

Article

High Pressure Behavior of Mascagnite from Single Crystal Synchrotron X-ray Diffraction Data

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Abstract: High-pressure synchrotron X-ray diffraction was carried out on a single crystal of mascagnite, compressed in a diamond anvil cell. The sample maintained its crystal structure up to ~18 GPa. The volume–pressure data were fitted by a third-order Birch–Murnaghan equation of state (BM3-EOS) yielding $K_0 = 20.4(7)$ GPa, $K'_0 = 6.1(2)$, and $V_0 = 499(1) \text{ \AA}^3$, as suggested by the F–f plot. The axial compressibilities, calculated with BM3-EOS, were $K_{0a} = 35(3)$, $K'_{0a} = 7.7(7)$, $K_{0b} = 10(3)$, $K'_{0b} = 7(1)$, $K_{0c} = 25(1)$, and $K'_{0c} = 4.3(2)$. The axial *moduli* measured using a BM2-EOS and fixing K'_0 equal to 4, were $K_{0a} = 52(2)$, $K_{0b} = 20(1)$, and $K_{0c} = 29.6(4)$ GPa, and the anisotropic ratio of $K_{0a}:K_{0b}:K_{0c} = 1:0.4:0.5$. The evolution of crystal lattice and geometrical parameters indicated no phase transition until 17.6 GPa. Sulphate polyhedra were incompressible and the density increase of 30% compared to investigated pressure should be attributed to the reduction of weaker hydrogen bonds. In contrast, some of them, directed along [100], were very short at room temperature, below 2 Å, and showed a very low compressibility. This configuration explains the anisotropic compressional behavior and the lowest compressibility of the *a* axis.

Keywords: mascagnite; high pressure; crystal structure; ammonium sulphates



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1. Introduction

Mascagnite $(\text{NH}_4)_2\text{SO}_4$ is a rare ammonium sulfate mineral occurring in active volcanic fumaroles (e.g., at Mount Vesuvius, Italy), hot springs, or burning coal mine dumps. It is soft (~2.5 on Mohs Scale), water soluble, and fertilizing. Its crystal structure was described by Schlemper and Hamilton [1] in the orthorhombic space group *Pnam* with $a = 7.782$, $b = 10.636$ and $c = 5.993$ Å, $V = 496.037 \text{ \AA}^3$, and density equal to $17,695 \text{ g/cm}^3$. With their pioneering paper, using neutron diffraction data, they showed the $(\text{NH}_4)_2\text{SO}_4$ structure is comprised of an isolated sulfate and ammonium tetrahedra connected with a complex hydrogen bond system (Figure 1). They found two groups of hydrogen bonds between the H atoms of ammonium groups and the oxygens of SO_4 tetrahedra: one with very short distances, under 2 Å, reported in red in Figure 1, and the second group with longer homologue H ... O distances, reported with dotted segments in the same figure. They proved that $(\text{NH}_4)_2\text{SO}_4$ undergoes a first-order phase transition at $T_c = 223 \text{ K}$ without changing the number of formula unit $Z = 4$. Below the T_c , the mirror plane perpendicular to the *c* axis and the center of inversion disappear, the space group becomes *Pna2₁*, and the unit cell parameters become $a = 7.783$, $b = 10.61$, and $c = 5.967$ Å. The transition produces less distorted ammonium groups and a reduction in the average O–H distances, with six O–H distances at low temperature below 2 Å, whereas there were only two in the room temperature phase. Overall, there is a strengthening of the hydrogen bonds and a reorientation of the ammonium groups. The phase transition involves a change in the electric properties of the mineral. At room temperature, mascagnite has a paraelectric

behavior, whereas at low temperature it has a ferroelectric behavior. The transition was studied by Iqbal and Christoe [2] using Raman scattering. The analyzed transition has both order-disorder and displacive characteristics [3]. In addition, Iqbal and Christoe [2] showed that by decreasing temperature until the transition, not only the order-disorder of the NH_4^+ group appears, but a decrease in the librations of the SO_4 ion coupled with a subtle distortion of the polyhedra through the enhancing hydrogen bond are also evident. Recently, Malec et al. [4] studied the H-bond dynamic in mascagnite and confirmed the intermediate character between a displacive and an order-disorder phase transition. Using ^{14}N NMR spectra collected around 223 °C, Lim [5] showed that the phase transition was caused by the change of the ^{14}N environment in the NH_4^+ groups, i.e., the temperature affects the degree of distortion of the tetrahedral H-N group, rather than the SO_4 group. In one type of ammonium group, $\text{NH}_4(1)$, N-H decreases from 1.075 to 1.053 Å, whereas in $\text{NH}_4(2)$, N-H decreases from 1.062 to 1.048 Å. Mikhaleva [6] showed the effect of temperature and pressure on thermodynamic parameters and the hysteresis at the ferroelectric phase transition.

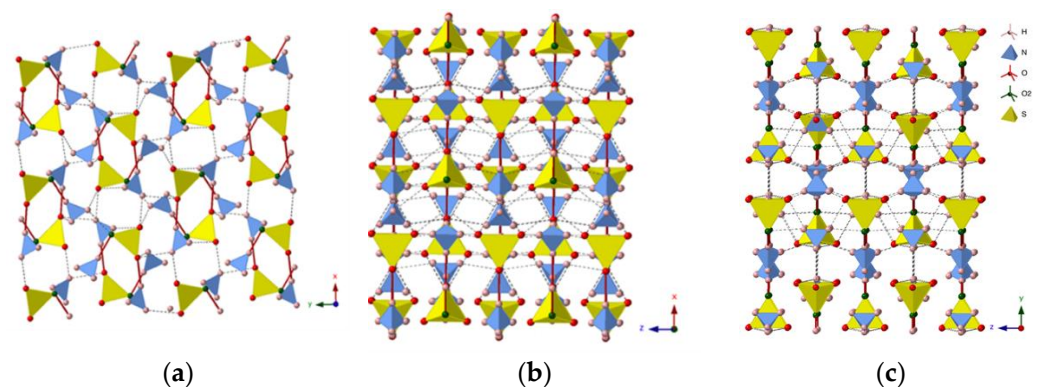


Figure 1. (a) Crystal structure of mascagnite projected along (a) [001], (b) [010], (c) [100]. The red segments indicate the H-O distances below 2 Å, whereas the dotted segments indicate the H-O distances above 2 Å.

