	Experiment title: High pressure – high temperature phase transition in gypsum	**Experiment number:**hs-3507
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Shifts: 9	**Local contact(s)**: Marco Merlini	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

*Paola Comodi – Dip. Scienze della Terra Università di Perugia-Perugia Italy

*Sabrina Nazzareni - Dip. Scienze della Terra Università di Perugia-Perugia Italy

*Leonid Dubrovinsky – Bayerisches Geoinstitut- Bayreuth Germany

Report:

A number of important industrial processes (production of phosphoric acid or phosphate fertilizers, gas desulfurization, hydrometallurgic production of Zn and Cu and recovery of natural gas and oil) are accompanied by the crystallization of calcium sulphate: $CaSO_4$ $2H_2O$ (gypsum), $CaSO_4$ ½ H_2O (bassanite), $CaSO_4$ (anhydrite). Ca-sulphates are found as the main constituting material for ground preparation by ancient Southern European painters [1]. In geology Ca-sulphates have an important role in the partitioning of sea-water cations during dehydration processes [2] and in recent years they were discovered in extra-terrestrial environments [3-5]. Moreover, taking into account that bassanite may be generated from acid sulphate alteration of carbonate, its presence can provide an insight into the environmental evolution of planets.

We performed H*P* - H*T* diffraction experiments on $CaSO_4$ + H_2O system to define the structural stability of Ca-sulphates, the EoS of gypsum at H*P* and the influence of temperature on the baric behaviour of bassanite along two isotherms at 109 °C (up to 22GPa) and 200 °C (up to 12GPa).

-GYPSUM: We carried out single-crystal and powder X-ray diffraction experiments up to 13 GPa to study the polymorphic transitions and the compression behaviour of gypsum-II polymorph. Powder was loaded in a DAC with a ruby chip as pressure calibrant, Ne and Ar as pressure transmitting media. H*P* single-crystal DAC setup: two crystals in different orientations, a ruby chip and He as pressure transmitting medium.

Gypsum-II appears just above 4 GPa and remains stable up to 8 GPa where a new change in the powder and single-crystal diffraction patterns does occur. The lattice parameters evolution was determined in the range 4 - 7.5 GPa by fitting the powder data with the Le Bail algorithm, while the single-crystal parameters were obtained by the CrysAlis software. At the transition the lattice parameters show a strong discontinuity in *a* parameter and $\boldsymbol{b}$ monoclinic angle, while *b* exhibits only a limited discontinuity and *c* change linearly before and after transition. The cell volumes were fitted with a 2nd-order Birch-Murnaghan EoS in the range 4.0 - 7.5 GPa, giving a bulk modulus $K_0 = 58(1)$ GPa . The axial compressibilities [$\beta a= 9.6(1.3)$, $\beta b= 2.4(1.1)$, $\beta c= 6.1(2.0)$ and $\beta_\beta = 3.1(5)$ GPa-1 (x10^{-3})] show a strong anisotropy with βa: βb: βc = 4:1:2.5. Bulk modulus increases from gypsum-I, $K_0= 44(3)$ with K'= 3.3 [6], to

gypsum-II and the compression behaviour from almost isotropic in gypsum-I ($\beta a: \beta b: \beta c = 1.1:1.1:1$) becomes strongly anisotropic. The monoclinic β angle increases with P up to the transition, and then decreases in the whole stability field of gypsum-II.

The crystal structure of gypsum-II was solved from single-crystal synchrotron X-ray data at 5.26, 5.88 and 6.74 GPa in the space group $P2_1/n$, using SHELX package [7]. All the refinements converged to a final R index around 3%. In gypsum-II both Ca and S are off their former special positions and the water oxygens are no more equivalent. The sulfur tetrahedra have <S-O> bond distances that slightly decreased to 1.42(2)Å at 5.26GPa and 1.41(3) Å at 6.74GPa, whereas the <Ca-O> changes of around 1% in the same P range. Structural refinements show that (010) layers shift along a changing the stacking sequence in the [010] direction at the transition, explaining the strong discontinuity observed for the a parameter and the β angle. The new structure configuration has longer hydrogen bonds (O…O from 2.75(3)Å to 2.84(3)Å at 5.26GPa) than those of gypsum-I (O...O from 2.73(2)Å to 2.69(3)Å at 3.9GPa) that allows to store water up to 8GPa. (*Nazzareni S., Comodi P., Dubrovinsky L., Bindi L. (2009) The crystal structure and HP behavior of gypsum-II from synchrotron single-crystal and powder X-ray diffraction. EHPRG09 Paris September 2009*)

