

Anisotropic compressional behavior of ettringite

Davide Comboni^{1*}, G. Diego Gatta¹, Paolo Lotti¹, Marco Merlini¹, Michael Hanfland²

¹ Dipartimento di Scienze della Terra, Università degli Studi di Milano, Via Botticelli 23, 20133 Milano, Italy

² ESRF – European Synchrotron Radiation Facility, 71 Avenue des Martyrs, CS40220, 38043 Grenoble Cedex, France.

* **Corresponding Author:** Davide Comboni, current email address davide.comboni@unimi.it

Abstract

The high-pressure behavior of a natural ettringite $[\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 27\text{H}_2\text{O}]$, $a = 11.2104(2)$ Å, $c = 21.4350(3)$ Å, Sp. Gr. $P31c$] has been studied by single-crystal X-ray diffraction with a diamond-anvil cell up to 4.22 GPa, using the methanol:ethanol= 4:1 mixture as a hydrostatic pressure-transmitting fluid. The isothermal bulk modulus ($K_0 = -V(\partial P/\partial V)$) was found to be 26.6(5) GPa. Ettringite shows a significant anisotropic compressional pattern, being more compressible on (001) than along [001] (*i.e.* the fibers growing axis), with $K(c)_0 \sim 2K(a,b)_0$. The mechanisms at the atomic scale, which govern the structure deformation, have been described by a series of structure refinements up to 2.3 GPa. The structure evolution in response to the applied pressure indicates a plausible densification of the hydrogen-bond network between the $\text{Ca}(\text{OH})_4(\text{H}_2\text{O})_4$ polyhedra and the SO_4 tetrahedra, which results in a softening and ultimately in a collapse of the whole structure at pressures > 3 GPa.

Keywords: ettringite, high pressure, compressibility, diamond anvil cell, H-bonds.

1. Introduction

A Portland cement is a complex multi-component system and, to predict its elastic properties, an exhaustive database of the thermodynamic parameters of the main constituents is needed. The synthetic counterpart of the mineral ettringite (ideally $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot n\text{H}_2\text{O}$, with $n = 24\text{--}27$), also known

as calcium aluminate trisulphate hydrate, is one of the most important crystalline phases in Portland cements. In Nature, ettringite is a rare mineral that occurs in metamorphosed limestone or as a low-temperature secondary-alteration phase, usually associated with portlandite, gypsum or afwillite. Ettringite-like phase plays different roles in Portland cements: i) in early hydration stages, its crystallization governs the set rate of the highly reactive $\text{Ca}_3\text{Al}_2\text{O}_6$ (“C3A”); ii) in aged cements, delayed formation of ettringite can promote degradation processes, in particular when limestone is used as a filler and a diffusion of sulphate-rich fluids occurs (*e.g.*, by contact with groundwater or sulphate-bearing soils) [1–4].

The crystal structure of ettringite is significantly complex (Fig. 1): its principal building units consist of $[\text{Ca}_3[\text{Al}(\text{OH})_6]\cdot 12\text{H}_2\text{O}]$ -columns, running parallel to $[001]$, in which $\text{Al}(\text{OH})_6$ -octahedra alternate with triplets of $\text{Ca}(\text{OH})_4(\text{OH}_2)_4$ -polyhedra, disposed around the 3-fold axis; these units are connected by sulphate groups *via* hydrogen bonds with H_2O molecules. A very recent paper by Gatta et al. [5] reported the structural model of ettringite based on single-crystal neutron diffraction data, with a full description of the complex H-bonding scheme of the structure.

Clark et al. [6] investigated, by X-ray diffraction and infrared spectroscopy, the high-pressure behavior of ettringite from ambient pressure up to 6.4 GPa. The authors found a transformation into an amorphous phase at ~3 GPa and estimated (by fitting only two P - V point) the isothermal bulk modulus ($K_0 = -V(\partial P/\partial V) = 1/\beta_0$, where β_0 is the volume compressibility coefficient at room conditions) of ettringite to 27(7) GPa, with the linear bulk moduli along the a and c crystallographic directions (*i.e.*, 23(10) GPa and 36(12)GPa, respectively). This K_0 value is similar to what obtained by Scholtzová et al. [7] and Speziale et al. [8] which, *via* Brillouin spectroscopy and density functional theory (DFT) simulations, determined the bulk modulus of ettringite to be in the range of 27-30 GPa. Using DFT, also Manzano et al. [9], simulated the crystal structure and electric properties of ettringite up to 5 GPa. The bulk modulus obtained from the fit of the calculated volumes between 0 and 2.5 GPa was found to be 29 GPa. Above about 2.5 GPa, the simulation evidences a sharp decrease in the bulk compressibility (by about 40%),

Table S2b. Refined anisotropic displacement parameters of Ca2 atom (in \AA^2) from the structure refinements.

Site	P (GPa)	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca2	0.0001	0.045(3)	0.023(3)	0.0035(8)	0.019(3)	0.001(2)	0.002(1)
	0.54(5)	0.041(3)	0.024(3)	0.0052(9)	0.0020(3)	0.005(2)	0.004(1)
	1.35(5)	0.041(2)	0.025(3)	0.0075(9)	0.020(3)	0.002(2)	0.002(1)
	1.84(5)	0.040(2)	0.024(3)	0.0078(9)	0.020(2)	0.003(2)	0.002(1)
	2.3(5)	0.041(2)	0.022(3)	0.0083(9)	0.019(3)	0.002(2)	0.002(1)

Table S3. Other O-O and O···O distances (in \AA)