Malec et al. [7] minutely described the mechanism of structural change from the para- to the ferroelectric phase of mascagnite for the development of new ferroelectric materials and their possible application as a new generation of electromechanical and optical devices. Significant interest has been paid in those materials in which changes in the hydrogen-bond system are crucial for the appearance of ferroelectric properties. Via the collection of structural data up to 163 K, Malec et al. [7] clarified the mechanism of the phase transitions, showing that it is strongly related to changes in the hydrogen-bond system. At 480 K a phase transition in electrical conductivity of the ammonium sulfate was found [8], but the crystal structural variation was not fully characterized.

Because ammonia is an important precursor to prebiotic chemistry, including in the formation of amino acids and a cascade of other biological chemicals of interest, mascagnite, as an ammonium mineral, has a strong impact on planetology [9,10]. Ammonia is expected to be one of the major constituents of giant planets in the solar system. For example, Neptune is thought to have a layered structure with a hot ice layer (a dense fluid with a C-H-O-N composition) localized between a rocky core and the gaseous atmosphere [11]. NASA's New Horizons space mission has found evidence of ammonia on the surface of Pluto, and it is unknown how this ammonia can survive on the surface of Pluto for such a long period without being destroyed by ultraviolet light, cosmic rays, or other radiation [12]. It has been hypothesized that ammonia comes from an underground ocean, which erupts ammonia-containing water toward the cold surface in a form of cryovolcanism. Ammonia not only allows the water to be liquid at cold temperatures (up to 176 K) [13] but it also is a further support to the hypothesis of an ocean under the cold crust of Pluto [14]. Moreover, Cook et al. [15] found a good fit to the shape and position of the

ammonium band in both Nix and Hydra observed with New Horizons, together with H₂O ice in the crystalline phase.

Moreover, the nitrogen cycle inside and outside the Earth's mantle and its retention mechanisms within the solid planets have been of considerable interest. The N degassing from the Earth mantle can be monitored using ¹⁵N isotope from volcanic gasses, and magmatic rocks, but the nitrogen stored in the mantle is much more difficult to quantify. Vennari et al. [16], who investigated the high-pressure behavior of buddingtonite, an ammonium feldspar, showed how the ammonium behaves within minerals in relation to pressure, how this is relevant to understand the stabilization of ammonium in the high-pressure environments on Earth or other planets, and how the nitrogen can be recycled in planet interiors. Despite a large number of scientific cases concerning the engineering of new technological materials, and terrestrial and planetary environments, this system has been barely explored. To the best of our knowledge, the present paper represents the first study on the high-pressure structure behavior of mascagnite, including an investigation of its compressibility at ambient temperature. By collecting structural data at different pressures using single crystal X-ray synchrotron diffraction measurements, the Equation of State (EoS), the density changes and the evolution of the crystal structure with pressure were determined. A comparison with the changes observed at low temperatures was made to understand whether the phase transition, with the change in the electrical characteristics, occurs at high pressure (HP).

2. Materials and Methods

HP-synchrotron X-ray single-crystal diffraction experiments were performed at the Extreme Conditions Beamline P02.2 at PETRA-III/DESY, Hamburg, Germany, using an incident beam with an energy of 42.7 keV and a focusing spot of ~8.5 (H) μ m 1.8 (V) μ m, from a compound refractive lens system consisting of 111 Be lenses with a radius of 50 μ m (400 μ m beam acceptance) and a focal length of 1221 mm. Several single crystals of mascagnite were tested prior to the compression experiment to assess the degree of crystallinity and the quality of each sample. The highest quality sample, having approximate dimensions of 50 $\times$ 40 $\times$ 20 μ m³, was loaded in a symmetric DAC, equipped with Boehler Almax design diamonds and seats [17] with 70° opening angles and culets having a size of 300 μ m. A 250 μ m thick rhenium gasket was squeezed between the two diamond anvils to achieve a final thickness of ~70 μ m. The sample chamber was then obtained by laser drilling a hole having a diameter of 200 μ m in the center of the indented area. A ruby sphere was loaded together with the selected mascagnite crystal in the sample chamber and served as the pressure calibrant. Pre-compressed neon gas was loaded in the sample chamber at 1.4 kbar using the gas loading system installed at PETRA-III and served as a quasi-hydrostatic pressure transmitting medium.

Diffraction images were acquired on a Perkin Elmer (Wiesbaden, Germany) XRD 1621 flat panel detector. The sample to detector distance (402.34 mm) and detector parameters were calibrated using a CeO₂ standard (NIST 674 a) and a natural enstatite single crystal, respectively.

At each pressure, X-ray step scans were collected upon continuous rotation of the DAC between +30 X° and −28 Y° in ω , with steps of 0.5° and an exposure time of 2 Ns. The CrysAlis package [18] was then used to search and index Bragg peaks, integrate intensities, correct them for Lorentz-polarization effects, and apply empirical absorption correction based on spherical harmonics. The structure refinements were carried out with ShelXle [19] starting from the atomic coordinates of the non-hydrogen atoms from Schlemper and Hamilton [1]. Crystal structures were plotted using CrystalMaker software [20]. Scattering curves for neutral atoms were used. Excellent quality of the data allowed anisotropic refinements for all non-H atoms. The limited data completeness due to the geometry of the diamond anvil cell made it difficult to determine the hydrogen positions under high pressure conditions. Thus, they were not refined. However, the present data enabled the description of the main structural features and their evolution, in addition to an expla-

nation of the anisotropic compression observed in the lattice parameters. Table 1 reports experimental and refinement details at different pressures, and Table 2 shows the fractional coordinates for all non-H atoms at different pressures with the equivalent thermal factors, U_{eq} . All of the crystal structure and hkl data are available as Supplementary Materials.

