EXPERIMENTAL SHOCK TRANSFORMATION OF GYPSUM TO ANHYDRITE: A NEW LOW PRESSURE REGIME SHOCK INDICATOR.

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Introduction: The shock behavior of gypsum is important in understanding the Cretaceous/Paleogene event and other terrestrial impacts that contain evaporite sediments in their targets (e.g., Mars Exploration Rover Spirit detected sulfate at Gusev crater, [1]). Most interest focuses on issues of devolatilization to quantify the production of SO_2 to better understand its role in generating a temporary atmosphere and its effects on climate and biota [2,3]. Kondo and Ahrens [4] measured induced radiation emitted from single crystal gypsum shocked to 30 and 40 GPa. They observed greybody emission spectra corresponding to temperatures in the range of 3,000 to 4,000 K that are a factor of 2 to 10 times greater than calculated pressure-density energy equation of state temperatures (Hugoniot) and are high enough to melt gypsum. Chen *et al*. [5] reported results of shock experiments on anhydrite, gypsum, and mixtures of these phases with silica. Their observations indicated little or no devolatilization of anhydrite shocked to 42 GPa and that the fraction of sulfur, by mass, that degassed is $\sim10^{-2}$ of theoretical prediction. In another report of shock experiments on calcite, anhydrite, and gypsum, Badjukov *et al*. [6] observed only intensive plastic deformation in anhydrite shock loaded at 63 GPa, and gypsum converted to anhydrite when shock loaded at 56 GPa but have not experimentally shocked gypsum in a step-wise manner to constrain possible incipient transformation effects. Schmitt and Hornemann [7] shock loaded anhydrite and quartz to a peak pressure of 60 GPa and report the platy anhydrite grains were completely pseudomorphed by small crystallized anhydrite grains. However, no evidence of interaction between the two phases could be observed and they suggested that recrystallization of anhydrite grains is the result of a solid-state transformation. They concluded that significant decomposition of anhydrite requires shock pressures higher than 60 GPa. Gupta *et al*. [8] reanalyzed the calcite and anhydrite shock wave experiments of Yang [9] using improved equations of state of porous materials and vaporized products. They determined the pressures for incipient and complete vaporization to be 32.5 and 122 GPa for anhydrite GPa which is a factor of 2 to 3 lower than reported earlier by Yang [9]. These studies are not in agreement regarding the onset of sulfate decomposition and documentation of shock effects in gypsum is incomplete.

Impactites produced in dominantly evaporate targets lack quartz, a commonly used shock indicator with well documented effects induced over a range of shock pressures beginning as low as ~10 GPa [10,11,12]. Bell [12] reports preliminary identification of gypsum transforming to anhydrite in systematic step-wise shock experiments from 10 to 47 GPa and documents a calibration scheme of shock effects in calcite and gypsum relative to those in quartz. The transformation of gypsum to anhydrite as evidenced by high relief and high birefringence is observed in the 18.4 GPa shock experiment and the effect is continuous through the 40.7 GPa experiment but whether or not calcium sulfate remains birefringent cannot be resolved in the 47.7 GPa experiment. The transition of gypsum to anhydrite (a stable polymorph) + H_2O is monotropic (irreversible) in which the temperature required to initiate the transformation is lowered with increasing pressure (200 °C at 1 atm). Raman spectroscopy can be used to detect the presence of water in gypsum which is characterized by peaks in the spectral region between 3200 and 3500 cm^{-1}. Peaks in this region are absent in anhydrite spectra. For anhydrite, the strongest Raman peak is found up-shifted to 1017 cm^{-1} from that of gypsum, found at 1008 cm^{-1}.

Results of Raman analyses have been used to verify the transformation of gypsum to anhydrite and results of that study are reported here. These shock-induced transformation effects in gypsum could provide a new low pressure regime shock indicator for impact deposits lacking quartz or other crystalline rock-forming minerals.

Experimental: Details of the shock experiments can be found in Bell, 2010. For this study, an additional 7 samples consisting of only quartz and gypsum (50:50%) were shocked in a step-wise manner to 6.4, 9.5, 19.4, 28.88, 40.1, 41.4, and 47.2 GPa. The samples were prepared and analysed according to the same protocols as Bell, 2010. Pure gypsum ($CaSO_4 \cdot 2H_2O$, Sigma Aldrich 255548-100G) and quartz (SiO_2, Montgomery Co., Arkansas) were used for the experiments. Raman spectra were collected using the Jobin-Yvon LabRAM HR800 at the Johnson Space Center Astromaterials Research and Exploration Science Directorate. The spectrometer is equipped with an argon ion (Ar+) gas laser using the 514.5cm^{-1} plasma line of that laser. Laser power was 80 mW at the sample to maximize spectral quality and minimize beam damage. The slit width was set at 100 µm and a data collection interval of 1 cm^{-1} was used in recording Raman spectra. Ten spectra were acquired per sample for each shock interval.

