EFFECTS OF SHOCK METAMORPHISM ON PHYLLOSILICATE STRUCTURES AND SPECTROSCOPY.

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Introduction:

Phyllosilicates detected on Mars using VNIR spectroscopy indicate that clay minerals were formed in the early history of Mars [1-4]. Clay formation has important implications for the climatic history of Mars, evolution of the martian crust and past habitability. Because the surface of Mars is also heavily cratered as a result of impacts, many of the minerals on Mars, including clays, have experienced shock metamorphism. Understanding shock effects in clay minerals and how shock metamorphism changes the spectral signatures of clay minerals is critical for the correct interpretation of remotely sensed spectroscopy from Mars.

During hypervelocity impacts on planetary surfaces, minerals in both the impacting body and the target experience a pulse of high pressure and temperature conditions as a result of shock compression. Shock stress and associated high temperature conditions results in structural changes including deformation, disorder and phase transitions, melting and crystallization [5-8] Shock induced structural changes can also affect infrared spectroscopy [9-10].

Spectroscopic studies aimed to understand how shock processes lead to volatile loss show that serpentine begins to lose water at 30 GPa and loses most structural water by 70 GPa [11-12] Weldon et al. [13] also noted changes in color and water content in nontronite related to shock pressure, where the nontronite became redder, darker, and less hydrated as a function of shock stress. Recent work on IR spectroscopy of shocked clays shows relatively little change in the VNIR and more significant changed in mid IR reflectance spectra [14]. These results have significant implications for the disconnected observations of phyllosilicate/amorphous materials on Mars.

Methods and Materials:

Samples. The samples used in this study include nontronite, montmorillonite, saonite, chlorite kaolinite and antigorite. We gently ground the samples and separated the < 2μm size fraction using the techniques described in [15].

Shock Experiments. Shock experiments were carried out using the Flat Plate Accelerator (FPA) at Johnson Space Center. The FPA uses a powder propellant gun to accelerate a metal flyer plate into a sample target assembly at velocities up to 2 km/s. The FPA can generate sample pressures up to 60 GPa. We used a 25-mm stainless steel assembly in a reverberation-type shock-recovery experiment. The internal energy added to a sample during shock loading, and therefore the shock temperature, is proportional to the volume change during compression. As a result, sample porosity leads to high bulk shock temperatures and temperature heterogeneities. To reduce the porosity of the clay samples and make them more like dense clay-bearing rocks, we compressed clay samples into pellets with resulting densities ranging from 1.97 g/cm^3 (kaolinite) to 2.44 g/cm^3 (chorite). In this type of reverberation experiment, the pressure of the sample rings up to that of the sample container by multiple reflection of the shock wave across the sample. The peak pressures of the sample, calculated from the shock impedance of the target assembly, the flyer plate and the flyer-plate velocity, ranged 10.0 to 40.0 GPa for our experiments.

Results:

So far, we have the largest pressure range (10 -40 GPa) for our nontranite sample so we will concentrate mostly on those results.

XRD. All of our samples show significant broadening of diffraction peaks, especially 001, with increasing shock pressure. This indicates a reduction in crystallite size or strain within those crystallites. In addition, kaolinite shows a distinct loss of stacking order between unshocked 20 GPa samples. In addition to broadening of reflections, nontronite shows a minor decrease in layer stacking order, going from the unshocked to 10 GPa. The most pronounced effect in nontranite is the almost complete loss of structural order after shock to 40 GPa. Based on XRD, the 40 GPa nontronite sample is essentially amorphous.

TEM. Bright-field TEM imaging and electron diffraction of the nontronite samples show a progressive decrease in structural order and reduction of coherent packets of nontronite layers (Fig. 1). Electron diffraction patterns of unshocked nontronite particles display strong ring patterns indicating orientation disorder. HRTEM images show curved crystallites with coherent packets up to about 20 (001) layers thick (Fig. 1a). The 20 GPa samples shows significantly weaker SAED patterns and smaller packets of choherent clay layers. The 40 GPa sample is nearly amorphous at the TEM scale. HRTEM images indicate locally amorphous material (Fig 1b) as well as highly disordered material with packets up to several 001 layers thick (Fig. 1c).

Mössbauer Spctroscopy, In general, samples with ferrous iron become slightly more oxidized with increasing shock pressure. In the case of nontronite, the

Mossbauer parameters stay nearly constant as a function of shock pressure, but the ferric Fe positions more distorted with increasing pressure.