Table 1. Data collection details and refinement parameters of $(\text{NH}_4)_2\text{SO}_4$ at different pressures.

P (GPa)	P0 (0.0001)	P1 0.29 (2)	P2 1.65 (2)	P3 3.88 (2)	P4 8.68 (2)	P5 10.53 (2)	P6 14.0 (1)	P7 15.83 (2)	P8 17.59 (2)
Space group	<i>Pnma</i>	<i>Pnma</i>	<i>Pnma</i>	<i>Pnma</i>	<i>Pnma</i>	<i>Pnma</i>	<i>Pnma</i>	<i>Pnma</i>	<i>Pnma</i>
<i>a</i> (Å)	7.7915 (6)	7.7584 (7)	7.6550 (5)	7.5489 (3)	7.4019 (2)	7.3509 (4)	7.2762 (3)	7.2360 (5)	7.2029 (7)
<i>b</i> (Å)	10.6522 (9)	10.595 (2)	10.379 (1)	10.0809 (6)	9.6899 (7)	9.580 (1)	9.434 (8)	9.370 (1)	9.328 (2)
<i>c</i> (Å)	5.9972 (5)	5.972 (1)	5.891 (1)	5.7630 (6)	5.5806 (6)	5.527 (1)	5.4425 (7)	5.398 (1)	5.361 (2)
<i>V</i> (Å ³)	497.74 (7)	490.88 (15)	468.01 (10)	438.56 (5)	400.26 (5)	389.24 (9)	373.59 (6)	365.99 (10)	360.20 (13)
Density (g/cm ³)	1.656	1.679	1.761	1.879	2.059	2.117	2.206	2.252	2.288
maximum 2θ	26	26	26	26	26	26	26	26	26
all reflections	1689	1057	989	936	815	776	758	738	716
unique reflections	1274	834	830	811	764	709	716	687	634
refine number parameters	41	41	41	41	41	41	41	41	41
R1 ($ F_0 > 4\sigma$)	0.0439	0.0407	0.0366	0.0385	0.0263	0.0394	0.0302	0.0340	0.0497
wR_2 , all reflections	0.1261	0.1094	0.087	0.0945	0.0778	0.1031	0.0795	0.0904	0.1402
wR_2 , all reflections	0.1136	0.0993	0.0815	0.0889	0.0738	0.0995	0.0761	0.0853	0.1339
goodness of fit	1.105	1.102	1.158	1.127	1.109	1.161	1.118	1.102	1.092
Residues (e [−] /Å ³) max	0.45	0.29	0.29	0.33	0.38	0.51	0.41	0.44	0.84
Residues (e [−] /Å ³) min	−0.49	−0.35	−0.28	−0.34	−0.36	−0.43	−0.37	−0.47	−0.95

Table 2. Atomic coordinates and U_{eq} for all non-H-atoms (Å²) of $(\text{NH}_4)_2\text{SO}_4$ at different pressures. *P* values are given in Table 1.

Sites	P	x	y	z	U_{eq}
S	P0	0.24417 (4)	0.41921 (3)	0.25	0.0218 (1)
	P1	0.24502 (4)	0.41931 (4)	0.25	0.0205 (2)
	P2	0.24859 (3)	0.41925 (3)	0.25	0.0168 (1)
	P3	0.25380 (4)	0.41816 (4)	0.25	0.0146 (1)
	P4	0.26095 (3)	0.41695 (3)	0.25	0.0104 (1)
	P5	0.26310 (5)	0.41701 (4)	0.25	0.0093 (2)
	P6	0.26632 (4)	0.41720 (4)	0.25	0.0088 (1)
	P7	0.26801 (4)	0.41750 (4)	0.25	0.0088 (1)
	P8	0.26933 (7)	0.41784 (7)	0.25	0.0093 (2)

Table 2. Cont.

