerstone status carbon has achieved in biological processes is due to this capability coupled with its ability to transition redox states, from -4 to +4. This broad range allows carbon to exist in the air we breathe (CO_2), the bones that stabilize us (CO_3^{2-}) and as waste products from biological processes (CH_4).

But these forms of carbon are not constrained to life processes. Indeed, these primitive forms of carbon have existed on the Earth for billions of years, far predating the earliest life forms. What flows through our bodies also cycles through the Earth, where it plays an influential role despite its low abundance. Compared to the solar and interstellar medium C/Si ratio of 10, the Earth only has a C/Si ratio on the order of ~ 0.0005 . *Lee et al.* [2010] attribute this loss of carbon in rocky planets to carbon burning that occurs during the accretionary stage in the rocky planet-forming portion of the disk. The bulk silicate Earth (BSE) is estimated to have only 735-3700 ppm carbon [*Marty*, 2012].

This relatively low abundance of carbon in the Earth does not restrict its importance in geologic processes. The amount of carbon contributed to the Earth during the accretionary phase is not easily determined and many theories include the introduction of additional volatile elements after the initial planet building stage via violent impacts [*Wood et al.*, 2013; *Albarède et al.*, 2013]. Carbonate minerals, a dominant form of oxidized carbon on Earth, have been found in CI and CM chondrites and were some of the first oxidized carbon minerals on Earth

[Hazen *et al.*, 2013] . The modern Earth is dominated by oxidized carbon species at the surface. Calcite (CaCO_3) is the primary constituent of limestone, a sedimentary rock that dominates ocean floor environments, and is one of the most common cementing minerals found in sandstone [Manning *et al.*, 2013] . Dolomite ($\text{CaMg}(\text{CO}_3)_2$) is another common oxidized carbon mineral, originating from the same environments as calcite and aragonite, a polymorph of calcite. Both calcite and dolomite adopt a rhombohedral structure, including Fe, Mg and Mn end-members of dolomite. These minerals are a major constituent of subducted slabs and are likely the source of the majority of the CO_2 released during arc volcanism. Indeed, much of the carbonate subducted at these tectonic interfaces is recycled back to the atmosphere. Dasgupta [2013] estimated that if the subduction flux of carbon were $(5.4\text{-}8.8) \times 10^{13}$ g C/yr, ~20-70% of that carbon would return as CO_2 to the atmosphere. Although this is not a hard limit on the modern flux of carbon, it does indicate that most carbon is likely involved in the surface global carbon cycle and that only a small percentage plays a role in the deep carbon cycle. For the carbon that does enter the mantle, the residence time is estimated at 1-4 Ga, a loose constraint at best [Dasgupta, 2013].

1.2 Deep Carbon

The life of carbon within the mantle is very different than on the surface. Due to higher mantle potential temperatures during the Hadean, Archean and Proterozoic Eons continuing until ~ 1 Ga, carbonate subduction likely only became efficient in Phanerozoic Eon [Dasgupta, 2013]. This recent influx of carbon to the mantle leads to questions of how carbon storage operates in the deep mantle. What are the dominant species? What are their residence times? How can we design experiments that answer these important questions? These interactions are beyond direct

observation, so some ingenuity is required to find appropriate experimental techniques to answer these questions.

Initially, the fate of the subducted carbonate minerals is determined by the relative depths of the decarbonation and melting reactions for the appropriate mineral assemblages and the temperature depth profile of the subducting slab. For carbonate bearing slabs the carbonated peridotite solidus governs the depth of decarbonation melting. The modern day mantle adiabat with a potential temperature of 1350° C intersects the carbonated peridotite solidus at ~300 km, providing a minimum depth for decarbonation melting.

Even if the carbonates survive to depth without loss to volatilization, the dominant magnesium-iron silicates of the mantle create a very different redox environment. The carbonates have limited solubility in the mantle silicates and remain in their own phases as either oxidized carbonate or reduced diamond/graphite/carbide [*Shcheka et al.*, 2006]. The mantle oxygen fugacity (f_{O_2}) changes with depth and reducing conditions dominate the deep mantle. At depth the mantle f_{O_2} is buffered by the exchange equilibria between Fe^{3+} and Fe^{2+} in mantle silicates. The resulting carbon species is then determined by the intersection of the carbonate-graphite/diamond transformation reactions and the oxygen fugacity imposed by iron redox [*Frost and McCammon*, 2008; *Stagno et al.*, 2013]. Experiments done by *Rohrbach and Schmidt* [2012] between 10-23 GPa and 1,400-1,900° C, with redox conditions relevant to the upper mantle and transition zone, found that the minimum f_{O_2} at which magnesite is stable is 2 log units above (more oxidized than) the Iron-Wustite Buffer (IW) to 23 GPa. Metal saturation at IW conditions is predicted at 8 GPa in the Earth's mantle, meaning that at this pressure carbonate is predicted to destabilize and reduce. Thus, below ~250 km reduced carbon (either diamond, graphite, carbide or another reduced form), is predicted to dominate.

Despite the dominance of decarbonation melting and reduction of carbonate in the mantle, arguments have been made that the mantle is heterogeneous and could contain influxes of carbonate rich subducted mantle lithosphere [Rohrbach and Schmidt, 2012; Stagno *et al.*, 2011]. These carbonate rich regions would oxidize the mantle silicate as they themselves are reduced and potentially would travel through the transition zone and even into the lower mantle [Stagno *et al.*, 2011]. There is experimental evidence for the coexistence of oxidized and reduced carbon phases at lower mantle conditions [Boulard *et al.*, 2013]. The prospect of these heterogeneities validates the study of carbonate phases at the pressures of the upper mantle, transition zone and lower mantle. Despite not being the predominant species, carbonates could still play a role in the introduction of carbon to the mantle and the deep carbon cycle.

1.3 Overview of the dissertation

The compilation of work in this dissertation is motivated by the desire to understand how carbonate and carbon dioxide behave at temperatures and pressures relevant to planetary interiors. Several different carbonate bearing minerals are studied at high pressure to examine their thermoelastic properties and phase stability: hanksite, tychite, kutnohorite and aragonite. Carbon dioxide is included in a study of the evolution of carbon bonding at pressure, specifically the change from molecular bonding to polyhedral bonding. Each of these studies is motivated by interest in generating equation of state data, examining phase stability, and carbon coordination at the conditions of planetary interiors.

1.3.1 Changing coordination of carbon at depth

The possibility of carbonate minerals as deep as the lower mantle motivates the experimental study of high pressure, high temperature carbonate minerals. This is a broad field and has been explored in depth for many years. Nevertheless, recently theoretical evidence

arose that the coordination of carbon with oxygen likely increases with depth across a range of carbon mineral systems, including the rhombohedral carbonates and CO₂ [Oganov *et al.*, 2008]. At ambient, atmospheric conditions, carbon is in planar triangular coordination with oxygen in CO₃²⁻. As pressure increases, studies have found that over a broad range of pressures (40-100+ GPa) carbon changes slowly to a tetrahedral coordination [Oganov *et al.*, 2008; Merlini *et al.*, 2012; Boulard *et al.*, 2011].

1.3.2 CO₂, carbon coordination and phase stability

The evidence for changing coordination of carbon at pressure invites a comparison of CO₂ phase transitions with the SiO₂ system that undergoes a change from tetrahedral coordination to octahedral coordination at transition zone pressures (~25 GPa). Several attempts have been made to map the CO₂ P,T phase diagram to that of silica to include quartz, coesite and stishovite-like phases [Sengupta and Yoo, 2010]. While these experimental attempts have been successful in finding several analog phases, the CO₂ phase diagram is full of metastable phases and path dependent phase transitions. The experiments conducted on CO₂ in this work attempt to elucidate some of these transitions and phases. Arguments can be made that is unlikely CO₂ will exist as a solid in the deep Earth due to low melting temperatures at depth (i.e. 1063 K at 24 GPa, 1408 K at 50 GPa and 2064 K at 135 GPa). Recent work on the high pressure, high temperature CO₂-V phase, however, indicates that at pressures above 20 GPa, this newly identified phase may be dense enough to significantly increase the melting temperature [Santoro *et al.*, 2012; Yoo *et al.*, 2013; Oganov *et al.*, 2008].

1.3.3 Carbonate and CO₂ experiment summaries

The predicted change coordination in both carbonate and CO₂ fundamentally affects how carbon is stored in the deep Earth and is an important part of understanding the role that oxidized

carbon takes in the mantle. Four separate studies are included in this work that examine the phase stability, carbon coordination and thermoelastic properties of carbon bearing minerals. The first study examines the complex ionically bonded salt, hanksite, using powder X-ray diffraction and Raman Spectroscopy methods. The second study probes the high-pressure phase transitions of the Mn-Dolomite end member, kutnohorite, using powder X-ray diffraction. The third study provides definitive high pressure, high temperature single crystal X-ray diffraction measurements of aragonite, which generate quality equation of state fits. Finally, a frontier study using neutron diffraction and resistive heating examines the CO₂-IV phase and its thermoelastic properties.

Each of these studies involved collaborations with different national and international laboratories using X-ray and neutron diffraction techniques. The techniques used in the CO₂ study (Chapter 5) at the Spallation Neutrons at Pressure (SNAP) instrument at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory involved engineering and pioneering the use of resistive heating with the panoramic diamond anvil cell, the first such study done using neutron diffraction techniques. Thus, the work encompassed in this dissertation not only represents achievement in basic mineral physics sciences, but also the development of novel techniques to further the experimental capabilities.

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Chapter 2: Spectroscopic and X-ray diffraction study of hanksite and tychite at high pressure, and a model for the compressibility of sulfate minerals

2.1 Introduction

Hanksite, $\text{Na}_{22}\text{K}(\text{SO}_4)_9(\text{CO}_3)_2\text{Cl}$, is a rare evaporite mineral most commonly found in the Quaternary lacustrine evaporite deposit at Searles Lake, San Bernadino, California [Pratt, 1897; Eugster and Smith, 1965]. Some of the sulfate rich deposits observed on Mars [Wang *et al.*, 2006; Steiger *et al.*, 2011] have been proposed to be evaporite beds caused by deposition from arid saline lakes, similar to Searles Lake [Barbieri and Stivaletta, 2011]. Hydrated salts with similar ionic constituents are thought to dominate the mantles of the icy moons of the outer planets [Chio *et al.*, 2004; Brand *et al.*, 2010]. Ganymede's outer icy mantle may contain 15-20 wt.% sulfates and studies predict a sulfate-dominated layer at the base of an 800 km icy mantle [Nakamura and Ohtani, 2011]. Therefore, understanding the behavior of sulfate rich minerals can provide insights into the chemical and physical properties of the surfaces and interiors of solar system bodies.

Only a handful of minerals including hanksite and tychite contain both sulfate and carbonate groups; hanksite is unique in that it contains (Na,K)Cl ionic groups as well. This ionic complexity combined with Hanksite's hexagonal symmetry make it an ideal mineralogical model for the behavior of complex ionic systems under pressure. Figure 2-1 illustrates the hanksite unit cell from the *a*-axis, *c*-axis and N(111) perspectives. Hanksite has cell parameters $a = 10.494(1)$ Å and $c = 21.190(3)$ Å, with a volume of $2020.8(8)$ Å³, a Z of 2, and 154 atoms in the unit cell. The hexagonal symmetry belongs to space group $P6_3/m$ [Kato and Saalfeld, 1972; Araki and Zoltai, 1973]. Carbonate triangles lie in a plane perpendicular to the *c*-axis. Chains of sodium and potassium octahedra run parallel to the *c*-axis and are connected by the sulfate tetrahedra and carbonate triangles [Araki and Zoltai, 1973]. The S-O bond lengths range from 1.463-1.485 Å, which is within the normal range of a non-distorted sulfate tetrahedron. As can be seen in Figure

2-1, the sulfate tetrahedra occupy two distinct bonding environments. Some sulfate groups are bonded to sodium polyhedra that include both oxygen and chlorine atoms while others are bonded only to regular sodium and/or potassium polyhedra including only oxygen atoms.

The high pressure behavior of sulfates gypsum and anhydrite have been studied both theoretically [Gracia *et al.*, 2012] and experimentally via X-ray diffraction and IR/Raman spectroscopy methods [Bradbury and Williams, 2009; Comodi *et al.*, 2008; Ma *et al.*, 2007; Knittle *et al.*, 2001; Chen *et al.*, 2001; Huang *et al.*, 2000]. In addition, much study has gone into MgSO_4 , BaSO_4 , various lithium sulfates and sulfate salts [Lemos *et al.*, 1991; Sakuntala and Arora, 1999; Sakuntala and Arora, 2000; Chen *et al.*, 2009; Chen *et al.*, 2010; Brand *et al.*, 2010; Machon *et al.*, 2010; Crichton *et al.*, 2011; Jahn and Schmidt, 2010; Zhang and Sekine, 2007; Santamaría-Pérez *et al.*, 2011; Antao, 2012]. Hydrated sulfates like gypsum undergo a number of structural changes below 10 GPa, while others like BaSO_4 exhibit few signs of transformation up to 20 GPa. The behavior of these compounds under pressure can be rationalized in terms of the local polyhedral behavior of the cations present in the structure, since SO_4 bond lengths and angles are expected to be relatively resistant to compression or distortion. Hanksite and tychite afford the opportunity to study this diverse behavior of sulfate under pressure in complex ionic compounds.

2.2 Experiment setup

The hanksite and tychite samples collected at Searles Lake were confirmed by X-ray diffraction. Powders were created by grinding samples in a mortar and pestle and were loaded into a 350 μm hole drilled in a precompressed steel gasket within a diamond anvil cell (500 μm culets). No additional pressure medium was included due to the high solubility of hanksite and tychite in most fluids. Effects of a possibly non-hydrostatic sample environment are addressed in

the discussion section. Small crystals of ruby were placed in multiple locations in the cell for ruby fluorescence pressure determinations [Mao *et al.*, 1986]. For hanksite the reported pressure is the average and standard deviation of pressures measured by several different ruby fluorescence measurements obtained between each pressure step. Two sets of Raman spectroscopy experiments were performed on hanksite and one X-ray diffraction experiment was performed on hanksite followed by another X-ray diffraction experiment on tychite. Fresh samples were used for each experiment.

Raman spectra of hanksite were collected as a function of pressure and room temperature using a microscope-based confocal Raman system in the UCLA Mineral Physics Lab equipped with a 488 nm Ar⁺ laser, a 750 mm monochromator, a grating of 1800 grooves/mm and a resolution of 0.50 cm⁻¹/pixel [Hunt *et al.*, 2011]. The spectrometer was calibrated using a neon gas lamp before each experiment. In a first experiment, the pressure was increased in ~2 GPa steps to 16.60(6) GPa. Spectroscopic data were collected between 800-1300 cm⁻¹, encompassing the ν_1 and ν_3 internal modes of sulfate and the ν_1 internal mode of carbonate. Data collection times ranged from 3-5 minutes with exposure time increasing with pressure. The cell was then left sitting for a week at high pressure. Upon decompression the signal to noise ratio was extremely poor and useful Raman signals could not be recovered below ~8 GPa. The cause of signal loss has not yet been determined. A second set of experiments examined the Raman spectra of hanksite under compression and subsequent decompression over the course of several hours. In this case, immediate decompression led to no signal loss.

In addition to the high-pressure Raman spectra, ambient-pressure spectra were collected on a number of additional species including laboratory grade MgSO₄ powder, single crystal gypsum, single crystal hanksite and single crystal tychite. For these measurements data was collected

from 200 to 1300 cm^{-1} and in the area of the O-H bonds $\sim 3400 \text{ cm}^{-1}$. During the measurements of hanksite, different crystal orientations produced different frequencies depending on the laser polarization and the orientation of the crystal.

Angle-dispersive powder X-ray diffraction patterns at ambient temperature and high pressure were obtained at Beamline 12.2.2 at the Advanced Light Source at Lawrence Berkeley National Labs using a wavelength of 0.6199 Å. The image detector distance was calibrated using a LaB_6 standard at the sample position. For hanksite, fifteen pressure steps of ~ 1 GPa were taken to reach a high pressure of 15(2) GPa and twelve measurements were taken during decompression. The experiment on tychite was taken to 17.2(8) GPa in pressure steps of ~ 2 GPa. The Mar345 image plate exposures were processed using the software Fit2D [Hammersley, 1996] to create a two-dimensional "caked" image (e.g., Figure 2-2). In-house software (M. Armentrout ms in preparation) was used to integrate the two-theta positions of each individual diffraction peak, yielding a best-fit d -spacing and error bar for each lattice plane. Best-fit lattice parameters were calculated using a weighted linear least squares fit to the collection of d -spacings at each pressure step, assuming hexagonal symmetry for hanksite and cubic symmetry for tychite (Table 2-1 and Table 2-2). Values for d -spacings at each pressure step are tabulated in Table 2-6 and Table 2-7. Unlike the X-ray pattern integration package in Fit2D, our approach allows for identification and resolution of close peaks and immediate awareness of spurious information in two-dimensional X-ray diffraction patterns.

In addition to the experimental X-ray diffraction and Raman spectroscopy, a model for the pressure dependence of tychite's volume was created using density functional theory, with the PBE Gradient corrected functional [Perdew *et al.*, 1996]. The software QUANTUM Espresso [Giannozzi *et al.*, 2009] and ultrasoft pseudopotentials (Table 2-3) were used to optimize the

primitive unit cell of tychite for a range of energy cutoffs from 40 to 80 Rydberg at a single electronic wave vector ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$). At 816 eV (60 Rydberg) the calculations were converged with respect to unit cell volume (0.05%) and with respect to energy (0.00019 eV/atom). The calculated primitive unit cell volume of 695.57 Å³ is 3.4% larger than the value of 671.96 Å³ from *Schmidt et al.* [2006]. This is typical and expected for a PBE model of an anhydrous crystal. Calculations were performed at several unit cell volumes, corresponding to a maximum pressure of 18.5 GPa.

2.3 Results and Discussion

2.3.1 Raman Spectroscopy

Figure 2-3 depicts the polarized Raman spectra of hanksite at ambient pressure and temperature. The most intense Raman vibration corresponds to the SO₄ ν_1 symmetric stretch, which dominates the ambient and high-pressure spectra. Our measured hanksite spectrum exhibits seventeen Raman peaks, including fifteen sulfate internal modes and two carbonate internal modes, compared with the 35 Raman-active modes predicted by our factor group analysis ($7A_g + 8E_{2g}^2 + 6E_{1g}^1 + 8E_{2g}^1 + 6E_{1g}^2$).

Table 2-4 gives a full listing of our ambient pressure experimental hanksite and tychite frequencies in comparison to previous sulfate vibrational data. The values of the sulfate internal modes depend on the local bonding structure. The aqueous SO₄ ion ν_1 is 980 cm⁻¹ [Nakamoto, 1997], but in a contact ion pair with MgSO₄ the frequency shifts to 988 cm⁻¹ [Jahn and Schmidt, 2010]. Comparing BaSO₄ and SrSO₄ illustrates the impact of bond length on sulfate modes. Sulfate ν_1 of SrSO₄ has a higher frequency than ν_1 of BaSO₄ because the shorter bond length between strontium and oxygen has a higher bond strength [Chen et al., 2009]. Further examples of shifts in ν_1 due to differing local polyhedral environments can be found in MgSO₄ hydrates

studied by *Wang et al.* [2006] and studies of lithium and sodium sulfates [*Matsumoto et al.*, 2009].

Figure 2-4 shows the Raman spectra as a function of pressure. Above 1.4(1) GPa the 992 cm^{-1} sulfate symmetric stretching mode (ν_1) becomes two distinct modes, each with a different pressure dependence. The carbonate ν_1 mode loses intensity above ~ 10 GPa and reappears upon decompression. A plot of the sulfate ν_1 and ν_3 and carbonate ν_1 modes as a function of pressure (Fig. 5) shows the pressure-reversibility and the reproducibility in experiments. The pressure dependence of these modes and their mode Grüneisen parameters are listed in Table 2-5.

Huang et al. [2000] and *Comodi et al.* [2008] observe a splitting in the sulfate ν_1 mode in gypsum at 4-6 GPa. They interpret the splitting as distortion of the sulfate tetrahedra due to changing water molecule geometry. *Knittle et al.* [2001] also observe the split at 4-6 GPa and conclude that the split is due to pressure-induced Fermi resonance with the overtone of the ν_2 symmetric bending vibration. In our case, no such overtones are readily apparent in our hanksite spectra, supporting the idea that the two distinct ν_1 peaks arise from the two distinct geometries of sulfate tetrahedra as indicated in Figure 2-1.

2.3.2 X-Ray diffraction

At ambient conditions the measured unit cell parameters of hanksite were $a = 10.494(1)$ Å and $c = 21.190(3)$ Å, with a unit cell volume of $2020.8(8)$ Å³, in good agreement with previously published values by *Kato and Saalfeld* [1972] of $a = 10.490(1)$ Å and $c = 21.240(1)$ Å and *Araki and Zoltai* [1973] of $a = 10.465(21)$ Å and $c = 21.191(43)$ Å. Figure 2-6 plots normalized volume as a function of pressure for hanksite and tychite diffraction data. For hanksite, the X-ray diffraction patterns are consistent with a hexagonal symmetry for all pressure steps. Integrated diffraction patterns are included in supplementary Figure 2-10 and lattice data

are tabulated in Table 2-7. A Birch-Murnaghan fit to the volume compression data between 0 and 8 GPa yields an isothermal bulk modulus of 66(1) GPa (with $K' = dK_{0,T}/dP$ fixed at 4). A Birch-Murnaghan fit of the unit cell parameters a and c with respect to pressure yield effective bulk moduli of 76(2) GPa for a and 50(2) GPa for c . This is consistent with the orientation of the carbonate triangles parallel to the a axis reducing the a axis compressibility and the large amount of compressible octahedra stacked along the c axis.

Tychite ($\text{Na}_6\text{Mg}_2(\text{CO}_3)_4(\text{SO}_4)$) has a cubic (Fd3) structure with similar polyhedral components (Schmidt et al. 2006). X-ray diffraction under pressure shows this structure is stable up to 10.61(8) GPa. A Birch-Murnaghan fit to the tychite high pressure data in this range gives an initial volume of 2693(2) $\text{\AA}^3$ and an isothermal bulk modulus of 85(1) GPa (with K' fixed at 4). This unit cell volume compares well with 2687.82(7) $\text{\AA}^3$ found by Schmidt et al. [2006]. The tychite experiment yields a bulk modulus smaller than the first principles model of tychite volume as a function of pressure, which yields $K_{0,T} = 132(1)$ GPa (with K' fixed at 4). In the diffraction experiments we observe evidence of a transition in the tychite unit cell structure by 12-15 GPa. Near 12 GPa the (111) lattice plane disappears, calling into question our assumption of Fd3 cubic symmetry. The new structure has not yet been identified. Tychite integrated diffraction patterns and lattice data are given in Table 2-6 and Figure 2-11.

2.3.3 Effects of non-hydrostaticity

Our sample, which could not be loaded with a liquid pressure medium due to its high solubility, may be subjected to a non-hydrostatic sample chamber. Generally these non-hydrostatic effects—which result in larger-than hydrostatic measured X-ray lattice parameters in the X-ray and diamond cell geometry employed in these studies—arise when a sample is able to support a great deal of differential stress. Figures depicting the pressure evolution of hanksite

and tychite diffraction patterns are provided in Figures 2-10 and 2-11. By 9-10 GPa notable broadening of peaks is seen in both hanksite and tychite patterns. Equation of state fits to the data were conducted below these pressures and only up to 8 GPa. Although we lack direct data on supported differential stress for this experiment, we can provide an estimate of our systematic bias on our measured bulk modulus by assuming that hanksite and tychite have similar strengths as those reported for NaCl [Meade and Jeanloz, 1988]. At 8 GPa, corresponding to the maximum pressure used to determine compressibility in the current study, NaCl supports a differential stress of ~ 0.25 GPa. If we assume that hanksite and tychite support a differential stress of ~ 0.5 GPa at 8 GPa, we calculate that our determined bulk moduli may be overestimated by $\sim 6\%$; e.g. 62 GPa for hanksite rather than 66 GPa. We acknowledge that lack of hydrostaticity may cause our measured bulk moduli to be systematically biased higher, but argue that the effect is small ($\sim 6\%$ maximum) and does not affect any of the main conclusions of our study.

2.3.4 Sulfate systematics

Figure 2-7 shows V/V_0 as a function of pressure for hanksite, tychite and several additional sulfate minerals. At pressures below ~ 8 GPa, hanksite's compressibility is similar to previous measurements of BaSO_4 compressibility [Lee *et al.*, 2003; Crichton *et al.*, 2011]. Beginning at 8 GPa and ending at 10 GPa the hanksite data show a volume drop of 5%, but with no apparent change of symmetry to indicate a first-order phase transition. A similar trend was determined from the ab initio calculations for mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) which undergoes a volume drop of 20% between 7 and 10 GPa [Brand *et al.*, 2010]. In contrast, tychite is slightly less compressible than hanksite and barite and its pressure-volume relationship is smooth until its structural change near 12 GPa. The first principles model of tychite is much less compressible and is most akin to the monazite-structured CaSO_4 [Bradbury and Williams, 2009].

Data from tychite, gypsum, SrSO_4 and LiCsSO_4 [Knittle *et al.*, 2001; Comodi *et al.*, 2008; Chen *et al.*, 2010; Shashikala *et al.*, 1993] all exhibit strong evidence for first order phase transitions. Lattice planes and symmetries change and the sulfate modes split near phase transitions. Hanksite shows no change in symmetry; diffraction peaks neither appear nor disappear during the volume shift between 8 and 10 GPa. Hanksite's behavior is closer to that of SrSO_4 and SnSO_4 . Raman studies of SrSO_4 by Chen *et al.* [2010] found a discontinuity of the ν_1 mode with respect to pressure at 10 GPa interpreted as a second order phase transition. The study of SnSO_4 by Hinrichsen *et al.* [2008] found a similar transition. Each of these transitions was iso-structural and caused by the reordering and/or distortion of the surrounding polyhedra affecting the less compressible SO_4 groups.

Figure 2-8 compares the compressibility of the a and c axes of the hanksite unit cell to the ratio of the two ν_1 modes above 1.4(1) GPa. All of these parameters exhibit a discontinuity in slope near 10 GPa. The c -axis is more compressible than the a -axis, but they both experience a drop in the same pressure range that the ratio of the ν_1 modes appear to flatten. The flattening of the ratio of the ν_1 modes corresponds to the slight kink seen in the Raman patterns (Fig, 5). These trends indicate a pressure-induced change in the local cation geometry surrounding the sulfate groups that does not affect the overall hexagonal symmetry.

Figure 2-7 demonstrates the wide range of compressibilities for sulfate minerals. We hypothesize that the elastic properties of sulfates are not controlled by the mechanical structure of the major functional SO_4 unit or unit cell properties, but rather by the local environment of the sulfate groups within a mineral structure. To test this hypothesis we examine the relationship between the average distance between sulfate groups (or other incompressible polyhedra) and the isothermal bulk modulus for several sulfate-bearing minerals (Figure 2-9). Minerals with large

distances ($>7 \text{ \AA}$) between sulfate groups and no other incompressible polyhedra have low bulk moduli (ettringite and mirabilite) [Brand *et al.*, 2010; Clark *et al.*, 2008]. As the distance between the sulfate groups decreases, the bulk modulus of the mineral increases exponentially. In tychite, the sulfate tetrahedra are far away from each other ($\sim 6 \text{ \AA}$) compared to the carbonate triangles ($\sim 4.3 \text{ \AA}$), so the carbonate groups are the important correlation factor. An estimate of the expected bulk modulus for a sulfate mineral can be achieved from this correlation given an idea of the distance between sulfate polyhedra.

2.4 Summary

The results of this study of hanksite and tychite primarily elucidate the compressibility of ionic salts, which are not closely bound and contain rigid polyhedral structures that control their compressional behavior. The control the carbonate group orientation and spacing has over the compressibility of a mineral is not limited to ionic salts. Similar behavior is found in the study of aragonite (Chapter 4). This study of hanksite and tychite serves to indicate the importance of the rigid polyhedral bodies in the compressibility of minerals and opens the door to further study of carbonate minerals and their thermoelastic properties at high-pressure and high-temperature.

2.6 Tables

Table 2-1. Hanksite hexagonal lattice parameters. Parameters a and c from ambient to 15(2) GPa.

Pressure (GPa)	a	c
0	10.487(1)	21.232(5)
2.8(2)	10.359(2)	20.859(6)
3.7(2)	10.347(3)	20.809(11)
4.6(5)	10.284(4)	20.662(14)
6.0(6)	10.257(3)	20.571(11)
6.7(7)	10.232(3)	20.507(12)
7.1(7)	10.213(3)	20.459(10)
8.1(8)	10.178(3)	20.364(10)
9.0(9)	10.135(4)	20.215(12)
9.8(8)	10.066(4)	20.048(10)
10.4(7)	10.010(4)	19.923(12)
11.5(15)	9.988(5)	19.833(13)
12.4(15)	9.957(4)	19.756(11)
13.0(15)	9.934(5)	19.695(12)
14(2)	9.910(4)	19.677(11)
15(2)	9.919(5)	19.713(13)

Note: Parameters a and c from ambient to 15(2) GPa.

Table 2-2. Tychite cubic lattice parameter. Parameter a from 0.41(6) GPa to 12.3(2) GPa. Diffraction patterns beyond this pressure have a different symmetry.

Pressure (GPa)	a
0.41(6)	13.886(2)
1.92(6)	13.833(4)
3.9(1)	13.715(5)
5.11(6)	13.656(4)
7.08(3)	13.573(4)
8.77(3)	13.519(3)
10.61(8)	13.450(4)
12.3(2)	13.423(8)

Notes: Parameter a from 0.41(6) to 12.3(2) GPa. Diffraction patterns beyond this pressure have a different symmetry.

Table 2-3. Pseudopotentials used in the first principles tychite model.

Carbon	C.pbe-rrkjus.UPF ¹
Magnesium	Mg_2-5-07.ncpp ²
Oxygen	O.pbe-rrkjus.UPF ¹
Sodium	Na.pbe-sp-van_ak.UPF ¹
Sulfur	S.pbe-van_ak.UPF ¹

¹ From <http://www.quantum-espresso.org>.

² Moynier et al. (2011).

Table 2-4. Raman frequencies of various sulfate minerals. The tychite and MgSO_4 studies in this work did not include the lower frequency range of modes ν_2 and ν_4 . ¹Raman data from this study; ²Schmidt et al., 2006; ³Wang et al. 2006; ⁴Knittle et al. 2001; ⁵Nakamoto 1997; ⁶Zhang and Sekine, 2007; ⁷Lee et al. 2003; ⁸Chen et al. 2010; ⁹Lemos et al. 1991.

