The compression behavior of blödite at low and high temperature up to ~10 GPa: implications for the stability of hydrous sulfates on icy planetary bodies

Comodi Paola¹, Stagno Vincenzo², Zucchini Azzurra¹, Fei Yingwei³, Prakapenka Vitali⁴

Abstract

Recent satellite inferences of hydrous sulfates as recurrent minerals on the surface of icy planetary bodies link with the potential mineral composition of their interior. Blödite, a mixed Mg-Na sulfate, is here taken as mineral representative of icy satellites surface to investigate its crystal structure and stability at conditions of the interior of icy bodies. To this aim we performed *in situ* synchrotron angle-dispersive X-ray powder diffraction experiments on natural blödite at pressures up to ~10 GPa and temperatures from ~100 K to ~570 K using diamond anvil cell technique to investigate the compression behavior and establish a low-to-high temperature equation of state that can be used as reference when modelling the interior of sulfate-rich icy satellites such as Ganymede.

The experimentally determined volume expansivity, α , varies from $7.6(6) \cdot 10^{-5} \text{ K}^{-1}$ at 0.0001 GPa (from 199 to 413 K) to $2.6(3) \cdot 10^{-5} \text{ K}^{-1}$ at 10 GPa (from 293 to 453 K) with $\partial\alpha/\partial P$ coefficient = $-5.6(8) \cdot 10^{-6} \text{ GPa}^{-1} \text{ K}^{-1}$.

The bulk modulus calculated from the least squares fitting of P - V data on the isotherm at 413 K using a second-order Birch - Murnaghan equation of state is 38 GPa, which gives the value of $\partial K/\partial T$ equal to $0.01(5) \text{ GPa}^{-1} \text{ K}^{-1}$. The thermobaric behavior of blödite appears strongly anisotropic with c lattice parameter being more deformed with respect to a and b .

Thermogravimetric analyses performed at ambient pressure showed three endotherms at 410 K, 500 K and 1000 K, with weight losses of approximately 11%, 11% and 43% caused by partial dehydration, full dehydration and sulfate decomposition. Interestingly, no clear evidence of dehydration was observed up to ~470 K and ~10 GPa, suggesting that pressure would act to stabilize the crystalline structure of blödite.

The data collected allow to write the following equation of state,

$$V(P,T) = V_0 [1 + 7.6(6) \cdot 10^{-5} \Delta T - 0.026(3)P - 5.6(8) \cdot 10^{-6} P\Delta T - 6.6(9) \cdot 10^{-6} P\Delta T]$$

from which the density of blödite can be determined at conditions of the ice mantle of the large icy satellites of Jupiter. Based on current thermal models for the interior of Ganymede, for instance, blödite is predicted to remain stable with the density almost unchanged to about 1000 km in depth in equilibrium with a deep saline ocean.

Blödite has higher density, bulk modulus and thermal stability than similar hydrous sulfates (e.g. mirabilite and epsomite) implying, therefore, a different contribution of these minerals to the extent of deep oceans in icy planets and their distribution over the local geotherms

Keywords Blödite, high pressure, icy satellite, sulfate, in situ angle-dispersive X-ray diffraction, synchrotron.

Introduction

Blödite [$\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$], $P2_1/a$ space group, $a=11.1136(3) \text{ \AA}$, $b= 8.2421(3) \text{ \AA}$, $c = 5.5328(2) \text{ \AA}$, $\beta=100.873(3)^\circ$, $V= 497,70(8) \text{ \AA}^3$, $Z=2$, is a common constituent of evaporitic sedimentary terrestrial environments (Garrett 2001; Mees et al 2011) consisting of parallel layers of $\text{MgO}_2(\text{H}_2\text{O})_4$ and $\text{NaO}_4(\text{H}^2\text{O})_2$ octahedra interconnected by SO_4 tetrahedra and hydrogen bonds (Figure 1; Rumanova 1958; Vizcayno and Garcia-Gonzales 1999). The occurrence of hydrated Mg- and Na- mineral sulfates end members within extra-terrestrial planets have been previously reported (Nash and Fanale 1977; McCord et al 1999, 2001; Shirley et al 2010; Dalton et al 2012, 2012b), and considered as a potential carrier of water in our solar system that might result in the stability of numerous Mg-Na solid solutions.

The presence of soluble sulfates in chondritic meteorites has led to the suggestion that multiply hydrated salts may have taken part during the accretion stage of icy planets, and might dominate the interior of icy moons of gas giant planets (Kargel 1991). In addition, the distorted H_2O absorption bands in the near infrared spectra of Galilean satellites was interpreted as mixture of Mg- Na_2 or H_2SO_4 hydrates (Dalton et al 2005; McCord et al 2001; Orlando et al 2005), establishing therefore a link between the interior and surface of icy planets that, however, remains matter of debate in light of recent collected spectra of the surface of icy satellites (Brown and Hand 2013).

Magnetometric data collected by the Galileo spacecraft on Jupiter's satellites Ganymede, Callisto and Europa supported by laboratory observations in the $\text{NaCl-H}_2\text{O}$ binary system indicate the existence of subsurface layers of significant electrical conductivity, most likely due to the presence of salty oceans beneath the icy crust (Clark 1980; Khurana et al 1998; Kivelson et al 2000; Valenti et al 2012; Hand and Carlson 2015; Hanley et al 2014).