Sites	P	x	y	z	U_{eq}
N1	P0	0.6895 (2)	0.4033 (1)	0.25	0.0302 (3)
	P1	0.6887 (2)	0.4034 (2)	0.25	0.0285 (4)
	P2	0.6863 (2)	0.4031 (1)	0.25	0.0234 (3)
	P3	0.6840 (2)	0.4036 (2)	0.25	0.0206 (3)
	P4	0.6842 (1)	0.4035 (1)	0.25	0.0148 (2)
	P5	0.6851 (2)	0.4032 (2)	0.25	0.0133 (3)
	P6	0.6874 (2)	0.4024 (1)	0.25	0.0121 (2)
	P7	0.6885 (2)	0.4018 (2)	0.25	0.0119 (3)
N2	P8	0.6902 (3)	0.4014 (3)	0.25	0.0119 (4)
	P0	0.9690 (2)	0.7045 (1)	0.25	0.0325 (3)
	P1	0.9686 (2)	0.7040 (2)	0.25	0.0303 (4)
	P2	0.9704(2)	0.7009 (1)	0.25	0.0245 (3)
	P3	0.9722 (2)	0.6943 (1)	0.25	0.0198 (3)
	P4	0.9684 (1)	0.6832 (1)	0.25	0.0145 (2)
	P5	0.9664 (2)	0.6803 (2)	0.25	0.0129 (3)
	P6	0.9628 (1)	0.6760 (1)	0.25	0.0120 (2)
O1	P7	0.9613 (2)	0.6739 (2)	0.25	0.0116 (3)
	P8	0.9597 (2)	0.6725 (2)	0.25	0.0129 (4)
	P0	0.0618 (2)	0.3888 (2)	0.25	0.0598 (5)
	P1	0.0609 (2)	0.3911 (2)	0.25	0.0537 (6)
	P2	0.0596 (1)	0.3970 (2)	0.25	0.0382 (4)
	P3	0.0602 (1)	0.4018 (2)	0.25	0.0265 (3)
	P4	0.0626 (1)	0.3996 (1)	0.25	0.0158 (2)
	P5	0.0635 (1)	0.3981 (2)	0.25	0.0142 (3)
O2	P6	0.0653 (1)	0.3953 (1)	0.25	0.0126 (2)
	P7	0.0662 (1)	0.3939 (1)	0.25	0.0125 (3)
	P8	0.0676 (2)	0.3925 (2)	0.25	0.0136 (4)
	P0	0.2697 (2)	0.5566 (2)	0.25	0.0453 (4)
	P1	0.2732 (2)	0.5571 (2)	0.25	0.0419 (5)
	P2	0.2857 (2)	0.5587 (1)	0.25	0.0322 (3)
	P3	0.2992 (2)	0.5602 (1)	0.25	0.0244 (3)
	P4	0.3070 (1)	0.5645 (1)	0.25	0.0159 (2)
O3	P5	0.3075 (2)	0.5661 (2)	0.25	0.0149 (3)
	P6	0.3073 (1)	0.5690 (1)	0.25	0.0131 (2)
	P7	0.3071 (2)	0.5704 (2)	0.25	0.0132 (3)
	P8	0.3061 (3)	0.5720 (2)	0.25	0.0142 (4)
	P0	0.3238 (1)	0.3662 (1)	0.0490 (2)	0.0479 (3)
	P1	0.3242 (1)	0.3653 (1)	0.0484 (3)	0.0436 (4)
	P2	0.3257 (1)	0.3613 (1)	0.0448 (2)	0.0344 (3)
	P3	0.3287 (1)	0.3555 (1)	0.0414 (2)	0.0253 (3)
	P4	0.33650 (7)	0.35124 (8)	0.0349 (2)	0.0162 (2)
	P5	0.3395 (1)	0.3510 (1)	0.0333 (2)	0.0142 (2)
	P6	0.3446 (8)	0.35107 (9)	0.0305 (2)	0.0129 (2)
	P7	0.34716 (9)	0.3513 (1)	0.0293 (2)	0.0124 (2)
	P8	0.3495 (2)	0.3518 (2)	0.0276 (3)	0.0120 (3)

3. Results

3.1. Compressibility

The evolution of lattice parameters with pressure was studied by collecting data at different pressures between 0.0001 and 17.6 GPa. The unit cell parameters are listed in Table 1 and the behavior of cell parameters with P is shown in Figure 2. The evolution of all lattice parameters did not show any discontinuity in the pressure range investigated. The P - V data, and the behavior of the cell parameters as a function of pressure, were fitted using the third-order Birch–Murnaghan Equation of State (BM3-EoS) as suggested by the F_E - f_E plots, namely the “Eulerian finite strain” versus “normalized stress” ($F_E = P/[3f_E(1 + 2f_E)^{5/2}$; $f_E = [(V_0/V)^{2/3} - 1]/2$), which is shown in Figure 3 [21–23]. The inclined linear regression lines suggest that the use of a truncated third-order BM3-EoS is appropriate to describe the elastic behavior of mascagnite. The volume–pressure data yielded the following values: $K_0 = 20.2(8)$ GPa, $K' = 6.1(2)$, and $V_0 = 499(1)$ Å³. Axis compressibility, calculated with a BM3-EoS, were $K_{0a} = 35(3)$ GPa, $K'_a = 7.7(7)$, $K_{0b} = 10(3)$ GPa, $K'_b = 7(1)$, $K_{0c} = 25(1)$ GPa, and $K'_c = 4.3(0.2)$. The axial moduli calculated using a second-order Birch–Murnaghan Equation of State (BM2-EoS), fixing K_0' equal to 4, were $K_{0a} = 52(2)$ GPa, $K_{0b} = 20(1)$ GPa, and $K_{0c} = 26.9(4)$ GPa, with a relatively strong anisotropic ratio of $K_{0a}:K_{0b}:K_{0c} = 1:0.4:0.5$, where the most incompressible parameter is a and the most compressible is b .

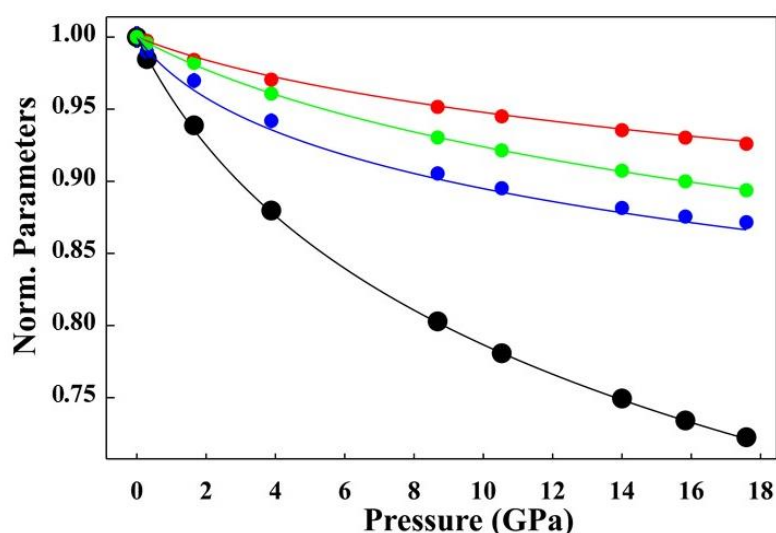


Figure 2. Lattice parameters and volume of mascagnite at different pressures (a lattice parameter—red dots, b lattice parameter—blue dots, c lattice parameter—green dots, V volume cell—black dots). The values are normalized to the room pressure value to highlight the reciprocal difference in the lattice parameters’ compressibilities.