Mode	Hanksite ¹	Tychite ¹	Tychite ²	MgSO_4 ¹	MgSO_4 ³	Gypsum ¹	Gypsum ⁴	SO_4 ion ⁵	Anhydrite ⁶	Barite ⁷	SrSO_4 ⁸	LiCsSO_4 ⁹
Sulfate ν_1	992.8	970 995 1049	967	983.8 1021.8 1051	1022.8 1052	1009	1002 1008	983	1016	988	1001	1016
Sulfate ν_2	459 470 474		493.8		451 475 499	419 497	412 492	450	416 498	451 461	50 8/9	448.1 461
Sulfate ν_3	1096 1117 1124 1135 1142 1156 1166 1190	1103 1137	1136.6	1136	1136 1220	1142	1120 1137 1150	1105	1111 1128 1159	1142 1169	1055 1094 1111 1158 1189	1108 1110.5 1125 1158.5 1198
Sulfate ν_4	620 625 634		629		608 681 697	621	605 621 670 672	611	608 627 674	617 646	622 639 656	620 623 650

Notes: The tychite and MgSO_4 studies in this work did not include the lower-frequency range of modes ν_2 and ν_4 . ¹Raman data from this study; ²Schmidt et al. (2006); ³Wang et al. (2006); ⁴Knittle et al. (2001); ⁵Nakamoto (1997); ⁶Zhang and Sekine (2007); ⁷Lee et al. (2003); ⁸Chen et al. (2010); ⁹Lemos et al. (1991).

Table 2-5. Hanksite sulfate ν_1 and ν_3 and carbonate ν_1 pressure dependence and mode Grüneisen parameters.

Mode	Pressure dependence ($\text{cm}^{-1}/\text{GPa}$)	Mode Grüneisen parameter
Sulfate ν_1	4.0(2)	0.27(1)
Sulfate ν_1 Shoulder	3.0(1)	0.199(7)
Carbonate ν_1	5.3(2)	0.32(1)
Sulfate ν_3	3.9(2)	0.23(1)

Notes: Mode Grüneisen parameters calculated from $\gamma_i = (K_{0,T}/\nu_0)(d\nu_i/dP)_T$ (Knittle et al. 2001) using the bulk modulus 66(1) GPa determined in the X-ray diffraction experiment. Mode Grüneisen parameters compare to sulfate ν_1 parameter of 0.21(2) in gypsum and a sulfate ν_1 parameter of 0.6(2) in pressurized anhydrite (Knittle et al. 2001; Bradbury and Williams 2009).

Table 2-6. Tychite *d*-spacings and standard deviations for all pressure steps.

Tychite Lattice Data														
Pressure	111		220		311		222		331		422		333	
(GPa)	<i>d</i> -space	σ	<i>d</i> -space	σ	<i>d</i> -space	σ	<i>d</i> -space	σ	<i>d</i> -space	σ	<i>d</i> -space	σ	<i>d</i> -space	σ
0.41(6)	8.00278	0.01878	4.91039	0.00235	4.18545	0.00098	4.00750	0.00314	3.18506	0.00098	2.83454	0.00124	2.67346	0.00056
1.92(6)	8.00545	0.00938	4.88579	0.00452	4.17308	0.00199	3.97816	0.00598	3.17017	0.00237	2.81973	0.00414	2.66360	0.00185
3.9(1)	7.92120	0.01119	4.84279	0.00511	4.13829	0.00224	3.94727	0.00983	3.14467	0.00248	2.78779	0.00415	2.64176	0.00188
5.11(6)	7.88396	0.01087	4.82193	0.00443	4.11879	0.00211	3.93409	0.00692	3.13077	0.00198	2.78484	0.00481	2.63167	0.00186
7.08(3)	7.83229	0.01130	4.78912	0.00462	4.09338	0.00172	3.91335	0.00714	3.11118	0.00191	2.76474	0.00490	2.61898	0.00196
8.77(3)	7.78863	0.01138	4.77433	0.00495	4.07677	0.00140	3.90211	0.00419	3.10064	0.00157	2.75513	0.00484	2.60551	0.00184
10.61(8)	7.81116	0.03870	4.76159	0.00855	4.05304	0.00168	3.88571	0.02487	3.08526	0.00223	2.74592	0.01259	2.59105	0.00156
12.3(2)	7.79311	0.02522	4.80062	0.02777	4.04426	0.00321	3.88292	0.02119	3.07863	0.00374			2.58487	0.00304
14(1)			4.80071	0.00945	4.08302	0.00880			3.13072	0.00946			2.56817	0.03837
15.3(8)			4.79079	0.00849	4.09293	0.00543			3.12318	0.00933				
17.2(8)			4.78385	0.00801	4.09592	0.00458			3.11751	0.00846				
13.88(2)			4.78362	0.00823	4.09853	0.00450			3.12119	0.00915				
13.0(6)			4.79901	0.00697	4.10778	0.00423			3.12173	0.00813				
11.16(2)			4.80883	0.00756	4.11204	0.00427			3.15342	0.00442			2.60217	0.02978
8.04(3)			4.85123	0.04129	4.07532	0.01084			3.08606	0.01807			2.60342	0.01062
5.25(2)	7.77131	0.06386	4.78220	0.01285	4.08378	0.00280			3.10398	0.00346			2.61152	0.00216
3.0(5)	7.90391	0.01994	4.81125	0.01285	4.11073	0.00322			3.12324	0.00452			2.62773	0.00264

Table 2-7. Hanksite *d*-spacings and standard deviations for all pressure steps.

Hanksite Lattice Data														
Pressure	002		010		013		110		020		023		006	
(GPa)	<i>d</i> -space	σ	<i>d</i> -space	σ	<i>d</i> -space	σ	<i>d</i> -space	σ	<i>d</i> -space	σ	<i>d</i> -space	σ	<i>d</i> -space	σ
2.8(2)	10.45417	0.04196	8.96863	0.01383	5.49522	0.01471	5.18245	0.00612	4.48668	0.00322	3.77123	0.00078	3.47456	0.00135
3.7(2)	10.56266	0.08233	8.98663	0.02127	5.46315	0.01843	5.17697	0.01008	4.48784	0.00414	3.76539	0.00126	3.46905	0.00272
4.6(5)	10.30519	0.11106	8.91938	0.02207	5.43543	0.03522	5.14874	0.01252	4.45565	0.00452	3.74100	0.00140	3.44602	0.00365
6.0(6)	10.32345	0.03735	8.88548	0.01342	5.41964	0.00875	5.12973	0.00429	4.44292	0.00361	3.73360	0.00182	3.42639	0.00372
6.7(7)	10.25783	0.05266	8.88080	0.01577	5.41178	0.01629	5.11767	0.00766	4.42917	0.00363	3.72094	0.00120	3.41697	0.00324
7.1(7)	10.28014	0.05200	8.85555	0.01546	5.41213	0.01585	5.10822	0.00681	4.42227	0.00301	3.71394	0.00125	3.40805	0.00256
8.1(8)	10.20269	0.04586	8.80447	0.01839	5.38270	0.01906	5.08767	0.00746	4.40487	0.00319	3.70016	0.00118	3.39153	0.00248
9.0(9)	10.16812	0.04286	8.76383	0.01495	5.33646	0.01589	5.05981	0.00811	4.38275	0.00413	3.68340	0.00143	3.36573	0.00282
9.8(8)	10.01506	0.03567	8.70589	0.01525	5.30762	0.01343	5.02028	0.00788	4.35458	0.00404	3.65338	0.00123	3.33141	0.00230
10.4(7)	9.97903	0.03788	8.66708	0.02657	5.26639	0.01332	4.99596	0.00976	4.32656	0.00499	3.63394	0.00128	3.30615	0.00289
11.5(15)	9.86523	0.04542	8.63900	0.02567	5.32085	0.01427	4.97757	0.01206	4.31243	0.00695	3.62353	0.00149	3.29577	0.00294
12.4(15)	9.89261	0.03634	8.61824	0.02837	5.29435	0.01295	4.96438	0.01039	4.30207	0.00747	3.61187	0.00138	3.28503	0.00229
13.0(15)	9.85926	0.03589	8.61316	0.02792	5.23406	0.01209	4.95120	0.01036	4.27748	0.00740	3.60205	0.00145	3.26976	0.00277
14(2)	9.82807	0.03668	8.58171	0.02999	5.21702	0.01321	4.92709	0.00975	4.28190	0.00763	3.59430	0.00138	3.27495	0.00228
15(2)	9.91671	0.03843	8.62786	0.03264	5.24199	0.01289	4.94435	0.01155	4.27967	0.00709	3.60059	0.00190	3.27573	0.00275
13(2)	9.83901	0.05122	8.57139	0.04051	5.27956	0.01505	4.95821	0.01309	4.29046	0.00798	3.60041	0.00212	3.28040	0.00245
12(2)	9.88468	0.04270	8.63566	0.03189	5.25709	0.01351	4.97549	0.01145	4.30200	0.00863	3.61042	0.00169	3.28687	0.00270
12(2)	9.97410	0.05221	8.66532	0.03709	5.25877	0.01454	4.98458	0.01411	4.31850	0.00973	3.61675	0.00247	3.29400	0.00309
11(2)	9.92607	0.05013	8.57521	0.03271	5.22856	0.01502	4.97864	0.01190	4.30784	0.00971	3.62091	0.00251	3.30281	0.00298
9.7(19)	9.96409	0.04778	8.70039	0.03288	5.26879	0.01476	4.99810	0.01354	4.33279	0.00659	3.63754	0.00192	3.31793	0.00319
8.4(16)	10.03191	0.03937	8.68767	0.03012	5.27333	0.01288	5.00897	0.01245	4.34346	0.00668	3.64796	0.00174	3.33670	0.00333
7.2(14)	10.06188	0.04745	8.73520	0.03141	5.30356	0.01414	5.02554	0.00955	4.36210	0.00800	3.65998	0.00175	3.34017	0.00271
6.0(12)	10.11346	0.04918	8.73864	0.03223	5.32458	0.01303	5.04345	0.01054	4.37157	0.00690	3.67669	0.00171	3.35576	0.00356
5(1)	10.15868	0.04669	8.76372	0.03395	5.36851	0.01947	5.06919	0.01237	4.40194	0.00968	3.69215	0.00218	3.36697	0.00405
4.0(8)	10.14322	0.03362	8.78124	0.02795	5.34085	0.01401	5.08606	0.01066	4.41500	0.00863	3.70479	0.00161	3.38310	0.00283
3.5(8)	10.14328	0.04988	8.80746	0.03789	5.43294	0.01614	5.08442	0.00927	4.41794	0.00759	3.71285	0.00171	3.40087	0.00419
2.9(6)	10.24210	0.05099	8.87671	0.03634	5.42191	0.01525	5.11166	0.01066	4.43002	0.00849	3.72335	0.00179	3.40253	0.00328

Pressure	120		121		122		017		026		220	
(GPa)	<i>d</i> -space	σ	<i>d</i> -space	σ	<i>d</i> -space	σ	<i>d</i> -space	σ	<i>d</i> -space	σ	<i>d</i> -space	σ
2.8(2)	3.38413	0.00290	3.34014	0.00200	3.23144	0.00473	2.82887	0.00281	2.74780	0.00063	2.58920	0.00102
3.7(2)	3.38390	0.00415	3.33895	0.00348	3.22039	0.00680	2.82652	0.00974	2.74115	0.00114	2.58477	0.00131
4.6(5)	3.36351	0.00432	3.31997	0.00515	3.19384	0.00573	2.81243	0.01733	2.72242	0.00144	2.57008	0.00159
6.0(6)	3.35323	0.00259	3.31297	0.00344	3.18927	0.00218	2.80374	0.00361	2.71098	0.00113	2.56475	0.00225
6.7(7)	3.34500	0.00307	3.30113	0.00344	3.17695	0.00441	2.79584	0.00618	2.70348	0.00128	2.55715	0.00199
7.1(7)	3.33745	0.00285	3.29595	0.00358	3.17086	0.00395	2.78044	0.00553	2.69846	0.00120	2.55209	0.00153
8.1(8)	3.32762	0.00301	3.28560	0.00366	3.15842	0.00408	2.76978	0.00851	2.68715	0.00128	2.54281	0.00168
9.0(9)	3.31642	0.00295	3.26928	0.00494	3.14260	0.00490	2.74656	0.00688	2.66935	0.00160	2.53160	0.00176
9.8(8)	3.29178	0.00440	3.25084	0.00489	3.12245	0.00351	2.75189	0.00425	2.65227	0.00146	2.51583	0.00190
10.4(7)	3.24570	0.00535	3.19748	0.00633	3.10669	0.00570	2.71074	0.00453	2.63913	0.00153	2.50480	0.00231
11.5(15)	3.26252	0.00548	3.21476	0.00500	3.10070	0.00524	2.69527	0.00438	2.62746	0.00173	2.49404	0.00243
12.4(15)	3.22175	0.00529	3.21152	0.00770	3.09210	0.00539	2.68325	0.00393	2.62092	0.00162	2.48330	0.00256
13.0(15)	3.23916	0.00472	3.17981	0.00803	3.07638	0.00606	2.67881	0.00475	2.61391	0.00169	2.48328	0.00291
14(2)	3.23816	0.00486	3.18711	0.00489	3.07246	0.00445	2.67412	0.00508	2.60726	0.00185	2.47993	0.00301
15(2)	3.23056	0.00551	3.18535	0.00805	3.07744	0.00559	2.68028	0.00516	2.61505	0.00244	2.47892	0.00357
13(2)	3.22893	0.00530	3.19004	0.00589	3.07858	0.00560	2.68203	0.00557	2.61183	0.00217	2.47981	0.00363
12(2)	3.24331	0.00597	3.19673	0.00498	3.08980	0.00580	2.66997	0.00419	2.61907	0.00195	2.48540	0.00332
12(2)	3.22513	0.00674	3.19244	0.00772	3.09025	0.00566	2.67855	0.00597	2.62505	0.00276	2.49191	0.00462
11(2)	3.23939	0.00647	3.21320	0.00721	3.08321	0.00680	2.69048	0.00727	2.62642	0.00252	2.50082	0.00511
9.7(19)	3.25357	0.00610	3.20612	0.00540	3.11700	0.00518	2.69046	0.00454	2.63843	0.00199	2.50947	0.00287
8.4(16)	3.27339	0.00516	3.23572	0.00599	3.10869	0.00508	2.71973	0.00482	2.64589	0.00189	2.51200	0.00282
7.2(14)	3.28285	0.00501	3.24313	0.00567	3.12762	0.00532	2.72267	0.00475	2.65719	0.00183	2.52092	0.00306
6.0(12)	3.29656	0.00581	3.25031	0.00604	3.13713	0.00536	2.74073	0.00525	2.66822	0.00165	2.53056	0.00296
5(1)	3.31472	0.00750	3.26339	0.00560	3.15009	0.00689	2.73630	0.00780	2.67572	0.00226	2.53821	0.00347
4.0(8)	3.34456	0.00500	3.28945	0.00623	3.18194	0.00824	2.76111	0.00475	2.69186	0.00150	2.54728	0.00284
3.5(8)	3.34252	0.00519	3.29568	0.00789	3.16675	0.00545	2.77283	0.00518	2.69486	0.00152	2.55195	0.00282
2.9(6)	3.35588	0.00713	3.29973	0.00701	3.18006	0.00682	2.77569	0.00747	2.70340	0.00155	2.55516	0.00296

Table 2-8. Ambient hanksite *d*-spacings and standard deviations.

Ambient Hanksite Lattice Data		
<u>hkl</u>	<u>d-spacing</u>	<u>σ</u>
002	10.6435	0.0653
010	9.1051	0.0225
013	5.5915	0.0122
110	5.2450	0.0056
020	4.5444	0.0052
023	3.8236	0.0013
006	3.5386	0.0020
120	3.4333	0.0018
121	3.3883	0.0011
115	3.2968	0.0029
122	3.2601	0.0021
030	3.0742	0.0015
116	2.9321	0.0013
017	2.8777	0.0013
026	2.7884	0.0007
220	2.6217	0.0004
311	2.5006	0.0009
043	2.1610	0.0007
231	2.0740	0.0005
038	1.9928	0.0003
046	1.9104	0.0004

2.7 Figures

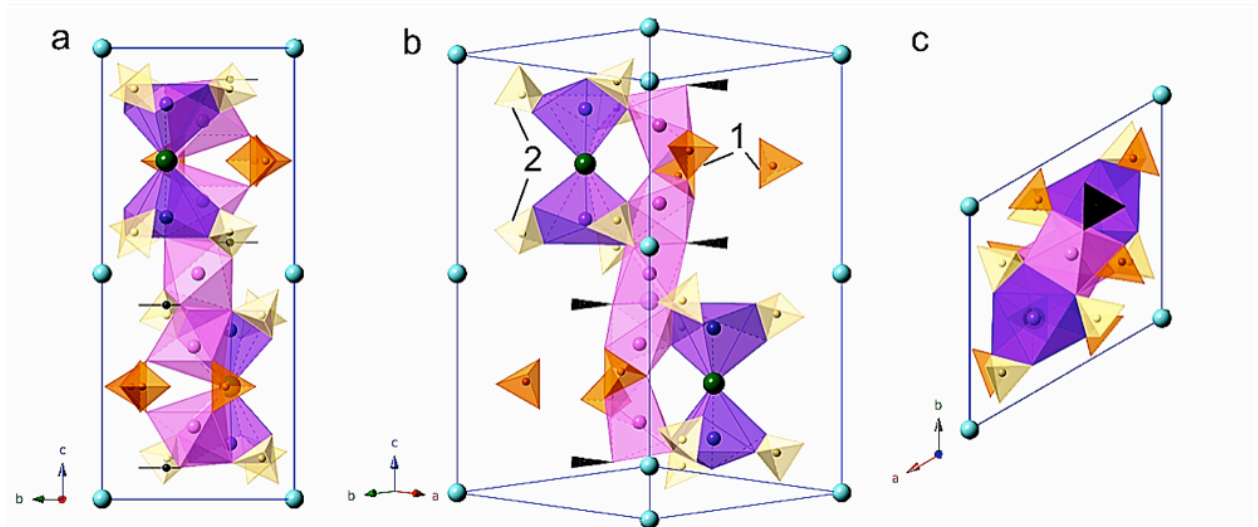


Figure 2-1. The hanksite unit cell from three perspectives. (a) view down a -axis, (b) view down $N(111)$ and (c) view down c -axis. Potassium atoms line the unit cell borders forming chains of potassium octahedra parallel to the c -axis. The two different types of sodium octahedra are shown in light (regular) and dark (coordinated with Cl). Carbonate triangles sit parallel to the a -axis in line with the chlorine atoms. Examples of the two distinct sulfate groups are labeled 1 (dark tetrahedra) and 2 (light tetrahedra). Dark sulfate groups are only bonded to regular sodium and potassium octahedra, while light groups are bonded to distorted octahedra.

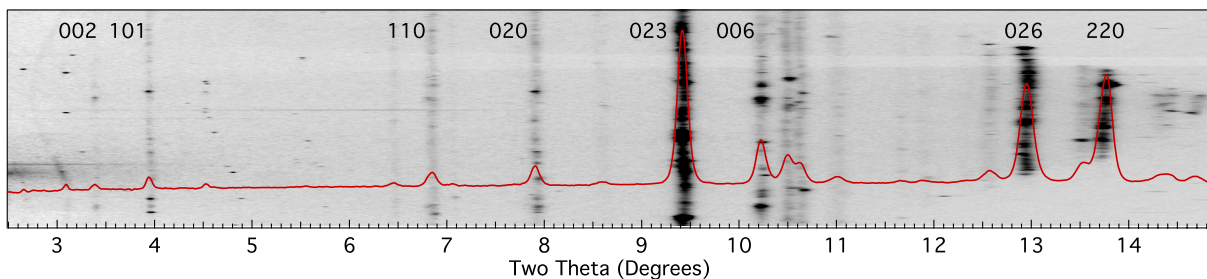


Figure 2-2. Diffraction pattern of hanksite at 2.8 GPa. Data integrated by Fit2D overlies the caked image. Selected lattice planes are labeled at the top left of their band. Note that instances of multiple peaks are much easier to identify in the "caked" image.

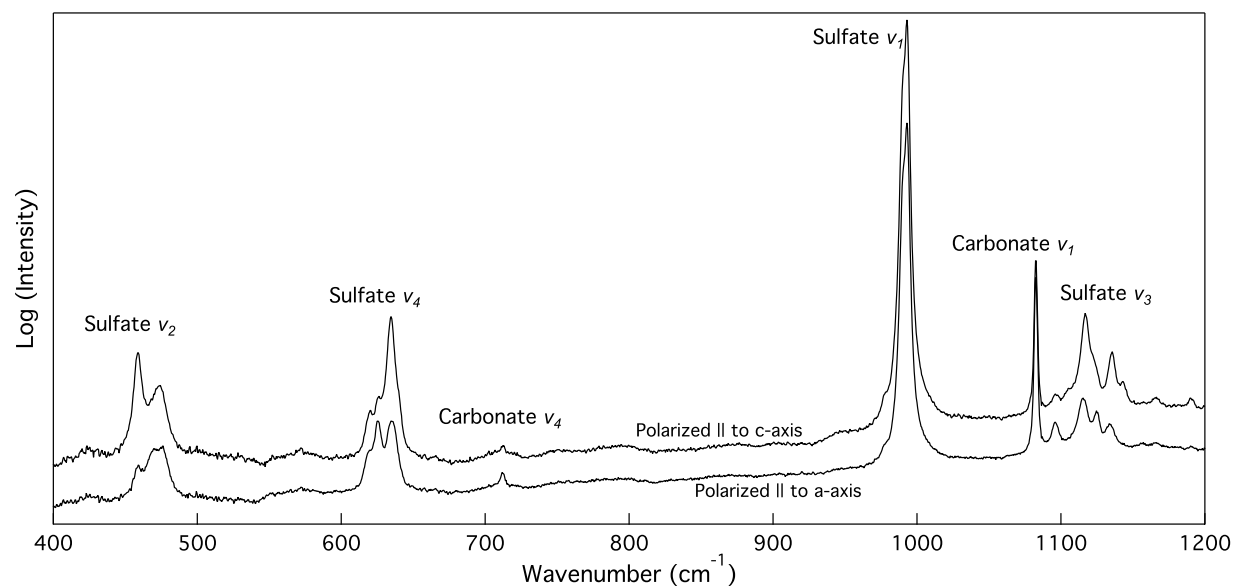


Figure 2-3. Ambient pressure polarized Raman spectra of hanksite. The ν_1 mode of the sulfate tetrahedra dominates the pattern at 992 cm^{-1} . The majority of the modes occur in the ν_3 antisymmetric stretch region between 1096 and 1190 cm^{-1} . Crystal orientation affects the presence and intensity of both carbonate and sulfate modes. In the upper pattern, the laser is polarized approximately parallel to the c axis while in the lower pattern it is polarized approximately parallel to the a axis.

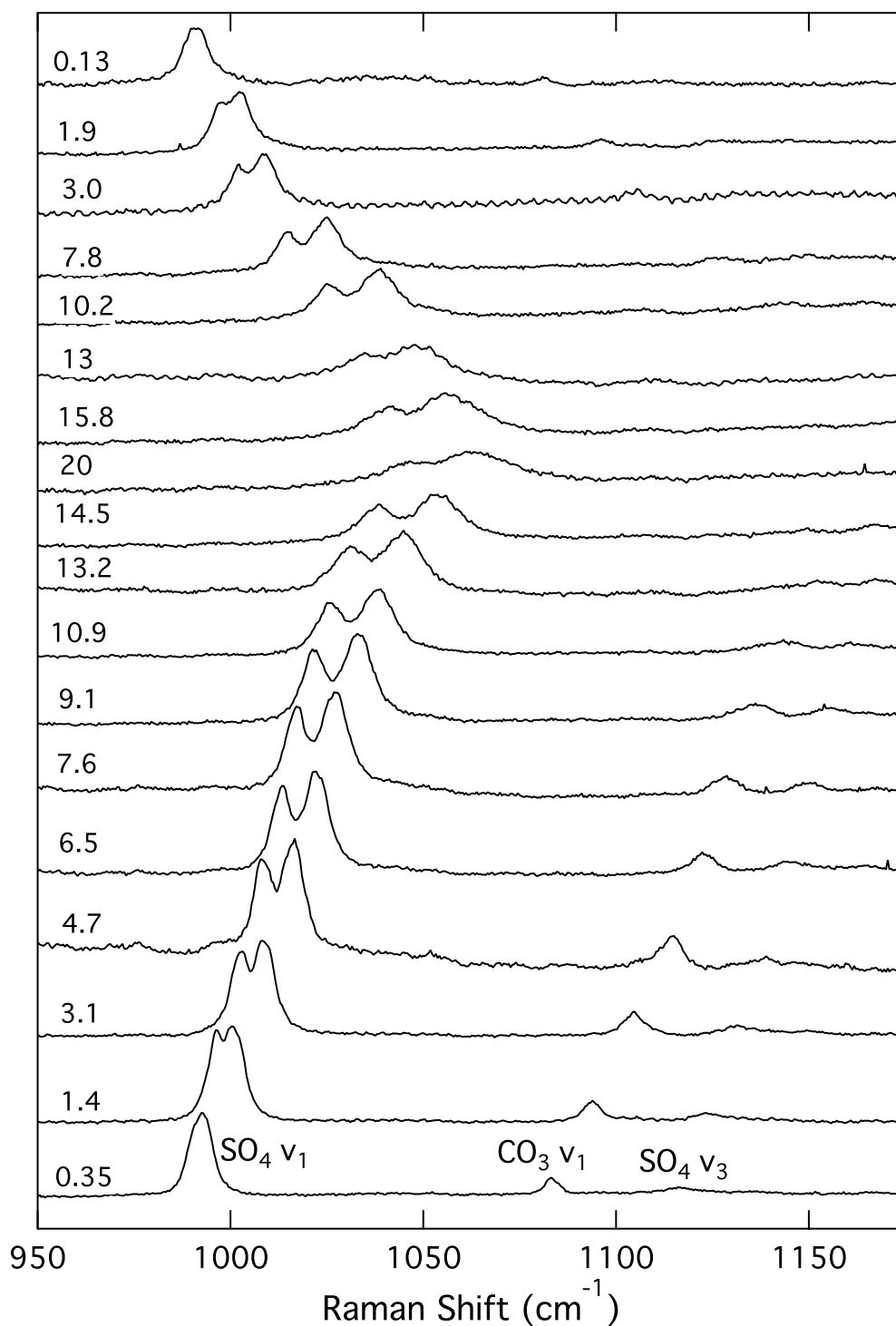


Figure 2-4. Raman spectra of hanksite as a function of pressure. Pressure in GPa of each spectrum is indicated to the top left of each pattern. Separation of the two ν_1 modes occurs immediately. Upon decompression, the modes return to their original frequencies and merge back together.

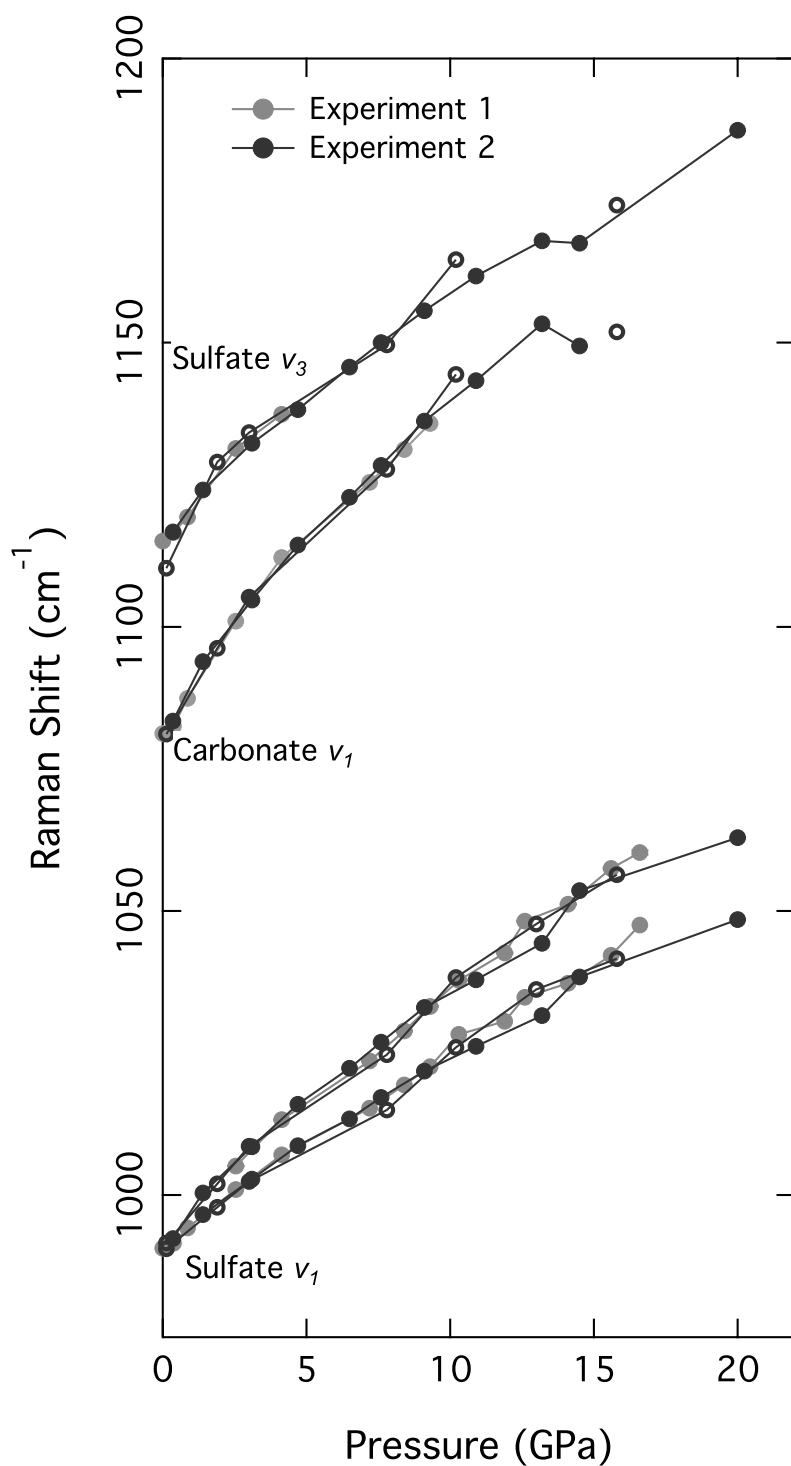


Figure 2-5. Raman shift versus pressure for both hanksite experiments. First hanksite experiment (gray circles), second hanksite experiment (dark gray circles) and second hanksite experiment decompression (open circles) are shown for three modes.