Spectra from Galileo's near infrared mapping spectrometer suggested the presence of hydrated minerals coexisting with carbonates and chlorides on the surface of Europa and Ganymede, which likely formed by evaporation of brines with compositions close to the $\text{H}_2\text{O-MgSO}_4\text{-NaSO}_4$ system that ascended from deep fluid layer (McCord et al 2001; Zolotov and Kargel 2009). Recently, Nakamura and Ohtani (2011) experimentally investigated high-pressure phase relations in the $\text{MgSO}_4\text{-H}_2\text{O}$ system, and hypothesized the possible composition of the icy mantle of Ganymede. They found ices VI and VII, magnesium sulfate heptahydrate and a liquid phase in $\text{MgSO}_4\text{-H}_2\text{O}$ system up to 4 GPa and 298 K. Hence, they suggested the presence of a deep ocean down to a depth

of about 800 km in the interior of Ganymede at the base of which a sulfate-rich sediment would be stable.

Given that the H_2O - MgSO_4 - NaSO_4 system appropriately describe the scenario above we point out that the effect of pressure and temperature on the stability of hydrous S-bearing phases such as blödite at conditions of the interior icy satellites is worthy of investigations. The knowledge of the stability of phases in the H_2O - MgSO_4 - NaSO_4 system at conditions of both cold and hot thermal regime has immediate implications on modeling the surface of icy satellites, understanding the control of thermal conditions on the weathering of sulfates (i.e. for H_2O storage and/or its release to the atmosphere), understanding (cryo-)volcanism (Pappalardo et al 2004), and related global cycle of sulfur in Jupiter's moons. Simple and complex hydrous sulfate might be actively involved in tectonic processes of several planets where temperature regimes at the surface span from around 100 K (e.g. Mars) to 670 K (e.g. Venus).

Although many studies have focused on the stability of sulfates at high pressure and temperature (Comodi et al 2008, 2012; Fortes et al 2013; Hawthorne 1985; Stoilova and Wildner 2004; Vance 2007; Yamamoto et al 196; Gromnitskaya et al 2013), only few studies were devoted to layered double sulfates such as blödite, mostly of which dealing with crystallographic aspects at ambient pressures (Hawthorne 1985; Stoilova and Wilder, 2004).

In contrast, the study by Comodi et al (2014) represents the only high-pressure study where the stability of blödite was investigated with volume-pressure data collected up to 11.2 GPa at ambient temperature. In particular, this study provided important details regarding the compression behavior of the sulfate polyhedra (harder) with respect to magnesium- and sodium- coordinated polyhedra (softer) within the whole structure. However, no data are available to date that describe the stability of blödite at low/high temperature needed to provide useful information about its possible presence in the interior of icy planets and satellites.

The present paper shows results on the behavior of blödite crystal structure with pressure both at low and high temperature using synchrotron angle-dispersive X-ray powder diffraction. The P-T conditions for the stability and dehydration of this mineral are then compared with the behaviour of other Na and Mg sulphate hydrated salts, such as mirabilite and epsomite.

1. Experimental methods

Natural blödite sample from Leopoldshall (Strassfurt, Germany; no. 1922.144 of the mineral collection of the Natural History Museum, Copenhagen) was used as starting material in this work. Its crystallinity and chemical composition were determined by X-ray diffraction, Raman spectroscopy and microprobe analysis available at the Department of Earth Sciences, University of Perugia (Italy). The starting sample was proved to be pure blödite and the chemical formula may be expressed as $\text{Na}_2\text{Mg}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ (Balic Zunic et al 2015).

Powder diffraction at room pressure and high temperature was measured by using a PANalytical X'PERT PRO diffractometer, PW3050 goniometer, equipped with an X'Celerator detector. The long fine focus (LFF) ceramic tube operated at 40kV and 40mA. PXRD patterns were collected with a 0.017° 2 theta scan step and 60 s/step counting time with the Cu $K\alpha$ radiation. Temperature dependent PXRD patterns were collected in the 293.15-453.15 K range by means of a custom-made sample holder equipped with a Peltier cell.

For measurements at high pressure at low and high temperature the sample was first broken into several small fragments, then a small chip was loaded in a diamond anvil cell (DAC) with culet size of 600 μm and crushed to a fine powder by hand loading. A small portion of the powder with dimensions of about $30 \times 30 \mu\text{m}$ was picked with a tungsten needle and placed at the center of a diamond anvil with 250 μm -culet size using a Re gasket as sample chamber with a 150 μm -diameter hole. Due to the highly hygroscopic behavior of the sample we cannot exclude contamination from the air moisture during the loading procedure. A couple of ruby spheres and gold powder were placed next to the sample as pressure markers using their equation of state (Fei et al 2007; Mao et al 1986). One diamond anvil was supported by a cubic boron nitride (c-BN) backing plate, and the other anvil by a tungsten carbide (WC) backing plate. In situ angle-dispersive powder X-ray diffraction measurements were performed at high pressure at the 13BM-B beamline, GSECARS (Advanced Photon Source, APS, Argonne National Laboratory, ANL). The DAC was loaded with neon used both as pressure medium and pressure marker (Hemley et al 1989), then mounted on a motor driven gearbox with the WC seat on the downstream side and the c-BN seat on the upstream side. Sample pressures were measured with the ruby luminescence method (Mao et al 1986) through an off-line system before and after each experiment. We also measured the lattice parameter of Au for selected experiments, and we calculated the pressure using the Au equation-of-state reported by Fei et al (2007). Only these latter values are reported here with an estimated error of ~ 0.05 GPa. Monochromatic 30 keV incident X-ray beams with wavelengths of 0.3344 Å was used. The beam was focused to a spot of $5 \times 15 \mu\text{m}$ using a pair of Kirkpatrick-Baez mirrors. The MAR345 image plate detector previously calibrated and corrected for sample-to-detector distance,

