Elastic properties of minerals: theory and practice

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SUMMARY

- ELASTIC PROPERTIES DEFINITIONS
- BULK MODULUS
- EQUATION OF STATE
- PHASE TRANSITION
- METHODS
- SOFTWARES DATA TREATMENTS
- EXAMPLES FROM EARTH SCIENCES
- EXAMPLES FROM MATERIAL SCIENCES
Knowledge on the elastic constants enables us to realize the elastic and mechanical properties of the crystals.

From https://www.tutorvista.com/content/physics/physics-iii/solids-and-fluids/elasticity-modulus.php#young's-modulus-of-elasticity
EoS: basic definitions

An equation of state can be expressed as a P-V relationship:

\[ \text{EQUATION OF STATE = RELATIONSHIP BETWEEN THE} \]
\[ \text{VOLUME OF A BODY AND THE PRESSURE TO WHICH IT} \]
\[ \text{IS SUBJECTED.} \]

Characterised by Volume \( V \) and pressure \( P \)

- Bulk modulus: \( K = -V \frac{\partial P}{\partial V} \)
- Bulk modulus derivative (curvature): \( K' = \frac{\partial K}{\partial P} \)
- Bulk modulus derivatives: \( K'' = \frac{\partial^2 K}{\partial P^2} \)

temperature and high-pressure crystal chemistry, Reviews in Mineralogy and Geochemistry, 41, 35-60.
BULK MODULUS AND EOS

- EOS MURNAGHAN = 1944 = the more a solid is compressed, the more difficult it is to compress further.

- VALID IF V/V₀ < 90%
- P(V) = K₀/K₀’[(V/V₀)EXP-K₀’ -1]
- K AND K’ = BULK MODULUS AND ITS PRESSURE DERIVATIVE
- HOW TO DETERMINE K AND K’
Equations of state: Murnaghan

- can be derived by assuming $K$ is linear with $P$

\[
-K \frac{\partial P}{\partial V} = K_0 + K'P
\]

\[
V = V_0 \left(1 + \frac{K'P}{K_0}\right)^{-\frac{1}{K'}}
\]

\[
P = \frac{K_0}{K'} \left[\left(\frac{V_0}{V}\right)^{K'} - 1\right]
\]

- Advantages
  - Can be inverted, easily integrated
  - ...great for thermo databases

- Disadvantages
  - Does not fit $P$-$V$ data for $V/V_0 < 0.9$
  - It is OK for volume reduction $< 10\%$

Birch-Murnaghan EoS

Finite strain EoS
- Assumes strain energy is a polynomial in \( f = \text{Eulerian strain} \)

\[
P = 3K_0 f_E \left( 1 + 2 f_E \right)^{\frac{3}{2}} \left( 1 + \frac{3}{2} (K' - 4) f_E + \frac{3}{2} \left( K_0 K'' + (K' - 4)(K' - 3) + \frac{35}{9} \right) f_E^2 \right)
\]

If it is trunked at second term \( f_e = 0 \) and \( K' = 4 \)

If it is trunked at third term \( f_e^2 = 0 \) and \( K'' = -1/K_0 (3-K')(4-K') + 35/9 \)

Birch-Murnaghan EoS

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

Truncation:

- **2nd order (in energy)**
  - Coefficient of \( f_E \) must be zero
  - \( V_0 \) and \( K_0 \) refined
  - \( K' = 4 \)

- **3rd order (in energy)**
  - Coefficient of \( f^2_E \) must be zero
  - \( V_0 K_0 K' \) refined

- **4th order (in energy)**
  - Coefficient of \( f^2_E \) non-zero
  - \( V_0 K_0 K' K'' \) refined

\[ K'' = \frac{-1}{K_0} \left[ (3 - K')(4 - K') + \frac{35}{9} \right] \]

How we can decide the order of BM EoS?

F- f plot
f-F plots

Rearrange BM4 Eos:

\[
P = 3K_0f_E \left(1 + 2f_E\right)^{5/2}\left(1 + \frac{3}{2}(K' - 4)f_E + \frac{3}{2}\left(K_0K'' + (K' - 4)(K' - 3) + \frac{35}{9}\right)f_E^2\right)
\]

Becomes a simple polynomial

\[
F_E = K_0 + \left(\frac{3K_0}{2}\right)(K' - 4)f_E + \left(\frac{3K_0}{2}\right)\left[K_0K'' + (K' - 4)(K' - 3) + \frac{35}{9}\right]f_E^2 + ...
\]

\[
f_E = \frac{\left(\frac{V_0}{V}\right)^{2/3} - 1}{2}
\]

\[
F_E = \frac{P}{3f(1 + 2f_E)^{5/2}}
\]

Eulerian strain: f

Vinet or Universal EoS

Derived from general inter-atomic potential

\[
f_V = \left( \frac{V}{V_0} \right)^{\frac{1}{3}} \quad \text{Vinet strain}
\]

\[
P = 3K_0 \left( 1 - \frac{f_V}{f^2_V} \right) \exp \left[ \frac{3}{2} (K' - 1)(1 - f_V) \right]
\]

It is valid also with very high pressure and \( V/V_0 < 0.6 \)

with \( K' = 1 \) and

\[
K'' = \frac{-1}{K_0} \left[ \left( \frac{K'}{2} \right)^2 + \left( \frac{K'}{2} \right)^{19} - \frac{19}{36} \right]
\]

Thermal Equation of State

The simplest isobaric EOS for a solid is just the definition for the thermal expansion coefficient, \( a \).

\[ a = \frac{1}{V} \frac{dV}{dT} = \frac{d\ln V}{dT} \]

A thermal EoS describes a material's reaction to temperature changes. When a material is heated, the thermal pressure in the system changes and results in thermal expansion.

