

Armstrongite at non-ambient conditions: An *in-situ* high-pressure single-crystal X-ray diffraction study

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Abstract

The high-pressure behavior of a natural armstrongite $[(\text{Ca}_{0.96}\text{Ce}_{0.01}\text{Yb}_{0.01})\text{Zr}_{0.99}\text{Si}_6\text{O}_{14.97}\cdot 2.02\text{H}_2\text{O}]$, $a\sim 14.03\text{\AA}$, $b\sim 14.14\text{\AA}$, $c\sim 7.85\text{\AA}$, $\beta\sim 109.4^\circ$, Sp. Gr. $C2/m$, a microporous heterosilicate, has been studied by single-crystal X-ray diffraction with a diamond-anvil cell up to 8 GPa, using the methanol:ethanol:H₂O=16:3:1 mixture as a pressure-transmitting fluid. A first-order phase transition, characterized by a triplication of the unit-cell volume, was detected between 4.01(5) and 5.07(5) GPa. The isothermal bulk modulus ($K_{V0} = -V(\partial P/\partial V)$) of the high-pressure polymorph was found to be ~50% higher than that obtained for the low-pressure one (*i.e.*, $K_{V0}=45(1)$ GPa for the high-pressure polymorph, $K_{V0}=31.2(6)$ GPa for the low-pressure polymorph), indicating a remarkable change in the structure compressibility. The mechanisms at the atomic scale, which govern the structure deformation of the low- P polymorphs, are described based on a series of structure refinements up to 4 GPa, and a comparison with those experienced by the structure at high temperature is provided. As observed for other microporous silicates, the polyhedral tilting is the main deformation mechanism able to accommodate the effects of the applied pressure. No evidence of crystal-fluid interaction, with a selective sorption of molecules of the pressure-transmitting fluid through the cavities, was observed at high pressure.

Keywords: armstrongite, heterosilicate, high pressure, compressibility, phase transition.

1. Introduction

Armstrongite, ideally $\text{CaZr}[\text{Si}_6\text{O}_{15}] \cdot 3\text{H}_2\text{O}$, is a rare mineral discovered for the first time in granite pegmatites and alkine granites of the Khan Bogdo massif (Mongolia) and described by Vladykin et al. [1], who indicated as possible space group Cm , $C2$ and $C2/m$ and assigned to armstrongite the ideal formula $\text{CaZr}[\text{Si}_6\text{O}_{15}] \cdot 2.5\text{H}_2\text{O}$. Concerns regarding the true space group of armstrongite were discussed by Karashaev and Sapozhnikov [2] and Jambor et al. [3]: on the basis of the reflection conditions (in particular $h + k + l \neq 2n$, $h0l$ with $h + l \neq 2n$ and $0k0$ with $k \neq 2n$), they reported the I -centered lattice with space group choices $I2/m$, $I2$ and Im . Kabalov et al. [4] re-investigated the structure of armstrongite solving and refining the structure in the space group $C2$, with a Rietveld full-profile fit with $R_{wp} = 2.75\%$, finding also the position of a new H_2O site and increasing the number of H_2O molecules up to 3 per formula unit (pfu). More recently, Mesto et al. [5], solved and refined the structure of a twinned crystal of armstrongite in the space group $C2/m$, with $a \sim 14.03 \text{ \AA}$, $b \sim 14.14 \text{ \AA}$, $c \sim 7.85 \text{ \AA}$, and $\beta \sim 109.4^\circ$. The structure of armstrongite (Fig. 1) consists of sheets made by $[\text{Si}_6\text{O}_{15}]^{6-}$ building units, which are generated by the condensation of xonolite-like chains running along the b axis (Fig. 1) [6]. The resulting $[\text{Si}_6\text{O}_{15}]^{6-}$ -sheets are characterized by four- and eight-member rings of tetrahedra alternating along $[100]$ and by four- and six-member rings alternating along $[010]$ (hereafter 4-, 6- and 8- mRs, respectively) (Fig. 2). ZrO_6 octahedra are connected with the SiO_4 tetrahedra to give the $(\text{ZrSi}_6\text{O}_{15})^{2-}$ heterogeneous framework, in which $\text{CaO}_5(\text{H}_2\text{O})_2$ -sevenfold coordination polyhedra are edge-connected to ZrO_6 octahedra to form columns running parallel to $[010]$ (Fig. 1).