tilting, and distortion by using the powder diffraction pattern of CeO_2 , was placed at a distance approximately of 298 mm from the sample. Diffraction peaks were collected using a continuous ω -oscillation scan mode over the range from -6° to $+6^\circ$ with an exposure time of 180 seconds. For measurements at low temperature and room pressure the sample was loaded in a glass capillary and cooled using an automatically-controlled nitrogen flow system. The temperature was monitored with a K-type thermocouple in contact with the capillary. The temperature was adjusted by varying the N_2 flow rate. Experiments at high pressure and low temperature were performed by flushing liquid nitrogen to the DAC and placing a K-type thermocouple wire in contact with the inner ceramic sleeve. Experiments at high pressure and high temperature were performed using a symmetric diamond anvil cell (DAC) with external resistance heating technique. In these experiments the sample was heated by a Pt-wire resistive micro-machined furnace placed around a pyrophyllite cylinder covering the two diamonds, which was then thermally insulated from the body of the cell using ceramic seats. During the heating procedure argon gas was always flushed inside the DAC to prevent oxidation of the diamonds. The temperature was measured using an S-type thermocouple in contact between the gasket and diamond (Antonangeli et al 2012). A sketch of the cell used for our measurements along with the recovered sample chamber are shown in Figure 2a and 2b.

The acquired diffraction patterns were integrated using the FIT2D software package (Hammersley et al 1998). EXP-GUI and GSAS softwares were also used to elaborate the spectra (Larson and Von Dreele 2004; Toby 2001)

2. RESULTS

The pressure-temperature conditions at which diffraction data were collected are shown in Figure 3. Lattice parameters were measured at ambient pressure from 119 K up to 453 K. At 1.4 and 5.1 GPa from 234 K to 250 K from 293K respectively, and at 10.4 GPa from 313 K to 580 K. Cell dimensions and standard reliability factors of the Le Bail analysis (Le Bail et al 1988) are listed in Table 1 and Table 2 with the number of observations used for the refinement.

The limited access to reciprocal space due to the absorption by DAC's steel components, usually reduce to one third or less the entire accessible data, and from the very strong reflections of the diamond anvils. As a consequence the number of observations between the ambient and non ambient diffraction is drastically reduced, and the uncertainties on the lattice parameter are very large with respect to the data collected without DAC. In addition, the uncertainty on the measured lattice parameters propagates from either quasi-hydrostatic conditions inside the diamond anvil cell using powder samples (Fei and Wang 2000) or the layered nature of blödite causing the observed preferred orientation when pressure is increased during our measurements.

3.1 Experiments at low/high temperature at ambient pressure

Experiments performed at ambient pressure show a linear increase of all lattice parameters as temperature increases, with the c lattice parameter being characterized by the largest thermal expansion (Figure 5a-b) determined at ~119-433 K. The calculated thermal expansion coefficients from 119 to 297 K (Figure 5a) are $\alpha_a = 1.2(2) \cdot 10^{-5}$; $\alpha_b = 1.6(3) \cdot 10^{-5}$; $\alpha_c = 4.5(4) \cdot 10^{-5} \text{ K}^{-1}$; $\alpha_v = 6.7(7) \cdot 10^{-5} \text{ K}^{-1}$ and the calculated thermal expansion coefficients from 300 to 433 K are $\alpha_a = 2.6(3) \cdot 10^{-5}$; $\alpha_b = 2.5(3) \cdot 10^{-5}$; $\alpha_c = 3.6(4) \cdot 10^{-5} \text{ K}^{-1}$; $\alpha_v = 8.4(6) \cdot 10^{-5} \text{ K}^{-1}$ (Figure 5b), with an average value for α_v between 119 and 433 K of $7.6(7) \cdot 10^{-5} \text{ K}^{-1}$.

The c lattice parameter remains the most deformable with respect to a and b that, therefore, show very similar thermal expansion values. Because the monoclinic symmetry of blödite with β angle significantly different from 90° , the principal directions of the expansion tensor should be investigated. The symmetry requires a direction parallel to b axis, and the other two axes free to rotate in the (010) plane. The Win-Strain software (Angel 2011) was used to calculate the magnitude and the orientation of the principal unit-strain coefficients in the investigated temperature (Table 3).

The principal strain axes of the finite Eulerian strain tensor were calculated from lattice parameters derived with the linear fit of the measured lattice parameter between 313 and 413 K, because of the relative scatter of the data that hindered the significance of the calculation point-by point. The

eigenvalues are $\alpha_1 = 1.67 \cdot 10^{-5}$, $\alpha_2 = 2.50 \cdot 10^{-5}$, $\alpha_3 = 4.27 \cdot 10^{-5}$, and the eigenvectors of that tensor have the following orientation $\alpha_1 \angle a = 35.5^\circ$, $\alpha_1 \angle b = 90^\circ$, $\alpha_1 \angle c = 65.5^\circ$; α_2 parallel to b ; $\alpha_3 \angle a = 54.5^\circ$, $\alpha_3 \angle b = 90^\circ$, $\alpha_3 \angle c = 155.5^\circ$.

