

High-pressure single-crystal X-ray diffraction and Raman spectroscopy of boltwoodite, $K_{0.63}Na_{0.37}[(UO_2)(SiO_3OH)](H_2O)_{1.5}$

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ABSTRACT

Uranyl silicates are common constituents of the oxidized portions of uranium ore deposits. They are also known to form on used nuclear fuel pellets under simulated geologic repository conditions. These phases can incorporate various cations, including higher actinides and fission products, which makes them relevant for studies that probe the stability of these phases in various contexts, including irradiation, high temperatures, and high pressures.

The changes in the single-crystal structure and Raman spectroscopy of the uranyl silicate mineral boltwoodite, $K_{0.63}Na_{0.37}[(UO_2)(SiO_3OH)](H_2O)_{1.5}$, have been investigated at 11 pressures from ambient to 16.8 GPa. The bulk modulus was determined to be 26.3(4) GPa from a third-order Birch-Murnaghan fit of the unit-cell volume vs. pressure. No obvious phase transition was observed between ambient pressure and 16.8 GPa. The structure is most easily compressed along the *a*-axis, which decreases by ca. 15% throughout the investigated pressure range, leading to distortions in the bonding geometries and higher coordination numbers of the interlayer cations. The *b*- and *c*-axes parallel to the uranyl silicate sheets are each compressed by ca. 4% compared to the ambient-pressure structure at 16.8 GPa, attributed to the uranyl silicate sheets becoming more highly corrugated with increasing pressure.

Previous experimental high-pressure work on uranium(VI) phases is limited due to the complexity of refining heavy atom crystal structures with disordered cations and/or water molecules, as well as the limitations imposed by the opening angle of the diamond-anvil cell used to achieve high pressures. A method for overcoming these challenges is presented here to facilitate further high-pressure studies of heavy element minerals and other phases.

Keywords: Boltwoodite, uranyl mineral, high-pressure X-ray diffraction, nuclear waste

INTRODUCTION

High-pressure studies of natural and synthetic uraninite, UO_{2+x} , abound because uraninite is the most abundant uranium ore and UO_2 is used as a fuel in many nuclear reactors (Gréaux et al. 2008; Idiri et al. 2004; Livneh and Sterer 2006). High-pressure studies of UO_2 and UO_{2+x} have identified a phase transition between the ambient-pressure fluorite-type phase, *Fm*3*m*, and the high-pressure cotunnite-type phase, *Pnma*, determined the bulk modulus of UO_2 , and described the changes in the Raman spectrum that accompany this phase transition (Idiri et al. 2004; Livneh and Sterer 2006). These characterizations inform geoscience and highlight how extreme conditions, such as high pressure, fundamentally change the structure and spectroscopic properties of well-known phases.

Previous high-pressure experimentation with U(VI) materials has employed powder X-ray diffraction (PXRD) techniques that are complimented with spectroscopic techniques or computational studies (Dyuzheva et al. 2001; Lipp et al. 2011; Shields et al. 2023; Zhang et al. 2014). PXRD is an attractive technique for high-pressure studies since diffraction from many crystallites in various orientations is collected regardless of the opening

angle of the DAC. The data collected from powder diffraction studies are sufficient for identifying phase changes, but do not allow for the refinement of individual atoms and a more detailed analysis of pressure-induced changes in the crystal structure, as would single-crystal X-ray diffraction (SC-XRD). Single-crystal experiments are more challenging due to the fixed orientation of the crystal(s) within the DAC and the limited opening angle of the DAC itself, but with sufficiently well-diffracting samples, high-pressure SC-XRD is possible.

Under simulated nuclear waste geological repository conditions, various minerals form on UO_2 and spent nuclear fuel, including uranyl-oxide hydrates, a uranyl silica hydrate, uranyl alkaline silica hydrates, uranyl peroxides, and a few phases not containing uranium (Finn et al. 1995; Hanson et al. 2005; Wronkiewicz et al. 1996). The uranyl alkaline silica hydrates uranophane $Ca[(UO_2)(SiO_3OH)]_2(H_2O)_5$, boltwoodite $K_{0.63}Na_{0.37}[(UO_2)(SiO_3OH)](H_2O)_{1.5}$, sodium boltwoodite $Na[(UO_2)(SiO_3OH)](H_2O)$, and sklodowskite $Mg[(UO_2)(SiO_3OH)]_2(H_2O)_6$, have a demonstrated ability to limit environmental mobility of uranium, fission products, and higher actinides that can be incorporated into their structures (Burns 1999; Burns and Klingensmith 2006; Finn et al. 1996; Klingensmith and Burns 2007). All four of these uranyl alkaline silica hydrates have crystal structures that contain sheets with the uranophane sheet anion topology (Fig. 1). Uranophane-type sheets consist of uranyl

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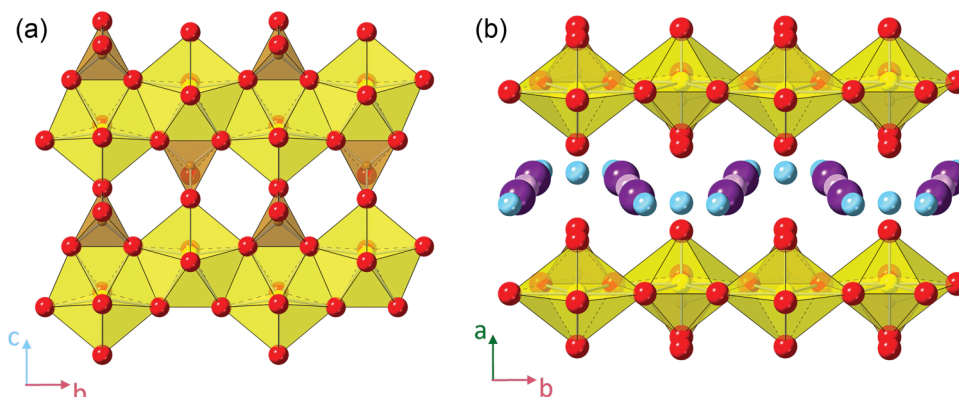


FIGURE 1. (a) The sheet structural unit of boltwoodite, $K_{0.63}Na_{0.37}[(UO_2)(SiO_3OH)](H_2O)_{1.5}$, comprised of uranyl pentagonal bipyramids (yellow) and silicate tetrahedra (orange) with O atoms shown in red. (b) Potassium cations (dark purple), sodium cations (pink), and water molecules (light blue spheres, with hydrogen atoms omitted) provide charge balance and bonding in the interlayer space of boltwoodite. All interlayer positions are partially occupied. (Color online.)

pentagonal bipyramids that share edges to form infinite chains that are connected into sheets via edge- and vertex-sharing with silicate tetrahedra (Fig. 1a). In the case of boltwoodite, the interlayer space is occupied by a mixture of potassium and sodium cations along with water molecules (Fig. 1b). All interlayer sites are partially occupied. Crystals of boltwoodite are well suited as a first uranium(VI) mineral for high-pressure single-crystal X-ray diffraction studies since they diffract strongly when exposed to X-rays. The methods established and results presented in this work lay the foundation for high-pressure SC-XRD study of other uranium(VI) phases relevant to the nuclear fuel cycle.

MATERIALS AND METHODS

Natural uranium minerals are radioactive owing to the presence of uranium and its decay products. All experiments were conducted by trained personnel in purpose-designed laboratories for handling radioactive isotopes.

Sample information

Boltwoodite $\{(K_{0.63}Na_{0.37})[(UO_2)(SiO_3OH)](H_2O)_{1.5}\}$ from near Rössing, Namibia, was investigated in this study. The same specimen was used for the first crystal structure determination by Burns (1998). The specimen consists of multiple clusters of orange to yellow blade-shaped crystals up to 1 cm in length. Single crystals with approximate dimensions of 15 μm by 30 μm and up to 100 μm in the third dimension were selected for study.

Characterization of boltwoodite at ambient pressure

Raman spectra for crystals of boltwoodite were collected using a Renishaw inVia instrument with a 785 nm excitation laser and a 20 $\times$ objective (Fig. 2). The laser power was attenuated to 5% to protect the sample from beam damage with 30 s exposure time and 3 accumulations per scan. The PeakFitPro package in OriginPro (2024) was used to fit the spectrum. Peaks were assigned according to the literature (Frankland et al. 2022; Frost et al. 2006). The two main regions of interest are the symmetric stretch, ν_1 , of the uranyl ion fit by two peaks at 789 and 796 cm^{-1} , and the ν_1 mode of the silicate tetrahedron fit by two peaks at 936 and 958 cm^{-1} (see Online Materials¹ Figs. S1 and S2). The presence of two peaks for the symmetric stretching mode of both the uranyl ion and the silicate tetrahedron is consistent with their coordination by a mixture of potassium and sodium cations in the interlayer space.

Single crystals of boltwoodite were mounted on cryogenic loops, and diffraction data were collected using a Rigaku XtaLAB Synergy-S diffractometer equipped with a microfocus MoK α radiation source. Data were processed using the CrysAlis Pro software package with absorption corrections applied using face

indexing methods (Agilent 2014). The structure was solved using intrinsic phasing (SHELXT) and refined by least-squares methods (SHELXL) through the OLEX2 graphical user interface (Dolomanov et al. 2009; Sheldrick 2015a, 2015b). The resulting structure is in accord with that reported earlier.