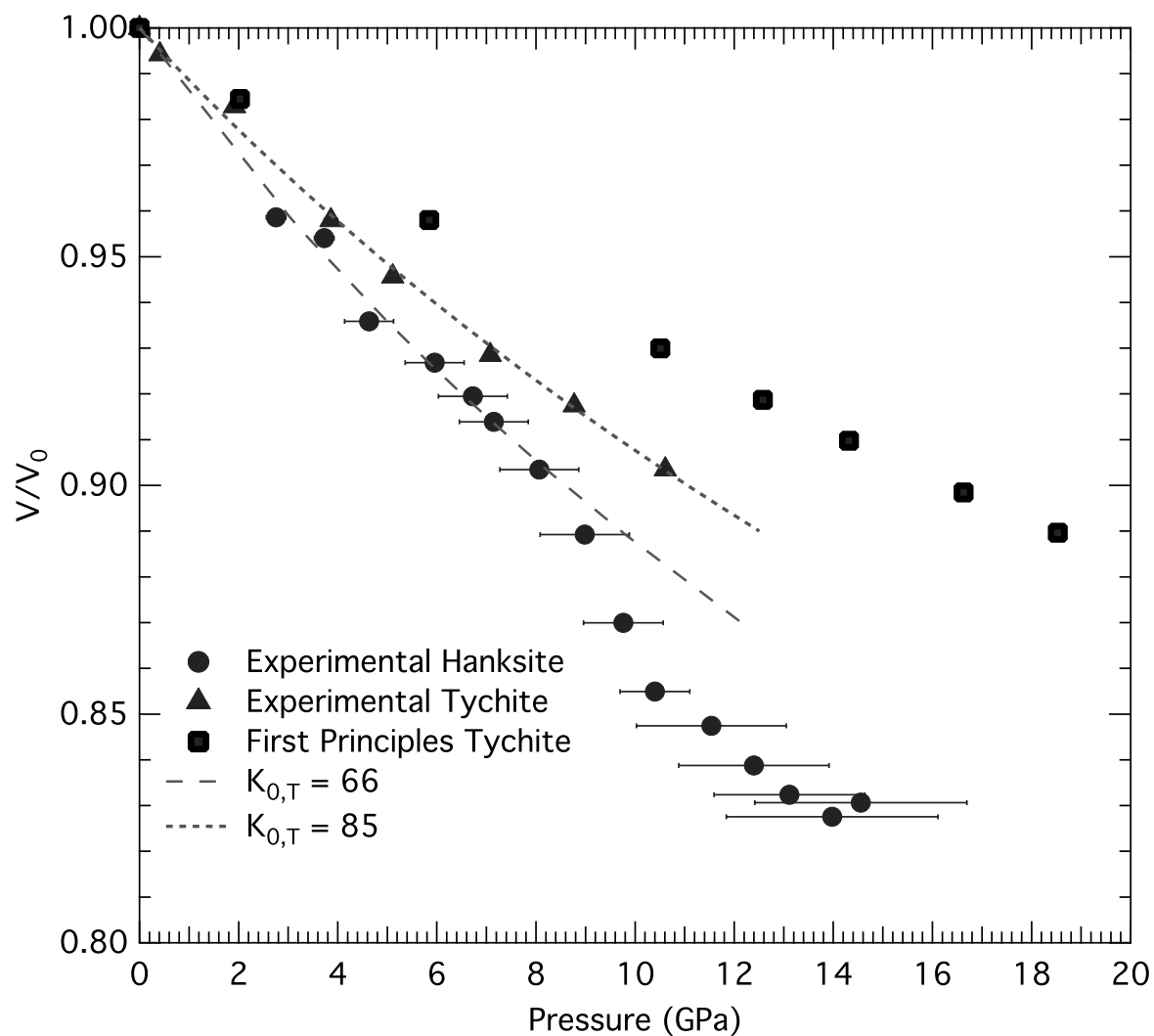


Figure 2-6. Plot of normalized volume as a function of pressure for hanksite (experimental: ●) and tychite (experimental: ▲, model: ■) from X-ray diffraction data and first principles model. Error bars on hanksite pressure represent the standard deviation of pressures measured in the DAC. Birch-Murnaghan fits to the experimental data are shown as dotted lines (hanksite $K_{0,T} = 66(1)$ GPa; tychite $K_{0,T} = 85(1)$ GPa).

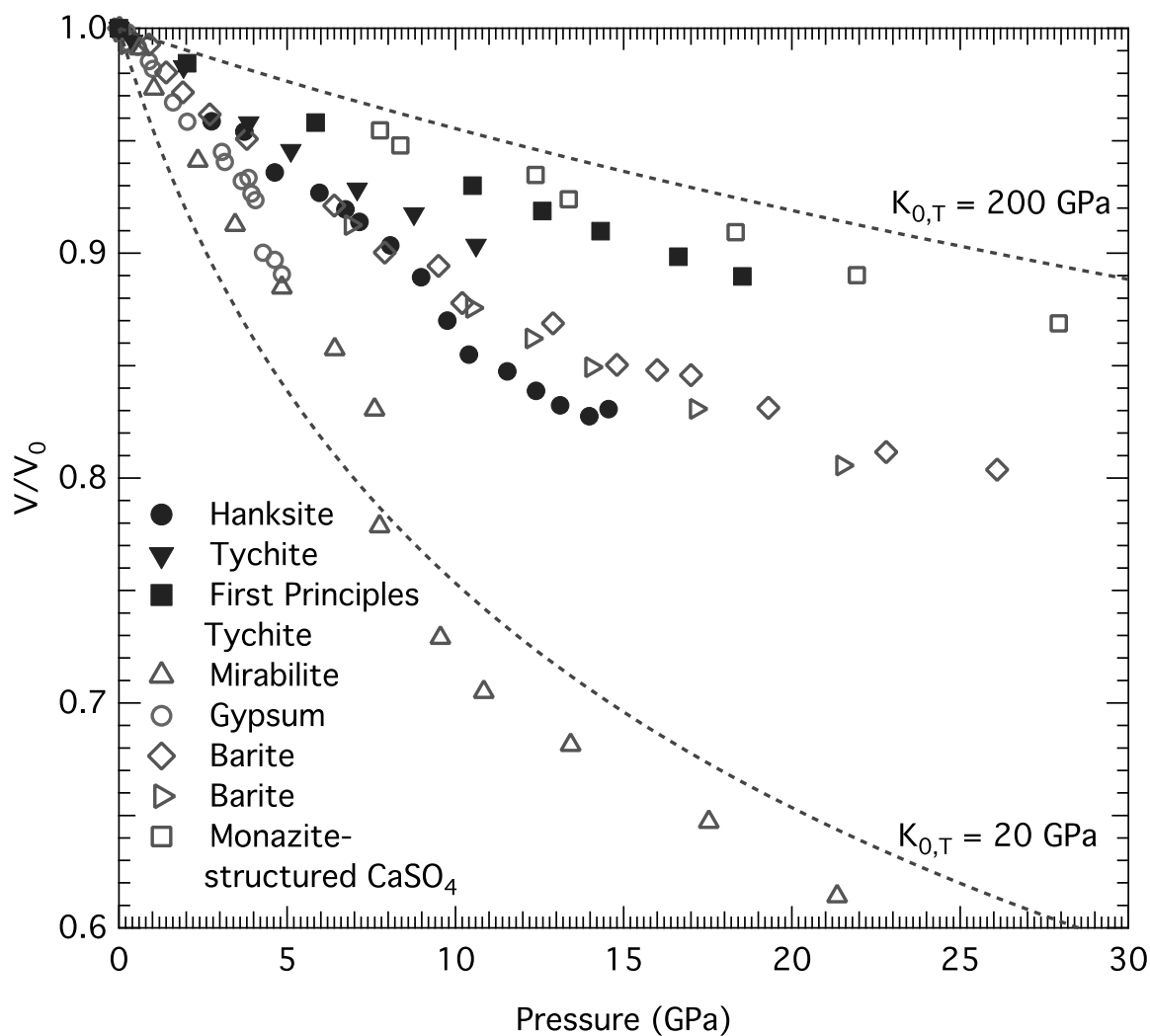


Figure 2-7. Plot of normalized volume as a function of pressure for a variety of sulfate minerals. Birch-Murnaghan P-V curves are shown for $K_{0,T} = 200 \text{ GPa}$ and $K_{0,T} = 20 \text{ GPa}$ (dotted lines, K' fixed at 4). Sulfate mineral data from *Lee et al.* [2003] (◇); *Comodi et al.* [2008] (○); *Bradbury and Williams* [2009] (□); *Brand et al.* [2010] (△); and *Crichton et al.* [2011] (▷). For clarity in seeing trends, we have omitted error bars from this plot.

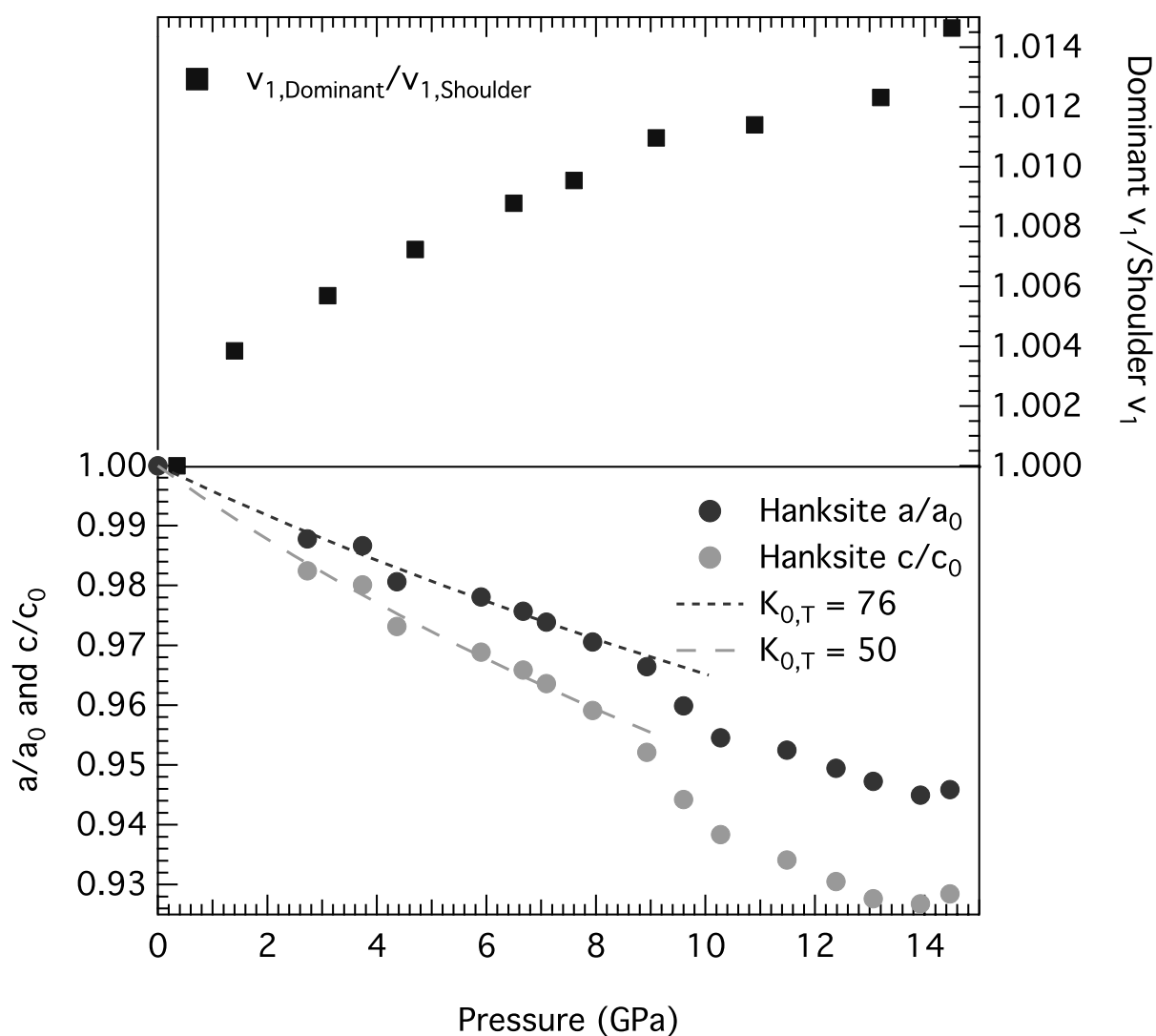


Figure 2-8. Ratio of sulfate ν_1 modes and normalized compressibilities of a and c axes. Fits to the Birch-Murnaghan equation of state from below 8 GPa are shown for both a and c . Note the discontinuity in both the Raman and X-ray data near 10 GPa.

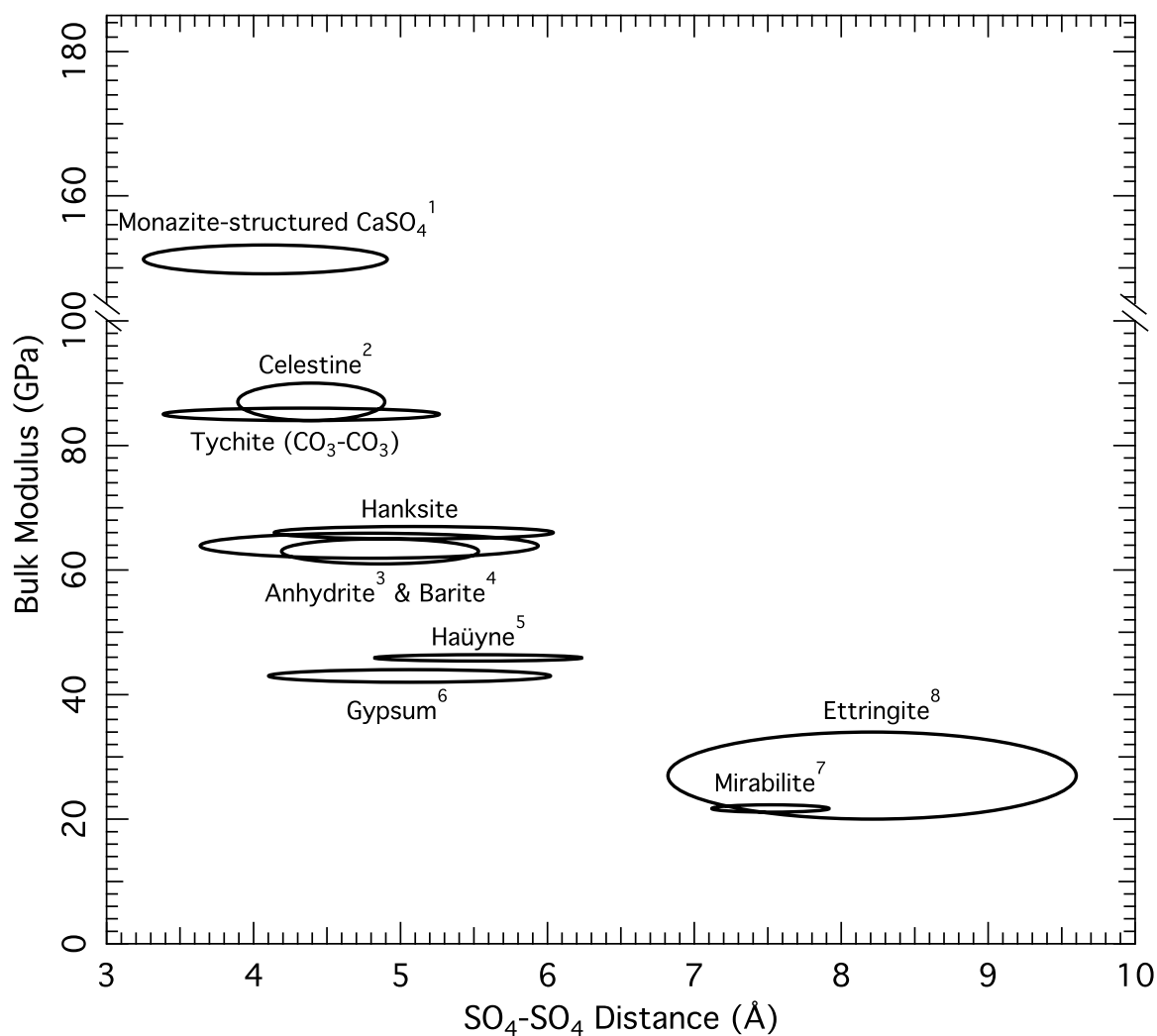


Figure 2-9. Correlation between isothermal bulk modulus and average SO₄-SO₄ distance in select minerals. Ellipses encompass standard deviation of SO₄-SO₄ distance in each mineral and the error in the isothermal bulk modulus calculation. Bulk modulus data from ¹Bradbury and Williams, 2009; ²Chen et al., 2010; ³Gracia et al., 2012; ⁴Crichton et al., 2011; ⁵Fan et al., 2011; ⁶Comodi et al., 2008; ⁷Brand et al., 2010; and ⁸Clark et al., 2008.

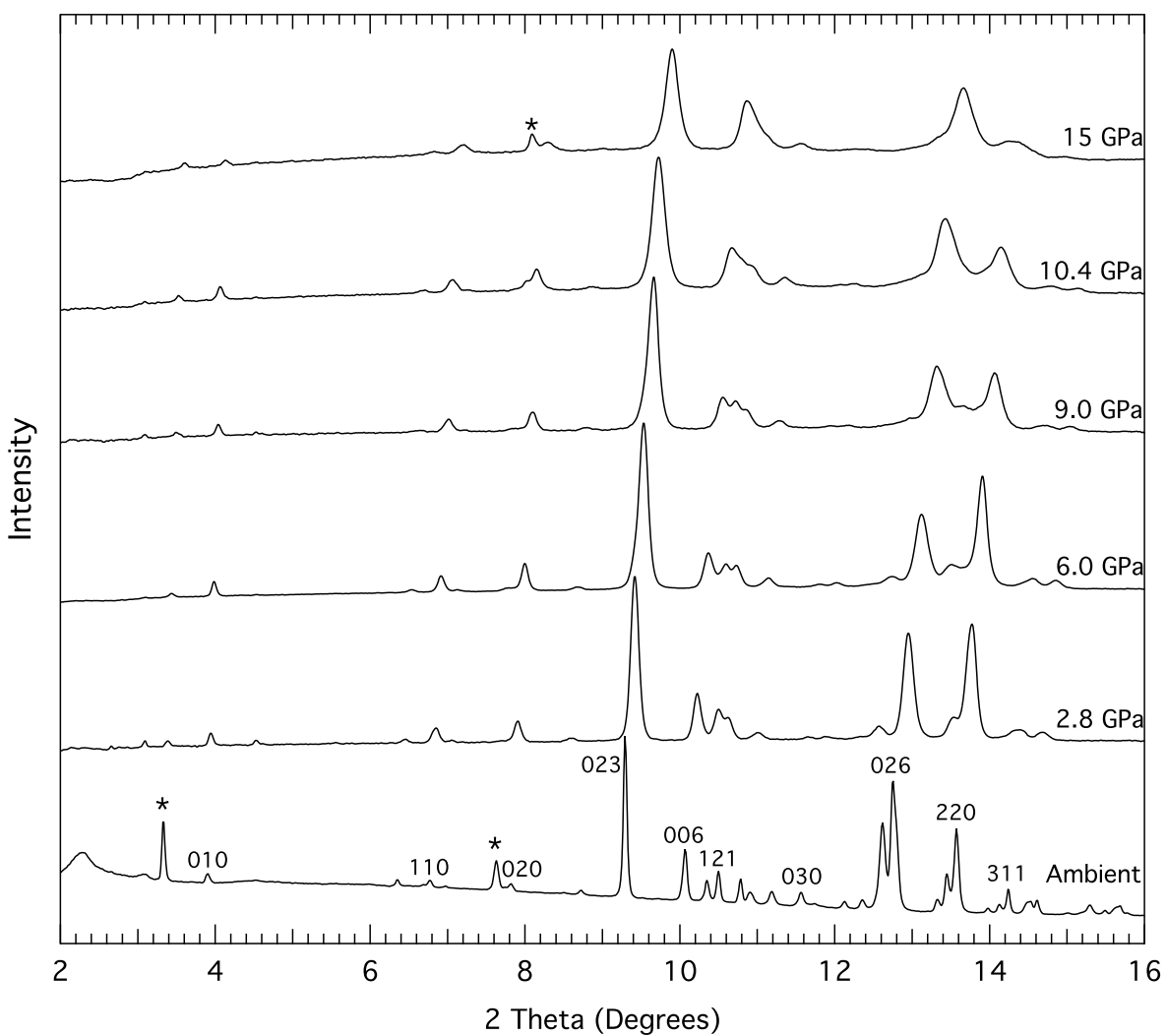


Figure 2-10. Selected hanksite diffraction patterns. Evolution of the Bragg maxima for five pressure steps. Several lattice planes used for structure determination are noted on the ambient pattern. Stars indicate peaks due to spurious information on the image plate. For additional diffraction data please see Tables 2-7 and 2-8.

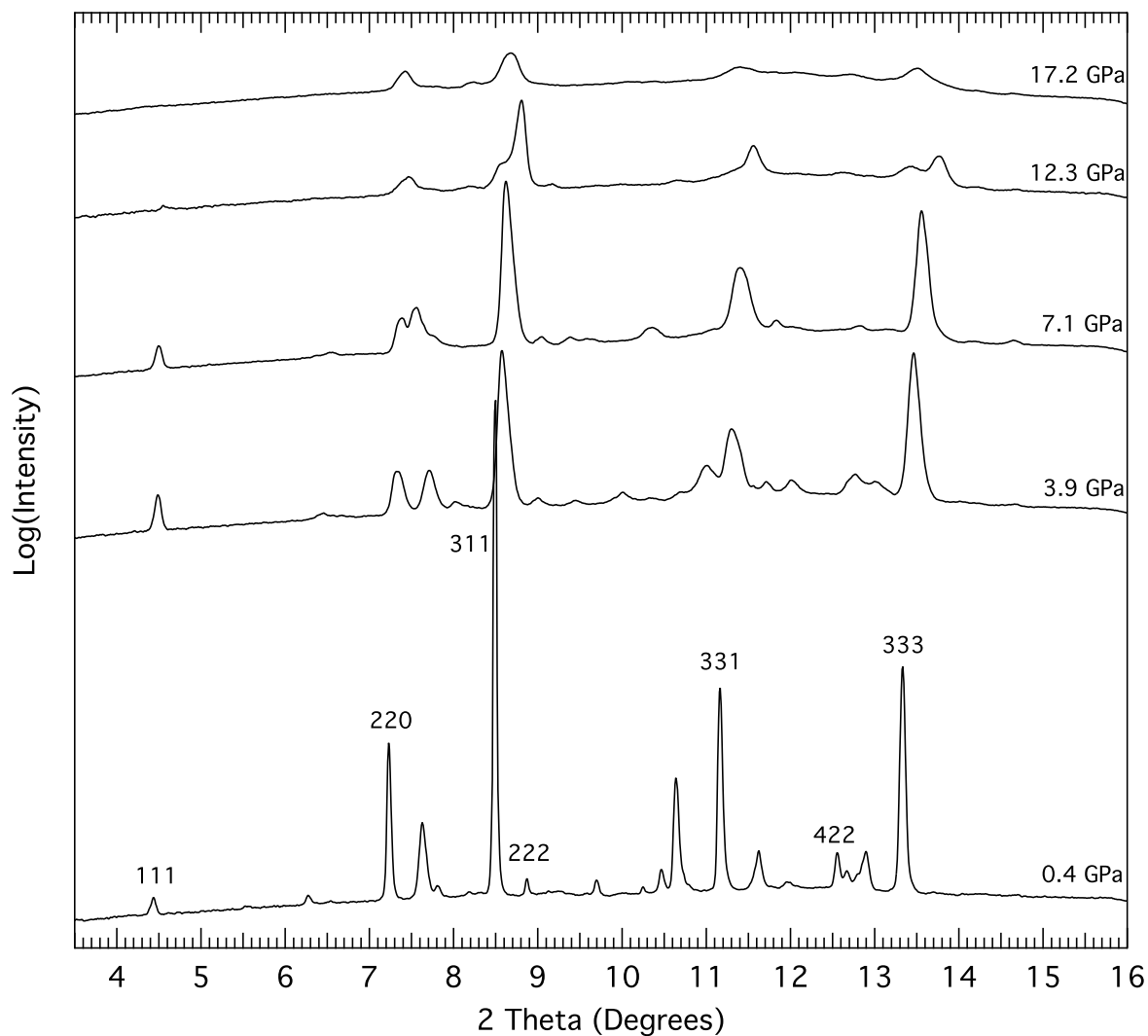


Figure 2-11. Selected tychite diffraction patterns. Evolution of the Bragg maxima for five pressure steps. Lattice planes used for structure determination noted on the 0.4 GPa pattern. Additional data in Table 2-6.

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Chapter 3: High-pressure compressibility and phase stability of Mn-dolomite (kutnohorite)

3.1 Introduction

Carbon in the deep Earth consists of a primordial component plus carbonate that has recycled into the Earth's mantle via subduction zones [Dasgupta and Hirschmann, 2010]. Carbon has limited solubility in mantle silicates and therefore exists as carbon-rich accessory phases, either as oxidized carbonate or reduced graphite/diamond/carbide [Shcheka, et al., 2006]. Therefore studying the high-pressure behavior of carbonate phases helps determine the role of the Earth's deep interior in the deep carbon cycle. In this paper, we present the high-pressure behavior of kutnohorite, an Mn-rich dolomite, and use the new data in conjunction with existing data to analyze the high pressure behavior of a series of rhombohedral carbonate phases.

Recent experimental studies demonstrate that dolomite, $(\text{CaMg}_{1-x}\text{M}_x)(\text{CO}_3)_2$, where $\text{M} = \text{Fe}, \text{Mn}, \text{Zn}$, undergoes a series of phase transformations with increasing pressures and temperatures. Dolomite I (rhombohedral *R*-3) is the ambient pressure phase. Dolomite II (triclinic *P*-1) was observed at ambient temperatures and pressures above ~ 20 GPa [Santillán et al., 2003; Mao et al., 2011; Merlini et al., 2012]. A third dolomite phase, Dolomite III, was recently observed in $\text{Ca}(\text{Mg}_{0.92}\text{Fe}_{0.08})(\text{CO}_3)_2$ by Mao, et al. (2011) and $\text{Ca}(\text{Mg}_{0.6}\text{Fe}_{0.4})(\text{CO}_3)_2$ by Merlini, et al. [2012], by compressing above 35 GPa and laser heating. This dolomite III phase is stable during temperature-quench, allowing Merlini et al. [2012] to refine a structure (triclinic *P*-1). These results raise the possibility of a dolomite-structured carbonate that may be stable at the high-pressures and high-temperatures of the lower mantle and motivate our study to expand the compositional range to include the Mn end-member dolomite, kutnohorite.

3.2 Experimental Methods

Our starting sample was kutnohorite from Franklin, NJ with a composition of $(\text{Ca}_{0.76}\text{Mn}_{0.24})\text{Mn}(\text{CO}_3)_2$ and with $\sim 5\%$ rhodochrosite (MnCO_3) vein impurities, determined by

electron microprobe. This Mn-enriched composition is in agreement with a previous determination by *Fron del and Bauer* [1955] and is not unusual for kutnohorite from Franklin, NJ. In addition, the Mn excess does not affect the structure of the kutnohorite, which is the dolomite structure comprised of alternating layers of cations interspaced with layers of carbonate triangles. Pieces of whole rock were ground and then mixed with 5-10 wt% Au, which was used as an internal X-ray pressure calibrant [*Takemura and Dewaele*, 2008].

Two separate diamond anvil cell experiments were performed, each gas-loaded with Ne to ensure hydrostatic pressure and including a small ruby chip for cross-reference pressure measurement [*Rivers et al.*, 2008]. In a first experiment, the kutnohorite-Au mixture was pressed, sandwiched between NaCl chips and then placed in a 150 x 70 μm hole in a pre-indented rhenium gasket in a diamond anvil cell equipped with 500 μm culets. This sample was compressed at room temperature to 19 GPa in steps of 3-5 GPa (Figure 3-1). A second diamond anvil cell equipped with 300 μm culets was loaded with prepressed kutnohorite-Au mixture placed in an 80 x 50 μm gasket hole with no NaCl calibrant. A verification X-ray diffraction pattern was taken at 0.5 GPa before this sample was compressed to 35 GPa and then laser-heated with the double-sided fiber laser heating system [*Clark et al.*, 2012].

Angle-dispersive X-ray diffraction data was collected on a MAR345 image plate at an energy of 28 KeV (0.4428 $\text{\AA}$) at beamline 12.2.2 at the Advanced Light Source, Lawrence Berkeley National Laboratory. All diffraction patterns were integrated using GSAS II to display intensity versus two-theta angles [*Toby and Von Dreele*, 2013]. Up to 19 GPa kutnohorite, Au and NaCl were indexed and both Rietveld Refinement methods (GSAS) and Gaussian fits to each of the diffraction peaks were used to find extract pressure-volume information. Pressure was measured before and after each pressure step using ruby fluorescence, and determined from

an internal calibrant using the lattice volume of the Au determined by the X-ray patterns and fitting to the equation of state of Au [Takemura and Dewaele, 2008]. Pressure error values were propagated from the uncertainty in the refinement fit to the Au lattice parameters. The second loading of kutnohorite did not include the NaCl and the kutnohorite starting structure was confirmed with a diffraction pattern obtained at 0.5 GPa after gas loading but before compression and heating (Figure 3-1). The patterns collected above 35 GPa show a change in the structure, indicating a change from the initial rhombohedral structure. While the pressure of the transformation is similar to the dolomite III transformation observed in the Mg and Fe-bearing dolomites, it is not clear from our current diffraction patterns whether the structures are related.

3.3 Results and Discussion

Upon compression in the diamond cell, we find kutnohorite to be stable in the dolomite I structure to 19 GPa at ambient temperature (300 K). For each diffraction pattern the best-fit rhombohedral lattice parameters were determined from Gaussian fits of each indexed peak and by Reitveld refinement (Figure 3-2). Although the error bars are much greater for the individual Gaussian fits, the volume data extracted from each method is nearly indistinguishable. As illustrated in Table 3-1 and Figure 3-2, the large Gaussian fit volume error originates from an under constraint of lattice parameter c . The available peaks in our two-theta range constrained the lattice parameter a much better. The c/a ratio of kutnohorite at 0.3 GPa is 3.366, similar to 3.354 found by Graf [1961]. The ratio steadily decreases with increasing pressure, lowering to 3.105 at 20 GPa, which is consistent with a more compressible c axis.

