

UNCERTAINTIES IN THE SHOCK DEVOLATILIZATION OF HYDRATED MINERALS: A NONTRONITE CASE STUDY. S. T. Stewart¹, R. G. Kraus¹, R. E. Milliken², and N. J. Tosca³, ¹Dept. of Earth & Planetary Sci., Harvard U., 20 Oxford St., Cambridge, MA 02138 (sstewart@eps.harvard.edu), ²JPL/Caltech, 4800 Oak Grove Dr., Pasadena, CA 91109, ³Dept. of Earth Sciences, U. Cambridge, Cambridge CB2 3EQ, U. K.

Introduction: Understanding the distribution of hydrated minerals on Mars in space and time will ultimately constrain paleo-surface conditions, providing insight into planetary evolution. Phyllosilicates, confined largely to Noachian terrains [1-3], appear contemporaneous with a period of intense impact cratering. So, in addition to aqueous chemistry, they may carry an overprint of crustal impact modification. Such pervasive shock processing may have significantly modified or destroyed phyllosilicates through mechanical and/or thermal processes, which would in turn modify their spectral signatures.

Shock processing can change the near- (NIR) and far- (FIR) infrared spectrum of hydrated minerals (e.g., $\sim 3 \mu\text{m}$ O-H stretching and Si-O vibration bands at approximately 9 and $20 \mu\text{m}$ in nontronite [1]). The O-H stretch feature is diminished and the Si-O vibrational bands are completely removed and replaced by a less distinct glassy spectrum at very high shock pressures. Spectral changes are interpreted as (1) loss of water; (2) collapse of the interlayer structure in smectites; and (3) at high pressures, shock-induced amorphization.

Despite previous experimental attempts aimed at understanding shock-induced structural and spectroscopic changes of phyllosilicates, the data in hand are sparse and difficult to interpret. Here we report new results on nontronite, a major phyllosilicate mineral identified in ancient Martian terrains [2].

Shock recovery of nontronite: Two specimens of nontronite (API Clay Mineral Standard #H-33b) were shocked simultaneously in a SS304 steel planar shock recovery capsule by a steel flyer plate impacting at 1207 m/s [e.g., 3, 4]. The nontronite was powdered, sieved to $<65 \mu\text{m}$, and pressed to a density of 2.3 g/cm^3 in $8 \times 2 \text{ mm}$ discs. The samples were vented by 4 grooves around the downrange plug. It is well known that venting is required to allow volume expansion of gases released during the experiment [e.g., 5, 6, 7].

During this experiment the front face of the sample capsule sheared in a manner identical to previous shock recovery experiments [8, on dolomite, calcite, and siderite]: a disc of the 1.5-mm thick steel impact face of the sample capsule with diameter equal to the specimen was found intact next to the recovered target assembly. Some of the nontronite was recovered within the sample capsule. The recovered material was unconfined and had unlimited volume for expansion during release from the shock state. Skala et al. [8]

interpreted the onset of front face failure of the recovery capsule to be indicative of the shock pressure required to begin ‘significant devolatilization.’ The shock conditions for failure were very reproducible and dependent on the sample material, and this failure mode was not observed in their (or our) experiments on nonhydrous silicates. Ivanov et al. [5] questioned this simple interpretation because of the complex material strength of the steel capsule. An alternative explanation is that the front face shears during compression (rather than release) because of the strong contrast in compressibility between the sample and the steel.

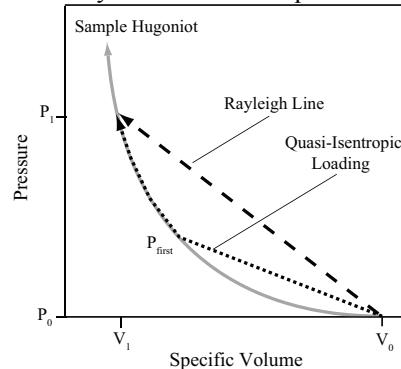


Fig. 1. Schematic of different thermodynamic paths to the same final shock pressure and volume via (1) a single shock wave or (2) multiple shock waves.

A shock pressure of 26 GPa was generated in the steel. The initial shock pressure in the nontronite is harder to determine. Given enough time, the nontronite sample will equilibrate with the steel via a series of shock wave reflections that ‘ring-up’ the pressure in the sample (Fig. 1). The sample is initially shocked to pressure P_{first} (determined by the impedance mismatch between the steel and the sample). The subsequent shock wave reverberations raise the pressure, and 4 to 5 reflections are required to reach within 10% of P_1 . The shock Hugoniot of nontronite has not been measured, so we estimate it based on shock experiments on different clays [9]. A reasonable range for P_{first} is 6-10 GPa. The achieved peak shock pressure depends on the thickness of the sample and time of arrival of the release waves; the sample may not have had time to reach the peak pressure before release. One of the main uncertainties in interpretation of shock-recovery experiments on hydrated minerals is the lack of Hugoniot data.