Results: The gypsum used in this study was characterized by Raman spectroscopy in the range 100 to 1400 cm^{-1} and peaks were assigned according to [13]. In the Raman spectra, the peaks around 100 and 210 cm^{-1} (rotational and translational lattice modes) are the result of stretch vibration modes of water, and no peaks for these modes of water were observed in any spectra from the shocked gypsum samples. With the exception of the 19.4 GPa sample, the spectral peaks for the v_1 (SO_4) symmetric stretch vibration mode of SO_4 tetrahedra are consistently located near 1017cm^{-1} which is up-shifted from the gypsum peak at 1008 cm^{-1} (Figure 1). Spectal peak intensity is diminished for all samples - a likely result of shock deformation of the covalently bonded SO_4 tetrahedra. Peaks in the region between 3200 and 3500 cm^{-1} (2 v_2, v_1, and v_3 stretch vibration modes of water) are absent in the Raman spectra (Figure 2). Again, the 19.4 GPa sample is the exception and has a hint of the v_3 mode in spectra collected from one spot analysed. However, all other spots analysed on this sample resulted in Raman spectra lacking the stretch vibration modes of water. These results indicate that all shocked gypsum samples are transformed to anhydrite across the entire pressure range from 10 to 47 GPa have been transformed to anhydrite.

Conclusions: Anhydrite can be useful as a low pressure shock indicator in naturally shocked rocks when the target strata can be documented to have contained gypsum in the absence of silicate rocks that might otherwise provide petrographic shock indicators. Anhydrite present in distal ejecta may be a useful tool to fingerprint the source of the material in the impact deposits as well. These data document the solid-state transformation of gypsum to anhydrite and demonstrate the stability of sulfate to shock pressures as high as 47 GPa. Modeling of the magnitude and duration of a toxic atmosphere genreated during large meteorite impacts into sulfate-rich targets can benefit from a documented upper stability limit for gypsum and anhydrite.

References: [1] Hecht, M.H. et al., (2008) *Science* v.325, 64-67. [2] Silver, L.T. and Schultz, P.H., eds. (1982) GSA Special Paper 190. 528 p.[3] Brett, R. (1992) *GCA* 56, 3603-3606. [4] Kondo, K.-I. and Ahrens, T.J. (1983) *Phys Chem of Mins* 9, 173-181.[5] Chen, G., Tyburczy, J.A., and Ahrens, T.J. (1994) *E & PSL* 128, 615-628. [6] Badjukov, D.D., Dikov, Yu P., Petrova, T.L., and Pershin, S.V. (1995) *LPSC XXVI* abst. # 63-64. [7] Schmitt, R.T. and Hornemann, U. (1998) *LPSC XXIX* abst. #1019, CD-ROM. [8] Gupta, S.C., Ahrens, T.J., and Yang, W. (1999) *in* Shock Compression of Condensed Matter,1259-1262. [9] Yang, W. and Ahrens, T.J. (1998) *E & PSL Letters* 156, 125-140. [10] Stöffler, D. and Langenhorst, F. (1994) *Meteoritics* 29, 155-181.[11] Grieve, A.F., Langenhorst, F., and Stoffler, D. (1996) *MAPS* 31, 6-35 [12] Bell, M.S. (2010) *GSA Special Paper* 465, 593-608. [13] Sarma et al. (1998) *J. Raman Spec.* 29, 851-856.
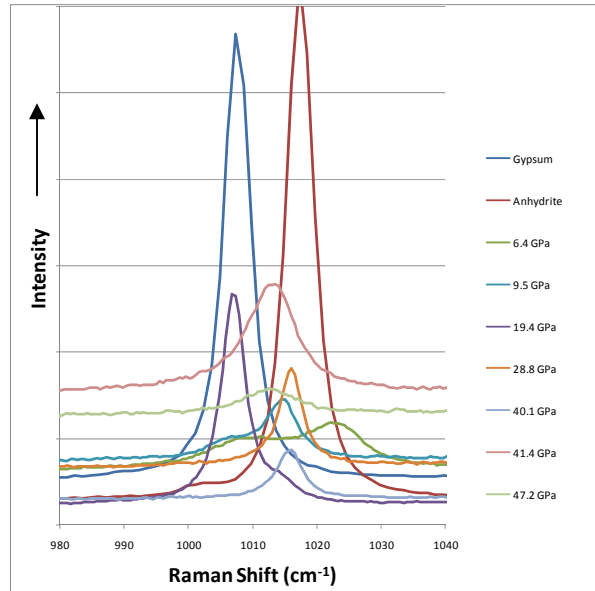

Figure 1. Raman spectra for the v_1 (SO_4) symmetric stretch vibration mode of SO_4 tetrahedra for samples shocked from 9.9 to 47.1 GPa. Raman spectra for unshocked gypsum and anhydrite are included for reference.
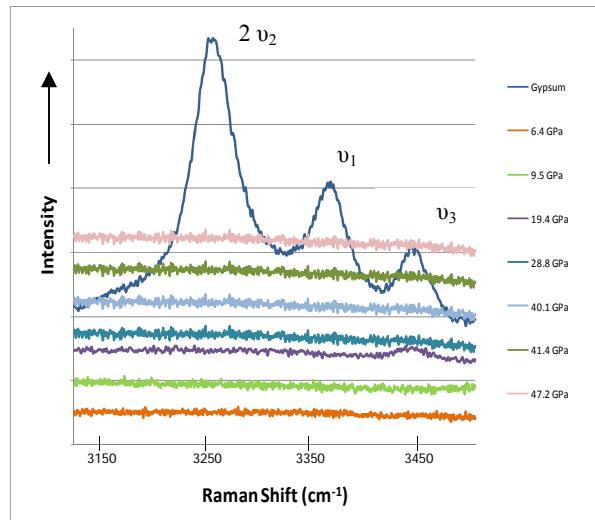

Figure 2. Peaks in the region between 3200 and 3500 cm^{-1} (2 v_2, v_1, and v_3 stretch vibration modes of water) are absent in the shocked gypsum Raman spectra. Raman spectra for unshocked gypsum is included for reference.