As shown in Figure 3-2, the best-fit of the pressure-volume data to a 2nd order Birch-Murnaghan equation of state (with $K'_{T,0}$ fixed at 4) yields an isothermal bulk modulus of 85(6) GPa and a V_0 of 332(2). A 3rd order fit is also shown in Figure 2 that yields a bulk modulus of

110(1) GPa, $K' = 1.9(1)$ and V_0 of 329.3(1). This study does not include sufficient data points to merit the use of this higher order equation of state. A later ambient-pressure single-crystal measurement was performed on the same sample and confirmed the dolomite I structure with a unit cell volume of 230(1) Å³, which is consistent with our fitted results. These ambient volumes are within the previous range of literature values (330-336 Å³) that depend on disorder [Graf, 1961; Farkas *et al.*, 1988]. The powder diffraction result is likely the average of many differently disordered crystallites, which would account for the disparity between the single crystal and powder diffraction results. This bulk modulus found in the 2nd order equation of state fit is comparable to those of Fe dolomite-type end-member ankerite, 91 GPa, and dolomite, 94 GPa [Ross and Reeder, 1992].

The compressibility-volume systematics of Mg, Fe and Mn-dolomite can be directly compared with other rhombohedral carbonates such as calcite (CaCO₃). These rhombohedral carbonates have been previously investigated under pressure in some detail [Ross, 1997; Zhang *et al.*, 1997; Zhang and Reeder, 1999; Ono, 2007; Litasov *et al.*, 2013]. In the rhombohedral carbonates, the marginally distorted cation octahedra are corner-linked through shared oxygen anions of carbonate groups. These carbonate planar triangles are the most incompressible elements in the structure. Studies by Ross [1997] and Ross and Reeder [1992] illustrate that the M-O-M and M-O-C angles in magnesite, dolomite and ankerite have very little variation with pressure. This means bond bending is not a major process in the compression of the rhombohedral carbonates. The cation range of these carbonates encompasses divalent alkaline earth elements, 3d transition metals and 4d transition metals ranging in size from 0.69 to 1.0 Å. The dolomite structure is a double carbonate and thus combines at least two different cations from this list, with one always being Ca²⁺, in alternating cation layers. The composition of our

kutnohorite sample, $(\text{Ca}_{0.76}\text{Mn}_{0.24})\text{Mn}(\text{CO}_3)_2$, shows a significant excess of manganese, raising the possibility that it is not ordered like a standard dolomite, but perhaps mixes Ca and Mn between the two layers.

In kutnohorite the compressibility of the unit cell is controlled primarily by the behavior of the Ca and Mn octahedra since the carbonate planar triangles are essentially incompressible in this pressure regime. This leads to anisotropic compression in all of the rhombohedral carbonates as evidenced by a significantly more compressible c axis. A linear relationship is predicted between the bulk moduli and the ambient unit cell volume. Figure 3-3 shows this trend for the rhombohedral carbonates. The deviation of MgCO_3 and CdCO_3 from the linear trend is of note. The higher compressibility of MgCO_3 is attributed to substantially higher a -axis compressibility than found in the other rhombohedral carbonates of similar ambient volume (i.e. CoCO_3 and ZnCO_3) [Zhang and Reeder, 1999]. Indeed, Zhang and Reeder [1999] found a linear relationship between c -axis compressibility and M-O bond length for all cation types.

Our new kutnohorite data fit within the linear relationship described by the rhombohedral carbonates (Figure 3-3). The dolomites have higher volumes and lower bulk moduli, and fall on a trend line of $-0.60(20) \text{ GPa}/\text{\AA}^3$ while the calcite-type carbonates show a slope of $-0.61(3) \text{ GPa}/\text{\AA}^3$, excluding the magnesite and otavite (CdCO_3) data points. In addition, unit cell volumes increase as the cation changes from $\text{Mg} > \text{Fe} > \text{Mn}$, both in the single and double carbonate series, consistent with other transition metal systematics within mineral structures. Depending on the new bonding environment high pressure polymorphs of dolomite might be expected to follow this linear trend since the elastic behavior of the structure is rooted in the constituent polyhedral compressibility and size of the cation sites.

3.4 Implications for dolomite structures

This work provides new measurements of the isothermal bulk modulus of kutnohorite, which is found to be 85(6) GPa. This is the first instance of this bulk thermoelastic property of kutnohorite being reported in the literature and we find it in good agreement with other bulk moduli found for ankerite and dolomite. The similarity to the bulk moduli in other dolomite end members suggests that compositional variation in the dolomites does not affect structural evolution. We have also found that the Mn end member of dolomite undergoes a change at high pressure (35 GPa) and temperature that may be in accordance with previous work done on Fe-bearing dolomites by *Mao et al.* [2011] and *Merlini et al.* [2012]. This finding has the important implication that dolomite may undergoes phase transitions regardless of composition and that these changes are perhaps inherent to the dolomite structure. In the unlikely case that a carbonate with dolomite stoichiometry is preserved in a cold subducting slab these results imply the dolomite will be stable at the P,T conditions of the lower mantle. Finally, we have highlighted the systematics of single and double rhombohedral carbonates. The compressional and structural characteristics of these minerals are linearly related for both single and double carbonates, implying that the compressibility of the constituent cation polyhedra governs the bulk compressibility of these rhombohedral carbonates. We hypothesize that the linear trend between compressibility and structure will continue in the high-pressure dolomite structures, but further study is needed to gain information on the structure and bulk thermoelastic properties of the high pressure forms of dolomite.

3.5 Summary

This study of kutnohorite was followed by a single crystal study at the European Synchrotron Radiation Facility in collaboration with Prof. Marco Merlini of the University of

Milan. The subsequent work validated the equation of state found during our powder diffraction study (Figure 3-4). Additionally the study illuminated the phase stability of kutnohorite, finding that it's stability is different from the Fe-rich dolomite I and II phases previously identified by both *Mao et al.* [2011] and *Merlini et al.* [2012]. Current work is underway to identify the new structure found in these single crystal experiments.

This study on the Mn-dolomite end member kutnohorite served to further elucidate the behavior of carbonate at high pressure. Although no evidence of a transformation from planar coordination to tetrahedral coordination was found in the kutnohorite sample, understanding the evolution of different end member of dolomite at high pressure does inform our knowledge of carbon in the deep earth. If carbonate did survive the subduction process, these dolomite phases might be stable structures to deep mantle pressures.

3.6 Tables

Table 3-1. Room temperature kutnohorite and Au unit cell parameters to 20 GPa from both GSAS refinements and Gaussian peak fitting. Note that the highest pressure refinement was not able to determine the kutnohorite parameters and thus the peak fitting data point is used in our analysis.

Kutnohorite fitted peaks			Kutnohorite GSAS refinement			Au GSAS refinement			R_{wp}
a	c	V	a	c	V	a	V	P	
4.834(25)	16.27(13)	329(5)	4.843(1)	16.239(4)	329.93(9)	4.0749(1)	67.663(7)	0.46409(2)	0.0746
4.854(24)	16.21(18)	330(4)	4.8524(9)	16.173(4)	329.81(6)	4.0735(3)	67.594(17)	0.63728(2)	0.0456
4.799(30)	15.64(16)	312(5)	4.8161(15)	15.691(6)	315.20(15)	4.0399(5)	65.939(22)	5.1245(14)	0.0591
4.77(2)	15.40(13)	303(4)	4.7704(7)	15.404(5)	303.58(9)	4.0118(2)	64.569(13)	9.3701(16)	0.0777
4.751(24)	15.19(18)	297(5)	4.761(3)	15.176(20)	297.94(35)	3.9990(7)	63.965(32)	11.413(5)	0.0639
4.737(21)	14.98(22)	291(5)	4.751(3)	14.957(14)	292.47(20)	3.9744(3)	62.741(15)	15.905(3)	0.0549
4.712(27)	14.63(17)	281(5)	^a	^a	^a	3.9562(3)	61.922(17)	19.197(5)	0.0834

^a The highest pressure refinement was not able to determine the kutnohorite parameters and thus the peak fitting data point is used in our analysis.

3.7 Figures

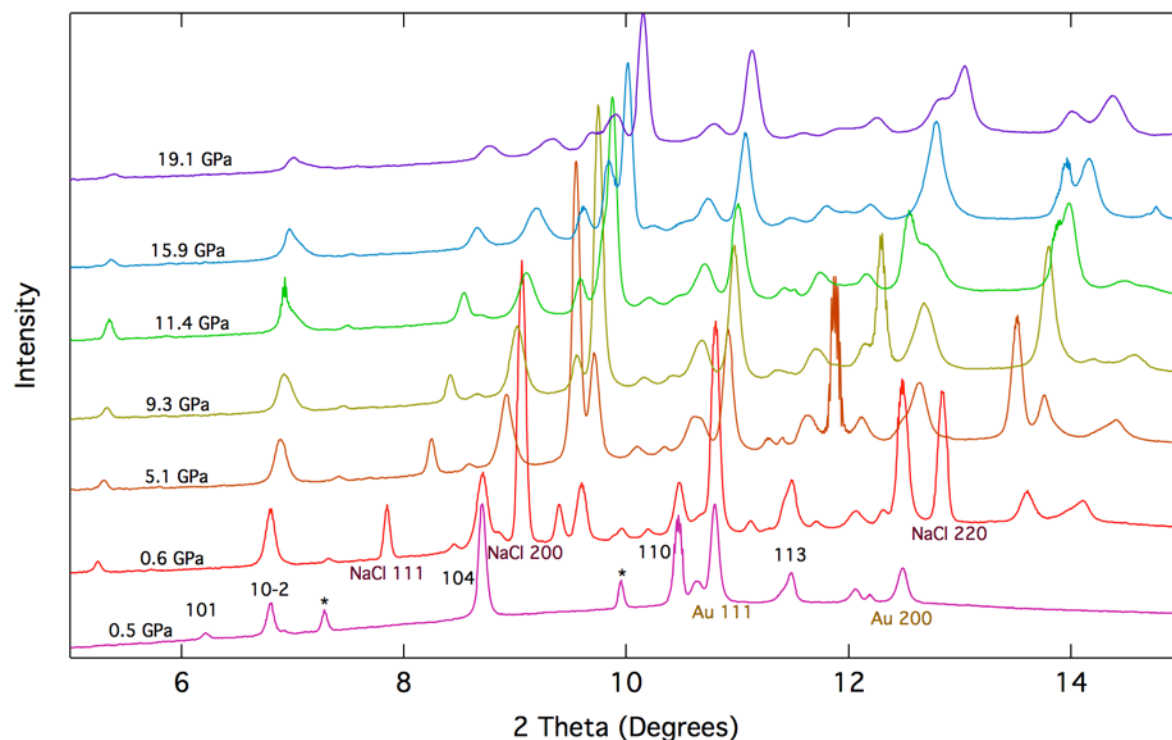


Figure 3-1. Diffraction patterns of kutnohorite to 19 GPa. Bottom pattern shows Au mixture used in the second high pressure experiments at 0.5 GPa before compression and heating. Other patterns were loaded with Au mixture and sandwiched between NaCl flakes. Rhombohedral kutnohorite is present to 20 GPa. The starred peaks represent an unidentified cubic phase.

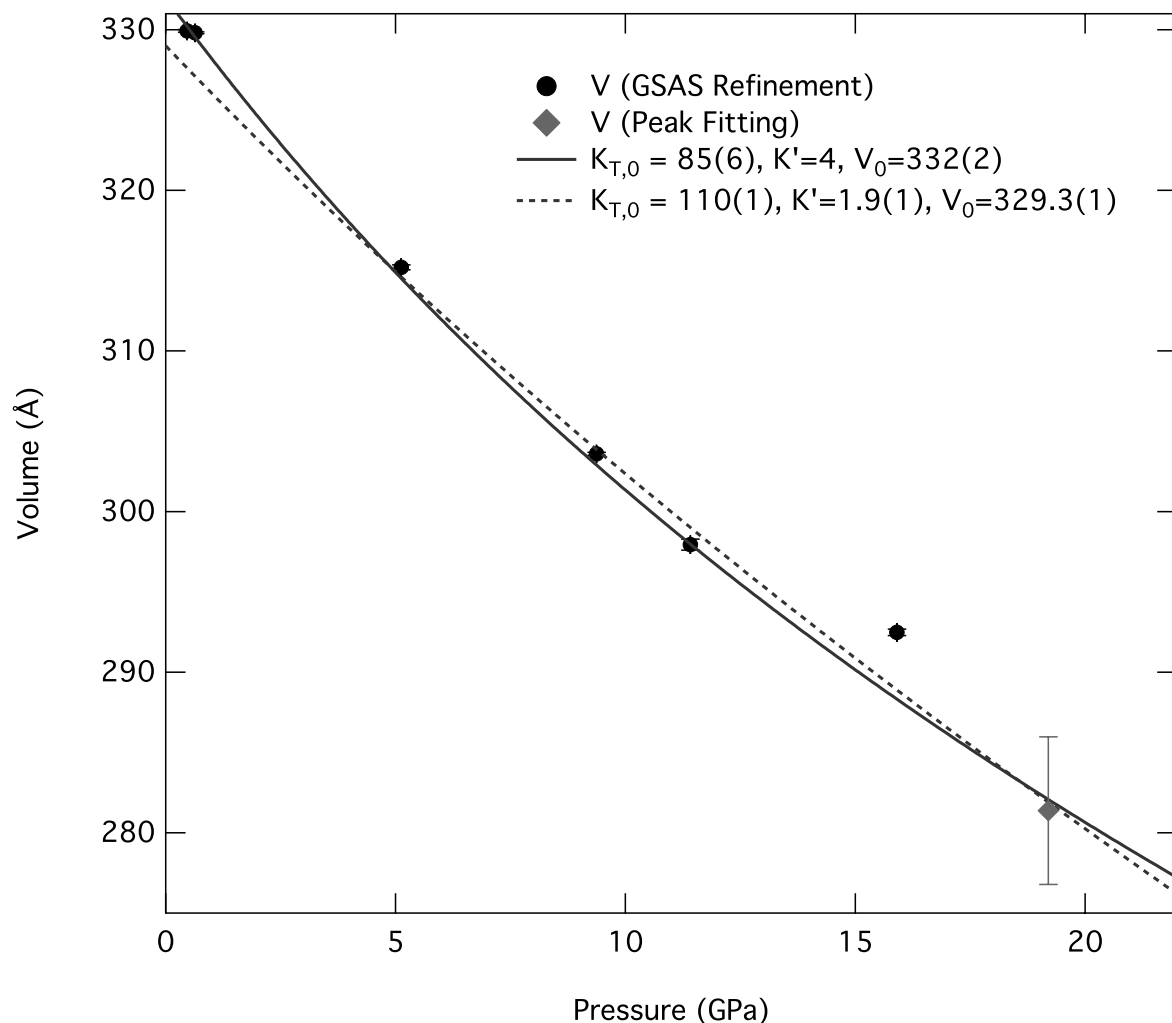


Figure 3-2. The unit cell volume of kutnohorite as a function of pressure as determined by both Rietveld Refinement (dark circles) and Gaussian peak fitting (final diamond point). Volume error bars for the Gaussian fit point reflect that the indexed peaks better constrain unit cell parameter a than c . For our equation of state fitting we used the refinement results except at the highest pressure where no refinement was possible and we used the Gaussian peak fitting result (19.2 GPa data point). Equation of state fit to the kutnohorite pressure-volume data as determined from both a 2nd and 3rd order Birch Murnaghan equation of state are shown.

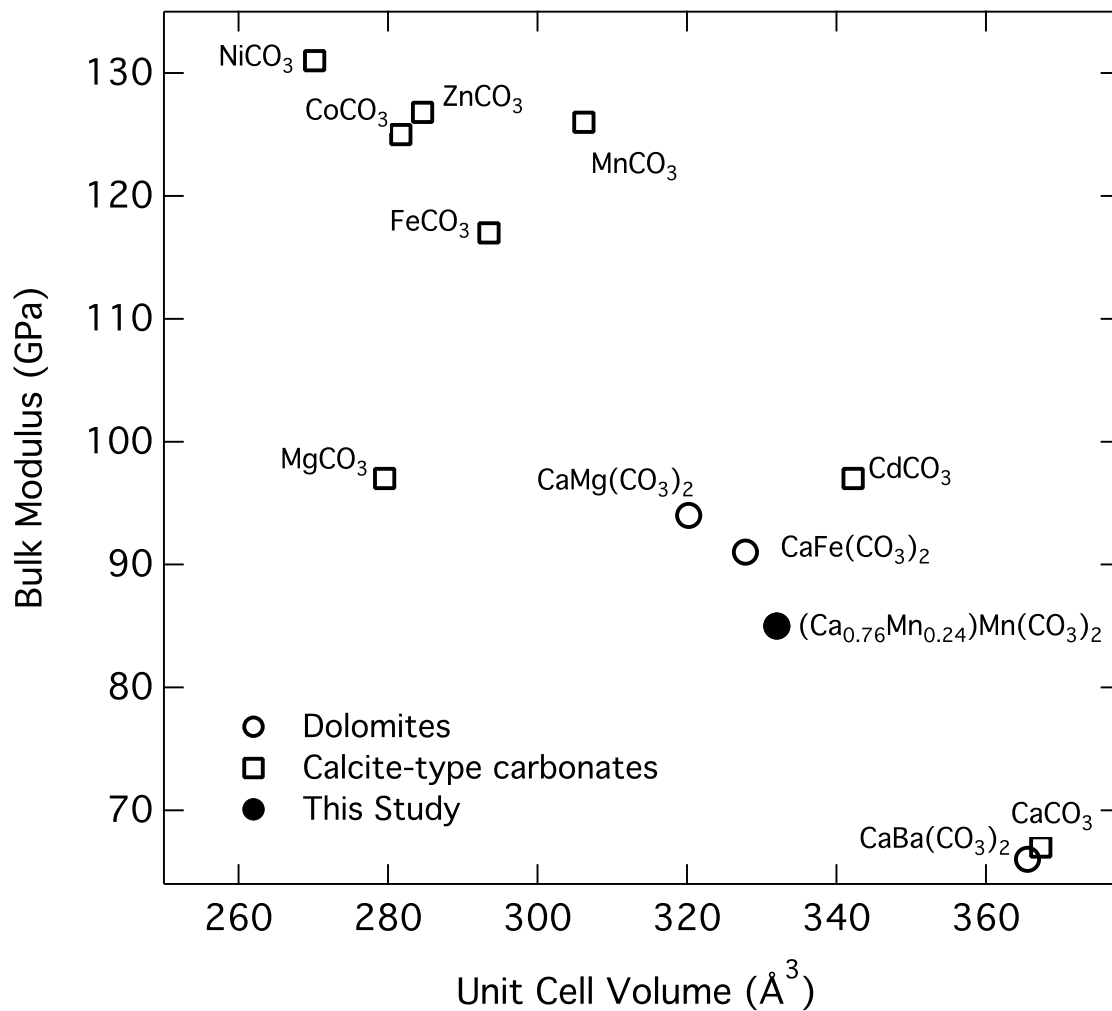


Figure 3-3. Calcite-type carbonate data and dolomite data examining the relationship between bulk modulus (GPa) and ambient unit cell volume ($\text{\AA}^3$). The dolomites fall on a trend line of $-0.6(2) \text{ GPa}/\text{\AA}^3$ while the calcite-type carbonates exhibit a slope of $-0.61(3) \text{ GPa}/\text{\AA}^3$.

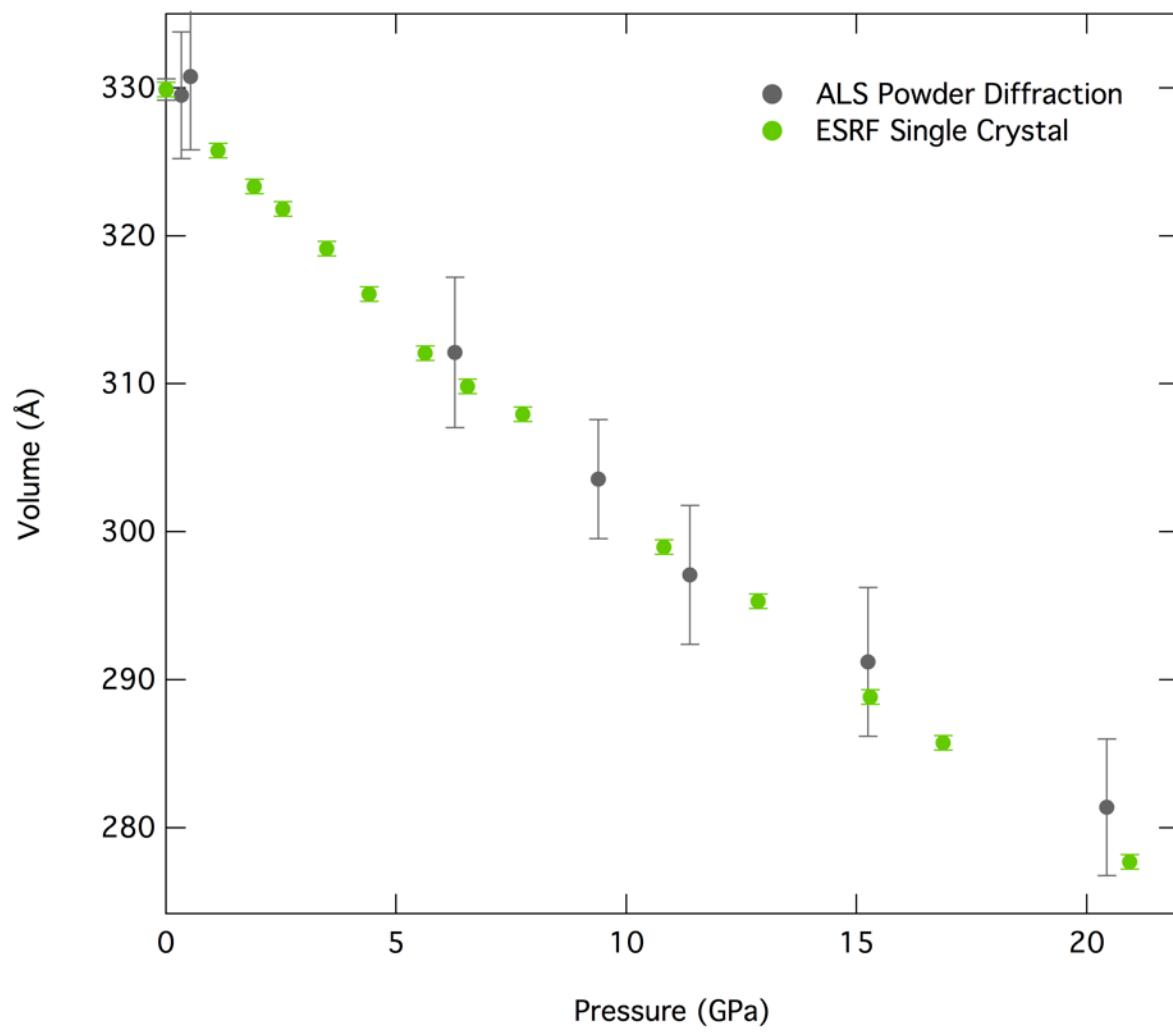


Figure 3-4. Single crystal X-ray diffraction data from ESRF overlaid on the kutnohorite data examined in Chapter 3.

3.8 References

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Chapter 4: High-Pressure Compressibility and Thermal Expansion of Aragonite

4.1 Introduction

Carbon in the deep Earth consists of a primordial component plus carbonate that has recycled into the Earth's mantle via subduction zones [Dasgupta and Hirschmann, 2010; Kelemen and Manning, 2015]. In the solid state, carbon has limited solubility in mantle silicates and therefore resides chiefly in carbon-rich accessory phases, either as oxidized carbonate or reduced graphite, diamond, or carbide [Shcheka, et al., 2006]. Aragonite is one of the two most common forms of calcium carbonate found at the Earth's surface and is formed by both biological and physical processes. Although aragonite is metastable at ambient conditions at the surface of the Earth, its biological formation and contribution to ocean floor deposits and high-pressure stability make it the predominant form of calcium carbonate contributing to deep-Earth recycling at subduction zones. Therefore, understanding the phase stability and compressibility of aragonite at high pressures and temperatures will help constrain the behavior of a key potential carbon reservoir in the deep carbon cycle.

At ambient conditions, aragonite has an orthorhombic $2/m\ 2/m\ 2/m$ structure and an average unit cell volume of $226.93(6)\ \text{\AA}^3$ and a Z of 4 (Figure 4-1) [Martinez et al., 1996; Santillán and Williams, 2004; Ono et al., 2005; Antao et al., 2010; Ye et al., 2012]. Aragonite becomes stable relative to calcite at ~ 0.3 GPa (e.g., Johannes and Puhan [1971]); however, the pressure of its transformation to a higher pressure (post-aragonite) phase is the subject of debate [Vizgirda and Ahrens, 1982; Kraft et al., 1991; Santillán and Williams, 2004; Ono, 2005; Martinez et al., 1996; Liu et al., 2005]. Early shock compression experiments suggested that aragonite undergoes a phase transition around 6 GPa with the possibility of another transition at ~ 16 GPa [Vizgirda and Ahrens, 1982]. However, subsequent vibrational spectroscopy experiments found no sign of these phase transitions to 40 GPa [Kraft et al., 1991]. X-ray

diffraction studies by *Santillán and Williams* [2004] and *Ono et al.* [2005] indicated a phase transition near 35-40 GPa but found differing behavior near the transition pressure. *Santillán and Williams* [2004] noted that strong lattice strain developed between 26 and 40 GPa and suggested that it marked the onset a sluggish transition to a trigonal structure that became complete at 40 GPa. In contrast, *Ono et al.* [2005] proposed that the transition was a new orthorhombic structure with $Z = 2$. Studies of high pressure CaCO_3 by *ab initio* methods focused chiefly on the transition to post-aragonite and pyroxene-type polymorphs [*Oganov et al.* 2006, 2008; *Arapan et al.* 2007; *Arapan and Ahuja*, 2010; *Pickard and Needs*, 2015] but in some cases results identify additional potentially stable structures in the vicinity of the aragonite to post-aragonite transition (e.g., *Pickard and Needs* [2015]).

Insights into the nature and location of the transition to a higher pressure phase can be gained by study of the compressional behavior of aragonite. However, existing X-ray diffraction studies [*Martinez et al.*, 1996; *Santillán and Williams*, 2004; *Ono et al.*, 2005] disagree and lack sufficient detail in the pressure range of the transition.

To address these issues, we conducted a single-crystal synchrotron X-ray diffraction study of aragonite under hydrostatic compression to 40 GPa at ambient temperature in a diamond anvil cell (DAC). We supplemented compressional results with thermal expansion data from powder X-ray diffraction at ambient pressure. The combination of these studies enables the creation of a complete thermoelastic equation of state for aragonite and provides detailed insights into the polyhedral and atomic distortions that accompany compression in the vicinity of the high pressure breakdown of aragonite.

4.2 Experimental Methods

The starting sample of aragonite was a natural specimen from Spain (Molina de Aragon) with a pure composition of CaCO_3 , within experimental accuracy as determined by electron microprobe analysis (University of Milano, Italy). We performed high-pressure single-crystal experiments at the undulator source ID09A beamline at the ESRF, Grenoble, France, following established procedures [Merlini and Hanfland, 2013]. The optical features of the beamline provide a near-parallel collimated X-ray beam of approximately $15 \times 10 \text{ microns}^2$ on the sample. The sample was loaded in a Ne pressure transmitting medium in a membrane-type diamond anvil cell of Boehler-Almax design equipped with $300 \text{ }\mu\text{m}$ culet size diamonds and opening windows of 60 degrees. Pressure was determined using ruby fluorescence [Mao *et al.*, 1986]. The DAC was mounted on a Omega-rotation goniometer, and single-crystal data were collected by integrated step-scans of 1 degree, in the 60 degree rotation range allowed by the geometry of the DAC. The diffraction patterns were recorded with the Mar555 flat panel detector, at a distance of 300 mm from the sample. Aragonite was compressed continuously from ambient pressure to 40 GPa in steps of 1-2 GPa to provide good statistics for equation of state fitting (Table 4-1). The data were processed with the CrysAlis software [Oxford Diffraction, 2008]. The instrumental geometrical parameters (sample to detector distance, beam center and detector tilt) were refined with a garnet standard single crystal. The refinement of crystal orientation matrix provided aragonite lattice parameters at variable pressures. The integrated intensity was used for structure refinement, using the software packages Superflip [Palatinus and Chapuis, 2007] and Jana2006 [Petricek *et al.*, 2006].

Ambient-pressure thermal expansion measurements were collected on the same natural aragonite sample. Powder diffraction data were collected using a wavelength of $0.689264 \text{ }\text{\AA}$ at

the MCX beamline at the Elettra synchrotron using previously described techniques (Rebuffi et al. 2014). Powdered aragonite was enclosed in a quartz capillary and mixed with quartz as internal standard. A hot glass blower maintained high temperature and measurements were performed in the temperature interval 298-700 K (Table 4-2). The temperature precision is estimated using the α - β quartz high temperature transition to be within $\pm 2^\circ\text{C}$. The diffraction patterns were analyzed using the Rietveld method and the GSAS software. The extracted unit cell volumes were used to fit a simple linear thermal expansion model [Fei, 1995; Angel et al., 2014].

4.3 Results

4.3.1 Phase stability and lattice compressibility

Single-crystal measurements at ambient pressure and temperature confirm the orthorhombic Pnma space group of aragonite and yield a unit cell volume of $226.932(5) \text{ \AA}^3$. Figure 4-2 shows the aragonite lattice compression to 36 GPa at ambient temperature. The data indicate a decrease in cell volume of $\sim 25\%$ over this pressure range. Below ~ 10 GPa, our results are in good agreement with powder X-ray diffraction studies that used cubic anvil [Martinez et al., 1996] and diamond-anvil cells [Ono et al., 2005; Santillán and Williams, 2004]. At higher pressures, the new data agree well with those of Martinez et al. [1996] and Ono et al. [2005], but differ from the Santillán and Williams [2004] data. The deviation of the volumes determined by Santillán and Williams [2004] above 10 GPa likely resulted from freezing of the methanol-ethanol mixture they used as a pressure medium, resulting in non-hydrostaticity in their diamond-cell experiments. Ono et al. [2005] addressed this problem by laser heating their aragonite sample in a DAC to reduce differential pressure effects in the sample chamber and to overcome kinetic inhibition of any phase transitions. Data were collected at ambient temperature

after cooling. Their data agree with our results to 27 GPa. The next pressure at which *Ono et al.* [2005] obtained data was 35 GPa, where they identified a large decrease in volume which they interpret to be due to transformation to post-aragonite structure.

The data were fitted to a 3rd order Birch-Murnaghan equation of state using a linear least-squares fitting method with V_0 fixed at 226.932(5) Å³, the ambient pressure measurement. Data at >31.5 GPa begin to depart from the Birch-Murnaghan functional form, perhaps due to lattice distortion signaling the onset of the phase transition. To ensure exclusion of data compromised by lattice distortion, only results from ≤ 31.5 GPa were used to derive the isothermal equation of state. This yields an isothermal bulk modulus of aragonite of 66.5(7) GPa with $K' = 5.0(1)$. The values agree well with previous values from X-ray diffraction [*Martinez et al.*, 1996; *Ono et al.*, 2005] and Brillouin scattering [*Liu et al.*, 2005] experiments, in which derived bulk moduli were respectively 64.8, 73(2) and 68.9(14) GPa ($K' = 4$). *Ono et al.* [2005] also fitted K' , obtaining a bulk modulus of 67(6) GPa and $K' = 4.7(8)$, again in excellent agreement with our result.