The average K:Na molar ratio of boltwoodite was determined by electron microprobe analysis at the Materials Characterization Facility of the University of Notre Dame. A Cameca SX100 with a 50 nA current, 15 kV power, and a 20 μm spot size, with 20 s counts on each peak, was used. Data were collected at three spots on two crystals, resulting in a total of six data points to determine the average ratio of K to Na. The following standards were used for electron-microprobe analysis: albite $[Na(AlSi_3O_8)]$ for Na, potassium feldspar $(KAlSi_3O_8)$ for K and Si, and a synthetic uranium dioxide pellet for U.

High-pressure experiments

Single-crystal X-ray diffraction data and Raman spectra were collected for crystals of boltwoodite contained within diamond-anvil cells (DACs) at elevated pressures. A One20DAC Diacell wide-angle DAC with a 120° full opening angle was used for pressures from 0.1 to 11 GPa. For pressures in the range of 11 to 20 GPa, a Spherical Seat DAC (SS-DAC) or iBX70 DAC, each with a 70° full opening angle, was used. All DACs were fitted with Boehler-Almax-style diamonds, featuring a culet diameter of 500 μm . Stainless steel gaskets of

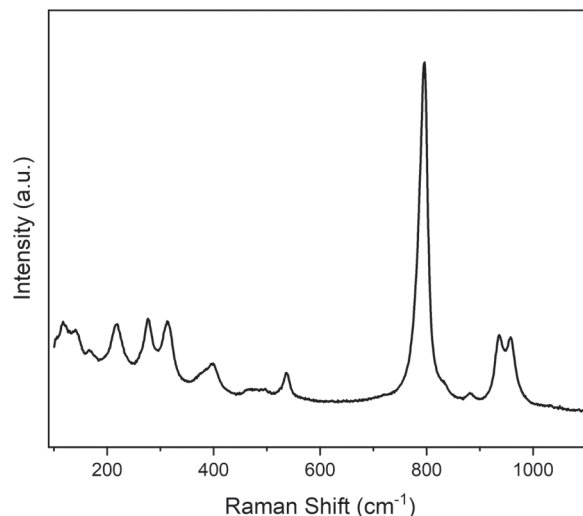


FIGURE 2. The ambient pressure Raman spectrum of boltwoodite, $K_{0.63}Na_{0.37}[(UO_2)(SiO_3OH)](H_2O)_{1.5}$.

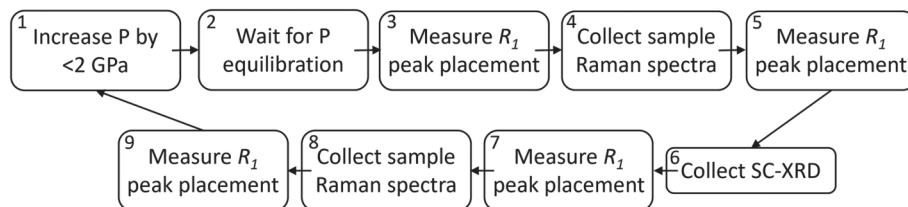


FIGURE 3. High-pressure data collection workflow.

250 μm thickness were pre-indented to a thickness of 40–60 μm with a central hole ca. 160 μm in diameter prepared by electro-discharge on a Boehler $\mu\text{Driller}$ equipped with a 160 μm tungsten carbide electrode.

In a DAC, there is a steep pressure gradient between the center of the diamond anvil and its edge (Bassett 2009). To ensure force is distributed equally in all directions, a hydrostatic pressure medium was used. A mixture of 4:1 methanol:ethanol (Me:EtOH) was used due to its comparatively high hydrostatic limit of 10.5 GPa (Klotz et al. 2009).

Ruby fluorescence was used to monitor the pressure applied to the sample in situ. One or two fragments of powdered “ruby” (corundum, $\text{Al}_2\text{O}_3\text{:Cr}^{3+}$) were loaded with each sample. Fluorescence spectra were collected using a Renishaw inVia instrument with a 532 nm excitation laser and a 20 $\times$ objective. The laser power was attenuated to 0.0001% to penetrate the diamond anvil while protecting the ruby from beam damage with 2 s exposure time and 3 accumulations per scan. When ruby is excited by a laser with a wavelength of 532 nm or less, its fluorescence spectrum exhibits a characteristic R_1 peak centered at 694.2 nm (Yamaoka et al. 2012). The shift of the R_1 peak has been well characterized with increasing pressure (Mao et al. 1978). In this work, the ruby fluorescence spectrum was fit using the PeakFitPro package in OriginPro (2024), and the pressure applied to the sample was calculated based on the following equation:

$$P = \frac{1904}{9.827} \left[\left(\frac{\lambda_0 + \Delta\lambda}{\lambda_0} \right)^{9.827} - 1 \right]$$

Here, P is the pressure in gigapascals (GPa), λ_0 is the initial placement of the R_1 peak, and $\Delta\lambda$ is the change in placement of the R_1 peak at elevated pressure (Lei et al. 2013; Mao et al. 1978).

Once the DAC was loaded, the general workflow of high-pressure experimentation followed the flow diagram shown in Figure 3.

The pressure calculated based on the position of the R_1 peak, measured in steps 3 and 5, was averaged and is reported as the pressure for Raman spectra collected prior to the diffraction experiments. Likewise, the pressures calculated based on the position of the R_1 peak, measured in steps 7 and 9, were averaged, and the value is reported as the pressure for Raman spectra collected after the diffraction experiments. The pressure calculated based on the position of the R_1 peak measured in steps 5 and 7 was averaged and is reported as the experimental pressure of the diffraction experiment. The difference in pressure before and after SC-XRD data was collected is reported as the error for each pressure.

Raman spectra for single crystals at high pressure were collected using a Renishaw inVia instrument with a 785 nm excitation laser and a 20 $\times$ objective. For the One20DAC the laser power was attenuated to 10% to penetrate the diamond anvil while protecting the sample from beam damage with 10 s exposure time and 5 accumulations per scan. For the SS/iBX DAC, the laser power was attenuated to 50% to penetrate the diamond anvil while protecting the sample from beam damage with 15 s exposure time and 5 accumulations per scan.

To maximize completeness despite the limited opening angle of the DAC, two or three crystals of boltwoodite in various orientations were loaded into a single DAC. When the blade-shaped crystals lie flat in their preferred orientation their a -axis is perpendicular to the surface (Fig. 4). In each loading, one crystal is placed in its preferred orientation while another is placed on its side (so the b - or c -axis is perpendicular to the surface) or placed on top of the first crystal also in its preferred orientation but offset by ca. 60° (Fig. 4). A crystal was milled using a focused ion beam (FIB) to cut the crystal at a 37° angle relative to its preferred orientation and then was loaded on the fabricated face so the crystal itself was oriented in such a way that none of its crystallographic axes were parallel to incident beams (Fig. 5). The results of the FIB-milling experiment did not provide significantly better crystallographic coverage.

Single-crystal X-ray diffraction (SC-XRD) data were collected at high pressures using a Rigaku XtalLAB Synergy-S diffractometer equipped with an AgK α radiation source. SC-XRD collections were optimized to obtain complete redundant data with a redundancy factor of 5, a resolution limit of 0.40 Å, and longer

collection times at higher angles. Single-crystal data were processed using the CrysAlis Pro software package with user-guided data reduction, including an imposed resolution limit of 0.70 Å since only diamond reflections were present in the 0.70 to 0.40 Å resolution range (Agilent 2014).

The effective opening angle of the DAC was optimized at each pressure by testing half-opening angles ranging from 60° to 52° for the 120° full-opening angle DAC and from 35° to 27° for the 70° full-opening angle DAC. The effective opening angle of the DAC is usually less than its full-opening angle, mainly due to the non-negligible thickness of the gasket around the sample (Tchoń and Makal 2021).

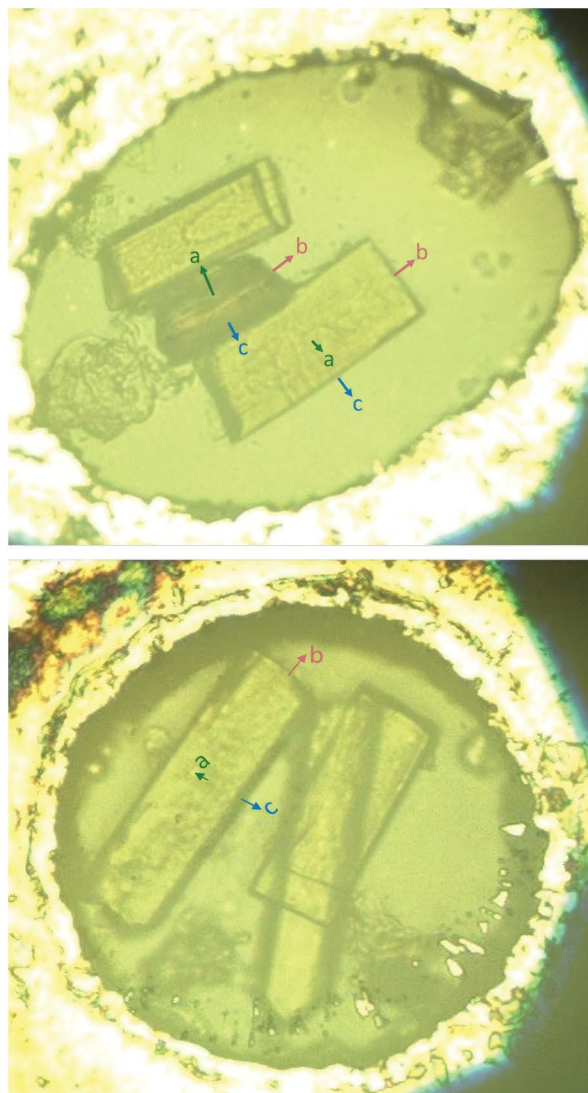


FIGURE 4. Crystals of boltwoodite loaded in the diamond-anvil cell in mixed orientations. (Color online.)