<u>BASSANITE</u>: Experimental setup for 1) isotherm 109°C: bassanite powder loaded on a externally heated DAC with ruby chip as pressure calibrant and Ne as pressure transmitting medium. 2) Isotherm 200°C: externally heated membrane-driven DAC loaded with bassanite powder, ruby chip as pressure calibrant and Ar, as pressure transmitting medium.

The pressure evolution of bassanite ($CaSO_4$ $1/2H_2O$) was investigated by synchrotron X-ray powder diffraction along three isotherms: at room temperature up to 33 GPa, at 109°C up to 22GPa and at 200°C up to 12GPa (Fig. 1, Fig. 2). The room temperature cell-volume data, from 0.001 to 33 GPa, were fitted to a 3rd-order Birch-Murnaghan EoS, and a bulk modulus $K_0 = 86(7)$ GPa with K' = 2.5(3) was obtained. The axial compressibility values are $\beta_a = 3.7(2)$, $\beta_b = 3.6(1)$ and $\beta_c = 2.8(1)$ GPa^{-1} $(x10^{-3})$ showing a slightly anisotropic behavior, with the least compressible direction along c axis. The strain tensor analysis showed that the main deformation occurs in the (010) plane at a direction 18° from the a axis.

The bulk moduli of isotherms 109 and 200 °C, were obtained by fitting cell-volume data with a 2nd-order Birch-Murnaghan EoS, with K' = 4, and are $K_{109} = 79(4)$ GPa and $K_{200} = 63(7)$ GPa, respectively. The axial compressibility values for isotherm 109 °C are $\beta_a = 2.4(1)$, $\beta_b = 3.0(1)$, $\beta_c = 2.5(1)$ $(x10^{-3})$ GPa^{-1} and for isotherm 200 °C they are $\beta_a = 3.5(3)$, $\beta_b = 3.4(3)$, $\beta_c = 2.6(4)$ $(x10^{-3})$ GPa^{-1}. These two bulk moduli and the 20°C bulk modulus, $K_{0,20} = 69(8)$ recalculated to a 2nd-order Birch-Murnaghan EoS to be consistent, as well as the axial compressibilities, are similar for the three isotherms indicating that the thermal effect on the bulk moduli is not significant up to 200°C. The size variation of the pseudo-hexagonal channel with P and T indicates that the sulfate "host" lattice and the H_2O "guest" molecule in bassanite do not undergo strong change up to 33GPa and 200°C. (*Comodi P., Nazzareni S., Dubrovinsky L., Merlini M., 2009 The high pressure-high temperature behavior of bassanite. Am. Mineral. in press*)
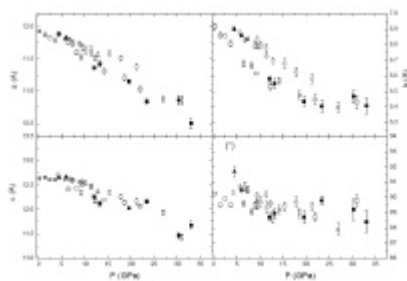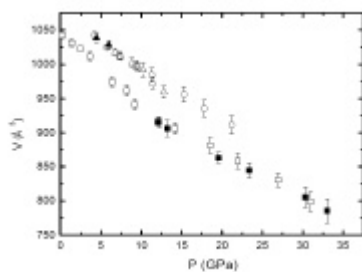

Fig. 1   Fig. 2

References

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