**High-temperature Birch-Murnaghan EoS**

Thermal expansion coefficient and bulk modulus are assumed to vary linearly with temperature,

\[ K(T) = K_0(T_0) + \left( \frac{\Delta K}{\Delta T} \right) (T - T_0) \]

where \( T_0 \) is the reference temperature (298 K).
Phase transitions @ HP

Polyhedral tilting
polyhedron regularization
Increase of coordination numbers
High spin – low spin transition
H-bond evolution
Structural deformation @ HP

Rule of thumb of HP crystalchemistry

Usually the largest deformation interest

Si-O-Si angle
Then
O-Si-O angle
Then Si-O

Polyhedral tilting
Zeolites at high pressure: A review

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[Received 17 May 2013; Accepted 8 September 2013; Associate Editor: F. C. Hawthorne]

ABSTRACT

This is a review of the elastic behaviour and pressure (P)-induced structural evolution of zeolites and presents a comparative analysis of the deformation mechanisms of the Si/Al-framework and the rearrangement of the extra-framework species in response to applied pressure. The interaction between P-transmitting fluids and zeolites, which can lead to phenomena such as “P-induced over-hydration”, is described. The comparative elastic analysis and the high-P structural data of zeolites reported so far allow us to make some generalizations: (1) The range of compressibility among this class of open-framework silicates is large, with bulk moduli ranging between 15 and 70 GPa; (2) Microporosity does not necessarily imply high compressibility, as several zeolites are less compressible than other non-zeolitic rock-forming minerals; (3) Compressibilities of zeolites do not seem to be directly related to microporosity, at least if we model microporosity with the “framework density”; (4) The flexibility observed in zeolites under hydrostatic compression is mainly governed by tilting of rigid tetrahedra around O atoms that behave as hinges within the framework. Pressure-induced tilting commonly leads to continuous rearrangement of the framework without any phase transition. More rarely, tilting induces displacive phase transitions and isothermal P-induced reconstructive phase transitions (i.e. with change in framework topology), have not been reported in this class of materials; (5) Deformation mechanisms in response to applied pressure are generally dictated by the topological configuration of the framework rather than the Si/Al-distribution or the extra-framework content. The channel content governs the compressibility of the cavities, leading to different unit-cell-volume compressibilities in isotypic structures.

Fig. 1. EDI framework type: SBU chains extend along [001] and undergo cooperative anti-rotation in response to applied pressure. The deformation mechanism leads to compression of the channels of eight-membered rings parallel to [001].
Pressure induce change in coordination number

With pressure the reduction of anionic radius (oxygen for example) is larger than that of cation (silicon).

As a consequence the ratio: cation radius/anion radius increases.
And so increase the coordination number.

The increase of coordination number produce an increase in packing efficiency.
## High pressure crystal-chemical paradox

<table>
<thead>
<tr>
<th>Ionic character</th>
<th>SiO$_4$(quartz)</th>
<th>SiO$_6$(stishovite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-O</td>
<td>1.62</td>
<td>1.78</td>
</tr>
<tr>
<td>O-O</td>
<td>2.63</td>
<td>2.51</td>
</tr>
</tbody>
</table>

Increase of packing efficiency
Both anions and cations increase the coordination number with pressure

\[
\text{XYO}_3
\]

- \( ^6\text{Mg}_4\text{Si}_3\text{O}_2\text{O} \) Enstatite
- \( ^8\text{Mg}_3^6(\text{MgSi})^4\text{Si}_3^4\text{O}_{12} \) Majorite
- \( ^6\text{Mg}_6\text{Si}_4\text{O}_3 \) Ilmenite
- \( ^8\text{Mg}_6^6\text{Si}_4^5\text{O}_5\text{O}_2 \) Si-Perovskite

From https://doi.org/10.1016/j.earscirev.2011.10.005
MINERALOGY

Discovery of bridgmanite, the most abundant mineral in Earth, in a shocked meteorite

Oliver Tschauker,1,2 Chi Ma,3 John R. Beckett,4 Clemens Fresacher,5 Vitali B. Prakapenka,6 George R. Rosman7

Meteories exposed to high pressures and temperatures during impact-induced shock often contain minerals whose occurrence and stability normally confine them to the deeper portions of Earth’s mantle. One exception has been MgSiO3 in the perovskite structure, which is the most abundant solid phase in Earth. Here we report the discovery of this important phase as a mineral in the Tenham LS chondrite and approved by the International Mineralogical Association (specimen IMA 2014-007). MgSiO3-perovskite is now called bridgmanite. The associated phase assemblage constrains peak shock conditions to ~ 24 gigapascals and 2300 Kelvin. The discovery concludes a half century of efforts to find, identify, and characterize a natural specimen of this important mineral.

In the sciences, the complexity of conceptions and the difficulty of scientifically and theoretically resolving any experiment and theory are measured. One of the most glaring omissions in the study of Earth’s mantle has been the inability to find naturally occurring specimens of what we believe to be Earth’s most abundant rock-forming phase, MgSiO3, in an orthorhombic, ABO3 perovskite structure. Despite appearing for decades in numerous experimental and theoretical studies (6-8), characteristics of possible natural samples have not been sufficient to meet International Mineralogical Association criteria for naming a new mineral (7). Consequently, any detailed chemical, structural, and petrographic analysis of natural MgSiO3-perovskite has remained impossible. In addition, having a formal mineral name for a phase that is so important is important in itself. Various ambiguous or incorrect terms such as “silicate perovskite” and “perovskite” have been used for describing this phase, but they convey ambiguity to the description of research findings. We put this ambiguity to rest by describing the natural occurrence of bridgmanite: MgSiO3 in the orthorhombic ABO3 perovskite structure. The name bridgmanite honors Percy W. Bridgman (1889-1953), the 1946 Nobel laureate in Physics, for his fundamental contributions to high-pressure mineralogy in particular, and to high-pressure research in general.

The importance of bridgmanite in the lower mantle of Earth has long been recognized. Several lines of evidence show that it forms through a

Fig. 1. Scanning electron microscope image of a bridgmanite-ekmoltite aggregate. The backscattered electron image reveals an aggregate of submicrometer-sized crystals of bridgmanite and ekmanolite enclosed in (Mg,Fe)SiO3 glass and within a Tenham shock-melt vein. Majorite is found in the vein matrix. The bridgmanite-ekmanolite clast is a pseudomorph after pyroxene that was trapped in the melt. This observation is consistent with an earlier report about the possible occurrence of bridgmanite with ekmanolite in Tenham (26).
Brigman (1882-1961) Nobel 1946
high pressure study 100000 kg/cm²

Tenham L6 chondrite and approved by the International Mineralogical Association (specimen IMA 2014-017). MgSiO₃-perovskite is now called bridgmanite. The associated phase assemblage constrains peak shock conditions to ~ 24 GPa and 2300 K. The discovery concludes a half century of efforts to find, identify, and characterize a natural specimen of this important mineral.
Si-Perowskite- post-Si-perowskite

Crystal structure of mantle silicate perovskite. The red spheres are Mg atoms in the dodecahedral sites and the light blue octahedra are SiO$_6$ units

Crystal structure of mantle silicate post-perovskite. The red spheres are Mg atoms in the dodecahedral sites and the light blue octahedra are SiO$_6$ units

From http://www.public.asu.edu/~sshim5/images/mantle_minerals.html
From Post-Perovskite Phase Transition in MgSiO$_3$
Motohiko Murakami$^{1,*}$, Kei Hirose$^{1,*}$, Katsuyuki Kawamura$^1$, Nagayoshi Sata$^2$, Yasuo Ohishi$^3$

*Clarified author names and affiliations, accurate URLing.