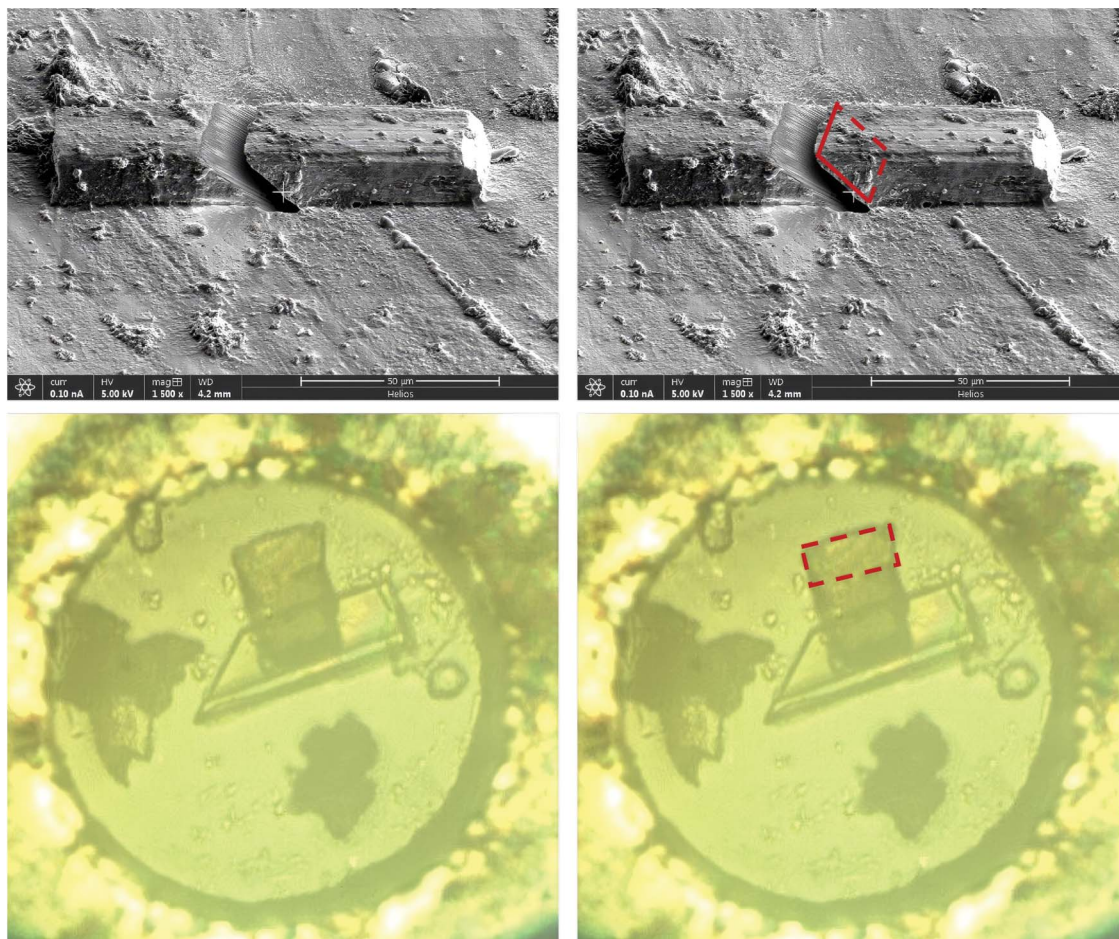


FIGURE 5. A crystal of boltwoodite cut at a 37° angle by FIB milling (top), loaded in a diamond-anvil cell on its fabricated face (bottom), with the fabricated face outlined in red (right). (Color online.)

Absorption corrections based on the crystal dimensions and chemistry, diamond-anvil thickness, hydrostatic pressure medium, gasket thickness, and sample chamber radius were applied using the ABSORB program (Angel 2004). The SORTAV package of the WinGX suite was used to merge the *hkl* files of each crystal after high-pressure absorption corrections had been applied to maximize the completeness of the model for refinement (Farrugia 2012). Structures were solved using intrinsic phasing methods (SHELXT) and refined by least-squares methods (SHELXL) through the OLEX2 graphical user interface (Dolomanov et al. 2009; Sheldrick 2015a, 2015b). Structure models were refined against the *hkl* file of the primary component and a merged *hkl* file created using SORTAV.

Continuous symmetry measurement (CSM) analysis was used to determine the distortion of the U, Si, and K coordination polyhedra of boltwoodite at each pressure. This method compares the crystallographically determined atomic positions to those of ideal polyhedra with the same number of vertices and reports the normalized root-mean-square deviation, *S*, from the ideal reference polyhedron, *S* = 0, where $0 \leq S \leq 100$ (Pinsky and Avnir 1998).

At the end of high-pressure experimentation, Raman spectra were collected for the samples in the de-pressurized DAC. Crystals were recovered if possible, and post-pressurization diffraction data and Raman spectra were collected as described in the “Preliminary Characterization” section.

RESULTS AND DISCUSSION

The ambient-pressure single-crystal structure of boltwoodite (Fig. 1), $\text{K}_{0.63}\text{Na}_{0.37}[(\text{UO}_2)(\text{SiO}_3\text{OH})](\text{H}_2\text{O})_{1.5}$, was refined in space group $P2_1$ with unit-cell parameters $a = 7.0412(5)$ Å,

$b = 7.0458(3)$ Å, $c = 6.6379(3)$ Å, and $\beta = 105.087(7)^\circ$. The ambient-pressure structure model agrees well with the previously reported structure (Burns 1998). However, the ratio of K to Na in the formula reported here differs slightly from that reported by Burns (1998), reflecting the results of electron microprobe data collected as part of this study (Table 1).

The ambient-pressure structure was used as the initial model for refining the structure of the first high-pressure data set collected at 1.2 GPa. The structure of boltwoodite for each consecutive pressure point was refined using the structure from the previous pressure point as the starting model. The structure models had R_1 values ranging from 2.42 to 4.61% and wR_2 values of 5.22 to 11.68% (Online Materials¹ Table S1) when refined against the *hkl* values of the primary component, and R_1 values from 2.28 to 4.30% and wR_2 values of 5.22 to 11.26% (Table 2) when refined against the merged *hkl* file. The level of completeness for structure refinement was substantially improved by merging the *hkl* files of multiple crystals at the same pressure, and these structures will be used in the following discussion. Ten high-pressure structures, ranging from 1.2 to 16.8 GPa, were refined. No H atom positions were refined. CIFs for all structures are available in the Crystallography Open Database.

TABLE 1. Electron microprobe data (wt%) of boltwoodite

	Average of 6	St. dev.		Struct.
Na ₂ O	2.61	0.13	Na	0.373(3)
K ₂ O	6.7	0.5	K	0.627(2)
SiO ₂	14.5	0.5	Si	1
UO ₃	64.8	1.3	U	1
H ₂ O	8.5 ^a			
Total	97.1			

^a Calculated from stoichiometry.

Whereas the sheet structure of boltwoodite at ambient pressure conforms to $P2_1/m$ the placement and variable occupancy of the interlayer cations requires $P2_1$, as discussed by Burns (1998). Because of this, the structures reported herein have been solved in $P2_1$, as discussed in the body of this work. Figure 6 illustrates the naming scheme for the atoms that will be used throughout the discussion that follows.

No obvious phase transition was observed for boltwoodite at pressures up to 16.8 GPa. A third-order Birch-Murnaghan fit of the unit-cell volume at each pressure point gave the bulk modulus, $K_0 = 26.3(4)$ GPa, and its pressure derivative, $K'_0 = 9.18(11)$ GPa (Fig. 7). Unsurprisingly, the sheet-based structure of boltwoodite is more compressible than the higher-dimensional structures of UO₂ or α -U₃O₈, which have bulk moduli of 198(2) and 78 GPa, respectively (Idiri et al. 2004; Shukla et al. 2023). A synthetic uranium(VI) carboxyphosphonate (UCP) compound, (UO₂)(O₃PCH₂CO₂H), crystallizes with the same sheet topology as boltwoodite and has a reported bulk modulus of 18.1(1) GPa (Spencer et al. 2014). The UCP compound features phosphate tetrahedra capped with carboxyl groups, oriented toward the interlayer space, whereas boltwoodite is composed of silicate tetrahedra capped by hydroxyl groups (Spencer et al. 2014). Where the sheets of the UCP compound are held together via hydrogen bonding of the carboxyl groups, the sheets of boltwoodite are held together by bonds with interlayer cations. Additionally, the sheets of the UCP compound are offset in an “ABAB” packing sequence, whereas the sheets of boltwoodite are aligned (Fig. 1). Due to these differences, it is not surprising that the bulk modulus of boltwoodite indicates it is less

compressible than the UCP compound. However, it is notable that the bulk modulus of boltwoodite is similar to that of the uranyl peroxide nanocluster U₆₀, [UO₂(O₂)(OH)]₆₀⁶⁰⁻, for which the bulk modulus is 25(2) GPa, more so than that of the UCP compound (Turner et al. 2017).

The lengths of a , b , and c decrease by 1.073(8), 0.2850(4), and 0.2742(13) Å over the studied pressure range, respectively (Fig. 8), corresponding to ca. 15% for a and ~4% for b and c . The a -axis is roughly parallel to the uranyl ion and perpendicular to the uranyl silicate sheets (Fig. 1). The decrease in the a -axis indicates some shortening of the uranyl bond and/or compression of the interlayer space. Interlayer cations form weak bonds with the uranyl ion O atoms, as well as weak bonds with O atoms of interlayer water molecules; therefore, it is more likely that the interlayer is modified rather than the stronger uranyl bonds.