Schingaro et al. [7] investigated the dehydration process of armstrongite by means of thermal analysis, *in-situ* X-ray powder diffraction and Fourier-transform infrared spectroscopy. In the companion manuscript of the present one [8], the structure of the fully dehydrated form of armstrongite has been solved and refined by *in-situ* high-temperature single crystal X-ray diffraction.

This study is aimed to extend the knowledge about the behavior of armstrongite under extreme conditions, with the description of its high-pressure behavior under hydrostatic compression. To date, no X-ray diffraction data at high pressure are available in the open literature and, consequently, the compressional parameters of this material are still unknown. In addition, in the last years, the crystal-fluid interaction promoted by pressure in zeolite-like compounds is being object of a raising interest, especially in the fields of materials science and mineralogy. Although armstrongite is a heterosilicate, its structure, with a framework density (FD) ~ 21.86 (lying in the range of zeolites), could be a potential candidate for molecular intrusion enhanced by increasing pressure. On this basis, we have investigated the high-pressure behavior of armstrongite up to 8 GPa by means of *in-situ* single-crystal synchrotron X-ray diffraction, using a diamond-anvil cell (DAC) and a potentially penetrating *P*-transmitting fluid.

2. Experimental methods

A single crystal of armstrongite (same specimen described by Mesto et al. [5] and in Lacalamita et al. [8]) from Khan Bogdo, Mongolia, with a prismatic habit ($\sim 50 \times 20 \times 20$ μm in size) was selected on the basis of its optical quality for the high-pressure experiment, performed at the ID15B beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. A parallel monochromatic beam operating with an $E = 30.16$ KeV ($\lambda \sim 0.411$ Å) was used. The crystal was loaded in a membrane-driven DAC, with 600 μm Boehler-Almax design anvils, along with some ruby spheres for pressure determination (pressure uncertainty ± 0.05 GPa [9]). A stainless steel foil (with thickness ~ 250 μm) was pre-indented to 70 μm and then drilled by spark-erosion, leading to a *P*-chamber of ~ 200 μm in diameter. Before adding the methanol:ethanol:H₂O = 16:3:1 mix, used as hydrostatic *P*-transmitting fluid [10], a first data collection was performed with the crystal in the DAC without any *P*-fluid. The adopted data collection strategy consisted in a pure ω -scan ($-32^\circ \leq \omega \leq +32^\circ$), with 1° step width and 1s exposure time per step. The X-ray diffraction patterns were collected by a MAR555 flat-panel detector (at a distance of 287.43 mm from the sample

position). Further details pertaining to the beamline experimental setup are reported in Merlini and Hanfland [11]. Indexing of the diffraction peaks and integration of their intensities (corrected for Lorentz-polarization effects) was done using the CrysAlis package [12]. Corrections for absorption (caused by the DAC components) and background were applied using the semi-empirical *ABSPACK* routine implemented in CrysAlis [12].

3. Structure refinement protocol

The structure refinements of the armstrongite structure at room and high pressure were performed using the software JANA2006 [13]. Starting with the structure model of Mesto et al. [5], a series of structure refinements were performed up to 4 GPa, at which the material experiences a *P*-induced phase transition with a triplication of the unit-cell volume. In the structure refinements of the low-*P* polymorph, in order to reduce the number of the refined variables, the atomic displacement parameters (D.P.) were modelled as isotropic. For the high-*P* polymorph, unfortunately, the low (reflections/parameters to be refined) ratio hindered the structure solution of the crystal structure. The unit-cell parameters with *P* are listed in Tab. 1 and the principal statistical parameters of the structure refinements are listed in Tab. S1 (supplementary materials, SM). Atomic coordinates, site occupancies and displacement parameters are given in Tab. S2 (SM), Si-O and Zr-O distances are listed in Tab. S3 (SM), whereas other relevant distances are reported in Tab. 2.