Science 07 May 2004:
Vol. 304, Issue 5672, pp. 855-858
DOI: 10.1126/science.1095932

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**Drastic change in X-ray diffraction pattern around 125 GPa and 2500 K**

**Unknown Phase**

**Pbnm Perovskite**

(M. Murakami and K. Hirose, private communication)
Perovskite to post-perovskite phase transition associated to D” layer

From http://www.iitaka.org/Post-perovskite.html
The spin state of the complex also affects an atom's ionic radius. For example:

- Octahedral high spin: Cr$^{2+}$, 64.5 pm.
- Octahedral low spin: Mn$^{3+}$, 58 pm.
- Octahedral high spin: Fe$^{3+}$, the ionic radius is 64.5 pm.
- Octahedral low spin: Fe$^{3+}$, the ionic radius is 55 pm.
- Octahedral high spin: Fe$^{2+}$, the ionic radius is 78 pm.
- Octahedral low spin: Includes Fe$^{2+}$ ionic radius 62 pm, Co$^{3+}$ ionic radius 54.5 pm, Ni$^{2+}$ ionic radius 48 pm.
- Octahedral high spin: Co$^{2+}$ ionic radius 74.5 pm.
- Octahedral low spin: Co$^{2+}$ ionic radius 65 pm, Ni$^{2+}$ ionic radius 56 pm.
- Octahedral high spin: Ni$^{2+}$ ionic radius 69 pm.
- Square planar low-spin: Ni$^{2+}$ ionic radius 49 pm.
The image depicts spin crossover of **ferromagnesite** at HP and HT. The color on the right represents the fraction of the low-spin state of iron in the sample.

High-Pressure Orthorhombic Ferromagnesite as a Potential Deep-Mantle Carbon Carrier

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Knowledge of the physical and chemical properties of candidate deep-carbon carriers such as ferromagnesite [(Mg,Fe)FeCO₃] at high pressure and temperature of the deep mantle is necessary for our understanding of deep-carbon storage as well as the global carbon cycle of the planet. Previous studies have reported different scenarios for the (Mg,Fe)FeCO₃ system at deep-mantle conditions including the chemical (Mg,Fe)CO₃, the occurrence of the tetrahedrally-coordinated carbonates based on CO₃²⁻ units, and various high-pressure phase transitions. Here, we have studied the phase stability and the compressional behavior of (Mg,Fe)FeCO₃ carbonates up to relevant lower-mantle conditions of 120 GPa and 2400 K. Our experimental results show that the rhombohedral siderite (Phase I) is an orthorhombic phase (Phase II with Pnma space group) at approximately 50 GPa and 1400 K. Structural transition is likely driven by the spin transition of iron accompanied by a volume collapse in Fe-rich (Mg,Fe)CO₃ phases; the spin transition stabilizes the high-pressure phase II at much lower conditions than its Mg-rich counterpart. It is conceivable that the low-spin ferromagnesite phase may be a major deep-carbon carrier at the deeper parts of the lower mantle below 1900 km in depth.

Figure 4: Comparison of the pressure-volume relations in the (Mg,Fe)CO₃ phases. (A) Unit cell volume of siderite I and II phases as a function of pressure at ambient temperature. The vertical axis is plotted as the unit cell volume per formula unit (V/Z). The number of molecules per unit cell [Z] is 6 for siderite I and 12 for siderite II. HS: high-spin state; LS: low-spin state. Solid curves: modeled EOS fits of the experimental results. The volume collapse of 9.2% (±0.5%) and 6.5% (±0.4%) for siderite I and II, respectively, can be associated with their respective spin transition at high pressures. Solid diamond: V/Z of magnesiowüstite re-calculated from Ishihara et al. (Table S3), Solid triangle: V/Z of the high-pressure phase of magnesiowüstite [(Mg₁₋ₓFeₓ)₃O₄] CO₃ re-calculated from Boulard et al. (Table S5). (B) Lattice parameters of the siderite I (as a function of pressure at 300 K). The lattice collapse in siderite II is 1.9%, 1.5%, and 1.0% for a₀, b₀, and c₀, respectively, at approximately 60 GPa. Filled symbols:
Stable intermediate-spin ferrous iron in lower-mantle perovskite

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The lower mantle is dominated by a magnesium- and iron-bearing mineral with the perovskite structure. Iron has the ability to adopt different electronic configurations, and transitions in its spin state in the lower mantle can significantly influence mantle properties and dynamics. However, previous studies aimed at understanding these transitions have provided conflicting results. Here we report the results of high-pressure (up to 110 GPa) and high-temperature (up to 1,800 K) experiments aimed at understanding spin transitions of iron in perovskite at lower-mantle conditions. Our Mössbauer and nuclear forward scattering data for two lower-mantle perovskite compositions demonstrate that the transition of ferrous iron from the high-spin to the intermediate-spin state occurs at approximately 30 GPa, and that high temperatures favour the stability of the intermediate-spin state. We therefore infer that ferrous iron adopts the intermediate-spin state throughout the bulk of the lower mantle. Our X-ray data show significant anisotropic compression of lower-mantle perovskite containing intermediate-spin ferrous iron, which correlates strongly with the spin transition. We predict spin-state heterogeneities in the uppermost part of the lower mantle associated with sinking slabs and regions of upwelling. These may affect local properties, including thermal and electrical conductivity, deformation (viscosity) and chemical behaviour, and thereby affect mantle dynamics.

Figure 3 Estimated Fe\textsuperscript{2+} spin-state distribution in the lower mantle. a, Silicate perovskite variation estimated from our data, previous XES data\textsuperscript{22} and current thermal models\textsuperscript{23,25}. The greatest contrast occurs in the uppermost region, and no spin transition is expected at the base of the mantle in the postperovskite phase\textsuperscript{25}. b, (Mg,Fe)O variation on the basis of previous data\textsuperscript{22} shows the greatest contrast in spin state to occur in the middle part of the lower mantle. Slab mineralogy excludes (Mg,Fe)O and the temperature effect is small in the upwelling and downwelling regions of the lower mantle\textsuperscript{25}.