In the same way the principal strain axes of the finite Eulerian strain tensor were calculated with data collected at low temperature, between 217 and 119 K. The eigenvalues and the orientation of eigenvectors are very near to those calculated at high temperature, $\alpha_1 = 1.23 \cdot 10^{-5}$, $\alpha_2 = 2.19 \cdot 10^{-5}$, $\alpha_3 = 4.32 \cdot 10^{-5}$ with $\alpha_1 \angle a = 29.6^\circ$, $\alpha_1 \angle b = 90^\circ$, $\alpha_1 \angle c = 71.1^\circ$; α_2 parallel to b ; $\alpha_3 \angle a = 60.4^\circ$, $\alpha_3 \angle b = 90^\circ$, $\alpha_3 \angle c = 161^\circ$.

3.2 Experiments at low/high temperature at different pressures

The lattice parameters at different temperatures along the isobars of 1.4, 5.3 and 10.4 GPa are summarized in Table 2. The thermal expansion coefficient measured between 199 K and 413 K is $7.6(6) \cdot 10^{-5} \text{ K}^{-1}$ at room pressure, and $\alpha_v = 2.6(3) \cdot 10^{-5} \text{ K}^{-1}$ measured between 313 K and 453 K at ~ 10 GPa. As consequence the pressure derivative of thermal expansion, $\delta\alpha/\delta P$, is $-5.6(9) \cdot 10^{-6} \text{ GPa}^{-1} \text{ K}^{-1}$. The bulk modulus at room pressure were determined by Comodi et al (2014) using single crystal synchrotron X-ray diffraction collected at different pressure up to 11.2 GPa. Data fitted by a second and a third-order Birch-Murnaghan equation of state, yielded to a bulk modulus of 39.5 (6) GPa fixing K' to 4, and to 36(1) GPa with K' refined to 5.1(4) GPa^{-1} , respectively.

Unfortunately, the limited collected data set allowed just a rough estimation of the $\delta K/\delta T$ as the K along the isotherm at 413 K was calculated from only two points. However, a second-order Birch-Murnaghan equation of state was determined and a K_0 (fixing $K' = 4$) of 38(5) GPa was obtained. These two K values (at 293 and 413 K) give the value of $\delta K/\delta T$ of $-0.01(5) \text{ GPa/K}$. The pressure derivative of the volume thermal expansion coefficient and the temperature derivative of bulk modulus are not independent from each other: the relation between them is $(\delta\alpha/\delta P)_T = -(\delta\beta/\delta T)_P = 1/K^2 (\delta K/\delta T)$. The data collected independently along the isotherms and the isobars, notwithstanding the large error, resulted in quite agreement since $\delta\alpha/\delta P$ calculated with the relationship $\delta\alpha/\delta P = 1/K^2 (\delta K/\delta T)$ gives a value of $6.6(9) \cdot 10^{-6} \text{ GPa}^{-1} \text{ K}^{-1}$.

The recovered sample from ~ 10 GPa after treatment up to ~ 500 K was analyzed by Raman spectroscopy (532 nm laser-equipped Jasco available at the Geophysical Laboratory, Carnegie Institution of Washington) to ensure that no dehydration occurred (Figure 6a-b). This also confirmed the general stability of blödite structure after the experimental runs by the presence of the main vibrational modes in agreement with those from the RRUFF database (sample ref. R050317; Lafuente et al. 2015), although the reduced intensity of water-related modes and the peak shift

observed for the crystalline phase over the sample chamber would suggest the possible, not certain, partial dehydration of the sample.

Based on spectroscopic evidences that blödite might be an abundant phase present on the surface of icy extraterrestrial bodies, the effect of pressure on the thermal behavior was also investigated at temperature lower than 273 K at 1.4 and 5.3 GPa, respectively. No pressure effect in the temperature range of 230-280 K was detected. The difference on the bulk moduli determined comparing the cell volume at 298-413 K at ambient pressure and 10 GPa respectively are not significant, which may imply the coefficient $\delta K/\delta T$ being equal to 0.

3.3 Dehydration experiments

Balic-Zunic et al (2015) described the mass loss of blödite on the basis of thermogravimetric data. They observed that the water loss occurs in two steps at 453 K and at 533 K at ambient pressure and with sample exposed in air, whereas the decomposition was observed between 973 K and 1173 K in good agreement with previous data by Madsen (1966). On the basis of the amount of the weight loss they associated the release of two water molecules per formula unit to the first step and the loss of the other two water molecules to the second step both corresponding to a total weight loss of approximately 11%. The final weight loss of approximately 48% can be referred to the release of SO_3 groups and decomposition of the mineral to Na and Mg oxides.

The present data allow us to determine the effect of the pressure on the dehydration temperature. At 430 K at ambient pressure a sharp decrease in volume is observed and also in the c lattice parameters, which agrees with Balic-Zunic et al (2015) data.

