

**IMPACT-INDUCED DEVOLATILIZATION OF NATURAL GYPSUM AND PLASTER OF PARIS: AN INFRA-RED AND RAMAN SPECTROSCOPIC STUDY.** K. Miljković<sup>1</sup>, M. C. Price<sup>2</sup>, P. J. Wozniakiewicz<sup>2</sup>, N. J. Mason<sup>3</sup> and J. C. Zarnecki<sup>3</sup>. <sup>1</sup>Univ Paris Diderot, Sorbonne Paris Cité, Institute de Physique du Globe de Paris, Paris, France, <sup>2</sup>School of Physical Sciences, University of Kent, Canterbury, Kent, CT2 7NH, UK. <sup>3</sup>Department of Physical Sciences, The Open University, Milton Keynes, MK7 6AA, UK. (miljkovic@ipgp.fr).

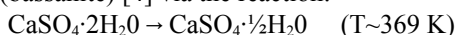
**Introduction:** Meteorites and comets impact the surfaces of all bodies within the Solar System causing high pressures (~10s GPa) and temperatures (~1000s K) that can induce significant mineralogical changes to the bodies' surfaces. In an effort to understand such change, several studies [1-6] have looked at the effect of pressure on gypsum (a simple hydrated sulphate mineral:  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ).

The aim of this study is to determine the quantity of trapped volatiles within a gypsum target that could be released during an impact and, conversely, what percentage of volatiles from the impactor might become entrapped within the surface material. We present preliminary results from three sets of impact experiments carried out onto natural gypsum, artificial gypsum targets made from plaster of paris (POP) and from POP projectiles fired into Al plates. Infra-red (IR) and Raman spectroscopy was used to probe targets after impact to ascertain the degree of devolatilization that had occurred.

**Methodology:** The first set of experiments was carried out using the hypervelocity impact lab at the Open University [7] onto natural gypsum [8]. The impacted targets were scanned with a Thermo Nicolet Fourier Transform Infra-Red (FTIR) spectrometer to identify any changes (reduction) in the OH lines arising from the devolatilization of water within the mineral polycrystalline structure. In order to compare and complement the natural gypsum, the second and third sets of experiments involve POP targets and projectiles using the University of Kent's light gas gun [9] and LabRam-HR Raman spectrometer equipped with a LN<sub>2</sub> cooled IR unit capable of performing concurrent Raman and IR spectra measurements.

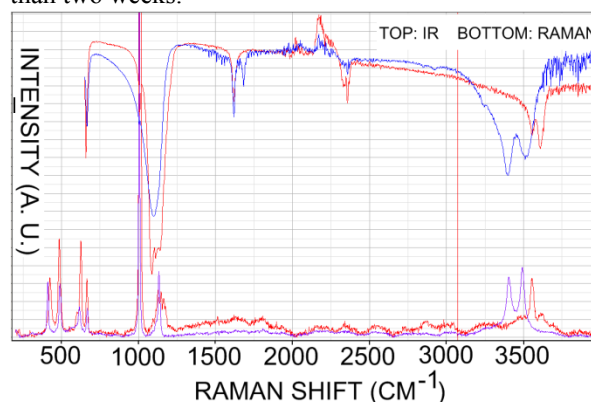
Although both natural and artificial gypsum targets are chemically very similar and give nearly identical IR and Raman spectra, their shock responses are significantly different, implying that shock pressure propagation and temperatures experienced within the targets are different. Hydrocode modelling has also been performed to estimate the peak shock pressures during the impacts.

**Results:** Upon heating, each gypsum molecule loses 1.5 water molecules and transforms to its hemihydrate form (bassanite) [4] via the reaction:



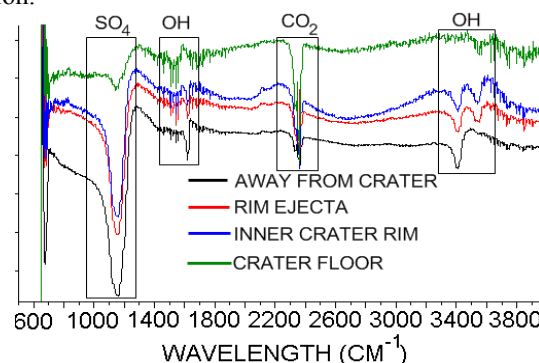
IR and Raman spectra observed from a test piece of POP heated until dehydration are shown in Fig. 1, (band assignments are shown in Fig. 2, as given in [2]).