At ambient pressure, the interlayer K cation is seven-coordinated by four uranyl O (O_{yl}) atoms (O1 and O2), two H₂O groups (O7), and one hydroxyl group (O6). The longest of these is K–O6 at 3.27(2) Å, with longer K–O separations being ignored because they are not necessary to meet the bond valence requirements of the K site (Tables 3 and 4) (Burns 1998). With increasing pressure, the coordination environment about the interlayer K cation changes, with additional O atoms moving into the range of likely bonding interactions. However, reported bond-valence parameters are not applicable to high-pressure structures, and it is not straightforward to determine which of the longer K–O interatomic distances may correspond to bonding interactions. If the 3.27(2) Å interatomic distance is used as an arbitrary threshold for coordination of the K cation, its coordination sphere is K- ϕ_9 at 3.4, 10.9, and 16.8 GPa and K- ϕ_{10} at 6.5, 7.8, 9.1, 12.3, and 14.8 GPa (Table 4). Because this threshold for considering an interaction to be a bond is relatively arbitrary, it is necessary to inspect the Raman spectra at each pressure to ascertain whether there is evidence for changed bonding environments. Above 10.5 GPa, the hydrostatic pressure medium hardens, leading to pressure gradients of up to 1.8 GPa across the face of the diamond anvil at an average pressure of 18 GPa (Klotz et al. 2009), and further necessitates complementary Raman spectroscopy.

TABLE 2. Crystallographic parameters for the ambient and high-pressure structures of boltwoodite, K_{0.63}Na_{0.37}[(UO₂)(SiO₃OH)](H₂O)_{1.5} refined against the merged hkl file of all components

P (GPa)	0.0	1.2	3.4	4.8	6.5	7.8	9.1	10.9	12.3	14.8	16.8
σP (GPa)	0	0.4	0.0018	0.16	0.07	0.2	0.03	0.30	0.3	0.2	0.05
a (Å)	7.05879(19)	6.9020(5)	6.6627(4)	6.5304(5)	6.430(2)	6.3684(13)	6.281(4)	6.239(3)	6.214(3)	6.094(9)	5.993(8)
b (Å)	7.04576(10)	7.0139(3)	6.9407(3)	6.9113(3)	6.8773(4)	6.8556(3)	6.8329(7)	6.8094(10)	6.8094(4)	6.7721(4)	6.7567(4)
c (Å)	6.63767(10)	6.6112(18)	6.5602(17)	6.5396(18)	6.5004(5)	6.4803(4)	6.4637(9)	6.4340(10)	6.380(12)	6.3815(15)	6.3602(13)
β (°)	104.955(2)	105.279(14)	105.443(12)	105.315(16)	105.365(18)	105.352(13)	105.28(3)	105.26(3)	105.67(12)	105.90(7)	105.77(7)
V (Å ³)	318.939(12)	308.77(9)	292.41(8)	284.67(8)	277.17(9)	272.83(6)	267.58(16)	263.71(16)	259.9(5)	253.3(4)	247.9(3)
ρ (g/cm ³)	4.366	4.509	4.761	4.891	5.024	5.104	5.204	5.28	5.357	5.498	5.619
Reflections collected	12086	932	906	662	609	580	521	505	264	282	266
Reflections int.	6949	2282	2614	2302	2189	2369	1916	825	1141	1651	1646
Data	3778	932	906	662	609	580	521	505	264	282	266
Data ($I > 2\sigma$)	3406	858	818	610	563	538	465	435	245	253	237
R_{int}	0.0352	0.0613	0.0453	0.0384	0.0385	0.0362	0.0541	0.0327	0.0295	0.0542	0.057
Restraints	1	1	1	1	1	1	1	1	1	1	1
Parameters	112	54	59	59	54	54	54	54	54	54	55
GOF	1.070	1.102	1.117	1.147	1.108	1.084	1.092	1.078	1.106	1.113	1.132
Restr. GOF	1.070	1.101	1.116	1.146	1.107	1.083	1.091	1.076	1.103	1.11	1.129
R_1 ($I > 2\sigma$)	0.0242	0.0348	0.0339	0.0256	0.0245	0.0228	0.0302	0.0346	0.0306	0.0342	0.0373
R_1 (all data)	0.0283	0.0394	0.0400	0.0294	0.0284	0.0271	0.0402	0.0455	0.0344	0.0420	0.0448
wR2 (all data)	0.0522	0.0825	0.0842	0.0582	0.0598	0.0558	0.0610	0.0816	0.0760	0.0851	0.0951
Largest diff. peak	5.816	5.066	6.232	2.118	1.797	2.066	1.837	2.675	2.272	1.832	2.102
Largest diff. hole	−1.524	−2.243	−1.352	−1.456	−1.151	−0.998	−1.317	−1.364	−0.89	−1.036	−1.118

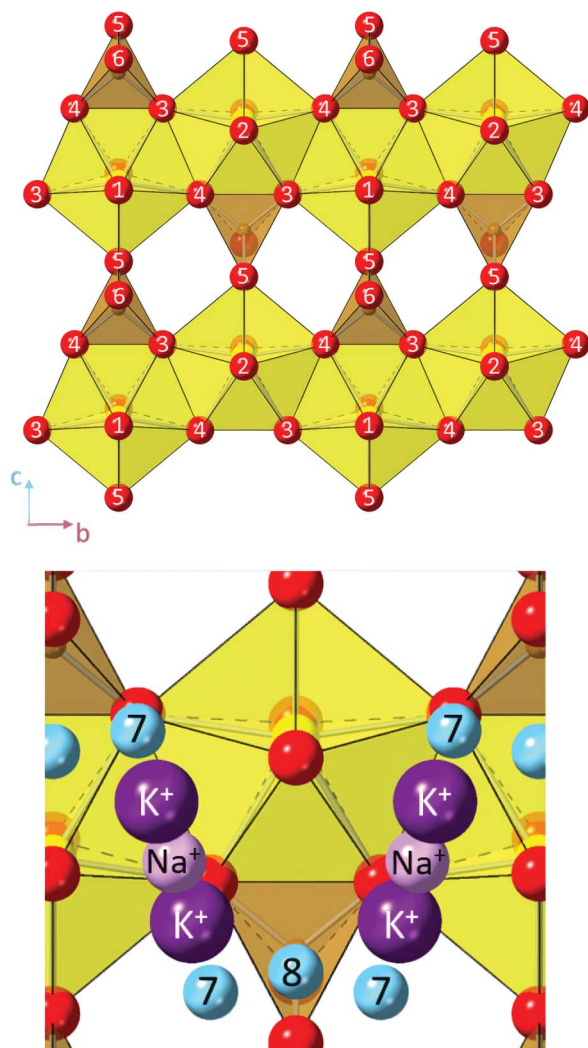


FIGURE 6. Labeled sheets and interlayer of boltwoodite. Uranyl pentagonal bipyramids (yellow) and silicate tetrahedra (orange) share O atoms (red spheres numbered for discussion) to form the sheet structure. The interlayer space is occupied by potassium cations (dark purple spheres), sodium cations (pink spheres), and water molecules (light blue spheres numbered for discussion). All interlayer sites are partially occupied. (Color online.)

At ambient pressure, the silicate symmetric stretching region in the Raman spectrum of boltwoodite is characterized by peaks at 936 and 958 cm^{-1} (Fig. 2). The existence of two peaks for the ν_1 stretch of the silicate tetrahedron likely reflects differences in coordination of the hydroxyl group (O6) that protrudes into the interlayer and coordinates to the partially occupied K site. In contrast, O3, O4, and O5 are shared between the Si and U centers and do not coordinate interlayer cations at ambient pressure.

For crystals at ambient pressure to 4.8 GPa, the silicate symmetric stretching peaks in the Raman spectra are consistently separated by 22 cm^{-1} and shift to higher wavenumbers with increasing pressure, indicating that the Si-O bond lengths shorten, but the silicate tetrahedron experiences no change in its local bonding environment (Fig. 9). The geometric

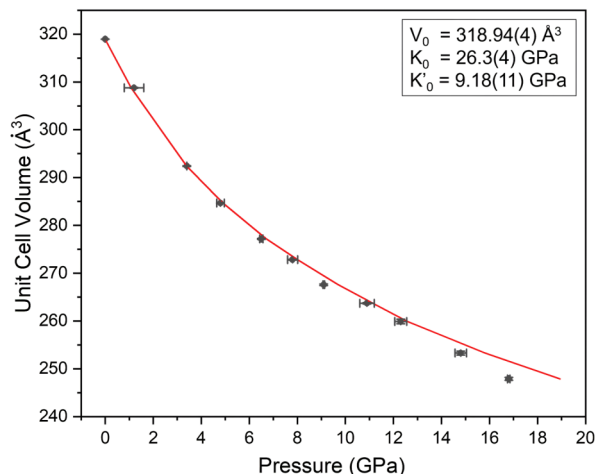
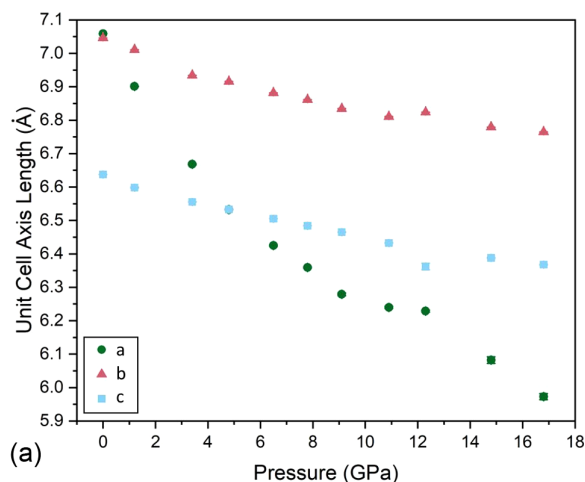
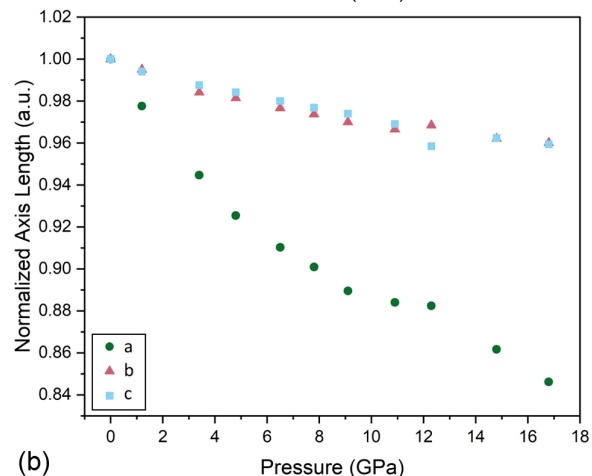