3.2. Crystal Structure Evolution with Pressure

The refined data of mascagnite structure at ambient conditions were in very good agreement with the literature data from Schlemper and Hamilton [1], with one S tetrahedron and two independent ammonium tetrahedra, N1 and N2. No tetrahedron shared vertexes or edges with another, and both S or N and the connections were secured by a complex system of N ... H ... O hydrogen bonds.

The single crystal high-pressure structural data were collected at eight different pressures until 17.6 GPa.

The comparison of high-pressure structural data shows that the volume and average S–O bond distances of sulfate tetrahedron remain almost unchanged, with the average distance $\langle S-O \rangle$ of 1.466 (1)–1.468 (1) Å, and polyhedral volume changing from 1.623 Å³ to 1.610 Å³, in the pressure range 0.0001–17.6 GPa (Table 3). The values are very near to those measured in other sulfate minerals, for example, in bloedite [24] or gypsum [25].

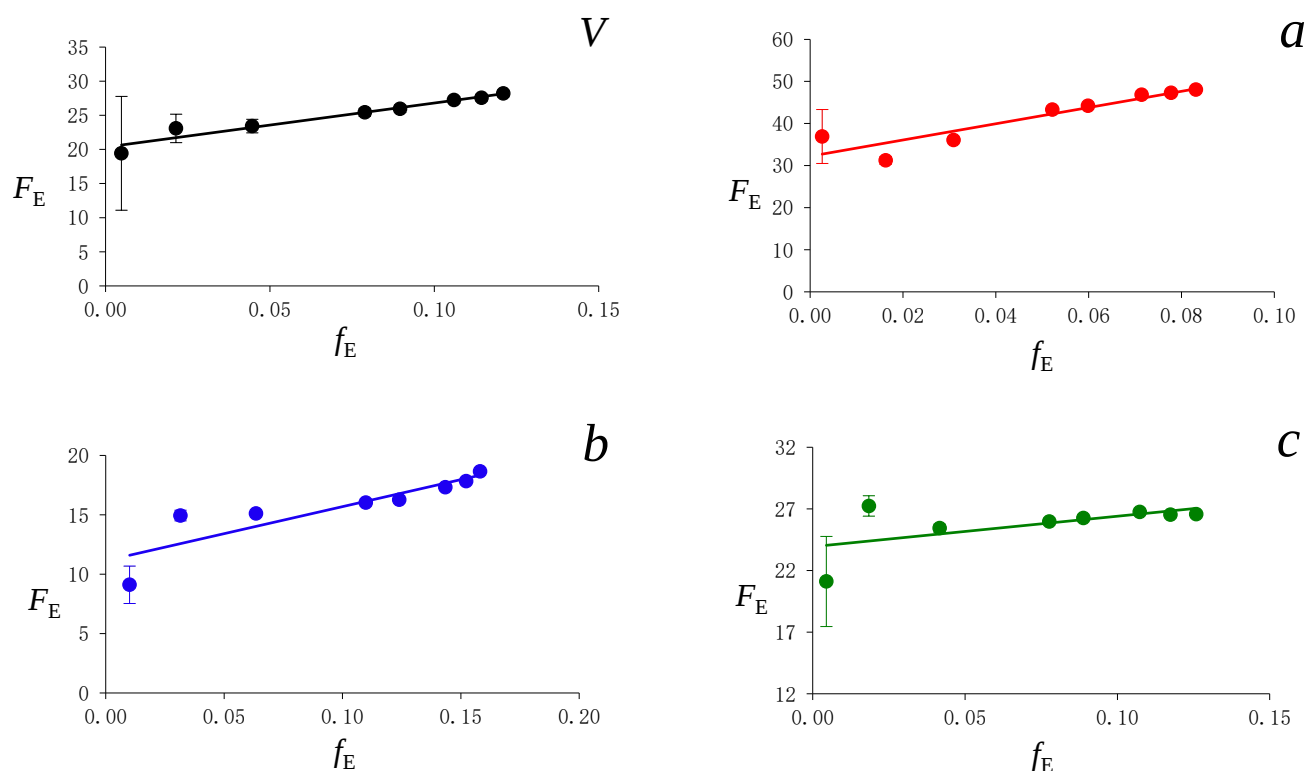


Figure 3. F-f plot. Eulerian finite (f_E) strain versus normalized stress (F_E) with the weighted linear regression through the volume cell data points (graph with black dots), through the a lattice parameters (graph with red dots), through the b lattice parameters (graph with blue dots) and through c lattice parameters (graph with green dots).

Table 3. Bond distances (Å), volume (Å³), and distortion parameters of the SO₄ polyhedron at different pressures.