The main spectral changes that occur upon heating the POP are: the OH lines at 3395 and 3510  $\text{cm}^{-1}$  shift to 3556 and 3610  $\text{cm}^{-1}$  and the  $\text{SO}_4$  line moves from 1100 to 1120  $\text{cm}^{-1}$ . This process appears long-lived, considering that repeated daily scans from our test sample showed no reversion to the hydrated state after more than two weeks.

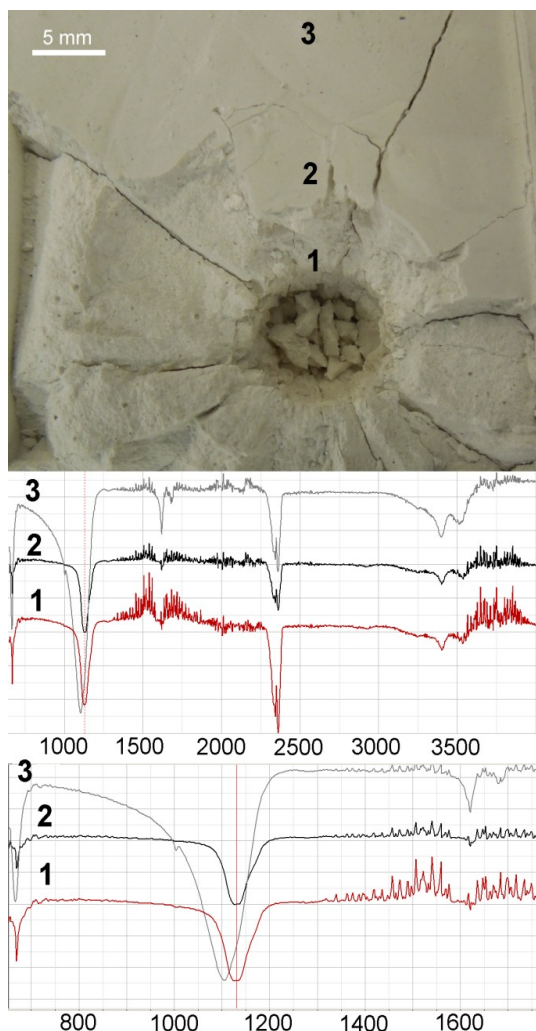


**Fig. 1.** Raman (bottom) and IR (top) spectra of POP upon heating to 369K for 1 hour and then cooled to room temperature. Blue spectra are hydrated and red spectra are the hemihydrated gypsum.

Fig. 2. shows the IR spectra of a crater made in a natural gypsum target taken: from the crater floor, the crater rim, well away from the crater and from ejecta spall. Similar to Fig. 1, there is a shift in both the OH and  $\text{SO}_4$  lines in addition to a loss in intensity of the OH lines indicating dehydration of the shocked target. AUTODYN hydrocode simulations (of 1 mm stainless steel projectile at 2 km/s impacting vertically natural gypsum target) showed that the region of the inner crater experienced pressures up to 4 GPa in compression.



**Fig. 2.** IR spectra showing the loss of OH vibrational lines at points within an impact crater made by a 1 mm diameter stainless steel sphere impacting natural gypsum at 2 km s<sup>-1</sup>.