FIGURE 7. Pressure dependence of the unit-cell volume of boltwoodite. Third-order Birch-Murnaghan EOS fit shown in red with fit parameters displayed in the legend. Error bars represent the range 1 σ from the reported value. (Color online.)



(a)



(b)

FIGURE 8. Pressure-induced change in (a) unit-cell axes lengths and (b) normalized unit-cell axes lengths. (Color online.)

TABLE 3. Interatomic distances between the potassium cation, K, and uranyl O atoms, O1 and O2, with increasing pressure

P (GPa)	K-O1 (Å)	K-O1 (Å)	K-O2 (Å)	K-O2 (Å)	<K- Φ uranyl> (Å)
0	2.75(2)	3.033(19)	2.56(2)	2.80(2)	2.79(4)
1.2	2.54(3) ^{a,b}	2.78(2) ^{a,b}	2.76(3) ^{a,b}	2.96(2) ^{a,b}	2.76(5)
3.4	2.55(2) ^a	3.031(18) ^b	2.415(14) ^{a,b}	2.780(14) ^b	2.69(3)
4.8	2.77(2)	2.891(17) ^{a,b}	2.392(16) ^a	2.780(16)	2.71(3)
6.5	2.76(2)	2.834(16) ^a	2.530(18) ^b	2.767(15)	2.72(3)
7.8	2.78(3)	3.16(2) ^{a,b}	2.74(2) ^{a,b}	2.97(2) ^{a,b}	2.91(5) ^b
9.1	2.56(3) ^{a,b}	3.01(2) ^b	2.44(3) ^{a,b}	2.76(3) ^b	2.69(6) ^b
10.9	2.87(6) ^b	3.43(4) ^{a,b}	3.01(6) ^{a,b}	3.04(5) ^{a,b}	3.09(11) ^b
12.3	2.58(5) ^{a,b}	3.29(6) ^a	2.61(4) ^b	2.97(8)	2.86(12)
14.8	2.41(4) ^a	2.83(4) ^{a,b}	2.40(4) ^{a,b}	2.62(4) ^{a,b}	2.57(8)
16.8	2.82(6) ^b	3.00(6)	2.68(5) ^b	3.00(4) ^{a,b}	2.88(11)

^a Indicates the listed interatomic distance and that of the ambient-pressure structure are statistically different.

^b Indicates the listed interatomic distance and that of the previous pressure structure are statistically different.

TABLE 4. Interatomic distances between the interlayer potassium cation and O atoms in the form of the hydroxyl group of the silicate tetrahedron (O6), the O atoms of the interlayer water molecules (O7), and the equatorial O atoms of the uranyl bipyramid (O3, O4, and O5)

P (GPa)	K-OH6 (Å)	K-H ₂ O7 (Å)	K-H ₂ O7 (Å)	K-O4 (Å)	K-O5 (Å)	K-OH6 (Å)	K-O3 (Å)
0	3.27(2)	2.87(2)	2.99(2)	3.312(19)	—	—	3.33(2)
1.2	3.296(17)	2.92(3)	2.97(3)	3.041(16) ^{a,b}	3.414(19)	3.322(16)	—
3.4	3.147(16) ^{a,b}	2.78(2) ^{a,b}	3.93(2)	2.961(13) ^{a,b}	3.205(15) ^b	3.257(17)	—
4.8	3.08(2) ^a	2.67(3) ^a	2.87(3) ^a	2.79(2) ^{a,b}	3.161(17)	3.280(15)	—
6.5	3.05(2) ^a	2.610(17) ^a	2.89(3)	2.76(2) ^a	3.037(16) ^b	3.262(17) ^b	—
7.8	2.47(2) ^{a,b}	2.616(15) ^a	2.69(2) ^{a,b}	3.03(3) ^{a,b}	2.83(2) ^b	2.98(3) ^b	—
9.1	2.66(3) ^{a,b}	2.47(4) ^{a,b}	2.97(5) ^b	—	3.01(2) ^b	3.20(3) ^b	3.00(4) ^a
10.9	2.08(5) ^{a,b}	2.53(4) ^a	3.32(5) ^{a,b}	—	2.65(6) ^b	2.85(5)	2.93(6) ^a
12.3	2.47(4) ^{a,b}	2.45(4) ^a	2.97(7) ^b	—	2.52(7)	3.08(6)	2.67(4) ^{a,b}
14.8	2.73(5) ^{a,b}	2.43(3) ^a	3.01(5)	2.56(4) ^a	2.72(4)	—	—
16.8	2.09(7) ^{a,b}	2.44(4) ^a	2.98(5)	—	2.50(6)	2.94(7)	2.74(6)

^a Indicates the listed interatomic distance and that of the ambient-pressure structure are statistically different.

^b Indicates the listed interatomic distance and that of the previous pressure structure are statistically different.

parameters of the silicate tetrahedron have been analyzed using continuous symmetry measurement (CSM) analysis (Pinsky and Avnir 1998), which indicates the silicate tetrahedron is minimally distorted (recall $0 < S < 100$ where $S = 0$ is the ideal polyhedron) compared to both its ideal geometry and its ambient-pressure shape from ambient pressure to 4.8 GPa (Table 5). Similarly, the geometry of the seven-coordinate polyhedron about the potassium cation is minimally distorted from ambient pressure to 4.8 GPa (Table 6; Fig. 10a).

For crystals at pressures between 6.5 and 7.8 GPa, the separation of the two silicate-related peaks in the ca. 950–1000 cm^{-1} region of the Raman spectrum is 11 cm^{-1} , indicating the local bonding environment around the silicon center has become more symmetric. The next nearest O atom after those considered coordinated to the potassium center at ambient pressure is O4 at 6.5 GPa and O5 at 7.8 GPa (Figs. 10b and 10c, respectively), each of which are within the 3.27(2) Å “threshold” for interaction with the potassium cation (Table 4). Therefore, the change in the silicate-related peak splitting of the Raman spectrum is attributed to the coordination of the potassium cation to an O atom shared between the U and Si centers of the sheet structure, with the potassium cation coordination increasing to eight-coordinate in the 6.5–7.8 GPa pressure range (Figs. 10b and 10c). At both 6.5 and 7.8 GPa, the eight-coordinate potassium cation polyhedra are best described as a biaugmented trigonal prism based on CSM analysis of 13 potential eight-coordinate polyhedra (Figs. 10b and 10c). CSM analysis reveals that the silicate tetrahedron is 0.715 to 0.989 units distorted from its ambient pressure structure at 6.5 and 7.8 GPa, respectively (Table 5).

At 9.1 GPa, the separation of the silicate-related peaks in the Raman spectrum is only 4 cm^{-1} , and the distortion of the tetrahedron is 0.748 units compared to the ambient-pressure structure. This change in the silicate symmetric stretching region of the Raman spectrum indicates that both O4 and O5 now coordinate to the potassium cation, as they are at a similar distance from it. The resulting nine-coordinate polyhedron is best described as a muffin based on CSM analysis of 13 potential nine-coordinate polyhedra (Fig. 10d).

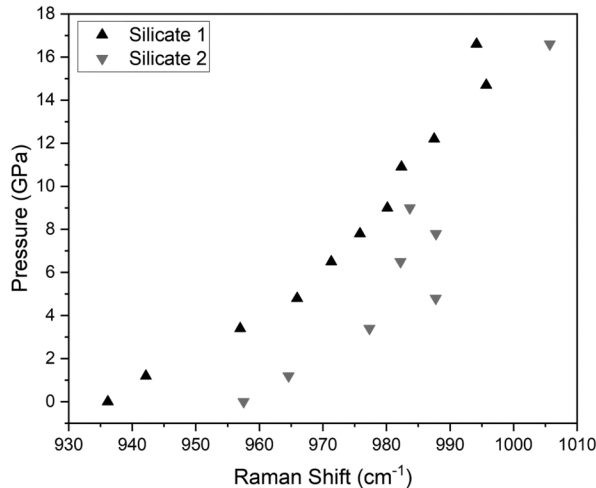


FIGURE 9. Pressure dependence of silicate peak placement in the Raman spectrum of boltwoodite.