4. Results

4.1. Phase transition, elastic behavior, and equation of state

The evolution of the unit-cell parameters as a function of pressure is shown in Fig. 3 and Fig. S1. Overall, the unit-cell parameters decrease steadily up to 4.01(5) GPa (Table 1). In this *P*-range, the lengths of the *b*- and *c*-edges decrease by 3.5 and 3.2%, respectively, whereas along *a* the edge length decreases by only 1.5%; the unit-cell volume is reduced by about 8.8% (Fig. 3). Between 4 and 5 GPa, armstrongite undergoes a phase transition characterized by a triplication of the unit-cell

volume (Table 1 and Fig. S1, S2 SM), as a result of the triplication of the c unit-cell edge (Tab. 1). The associated volume discontinuity reflects a first-order phase transition. Comparing the unit-cell volume of the low- P polymorph at 4.01(5) GPa and the $V/3$ of the high- P one at 5.07(5) GPa, a difference of about 5.2% occurs. In order to maintain the metrical configuration, the lattice of the high- P polymorph is better described as I -centered, and the reflection conditions suggests the space group $I2/m$ as highly likely. The metrical relationship between the lattice of the low- P ($C2/m$) and high- P ($I2/m$) polymorphs can be ideally expressed as: $a' = a$, $b' = b$, $c' = 3c$. The phase transition affects also the value of the monoclinic β angle: as shown in Fig. 3, in the low- P form, β progressively increases from $109.37(1)^\circ$ at ambient pressure to $110.38(4)^\circ$ at 4.01(5) GPa; for the high- P polymorph, the β value appears to be nearly unaffected by P with an average value of $103.1^\circ (\pm 0.2^\circ)$ (Fig. 3, S2 SM). In order to describe the (isothermal) compressional behavior of both low- and high- P polymorph, the experimental V - P data, weighted by their uncertainties, were fitted to a third-order (BM3-EoS) and a second-order (BM2-EoS) Birch-Murnaghan Equations of State [14, 15], respectively, using the EoS Fit 7.0 software [16]. The refined elastic coefficients of the fit are reported in Tab. 3. The high- P polymorph has a bulk modulus K_{V0} (*i.e.*, $K_{V0} = -V_0(\partial P/\partial V)_{P=0} = 1/\beta_{V0}$, where β_{V0} is the volume compressibility coefficient) $\sim 50\%$ higher than that obtained for the low- P one, indicating a significant increase in stiffness in response to the phase transition. Moreover, a remarkable change of the “axial bulk moduli” (calculated simply by substituting the cube of the individual lattice parameter a^3 , b^3 , c^3 for the volume in the EoS) [15] occurs from the low- to the high- P polymorph: K_b and K_c increase from 23 to 50 GPa and from 26 to 46 GPa, respectively, whereas K_a falls from 78 to 35 GPa. Therefore, the phase transition leads to a pronounced decrease of the compressibility along [010] and [001] coupled with a marked increase along [100]. Data collected in decompression show a significant hysteresis loop, as the high- P phase is stable (at least) down to 2.91(5) GPa (Fig. 2, Tab. 1).

4.2. Structure evolution at increasing pressure

The Zr-O distances of the low- P polymorph (reported in Tab. S3, SM) do not change drastically with P . Though the intra-tetrahedral Si-O distances (reported in Tab. S3, SM) do not show drastic changes up to 3.27(5) GPa, it is worth noting that a considerable distortion of the Si(1)-O₄ and Si(2)-O₄ tetrahedra is observed in the structural model refined at 4.01(5) GPa. This distortion is mainly governed by the sharp decrease of the Si(1)-O(2) distance coupled with an increase of the Si(2)-O(2) distance (Tab. S3, SM).

Nevertheless, similarly to zeolites (*e.g.* [17-19]) and others open-framework materials ([20] and references therein), the bulk compression is mainly accommodated through the tilting of the TO₄ units around the shared oxygen hinges. In armstrongite, the effects of such a behavior affect especially the diameters of the 6-mRs and 8-mRs (reported in Tab. 2 and shown in Fig. 3). For the 6-mRs, for example, the extension of the O7-O7 diameter with P is coupled with the compression of the O8-O8 one, leading to a noticeable distortion of this building unit (Fig. 4). Likewise, the distortion of the 8-mRs at high pressure is mainly due to the increase of the O6-O6 diameter, coupled with the decrease of O7-O7 and O1-O1 (Fig. 4).

With increasing pressure, the rotation of the ZrO₆ octahedra is reflected by the change of the O1-O7-O2, O8-O1-O9, O1-O9-O3 and O2-O4-O3 angles (Tab. 4). The O1-O9-O3 and O2-O4-O3 angles, for example, increase respectively by about 10.6 and 10.3 % ($\Delta P \approx 4$ GPa). The distortion of the 5-mRs is mainly governed by the decrease of the O1-O7-O2 and O8-O1-O9 angles (Fig. 4). Further (O-O-O) angles, related to the 5-mRs, are given in Tab. S4 (SM). Fig. 2 shows a 5-mR (formed by four SiO₄ tetrahedra and one ZrO₆ octahedra) at ambient pressure and at 4.01(5) GPa, respectively.