Figure 1 High-pressure XES spectra of Mg\textsubscript{0.5}Fe\textsubscript{0.5}O\textsubscript{2}, perovskite. a, Mössbauer spectra collected at room temperature (top five spectra) and high temperature (bottom spectrum). Pressures are given in GPa and quadruple doublets are coloured as follows: HS Fe\textsuperscript{2+}: blue; high-spin Fe\textsuperscript{2+}: red, minor component including Fe\textsuperscript{3+} green. b, XES spectra collected at room temperature (top three spectra) and high temperature (bottom spectrum). Pressures are given in GPa.
Table 1. The calculated parameters of the 8th-order Birch-Murnaghan Equation of State (energy per formula unit \(E\_\text{fu} \)) for different Fe\(_3\)S\(_4\) phases.

<table>
<thead>
<tr>
<th>Phase</th>
<th>(E_\text{fu}(\text{Mbar}))</th>
<th>(V_\text{fu}(\text{Å}^3))</th>
<th>(K_\text{f}(\text{GPa}))</th>
<th>(K_\text{f}(\text{GPa}))</th>
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<tr>
<td>STD-SP</td>
<td>-60.70</td>
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<td>56.6</td>
<td>3.6</td>
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<tr>
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</tr>
<tr>
<td>FM CM</td>
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<td>113.5</td>
<td>62.3</td>
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<td>113.0</td>
<td>50.0</td>
<td>3.5</td>
</tr>
</tbody>
</table>

![Graph of pressure-induced structural and spin transitions of Fe\(_3\)S\(_4\)](image)

**OPEN**

**Pressure-induced structural and spin transitions of Fe\(_3\)S\(_4\)**

Shengxuan Huang\(^1\), Duan Kang\(^1\), Xiang Wu\(^1\), Jingjing Niu\(^2\) & Shan Qin\(^1\)

Greigite (Fe\(_3\)S\(_4\)), a structurally rich material with Fe\(_{3+}\), has recently attracted great scientific interest from material science to geology due to its complicated structure and electronic and magnetic configurations. Here, an investigation into the structural, magnetic, and electronic properties of Fe\(_3\)S\(_4\) under high pressure has been conducted by first-principle calculations based on density functional theory. The results show that a first-order phase transition of Fe\(_3\)S\(_4\) would occur from the inverse spinel (ISP) structure to the Cs\(_2\)S\(_4\)-type (CT) structure at 2.4 GPa, accompanied by a collapse of 0.2% in the volume, a redistribution of iron cations, and a half-metal to metal transition. In the Cs\(_2\)S\(_4\)-type Fe\(_3\)S\(_4\), Fe\(_{3+}\) localized at octahedral environment firstly undergoes a transition from high-spin (HS) state to low-spin (LS) state at 1.6 GPa and Fe\(_{3+}\) subsequently closes at 1.76 GPa. The Equation of State for different phases of Fe\(_3\)S\(_4\) are also determined. Our results not only give some clues to explore novel materials by utilizing Fe\(_3\)S\(_4\), but also shed light on the fundamental information of Fe\(_{3}\)S\(_4\), as well as other Fe\(_{3}\)S\(_4\) compounds.

![Figure 2. Calculated net magnetic moments (a) and sub-lattice magnetic moments per Fe of A-type and B-site for Fe\(_3\)S\(_4\) phases. The magnetic moments of Fe\(_{3+}\) on the B-site are defined as positive and the reference of Fe\(_{3+}\) on the A-site in the Fe\(_3\)S\(_4\) structure is arbitrary. The grey, pink, blue and yellow regions represent FM-ISP, FM-CT, FM-CL, and FM-CS phases, respectively. The previous data marked with "esp" is experimental results. Blue (Fe\(_{3+}\)), green (Fe\(_{3+}\)), and pink (Fe\(_{3+}\)) points are extracted from refs 30, 40 and 42, respectively for comparison.](image)

![Figure 5. Calculated results of volume per formula unit of different Fe\(_3\)S\(_4\) phases as a function of pressure. The solid line segments are fitted by the third-order Birch-Murnaghan Equation of State. The volume collapse of each phase transition is marked. HS and LS represent high-spin and low-spin states, respectively. The previous data marked with red (Exp.), blue (Exp.), green (the.), and pink (the.) points are extracted from refs 38, 40 and 42, respectively for comparison.](image)
How to determine EoS and structural evolution @ HP?

Pressure-temperature range for diamond cell experiments.

- A: Ambient
- C: Cryogenic (not shown)
- R: External Resistance Heating
- L: Laser Heating
- Geotherm: Temperature range in Earth’s interior.

Dotted curves indicate estimated P-T in Jovian planetary interiors, with the conditions of the center shown at the end of each curve.

From GSECARS, APS web page
Diamond Anvil Cell

https://serc.carleton.edu/NAGTWorkshops/mineralogy/mineral_physics/diamond_anvil.html

Pressure transmitting media

<table>
<thead>
<tr>
<th>Media</th>
<th>Previous max “Hydro Pressure”</th>
<th>Diffraction broadening (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol:Ethanol</td>
<td>10.4</td>
<td>10.1</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>4.3</td>
<td>3.9</td>
</tr>
<tr>
<td>Silicone oil</td>
<td>5-7</td>
<td>&lt; 2.0</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>13.0</td>
<td>3</td>
</tr>
<tr>
<td>Argon</td>
<td>9</td>
<td>2</td>
</tr>
<tr>
<td>Fluorinert</td>
<td>5-10</td>
<td>1</td>
</tr>
</tbody>
</table>

Optical view through the DAC

Gypsum at 4.0 GPa

Gypsum at 4.8 GPa
HP – microraman spectroscopy

$\text{Ar}^+ = 514.5 \text{ nm (green laser)}$

$\text{He/Ne} = 632.8 \text{ nm (red laser)}$
Splitting of $\nu_1$ of sulphate at the transition
HP- single crystal X-ray diffraction

Xcalibur single crystal diffractometer (Oxford instrument) @ Dipartimento Scienze della Terra, Perugia, Italy

Point detector = lattice parameters at different P up to 5 GPa

CCD = structural data collection
At different P up to 4 GPa
• Limited access = limited part of reciprocal lattice can be measured
• Low signal (about one half with respect to signal with crystal in air, due to the absorption of the diamonds)
• Absorption by cell components
• Several phases contemporaneously in diffraction (diamond, beryllium, quartz, ruby)
HP-X-ray diffraction at synchrotrons
beamline 13BM-C (GSECARS) at the Advanced Photon Source (APS) synchrotron (Argonne National Laboratory, USA)