P (GPa)	O1-O1	O1-O2	O1-O2	O1-O3	O2-O2	O2-O6	O2-O9	O3-O3
0.0001	2.374(1)	2.709(1)	2.826(1)	3.024(1)	2.731(1)	2.899(1)	2.950(1)	2.619(1)
0.54(5)	2.444(2)	2.695(2)	2.848(2)	3.005(3)	2.699(2)	2.886(2)	2.976(2)	2.602(2)
1.35(5)	2.428(2)	2.728(2)	2.829(2)	2.982(3)	2.714(2)	2.857(2)	2.950(2)	2.653(2)
1.84(5)	2.420(2)	2.706(2)	2.823(2)	2.959(3)	2.722(2)	2.827(2)	2.920(2)	2.634(2)
2.30(5)	2.415(2)	2.710(2)	2.792(2)	2.933(3)	2.707(2)	2.796(2)	2.924(2)	2.634(3)

P (GPa)	O3-O4	O3-O4	O3-O12	O4-O4	O6-O2	O9-O11	O10-O12	O10···O14
0.0001	2.766(1)	2.811(1)	2.947(1)	2.512(2)	2.899(1)	2.953(1)	2.878(1)	2.858(1)
0.54(5)	2.757(2)	2.790(2)	2.941(2)	2.507(2)	2.886(2)	2.950(2)	2.826(2)	2.894(2)
1.35(5)	2.753(2)	2.791(2)	2.913(2)	2.484(2)	2.857(2)	2.885(2)	2.830(2)	2.830(2)
1.84(5)	2.744(2)	2.789(2)	2.894(2)	2.515(2)	2.827(2)	2.882(2)	2.808(2)	2.827(2)
2.30(5)	2.735(2)	2.776(2)	2.891(2)	2.483(2)	2.796(2)	2.879(2)	2.766(2)	2.820(2)

P (GPa)	O11-O2	O11-O9	O14-O16	O17-O18	O16-O16	O18-O18	O15-O15	O19-O19
0.0001	2.983(2)	2.953(1)	2.426(2)	2.430(2)	2.426(2)	2.507(2)	2.369(2)	2.155(2)
0.54(5)	3.078(2)	2.950(2)	2.412(2)	2.469(2)	2.376(2)	2.471(2)	2.356(2)	2.188(2)
1.35(5)	3.049(2)	2.852(2)	2.469(2)	2.480(2)	2.411(2)	2.449(2)	2.398(2)	2.185(2)
1.84(5)	3.052(2)	2.882(2)	2.459(2)	2.475(2)	2.434(2)	2.460(2)	2.390(2)	2.222(2)
2.30(5)	3.038(2)	2.879(2)	2.473(2)	2.476(2)	2.405(2)	2.456(2)	2.274(2)	2.198(2)

Site	P (GPa)	$S.o.f$	X	Y	Z	U_{iso}
O12	2.30(5)	1	0.252(2)	0.409(2)	0.1250(7)	0.031(4)
	0.0001	1	0.740(2)	0.597(2)	0.8678(7)	0.053(6)
	0.54(5)	1	0.744(2)	0.598(2)	0.8688(7)	0.039(5)
	1.35(5)	1	0.742(2)	0.596(2)	0.8698(6)	0.039(5)
	1.84(5)	1	0.743(2)	0.596(2)	0.8700(6)	0.039(5)
O13	2.30(5)	1	0.739(2)	0.595(2)	0.8712(7)	0.053(6)
	0.0001	1	1/3	2/3	0.4241(9)	0.08
	0.54(5)	1	1/3	2/3	0.4232(9)	0.08
	1.35(5)	1	1/3	2/3	0.4234(9)	0.08
	1.84(5)	1	1/3	2/3	0.4238(9)	0.08
O14	2.30(5)	1	1/3	2/3	0.4238(9)	0.08
	0.0001	1	1/3	2/3	0.8142(8)	0.059(7)
	0.54(5)	1	1/3	2/3	0.8146(9)	0.061(9)
	1.35(5)	1	1/3	2/3	0.8161(8)	0.056(6)
	1.84(5)	1	1/3	2/3	0.8154(8)	0.051(6)
O15	2.30(5)	1	1/3	2/3	0.8153(8)	0.043(5)
	0.0001	1	0.442(2)	0.799(2)	0.5101(9)	0.08
	0.54(5)	1	0.436(2)	0.802(2)	0.509(1)	0.08
	1.35(5)	1	0.438(2)	0.806(2)	0.509(1)	0.08
	1.84(5)	1	0.437(2)	0.807(2)	0.509(1)	0.08
O16	2.30(5)	1	0.439(2)	0.809(2)	0.509(1)	0.08
	0.0001	1	0.191(2)	0.622(2)	0.7222(6)	0.08
	0.54(5)	1	0.195(2)	0.627(2)	0.7216(8)	0.08
	1.35(5)	1	0.191(1)	0.624(2)	0.7201(8)	0.08
	1.84(5)	1	0.189(2)	0.623(2)	0.7200(7)	0.08
O17	2.30(5)	1	0.190(2)	0.623(2)	0.7184(8)	0.08
	0.0001	1	1/3	2/3	0.0674(9)	0.08
	0.54(5)	1	1/3	2/3	0.070(1)	0.08
	1.35(5)	1	1/3	2/3	0.070(1)	0.08
	1.84(5)	1	1/3	2/3	0.070(1)	0.08
O18	2.30(5)	1	1/3	2/3	0.070(1)	0.08
	0.0001	1	0.186(2)	0.576(2)	-0.0239(8)	0.08
	0.54(5)	1	0.188(2)	0.569(2)	-0.0249(9)	0.08
	1.35(5)	1	0.188(2)	0.568(2)	-0.0261(8)	0.08
	1.84(5)	1	0.187(2)	0.567(2)	-0.0260(8)	0.08
O19	2.30(5)	1	0.186(2)	0.568(2)	-0.0260(9)	0.08
	0.0001	0.30(1)	0.376(4)	0.583(4)	0.234(1)	0.03
	0.54(5)	0.29(1)	0.377(5)	0.581(4)	0.233(2)	0.03
	1.35(5)	0.30(1)	0.378(4)	0.581(4)	0.232(2)	0.03
	1.84(5)	0.30(1)	0.380(2)	0.580(4)	0.231(1)	0.03
O20	2.30(5)	0.29(1)	0.378(5)	0.579(4)	0.229(2)	0.03
	0.0001	0.74(3)	1/3	2/3	0.242(2)	0.03
	0.54(5)	0.78(3)	1/3	2/3	0.244(2)	0.03
	1.35(5)	0.74(3)	1/3	2/3	0.245(2)	0.03
	1.84(5)	0.74(3)	1/3	2/3	0.245(2)	0.03
	2.30(5)	0.78(3)	1/3	2/3	0.245(2)	0.03