<i>P</i> (GPa)	P0 (0.0001)	P1 0.29 (2)	P2 1.65 (2)	P3 3.88 (2)	P4 8.68 (2)	P5 10.53 (2)	P6 14.0 (1)	P7 15.83 (2)	P8 17.59 (2)
S-O1	1.458 (2)	1.459 (2)	1.465 (1)	1.470 (1)	1.4779 (8)	1.479 (1)	1.478 (1)	1.477 (1)	1.472 (2)
S-O2	1.477 (2)	1.477 (2)	1.475 (1)	1.472 (2)	1.470 (1)	1.465 (2)	1.462 (1)	1.460 (2)	1.462 (3)
S-O3 (x2)	1.469 (1)	1.468 (2)	1.474 (1)	1.471 (1)	1.4693 (9)	1.466 (1)	1.463 (1)	1.460 (1)	1.461 (2)
<S-O>	1.468	1.467	1.471	1.471	1.4715	1.469	1.466	1.464	1.464
<i>V</i>	1.623	1.622	1.636	1.634	1.635	1.627	1.618	1.611	1.610
Dist. index	0.0035	0.003	0.0022	0.0004	0.0022	0.0032	0.0038	0.0043	0.0028
Quad. elongation	1.0002	1.0001	1.0001	1.0000	1.0000	1.0000	1.0000	1.0000	1.0001

The tetrahedral distortion [26] measured by quadratic elongation and angle distortion (Table 3) shows that the tetrahedra are quite regular at room pressure and become more regular with increasing pressure. In general, under high pressure, the polyhedra become more regular because the longer distances have higher compressibility than that of the shorter distances, and, as a result, regular polyhedra have smaller volumes than those of the distorted polyhedra [27,28]. Otherwise, this may not be true, as a change in free energy establishes the sequence of overall structural evolutions, and exclusions to this general behavior can be found in many compounds. A closer examination of the evolution of bond distances shows that the shortest distance (S-O1) increases, and the longest distance (S-O2) decreases, with pressures of approximately the same quantities, leaving the average bond distances and volumes almost unchanged.

The S-O1 bond distances are directed along the a axis, whereas the S-O2 bond distances are directed along the b axis, and these may explain the strong compressional anisotropy of the lattice parameter.

To analyze the structural evolution with pressure in greater detail, the intermolecular distances between sulfur and nitrogen were measured, without considering the hydrogens' positions (negligible contribution due to low scattering). Figure 4a–c shows simplified representations of mascagnite structures without hydrogen in order to highlight the topological arrangement of S and N tetrahedra. Along the [010] direction, the mascagnite structure can be described as an alternation of two types of layers: one layer with S and N1 tetrahedra, and another layer where there are only N2 tetrahedra. The S-N values are reported in Table 4. The relative compressibility of the different distances, and a plot of the evolution of S-N bond lengths relative to the room pressure value for each distance are reported and evaluated in Figure 5.

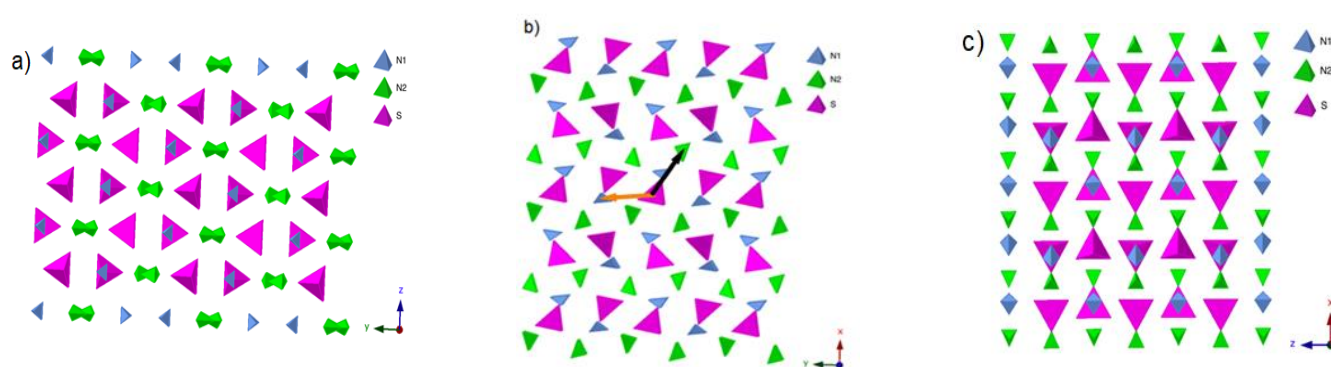


Figure 4. (a) (100) Projection with the y -axis horizontal; (b) (001) projection with the y -axis horizontal; (c) (010) projection with the z -axis horizontal. The polyhedral colors are: cyan for N1H₄, green for N2H₄, purple for SO₄. The segments in Figure 4b represent, in black, the distance S-N1, inclined with the largest component oriented along the x axis; and, in orange, the distance S-N2 oriented along the y axis.

Table 4. Sulfur-nitrogen distances (Å) at different pressures.

P (GPa)	P0 (0.0001)	P1 0.29 (2)	P2 1.65 (2)	P3 3.88 (2)	P4 8.68 (2)	P5 10.53 (2)	P6 14.0 (1)	P7 15.83 (2)	P8 17.59 (2)
S-N1	3.46209	3.446	3.3548	3.2508	3.13572	3.10492	3.06735	3.04636	3.03189
S-N1	3.47368	3.44678	3.37908	3.28566	3.15655	3.12033	3.06881	3.04745	3.03536
S-N1 (x2)	3.58222	3.56501	3.51059	3.4284	3.31328	3.27882	3.22738	3.20152	3.18018
S-N1' (*)	4.32525	4.31984	4.30769	4.30396	4.27089	4.25089	4.21437	4.19469	4.17423
S-N2 (x2)	3.67258	3.65642	3.61096	3.53532	3.40715	3.36928	3.31028	3.28208	3.2584
S-N2	3.71909	3.70159	3.61655	3.5023	3.36808	3.33443	3.31028	3.27069	3.25832
S-N2'	4.37438	4.35128	4.29272	4.24069	4.16793	4.1372	4.09556	4.076	4.02893
S-N2 (x2) (**)	4.38355	4.36508	4.29407	4.20418	4.11473	4.09088	4.05802	4.04095	4.05984

* principal component along the x axis, ** principal component along the y axis.