Figure 7 shows the evolution of volume cell up to 580 K at ~10 GPa. A sharp discontinuity on the lattice parameter evolution in particular for V occurs at 543 K. The behavior is not reversible as observed during decreasing temperature. We are confident that while the onset of dehydration at ambient pressure starts at ~420 K, at 10 GPa our data would suggest a possible change in the structure of blödite likely due to re-arrangement of the atomic structure following partial water loss. This would be also supported by the Raman spectrum showing a decrease of intensity relative to the H_2O bands. A more accurate interpretation of this sharp discontinuity would certainly benefit of future detailed *in situ* study at HP-T. In contrast, no effect relative to the O-H atomic structure was observed decreasing temperature down to ~110 K both at both ambient and high pressure.

These results can be interpreted as a first indication that the water molecules are retained in the blödite structure at high pressure similarly to what observed for gypsum at high pressure (Comodi et al 2012).

3. DISCUSSION AND CONCLUSIONS

The presence of hydrated sulfates in the interior of icy planetary bodies depends on the chemical nature of the primordial accreted rocks and ices, the redox activity and physical–chemical processing of materials, the extent of equilibrium in seawater-seafloor water/rock interactions, the fate of gases released during chemical processing, and other parameters that are generally poorly constrained as limited to satellite observations (Zolotov and Kargel 2009). In our justification for this study, we assumed a scenario such as that modeled by Kargel (1991) and Kargel et al (2000) regarding the deep interiors of the icy Galilean satellites. Modern studies on simplified binary diagrams in the $\text{MgSO}_4\text{-H}_2\text{O}$ systems resulted, then, in the proposal of a deep single (Nakamura and Ohtani 2011) or thin multi-ocean layers (Vance and Brown 2013).

Here, we reported the structural stability of blödite, a stable phase in the $\text{MgSO}_4\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$ system, over a wide pressure interval up to ~10 GPa and temperature range from ~110 to 500 K. The positive and negative thermal expansion at low and high T are similar and anisotropic with the largest variation along the c axis. Similar anisotropic behavior was observed increasing P (Comodi et al. 2014). The first implication is, therefore, relative to the structural stability of primordial hydrous sulfates during high-pressure impacts representative of accretion processes.

With the data collected and on the basis of thermos-elastic parameters, it is possible to write the following equation of state

$$V(P,T) = V_0(1+\alpha\Delta T)(1-\beta P)$$

where V_0 is the molar volume at 298 K and room pressure, P is the pressure in GPa and ΔT is T (in K) - 298. Since $\alpha = \alpha_0 + (\delta\alpha/\delta P)_T P$ and $\beta = \beta_0 + (\delta\beta/\delta T)_P \Delta T$, we can re-write the equation of state in the form:

$$V(P,T) = V_0[1 + \alpha\Delta T - \beta P + (\delta\alpha/\delta P)_T P\Delta T - (\delta\beta/\delta T)_P P\Delta T].$$

Taking into account the values from the experiments, for $\alpha, \beta, (K_0^{-1}), (\delta\alpha/\delta P)_T$ and $(\delta\beta/\delta T)_P$ we obtain for blödite

$$V(P,T) = V_0[1 + 7.6(6) \cdot 10^{-5} \Delta T - 0.026(3) P - 5.6(8) \cdot 10^{-6} P\Delta T - 6.6(9) \cdot 10^{-6} P\Delta T] \text{ with } P \text{ in GPa and } T \text{ in K.}$$

$$V(P,T) = V_0[1 + 7.6(6) \cdot 10^{-5} \Delta T - 0.026(3) P - 5.6(8) \cdot 10^{-6} P\Delta T - 6.6(9) \cdot 10^{-6} P\Delta T] \text{ with } P \text{ in GPa and } T \text{ in K.}$$

To determine the condition for the dehydration of blödite in planetary bodies the paramount parameter to take into account is the thermal model. So, starting from the thermal model of Ganymede (Montesi and Collins 2005) where an average surface temperature of 110 K is taken, and

a constant thermal gradient of 6-7 K/km, we predict blödite being a stable hydrous phase stable down to ocean depths, and further down to depth > 800 km as sediment precipitated from the saturated saline ocean. Beyond this depth, the local thermal regime will favor the stability of sulfate phases less hydrated taking into account the small effect of pressure on the dehydration.

A comparison of the compression behavior of blödite with other of Na-Mg sulfates allows further predictions regarding the stability of hydrous minerals in the interior of icy bodies. High pressure of mirabilite, the sodium sulphate decahydrate ($\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$), was studied by Fortes et al (2013), who determined the bulk modulus by using powder neutron diffraction data at 270 K being equal to 19.6 (1) GPa, its first pressure derivative $\delta K/\delta P = 5.8(5)$, and its temperature dependence $\delta K/\delta T = -0.0175(6) \text{ GPa K}^{-1}$. The high pressure behavior of epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) was studied by Fortes et al (2006), who determined a bulk modulus of 21.5(4) GPa and a $K' = 5.5$ along the isotherm of 290 K. Thermogravimetric analyses of mirabilite and epsomite (Prieto et al 2000) showed that mirabilite dehydrates in two steps at 310 and 333 K, whereas epsomite loses water in three steps at 319, 324 and 347 K.

The here presented new data on blödite show that this phase is more incompressible than Na or Mg hydrated salts, and that water molecules are likely to be released at higher temperature than mirabilite and epsomite.