<table>
<thead>
<tr>
<th>Source</th>
<th>Bending Magnet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monochromator Type</td>
<td>Si 111</td>
</tr>
<tr>
<td>Energy Range</td>
<td>10-10 keV</td>
</tr>
<tr>
<td>Resolution (ΔE/E)</td>
<td>5 x 10^-5</td>
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<tr>
<td>Flux (photons/sec)</td>
<td>1 x 10^{12} @10 keV</td>
</tr>
<tr>
<td>Beam Size (HxV)</td>
<td>Focused: 23µm x 28µm, Unfocused: 10mm x 3mm</td>
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<table>
<thead>
<tr>
<th>Source</th>
<th>Bending Magnet</th>
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<tr>
<td>Monochromator Type</td>
<td>Si 111</td>
</tr>
<tr>
<td>Energy Range</td>
<td>18-18 keV</td>
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<td>Resolution (ΔE/E)</td>
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<tr>
<td>Flux (photons/sec)</td>
<td>8 x 10^{11} @18 keV</td>
</tr>
<tr>
<td>Beam Size (HxV)</td>
<td>Focused: 26µm x 28µm, Unfocused: 10mm x 3mm</td>
</tr>
</tbody>
</table>
Double sided laser heated diamond cell for in-situ high P-T diffraction study. The double-sided heating approach allows one to combine different lasing modes to optimize temperature uniformity.

From GSECARS, APS web page
Multi-anvil with X-ray access = in situ synthesis and analysis of phase transformation

(BL04B1)
Why to determine physical properties?

1) To know the density changes

1) To know the structural changes (dehydration, phase transition….)

2) To know the physical properties changes (conducibility, seismic velocity,…..)

Examples from my experience and from literature

a) Storage of deep water in the earth

b) Water in solar system

c) Phase transition and bad gap evolution

d) High spin-low spin transition: effects

e) Very deep earth
examples

1) 10 A e acqua all'interno della terra e terremoti
2) Solfosali e proprietà fisiche band gap
3) Bloedite planetologia
Deep water

https://www.see.leeds.ac.uk/structure/dynamicearth/subduction/thermalbig.htm
L’acqua l’influenza…
La solubilità
La miscibilità
Il calore di mixing
I coefficienti di ripartizione
Le proprietà elastiche
Le proprietà elettriche

**Il punto di fusione**
La viscosità
La velocità delle onde simiche
L’anisotropia
La resistenza sforzi di taglio
Fig. 1. (a) Time and temperature series of XRD spectra acquired during antigorite dehydration at 3.6 GPa (sample Ant11). (b) Selected patterns at 300, 580 and 700 °C. Diffraction peaks are labelled as: Ag: antigorite, En: enstatite, Fs: forsterite, Gr: graphite, hBN: hexagonal boron nitride, hKL: “talc-like” phase.
DHMS = Dense Hydrous Magnesium silicates

Here we report the results of the first three-dimensional refinement of the 10 Å phase performed with single-crystal X-ray data.

The 10 Å phase, Mg₅Si₄O₁₀(OH)₂H₂O, is monoclinic, space group C2/m, a = 5.32(1)Å, b = 9.20(3)Å, c = 10.21(3)Å, β = 99.98(1)°, V = 492.9(2) Å³; the calculated density, assigning Z = 2, is 2.676 g cm⁻³. The structure has been solved by direct methods and refined by least-squares method with anisotropic displacement parameters. The final agreement index (R) was 0.088 for 54 refined parameters and 499 unique observed reflections collected with a diffractometer with a CCD detector.

The structure of the 10 Å phase is very similar to that of a homotetrahedral, 1 Å tetrahedral silica. It is a silicate consisting of 2.1 tetrahedral-dihedral layers parallel to (001). The mean Si-O, Mg-O, and O-H bond lengths are 1.626, 2.082, and 2.081 Å, respectively. The trigonal rotation angle α is 35°. The interlayer of the 10 Å phase is occupied by water molecules. According to the oxygen occupancy, 1 H₂O p.f.u. is assumed in the investigated sample. Although the average water oxygen position is in the mid-plane, structural refinement suggests disorder along α. Twelve hydrogen bonds are located between the water molecule and the 6 + 6 oxygen atoms of the basal rings of adjacent tetrahedral sheets (water-oxygen distances averaging 3.19 Å). Therefore there are six possible orientations for the water molecule, with six hydrogen bonds pointing toward the upper basal ring and six pointing toward the lower ring of tetrahedral sheets. The orientational disorder of water, in agreement with previous Raman spectroscopy data, is a feature relevant to the evaluation of thermodynamic functions and thermal stability of the 10 Å phase, which is a possible water carrier (9.1 wt%) in subducting slabs at high pressure.

The 10Å in the MgO-SiO₂-H₂O system
Mg₃Si₄O₁₀(OH)₂ * H₂O

C2/m, 1 H₂O p.f.u, 9.1 wt%
Fitting a third-order Birch-Murnaghan equation of state to the $P-V$ data yields values of $V_0 = 492.9(3)$, $K_0 = 39(3)$ GPa and $K' = 12.5(8)$. No significant
Modificata da Fumagalli and Poli, 2005
Crystal structure of the dense hydrous magnesium silicate, phase D

Hexiong Yang, Charles T. Prewitt, and Daniel J. Frost

Geophysical Laboratory and Center for High Pressure Research, Carnegie Institution of Washington, 5251 Broad Branch Road, NW, Washington, DC 20015, U.S.A.

ABSTRACT

Liu (1986, 1987) reported the diffraction pattern of a hydrous magnesium silicate resulting from the breakdown of serpentine at 22 GPa and 1000 °C and named this material "phase D." Since that time there have been several reports of the synthesis of phase D, but its confirmed composition and crystal structure have not yet been reported. We synthesized a new dense hydrous magnesium silicate at 20 GPa and 1200 °C and solved its crystal structure (a = 0.015 Å and c = 0.014 Å). The single crystal has composition Mg$_{18}$Si$_{15}$H$_{16}$O, (ideal formula: Mg$_8$Si$_3$H$_4$O$_2$), cell parameters a = 4.3453(4), c = 4.3450(5) Å, and V = 84.74(2) Å$^3$, and space group P31m. The crystal structure is relatively simple with all the Si occupying octahedral sites in a layer similar to that of brucite, with one of every three octahedra vacant. The Mg$_8$ octahedra are located above and below each vacant octahedral site. All O-H bonding occurs between SiO$_4$ octahedral layers. This is the only high-pressure hydrous magnesium silicate structure reported to date that contains all octahedrally coordinated Si. The calculated density of phase D (d$_0$ = 3.50 g/cm$^3$) is substantially greater than any other high-pressure hydrous magnesium silicate phase.