It is evident that, although the reduction of the S-N distance below 4 Å is almost the same for most bonds, relevant differences are evident in the evolution of S-N distances larger than 4 Å. We observed that the most incompressible distance is S-N1', which has about half of the compressibility of S-N2': $\beta_{S-N1'} = 0.0022 \text{ GPa}^{-1}$, $\beta_{S-N2'} = 0.0044 \text{ GPa}^{-1}$. Figure 4b indicates that S-N1' has the strongest component along the a axis and S-N2' along the b axis; thus, the strong anisotropy in the lattice parameters can be explained.

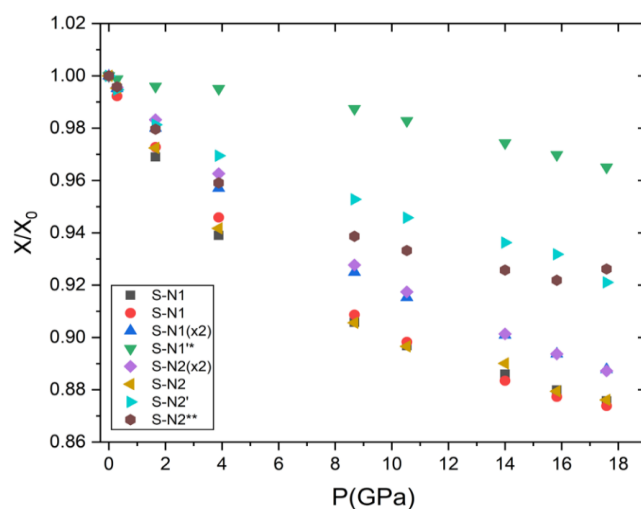


Figure 5. Evolution with pressures of sulfur-nitrogen distances. Values are given relative to their zero-pressure values. * S-N1' principal component along the x axis. ** S-N2 principal component along the y axis.

4. Discussion

The present data thoroughly describes the main structural evolution of mascagnite and explains the anisotropic compression observed in lattice parameters. The following considerations are outlined:

- (1) A strong increase in the density of mascagnite was found in the investigated change in the pressure density from 1.656 g/cm^3 at room pressure to 2.288 g/cm^3 at 17.6 GPa, which represents an increase of approximately 30%. The strong anisotropic contraction was observed in the evolution of the lattice parameters, with the a axis the least sensitive parameter and b the most sensitive parameter. The comparison between the structures refined at room temperature and those under 233 K [1] showed that the a parameter slightly increases, whereas b and c decrease. Shmyt'ko et al. [29] reported an anomalous increase in the lattice parameter a and the unit cell volume at temperatures below the ferroelectric phase transition point ($T_c = 223 \text{ K}$).
- (2) The bulk modulus of mascagnite was compared with those of other sulfates in combination with different metals, Na, Ca, and Mg, and a different amount of water molecules (Table 5 and Figure 6). Specifically, the K_0 and K'_0 of mirabilite, gypsum, bassanite, anhydrite, and other hydrated magnesium-sulfates, such as kieserite, epsomite, and meridianiite, were compared. An inverse relationship between K' and K_0 is evident, which usually occurs in materials with a large range of bulk moduli values. High K' values are found in soft materials, where the compressibility decreases drastically with the increase in pressure. In contrast, hard materials, with high K_0 values, usually have low K' values. In addition, we observed that sulfates with large monovalent cations (NH_4^+ and Na^+ : mascagnite and mirabilite) have a lower bulk modulus with respect to sulfates with small earth alkaline cations, namely, Ca and Mg. (e.g., gypsum and kieserite). Verma and Kumar [30] found a linear relation between the cation charges and the bulk modulus in a large suite series of cubic perovskites. Moreover, the number of water molecules appears to affect the bulk moduli, as observed in the Mg-sulfates suite of kieserite, epsomite, and meridianiite, with 1, 7, and 11 water molecules, respectively. The same results were observed by Comodi et al. [31] in a suite of amphiboles with different numbers of water molecules, where the bulk moduli increased as the oxo-component increased, thus reducing the OH content.
- (3) The SO_4 tetrahedral group is almost incompressible. The reduction in the average bond distances and volumes are not significant, in agreement with those observed

in other sulfates. The distortion parameters do not indicate any relevant changes, and the polyhedra are quite regular at room and high pressures. Nonetheless, the different evolutions of the S-O bond distance along the *a* and *b* axes partially explain the different compressibility of the lattice parameters: the S-O1 bond length along the *a* axis slightly increases with *P*, whereas the S-O2 bond distance directed along the *b* axis decreases with *P*.

- (4) The representation of the mascagnite structure can be simplified with the [010] layer formed by lamellas, which consists of two layers of tetrahedra: layers with SO₄ and N1H₄ tetrahedra are alternated with layers containing only N2H₄ groups. The interlayer connections, determined by measuring the S-N distances along the *b* axis, are softer than the connections along *a* and *c* axes. Indeed, the strongest hydrogen bonds, with distances below 2 Å, are along the *a* axis, thus explaining the anisotropic behavior of mascagnite.
- (5) The evolution of bonds and intermolecular distances, as already described for lattice parameters, did not show any discontinuity within the investigated pressure range. This was a definitively different behavior than that observed at low temperature by Malec et al. [4,7], who, with a series of single crystal X-ray diffraction measurements in the temperature range of 273–163 K, showed a dynamical effect at the ferroelectric phase transition. A strong discontinuity in the evolution of tetrahedral bond lengths and angles, and in those intermolecular distances at 233 K, was described by Iqbal and Christoe [2]. The characterization of the transition as a mix of displacive and order-disorder natures involving an H-bond system reorganization, as reported by Iqbal and Christoe [2], could not be verified at high pressure. It is likely that, at ambient temperature compression, the pressure did not affect the order-disorder and the displacive effects were too small to be detected by X-ray diffraction analysis.
- (6) In ammonium silicate buddingtonite collected by infrared spectroscopy under pressure, Vennari et al. [16] found that the increased hydrogen bonds between the ammonium group and the silicate framework does not occur under compression and the NH₄⁺ group only appears as a guest ion in the aluminosilicate framework. They concluded that this lack of interaction may have an impact on the stability of ammoniated minerals and may favor nitrides of fluid phases as the N carrier in the deep mantle. However, they suggested that, in cold environments, specifically, at low temperature and high pressure, ammonium may be retained and thus play a primary role in the processing of N in the mantle through the subduction zone.