As consequence the presence of mixed Na-Mg salts, such as blödite, between the salt hydrates on the icy satellites crust, might have a great effect on the density as well as on the buoyancy due to the significant difference in density and bulk moduli measured for these phases. The fluid phase formed may determine dramatic rheological changes, and a contrast in material properties with different viscosity. The different depth of the nucleation of the fluid phase related to different chemistry of hydrated salts, may affect the complex structure observed on Galilean satellites surface. Moreover, features on Europa and Ganymede related to cryovolcanic activity (Prockter et al 1998), namely eruption 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 sulphate phases. This and other possible implications derived from high pressure investigations require more focused systematic studies on the stability of hydrous sulfates at relevant conditions for the interior of icy planets.

ACKNOWLEDGMENTS

This work was supported as part of Energy Frontier Research in Extreme Environments Center (EFree), an Energy Frontier Research Center funded by the US Department of Energy, Office of Science under Award Number DE-SC0001057. V.S gratefully acknowledges financial support from WDC Research Fund at the Geophysical Laboratory. *Part of this work was performed at GeoSoilEnviroCARS (Sector 13), Advanced Photon Source (APS), Argonne National Laboratory (ANL). GeoSoilEnviroCARS is supported by the National Science Foundation award EAR-1128799 and DOE award DEFG02-94ER14466.* The Advanced Photon Source is a DOE Office of Science User Facility operated for the DOE Office of Science by ANL under Contract DE-AC02-06CH11357. P.C. sincerely thanks Tonci Balic Zunic for the bloedite sample and the useful comments. The study was also supported by MIUR Italian Ministero dell'Istruzione dell'Università e della Ricerca (PRIN-2010-2011 to Paola Comodi). The two anonymous referees are acknowledged for their comments, which allowed us to improve the quality of this manuscript.

REFERENCES

- Angel, R.J. (2011) Win-Strain. Crystallography laboratory, Virginia Tech. Blackburg.
- Antonangeli, D., Komabayashi, T., Occelli, F., Borissenko, E., Walters, A. C., Fiquet, G., Fei, Y. (2012). Simultaneous sound velocity and density measurements of hcp iron up to 93 GPa and 1100 K: An experimental test of the Birch's law at high temperature. *Earth Planet Sci Lett*, 331: 210–214.
- Balic-Zunic, T., Birkedal, R., Katerinopoulou, A., Comodi, P. (2015). Deyhdration of bloedite, $\text{Na}_2\text{Mg}(\text{SO}_4)(\text{H}_2\text{O})_4$, and Leonite, $\text{K}_2\text{Mg}(\text{SO}_4)_2(\text{H}_2\text{O})_4$. *Eur. J. Mineral.* DOI: 10.1127/ejm/2015/0027-2487.
- Brown, M. E., and K. P. Hand (2013), Salts and radiation products on the surface of Europa, *Astron. J.*, 145(4), 110, doi:10.1088/0004-6256/145/4/110.
- Clark, R. N. (1980). Ganymede, Europa, Callisto, and Saturn's rings: Compositional analysis from reflectance spectroscopy. *Icarus*, 44: 388-409.
- Comodi, P., Nazzareni, S., Zanazzi, P. F., Speziale, S. (2008) High-pressure behavior of gypsum: A single-crystal X-ray study. *American Mineralogist* 93 (10): 1530-1537.
- Comodi, P., Kurnosov, A., Nazzareni, S., Dubrovinsky, L. (2012) The dehydration process of gypsum under high pressure. *Physics and Chemistry of Minerals* 39(1): 65-71.
- Comodi, P, Nazzareni, S, Balic-Zunic, T, Zucchini, A, Hanfland, M (2014). The high-pressure behavior of bloedite: A synchrotron single-crystal X-ray diffraction study. *Am Mineral*, 99 (2-3): 511-518.
- Dalton, B., Prieto-Ballesteros, O., Kargel, J. S., Jamieson, C. S., Jolivet, J., Quinn, R. (2005). Spectral comparison of heavily hydrated salts with disrupted terrains on Europa. *Icarus* 177, 472–490.
- Dalton III, J. B., Shirley, J. H., Kamp, L. W. (2012). Europa's icy bright plains and dark linea: Exogenic and endogenic contribution to composition and surface properties *Jour of Geophys Res*, 117: E 03003.
- Dalton III, J. B., Pitman, K. M. (2012b). Low temperature optical constants of some hydrated sulfates relevant to planetary surfaces. *J Geophys Res*, 117: E09001.
- Fei, Y., Ricolleau, A., Frank, M., Mibe, K., Shen, G., Prakapenka, V. (2007). Toward an internally consistent pressure scale. *Proc Natl Acad Sci USA* doi:10.1073/pnas.0609013104.
- Fei, Y., and Wang, Y. (2000). *High-pressure and high temperature powder diffraction. Rev. Mineral Geochem.* 41, 521-557.