The compressibility of the lattice parameters of aragonite provides insight into the lattice-dependent elasticity, the mechanism of compressibility, and the onset of phase transformations. The pressure evolution of the normalized values of the a , b , and c lattice parameters of aragonite is shown in Figure 4-3. The lattice compressibilities were determined by fitting a 3rd order Birch-Murnaghan equation to the cubed lattice parameters as a function of pressure. The a -axis is most compressible, with a bulk modulus of 46.0(5) GPa and $K'=2.93(5)$. The c -axis is the least compressible with $K = 122(2)$ GPa and $K'=5.6(3)$. The b -axis displays a change in compressibility at ~15 GPa. Below this pressure, the fit to the data yields a bulk modulus of 59(2) GPa with $K'=11.4(7)$. In contrast, at >15 GPa the pressure dependence flattens, indicating a stiffening of the b -axis. Although the relative compressibilities of each lattice parameter follow

trends similar to those determined by *Santillán and Williams* [2004] and *Martinez et al.* [1996], our values disagree in detail. *Martinez et al.* [1996] found both the b and c axes to be more compressible to their highest pressure of 7 GPa. The small pressure range of their experiment limits the accuracy of their results when applied to higher pressure data such as our own. We interpret the difference between our measured compressibilities and the apparent lower compressibility inferred from the *Santillán and Williams* [2004] data as arising from non-hydrostatic pressure in their sample chamber above 10 GPa.

4.3.2 Axial ratios and polyhedral evolution

Figure 4 shows the c/a , b/a and b/c axial ratios as a function of pressure. These plots demonstrate significant mechanical distortion of the aragonite unit cell volume with compression. The c/a and b/a ratios increase continuously as pressure rises. The c/a and b/c ratios of *Martinez et al.* [1996] agree reasonably well with our data to 7 GPa, the highest pressure in their study. Our results also agree with those of *Santillán and Williams* [2004] below 10 GPa; however, their data become scattered at higher pressures where their cell lost hydrostaticity. The new, more densely spaced measurements reveal that the change in c/a ratio on compression is slightly nonlinear (Figure 4-4a). The curvature indicates that the a -axis increases in compressibility relative to the c -axis, which is the least compressible axis (Figure 4-3). The change in the ratio above 29.1 GPa (dashed black line in Figure 4-4a) indicates a large increase in the compressibility of the a -axis relative to the c -axis. The b/a ratio is linear throughout its pressure range. A dramatic shift occurs at ~30 GPa where the b -axis becomes significantly less compressible than the a -axis (Figure 4-4b). The large change in slope arises from commensurate increase in a -axis compressibility and decrease in b -axis compressibility above 30 GPa.

The b/c ratio (Figure 4-4c) decreases to a minimum at ~15 GPa and then increases slightly to ~30 GPa. The b/c ratio rises dramatically above this pressure. This behavior is confirmed (as well as the patterns in Figs. 4a and 4b) by an additional dataset taken at high pressure and included in this study as Figure 4-11. Data from *Martinez et al.* [1996] and *Santillán and Williams* [2004] show a similar trend to ~10 GPa, as with c/a and b/a , the data of *Santillán and Williams* [2004] deviate at higher pressure. As with the b/a ratio, the change in slope in b/c at ~30 GPa is an indication of severe stiffening of the b -axis (Figure 4-3). *Santillán and Williams* [2004] noted that when the b/c ratio reaches 1.73 the orthorhombic symmetry degenerates to trigonal symmetry. *Santillán and Williams* [2004] found this to occur at 40 GPa and our data support evolution toward this value due to the stiffening of the b -axis. Subsequent work by *Ono et al.* [2005] and [2007] indicate that the post-aragonite phase is orthorhombic and that the transition pressure is lower than that expected for the breakdown to trigonal symmetry. We are likely seeing evidence for structural distortions at or near conditions of aragonite breakdown as the axial ratios diverge abruptly from their previous trends.

The compressibility of the axes is directly related to the orientation and compressibility of the constituent polyhedra. The plane created by the b and c axes is parallel to the carbonate groups in the aragonite structure, whereas the a -axis is perpendicular to them (Figure 4-5). The high compressibility of the a -axis results from the orientation the relatively rigid carbonate groups, which give no support to compression along the a -axis (*Ross and Reeder*, 1992). Accordingly, compression is accommodated by geometric changes in the Ca-O polyhedra. The average compression of the Ca-O polyhedra below 31.5 GPa, as fit to the 3rd order Birch-Murnaghan equation of state, gives a bulk modulus of 62(2) GPa with $K'=7.1(5)$. This is within

error of the compressibility of the b -axis below 15 GPa and is likely the initial driving force of its compression.

Unlike the Ca-O polyhedra, the carbonate groups are relatively incompressible at these pressures (though they do exhibit small but significant distortions; see below). At ambient pressure and temperature, the distance between triangular carbonate groups is 2.881(13) Å along the a -axis, 4.949(5) Å along the c -axis and 7.942(15) Å along the b -axis. The change in these separations with pressure is a good indicator of the compressibilities of the axes with which they are aligned. Figure 4-5 compares the aragonite unit cell at ambient pressure and at 32.9 GPa. The carbon and O2 atoms lie along the b -axis and the base of the carbonate triangle lies along the c -axis. A decrease in the end-to-end separation of the relatively rigid carbonate triangles and the alignment of the triangle base with the c -axis account for its lower compressibility. The increasing compressibility of the a -axis is due in part to the small tilting of the carbonate groups, identifiable by the O2 atoms dipping out of the b - c plane toward the a -axis.

Figure 4-6 compares the ratio of the distances between the carbonate groups along the c and b axes to the b/c ratio (Figure 4-4c). The nearly identical dependence on pressure suggests that the intercarbonate distances control the changes in b/c axial ratio. Study of the carbonate-carbonate distances identifies two dips in b/c at ≥ 30 GPa. These dips may be caused by the effects of the distortion of the carbonate groups on the lattice parameters and intracellular dynamics (discussed further in the next section). Measurements of the carbonate separation distance indicate that the b -axis becomes less compressible starting at ~ 15 GPa and that it becomes stiffer than the c -axis between 25-30 GPa. This is consistent with an upcoming phase transition between 30 and 40 GPa, as found experimentally by *Santillán and Williams* [2004] and *Ono et al.* [2005], and predicted by ab initio studies [*Oganov et al.*, 2006; *Arapan and Ahuja*,

2010; *Pickard and Needs*, 2015]. The post-aragonite structure found by *Ono et al.* [2005] has a lower Z (2, not 4) and its b -axis is $\sim 40\%$ shorter with respect to the a and c -axes than that found in the ambient orthorhombic aragonite structure. This reduction in the relative b -axis length is smaller than the 50% decrease in formula unit (Z) and indicates that the b -axis remains stiff in the new structure. Experimental work on the lattice geometry of post-aragonite is needed to confirm this conclusion.

4.3.3 Atomic evolution and polyhedral distortion

The evolution with pressure of the atomic positions in the unit cell is shown in Figure 4-7. The carbon atoms at the center of the carbonate groups move with the O1 atomic position in both a and c axial directions. With compression, the carbon and O1 positions show little movement and no correlation along the b -axis, which is consistent with their nearly perpendicular alignment in this direction (Figure 4-5). The Ca atomic position moves linearly in each axial direction and undergoes only a minor shift in position, consistent with the oxygen atoms compressing around a relatively stationary Ca atom. The O2 atomic position remains fairly constant in its position along the c -axis, but undergoes notable changes in the other two atomic planes. This observation is consistent with large compressional displacement along the a -axis as the stacked carbonate groups move closer together and tilt and with the changing compressibility of the c -axis. Along the a -axis, the O2 position increases with respect to its original position to ~ 25 GPa, and then dips back toward its original coordinate at 25-30 GPa, the same pressure range as the dip in $\text{CO}_3\text{-CO}_3$ distance along the b -axis (Figure 4-6). Similar behavior is seen in the b -axis where the O2 position initially has a negative linear trend compared to its initial position that becomes a reversal near 25 GPa, much like the behavior seen in the b/c axial ratio in Figure 4-4c and the evolution of the carbonate spacing ratio in Figure 4-6.

These shifts bring the O2 position out of initial alignment with both carbon and calcium atoms as can be seen in the *b-c* plane slices at 0 and 32.9 GPa in Figure 4-5. Figure 4-5 shows that the central carbon atom in both carbonate groups displaces to left during pressure increase, creating a distortion of the CO₃ triangles in the *b-c* plane. In addition, the O2 atoms dip into *a*-axis as the carbonate planar groups tilt slightly into the *b-c* plane with the O2 arrow side tilting down.

The carbonate groups undergo small but important changes in geometry. Figure 4-8 gives the evolution of the bonds (Fig. 8a) and angles (Fig. 8b) within the carbonate structure. Both the C-O1 and C-O2 bond lengths remain close to their ambient values at pressures ≤ 20 GPa. Above this pressure the C-O1 and C-O2 bond lengths diverge. The C-O2 bond continuously shortens between 20 GPa and 29.1 GPa; beyond this pressure the C-O bond length measurements became unreliable due to lattice distortion. The C-O1 bond length increases over the same pressure range, although at a less dramatic rate. The bond angles reflect the changing geometry demonstrated in the bond lengths. At ambient pressure, the carbonate groups define equilateral triangles, with both bond angles equal to 120°. Distortion begins almost immediately and the bond angles do not return to 120° as compression continues. The O1-C-O1 bond angle decreases while the two O1-C-O2 bond angles increase before relaxing slightly near ~ 20 GPa. This divergence occurs before any noticeable changes in bond length arise in the same pressure range (Figure 4-8a). Above ~ 20 GPa the two O1-C-O2 bond angles continually diverge from the O1-C-O1 angle and the two types end with a 10° difference in angle at 29.1 GPa.

These changes in the carbonate groups are visualized in the overlaid carbonate triangles in Figure 4-9. The groups clearly evolve from an equilateral to an isosceles triangle at high pressure. The tilt of the O2 atoms in the *a*-axis is apparent in Figure 4-9a and 4-9c, which also shows a small deflection of the O1-C-O1 stacking from linear. The stages of change in the

carbonate groups are in alignment with the changes observed in the b/c ratio. The decrease in bond length and divergence in angle are concurrent with the reversal in the b/c ratios in Figure 4-4c and 4-6. The increase in slope and significant reduction in the compressibility of the b -axis correlate directly with the divergence in both bond length and angle and the shift from equilateral to isosceles. Compression along the b -axis begins to stiffen as soon as the carbonate groups begin to distort affecting the overall lattice and leading the rebound in the b/c ratio. Effects on other lattice parameters are not apparent until near ~ 30 GPa when all the ratios under and abrupt change in slope (Figure 4-4).

The distance from the O2 atoms to the base of the triangular carbonate group decreases by 1.9% to 32.9 GPa while the b -axis itself compresses 6.2%. This difference is another illustration of how the distortion of the carbonate group contributes to increasing stiffness along the b -axis with pressure. The c -axis compresses evenly despite the bond angle between O1-C-O1 decreasing by 9° over the entire pressure range. The carbonate group O1-O1 distance decreases by 5.6% to 32.9 GPa, essentially the same as the c -axis at 5.2% compression over the same range. Thus, the compressional behavior of aragonite can be seen to be a consequence of small, but significant, changes in the most rigid polyhedral elements, the carbonate groups.

4.3.4 Thermal expansion

Figure 4-10 shows the ambient pressure thermal expansion data gathered during the powder X-ray diffraction experiment. The measurements are in good agreement with previous data from both *Antao et al.* [2010] and *Ye et al.* [2012]. The thermal expansion of aragonite was fitted using the formalism:

$$V(T) = V_0 \text{Exp} \left\{ \int_{T_{Ref}}^T \alpha_V(T) dT \right\} \quad (1)$$

$$\alpha_V(T) = a_0 + a_1(T) \quad (2)$$

Where $\alpha_v(T)$ is thermal expansion, a_0 and a_1 are fitted constants, V_0 is the ambient temperature volume, T is the temperature and T_{ref} is a reference temperature, usually 300 K. The fit of the new thermal expansion data provide the following coefficients: $a_0 = 4.9(2) \times 10^{-5}$ and $a_1 = 3.7(5) \times 10^{-8}$. These results are in agreement with recent measurements by *Ye et al.* [2012] yielding $a_0 = 4.6(2) \times 10^{-5}$ and $a_1 = 5.4(4) \times 10^{-8}$ (143-586 K), but conflict with other literature data [*Antao et al.*, 2010; *Martinez et al.*, 1996]. *Antao et al.* [2010] found $a_0 = 5.47(4) \times 10^{-5}$ and $a_1 = 6.1(2) \times 10^{-8}$ (300-750 K), which is 11% greater in a_0 and 64% larger in a_1 . Figure 10 indicates that the data from *Antao et al.* [2010] are in exceptional agreement with the new measurements, which implies that the discrepancy must be in the fitting process. All the experiments indicate that the a -axis exhibits the greatest thermal expansion, and the c -axis the least. The thermal results correlate well with the compressibility study. The a -axis is the most compressible and the most expandable. The c -axis is the least compressible and the least expandable.

4.4 Implications

This study has generated a new isothermal equation of state for aragonite up to 40 GPa, where aragonite likely undergoes a phase transformation. Our new equation of state agrees with previous hydrostatic data [*Ono et al.*, 2005; *Liu et al.*, 2005] and our observation of structural changes at high pressures agrees with previous observations [*Martinez et al.*, 1996; *Santillán and Williams*, 2004; *Ono et al.*, 2005], but the equation benefits from higher sampling density and improved precision in the present study. Our measurements also permit quantification of the evolution with pressure of the aragonite axial parameters and the internal behavior of the polyhedral constituents of the unit cell. Significantly, we have identified a reduction in the compressibility of the b -axis, which is directly linked to distortions of the carbonate groups and their change from equilateral to isosceles. The distortion of the carbonate groups through the

divergence of the C-O1 and C-O2 bond lengths is especially intriguing. Future study of such internal displacements in the carbonate group may give insight into its transformation into a 4-coordinated tetrahedral as predicted by *Oganov et al.* [2006], *Arapan et al.* [2007] and *Arapan and Ahuja* [2010] and experimentally observed in aragonite by *Ono et al.* [2007], in Fe-rich carbonates by *Boulard et al.* [2012], in ferromagnesite by *Boulard et al.* [2015] and in $\text{Mg}_2\text{Fe}_2\text{C}_4\text{O}_{13}$ by *Merlini et al.* [2015].

These results also provide insight into the distortion of the aragonite structure before the phase transition, which is both predicted [*Oganov et al.*, 2006; *Arapan and Ahuja*, 2010; *Pickard and Needs*, 2015] and observed between 30-40 GPa [*Santillán and Williams*, 2004; *Ono et al.*, 2005]. Using *ab initio* calculations *Pickard and Needs* [2015] predict a monoclinic $\text{P2}_1/\text{c}$ structure to be most stable between 32-48 GPa, which correlates directly with our abrupt change in axial ratios and the appearance of large lattice distortion above 29.1 GPa. Our data validate a transition in the range, but give no further insight in the exact structure adopted by Aragonite at these pressures. Indeed, this new structure does not exactly fit previous experimental data of post aragonite found by *Ono et al.* [2005], but there may be kinetic effects hindering the transition or discrepancies caused by the laser heating techniques used in the experimental study. Nevertheless, the aragonite data in this study provides significant insight into the behavior of aragonite and its constituent polyhedra as these transition pressures approach. Kinetic effects may explain why our data maintain the distorted aragonite structure to the highest pressure we could extract good data from, 34.8 GPa, instead of undergoing a transition. The diverging axial ratios and distortion of the lattice indicate that a transition may be taking place sooner than the 40 GPa pressure reported in previous studies.

Our thermal expansion data bolsters the database of aragonite's thermal expansion measurements and confirms the findings of previous studies [Ye *et al.*, 2012]. The combination of the new thermal expansion data with the equation of state generated in this work will provide an accurate thermoelastic equation of state. This thermal equation of state can be used to model planetary interiors and provide further insight into carbon storage within the deep earth.

4.5 Summary

The data found in this study provide definitive thermoelastic constants to be used in the modeling of planetary interiors, both relevant to the earth and extrasolar planets rich in carbon phases. The distortion of the carbonate groups seen in this study motivates further study of carbonate evolution in aragonite and other carbonate minerals. While the distortions we found were notable, the C-O bond length found at the top of the isosceles triangle is in the range of the C=O bond found in CO₂, ~1.16 Å, significantly shorter than expected for a single bond. Further study is needed to verify this result. Nevertheless, this study informs the importance of studying the evolution of not only the malleable polyhedra, but also the rigid ones, especially in search of the changing coordination of carbon.

The high resolution taken during the single crystal portion of this study emphasizes how important single crystal studies are to the field of mineral physics. The equation of state data generated by these experiments is a definitive basis for any modeling needing the thermoelastic properties of aragonite. In the larger picture of the deep carbon cycle, this study brings us one step closer to understanding the possibility structure and phase that carbon could be stored in the deep earth.

4.6 Tables

Table 4-1. Unit cell parameters of aragonite from ambient to 34.8(3) GPa.

Pressure	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Volume (Å ³)
0	5.741(4)	7.97(1)	4.959(5)	226.9(2)
0.570(1)	5.712(4)	7.942(2)	4.9491(8)	224.5(2)
1.2(1)	5.690(4)	7.922(2)	4.9433(6)	222.8(2)
2.28(9)	5.651(4)	7.886(2)	4.9276(7)	219.6(2)
2.96(7)	5.627(4)	7.865(2)	4.9192(7)	217.7(2)
3.8(2)	5.602(4)	7.846(3)	4.913(6)	215.9(2)
6.0(1)	5.533(4)	7.789(3)	4.8866(6)	210.6(2)
8.0(2)	5.474(4)	7.743(3)	4.8655(4)	206.2(2)
9.9(2)	5.429(4)	7.711(3)	4.8511(6)	203.1(2)
11.6(2)	5.383(4)	7.675(3)	4.8327(7)	199.6(2)
13.8(3)	5.339(4)	7.651(3)	4.8190(8)	196.9(2)
15.7(6)	5.287(4)	7.616(3)	4.7997(7)	193.2(2)
17.5(5)	5.257(4)	7.598(3)	4.7874(8)	191.2(2)
19.5(3)	5.216(4)	7.580(3)	4.7749(8)	188.8(2)
21.1(4)	5.184(4)	7.558(3)	4.7583(8)	186.4(2)
22.8(2)	5.153(4)	7.542(3)	4.7487(8)	184.5(2)
24.03(2)	5.130(4)	7.538(3)	4.7408(8)	183.3(2)
25.38(7)	5.117(4)	7.527(3)	4.7367(8)	182.4(2)
26.7(1)	5.09(4)	7.514(3)	4.7270(8)	180.9(2)
27.9(1)	5.076(4)	7.504(3)	4.7168(8)	179.6(2)
29.1(2)	5.058(4)	7.490(3)	4.7130(8)	178.5(2)
31.4(2)	5.026(4)	7.475(4)	4.6980(8)	176.5(2)
32.9(2)	4.986(2)	7.502(4)	4.687(4)	175.3(2)
34.8(3)	4.948(2)	7.507(4)	4.663(4)	173.2(2)

Table 4-2. Thermal expansion of aragonite unit cell parameters from ambient temperature to 673 K.

T (K)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Volume (Å³)
298	5.7457(2)	4.9638(2)	7.9728(3)	227.39(2)
303	5.7462(2)	4.9634(2)	7.9722(3)	227.37(2)
323	5.7501(2)	4.9644(2)	7.9748(3)	227.65(2)
348	5.7553(2)	4.9655(2)	7.9789(3)	228.02(2)
373	5.7603(2)	4.9671(2)	7.982(3)	228.38(2)
398	5.7661(2)	4.9676(2)	7.9858(3)	228.75(2)
423	5.7716(2)	4.9687(2)	7.9899(3)	229.13(2)
473	5.7822(2)	4.9711(2)	7.9961(3)	229.84(2)
523	5.7931(2)	4.9734(2)	8.0054(3)	230.65(2)
573	5.8035(2)	4.9754(2)	8.0151(3)	231.44(2)
623	5.8149(2)	4.978(2)	8.024(3)	232.27(2)
673	5.8279(2)	4.9794(2)	8.033(3)	233.11(2)

4.7 Figures

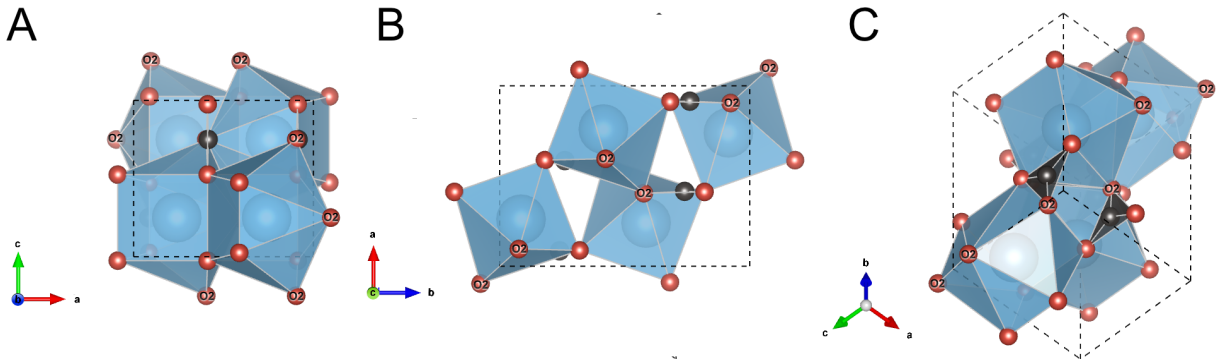


Figure 4-1. Structure of aragonite at ambient pressure and temperature. A. View along the *b*-axis; B. View along the *c*-axis; C. Slice through the *a*, *b* and *c* planes. Aragonite is comprised of two planes of triangular carbonate groups in opposite orientation with 9-coordinated Ca ions between the carbonate groups. Oxygen atoms are red, Ca atoms and polyhedra are blue and C atoms and triangles are grey. The oxygen atoms in the O2 position are marked accordingly in each orientation.

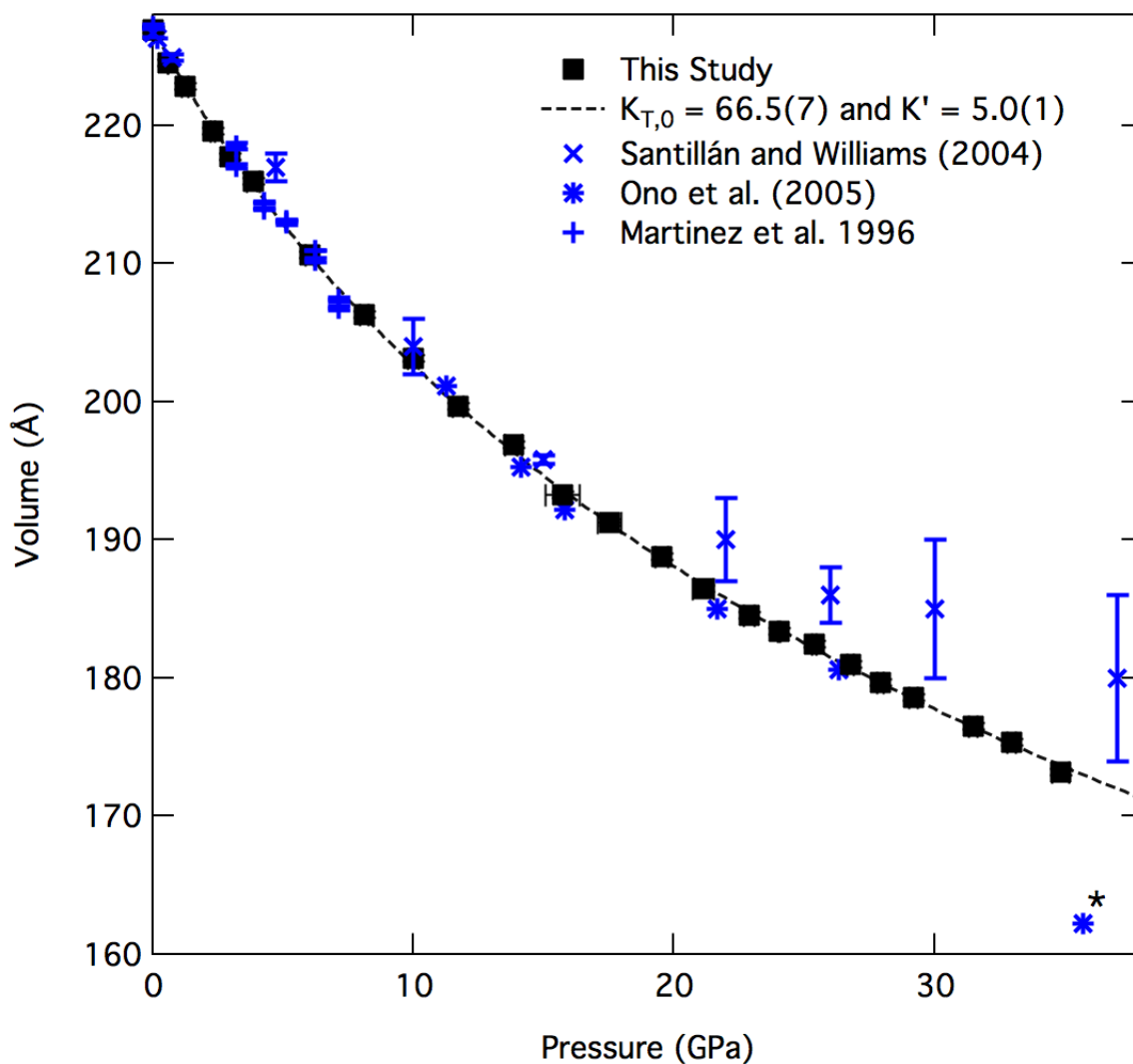


Figure 4-2. Aragonite unit cell volume versus pressure. Volume versus pressure data from this study and three previous investigations of aragonite. The dashed black line represents the fit of the data to the 3rd order Birch-Murnaghan equation of state. The starred point in *Ono et al.*'s [2005] data is a post-aragonite structure found after heating by the authors at 35 GPa.

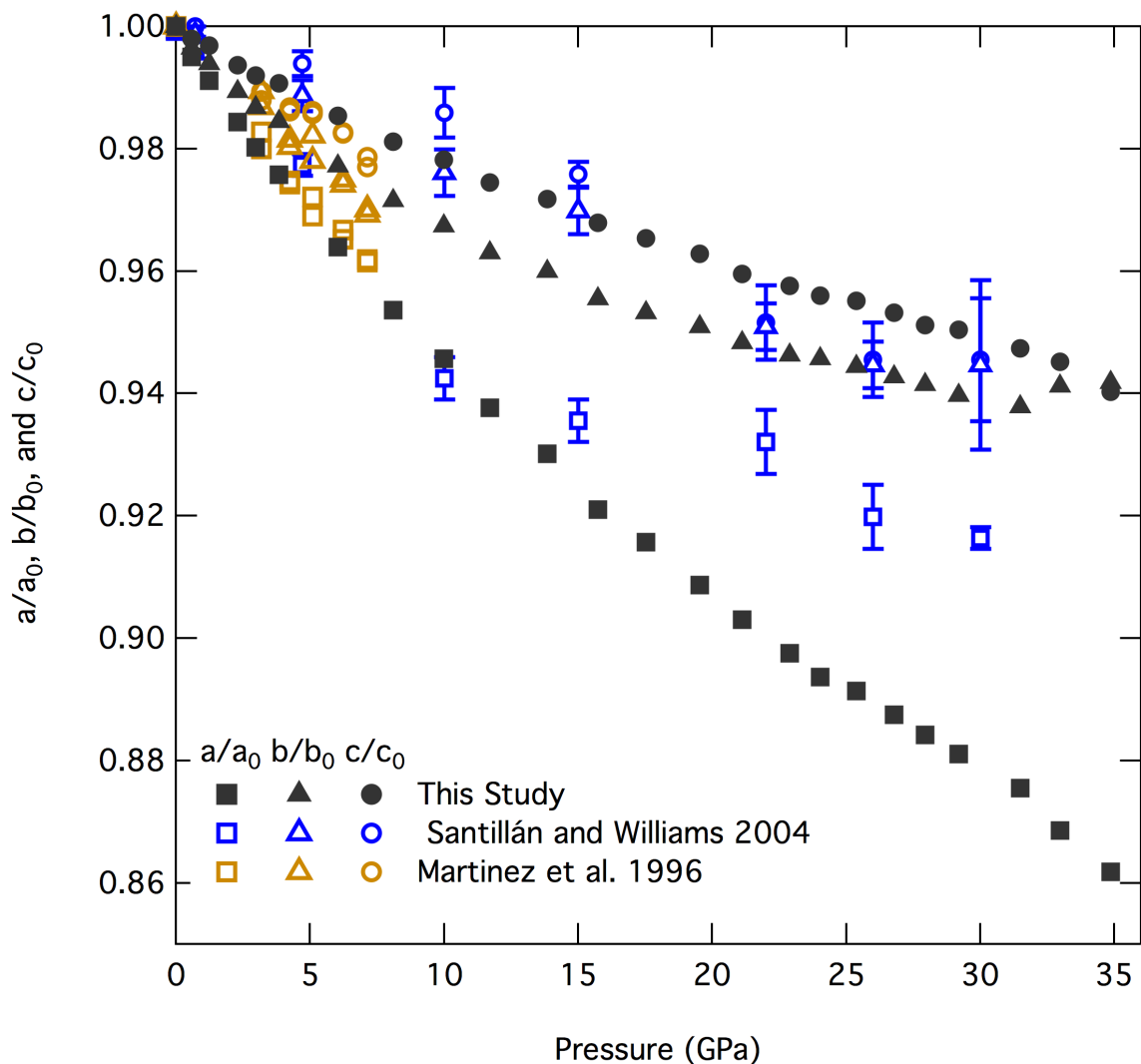


Figure 4-3. Compressibility of a , b , and c crystallographic axes of aragonite. The a -axis is the most compressible and the c -axis is the least compressible. The b -axis changes its compression behavior and begin to stiffen ~ 20 GPa. The data from *Santillán and Williams* [2004] is consistent to 10 GPa, which is the pressure at which their methanol:ethanol pressure medium freezes and becomes non-hydrostatic.