The role played by the CaO₅(H₂O)₂-sevenfold coordination polyhedra, in order to accommodate the effects of pressure, appears to be only secondary (Tab. S3, SM) and subordinate to the tilting of Si-tetrahedra and Zr-octahedra.

5. Discussion and concluding remarks

In this study, we have investigated, for the first time, the behavior of armstrongite at high pressure, on the basis of *in-situ* single crystal X-ray diffraction data collected up to 8.01 GPa. Data collected at high pressure show a first-order phase transition, bracketed between 4.01(5) and 5.07(5) GPa. The unit-cell volume of the high-*P* polymorph triplicates (Tab. 1). The bulk compression of the low-*P* polymorph is mainly accommodated through the tilting of both SiO₄ tetrahedra and ZrO₆ octahedra, around the shared oxygen hinges. In fact, these polyhedra behave as quasi-rigid units; in this respect, armstrongite behaves similarly to other microporous minerals, such as zeolites [*e.g.* 17-19, 21] or heterosilicates, such as its Na- analogue, elpidite (Na₂ZrSi₆O₁₅•3H₂O) [22]. In elpidite, one of the major distortion mechanisms in response to hydrostatic compression is represented by the opposite rotations of the Zr-octahedra. Also elpidite experiences a *P*-induced phase transition, between 1.2-1.9 GPa, with doubling of the *a* cell parameter (and consequently of the unit-cell volume). Tilting of the Zr-octahedra is the common deformation mechanism between elpidite and armstrongite (either at high temperature and high pressure [8, 22 and this paper]), whereas the role played by Ca (or Na) appears to be only secondary in armstrongite at high pressure but it is critical in elpidite at *HP* and in armstrongite at *HT* [8, 22]. Unfortunately, the triplication of the unit-cell volume prevented the structure solution of the high-*P* polymorph of armstrongite, hindering a comparison between the high-pressure structures of armstrongite and elpidite. However, armstrongite seems to be more stable to pressure with respect to its Na-analogue, which undergoes a (presumably) second-order phase transition between 1.2-1.9 GPa [22].

The lack of the structure model of the high-*P* polymorph of armstrongite does not allow any speculation about the character of the first-order phase transition observed between 4.01(5) and 5.07(5) GPa: displacive or reconstructive? Overall, the high-*P* polymorph of armstrongite is found to be stiffer than the low-*P* one (*i.e.*, K_{V0} increases by about 50%, Tab. 3), and a remarkable change of the elastic anisotropic scheme occurs: $K_c \sim K_b \sim \frac{1}{3}K_a$ for the low-*P* form, $K_c \sim K_b \sim 1.4K_a$ for the high-*P* form (Tab. 3).

On the basis of the structure refinements of the low- P polymorph, we can infer that no evidence of crystal-fluid interaction, with a selective sorption of molecules of the P -transmitting fluid through the cavities, occurs. This kind of effect was observed in several open-framework materials when compressed in fluids made by small molecules (*e.g.*, with kinetic diameter shorter than the free diameters of the structural cavities), recently reviewed by Gatta et al. [20]. It is highly likely that the channel population in armstrongite structure hinders the penetration of the new molecules (*e.g.*, H₂O) in response to the applied pressure.

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Table 1. Unit-cell parameters of armstrongite at high pressure (* in decompression).