which was explained by a “densification” of the hydrogen bond network. Recently, Cuesta et al. [10] compressed ettringite powder in silicone oil up to 3 GPa, obtaining a bulk modulus value of 30(3) GPa, *i.e.*, within 1σ to what previously reported.

Up to now, at the best of our knowledge, the only experiments on the high-pressure behavior of ettringite are those of Cuesta et al. [10] and Clark et al. [6]. Despite the previous studies at high pressure provided a general view of the compressional behavior of ettringite, a description of the deformation mechanisms at the atomic scale is still missing, as the quality of the X-ray powder diffraction data at high pressure, coupled with the structural complexity of ettringite, hindered the structure refinements. Furthermore, the K_0 value obtained by Clark et al. [6] is merely qualitative as it is the result of the fit through only two P - V points. On the other hand, Cuesta et al. [10] compressed the ettringite powder in silicone oil, considering an hydrostatic limit of 3 GPa according to Klotz et al. [11]. However, Ross et al. [12] described silicone oil as hydrostatic only up 0.8 GPa, and the poor data fit of Cuesta et al. [10], with one single function between 0 and 3 GPa, could be the result of using silicone oil out of its effective hydrostatic limit.

In this light, we have investigated the compressional behavior of ettringite up to 4.2 GPa by means of *in-situ* single-crystal synchrotron X-ray diffraction, using a diamond-anvil cell (DAC) and the mix methanol:ethanol (4:1) P -transmitting fluid, which allow a description of the structure deformation mechanisms at the atomic scale and the determination of the bulk elastic parameters of ettringite, based on hydrostatic conditions within the P -range investigated [11,12].

2. Experimental methods and structure refinement protocol.

A preliminary single-crystal X-ray diffraction data collection was performed using an Xcalibur Oxford Diffraction diffractometer equipped with a CCD detector, graphite-monochromatized Mo- $K\alpha$ radiation, and operating at 50 kV and 30 mA at the Earth Sciences Department – University of Milan. Diffraction data from a series of crystals of ettringite from N’Chwaning mine (*i.e.*, the same specimen described by Gatta et al. [5]), were collected by a combination of ω and ϕ scans, in order to maximize the reciprocal

space coverage, with a step size of 1° and an exposure time of 30 s per frame. Afterwards, a crystal with a prismatic habit (~90 x 30 x 20 µm in size) was selected for the high-pressure experiment, performed at the ID15B beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. A parallel monochromatic beam ($E \sim 30$ KeV, $\lambda \sim 0.414$ Å) was used for the diffraction experiment. The diffraction patterns were collected by a MAR555 flat-panel detector, positioned at 287.43 mm from the sample position. Further details on the beamline setup are reported in Merlini and Hanfland [13]. The crystal was loaded in a membrane-driven DAC, with 600 µm culet Boehler-Almax design anvils, along with few ruby spheres for pressure determination (pressure uncertainty ± 0.05 GPa, Mao et al. [14]). 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 = 4:1 mixture, used as hydrostatic P -transmitting fluid, a first data collection was performed with the crystal in the DAC without any P -fluid, whereas fourteen data collections (two of which in decompression) have been performed at different pressures up to 4.22 GPa. 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. Indexing of the diffraction peaks and integration of their intensities (corrected for Lorentz-polarization effects) was performed using the CrysAlis package [15]. Corrections for absorption (caused by the DAC components) was applied using the semi-empirical *ABSPACK* routine implemented in CrysAlis [15]. All the structure refinements were performed using the package JANA2006 [16], in the space group $P31c$, as suggested by the diffraction patterns and by the reflection conditions, using the initial fractional coordinates from Gatta et al. [5]. The positions of the inter-column “free” H₂O sites were obtained by a careful analysis of the difference-Fourier maps of the electron density, based on the structure refinements performed with the crystal in air. The analysis of the difference-Fourier maps of the electron density function revealed a cigar-like shape of the Ca atom occupying the Ca2 site, so this site was refined with an anisotropic displacement parameter. In order to reduce the number of the refined variables, the displacement parameters (D.P.) of all the sites (excluding Ca2) were refined as isotropic. Moreover, the