Figure 4: Stability fields of major hydrous phases in the subducted slabs in a pyrolite = 2 wt% H$_2$O system. Those of δ-AlOOH (ref. 20) and alumino-phase H (10) are shown by a green dashed line and light blue region, respectively. Coloured areas represent the regions where water is retained in the high-pressure phases. Typical in cold slabs the mantle geotherm is shown by thick Atg, antigorite A, phase A; Wd, wadsleyite; Rw, ringwoodite; superhydrous phase B; D, phase D.

mined by Frost and Fei (in preparation) from unit-cell volume compression data, is 200(4) GPa, the largest of all high-pressure hydrous magnesium silicates. Li and Jeanloz (1991) synthesized an assemblage of perovskite and phase D from a mixture of Mg$_{68}$Fe$_{32}$SiO$_3$ pyroxene with 4 wt% H$_2$O at ~40-60 GPa and ~1700 °C, which suggests that phase D is stable under lower mantle conditions. Given its large bulk modulus, high density, large
Phase D transforms to Phase H at 48 GPa

The stability of hydrous silicate at high pressures and water transport to the deep lower mantle

M. Nishi1,2*, T. Irfune1,2, J. Tsuchiya1,2, Y. Tange1,2, Y. Nishihara1, K. Fujino1 and Y.

The presence of water strongly influences the structure, composition and dynamics of the Earth's deep mantle. Hydrous magnesium-rich silicates play an important role in transporting water into the deep mantle when oceanic plates subduct as slabs. The highest-pressure form of such hydrous silicates, phase D, was reported to dissociate into an assemblage of nominally anhydrous phases plus water at pressures of about 45 GPa, equivalent to 1,250 km depth. In this way, free water would be released in the middle region of the lower mantle, which suggests that no water can reach the deeper regions of the lower mantle. Here we use in situ X-ray measurements in conjunction with a multi-anvil apparatus using sintered diamond anvils to show that hydrous phases are stable under lower mantle conditions up to 50 GPa. We found that phase D transforms to an assemblage with another hydrous silicate (Mg,SiH,O), named phase H, at pressures above about 45 GPa. Our results suggest that phase H is the dominant hydrous silicate in descending slabs, and may be found at depths for deeper than 1,250 km. We conclude that a significant amount of water is retained in the descending slabs and may be delivered to the deepest part of the lower mantle.

Which the structure of phase H?
Crystal chemistry of dense hydrous magnesium silicates: The structure of phase H, MgSiH₂O₄, synthesized at 45 GPa and 1000 °C

Luca Bindi, Masayuki Nishi, Jun Tsujiya, and Tetsuo Irfune

The crystal structure of the dense hydrous magnesium silicate phase H, MgSiH₂O₄, synthesized at 45 GPa and 1000 °C, was investigated by single-crystal X-ray diffraction. Although showing a deterioration process under the X-ray beam, the compound was found to be orthorhombic, space group Pnmm (CaCl₂-type structure), with lattice parameters a = 4.733(2), b = 4.3250(10), c = 2.6420(10) Å, V = 58.18(3) Å³, and Z = 1. The structure was refined to R₁ = 0.0387 using 53 observed reflections [2θ(0) level]. Magnesium and silicon were found to be disordered at the same octahedral site (with a mean bond distance of 1.057 Å). Hydrogen was not located in the difference Fourier maps, but it is very likely disordered at a half-occupied 4g position. The centrosymmetric nature of the structure of phase H is examined in relation to that reported for pure MgAl₂O₄ [ambient conditions (non-centrosymmetric, P2₁/n)], and the possibility that these two compounds can form a solid solution at least at high pressure is discussed.

Keywords: Phase H, dense hydrous magnesium silicates, lower mantle, crystal structure, synthesis

Figure 3. The crystal structure of phase H down [001]. The horizontal direction is the a axis. Gray polyhedra refer to (Mg,Si)-O octahedra; white circles refer to oxygen atoms, whereas the hydrogen atoms (small black circles) have been tentatively drawn at the Wyckoff position 4g (0.475, 0.042, 0) and bonded (dashed lines) to oxygen. The fact that hydrogen is half occupied does impede the formation of the unrealistic H–H distance of 0.43 Å.

It crystallizes with the CaCl₂-type structure, Pnmm space.
Crystal structure, equation of state, and elasticity of phase H (MgSiO₃H₂) at Earth's lower mantle pressures

Joe Tinkham* & Marlan Moodie1,2

Figure 2. Pressure dependence of unit-cell volume and lattice parameters. The left panel shows the plot of unit-cell volume as a function of pressure for phase H with ordered Mg and Si atoms (model-1) (light blue filled symbol). Also, shown are the metastable extensions of unit-cell volume for the symmetric hydrogen bonded structure (light blue open symbols). Inset shows the plot of $r_{O-O}$ as a function of $r_{O-D}$ at around 30 GPa. $r_{O-O}$ becomes (1/2) of $r_{O-D}$, i.e., hydrogen bond symmetrizes. The right panel shows the plots of the $a$, $b$, and $c$-axes as a function of pressure. Inset shows the plot of $\gamma$ as a function of pressure. For comparison, the experimental results are also plotted (open symbols) and (grey filled symbols).

Table 1. Cell parameters, bond distances, oxygen-oxygen (O-O) bond distances, and idealized volumes of phase H (model-1) as a function of pressure.

Figure 5. Density, velocity, and impedance contrast. Plot of (a) density, (b) primary wave velocity ($V_p$), and (c) shear wave velocity ($V_s$) vs. pressure for phase H (model-1) (light blue open symbols), phase I (D, light green open symbol), and stishovite (at red open symbols). (d) plot of impedance contrast ($\Delta\Gamma$) (open triangles) defined as the sum of shear velocity contrast and density contrast across the reaction phase D → phase H → stishovite. Also shown are the depth dependent impedance contrasts from seismological observations (filled grey triangles).
Sulfosalts

Complex salts:
(analogue of oxysalts = simple cation + complex anion $(\text{MeO}_m)^{n-}$)
$(\text{Me}^+, \text{Me}^{2+}, \text{etc.})_x [(\text{Bi, Sb, As})^{3+}, \text{Te}^{4+}]_y [(\text{S, Se, Te})^{2-}]_z$

Important for:

Extraction of $(\text{Cu, Pb, Ag, Fe})$ metals

Photovoltaic cell
Photo-voltaic materials beyhod c-Si

CdTe and CIGS (CuIn$_{1-x}$Ga$_x$Se$_y$S$_{2-y}$) absorber systems have been developed for thin-film PV (photovoltaic) devices, instead of silicon because they absorb light more strongly (directly instead of indirectly) but...

They are limited in the long-term by the scarcity of Te, Ga, In.