TABLE 5. Pressure-dependent CSM analysis of the silicate tetrahedron

P (GPa)	Dev. from Ideal
0	0.333
1.2	0.320
3.4	0.421
4.8	0.311
6.5	0.715
7.8	0.989
9.1	0.748
10.9	1.336
12.3	0.346
14.8	0.874
16.8	0.992

For crystals between 10.9 and 14.8 GPa, there is no resolvable separation between the silicate-related peaks in the Raman spectrum. This indicates a symmetric bonding environment around the silicon center, which in turn indicates O3, O4, O5, and O6 all

interact with the interlayer K cation throughout the 10.9 to 14.8 GPa pressure range. The resulting 10-coordinate K cation polyhedron is best described as a sphenocorona based on CSM analysis of 13 potential 10-coordinate polyhedra (Fig. 10e).

At 16.8 GPa, the silicate-related peaks in the Raman spectrum are split with a separation of 11 cm^{-1} , indicating the K cation is likely no longer 10-coordinate as it was from 10.9–14.8 GPa (Fig. 10e). One could argue that a separation of 11 cm^{-1} indicates the potassium cation is eight-coordinate, as in the 6.5 or 7.8 GPa structure (Figs. 10b and 10c). Since the interlayer space has been compressed by ca. 0.4 Å from 7.8 to 16.8 GPa, it seems more likely that the potassium cation is either nine-coordinate, as in the 9.1 GPa structure (Fig. 10d), or 11-coordinate by coordinating O3 O atoms from the sheet above and below (Fig. 10f). At 16.8 GPa, an O6 hydroxyl group is only $2.09(7)\text{ Å}$ from the potassium center, which is an unrealistically short K-O interaction distance

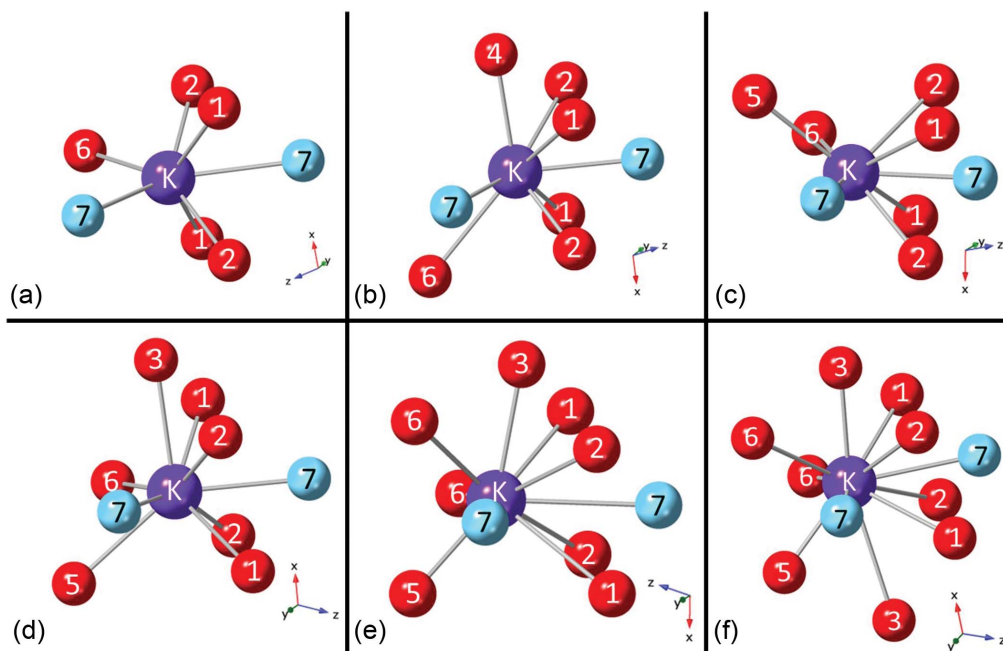


FIGURE 10. Proposed coordination of the interlayer potassium cation (purple spheres) with interlayer water molecules (light blue spheres) and O atoms from the uranyl silicate sheet structure (red spheres) at (a) ambient pressure to 4.8 GPa, (b) 6.5 GPa, (c) 7.8 GPa, (d) 9.1 GPa, (e) 10.9 to 14.8 GPa, and (f) 16.8 GPa. (Color online.)

TABLE 6. Pressure-dependent continuous symmetry measurement results for the interlayer potassium cation coordination sphere in boltwoodite

P (GPa)	Coord. #	Polyhedral Shape	Additional O Atoms	Dev. from Ideal
0	7	Capped trigonal prism	—	3.385
1.2	7	Capped trigonal prism	—	4.427
3.4	7	Capped trigonal prism	—	7.666
4.8	7	Capped trigonal prism	—	7.708
6.5	8	Biaugmented trigonal prism	O4	6.559
7.8	8	Biaugmented trigonal prism	O5	9.195
9.1	9	Muffin	O3 and O5	4.051
10.9	10	Sphenocorona J87	O3, O5, and O6	5.892
12.3	10	Sphenocorona J87	O3, O5, and O6	5.049
14.8	10	Sphenocorona J87	O3, O5, and O6	3.830
16.8	9	Muffin	O3 and O5	11.181
16.8	10	Sphenocorona J87	O3, O5, and O6	5.676
16.8	11	Capped pentagonal antiprism J11	2 × O3, O5, and O6	7.366

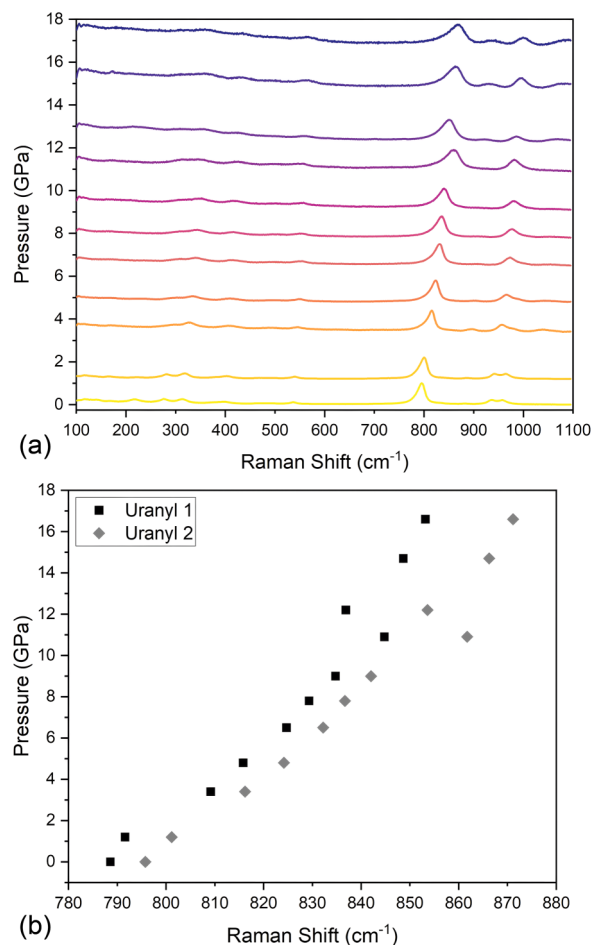


FIGURE 11. (a) Raman spectra of boltwoodite from ambient pressure to 16.8 GPa. (b) Placement of the uranyl peaks in the Raman spectra relative to pressure. (Color online.)

that may favor a nine-coordinate environment around the K cation. In the 11-coordinate case, O3 atoms can be shared by a K cation above and below the sheet, thereby decreasing the electron density available for donation to each and creating a less symmetric bonding environment around the silicon center. Based on the CSM analysis of the 9- and 11-coordinate potassium polyhedra, it seems the 11-coordinate case is more likely.

The interlayer Na cation coordination cannot be described in detail owing to the difficulty in refining the water molecules that

are vital to its coordination environment at pressures above 3.4 GPa (Burns 1998). In the 16.8 GPa structure, the O8 site could not be adequately refined, so the occupancy of O7 was increased to satisfy the coordination needs of both the potassium and sodium interlayer cations and the overall 7.5 O atoms present within the structure. Due to these uncertainties, tables related to the changing coordination of the sodium cations are presented in the SI (Online Materials¹ Tables S2–S4).

The uranyl pentagonal bipyramid remains mostly undisturbed throughout the studied pressure range, and maintains a polyhedral structure best described as a Johnson pentagonal bipyramid (Online Materials¹ Table S5). However, the uranyl symmetric stretching peak positions in the Raman spectrum shift to higher wavenumbers with increasing pressure (Fig. 11). Although the U–O_{yl} bond lengths change modestly compared to the ambient pressure structure through the studied pressure range, the bonding environment of the O_{yl} atoms changes as the coordination of the interlayer potassium cation changes. From ambient pressure to 16.8 GPa, the K–O_{yl} interactions are the strongest of the potassium cation. However, as the interlayer space is compressed and the potassium cation interacts with O atoms that were previously out of bonding range (O3, O4, O5, and a second O6), less electron density may be required from the O_{yl} atoms as the K cation is otherwise satisfied. Therefore, although the uranyl bond lengths are not changing appreciably, there may be slightly more effective electron density between U–O_{yl} since the bond valence requirements of K⁺ can be otherwise met. At all pressures other than 10.9 GPa, the calculated uranyl bond lengths based on the uranyl peak placement in the Raman spectrum are consistent within 1–3 σ of the reported crystallographic values (Online Materials¹ Table S6) (Bartlett and Cooney 1989).

From ambient pressure to 9.1 GPa, the separation of the uranyl peaks in the Raman spectra is 7–9 cm^{−1}, whereas over the range of 10.9–16.8 GPa, the peak separation is ca. 17 cm^{−1} (Fig. 11). The splitting of the uranyl-related peaks in the Raman spectrum indicates there is an asymmetric bonding environment around the uranyl ion, which can be attributed to the variation in the interlayer cation occupancies. The increased separation of the uranyl-related peaks in the Raman spectrum coincides with the pressure range at which the interlayer K cation coordinates with the O atoms shared between U and Si of the sheet structure (O3, O4, and O5) and becomes 10-coordinate (Table 6).