Site	P (GPa)	$S.o.f$	X	Y	Z	U_{iso}
O3	2.30(5)	1	0.995(2)	0.854(1)	0.0470(5)	0.013(3)
	0.0001	1	-0.010(1)	0.129(2)	0.7986(5)	0.017(1)
	0.54(5)	1	-0.010(1)	0.130(2)	0.7980(5)	0.017(1)
	1.35(5)	1	-0.010(1)	0.134(1)	0.7980(5)	0.017(1)
	1.84(5)	1	-0.011(1)	0.133(1)	0.7982(5)	0.017(1)
O4	2.30(5)	1	-0.011(1)	0.134(1)	0.7987(5)	0.017(1)
	0.0001	1	-0.005(1)	0.868(1)	0.1884(4)	0.010(2)
	0.54(5)	1	-0.006(1)	0.867(1)	0.1880(5)	0.010(2)
	1.35(5)	1	-0.005(1)	0.867(1)	0.1877(4)	0.011(2)
	1.84(5)	1	-0.006(1)	0.865(1)	0.1880(5)	0.012(2)
O5	2.30(5)	1	-0.006(2)	0.865(1)	0.1886(5)	0.015(2)
	0.0001	1	-0.006(1)	0.348(1)	0.0434(4)	0.032(3)
	0.54(5)	1	-0.007(1)	0.348(1)	0.0444(4)	0.030(3)
	1.35(5)	1	-0.005(1)	0.349(1)	0.0436(5)	0.032(3)
	1.84(5)	1	-0.005(1)	0.351(1)	0.0436(4)	0.032(3)
O6	2.30(5)	1	-0.004(2)	0.351(1)	0.0426(5)	0.034(3)
	0.0001	1	0.007(1)	0.669(1)	0.9591(4)	0.018(2)
	0.54(5)	1	0.006(1)	0.668(1)	0.9589(4)	0.016(2)
	1.35(5)	1	0.006(1)	0.668(1)	0.9587(4)	0.021(2)
	1.84(5)	1	0.006(1)	0.667(1)	0.9590(4)	0.020(2)
O7	2.30(5)	1	0.006(1)	0.668(1)	0.9592(4)	0.025(2)
	0.0001	1	-0.002(1)	0.331(1)	0.2060(5)	0.029(3)
	0.54(5)	1	-0.001(1)	0.334(1)	0.2055(4)	0.023(2)
	1.35(5)	1	-0.001(1)	0.335(1)	0.2056(4)	0.024(2)
	1.84(5)	1	0.001(1)	0.337(1)	0.2064(4)	0.025(2)
O8	2.30(5)	1	0.002(1)	0.338(1)	0.2067(4)	0.027(2)
	0.0001	1	0.996(2)	0.641(2)	0.7900(5)	0.047(4)
	0.54(5)	1	0.997(2)	0.638(2)	0.7900(6)	0.059(5)
	1.35(5)	1	0.998(2)	0.637(2)	0.7901(6)	0.059(5)
	1.84(5)	1	0.998(2)	0.635(2)	0.7908(5)	0.058(4)
O9	2.30(5)	1	0.997(2)	0.633(2)	0.7914(6)	0.064(5)
	0.0001	1	0.259(2)	0.405(2)	0.6186(7)	0.035(5)
	0.54(5)	1	0.258(2)	0.406(2)	0.6216(7)	0.037(5)
	1.35(5)	1	0.262(2)	0.407(2)	0.6221(7)	0.036(5)
	1.84(5)	1	0.260(2)	0.407(2)	0.6216(7)	0.031(5)
O10	2.30(5)	1	0.260(2)	0.407(2)	0.6214(6)	0.023(4)
	0.0001	1	0.744(2)	0.592(2)	0.3726(6)	0.037(5)
	0.54(5)	1	0.744(2)	0.596(2)	0.3739(6)	0.032(5)
	1.35(5)	1	0.743(2)	0.593(2)	0.3741(6)	0.029(4)
	1.84(5)	1	0.742(2)	0.593(2)	0.3745(6)	0.031(4)
O11	2.30(5)	1	0.742(2)	0.593(2)	0.3758(6)	0.040(5)
	0.0001	1	0.240(2)	0.398(2)	0.1218(7)	0.037(4)
	0.54(5)	1	0.247(2)	0.405(2)	0.1243(8)	0.042(5)
	1.35(5)	1	0.249(2)	0.406(2)	0.1256(7)	0.043(5)
	1.84(5)	1	0.251(2)	0.408(2)	0.1259(7)	0.040(5)

Table S2a Refined positional and displacement parameters of ettringite as a function of pressure (* see table S2b).