P (GPa)	V (Å ³)	a (Å)	b (Å)	c (Å)	β (°)
0.0001	1469.3(5)	14.0312(6)	14.1385(2)	7.851(2)	109.37(1)
0.01(5)	1466.7(6)	14.0248(9)	14.1368(2)	7.843(2)	109.39(2)
0.15(5)	1456.6(6)	14.016(1)	14.0970(3)	7.822(3)	109.53(2)
0.28(5)	1450.3(6)	14.0079(9)	14.0670(2)	7.814(2)	109.62(2)
0.48(5)	1440.3(6)	13.997(1)	14.0286(3)	7.793(3)	109.73(2)
0.71(5)	1430.5(6)	13.9810(8)	13.9877(2)	7.774(2)	109.80(2)
1.15(5)	1416.1(5)	13.958(1)	13.9303(3)	7.746(2)	109.92(2)
1.48(5)	1405.8(5)	13.940(1)	13.8924(3)	7.725(3)	109.99(2)
2.03(5)	1391.4(6)	13.914(1)	13.8345(3)	7.698(3)	110.11(2)
2.76(5)	1371.5(6)	13.874(2)	13.7579(4)	7.658(4)	110.23(3)
3.27(5)	1358.1(6)	13.840(1)	13.7064(2)	7.633(2)	110.29(2)
4.01(5)	1340.7(6)	13.801(2)	13.6435(5)	7.596(4)	110.38(4)
5.07(5)	3813(1)	12.684(1)	13.4750(4)	22.917(8)	103.23(2)
5.67(5)	3779(1)	12.642(2)	13.4402(6)	22.84(1)	103.16(3)
6.33(5)	3742(1)	12.596(2)	13.3944(7)	22.78(1)	103.15(3)
7.18(5)	3701(1)	12.535(3)	13.359(1)	22.68(2)	102.98(5)
7.68(5)	3674(1)	12.498(2)	13.3415(9)	22.61(2)	102.91(4)
8.01(5)	3654(1)	12.476(2)	13.3124(9)	22.56(2)	102.96(4)
*7.31(5)	3682(1)	12.501(2)	13.3443(9)	22.65(2)	102.90(4)
*5.31(5)	3792(1)	12.651(3)	13.459(1)	22.86(2)	103.05(5)
*4.19(5)	3860(1)	12.740(3)	13.544(1)	22.96(2)	103.06(5)
*3.45(5)	3912(1)	12.812(2)	13.5791(9)	23.11(2)	103.32(4)
*2.91(5)	3957(1)	12.865(2)	13.6428(7)	23.16(2)	103.24(3)
*2.00(5)	1382.7(7)	13.904(3)	13.8099(6)	7.676(6)	110.26(5)
*1.15(5)	1411.2(7)	13.991(4)	13.9608(10)	7.694(9)	110.11(7)

Table 2. Relevant interatomic distances (in Å) of armstrongite pertaining to the 6- and 8-mRs diameters at different pressure (* in decompression).

<i>P</i> (GPa)	O7-O7 _(6-mRs)	O8-O8	O1-O1	O6-O6	O7-O7 _(8-mRs)
0.0001	6.091(8)	5.630(6)	6.577(1)	5.922(8)	6.792(6)
0.01(5)	6.080(13)	5.606(9)	6.581(1)	5.875(11)	6.765(8)
0.15(5)	6.108(14)	5.531(9)	6.493(1)	5.833(14)	6.790(11)
0.28(5)	6.133(13)	5.517(8)	6.430(1)	5.896(11)	6.800(8)
0.48(5)	6.174(14)	5.450(8)	6.326(1)	5.797(14)	6.837(12)
0.71(5)	6.223(14)	5.436(8)	6.246(1)	5.775(11)	6.885(8)
1.15(5)	6.238(14)	5.391(8)	6.151(1)	5.764(11)	6.908(8)
1.48(5)	6.297(14)	5.345(8)	6.126(1)	5.680(11)	6.975(9)
2.03(5)	6.335(2)	5.306(8)	5.967(1)	5.64 (14)	6.981(13)
2.76(5)	6.378(2)	5.223(11)	5.859(2)	5.62(2)	7.07(2)
3.27(5)	6.381(2)	5.20(2)	5.808(1)	5.544(11)	7.076(9)
4.01(5)	6.478(2)	5.075(6)	5.702(1)	5.511(11)	7.163(9)
*1.15(5)	6.23(5)	5.37(3)	6.21(4)	5.75(5)	6.90(4)

Table 3. Refined elastic parameters pertaining the low- and the high- P polymorphs of armstrongite, based on isothermal III- and II-BM Equation of State fits.

	V_0, x_0 ($\text{\AA}^3, \text{\AA}$)	K_{V_0, x_0} (GPa)	K'	β_{V_0, x_0} (GPa^{-1})	χ^2
<i>Elastic parameters of the low pressure polymorph of armstrongite fitted with a third-order Birch-Murnaghan EoS</i>					
V	1465(1)	31.2(6)	8.6*	0.0321(5)	1.25
a	14.028(1)	78(4)	2(2)	0.0043(2)	0.59
b	14.131(4)	23(2)	10*	0.015(1)	0.89
c	7.844(2)	26(2)	10*	0.0128(9)	0.74
	V_0, x_0 ($\text{\AA}^3, \text{\AA}$)	K_{V_0, x_0} (GPa)	K'	β_{V_0, x_0} (GPa^{-1})	χ^2
<i>Elastic parameters of the high pressure polymorph of armstrongite fitted with a second-order Birch-Murnaghan EoS</i>					
V	4185(8)	45(1)	4*	0.0222(5)	0.77
a	13.17(2)	35(1)	4*	0.0095(3)	4.95
b	13.87(1)	50(2)	4*	0.0067(3)	5.99
c	23.62(4)	46(3)	4*	0.0072(5)	1.64