In the uranyl silicate sheets, the only bond lengths that significantly differ between the ambient-pressure structure and that at 16.8 GPa are those of U–O4 and U–O5

TABLE 7. Bond lengths of uranyl pentagonal bipyramids in boltwoodite from 0 to 16.8 GPa

P (GPa)	U–O1 (Å)	U–O2 (Å)	U–O3 (Å)	U–O3 (Å)	U–O4 (Å)	U–O4 (Å)	U–O5 (Å)
0	1.801(5)	1.805(5)	2.319(11)	2.437(11)	2.303(10)	2.446(10)	2.250(3)
1.2	1.777(10)	1.807(9)	2.263(11) ^{a,b}	2.485(12) ^{a,b}	2.356(14) ^{a,b}	2.392(15) ^{a,b}	2.248(10)
3.4	1.801(10)	1.780(9)	2.386(13) ^{a,b}	2.403(14) ^b	2.207(11) ^{a,b}	2.450(12) ^b	2.244(9)
4.8	1.728(16) ^{a,b}	1.765(17)	2.287(10) ^b	2.450(10) ^b	2.286(10) ^b	2.394(9) ^{a,b}	2.235(6)
6.5	1.741(17) ^a	1.730(19) ^a	2.380(10) ^{a,b}	2.402(10) ^b	2.208(8) ^{a,b}	2.420(8)	2.231(7)
7.8	1.757(19)	1.729(18) ^a	2.276(10) ^{a,b}	2.383(9) ^a	2.285(10) ^b	2.424(10)	2.226(7) ^a
9.1	1.65(3) ^{a,b}	1.66(4) ^a	2.362(13) ^b	2.385(15)	2.202(12) ^{a,b}	2.393(11) ^a	2.227(8)
10.9	1.64(3) ^a	1.67(3) ^a	2.391(16) ^a	2.394(16)	2.141(15) ^{a,b}	2.424(13)	2.227(11)
12.3	1.82(3) ^b	1.78(3)	2.29(3) ^b	2.29(4) ^a	2.26(3) ^b	2.43(5)	2.19(4)
14.8	1.80(3)	1.73(2) ^a	2.34(3)	2.38(4)	2.16(3) ^a	2.39(4)	2.19(3)
16.8	1.80(5)	1.70(3) ^a	2.34(4)	2.37(5)	2.19(3) ^a	2.33(5)	2.16(3) ^a

^a Indicates the listed interatomic distance and that of the ambient-pressure structure are statistically different.

^b Indicates the listed interatomic distance and that of the previous pressure structure are statistically different.

(Table 7; Online Materials¹ Table S7). However, the *b*- and *c*-axis parameters at 16.8 GPa are smaller than those of the ambient-pressure structure by 0.270 and 0.2742 Å, respectively. The minimal changes in U–O and Si–O bond lengths from ambient pressure to 16.8 GPa point to increasing corrugation of the uranyl silicate sheets with increasing pressure, which accounts for the changes in the *b*- and *c*-axis parameters. Along the *b*-axis, the dihedral U–O3/O4–U angle decreases by ca. 10.5° from ambient pressure to 16.8 GPa, indicating the sheet becomes more corrugated along the *b*-axis, which decreases the unit-cell parameter value. Along the *c*-axis, the U–O5–Si angle decreases by ca. 9°, and the U–O3/O4–Si dihedral angle increases by ca. 0.5° from ambient pressure to 16.8 GPa, which is consistent with the sheet becoming more corrugated along the *c*-axis, thereby causing the unit-cell parameter to decrease.

IMPLICATIONS

Crystal structure determination is non-trivial for heavy atom mineral structures, particularly those with disordered cations or water molecules and/or partially occupied sites, such as boltwoodite, $K_{0.63}Na_{0.37}[(UO_2)(SiO_3OH)](H_2O)_{1.5}$, which is known to form on used nuclear fuel under simulated geologic repository conditions. High-pressure structure determination is further limited by the opening angle of the diamond-anvil cell, which limits the possible completeness of data collection for a given crystal orientation. These difficulties have been overcome for the structural determination of boltwoodite at pressures up to 16.8 GPa, and Raman spectroscopy aided in the validation of crystallographic structure models. Until now, powder X-ray diffraction and computational methods have been favored for high-pressure studies of uranium(VI) phases due to the complications associated with refining the structure of heavy elements, particularly with the limited opening angles of diamond-anvil cells. Due to this limitation in the techniques used, previous works have not directly determined pressure-induced structural changes at the atomic level, except through computational methods. The current work shows that the body of experimental literature can be expanded to validate computational work, and furthermore, to investigate the structure-property relationships of uranium(VI) minerals and other heavy element structures at the atomic level.

Comparing the bulk moduli of boltwoodite from this work and the uranium(VI) carboxyphosphonate (UCP) compound, $(UO_2)(O_3PCH_2CO_2H)$, which are 26.3(4) and 18.1(1), respectively (Spencer et al. 2014), it is clear that similar ambient-pressure crystal structures are not indicative of similar compressibilities. Furthermore, the bulk modulus of boltwoodite is more similar to that of the uranyl peroxide nanocluster U_{60} , $[UO_2(O_2)(OH)]_{60}^{60-}$, for which the bulk modulus is 25(2) GPa (Turner et al. 2017). By expanding the body of high-pressure literature, future work can be done to describe the similarities in structure-property relationships that may have implications for how structures will respond in other extreme conditions.

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High Pressure Structure and Spectroscopy of Boltwoodite, $\text{K}_{0.63}\text{Na}_{0.37}[(\text{UO}_2)(\text{SiO}_3\text{OH})](\text{H}_2\text{O})_{1.5}$

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Supplementary Information

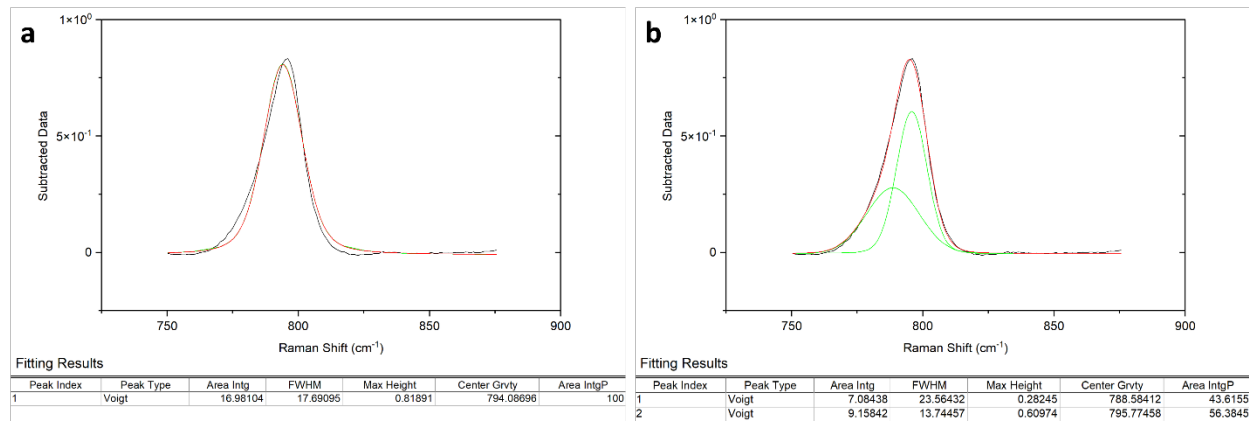


Figure S-1: a) Single curve fit results and b) dual curve fit results of the uranyl ν_1 region of the ambient pressure Raman spectrum of boltwoodite. Akaike's Information Criterion Test results indicate the fit shown in (b) is 6.88292×10^{60} times more likely than the fit shown in (a). Likewise, Bayesian Information Criterion Test results in a difference greater than 10, conclusively indicating the fit shown in (b) is correct.

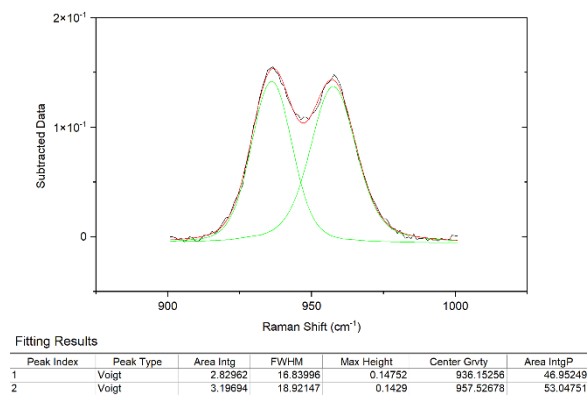


Figure S-2: Fit of the silicate ν_1 stretching region of the ambient pressure Raman spectrum of boltwoodite.

Table S-1: Crystallographic parameters for the ambient and high pressure structures of boltwoodite, $K_{0.63}Na_{0.37}[(UO_2)(SiO_3OH)](H_2O)_{1.5}$ refined against the primary component *hkl* file.