Site	<i>P</i> (GPa)	<i>S.o.f</i>	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>U_{iso}</i> (Å ²)
Ca1	0.0001	1	0.0040(5)	0.8101(6)	0.8101(6)	0.017(1)
	0.54(5)	1	0.0042(5)	0.8085(6)	0.8687(2)	0.016(1)
	1.35(5)	1	0.0045(5)	0.8082(6)	0.8684(2)	0.016(1)
	1.84(5)	1	0.0039(5)	0.8068(5)	0.8681(1)	0.015(1)
	2.30(5)	1	0.0033(6)	0.8063(5)	0.8681(2)	0.017(1)
Ca2	0.0001	1	0.9971(6)	0.1900(6)	0.1189(2)	0.023(2)*
	0.54(5)	1	0.9968(6)	0.1904(6)	0.1185(2)	0.022(2)*
	1.35(5)	1	0.9974(6)	0.1921(6)	0.1184(2)	0.022(2)*
	1.84(5)	1	0.9976(6)	0.1927(6)	0.1182(2)	0.022(2)*
	2.30(5)	1	0.9976(6)	0.1934(6)	0.1182(2)	0.022(2)*
Al1	0.0001	1	0	0	-0.0055(7)	0.0108(9)
	0.54(5)	1	0	0	-0.0061(7)	0.0122(9)
	1.35(5)	1	0	0	-0.0063(6)	0.0120(9)
	1.84(5)	1	0	0	-0.0063(6)	0.0116(9)
	2.30(5)	1	0	0	-0.0068(6)	0.0123(9)
Al2	0.0001	1	0	0	0.2440(6)	0.0120(9)
	0.54(5)	1	0	0	0.2436(7)	0.0115(9)
	1.35(5)	1	0	0	0.2433(6)	0.0109(9)
	1.84(5)	1	0	0	0.2433(5)	0.0108(8)
	2.30(5)	1	0	0	0.2432(6)	0.0118(9)
S1	0.0001	1	1/3	2/3	0.4853(5)	0.0365(8)
	0.54(5)	1	1/3	2/3	0.4855(5)	0.0346(8)
	1.35(5)	1	1/3	2/3	0.4862(5)	0.0332(8)
	1.84(5)	1	1/3	2/3	0.4870(5)	0.0324(7)
	2.30(5)	1	1/3	2/3	0.4873(5)	0.0341(8)
S2	0.0001	1	1/3	2/3	0.7473(5)	0.0365(8)
	0.54(5)	1	1/3	2/3	0.7471(5)	0.0346(8)
	1.35(5)	1	1/3	2/3	0.7472(5)	0.0332(8)
	1.84(5)	1	1/3	2/3	0.7472(5)	0.0324(7)
	2.30(5)	1	1/3	2/3	0.7475(5)	0.0341(8)
S3	0.0001	1	1/3	2/3	0.0004(5)	0.0365(8)
	0.54(5)	1	1/3	2/3	0.0006(5)	0.0346(8)
	1.35(5)	1	1/3	2/3	0.0005(5)	0.0332(8)
	1.84(5)	1	1/3	2/3	0.0006(4)	0.0324(7)
	2.30(5)	1	1/3	2/3	0.0007(4)	0.0341(8)
O1	0.0001	1	0.992(1)	0.119(1)	0.9395(5)	0.014(3)
	0.54(5)	1	0.990(1)	0.122(1)	0.9388(5)	0.012(3)
	1.35(5)	1	0.994(1)	0.124(1)	0.9383(5)	0.013(3)
	1.84(5)	1	0.994(1)	0.124(1)	0.9379(4)	0.012(3)
	2.30(5)	1	0.996(1)	0.126(1)	0.9374(5)	0.016(3)
O2	0.0001	1	0.994(1)	0.857(1)	0.0485(5)	0.013(3)
	0.54(5)	1	0.992(1)	0.856(1)	0.0482(5)	0.014(3)
	1.35(5)	1	0.993(1)	0.855(1)	0.0484(5)	0.014(3)
	1.84(5)	1	0.993(1)	0.124(1)	0.9379(4)	0.012(3)

D.P. of the H₂O-oxygen occupying the O19 and O20 sites were fixed to $U_{iso} = 0.03 \text{ Å}^2$ and those occupying the sites O13, O15, O16, O17 and O18 were fixed to $U_{iso} = 0.08 \text{ Å}^2$, leading to the best figures of merit. As common for high-pressure experiments based on X-ray diffraction, no H-sites were located and refined. It is worth to underline that, differently from the structural model of Gatta et al. [5], in this study the maximum of the electron density function corresponding to O20 is positioned on the three-fold axis. This is probably a mere artifact of the structure refinement, induced by the low number of reflections available with the crystal in the DAC (due to the limited portion of the reciprocal space actually accessible).

The refined unit-cell parameters at high pressure are listed in Tables 1 and shown in Fig. 2. The principal statistical parameters of the structure refinements are listed in Table S1 (supplementary materials, SM). Atomic coordinates, site occupancy factors and displacement parameters of selected structure refinements are given in Table S2 (SM). Relevant inter-atomic distances are reported in Tables 2, 3 and S3.

3. Results and discussion

Compressional behaviour

The evolution of the unit-cell volume of ettringite with pressure (data listed in Table 1) is shown in Fig. 2. The compressional pattern appears to be monotonic up to 3 GPa, where a change of the compressional behavior occurs. Above 3 GPa, a marked increase of the volume compressibility takes place, mainly due to a softening on the *ab* plane (see Fig. 2). It is worth to note that such a softening is coupled with a sharp decrease of the number of observed reflections, which ultimately hindered any structure refinements above 2.3 GPa (see next section). **Data collected in decompression at 1.16 and 0.25 GPa (blue triangles in Fig. 2) are perfectly in trend with the data collected during compression. This proves an ideal elastic behavior of ettringite within the *P*-range investigated.**

To describe the (isothermal) compressional behavior of ettringite, the unit-cell volume vs. pressure data were fitted, using the EoS Fit 7.0 software, to an isothermal Birch-Murnaghan equation of state

(BM-EoS), truncated to the second order in energy [17,18]. The Birch-Murnaghan EoS [17] is based upon the assumption that the high-pressure strain energy in a solid can be expressed as a Taylor series in the Eulerian finite strain, defined as:

$$f_E = [(V_{P0}/V_P)^{2/3} - 1] / 2.$$

Expansion in the Eulerian strain polynomial has the following form:

$$P(f_E) = 3K_0 f_E (1 + 2 f_E)^{5/2} \{ 1 + \frac{3}{2}(K' - 4) f_E + 3/2[K_0 K'' + (K' - 4)(K' - 3) + \frac{35}{9}] f_E^2 + \dots \}.$$

This isothermal equation of state allows to obtain the isothermal bulk modulus of a given material K_0 [$K_0 = -V \cdot (\partial P / \partial V)_{P0}$, which is the reciprocal of the thermodynamic volume compressibility coefficient $\beta_0 = 1/K_0 = -1/V \cdot (\partial V / \partial P)_{P0}$], and its P -derivatives ($K' = \partial K_0 / \partial P$, $K'' = \partial^2 K_0 / \partial P^2$). For the experimental data of ettringite, the fit was performed using the data weighted by the uncertainties in P and V , and the refined elastic parameters obtained by the least-squares fit are listed in Table 4. The refined bulk modulus at ambient conditions ($K_0 = 26.6(5)$ GPa) is comparable (although significantly more precise) to those obtained experimentally by Clark et al. [6] and calculated on the basis of DFT simulation by Manzano et al. [9] (*i.e.*, 27(7) and 29 GPa, respectively).