Cd is toxic.

http://rsta.royalsocietypublishing.org/content/369/1942/1840.figures-only
New photovoltaic generation characteristics:

Optimal band gap ($E_g = 1.4-1.5$ eV)
High absorption coefficient in the visible range (about $10^4$ cm$^{-1}$)
High power conversion efficiency (theoretical limit 30%)
Earth-abundant
Low cost
Non toxic constituent

http://energyeducation.ca/encyclopedia/Conduction_band
New materials
quaternary semiconductor - CZTS

CZTS = Kesterite = Cu$_2$ZnS
Alternative ternary copper sulfides based on Cu-Bi-S or Cu-Sb-S type materials

Structural and electronic properties of CuSbS$_2$ and CuBiS$_2$: potential absorber materials for thin-film solar cells

Jesse T. R. Dufton, Aron Walsh, Pooja M. Panchmatia, Laurie M. Peter, Diego Colombara and M. Saiful Islam*

Received 19th January 2012, Accepted 27th March 2012
DOI: 10.1039/c2cp40916j

Sulfosalts — A new class of compound semiconductors for photovoltaic applications

Herbert Dittrich *, Anna Bieniok, Uwe Brendel, Michael Grodzicki, Dan Topa

Department of Materials Science, Div. of Mineralogy, University of Salzburg, Hellbrunnerstr. 34, A-5020 Salzburg, Austria

Available online 1 February 2007

Lone electron pair

A lone pair refers to a pair of valence electrons that are not shared with another atom and is sometimes called a non-bonding pair.

$\text{As}^{3+}, \text{Sb}^{3+}, \text{Bi}^{3+}, \text{Sn}^{2+}, \text{Ge}^{2+}$ required an usually asymmetrically situated structural space for their non bonding $s^2$ pair.

The degree of sterochemical activity of the lone pair (namely the influence of the lone pair in the relative spatial arrangement of atoms in a structure) varies with the species (decreasing with increasing $Z$, lower with Bi and higher with Sb) and with structure type.
Chalcostibite CuSbS$_2$
Emplectite CuBiS$_2$
SnS- archetype
Herzenbergite (mineral)
Table 1. Coordination numbers and hybridization types for the cations commonly occurring in chalogenides.

<table>
<thead>
<tr>
<th>Type of Hybridization</th>
<th>Coordination Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>sp²</td>
<td>2</td>
</tr>
<tr>
<td>sp³</td>
<td>3</td>
</tr>
<tr>
<td>d⁴</td>
<td>4</td>
</tr>
<tr>
<td>d⁵</td>
<td>5</td>
</tr>
<tr>
<td>d⁶</td>
<td>6</td>
</tr>
</tbody>
</table>

Examples:
- Fe²⁺, Fe³⁺, Co²⁺, Ni²⁺, Pd²⁺, Br⁻, Sb²⁻, Bi³⁻, P₆⁺-
- Ni⁴⁺, Ni₂⁺, Ni³⁺, Cu²⁺, Ag⁺, Hg²⁺}

Diagram: A molecular structure with atoms connected, possibly representing a chalogenide.
High pressure study of chalcostibite: why

- Pressure can change structure and structural properties
- LEP evolution with P
- LEP effect on the baric behaviour
- Pressure is an important parameter which could be used to tune
  - the thermoelectric properties of materials

Thermoelectric efficiency
Seebeck effect = converting T to current
Peltier effect = converting current to T
Thomson effect = conductor heating/cooling
   All material have a non zero thermoelectric effect, but quite small to be useful.

explore the physical properties as a means of improving its photovoltaic performance
High pressure study of chalcostibite: where

Experiment @GSECAR-BM13
High pressure study of chalcostibite: how

ETH-type DAC with diamond backing plates

600 μm diamond culet

pre-indented rhenium gasket with a 250 μm hole

ruby chip and a gold crystal as internal pressure calibrants.

Ne as P transmitting medium

Multi-samples mounting
High pressure study of chalcostibite: how

fixed wavelength of 0.3344 Å

MarResearch Mar165 detector calibrated for sample-to detector distance, tilting and distortion by the powder diffraction pattern of CeO$_2$ DAC rotation = 50° around the omega-axis
GSE_ADA/RSV is a free software package for custom analysis of single-crystal micro X-ray diffraction (SCμXRD) data, samples enclosed in diamond anvil cells.

The package has been in extensive use at the high pressure beamlines @ APS.

The software is optimized for processing of wide-rotation images and includes a variety of peak intensity corrections to make data management from SCμXRD easier and more reliable.
Results - EOS
Evolution of Sb eccentricity with pressure
(Ivton software, Balic-Zunic, 2007)

Sb-coordination polyhedron = 5+2
At HP:
short distance stay constants
Long distance decreasing
Sphericity evolution with P

![Graph showing sphericity evolution with pressure for CN7 and CN6]
Movement of LEP of Sb closer to the parent atom with P up to 12 GPa
chalcostibite
α-β transition Sb CN from 5 + 2 to 6
Along [100]
Cu$^{+1}$ change coordination from IV to V
at the transition relative displacement of SnS-like slabs parallel to (001), at 13.5 the displacement is about 2 Å. This way the Cu change coordination from 4 to 5, note the change of distance in red
@ the transition increases the Sb coordination from 5+2 to 6+1
α - β transition

Moving toward the coordination of Sb from 5+2 to 6+1
α - β transition
β-Chalcostibite
Conclusion

Cu change coordination from 4 to 5 (unknown Cu coordination!!)

Square coordination and square pyramid coordination (found in the nickel sulfide millerite) has the same geometry as conventional octahedral coordination with one or two atoms removed.

Tetragonal pyramidal coordination with Cu$^{++}$ for example in Azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$)

Sb change coordination from 5 plus 2 to 6 plus 1

LEP stereo chemistry – activity reduced with P, allowing a better structural packing…really

Density increase of about 2.2 %

Reversible transition
Remote-sensing infrared spectroscopy is the principal field of investigation for planetary surfaces composition. Past, present and future missions to the solar system bodies include in their payload, instruments measuring the emerging radiation in the infrared range. Apart from measuring the reflected radiance, more and more spacecrafts are equipped with instruments measuring directly the emitted radiation from the planetary surface. The emitted radiation is not only a function of the composition of the material but also of its texture and especially the grain size distribution.

https://www.researchgate.net/project/Surface-Mineralogy-of-Planet-Mercury/figures
Ganymede may have a crust about 300 km thick composed of a 10:1 ratio of ice:mirabilite, and a mantle 500 km thick composed of 50% ice phases plus 50% hydrated Mg and Na sulfates.