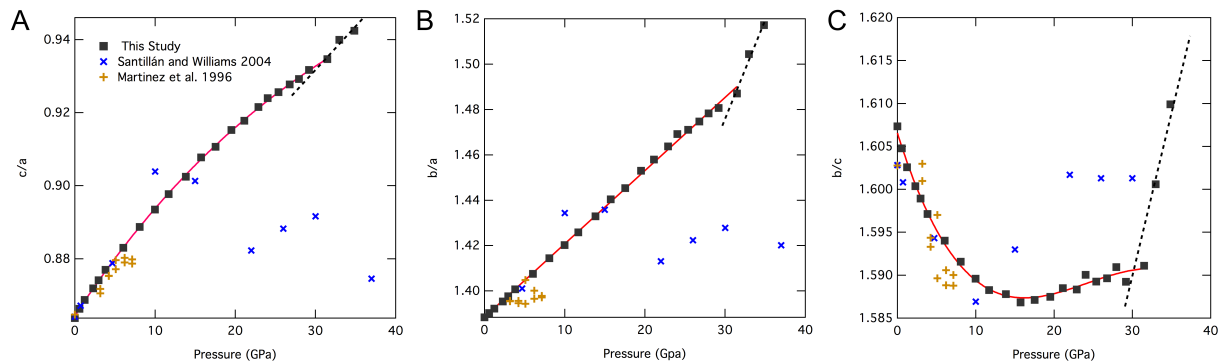
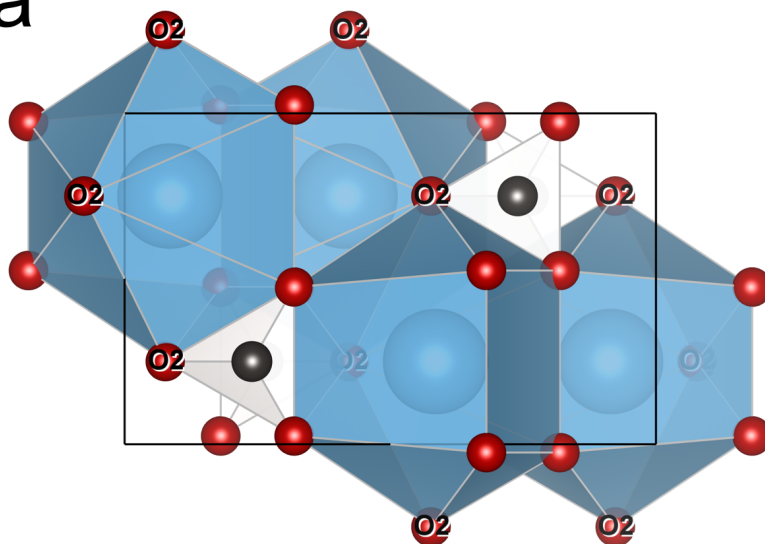


Figure 4-4. c/b (a), b/a (b) and b/c (c) ratios of aragonite. Data from two previous studies are included in all three figures. The c/b ratio in (a) maintains a constant trend (red line) until 30 GPa and then changes to steeper slope (dashed line). The b/a ratio is linear throughout. The ratio with constant slope to ~30 GPa (red line) before dramatically shifting to a steeper grade (dashed line). The b/c ratios declines steadily to 15 GPa and begins to bottom out, remaining nearly constant to 30 GPa (red line) where it shoots up in a linear trend (dashed line). Each of these changes are consistent with the stiffening of the b -axis relative to the a and c axes.

0 GPa



32.9 GPa

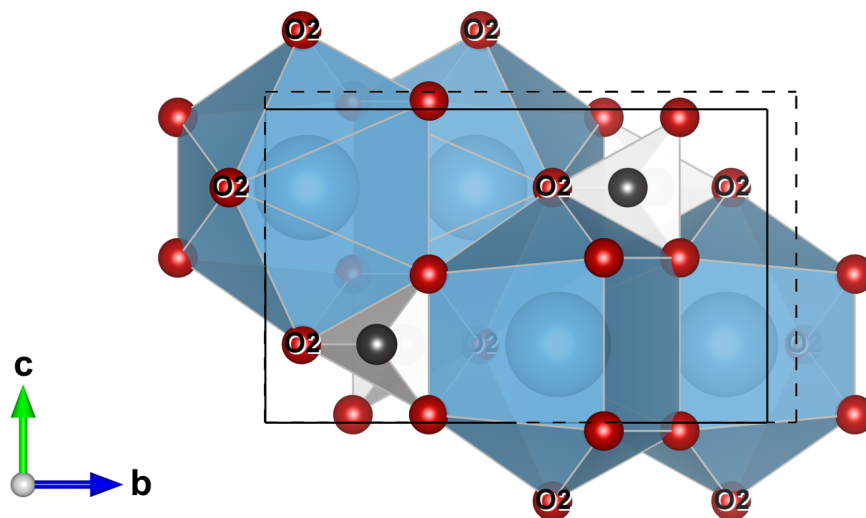


Figure 4-5. Unit cell comparison at ambient and 32.9 GPa. Shows slice through the a-axis, with the c-axis in the vertical and b-axis in the horizontal. Oxygen atoms are red, carbon are black and Ca are light blue. The carbonate groups are white. The ambient pressure unit cell is overlaid (dashed rectangle) over the unit cell at 32.9 GPa to emphasize the changes in both the b and c axes.

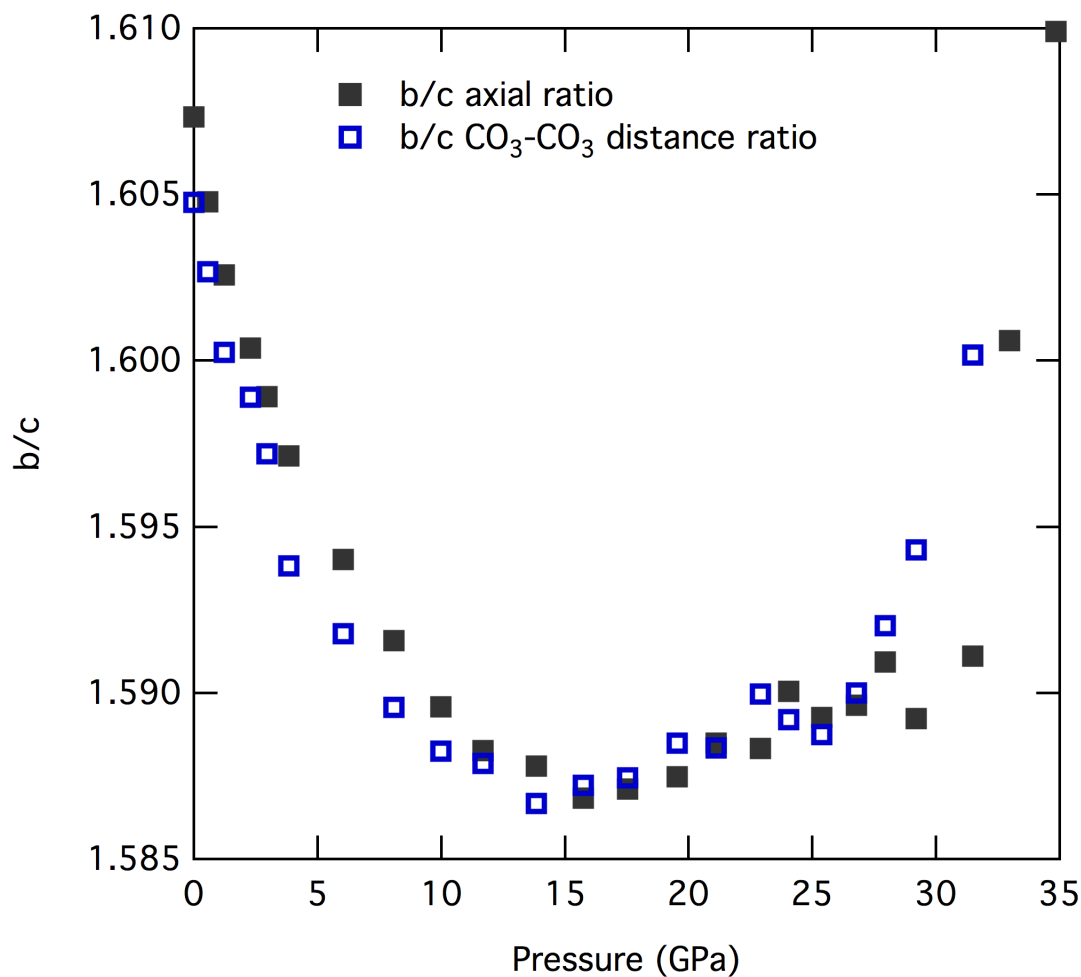


Figure 4-6. b/c ratio from unit cell parameters and $\text{CO}_3\text{-CO}_3$ distances. The solid black squares are the same as those found in Figure 4c. The open blue squares give the ratio of the distance between carbonate groups along the b -axis and carbonate groups along the c -axis (best visualized in Figure 4-5). The ratio of the inter-carbonate distances is nearly identical to that of the unit cell parameters and follows the decreasing trend followed by a change in slope at 30 GPa, which is consistent with the distance between carbonate groups along the b -axis ceasing to decrease after ~20 GPa due to the elongation of the carbonate triangles along the b -axis.

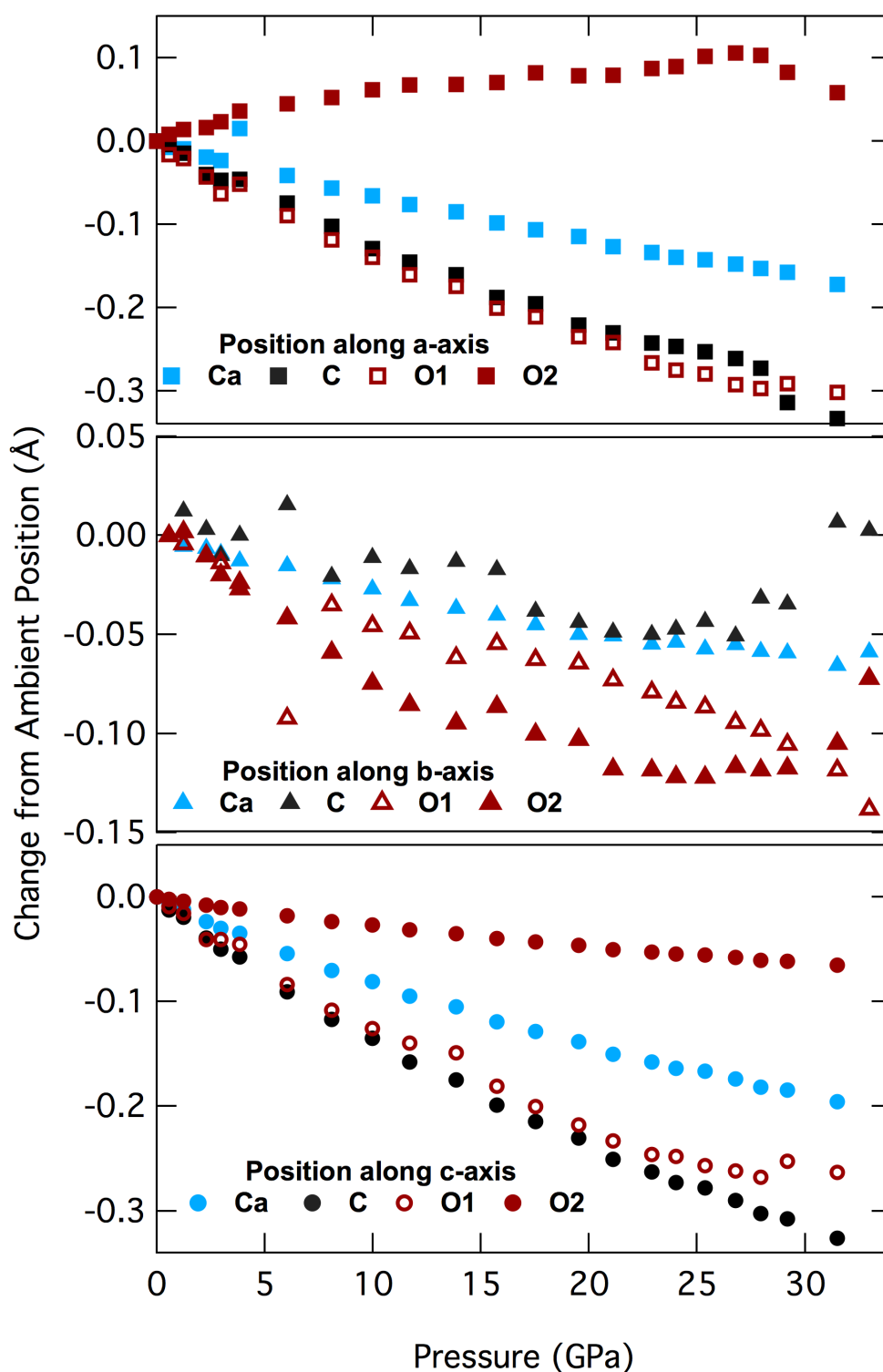


Figure 4-7. Pressure-dependent atomic positions. From the single crystal refinement data the evolution of the atomic sites is plotted as a function of pressure in the *a*, *b* and *c* orientations. Positions are plotted as distance from original position in Angstroms, normalized for contracting unit cell volume.

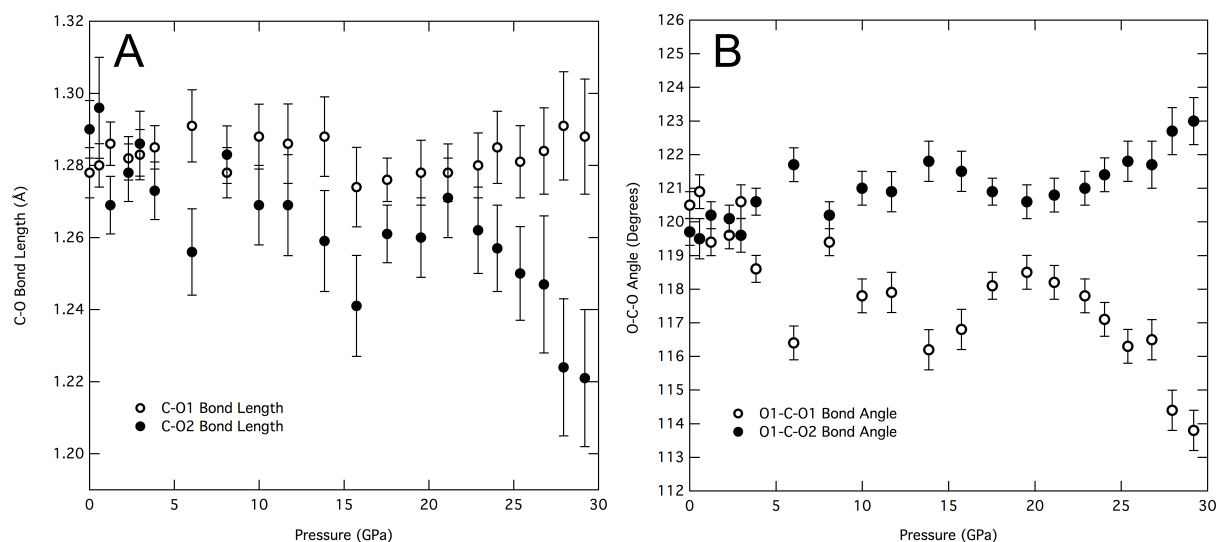


Figure 4-8. C-O bond lengths (a) and O-C-O bond angles (b). The carbon and oxygen bond lengths are shown for both the O1 and O2 sites. The O1 sites are parallel to the c -axis, comprise the base of the carbonate triangle and change very little with pressure. The O2 site bisects the base of the triangle and is in alignment with the b -axis. At ~ 20 GPa the C-O2 bond distance rapidly decreases and in turn leads to the U-shaped behavior in the b/c ratio and eventual lattice distortion between 25-30 GPa. The bond angles steadily diverge from ~ 20 GPa onward, in alignment with the U-shape in Figure 4-4c and 4-6.

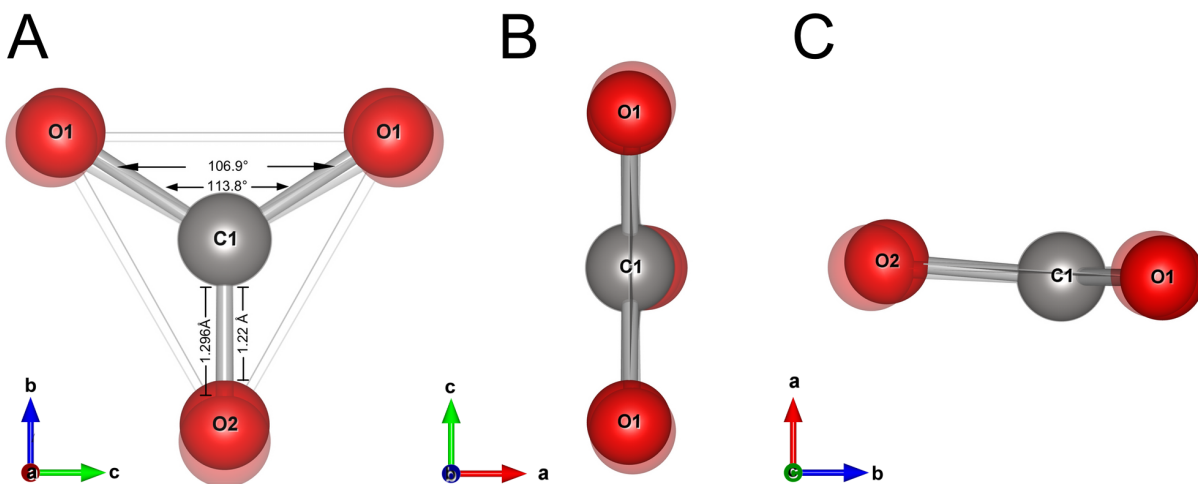


Figure 4-9. Evolution of the carbonate groups in the aragonite structure overlaid at two pressures from three angles: b-c planar view with significant changes in bond lengths and angles labeled (a), a-c planar view where the displacement of the O2 oxygen is noticeable (b) and a-b planar illustrating the change in angle between O1-C-O2. The carbonate groups with all atoms gray are extracted from data at 0 GPa. Carbonate groups with oxygen atoms in red are extracted from data at 29.1 GPa. Carbonate is shown in gray in the center and oxygen is light red at ambient pressure and dark red at 29.1 GPa. O1 and O2 oxygen sites are labeled.

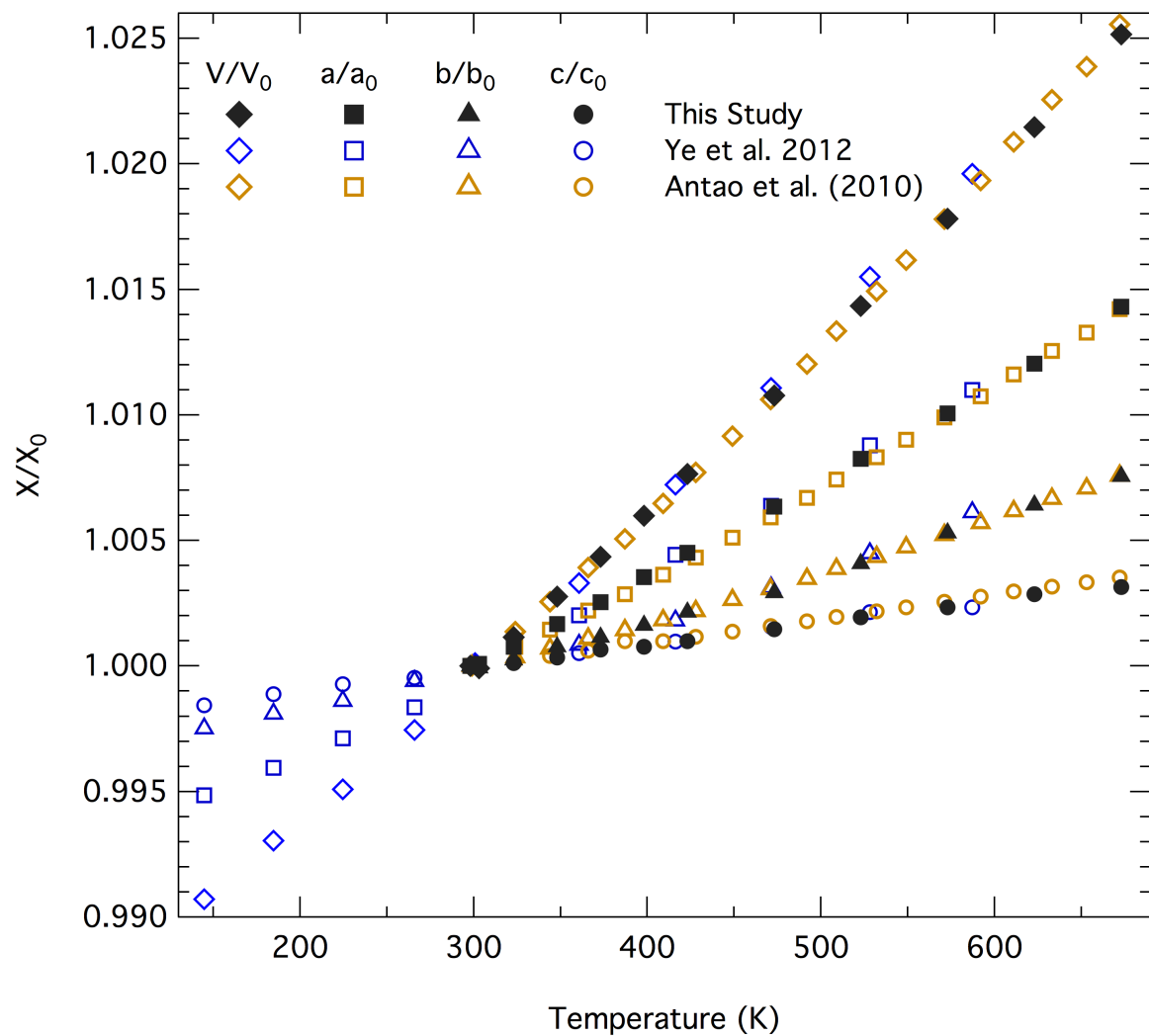


Figure 4-10. Thermal expansion of aragonite unit cell volume and axial crystallographic parameters. Thermal expansion data from our study is shown in solid black. Data from *Ye et al.* [2012] and *Antao et al.* [2010] is provided for comparison. We find the *c*-axis to exhibit the most expansion and the *a*-axis to be the least expansive. This is in direct contrast to the compressional behavior where *a* is the most compressible and *c* is the least.

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Chapter 5: Structure, stability, and thermoelastic properties of CO₂-IV

5.1 Introduction

The study of solid CO₂ at elevated pressures and temperatures is important in many facets of science including geology, condensed matter physics and material science. CO₂ plays a fundamental role in the carbon cycle of Earth, both atmospherically and through subduction processes feeding the mantle. Studies of high pressure, high temperature phases of solid CO₂ help understand the forms that carbon may adopt at the pressures and temperatures of planetary interiors, both in the solar system and beyond. Knowledge of these forms gives insight into the possible composition of carbon reservoirs in the deep earth and carbon storage on icy outer solar system bodies such as Titan or even icy exoplanets.

CO₂ phases have been found to have changing coordination from two-fold linear to four-fold tetrahedral at high P,T [*Oganov et al.*, 2008]. Due to the perceived similarities with SiO₂ several attempts have been made to map the CO₂ P,T phase diagram to that of silica to include quartz, coesite and stishovite-like phases [*Sengupta and Yoo*, 2010]. While these experiments have been successful in finding several analog phases, the CO₂ phase diagram is replete with metastable phases and path dependent phase transitions. Despite nearly two decades of research into CO₂ between the stable, well characterized dry ice CO₂-I phase and the high P,T polymeric CO₂-V phase, the phase diagram of CO₂ is still not clear. Our experiments are geared toward further elucidating this enigmatic region by studying one of its phases, CO₂-IV.

Arguments can be made that is unlikely CO₂ will exist as a solid in the deep Earth due to low melting temperatures at depth (i.e. 1063 K at 24 GPa, 1408 K at 50 GPa and 2064 K at 135 GPa). Recent work, however, on the high P,T CO₂-V phase indicates that at pressures above 20 GPa this newly identified phase may be dense enough to significantly increase the melting temperature [*Santoro et al.*, 2012; *Yoo et al.*, 2013; *Oganov et al.*, 2008]. Regardless of the

presence of isolated CO₂ in the deep interior, the predicted change in coordination in CO₂ fundamentally affects how carbon is stored in the deep Earth and is an important part of understanding the role that carbon plays in the mantle.

CO₂-IV has been studied by theoretical, Raman, infrared and X-ray techniques since its discovery in the early 2000s [*Iota and Yoo*, 2001; *Yoo et al.*, 2001; *Yoo et al.*, 2002; *Park et al.*, 2003; *Gorelli et al.*, 2004; *Datchi et al.*, 2009; *Contreras-García and Recio*, 2009]. The structure of CO₂-IV has been controversial since its discovery in 2001. Work by *Yoo et al.* [2001] and *Park et al.* [2003] concluded that the CO₂ molecule is bent in phase IV, giving longer C=O bond lengths of up to 1.3-1.5 Å in comparison to the 1.168 Å found at ambient conditions [*Datchi et al.*, 2009]. In contrast more recent work by *Gorelli et al.* [2004] and *Datchi et al.* [2009] using IR absorption spectra and X-ray diffraction respectively show that the CO₂ molecule is linear and has a double bond length closer to that at ambient conditions. Consequently, these studies disagree on the structure of CO₂-IV. The following space groups have been proposed: tetragonal *P4₁2₁2*, orthorhombic *Pbcn* and rhombohedral *R-3c*. The need for further data to help settle this controversies and to identify the basic thermo-elastic properties of CO₂-IV phase motivates our study.

5.2 Experimental Methods

We performed several experiments on CO₂-IV at the Spallation Neutrons at Pressure (SNAP) instrument at the Spallation Neutron Source (SNS), Oak Ridge National Laboratory (ORNL). Three different panoramic diamond anvil cells (DACs) with 1.6 mm culets in supported conical tungsten carbide seats were used. T301 steel of 250 µm thickness was precompressed to ~ 160 µm and drilled by EDM to form 650 µm gasket holes. The samples were gas loaded with CO₂ at the Mineral Physics Laboratory at the University of Texas at Austin. All

DACs were loaded with liquid CO₂ and pressurized to 1 GPa, crystallizing into dry ice at this pressure and ambient temperature. The samples were checked by optical microscope to confirm the quality of the powder.

The development of resistive heating at the SNAP instrument occurred concurrently with our experiment. The panoramic DAC was placed between two grooved cooper disks with a flexible metal heater that fits within the grooves. Outside this a 5 mm macor machinable ceramic disk is used an insulator between the heaters and the tie-rod double-membrane-driven press is used to pressurize the sample chamber. For further details of the press design see Boehler et al. (2013). To cool the press and prevent heating of the neutron detectors and other nearby machinery, copper cooling clamps were engineered to encompass both ends of the press. Cold water was pumped through these copper sleeves throughout the experiment. K-type thermocouples were attached to the press and inserted into one of the hole in the panoramic DAC to contact the seat near the anvil. Figure 5-1 shows a picture of the panoramic DAC seated in the press with the pressure lines, cooling water lines and thermocouples attached. The heating system was found to be very stable with a consistent ~5 K variation between thermocouple reading on the anvils and on the steel cell. The water-cooled press never reached temperatures greater than 375 K despite long data collection periods (6-12 hours) and temperatures up to 625 K.

All three of the DACs were pressurized then heated to achieve CO₂-IV, which is only formed at high temperature and pressure. Figure 5-2 illustrates the data points taken during both experiments in a diagram of the known stabilities of CO₂ phases. Due to the metastable behavior of the CO₂ phases between 11-50 GPa and up to 1000 K the lines in this diagram serve as a record of experimental results and stabilities rather than a formal phase diagram. The first

powdered sample was pressurized to 7.88 GPa and heated to 500 K, but was unable to pressurize above 13 GPa due to the variable thermal expansion experienced by the DAC and membrane press assembly.

The second DAC containing powdered CO₂ was initially pressurized to 18.0(2) GPa at ambient temperature in the panoramic DAC using the membrane press and helium gas. Pressure was recorded before and after each data acquisition using the Ruby fluorescence system installed at the instrument. Difference in pressure before and after the run was never more than 0.4 GPa and often less. The resistive heating system was initialized after pressurization and heated to 600 K. Temperature was adjusted to 625 K, 525 K, 450 K, 375 K and 300 K to study the thermal expansion of CO₂-IV and examine the P, T stability range of CO₂-IV.

In the third DAC, the powdered CO₂ was pressurized to several points within the stability range of CO₂-I before compressing at ambient temperature to 21 GPa. After data was taken at 21 GPa to confirm the formation of CO₂-III (Fig. 5-2), the heating system was initialized using the same setup as in the other DAC experiments. The sample was heated to 525 K and the pressure dropped to near 16 GPa as the CO₂-III lattice transformed to both CO₂-II and CO₂-IV. This point clearly lies on the II-IV stability line in Figure 5-2 and our data confirms that both phases are present at this point. After further heating to 625 K, only CO₂-IV was found. Data was then taken at various temperatures before quenching the sample to room temperature. At room temperature, CO₂-IV remained stable and was pressurized in steps of ~1 GPa from 18 GPa to 24.8 GPa.

In all experiments the incident neutron beam was focused by parabolic mirror to ~2 mm diameter and then directed through a 400 μ m diameter hexagonal boron nitride collimator that contacted the back of the upstream diamond. Diffraction data from each temperature step were normalized

to the intensity measured from a 2 mm x 1.5 mm vanadium disk placed between the anvils at the same position that CO₂ data acquisition occurred.

Neutron diffraction data above 525 K were confirmed as CO₂-IV during the experiments by comparison with data taken by *Park et al.* [2003] and *Datchi et al.* [2009]. Further analysis was undertaken after the normalization to the vanadium and background correction. Rietveld Refinements were carried out using GSAS and both the tetragonal $P4_12_12$ space group proposed by Park et al. (2003) and the $R-3c$ space group proposed by *Datchi et al.* [2009]. While the R values of both refinements are close (7.7% for Park et al. and 5.5% for Datchi et al.) at 18.2 GPa and 625 K, the intensities and peaks of the tetragonal structure do not match as well as those of the rhombohedral structure (Figure 5-3). The lattice parameters and refinement results for CO₂-IV using the $R-3c$ symmetry from all runs are shown in Table 5-1a.