Analyses: The nontronite samples were characterized by NIR and FIR spectroscopy, x-ray diffraction (XRD), and thermogravimetric analyses (TGA). The

TGA results on unshocked samples were consistent with previous work [10]. The XRD and infrared spectra of shocked and unshocked nontronite are shown in Figs. 2 and 3. Also, as expected, the shocked nontro-nite experienced a dramatic change in color, changing from green-yellow to a reddish black [11]. Changes in Si-O bonding are observed in the FIR. In this experiment, the smectite structure has been completely de-stroyed and the resulting material would not be identified as a clay via NIR reflectance spectroscopy.

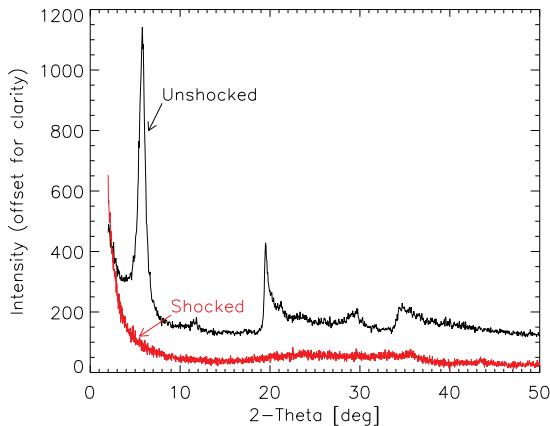


Fig. 2. X-ray diffraction spectra of shocked (red, 6-10 GPa P_{first} , 26 GPa peak shock) and unshocked nontronite (black). The basal layer (arrows) has collapsed completely in the shocked sample, but there are weak peaks remaining at larger 2θ (20-40°).

Comparison to previous work on nontronite: Boslough et al. conducted two impact shock recovery experiments on nontronite [1, 11]. In their experiment at 30 GPa (P_1 in the steel capsule), they found that the basal layer collapsed from 14.9 to 11.7 Å and that some of the bound OH was lost. Their results on un-vented samples are in stark contrast to our new results on vented samples. We find that none of the basal structure is preserved under lower shock pressures.

In a subsequent study, Boslough et al. [12] conducted a series of explosively-driven shock recovery experiments (13-48 GPa peak pressures) on 37-62% porous nontronite in unvented copper fixtures to measure magnetic properties, XRD, and Mössbauer spectroscopy. These experiments suffered from severe heterogeneity in the shock pressure across the sample. In two cases, the capsules ruptured and the results were different than for the enclosed samples, but it was not discussed in detail in their work.

Recently, preliminary near-infrared data have been collected on shock recovered nontronites [13-15]. These experiments utilized a sealed recovery capsule and non-planar impact conditions. The highly heterogeneous shock pressure histories were estimated by modeling the laboratory experiments [14]. Samples subjected to peak pressures of 5.4-17.5 GPa and

average shock pressures of 0.9-1.6 GPa did not exhibit any significant changes in the NIR spectra. These experiments are extremely difficult to interpret because of the combined problems of heterogeneous, nonplanar shock loading, unvented capsules, and unknown Hugoniot of the sample.

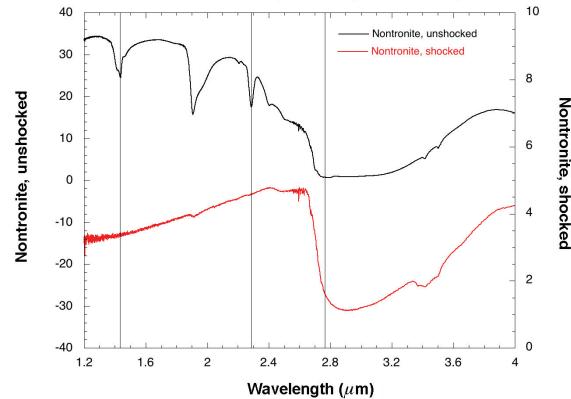


Fig. 3. NIR reflectance spectra of shocked and unshocked nontronite. The shocked sample has lost the OH bands (vertical lines: Fe-OH bands). Adsorbed H₂O is present (broad absorption feature around 2.9 μm). The smectite basal layer has been destroyed.

Application of shock recovery data to remote sensing observations: The basal layer of nontronite is modified and eventually destroyed by shock, which leads to permanent removal of OH bonding sites. As a result, the spectra is modified. However, we do not presently understand the shock conditions under which the structural changes are initiated or when amorphization is reached. In general, shock recovery data on hydrated materials that are obtained in sealed capsules should be applied to observations with extreme caution given the significant discrepancies compared to vented capsules. Understanding of shock modification of hydrated minerals on Mars remains poor without more Hugoniot measurements, equation of state information (sound speeds under pressure and temperatures), and vented shock recovery data.

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