- Fortes A.D., Wood I.G., Vocadlo L., Brand H.E.A., Grindrod, P.M., Joy K.H., Turcker M.G. (2006) The phase behavior of epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) to 50 Kbar: Planetary implications. *Lunar and Planetary Science XXXVII*, 1029.pdf
- Fortes, A. D., Vočadlo, L., Lindsay-Scott, A., Wood, I. G., Brand, H. E. A., Fernandez-Alonso, F. (2013). P-V-T equation of state of synthetic mirabilite ($\text{NaSO}_4 \cdot 10\text{H}_2\text{O}$) determined by powder neutron diffraction. *Journal of Applied Crystallography*, 46(2): 448-460.
- Garrett, D. E. (2001). Sodium Sulfate. *Handbook of Deposits, Processing, Properties, and Use*, Academic Press, San Diego, 365.
- Gromnitskaya E.L., Yagafarov O.F., Lyapin A.G., Brazhkin V.V., Wood I.G., Tucker M.G. Fortes A.D. (2013) The high-pressure phase diagram of synthetic epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{D}_2\text{O}$) from ultrasonic and neutron powder diffraction measurements. *Phys. Chem. Mineral.* 40,271-285.
- Hammersley, A. P. (1998). FIT2D V12.077 Reference Manual, European Synchrotron Radiation Facility, Grenoble, France, Version 4.0.
- Hand, K. P., and R. W. Carlson (2015), Europa's surface color suggests an ocean rich with sodium chloride, *Geophys. Res. Lett.*, 42, 3174–3178, doi:10.1002/2015GL063559.
- Hanley, J., J. B. Dalton III, V. F. Chevrier, C. S. Jamieson, and R. S. Barrows (2014), Reflectance spectra of hydrated chlorine salts: The effect of temperature with implications for Europa, *J. Geophys. Res. Planets*, 119, 2370–2377, doi:10.1002/2013JE004565
- Hawthorne, F. C. (1985). Refinement of the crystal structure of bloedite: structural similarities in the $[\text{VI}^{\text{M}}(\text{IV}^{\text{T}}\Phi_4)_2 \Phi_n]$. *Canadian Mineralogist*, 23: 669-674.
- Hemley, R. J., Zha, C. S., Jephcoat, A. P., Mao, H-K., Finger, L. W., Cox, D. E. (1989). X-ray diffraction and equation of state of solid neon to 110 GPa. *Physical Review B* 39(16): 11820-11827.
- Kargel, J. S. (1991). Brine volcanism and the interior structures of asteroids and icy satellites. *Icarus* 94, 368–390.
- Kargel, J.S., Kaye J.Z., Head J.W, Marion G.M., Sassen R., Crowley J.K., Ballesteros O.P., Grant S.A, Hogenboom D.L, (2000): Europa's crust and ocean: origin, composition, the prospects for life. *Icarus* 148, 226–265
- Khurana, K. K., Kivelson, M. G., Stevenson, D. J., Schubert, G., Russell, C. T., Walker, R. J., Polanskey, C. (1998). Induced magnetic fields as evidence for subsurface oceans in Europa and Callisto. *Nature*, 395: 777-780.

- Kivelson, M. G., Khurana, K. K., Russell, C. T., Volwerk, M., Walker, R. J., Zimmer, C. (2000). Galileo Magnetometer Measurements: A Stronger Case for a Subsurface Ocean at Europa. *Science*, 289: 1340-1343.
- Lafuente, B., Downs, R. T., Yang, H., Stone, N. (2015). The power of databases: the RRUFF project. In: Highlights in Mineralogical Crystallography, T Armbruster and R M Danisi, eds. Berlin, Germany, W. De Gruyter, pp 1-30.
- Larson, A.C. and Von Dreele R.R. (2004) General Structure Analysis System (GSAS), Los Alamos National Laboratory Report LAUR 86-748.
- Le Bail, A., Duroy H., Fourquet, J. L. (1988). Ab-initio structure determination of LiSbWO_6 by X-ray powder diffraction, *Mat. Res. Bull.*, 23, 447-452.
- Madsen, B. M. (1966). Loewite, vanthoffite, bloedite, and leonite from southeastern New Mexico. U.S. Geological Survey Professional Paper, 550-8, 125-129.
- Mao, H-K., Xu, J., Bell, P. M. (1986). Calibration of the ruby pressure gauge to 800 kbar under quasi-hydrostatic conditions. *Journal of Geophysical Research*, 91(B5): 4673–4676.
- McCord, T. B., Hansen, G. B., Matson, D. L., Johnson, T. V., Crowley, J. K., Fanale, F. P., Carlson, R. W., Smythe, W. D., Martin, P. D., Hibbitts, C. A., Granahan, J. C., Ocampo, A., NIMS Team (1999) Hydrated salt minerals on Europa's surface from the Galileo NIMS investigation. *Journal of Geophysics Research*, 1046: 3311-3319.,
- McCord, T. B., Hansen, G. B., Hibbitts, C. A. (2001) Hydrated Salt Minerals on Ganymede's Surface: Evidence of an Ocean Below. *Science*, 292: 1523-1525.
- Mees, F., Castañeda, C., Herrero, J., Van Ranst, E. (2011). Bloedite sedimentation in a seasonally dry saline lake (Salada Mediana, Spain). *Sedimentary Geology* 238(1-2): 106-115.
- Montési, L. G. J., Collins, G. C., (2005). On the mechanical origin of two-wavelength tectonics on Ganymede. *Lunar Planet. Sci.* 36. Abstract 2093.
- Nakamura, R., Ohtani, E. (2011) The high-pressure phase relation of the $\text{MgSO}_4\text{--H}_2\text{O}$ system and its implication for the internal structure of Ganymede. *Icarus*, 211: 648-654.
- Nash, D. B., Fanale, F. P. (1977). Io's surface composition based on reflectance spectra of sulfur/salt mixtures and proton-irradiation experiments. *Icarus*, 31: 40-80.
- Orlando, T. M., McCord, T. B., Grieves, G. A. (2005). The chemical nature of Europa surface material and the relation to a subsurface ocean, *Icarus*, 177, 2, 528-533.
- .
- Pappalardo, R. T., Collins, G. C., Head, J. W., Helfenstein, P., McCord, T. B., Moore, J. M., Prockter, L. M., Schenk, P. M., Spencer, J. R. (2004). Geology of Ganymede. In: *Jupiter. The*