Ettringite shows a significant anisotropic compressional pattern, with $K(c)_0 \sim 2K(a,b)_0$ (being the axial moduli defined as $K_{j0} = 1/3\beta_{j0} = -1/3l_j \cdot (\partial l_j / \partial P)_{P0}$, with l_j as a given unit-cell edge length), in fair agreement with the previous high-pressure investigations and simulations (Table 4). At $P > 3$ GPa, ettringite experiments an abrupt increase in the bulk compressibility. Into detail, by fitting the data between 3 and 4.2 GPa, the K_0 drops from 26.6(5) to 10.4(8) GPa. Such a softening is largely anisotropic, as it affects particularly the ab plane (*i.e.*, $K(a)$ drops from 21(1) to 7.3(8) GPa), whereas the linear bulk moduli $K(c)$ is far less affected (Tab. 4).

Structure evolution at increasing pressure

The evolution of the bond-distances with P shows that the SO₄ tetrahedra are almost incompressible within the P -range investigated. The Al-octahedra are more compressible, as the Al-O

Supplementary material

Table S1a. Details pertaining to the structure refinements of ettringite as a function of pressure.

P (GPa)	0.0001	0.54(5)	1.35(5)	1.84(5)	2.30(5)
$\min \leq h \leq \max$	-16; +15	-4; +4	-15; +15	-16; +15	-15; +15
$\min \leq k \leq \max$	-17; +16	-16; +16	-15; +15	-15; +15	-5; +5
$\min \leq l \leq \max$	-34; +34	-33; +33	-33; +32	-33; +33	-33; +33
Unique reflections	2963	3216	3116	3077	3022
Observed reflections $I > 3\sigma(I)$	1326	1260	1261	1245	1192
R_{int} (obs)	0.038	0.076	0.063	0.055	0.058
R_{int} (all)	0.042	0.080	0.066	0.058	0.060
R_1 (obs)	0.092	0.101	0.099	0.098	0.099
R_1 (all)	0.175	0.182	0.167	0.167	0.169
wR_1 (obs)	0.112	0.119	0.118	0.115	0.119
wR_1 (all)	0.115	0.124	0.120	0.118	0.121
Residuals ($e^-/\text{\AA}^3$)	-1.11; +1.08	-1.31; +1.04	-1.35; +1.05	-1.30; +0.87	-1.07; +1.08

Table S1b. Details pertaining to the structure intensity data reduction of ettringite as a function of pressure, only the number of observed reflections (with $I > 3\sigma(I)$) are shown.

P (GPa)	0.0001	0.08(5)	0.13(5)	0.25(5)	0.54(5)	0.91(5)	0.93(5)	1.35(5)	1.84(5)
Number of reflections	1326	1011	1262	1361	1260	1264	1379	1261	1245

P (GPa)	2.30(5)	2.81(5)	3.41(5)	4.22(5)	1.16(5)	0.27(5)
Number of reflections	1192	405	217	120	953	980

distances are compressed by 0.01-0.04 Å within the *P*-range investigated (Tab. 2). The Ca-O distances are more significantly affected by the applied pressure, with a contraction ranging between 0.02 and 0.08 Å, between 0.001 and 2.30 GPa (Tab. S1). Even the O19···O19 distance (distance between the inter-column “free” H₂O molecules generated by the three-fold axis) and the O19···O15 and O19···O13 ones (which represent, respectively, the distances between the H₂O molecule and the oxygen atoms of the S1- and S3-tetrahedra) are only slightly affected in response to the applied pressure. The most prominent changes in the ettringite structure at high pressure affect the O···O distances involving the oxygen atoms of the SO₄-tetrahedra and those of the Ca(OH)₄(OH₂)₄-polyhedra (Tab. 3, Fig. 3). These inter-atomic distances lie on the *ab* -plane and decrease pronouncedly in response to the applied pressure (*e.g.*, O9···O16 and O5···O15 decrease by almost 0.2 Å), which is consistent with the fact that the linear bulk modulus along the *c* direction is almost twice that along the *a* (or *b*) direction. It is worth to remember that O5, O6, O8, O9, and O19 are all oxygen sites of H₂O molecules and that, unfortunately, it is impossible to localize the corresponding H atoms in high-pressure experiments. Nevertheless, based on the hydrogen atoms configuration recently reported by Gatta et al. [5], on the basis of a single-crystal neutron structure refinement, it is possible to draw some considerations. For instance, O15 site is at ~1.82 Å from H16, H7 and H1. O6 is the oxygen site of the H₂O molecule having H1 and H6 as proton sites. Similarly, O16 is also at ~1.82 Å from H12, H11 and H15, and O9 is the H₂O oxygen site having H15 and H16 as proton sites. O18 is at ~1.80 Å from H3, H2 and H6, and O5 is the H₂O oxygen site having H3 and H7 as proton sites, whereas O6 has H6 and H1 as proton sites. This means that, overall, the interaction O15···O6, O16···O9, O18···O5 and O18···O6 are mediated by H-bonds. As pressure increases, the distances between the oxygen sites drastically decrease (Tab. 3, Fig. 3). This is consistent with the findings of Clark et al. [6], which indicated that the amorphization process takes place at ~3 GPa.