Table 5. K₀ and K' measured in sulfates of different alkaline (Na) and earth alkaline (Ca, Mg) metals, and with different numbers of water molecules.

Mineral	Chemical Formula	K ₀ (GPa)	K'	Density (g/cm ³)	Reference
Anhydrite	CaSO ₄	63.9	5.9	2.96	Gracia et al. [32]
Bassanite	CaSO ₄ ·1/2 H ₂ O	86 (7)	2.5 (3)	2.77	Comodi et al. [33]
Gypsum	CaSO ₄ ·2 H ₂ O	44 (3)	3.3 (3)	2.318	Comodi et al. [25]
Bloedite	Na ₂ Mg(SO ₄) ₂ ·4 H ₂ O	36 (1)	5.1 (1)	1.196	Comodi et al. [34]
Kieserite	MgSO ₄ ·H ₂ O	48.1 (5)	8.1 (6)	2.58	Meusburger et al. [35]
Epsomite	MgSO ₄ ·7 H ₂ O	21.5 (1)	5.4	1.68	Fortes et al. [36]
Meridianiite	MgSO ₄ ·11 H ₂ O	19.9 (4)	9 (1)	1.50	Fortes et al. [37]
Mirabilite	Na ₂ SO ₄ ·10 H ₂ O	19.6 (1)	5.8 (5)	1.47	Fortes et al. [38]
Mascagnite	NH ₄ SO ₄	20.4 (7)	6.1 (2)	1.77	Present paper

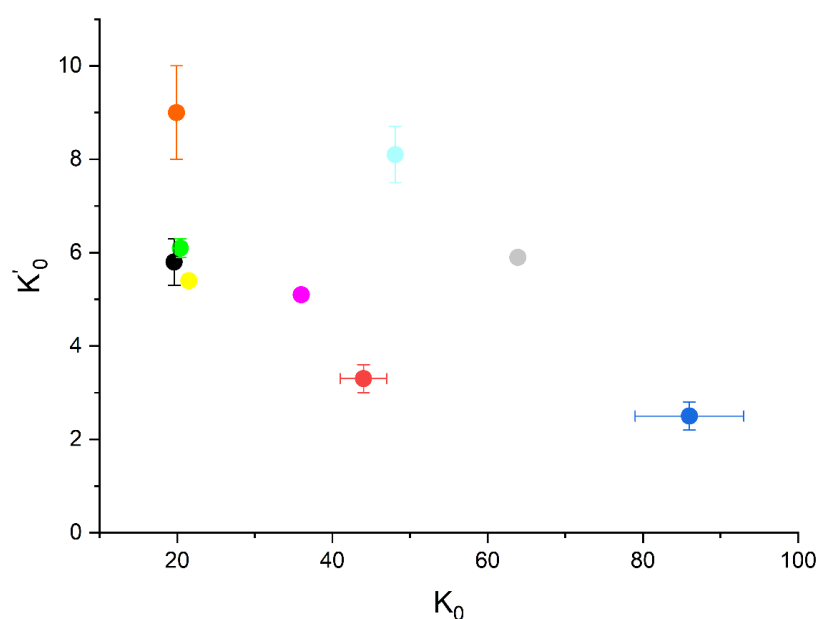


Figure 6. Comparison between bulk modulus (K_0) and its derivative (K'_0) of some sulfate minerals reported in Table 5. Bassanite (blue), anhydrite (grey), kieserite (cyan), gypsum (red), bloedite (magenta), epsomite (yellow), meridianiite (orange), mirabilite (black), and mascagnite (green).

In the structure of mascagnite, ammonium is not a guest component and strongly interacts with sulfate groups through a complex system of hydrogen bonds. The data collected at high pressure show that although mascagnite has a high compressibility, it remains stable up to ~18 GPa due to the increase in the hydrogen bonds between ammonium and sulfate groups at high pressure. We could not localize H in our structures. However, the intramolecular (S-N) distance evolutions indirectly show that the pressure affects the weaker hydrogen bonds (those directed along the b axis) and contribute to the stabilization of NH_4^+ in the structure.

5. Conclusions

The evolution at high pressure of mascagnite confirmed the exceptional stability of the structure's framework up to ~18 GPa. The structures usually show the opposite behavior at high pressure and high temperature [39], and, thus, they may have similar behavior at high pressure and low temperature, but it did not occur in mascagnite. The ammonia groups are fixed in the crystal structure with a complex network of hydrogen bonds, which remain at high pressure and evolve through the strengthening of the weaker hydrogen bonds (those directed along the b axis, which have the highest compressibility).

This evidence suggests that mascagnite can be considered to be a good candidate for nitrogen storage in the depths of icy planets under high pressure conditions, and may be a nitrogen carrier within the sub-surface in the Earth, in addition to cold planetary bodies. In the case of the latter, this may enable the nitrogen to return to the surface via cryo-vulcanism phenomena.

To fully understand the behavior of hydrogen bonds, in the future it will be necessary to perform neutron diffraction, which will provide further details on the evolution of hydrogen during compression.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/cryst11080976/s1>, Crystal information files and hkl tables for each pressure point mentioned within the manuscript.

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