- planet, satellites and magnetosphere. Edited by Fran Bagenal, Timothy E Dowling, William B McKinnon. Cambridge University Press: 363-396.
- Prieto, O., Gutierrez Florez, M., Kargel, J. S., Quilez, E. (2000). Thermal analysis of some hydrated salts; implications for Europa's satellite. Abstracts of Papers Submitted to the Lunar and Planetary Science Conference 31: abstract 1728.
- Prockter, L. M., Head, J. W., Pappalardo, R. T., Senske, D. A., Neukum, G., Wagner, R., Wolf, U., Oberst, J., Giese, B., Moore, J. M., Chapman, Clark, R., Helfenstein, P., Greeley, R. Breneman H. H., Belton M. J. S. (1998). Dark Terrain on Ganymede: Geological Mapping and Interpretation of Galileo Regio at High Resolution. *Icarus*, 135, 317-344.
- Rumanova, I. M. (1958). Crystal structure of bloedite. *Dokladi Akademii Nauk SSSR* 118: 84-87.
- Shirley, J., Dalton, J., III, Prockter, L., and Kamp, L. (2010). Europa's ridged plains and smooth low albedo plains: distinctive compositions and compositional gradients at the leading sidetrailing side boundary. *Icarus*, 210:358–384.
- Stoilova, D., Wildner, M. (2004). Bloedite-type compounds $\text{Na}_2\text{Me}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (Me = Mg, Co, Ni, Zn): crystal structures and hydrogen bonding systems. *Journal of Molecular Structure*, 706: 57-63.
- Toby, B. H. (2001), EXPGUI, a graphical user interface for GSAS, *J. Appl. Cryst.*
- Valenti, P., Bodnar, R. J., Schmidt, C. (2012). Experimental determination of H_2O -NaCl liquids to 25 mass% NaCl and 1.4 GPa: Application to the Jovian satellite Europa. *Geochimica et Cosmochimica Acta*, 92: 117-128.
- Vance, S. (2007). High pressure and low temperature equations of state for aqueous magnesium sulfate: applications to the search for life in extraterrestrial oceans, with particular reference to Europa. PhD Thesis.
- Vance, S., and Brown, J. (2013). Thermodynamic properties of aqueous MgSO_4 to 800 MPa at temperatures from -20 to 100°C and concentrations to 2.5 mol kg⁻¹ from sound speeds, with applications to icy world oceans. *Geochimica et Cosmochimica Acta*, 110:176-189.
- Vizcayno, C., Garcia-Gonzales, M. T. (1999). $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, the Mg end-member of the bloedite-type of mineral. *Acta Crystallographica*, C55: 8-11.
- Yamamoto, H., Kennedy, G. C. (1969). Stability relations in the system $\text{CaSO}_4\text{-H}_2\text{O}$ at high temperatures and pressures. *Amer J of Science*, 267 (A): 550-557.
- Zolotov, M. Y., Kargel, J. S. (2009). On the Composition of Europa's Icy Shell, Ocean and Underlying Rocks. In Europa (R Pappalardo, WB McKinnon, K Khurana, Editors). University of Arizona Press, Tucson: 431-457.

Captions

Figure 1. Shown is the crystal structure of blödite projected along a) (001) and b) (100) axes, respectively. Mg coordination polyhedra are represented by pink octahedra, S coordination polyhedra are represented by grey tetrahedra. Yellow, bright grey and dark grey spheres represent Na, O and H atoms respectively. Dashed red lines indicate the hydrogen bonds.

Figure 2 a) Cross-section of the used diamond anvil cell with resistive heating (Antonangeli et al. 2012). The inset in b) shows the recovered sample chamber with gold and ruby used as pressure markers (see main text).

Figure 3 Summary of the pressure-temperature conditions for the data collection. Runs at ambient temperature and high pressure by Comodi et al (2014) are also shown for comparison.

Figure 4 Representative angle-dispersive X-ray diffraction pattern of blödite refined by using EXPGUI-GSAS software. Red crosses are measured data, green line is the calculated spectra on the base of a refined structural model, black tick marks under the diffraction patterns are the calculated peak positions. Miller indices for more intense peaks of blödite are reported.

Figure 5 a) Reciprocal lattice evolution of blödite at temperature $< 250\text{K}$ and b) $>250\text{K}$. Dashed line are representative surface temperatures of Ganymede, , Callisto Jupiter and Mars.

Figure 6 Raman spectra of blödite sample recovered from DAC after 10.4 GPa and 573 K.

Figure 7. Comparison of dehydration temperature of blödite at ambient pressure and 10.4 GPa

Figures

Figure 1a-b

Figure 2a-b

2
3
4

Figure 3

5
6
7
~

Figure 4

Figure 5 a and b

Figure 6

Figure 7