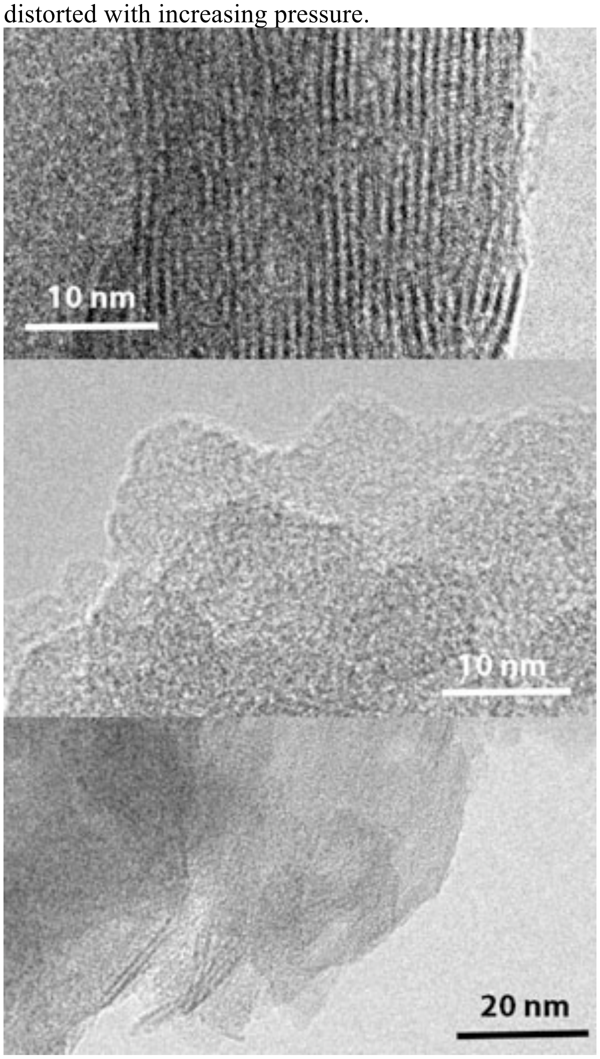

Fig.1 Bright fied TEM images of (a) nontronite 001 layers in unshocked material, (b) amourphous nontronite in material shocked to 40 GPA and (c) short-range layering in nontronite shocked to 40 GPa.

VNIR and MIR Spectroscopy. Details of the VNIR and MIR spectroscopy results for nontronite are presented in a separate abstract [16]. Distinct differences between pre- and post-shock nontronite samples are visible for shock pressures as low as 10 GPa, but the most dramatic structural changes occurred between 20 and 40 GPa. Changes in the feature at ~0.6 µm, in samples shocked to 20 and 40 GPa as well as visible color changes are consistent with Mossbauer observations of changes in ferric Fe site geometries. 1.4 and 1.9 µm absorption features broaden and shallow with increasing shock pressure, consistent with dehydration and dehyroxilation during shock. In thermal emission spectra, the amplidude of the Si-O stretching feature at ~ 1100 cm^{-1} and the Si-O and metal-O features between ~ 200 and 600 cm^{-1} are greatly reduced in 20 and 40 GPa samples.

Discussion: Our shock recovery experiments and subsequent detailed sample characterization are helping us to better understand shock metamorphic effects in phylosilicates and spectral changes that will affect remote sensing observations from Mars. However, the reverberation method used in these shock recovery experiments results in lower shock temperatures than the single-shock loading of natural impacts. This limitation means that the pressure values associated with shock metamorphic effects we observe cannot be directly correlated with the pressures of natural shock effects in clay minerals.

The shock metamorphic effects that we see in nontronite, from 10 to 40 GPa, represent increasing strain and structural disorder with increasing shock stress. Nontronite shocked to 40 GPa is essentially amorphous to X-ray diffraction, but TEM results show that the nanometer-scale structural disorder and deformation are heterogeneous. Mossbauer spectroscopy of the nontronite shows that the ferric iron sites become increasingly distorted with pressure, consistent with amorphization at the X-ray and electron diffraction scales. Changes in the ~ 0.6 µm feature in VNIR spectra are consistent with the changes in ferric iron site distortions. The significant changes observed in VNIR spectra and the near elimination of spectral features in MIR emission spectra of nontronite at pressure up to 40 GPa are important to the interpretation and identification of clay minerals and poorly crystalline clay-like materials on Mars. Shock effects could help explain why clays are more readily observed with VNIR rather than TIR data sets. More work is needed to understand the shock features and associated prectral properties.

References:

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