As no other inter-atomic distances evolve in a significant way, the only realistic explanation to the collapse of the structure it is connected to the increasing interaction between the oxygen atoms of the

Ca-polyhedra and those of the SO₄ tetrahedra, as well as to the likely collapse of the H-bonding system. Considering that the crystal structure of ettringite consists of [Ca₃[Al(OH)₆]·12H₂O]-columns parallel to [001], and connected by sulphate groups *via* hydrogen bonds with H₂O molecules, a significant change in the H-bonding scheme could lead to critical derangements. As the hydrogen bond strength follows the same exponential trend that dipole-dipole interactions follow, it decays with r^3 (where r is the distance between the two dipoles). In this light, a decrease of 0.20 Å of the $O_{donor} \cdots O_{acceptor}$ distance (*i.e.*, as revealed by the structure refinements) is pronounced and may lead to a dramatic change of the bonding configuration, ultimately resulting in weakening of the structure itself, which is consistent with the elastic softening observed by the P - V plot (Fig. 2, Tab. 4).

Based on their DFT simulations, Manzano et al. [9] calculated the K_{P0} of ettringite and predicted the densification of the hydrogen bonds scheme, which is indirectly corroborated by the structure refinements of our study. The authors, however, indicated a decrease of the bulk compressibility in response to such a densification. Nevertheless, the interactions between the hydrogen bonds network and the oxygen sites of the SO₄-tetrahedra ultimately enhance the bulk compressibility, given rise to the opposite elastic behavior, as experimentally observed. It is highly likely that the complex network of weak inter-atomic interactions in the ettringite structure is the cause of the discrepancy between DFT modelling and experimental behavior.

4. Concluding remarks

In this study, the bulk modulus of ettringite is more precisely determined, based on a second-order Birch-Murnaghan EoS fit, with respect to the previous studies: $K_0 = 26.6(5)$ GPa (with $\beta_0 = 0.038(1)$ GPa⁻¹). The compressibility of ettringite is significantly anisotropic, being $K(c)_0 \sim 2K(a,b)_0$. At $P > 3$ GPa, a pronounced softening of the structure, mainly governed by a sharp increase of the (001) compressibility, occurs; such a softening is accompanied and followed by a severe decrease of the number of observed reflections, which hinders any structure refinement above 2.2 GPa. The high-pressure behavior of

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Fig. 1. (*Right side*) Crystal structure of ettringite, viewed down [001], and (*left side*) view of the $[\text{Ca}_3[\text{Al}(\text{OH})_6]\cdot 12\text{H}_2\text{O}]$ -column running along [001] (SO_4 -tetrahedra in green, $\text{Al}(\text{OH})_6$ -octahedra in light blue and $\text{Ca}(\text{OH})_4(\text{OH}_2)_4$ -polyhedra in yellow).

Fig. 2. (*Left side*) Evolution of the unit-cell volume of ettringite with pressure (*black squares* and *red circles*: compression path; *blue diamonds*: decompression path). (*Right side*) Evolution of the normalized (to P_0) unit-cell parameters of ettringite (a/a_0 in *black squares* for the compression path, in *upward-blue triangles* for the decompression path; c/c_0 in *red circles* for the compression path, in *downward-green triangles* for the decompression path).

Fig. 3. High-pressure evolution of the relevant $\text{O}\cdots\text{O}$ distances: (*left*) $\text{O5}\cdots\text{O18}$ in black squares, $\text{O5}\cdots\text{O15}$ in red circles, $\text{O6}\cdots\text{O18}$ in upward-blue triangles, $\text{O6}\cdots\text{O15}$ in downward-green triangles, (*mid*) $\text{O7}\cdots\text{O16}$ in black squares, $\text{O7}\cdots\text{O19}$ in red circles, $\text{O8}\cdots\text{O19}$ in upward-blue triangles, $\text{O8}\cdots\text{O16}$ in downward-green triangles; (*right*) $\text{O9}\cdots\text{O15}$ in black squares, $\text{O9}\cdots\text{O16}$ in red circles, $\text{O10}\cdots\text{O18}$ in upward-blue triangles, $\text{O11}\cdots\text{O17}$ in downward-green triangles, $\text{O12}\cdots\text{O13}$ in pink diamonds.

ettringite, at the atomic level, is here described, for the first time, from ambient pressure up to 2.2 GPa. Despite no dramatic changes are observed for the SO_4 -tetrahedra, $\text{Al}(\text{OH})_6$ -octahedra and $\text{Ca}(\text{OH})_4(\text{OH}_2)_4$ -polyhedra, a significant shortening of the $\text{O}_{\text{donor}}\cdots\text{O}_{\text{acceptor}}$ distances between the oxygen sites of the $\text{Ca}(\text{OH})_4(\text{OH}_2)_4$ -polyhedra (*donors*) and SO_4 -tetrahedra (*acceptors*) occurs. Such an effect leads to a pronounced change of the H-bonding configuration (“*densification of the hydrogen bond network*”, as defined by Manzano et al. [9]) but, contrarily to the compressional behavior modeled by Manzano et al. [9], the final result is a significant softening of the structure, as our P - V data evolution shows.

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Table 1: Unit-cell parameters of ettringite with pressure (* data collected in decompression).