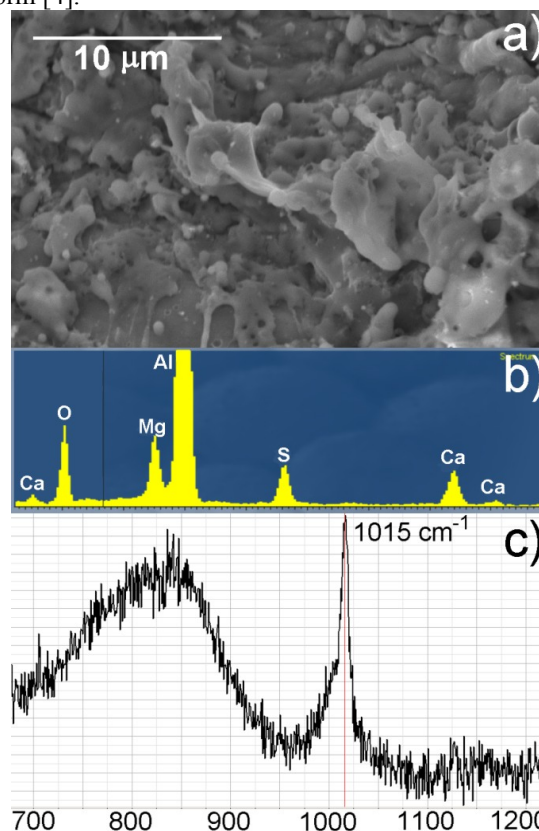


**Fig. 3:** Crater in POP (top) made by 2 mm dia. basalt sphere at 5.15 km s<sup>-1</sup>. The IR spectra 1, 2 and 3 (bottom) are also labelled on the crater. The bottom spectra shows an expanded region around the SO<sub>4</sub> line. X-axis units are cm<sup>-1</sup>.

Fig. 3 shows an impact into a POP target, along with the associated FTIR spectra at: ~2 mm (1), ~7 mm (2) and ~17 mm (3) away from the crater centre. The FTIR spectra also shows a shift in the SO<sub>4</sub> line from 1130 cm<sup>-1</sup> (close to crater) to 1104 cm<sup>-1</sup> (far from crater) and possible loss/reduction in the intensity of the OH lines as seen in the natural gypsum targets. The Raman spectra do not show any significant difference between the three sample positions on the target, with no shift/decrease in OH line intensity. However, a small shift (a few wavenumbers) is observed in the position of the SO<sub>4</sub> line, which may reveal the pressure history of the gypsum as described by [10]. Work is ongoing to verify this.

A third experiment was carried out in which a 1.5 mm cube of POP was fired into a 5 mm thick Al target at 6.05 km s<sup>-1</sup>. Ca and S rich residues were detected in the resulting impact craters via SEM-EDX (Energy

Dispersive X-ray spectroscopy) and SEM images show a molten, globular structure to the residue (Fig 4b). Impact craters were then scanned to find any indication of OH lines and although the SO<sub>4</sub> line is present (Fig 4c), it is shifted from 1005 cm<sup>-1</sup> to 1015 cm<sup>-1</sup> indicating complete dehydration of the gypsum to its anhydrite form [4].



**Fig. 4:** a) Molten residue within the impact crater: b) EDX spectrum of projectile residue c) Raman spectrum of residue showing the shifted SO<sub>4</sub> vibration at 1015 cm<sup>-1</sup>

**Conclusions:** i) Shocked and slowly heated gypsum does not re-hydrate from the ambient air moisture; ii) both IR and Raman spectroscopy show the ability to quantify the degree of devolatilization that occurs during an impact; iii) IR appears to be a more sensitive tracer of water loss than Raman spectroscopy. Ongoing work is investigating the IR/Raman spectral differences in greater detail.

**References:** [1] Bell M. S. (2010). *GCA special papers*, 465, 593. [2] Knittle E. et al. (2001). *Phys. Chem. Minerals*, 28, 630. [3] Sarma L. P. et al. (1998). *J. Raman Spec.*, 29, 851. [4] Prasad P. S. R et al. (2001). *Curr. Science*, 80, 9. [5] Prasad P. S. R. (1999). *J. Raman Spec.*, 30, 693. [6] Chen G. et al. (1994). *E & PSL*, 128, 615. [7] McDonnell, J.A.M. et al. (2006). *Int. J. Impact Eng.* 33, 410. [8] Miljković K. et al. (2011). *Icarus* 214, 739. [9] M. J. Burchell et al., (1999). *Meas. Sci. & Tech.*, 10, 41. [10] Bell M. S. & Zolensky M. E. (2011). *LPSC XXXXII*, abstract # 2008