Some variation in the centering of the cell existed between the runs. This technical issue was dealt with after the data had been collected by a recalibration to the CO₂-I data collected from each cell before heating. The equation of state (EOS) of CO₂-I is known, as reported by *Liu et al.* [1984] and *Giordano et al.* [2010] and the EOS parameters of CO₂-I using both the sets of data of Giordano and Liu are $V_0 = 50$ (fixed), $B_0 = 2.67(29)$ GPa and $B'_0 = 11.4(13)$. The unit-cell volume of CO₂-I was estimated from this equation of state for the pressures of the DAC experiments. From this, the d -spacings of the Bragg reflections were calculated and compared to the d -spacings observed experimentally. The first DAC experiment showed no deviation from the EOS and thus did not need correction. The ratio $d(\text{obs})/d(\text{calc})$ is 0.99656 in the second DAC run, where the thermal expansion data were taken. The ratio $d(\text{obs})/d(\text{calc})$ is 0.98764 for the final DAC run, which included the collection of high pressure data on quenched CO₂-IV. The

corrected patterns then underwent a background fitting, Vanadium correction and attenuation correction using software designed for use at SNAP by M. Guthrie.

5.3 Results and Discussion

5.3.1 Phase stability

The powder neutron diffraction results obtained during our experiments provide new evidence, obtained in a novel manner, for the interpretation of the controversial CO₂ “phase” diagram. Previous studies, both experimental and theoretical, on CO₂-IV and CO₂-II are divided in their results, making our contribution using a new method relevant [*Datchi et al.*, 2014; *Park et al.*, 2003; *Yoo et al.*, 2001; *Bonev et al.*, 2003; *Datchi et al.*, 2009; *Yoo et al.*, 2011]. The second DAC experiment confirms that the CO₂-IV structure is stable at 18.0(2) GPa from 625 K, the highest temperature achieved with our resistive heating system, to 300 K. In addition to the formation of CO₂-IV in the expected stability field, CO₂-IV is found to be stable a several temperature steps down to 295 K. The third DAC experiment investigated the elastic properties of CO₂-IV at ambient temperature.

Previous experiments on CO₂ phases between dry ice (CO₂-I) and the high P,T polymeric phases such as CO₂-V have used X-ray single crystal diffraction and Raman spectroscopy to study CO₂-IV in its presumed field of stability, above ~460 K and 11 GPa [*Park et al.*, 2003; *Yoo et al.*, 2011; *Datchi et al.*, 2009]. Previously, crystals have been grown at high temperature and quenched, presumably fairly quickly, to study pressure dependent behavior. While our neutron diffraction experiments made use of quenching during the third phase of the experiment for the same purpose, we did not instantly quench CO₂-IV in any of our experiments. In all experiments CO₂ underwent a long cooling process, especially in the thermal experiments where temperature steps of 75-100 K were conducted over runs of 8-12 hours in duration. Both Raman and X-ray

diffraction have relatively fast data collection intervals, far shorter than the 12 hour runs used in our high-pressure neutron diffraction experiments at SNAP. This time difference is relevant when phase transition kinetic effects are considered and give credence to CO₂-IV being stable at each of our data collection points. Unlike previous compilations of the phases stable in the high-pressure CO₂ P,T space, we find that CO₂ is stable throughout the P,T conditions assumed to belong to both phases II and III. Phase III has been previously identified as metastable, so this is unsurprising, but phase II has not been projected to be unstable with respect to phase IV before [Yoo, 2013], however, no experiment has been conducted to particularly investigate the stability relationship between CO₂-II and CO₂-IV.

5.3.2 Compression and bulk modulus

Although much work in the past two decades has focused on the intermediate portion of the CO₂ phase diagram, very few studies have looked into the compressional or thermal behavior of these phases. The final DAC run included a compressional study of CO₂-IV at ambient temperature. All of the CO₂ data generated during this third and final run are shown in Figure 5-4, as well as some CO₂-I data from the previous DAC experiments. The data taken at 295 K from 18 GPa to 24.8 GPa were used to fit both 2nd and 3rd order Birch-Murnaghan equations of state. The 2nd order fit yields $V_0 = 37.3(5) \text{ \AA}^3$, a bulk modulus of $K_{T,0} = 34(2)$ with $K' = 4$ while the 3rd order fit yields $V_0 = 41(1) \text{ \AA}^3$, a bulk modulus of $K_{T,0} = 15.8(6)$ and $K' = 5.5(19)$. Both fits are shown in Figure 4 with the notable difference being the low pressure behavior where the 3rd order fit passes more closely through the CO₂-I data than 2nd order fit does. Previous studies, notably *Giordano et al.* [2007], found a volume drop during the phase change from CO₂-I to CO₂-IV or CO₂-VII, which is consistent with our fit falling below the CO₂-I data, but following a similar trajectory.

Figure 5-5 combines a number of studies [*Liu*, 1984; *Park et al.*, 2003; *Datchi et al.*, (2009, 2014); *Giordano et al.*, 2010] to give context to the new CO₂-IV data presented. The plot includes phases I, II, and IV. The data collected during this experiment on CO₂-I are consistent with previous CO₂-I data, validating our novel neutron diffraction results. The difference between CO₂-II and CO₂-IV is subtle but can be seen in the slightly smaller volume taken on by CO₂-II, which mirrors the shock experiment results from *Liu* [1984]. Both the new CO₂-IV data and the data taken by *Park et al.* [2003] show a larger volume at similar pressures, with the two phases diverging as pressure increases.

A closer look at the compressibility of CO₂-IV is given in Figure 5-6, which shows all of the currently available data for the phase. Both equation of state fits are shown to illustrate the divergence of previous data from the fit to the new CO₂-IV data. Indeed, the CO₂-IV data collected by *Park et al.* [2003] via X-ray diffraction indicates a stiffer phase, with data points clearly falling above the equation of state fits above 25 GPa. Our experiment was limited in pressure due the large diamond culets required for successful neutron diffraction experiments. Regardless of this limitation, the data points were taken at even (~ 1 GPa) pressure intervals and represent the best available data for equation of state fitting. Indeed, no equation of state fitting was attempted in the *Park et al.* [2003] analysis. There are only two other data points, from the work by *Datchi et al.* [2009], which fit generally well with both our data and the equation of state fits. Clearly this is an area rich for future experiments geared toward equation of state formulation, not just structural inquiries.

The development of equations of state for CO₂ through experiment is still a nascent field of study. Table 5-2 lists several literature studies of CO₂ and their equations of state, derived experimentally or theoretically. Interestingly, the 3rd order Birch-Murnaghan equation of state

from this study is on par with the equation of state found by *Datchi et al.* [2014] for CO₂-II, $V_0 = 41(2) \text{ \AA}^3$, $K_{T,0} = 16(5)$ and $K' = 5.2(4)$, in comparison to $V_0 = 41(1) \text{ \AA}^3$, $K_{T,0} = 15.8(6)$ and $K' = 5.5(19)$ for CO₂-IV in this study. *Datchi et al.* [2009] report a different value for the bulk modulus by fixing $K' = 6.29$ based on theoretical calculations by *Gohr et al.* [2013], but this adherence to theoretical values may lead to a bias not present in the experimental data. The similarities between the two equation of state fits to the data for two different phases of CO₂ are notable and indicate the phases exhibit similar elastic properties. *Datchi et al.* [2009] used a single crystal of CO₂-II in Ne formed at 15 GPa and 490 K quenched the sample to 295 K and then compressed to 57.7 GPa using membrane DACs and synchrotron radiation [*Datchi et al.*, 2014] in a similar manner to the methods of our neutron experiments.

As can be seen in Table 5-2, the only previous data on CO₂-IV is entirely computational. Previous computational studies of CO₂-IV indicate its compressibility is similar giving a bulk modulus between 2.5(2)-10.7(1) with a pressure derivative between 7.9(2)-7.06(3) for GGA and LDA, respectively, density functional theory results [*Datchi et al.*, 2009]. Our results yield a stiffer bulk modulus, but since they are the only published CO₂-IV compressional data at present, the slight difference is unsurprising. In general, CO₂ phases both experimentally and theoretically yield low bulk moduli, indicating high compressibility, and pressure derivatives greater than $K' = 4$. The only exception to these parameters during equation of state fitting is in the work of *Yoo et al.* [2002], which presents a bulk modulus of 131 GPa and a pressure derivative of 2.1 for CO₂-II. Our current experiment adds to the body of work that supports highly compressible CO₂ phases that have bulk moduli closer to 10-15 GPa and pressure derivatives above $K' = 4$.

5.3.3 High temperature data

Neutron diffraction patterns of CO₂-IV from each temperature step in the thermal expansion experiment (the 2nd DAC experiment) are shown in Figure 5-7. Each pattern was collected for 8-12 hours due to the low neutron flux, several orders of magnitude less than synchrotron X-ray, and the small volume of material used in high-pressure experiments. The powder diffraction patterns of CO₂-IV are very close to those generated by the crystallographic data from previous experiments. As discussed in the methods section, GSAS Refinements used the rhombohedral structure found by *Datchi et al.* [2009]. In general, the high temperature data taken were between 16 and 21 GPa and mostly centered around 18 GPa, the pressure used in the thermal expansion experiment.

Figure 5-8 shows data taken in nearly isobaric conditions (18 ± 0.3 GPa, see Table 5-1a) and a thermal expansion fit to the data. We use a linear parameterization of thermal expansion:

$$V = \text{Exp} \left\{ a_{300}(T - 300) + a_1 \left[\frac{(T^2 - 300^2)}{2} - 300(T + 300) \right] \right\} V_0 \quad (1)$$

$$\alpha_T = a_{300} + a_1(T - 300) \quad (2)$$

Where V is volume, V_0 is volume at ambient temperature, T is temperature, T_0 is room temperature (300 K), α_T is thermal expansion at temperature T , and a_{300} and a_1 are fitting parameters. We find $a_{300} = 8.15(95) \times 10^{-5}$ and $a_1 = 1.4(11) \times 10^{-8}$. At 625 K and 18 GPa, the thermal expansion of CO₂-IV is $8.6(5) \times 10^{-5} \text{ K}^{-1}$. No previous thermal expansion experiments have been conducted on CO₂-II or CO₂-IV, but *Giordano et al.* [2010] found α_T at 295 K to be $1.296(30) \times 10^{-3} \text{ K}^{-1}$ for CO₂-I. This value is significantly larger than the value found for CO₂-IV, which is just $a_{300} = \alpha_{300}$ since our values are normalized to 300 K. Further study of thermal expansion in the CO₂ phases is needed to confirm these results.

All of the data collected at high temperature are pictured in Figure 5-9. The equation of state for CO₂-IV determined during the compressional experiment (3rd DAC experiment) is shown as well as contour lines that highlight the deviation of the high temperature data from the equation of state (Fig. 9a). In particular, data taken at 525 K show remarkable variability, ranging from nearly 30 Å³ per molecule of CO₂ at 16.3 GPa to under 28.5 Å³ per molecule at 18 GPa, with an intermediate volume found at higher pressure. This anomaly is not easily explained since data at other isotherms exhibit more predictable behavior that is reflected in their similarities to the equation of state contours. Adding literature data to the mix serves to illustrate how much further study is needed to fully quantify the high temperature behavior of CO₂-IV (Fig. 9b). Data from the previous CO₂-IV studies by *Park et al.* [2003] and *Datchi et al.* [2009] create even more of a scatter plot. Despite *Park et al.* [2003] using a different unit cell, tetrahedral to the rhombohedral used by this study and *Datchi et al.* [2009], volume per molecular formula unit should be consistent between the studies. Indeed, Park et al.'s data points at 429 K and 548 K generally fit the trends of data from the current study. Beyond that, however, notable deviation is seen at 473 K and perhaps at 322 K. The sole data point at high temperature from *Datchi et al.* [2009] generally fits, if falling a bit below expected volume. Regardless, combining these studies indicates that further study is needed at high temperature to fully understand the thermal properties of CO₂-IV.

5.4 Implications

Our thermal expansion experiment is the first of its kind on these mid-pressure solid CO₂ phases. The success of our experiment should encourage further in situ compressional and thermal experiments. The pressures and temperatures encountered along the geothermal gradient found in the Earth do not include the stability field of CO₂-IV, which has been reported to form

above ~ 460 K between ~ 12 and ~ 50 GPa. CO_2 subducted into the Earth is likely in the liquid state as the geotherm is above its melting curve for all interior pressures. Up to 70% of the carbon subducted at convergent plate boundaries is recycled back to the surface through arc volcanism, reducing the influx of CO_2 to $\sim 4\text{--}6 \times 10^{13}$ g C/yr. In the case that carbon does make it into the interior of the Earth within a cold lithospheric slab, $\text{CO}_2\text{-IV}$ could occur below 1000 K at 12 GPa. Increasing pressure finds the melting temperature of CO_2 only increasing by 200 K across 20 GPa. Therefore, there is a possibility of finding solid carbon dioxide if a slab remains sufficiently cold to the top of the transition zone (410 km and ~ 14 GPa).

Ice giants such as the Solar System's Uranus and Neptune present another possible candidate for $\text{CO}_2\text{-IV}$ and the other mid-pressure carbon dioxide phases. The surface of these planets is 70-75 K, but despite this promising starting temperature, these giant balls of gas and dust have such mass that the internal temperature gradient is very steep. A third of the way to the core, the temperature has already reached 2500-3000 K and pressures of 10 GPa. While this is realistic pressure for the stability of $\text{CO}_2\text{-IV}$, the temperature ensures that carbon dioxide is only found in a gaseous state. If both the Earth and ice giants are too warm, perhaps a different type of planet is needed for this phase of CO_2 . Exoplanets come in many shapes and sizes and one can imagine an ocean planet with majority water that contains the usual gases including carbon dioxide. The temperature profile of this planet would be different from the silicate Earth and the giant balls of ice and dust, most importantly containing a depression in the temperature. Instead of a temperature of near 2000 K at 18 GPa, this water world would be a temperate 500-700 K, the exact temperature range in which $\text{CO}_2\text{-IV}$ is stable.

The neutron diffraction measurements presented in this study are cutting edge with respect to not only the study of $\text{CO}_2\text{-IV}$, but also the methods used during the study. These results

indicate that resistively heated DAC experiments are possible using neutron diffraction and encourage the development of further heating systems for DAC experiments in these settings. In addition, we verify the structure of CO₂-IV while presenting new findings on its phase stability with respect to the other “intermediate” CO₂ phases. This study introduces the first compressional study of CO₂-IV and yields foundational thermal expansion data. These experiments help to determine the thermoelastic properties of CO₂-IV and inform planetary interior models. This study is the first step toward expanding the range of DAC neutron diffraction experiments and compiling data to yield definitive thermoelastic properties for CO₂ phases.

5.5 Summary

The experimental scope of the CO₂ project went far beyond the scope of any other study contained in this dissertation. The work produced here is the result of a foundational collaboration between the SNAP instrument and the Deep Carbon Observatory, which funded and supported this work. The studies, although important in their scientific additions to the field of carbon dioxide at high pressures and temperature, were the first of their kind at a neutron diffraction facility. The legacy of this study is not only important new thermoelastic data on CO₂-IV, but also the inauguration of a new era of neutron diffraction diamond anvil cell studies. The success of this work will help to motivate other daring studies that will help push the envelope of mineral physics and its techniques.

The data generated by this study supports the existence of molecular carbon dioxide until the transition to CO₂-V at higher temperature and pressure. These results support the theory that there is no “intermediate” bonding situation encountered by the carbon dioxide molecule and

predict an abrupt phase transition at the CO₂-IV/CO₂-V boundary. Further study into CO₂ phase stability and structure is needed to fully verify this prediction.

5.6 Tables

Table 5-1a. The Rietveld Refinement results and lattice parameters at each temperature for the rhombohedral CO₂-IV structure.

P (GPa)	T (K)	Run #	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	<i>V</i> / <i>Z</i> (Å ³)	wRp
19.5	625	20033	8.594(2)	10.631(3)	680.2(3)	28.34(1)	0.0081
18.9	525	20034	8.596(2)	10.631(2)	680.5(3)	28.35(1)	0.0078
18	450	20035	8.587(2)	10.618(3)	678.1(3)	28.25(1)	0.0084
18	295	20036	8.555(2)	10.578(3)	670.6(3)	27.94(1)	0.0093
19	295	20037	8.510(2)	10.535(3)	660.9(3)	27.54(1)	0.0103
20.3	295	20038	8.479(2)	10.496(3)	652.9(3)	27.21(1)	0.01
21.5	295	20039	8.438(2)	10.467(3)	645.5(3)	26.90(1)	0.0108
23	295	20040	8.400(3)	10.426(5)	637.2(5)	26.55(2)	0.0145
24.8	295	20041	8.353(2)	10.398(4)	628.5(4)	26.19(1)	0.0108
17.6	600	15893	8.640(1)	10.696(2)	691.6(2)	28.816(8)	0.0039
18.2	625	15895	8.622(1)	10.677(2)	687.6(2)	28.648(8)	0.0039
17.9	525	15897	8.580(1)	10.630(2)	677.8(2)	28.242(9)	0.0048
18.3	450	15898	8.566(1)	10.611(2)	674.4(2)	28.100(8)	0.0047
18	375	15899	8.557(1)	10.598(2)	672.1(2)	28.004(9)	0.0048
17.9	300	15901	8.450(1)	10.580(2)	668.3(2)	27.845(8)	0.0049

Table 5-1b. The Rietveld Refinement results and lattice parameters at each temperature for CO₂-I.

P (GPa)	T (K)	Run #	<i>a</i> (Å)	<i>V</i> (Å ³)	wRp	Rp
5.3(2)	295	20030	5.1657(9)	137.84(7)	-	-
7.7(2)	295	14352	5.0442(5)	128.34(4)	0.0058	0.0048
1.3(2)	295	15892	5.5202(8)	168.22(7)	0.0072	0.0062
6.1(2)	295	15869	5.1286(7)	134.89(6)	0.0107	0.0061
9.8(2)	295	15870	5.0200(8)	126.51(6)	0.011	0.0067

Table 5-2. Bulk modulus, pressure derivative and initial volume for several CO₂ phases from the literature. * denotes a set value in the equation of state fit. Results from the current study are shown in bold.

Study	Phase	Method	K _{T,0} (GPa)	K _{T,0'}	V ₀ (Å ³)
This Study	IV	Neutron Diffraction	15.8(6) 34(2)	5.5(19) 4*	41.1(13) 37.3(5)
This Study, Liu (1984) and Giordano et al. (2010)	I	Fit to Previous Data	2.67(29)	11.4(13)	50*
Datchi et al. (2009)	IV	XRD/GGA	2.5(2)	7.9(2)	-
		XRD/LDA	10.7(1)	7.06(3)	-
Datchi et al. (2014)	II	XRD/Raman	8.5(3) 16(5)	6.29* 5.2(4)	44.4(4) 41(2)
Bonev et al. (2003)	II	DFT/PBE	4.37	6.66	51.21
Gohr et al. (2013)	II	DFT/PBE-D3	7.46	6.29	45.82
Yoo et al. (2002)	I	XRD	6.2	6.1	-
	II		131	2.1	29.8
	III		87	3.3	-
Zhang et al. (2014)	I	Bruillion Scattering	3.4(6)	7.8(3)	-
Giordano et al. (2010)~	I	XRD/Raman/IR	3(1)	8.4(8)	50(2)
Liu (1984)~	I	Shock	3(5)	9(1)	50(9)

5.7 Figures

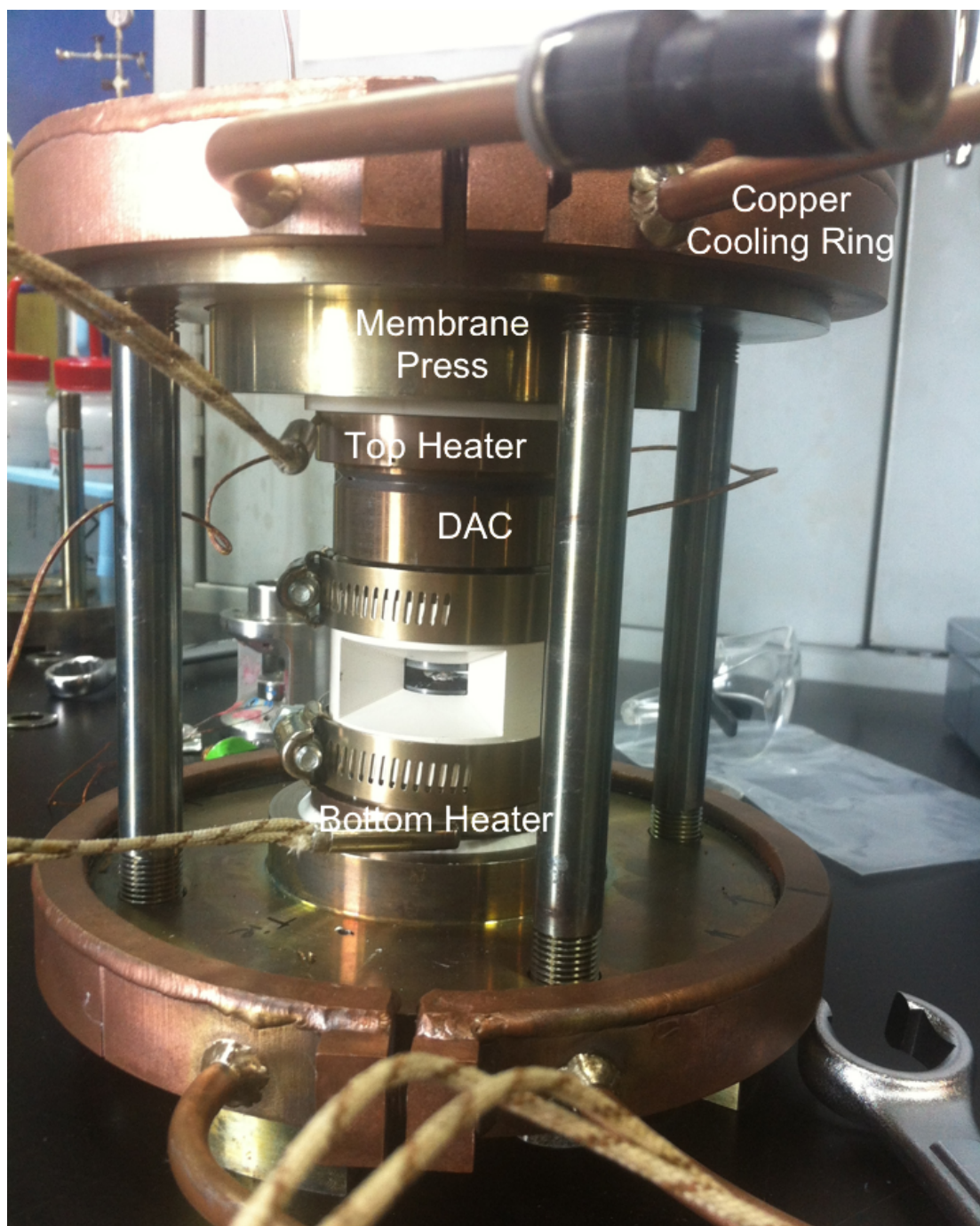


Figure 5-1. The DAC assembly in the membrane press. The diamond anvils are visible in the middle of the assembly. The panoramic DAC supports the anvils and is surrounded by resistive heaters and ceramic insulators on either end. This assembly is then place within the membrane press and the copper cooling system is installed on the press.

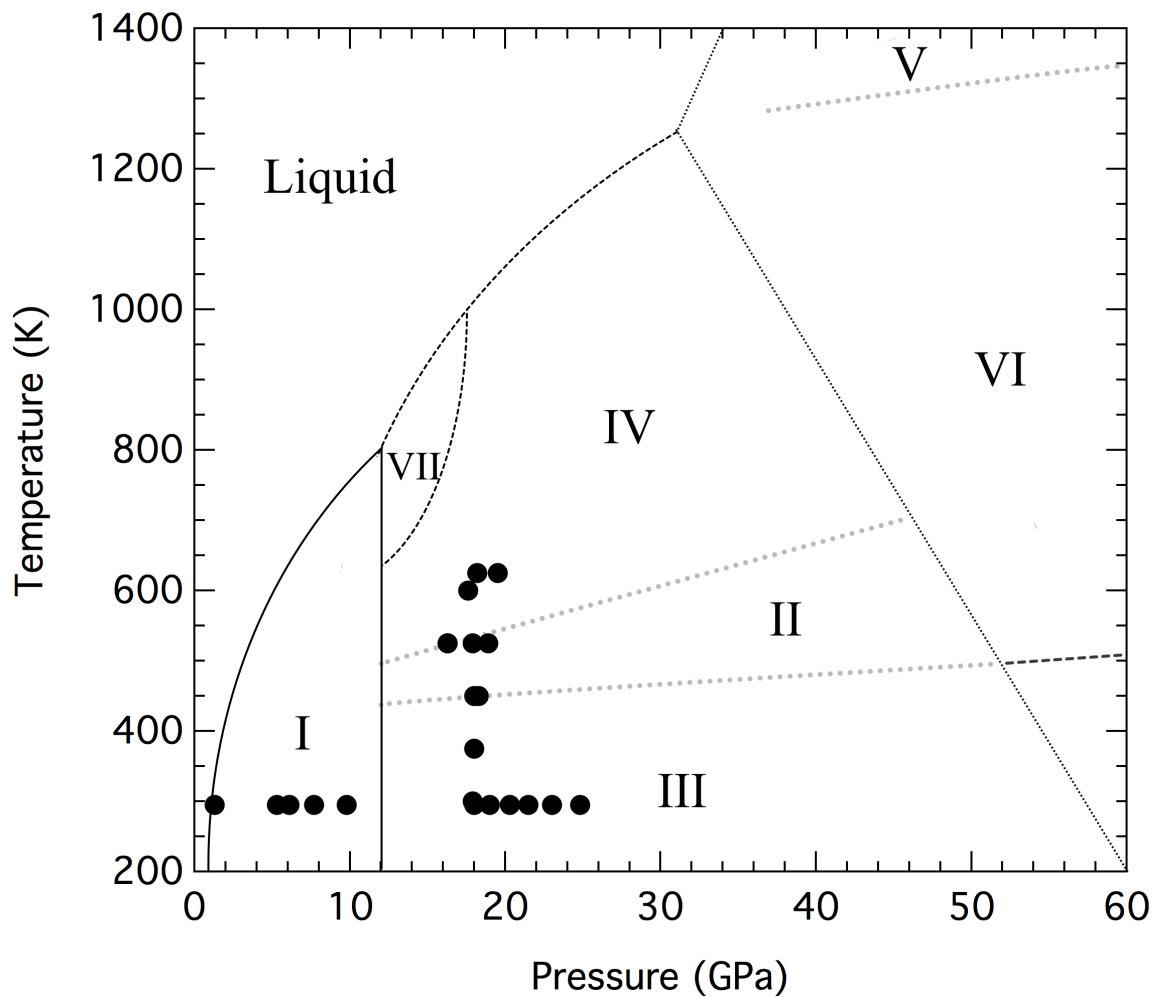


Figure 5-2. Stability diagram of CO₂. Black dots mark the different data collection points taken during all CO₂ DAC experiments.

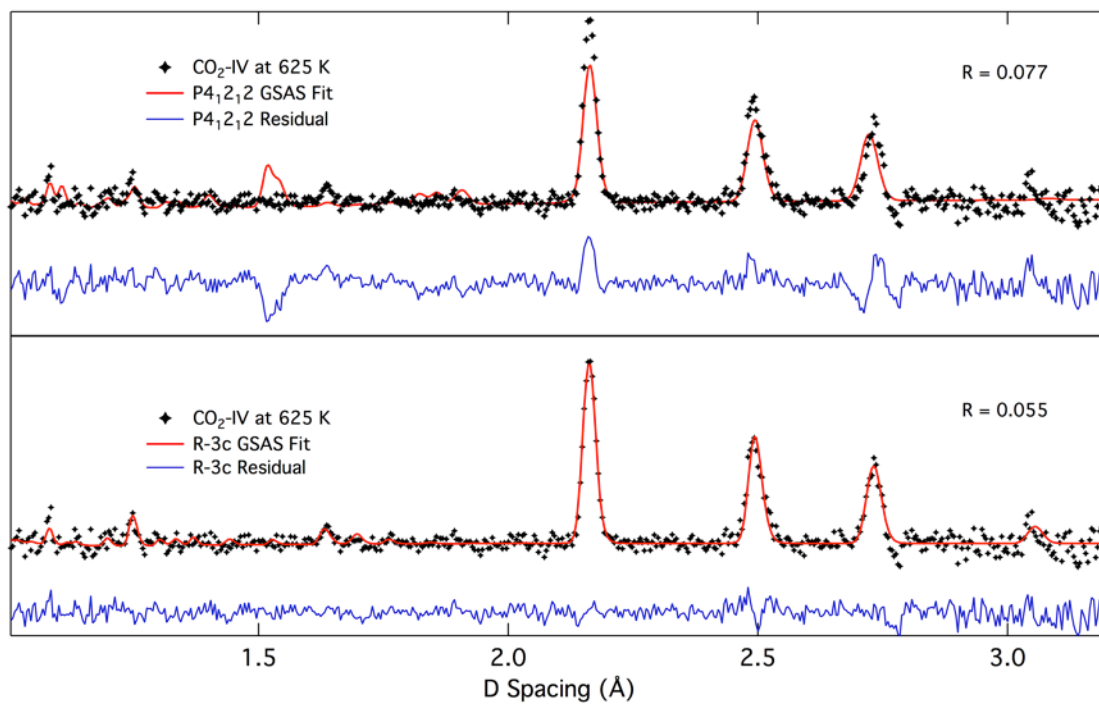


Figure 5-3. Comparison of Reitveld refinements of the structure of CO₂-IV using our neutron data. The rhombohedral structure found by *Datchi et al.* [2009] is the best fit to our data.