Note: The value of $K' = \partial K_{V_0}/\partial P$ for the unit-cell volume of the low- P polymorph was fixed to 8.6: the free refined value was too high to be reasonable (*e.g.* $\sim 12.5(8)$), likely biased by the impending phase transition.* fixed value.

Table 4. Relevant O-O-O angles (in °) of armstrongite, pertaining to the 5-mRs, at different pressure (* in decompression).

<i>P</i> (GPa)	O7-O1-O9	O1-O9-O4	O2-O4-O9	O4-O2-O7	O4-O3-O9
0.0001	131.34(1)	89.42(1)	104.22(1)	118.26(5)	58.67(1)
0.01(5)	131.39(1)	88.52(1)	105.38(1)	117.09(6)	58.33(1)
0.15(5)	132.12(2)	87.64(1)	104.88(1)	117.63(8)	58.70(1)
0.28(5)	132.54(3)	86.87(2)	104.77(2)	117.71(7)	58.87(1)
0.48(5)	133.03(2)	86.20(1)	104.23(1)	118.22(8)	58.97(1)
0.71(5)	133.06(1)	85.74(1)	103.90(1)	118.99(6)	58.93(1)
1.15(5)	133.26(2)	84.51(1)	103.85(1)	118.56(6)	59.25(1)
1.48(5)	133.20(2)	84.85(1)	103.16(1)	120.11(6)	59.12(1)
2.03(5)	132.52(2)	84.33(1)	101.77(1)	121.49(8)	59.45(1)
2.76(5)	132.00(2)	83.49(2)	102.16(2)	124.07(11)	59.82(1)
3.27(5)	131.95(1)	82.31(1)	102.29(1)	125.05(6)	59.92(1)
4.01(5)	131.46(1)	80.58(1)	105.52(1)	124.83(6)	59.14(1)
*1.15(5)	132.73(5)	84.01(4)	105.34(4)	117.6(3)	58.64(2)

Fig. 1. (*Left*) Crystal structure of armstrongite viewed down [001], (*middle*) the xonolite-like chain of armstrongite and (*right*) a column of ZrO_6 octahedra and $CaO_5(H_2O)_2$ polyhedra viewed perpendicular to the bc plane.

Fig. 2. Configuration of the 8-mRs (*right*), 6-mRs (*middle*) and 5-mRs (*left*) at ambient pressure (*top*) and at 4.01(5) GPa (*bottom*).

Fig. 3. (*Left*) High-pressure evolution of the normalized (to P_0) unit-cell volume and axial parameters of armstrongite (V/V_0 in *black squares*, a/a_0 *red circles*, b/b_0 *blue triangles*, c/c_0 *cyan triangles*) from ambient pressure to 4.01(5) GPa (*i.e.*, only for the low- P polymorph). High-pressure evolution of the normalized (to P_0) monoclinic β angle (*middle*) and unit-cell volume V (*right*) up to 8 GPa; *black squares* represent the compression path, whereas *red circles* the decompression path (*above the phase transition pressure, $V/3$ is reported).

Fig. 4. Evolution of the (relevant) normalized diameters and angles of the 6- (O7-O7 in *black squares*, O8-O8 in *red circles*), 8- (O1-O1 in *black squares*, O6-O6 in *red circles*, O7-O7 in *blue triangles*) and 5-mRs (O1-O7-O2 in *black squares*, O8-O1-O9 in *red circles*, O1-O9-O3 in *blue triangles* and O2-O4-O3 in *green triangles*) at left, middle and right side, respectively.

Fig. S1 Evolution with P of the axial parameters of the high- P polymorph of armstrongite (a/a_0 *black squares*, b/b_0 *red circles*, c/c_0 *blue triangles*).

Fig. S2 Idealised metrical relationship between the unit cell of the low- P (continuous line) and high- P (dashed line) polymorphs of armstrongite (viewed down to the b axis).