P (GPa)	V (Å ³)	a (Å)	c (Å)
0.0001	2332.9(9)	11.2104(2)	21.4350(3)
0.08(5)	2320(1)	11.1880(3)	21.4063(3)
0.13(5)	2317(1)	11.1816(3)	21.3988(4)
0.25(5)	2307(1)	11.1630(3)	21.3784(4)
0.54(5)	2288(1)	11.1216(4)	21.3406(5)
0.91(5)	2261(1)	11.0748(3)	21.2850(4)
0.93(5)	2260.6(8)	11.0740(3)	21.2852(4)
1.35(5)	2230.8(8)	11.0160(2)	21.2267(3)
1.84(5)	2197.9(9)	10.9505(2)	21.1647(3)
2.30(5)	2169(1)	10.8902(2)	21.1164(3)
3.00(5)	2126(1)	10.803(2)	21.038(2)
3.41(5)	2048(2)	10.609(5)	21.015(6)
4.22(5)	1930(4)	10.345(6)	20.827(11)
1.16(5)*	2235.7(9)	11.0254(3)	21.2367(4)
0.27(5)*	2296(1)	11.1415(4)	21.3556(6)

Table 2: Ca-O distances and Al-O distances (in Å) based on the structure refinement at high pressure.

P (GPa)	Ca1-O1	Ca1-O3	Ca1-O1	Ca1-O6	Ca1-O3	Ca1-O8	Ca1-O10	Ca1-O12
0.0001	2.378(1)	2.377(1)	2.454(1)	2.500(1)	2.497(1)	2.517(1)	2.635(1)	2.721(1)
0.54(5)	2.363(1)	2.384(1)	2.464(2)	2.483(2)	2.489(1)	2.506(2)	2.596(2)	2.662(2)
1.35(5)	2.372(1)	2.373(1)	2.420(1)	2.469(2)	2.476(1)	2.492(2)	2.580(2)	2.657(2)
1.84(5)	2.362(1)	2.350(1)	2.419(1)	2.466(2)	2.474(1)	2.468(2)	2.575(2)	2.627(2)
2.30(5)	2.362(1)	2.335(1)	2.389(1)	2.455(2)	2.462(1)	2.461(2)	2.572(3)	2.639(2)

P (GPa)	Ca2-O4	Ca2-O5	Ca2-O7	Ca2-O5	Ca2-O4	Ca2-O2	Ca2-O11	Ca2-O9
0.0001	2.358(1)	2.358(1)	2.443(1)	2.414(1)	2.470(1)	2.503(1)	2.544(1)	2.661(1)
0.54(5)	2.341(1)	2.341(1)	2.438(2)	2.380(2)	2.462(1)	2.505(1)	2.505(2)	2.632(3)
1.35(5)	2.337(1)	2.337(1)	2.424(2)	2.358(2)	2.443(1)	2.485(1)	2.596(2)	2.639(3)
1.84(5)	2.337(1)	2.355(1)	2.435(2)	2.355(2)	2.448(1)	2.483(1)	2.601(2)	2.607(3)
2.30(5)	2.336(1)	2.336(1)	2.430(2)	2.353(2)	2.446(1)	2.476(1)	2.589(2)	2.592(3)

P (GPa)	Al1-O1	Al1-O2	Al2-O3	Al2-O4
0.0001	1.806(1)	1.957(1)	1.913(1)	1.877(1)
0.54(5)	1.838(1)	1.941(1)	1.898(1)	1.873(1)
1.35(5)	1.830(1)	1.950(1)	1.922(1)	1.856(1)
1.84(5)	1.821(1)	1.940(1)	1.913(1)	1.847(1)
2.30(5)	1.826(1)	1.932(1)	1.920(1)	1.840(1)

Table 3: Relevant O···O distances between the oxygen sites of the SO₄-tetrahedra, Ca(OH)₄(OH₂)₄-polyhedra and inter-column “free” H₂O (in Å).

P (GPa)	O5···O18	O5···O15	O6···O18	O6···O15	O7···O16	O7···O19	O8···O19
0.0001	2.787(1)	2.946(1)	2.701(1)	2.683(1)	2.868(1)	2.990(1)	2.693(1)
0.54(5)	2.755(1)	2.843(2)	2.777(2)	2.665(2)	2.884(2)	2.927(2)	2.648(1)
1.35(5)	2.721(1)	2.807(2)	2.744(2)	2.613(2)	2.814(2)	2.881(2)	2.617(1)
1.84(5)	2.690(1)	2.760(2)	2.714(2)	2.588(2)	2.785(2)	2.807(2)	2.599(1)
2.30(5)	2.658(1)	2.748(2)	2.692(2)	2.561(2)	2.766(2)	2.787(2)	2.596(1)

P (GPa)	O8···O16	O9···O15	O9···O16	O10···O18	O11···O17	O12···O13
0.0001	2.706(1)	2.763(1)	2.770(1)	2.827(1)	2.899(1)	2.905(2)
0.54(5)	2.692(2)	2.860(2)	2.670(1)	2.722(2)	2.819(2)	2.869(2)
1.35(5)	2.654(2)	2.830(2)	2.604(2)	2.662(2)	2.801(2)	2.820(2)
1.84(5)	2.628(2)	2.833(2)	2.604(2)	2.641(2)	2.771(2)	2.806(2)
2.30(5)	2.650(2)	2.802(2)	2.575(2)	2.609(2)	2.730(2)	2.781(2)

Table 4: Refined isothermal elastic parameters of ettringite based on an II-BM equation of state fits.

	V_0, x_0 (Å ³ , Å)	K_0 (GPa)	K'	$\beta_{V,l}$ (GPa ⁻¹)
Data fitted up to 3.0 GPa (see section 3. Results)				
V	2331(2)	26.6(5)	4	0.038(1)
a	11.213(3)	21(1)	4	0.0159(8)
c	21.421(3)	47(1)	4	0.0071(2)
*Average compressibility between 3 and 4.22 GPa (see section 3. Results)				
V	-	10.4(8)	4	0.0756*
a	-	7.3(8)	4	0.0348*
c	-	34(11)	4	0.0082*