P (GPa)	0.0	1.2	3.4	4.8	6.5	7.8
σP (GPa)	0	0.4	0.0018	0.16	0.07	0.2
<i>a</i> (Å)	7.05879(19)	6.9029(5)	6.6626(4)	6.5304(5)	6.430(2)	6.3684(13)
<i>b</i> (Å)	7.04576(10)	7.0139(3)	6.9407(3)	6.9113(3)	6.8773(4)	6.8556(3)
<i>c</i> (Å)	6.63767(11)	6.6112(18)	6.5602(17)	6.5396(18)	6.5004(5)	6.4803(4)
β (degrees)	104.955(2)	105.279(14)	105.440(12)	105.315(16)	105.365(18)	105.352(13)
<i>V</i> (Å ³)	318.939(12)	308.42(10)	292.43(8)	284.67(9)	277.17(9)	272.83(6)
ρ (g/cm ³)	4.366	4.515	4.761	4.891	5.024	5.104
reflns	12086	4602	4201	3197	2976	3303
collected						
reflns int.	6949	2298	2614	2302	2189	2369
data	3778	1085	991	939	875	948
data (<i>I</i> >2 σ)	3406	958	854	861	814	878
R _{int}	0.0352	0.0613	0.0453	0.0384	0.0385	0.0362
restraints	1	1	1	1	1	1
params	112	67	59	59	59	54
GOF	1.070	1.048	1.100	1.060	1.073	1.075
restr. GOF	1.070	1.047	1.099	1.060	1.072	1.074
R1 (<i>I</i> >2 σ)	0.0242	0.0322	0.0461	0.027	0.0267	0.0282
R1 (all data)	0.0283	0.0401	0.0547	0.0319	0.0303	0.0320
wR2 (all data)	0.0522	0.0683	0.1168	0.0653	0.0642	0.0701
lrgst diff peak	5.816	1.726	5.742	1.352	1.331	1.877
lrgst diff hole	-1.524	-1.407	-1.898	-1.267	-0.853	-0.983

Table S-1 continued

P (GPa)	9.1	10.9	12.3	14.8	16.8
σ P (GPa)	0.03	0.3	0.3	0.2	0.05
<i>a</i> (Å)	6.281(4)	6.239(3)	6.214(3)	6.094(9)	5.985(8)
<i>b</i> (Å)	6.8329(7)	6.8094(10)	6.8094(4)	6.7721(4)	6.7608(4)
<i>c</i> (Å)	6.4637(9)	6.4340(10)	6.380(12)	6.3815(15)	6.3635(13)
β (degrees)	105.28(3)	105.26(3)	105.67(12)	105.90(7)	105.77(6)
<i>V</i> (Å ³)	267.58(16)	263.71(16)	259.9(5)	253.3(4)	247.8(3)
ρ (g/cm ³)	5.204	5.280	5.357	5.498	5.619
reflns collected	2749	1182	1433	2557	2578
reflns int.	1916	825	1141	1651	1939
data	902	634	280	277	266
data (<i>I</i> >2 σ)	811	565	258	241	229
R _{int}	0.0541	0.0327	0.0295	0.0542	0.0570
restraints	1	1	1	1	1
params	54	54	54	54	50
GOF	1.028	1.073	1.151	1.059	1.091
restr. GOF	1.028	1.072	1.149	1.057	1.088
R1 (<i>I</i> >2 σ)	0.0341	0.0404	0.0341	0.0297	0.0333
R1 (all data)	0.0414	0.0465	0.0377	0.0368	0.0446
wR2 (all data)	0.0845	0.0943	0.0853	0.0710	0.0802
largst diff peak	2.096	2.126	1.202	0.691	0.603
largst diff hole	-1.527	-1.353	-0.495	-0.663	-0.462

Table S-2: Interatomic distances between the sodium cation and uranyl oxygen atoms.

P (GPa)	Na-O1 (Å)	Na-O1 (Å)	Na-O2 (Å)	Na-O2 (Å)
0	2.72(5)	2.76(5)	2.41(4)	2.62(4)
1.2	2.46(4)	2.52(4)	2.61(4)	2.76(4)
3.4	2.46(4)	2.78(4)	2.46(4)	2.78(4)
4.8	2.49(4)	2.73(4)	2.26(4)	2.58(4)
6.5	2.51(5)	2.61(5)	2.22(5)	2.52(6)
7.8	2.75(6)	-	2.89(5)	-
9.1	2.53(6)	2.69(7)	2.33(9)	2.53(6)
10.9	2.42(8)	2.70(7)	2.29(8)	2.44(9)
12.3	2.48(7)	2.54(8)	2.13(13)	2.52(8)
14.8	2.24(7)	2.63(7)	1.99(8)	2.62(6)
16.8	1.86(15)	-	2.04(11)	-

Table S-3: Interatomic distances between the sodium cation and oxygen atoms other than O_{yls} from ambient pressure to 16.8 GPa.

P GPa)	Na-O9/O8 (Å)	Na-O9/O8 (Å)	Na-O6 (Å)	Na-O6 (Å)	Na-O3 (Å)	Na-O4 (Å)	Na-O5 (Å)
0	2.32(7)	2.55(6)	-	-	-	-	-
1.2	2.30(10)	2.42(9)	-	-	-	-	-
3.4	2.62(7)	2.63(7)	-	-	-	-	-
4.8	2.54(7)	-	-	-	-	-	-
6.5	2.66(7)	-	-	-	-	-	-
7.8	2.58(6)	-	2.29(6)	2.77(5)	2.93(6)	-	-
9.1	2.53(8)	-	-	-	-	2.67(9)	3.41(6)
10.9	1.77(9)	2.75(7)	-	-	-	2.71(9)	-
12.3	2.7(2)	-	2.92(12)	-	-	-	-
14.8	2.63(13)	-	-	-	2.96(8)	-	-
16.8	2.11(19)	-	-	-	2.2(2)	2.65(19)	-

Table S-4: Na cation bond valence, coordination number, polyhedral shape, and CSM deviation from ideal.

P (GPa)	Na-O b.v.	Coord. #	Polyhedral Shape	Dev. from Ideal
0	0.816	6	Octahedron	3.015
1.2	0.909	6	Octahedron	3.628
3.4	0.693	6	Octahedron	4.339
4.8	0.752	5	Vacant octahedron	3.169
6.5	0.784	5	Vacant octahedron	2.120
7.8	0.634	6	Octahedron	14.106
9.1	1.005	7	Capped trigonal prism	9.096
10.9	1.688	7	Capped trigonal prism	8.519
12.3	0.929	6	Octahedron	12.130
14.8	1.144	6	Pentagonal pyramid	10.284
16.8	1.891	5	Vacant octahedron	4.625

Table S-5: CSM results for the uranyl pentagonal bipyramid from ambient pressure to 16.8 GPa.

P (GPa)	Dev. from Ideal
0	1.325
1.2	1.529
3.4	1.705
4.8	1.857
6.5	1.410
7.8	1.860
9.1	1.345
10.9	1.776
12.3	2.111
14.8	2.028
16.8	1.991

Table S-6: Comparison of uranyl peak placement in the Raman spectrum of boltwoodite and the calculated uranyl bond lengths (Bartlett and Cooney 1989).

P (GPa)	Uranyl 1 (cm^{-1})	BC length ($\text{\AA}$)	Uranyl 2 (cm^{-1})	BC length ($\text{\AA}$)
0	789	1.82(3)	796	1.82(3)
1.2	792	1.82(3)	801	1.81(3)
3.4	809	1.80(3)	816	1.79(3)
4.8	816	1.79(3)	824	1.79(3)*
6.5	825	1.79(3)	832	1.78(3)*
7.8	829	1.78(3)	837	1.77(3)*
9.1	835	1.78(3)	842	1.77(3)*
10.9	845	1.77(3)**	862	1.75(3)**
12.3	837	1.77(3)	854	1.76(3)
14.8	849	1.76(3)	866	1.75(3)
16.8	853	1.76(3)	871	1.74(3)

*Values are within 3σ .**Values are beyond 3σ .

Table S-7: Silicate tetrahedron bond lengths, interatomic distances, and U-O5-Si angle.

P (GPa)	Si-O3 (Å)	Si-O4 (Å)	Si-O5 (Å)	Si-OH6 (Å)	<Si-O> (Å)	U-Si (Å)	U-O5-Si (°)
0	1.620(12)	1.630(11)	1.603(4)	1.589(8)	1.611(19)	3.1532(12)	133.61(17)
1.2	1.61(2)	1.67(2)	1.602(10)	1.600(13)	1.62(3)	3.148(4)	132.6(4)
3.4	1.59(2)	1.648(19)	1.585(9)	1.604(15)	1.61(3)	3.137(4) ^a	131.3(4) ^a
4.8	1.586(17)	1.681(16)	1.606(10)	1.55(2)	1.61(3)	3.128(3) ^a	129.5(5) ^a
6.5	1.528(16) ^a	1.698(15) ^a	1.599(11)	1.53(3)	1.59(4)	3.115(3) ^{a*}	129.2(5) ^a
7.8	1.774(13) ^{a*}	1.483(11) ^{a*}	1.596(11)	1.62(3)	1.62(4)	3.106(3) ^a	128.7(5) ^a
9.1	1.623(14) [*]	1.632(17) [*]	1.571(14)	1.60(4)	1.61(5)	3.108(3) ^a	129.4(6) ^a
10.9	1.436(18) ^{a*}	1.84(2) ^{a*}	1.588(15)	1.67(4)	1.63(5)	3.098(5) ^a	127.5(7) ^a
12.3	1.69(6) [*]	1.54(6) [*]	1.571(19)	1.61(5)	1.60(10)	3.058(15) ^a	128.9(18)
14.8	1.54(6)	1.72(6)	1.63(2)	1.48(5)	1.59(10)	3.086(10) ^a	125.3(11) ^a
16.8	1.52(7)	1.71(7)	1.68(3)	1.58(8)	1.62(13)	3.068(13) ^a	124.9(13) ^a