Europa probably has a layered crust composed of anhydrous Mg-Na sulfates near the base and a frozen or partially molten eutectic mixture of ice and hydrated Mg and Na sulfates near the surface.
Do Ganymede and/or Europa have water?

The possible internal structures of Ganymede and Callisto are shown in Fig. 7. The interior of Ganymede has been modeled from gravity data, and appears to be differentiated into an outermost ~800-km-thick ice layer and an underlying silicate mantle. A central iron core might also be present, which would explain the existence of a magnetic field. Ganymede has internal mass anomalies, perhaps related to topography on the ice-rock interface [24], [25]. Results from the magnetometer onboard the Galileo probe may indicate the presence of an internal ocean within 100–200 km of Ganymede’s surface, but inference is less robust than at Europa and Callisto [26]. The Ganymede surface is more cratered and ancient than Europa’s, consistent with a much thicker outer shell of solid ice. The role of icy volcanism in modifying the surfaces of outer planet moons is an outstanding question about which little is truly understood. Like many other icy moons, there is ambiguous evidence for cryovolcanic processes modifying the surface of Ganymede.

Which are the P-T stability conditions of the MgSO₄-Na₂SO₄-H₂O phases?

At which condition hydrated minerals become anhydrous minerals?

At which T and P we have free water?

How do evolve the density of the phases with P-T?
Bloedite

\((\text{Na}_2\text{Mg(SO}_4\text{)}_2 \cdot 4\text{H}_2\text{O})\)
Beamline ID09A is dedicated to the determination of structural properties of solids at HP using angle-dispersive-diffraction with DACs.

Energy 30 keV flux of $10^{11}$ photons/s at 200 mA.
Sample dimensions up to $10 \times 10 \, \mu m^2$ for megabar experiments

The scattered radiation is collected by an image-plate detector, an on-line Mar555 reader, which has a 430 x 350 mm (555mm diagonal) active area.

A laser spectrometer is available for pressure determination by the ruby fluorescence method.
It is also possible to perform Raman scattering experiments simultaneously.

The beamline is equipped with several membrane-type diamond anvil cells (0-40 GPa), a Liquid He cooled cryostat to perform HP experiments at low temperatures (down to 50 K), and external resistive heating equipment for high temperatures up to 600 K.

A Nd-YAG laser system is available externally for high temperature annealing of samples inside the diamond anvil cell.
Equation of state

**EoS BM2**

- $K_0 = 39.7(7)$
- $V_0 = 496.1 (9)$

**EoS BM3**

- $K_0 = 34.1 (10)$
- $K' = 5.5 (4)$
- $V_0 = 497.9(8)$

**EoS Vinet3**

- $K_0 = 33.9 (14)$
- $K' = 5.7 (4)$
- $V_0 = 497.9 (8)$

Lattice parameters vs P

- $P(GPa)$: [0.0001, 0.005, 0.01, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3.0, 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9, 4.0, 4.1, 4.2, 4.3, 4.4, 4.5, 4.6, 4.7, 4.8, 4.9, 5.0, 5.1, 5.2, 5.3, 5.4, 5.5, 5.6, 5.7, 5.8, 5.9, 6.0, 6.1, 6.2, 6.3, 6.4, 6.5, 6.6, 6.7, 6.8, 6.9, 7.0, 7.1, 7.2, 7.3, 7.4, 7.5, 7.6, 7.7, 7.8, 7.9, 8.0, 8.1, 8.2, 8.3, 8.4, 8.5, 8.6, 8.7, 8.8, 8.9, 9.0, 9.1, 9.2, 9.3, 9.4, 9.5, 9.6, 9.7, 9.8, 9.9, 10.0, 10.1, 10.2, 10.3, 10.4, 10.5, 10.6, 10.7, 10.8, 10.9, 11.0, 11.1, 11.2, 11.3, 11.4, 11.5, 11.6, 11.7, 11.8, 11.9, 12.0]

- Collected @ PG

β_a = 0.0073(4) (GPa^{-1})

β_b = 0.0046(3) (GPa^{-1})

β_c = 0.0049(4) (GPa^{-1})

bloedite structure resulted most incompressible along [010], the direction perpendicular to open sheet.
The compression behavior of blöditc at low and high temperature up to $\sim 10$ GPa: Implications for the stability of hydrous sulfates on icy planetary bodies

Paola Comodi, Vincenzo Stagno, Azzurra Zucchi, Yingwei Fei, Vitali Prakapenka

Department of Physics and Geology, University of Perugia, Italy
Department of Earth Sciences, Sapienza University of Rome, Italy
Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20055, USA
Argonne National Laboratory, University of Chicago, US

Moreover, the data presented allowed to determine the depth of the dehydration of Na and Mg salts as well as that of mixed Na-Mg salts in planetary bodies where the thermal model is known. Fig. 8 shows a cartoon reporting a scenario of the different depths for the dehydration of simple and mixed Na-Mg salts in Ganymede, where an average surface temperature of 110 K and a constant thermal gradient of 6.3 K/km are estimated (Montanari and Cod言, 2005). Whereas the dehydration of mirabilite and epsomite occurs in a narrow temperature range, between 310 and 347 K (determined with thermogravimetric analyses by Prinz et al., 2000) namely at around 30 km, our data for blöditc indicate that the dehydration condition starts at 443 K (with a limited effect of pressure) forming a hemihydrate phase, and it is complete at 570 K (Rah-Charal et al., 2015) between 50 and 70 km of depth.

Because the dehydration temperatures of blöditc are higher with respect to those of mirabilite and epsomite, the liquids beyond 100 km as drawn in fig. 8 should increase in volume due to blöditc dehydration from the brines. As consequence, perched ocean, increasing in salinity with depth, can exist as some planeto-magmatic models hypothesize (Vones and Brown, 2013)

Moreover, the fluid phase formed at different depths may determine dramatic rheological changes and a comsine in material properties with different viscosity which, in turn, affect the complex structure observed on Ganymede satellite surface. For example, features on Europa and Ganymede related to cryovolcanic activity (Pappalardo et al., 1998) as ejection of aqueous solution or partly crystallized slurry derived from partial melting of ice-bearing materials, may be associated to different dehydration conditions of the deeply stored hydrous sulfate phases. This and other possible implications deriving from high pressure investigations require more focused systematic studies on the stability of hydrous sulfates at relevant conditions for the interior of icy planets.
Conclusion

To know elastic properties of materials,
You need collect data *in situ*

Poor but not bad quality of data

Several times you have to collect data with different techniques

Eos and phase transitions are important tools to know in deep the material behavior

Sometime they represent unique data for earth and material sciences
Thank you for your attention