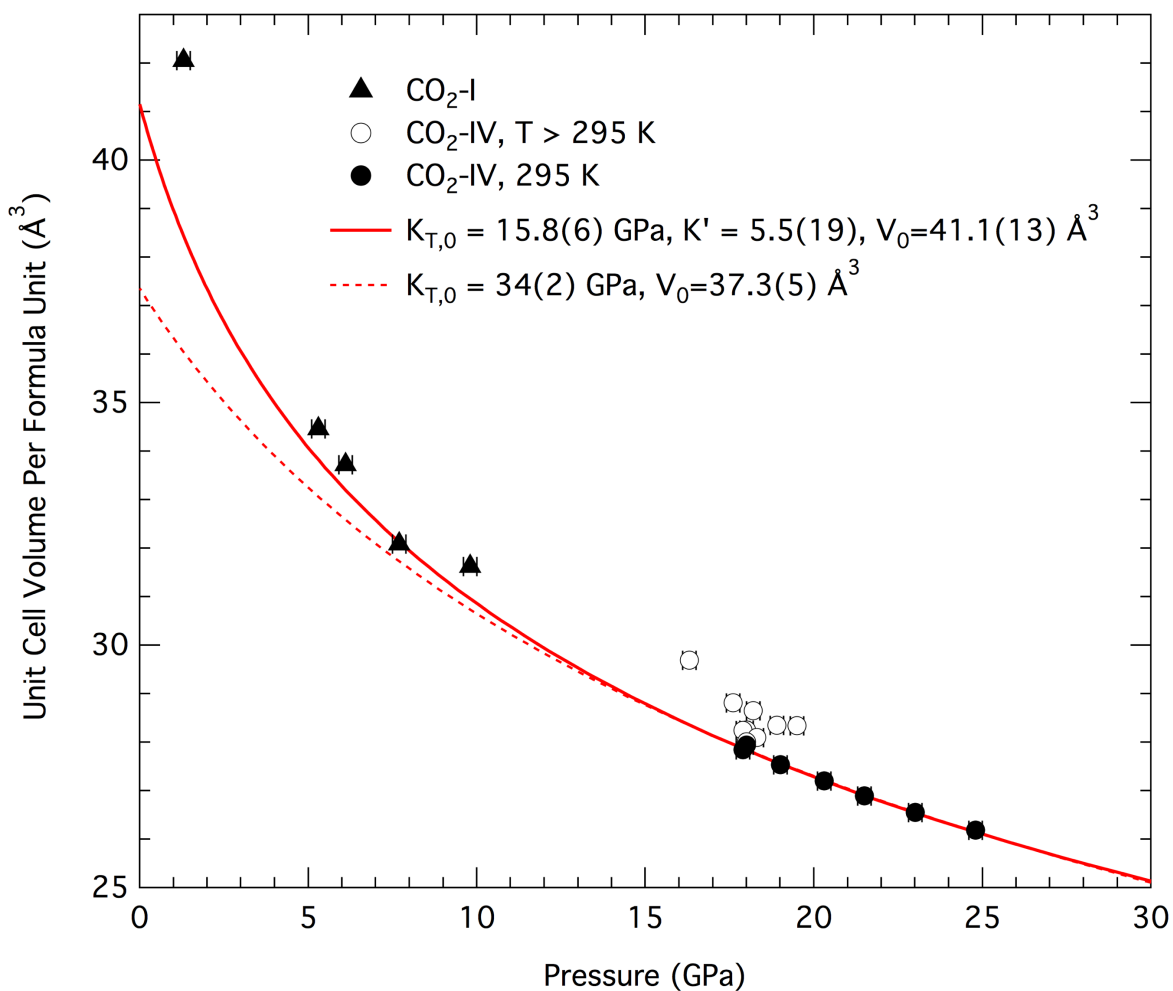


Figure 5-4. CO_2 -IV data fit to the Birch-Murnghan equation of state. Note that all of the CO_2 data is plotted, including both CO_2 -I and CO_2 -IV. Only CO_2 -IV data from our experiment was used in the fitting of the equation of state. Both the 2nd (dotted) and 3rd (solid) order fits to the data are shown.

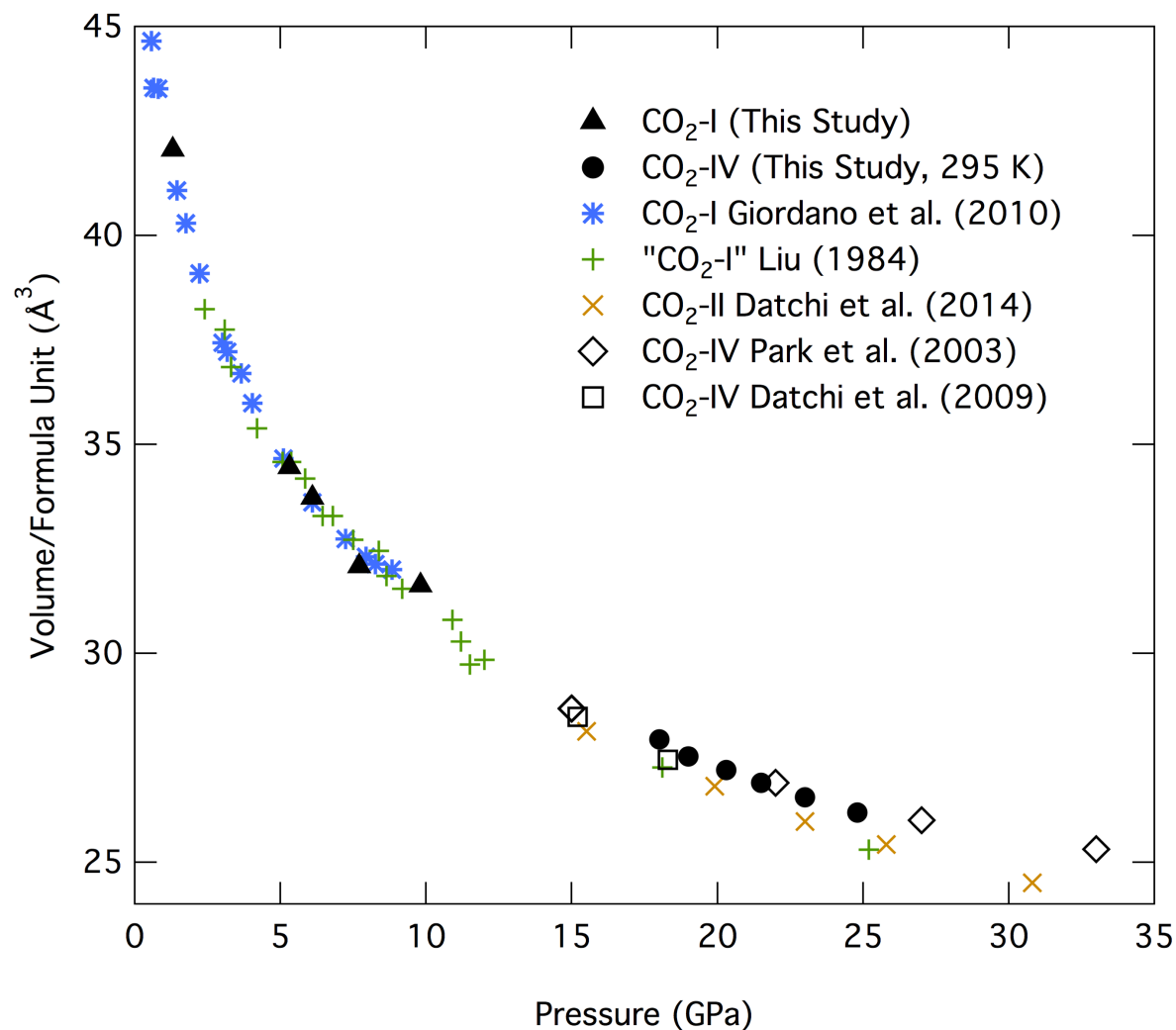


Figure 5-5. Ambient temperature CO_2 data from various studies encompassing several phases (I, II and IV). The volume per molecular formula unit difference between CO_2 -II and CO_2 -IV is apparent as the two phases begin to diverge by 20 GPa.

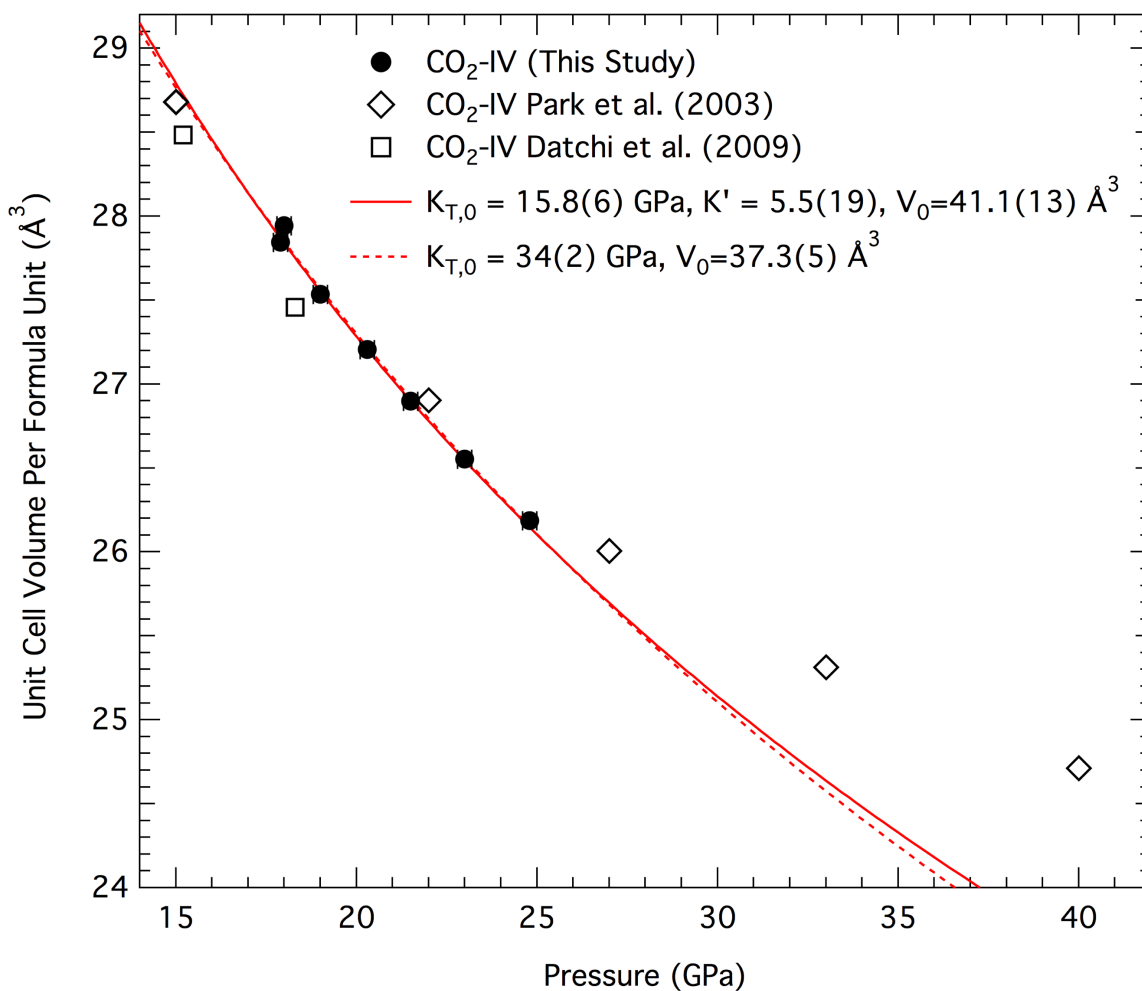


Figure 5-6. CO_2 -IV data (closed symbols) and equation of state in comparison to previous CO_2 -IV studies (open symbols). Both the 3rd order and 2nd order equation of state fits are shown. Both fits indicate that the new CO_2 -IV data indicate the phase is more compressible than the data in *Park et al.* [2003], but not *Datchi et al.* [2009].

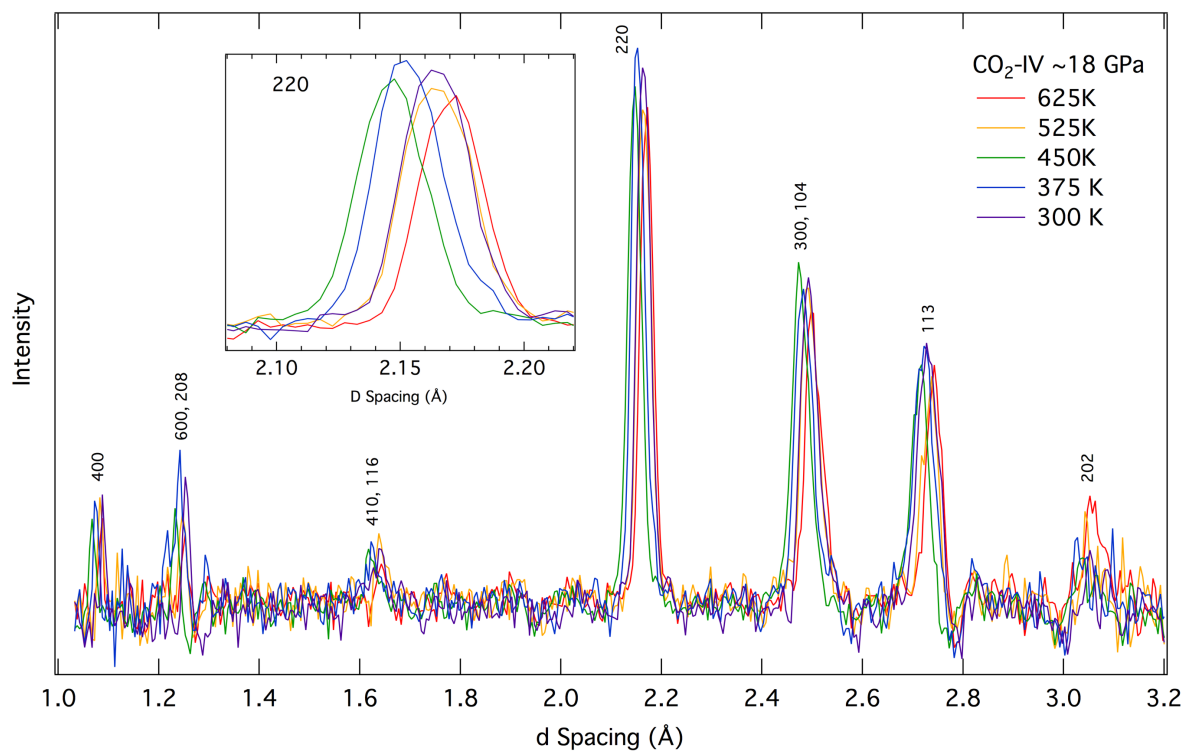


Figure 5-7. Neutron diffraction data from the thermal expansion experiment. Data shown is from 300 K to 625 K, with colors corresponding to temperature. The inset clearly shows the shift in the diffraction peaks with temperature. Note that there is some variation of pressure (± 0.3 GPa), which accounts for the ambient temperature 220 peak sitting in a similar position to the 625 K peak (see Table 5-1a).

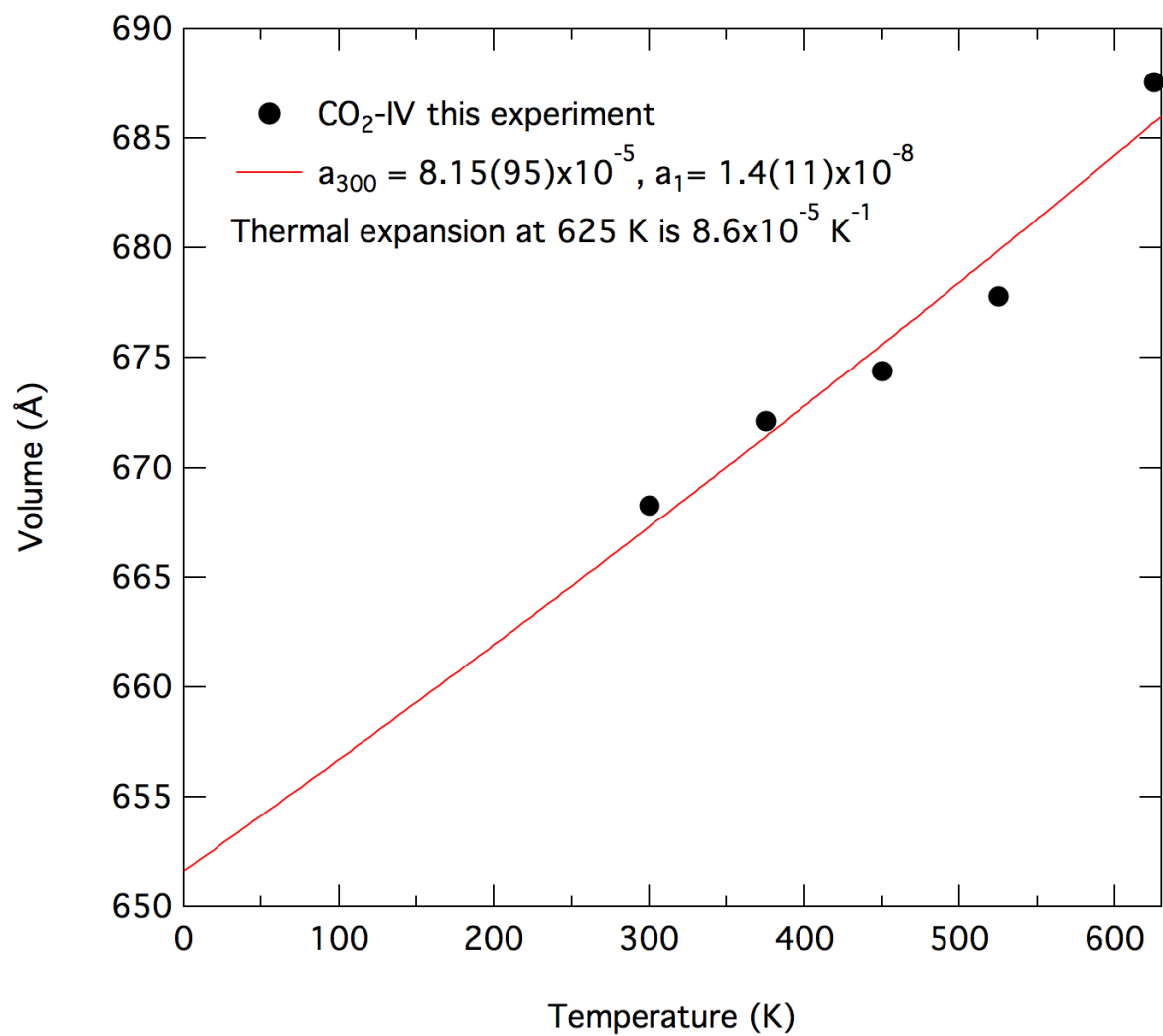


Figure 5-8. Linear thermal expansion fit by our data. Error bars are smaller symbols in volume.

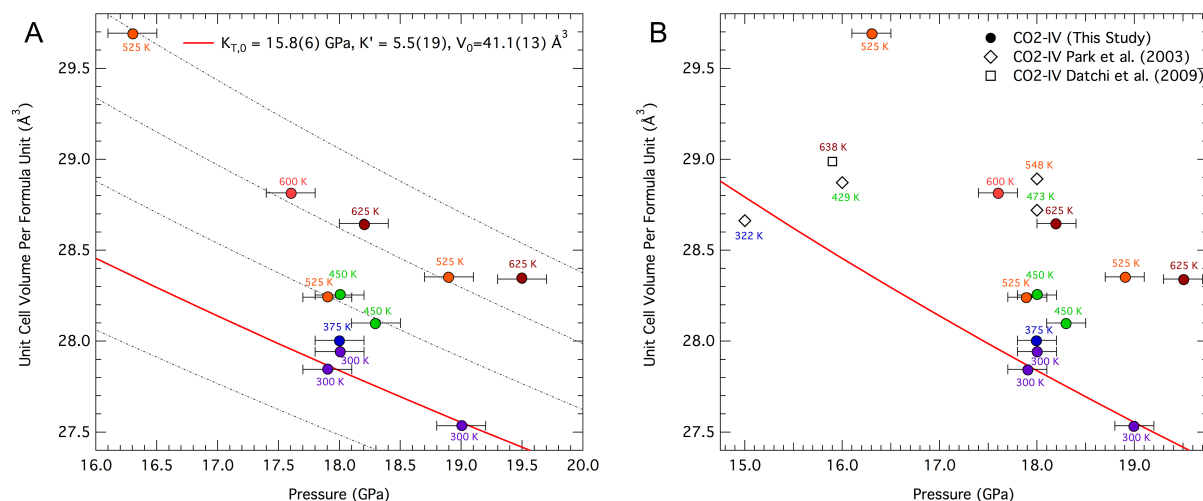


Figure 5-9. a) Thermal data in P,V space with equation of state contour lines corresponding to the 3rd order fit to the data. Different temperature regimes have different solid colors and all points are labeled with their temperature. b) Literature data is added to the previous plot, highlighting the large variability in current data.

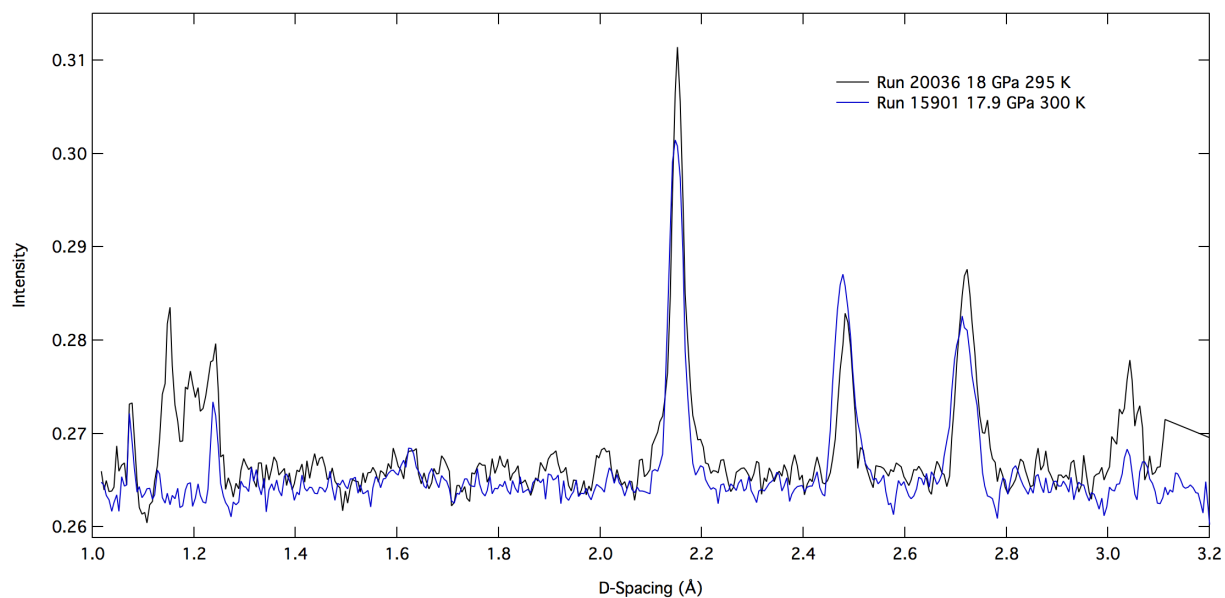


Figure 5-10. Normalized CO₂ patterns at ~18 GPa from both DAC experiments. The alignment of the DAC in the beam was slightly different between experiments and data were normalized to CO₂-I, whose equation of state is well known.

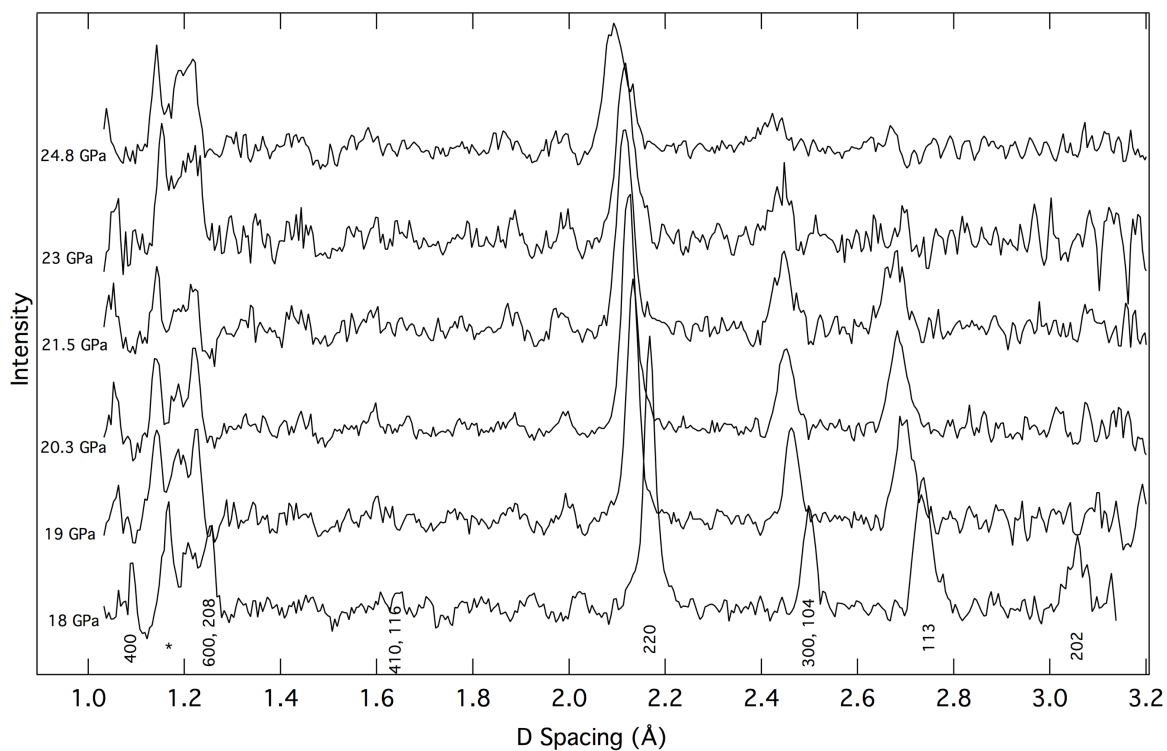


Figure 5-11. Data from the compressional experiment showing the evolution of the neutron diffraction patterns with pressure. The starred peak around 1.2 Å is a product the normalization process and not a lattice peak. Pressures and lattice planes are labeled.

5.8 References

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Chapter 6: Conclusions

6.1 Carbon in the deep earth

The studies included in this dissertation exhibit both breadth and depth in the study of carbon in the deep earth. A range of pressures (ambient to ~ 40 GPa) are covered in several studies that examine the high pressure role of carbon in various mineral systems. The work on hanksite emphasizes how compression of ionically bonded salts is controlled by the rigid polyhedral elements of the mineral. The work also provides a model for predicting sulfate compression. A similar model could be generated for carbonate compressibilities, since each study on carbonate minerals in this work found that the orientation and spacing of the carbonate groups had a direct impact on the compressibility of the lattice. Indeed, as we search for the changing coordination of carbon special attention should be paid to the orientation of the carbonate groups within the unit cell.

The work on kutnohorite provided important insights into the spectra of dolomite structures adopted at high pressure. Subsequent single crystal work done by the author in collaboration with Prof. Marco Merlini demonstrated that although kutnohorite adopts the dolomite structure, the exchange of Mn for Mg in the structure directly impacts the high-pressure phase stability and structural changes. In Merlini et al. (2012), the carbonate groups were shown to rotate and distort, indicating the high pressure dolomite phases might be a road map to the changing coordination of carbon. The different behavior adopted by kutnohorite shows no such distortion of the carbonate groups, only modification of the unit cell symmetry due to rotations. It is significant to note that a different cation fundamentally changes the evolution of the structure.

The aragonite study first and foremost provides a definitive equation of state for aragonite that can be used in modeling, both of the earth, moons and planets. Our work also further

characterizes the compressional behavior of aragonite before its predicted phase transition at 40 GPa and provides some evidence for the transition between 30 and 40 GPa predicted by Pickard and Needs (2015). While the interest in this transition comes mostly from a material science perspective, the possible subduction of aragonite to transition zone pressures makes this work valuable to the study of deep carbon within the earth. Assuming the carbonate does make it to transition zone and beyond, this study informs the phase stability of aragonite in oxidizing conditions possible in a heterogeneous mantle and provides the foundation for understanding possible deep mantle reservoirs of carbon.

The carbon dioxide study veers away from the carbonate mineral track and investigates the possibility of high-pressure, high temperature CO₂ phases in the Earth, other planets and icy moons. As noted in Chapter 5, although CO₂ is not predicted to be stable at earth mantle conditions, these studies provide a basis for the thermoelastic properties relevant to icy moons and exoplanets. In addition, the results of our neutron diffraction studies inform the debate over the transition from molecular to polymeric carbon dioxide and elucidate some of the mystery found in the CO₂ stability diagram. Indeed, our findings that CO₂-IV is the stable species at ambient temperatures (over nearly 12 hours) indicate that much work to be done before a reliable and believable CO₂ phase diagram can be constructed.

6.2 Future work

Each of the chapters included in this dissertation leaves a pathway toward future work. The hanksite and tychite study brings up questions surrounding modeling compressibilities based on inter-polyhedral distances and supports future examinations of salts at high pressure and temperature, especially in respect to icy moons and exoplanets. Future experiments involving ionic carbonate salts could include high-pressure studies, with a focus on finding a

decomposition pressure and examining the structure of the carbonate groups through this transition.

Further research into the high-pressure behavior of kutnohorite has already begun during the experiments at ESRF noted in Chapter 2. Since the single crystal study indicates that kutnohorite does not transition to a dolomite II type structure, future studies will need to focus on identifying the new structure and tracking the unique phase stability of kutnohorite. In addition, special consideration will need to be given to the orientation and compressibility of the carbonate groups in this new structure. To this end, single crystal X-ray and Raman or IR spectroscopy studies will be preferable to powder diffraction ones.

While the study of aragonite in Chapter 3 produced a solid equation of state and thermal expansion data, much is still unknown about the nature of the phase changes aragonite undergoes between 30 and 40 GPa. A future study aimed at studying the nature of the transition that includes laser heating to reduce kinetic effects would be a good next step. In addition, the evolution of the carbonate groups identified in our study will need to be verified, preferably with the use of heating to reduce kinetic effects that may lead to high lattice strain. Beyond the 40 GPa pressure range studies of aragonite at higher pressure can help identify the exact behavior and evolution of the carbonate groups at the high pressure experienced in the Earth's mantle.

Studies of carbon dioxide are truly in their infancy and further study of all facets of CO₂ and its phases are important to understand the basic physics of carbon dioxide and to driving the modeling of planetary interiors that require a CO₂ element. Systematic studies of the phase stability of each of the CO₂ phases need to be conducted to produce a useable phase diagram. The current studies (both previously and contained within Chapter 5) indicate this will be a

difficult process and that multiple techniques such as Raman spectroscopy and X-ray or neutron diffraction will be needed to complete this non-trivial task. In addition to further study of the phase stability of CO₂, studies into the symmetries adopted by different carbon dioxide phases are needed, preferably using a combination of spectroscopic and single crystal X-ray diffraction.

Beyond these scientifically based studies, further engineering remains to be done to increase the capabilities of the SNAP beamline with respect to high temperature diamond anvil studies. Additional work into the material of the diamond seats used in the panoramic cells and the membrane press will significantly help to increase the heating capabilities of the beamline. Currently the thermal expansion experienced by the membrane press is an obstacle to running compressional experiments at high temperatures. Also, refining the system to restrict heating to the diamond anvil cell instead of the press would be a significant step forward.

Each of the chapters included in this work is merely a stepping-stone toward future experiment and understanding. Nevertheless, each experiment detailed within this dissertation provided a notable contribution to the understanding of carbon in the deep Earth, including implications for the structure and stability of carbon found in a possible deep carbon reservoir.

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