THERMAL ALTERATION OF NONTRONITE AND MONTMORILLONITE: IMPLICATIONS FOR THE MARTIAN SURFACE. P. Gavin, V. Chevrier. W. M. Keck Laboratory for Space Simulations, Arkansas Center for Space and Planetary Sciences, 202 Old Museum Building, University of Arkansas, Fayetteville, AR 72701.

Introduction:

OMEGA/Mars Express data was confirmed by CRISM/MRO data of the existence of clay minerals on the surface of Mars [1, 2]. These clays have been found in some of the oldest terrains of Mars and because of their Noachian age, they hold clues to the earliest history of the martian surface. Clays have been detected in outcrops surrounded by lava flows and in the ejecta of small impact craters [3, 4]. Previous studies have suggested that clays may form by impact-induced hydrothermal processes [5] while others imply that they formed much earlier and that thermally altered clays may be responsible for the properties of the red dust that covers the martian surface [6, 7]. In this study, we investigate the effects of thermal treatment on the spectral properties of clays, focusing on nontronite and montmorillonite, and their relation to the martian surface.

Experimental and Analytical Methods:

One-gram samples of nontronite (Fe^{3+}, Mg) and montmorillonite (Al, Ca) were heated in a Lindberg tube furnace to temperatures ranging from 350°C to 1150°C for 4 to 24 hours. Samples were heated in air as well as under a steady flow of CO_2 to more closely replicate early martian conditions. Each sample was allowed to cool overnight and weighed after heating.

The samples' extreme color change after heating was precisely characterized using Munsell soil color charts. Samples were analyzed using X-ray diffraction and near-infrared reflectance spectroscopy.

Results and Discussion:

Each heated sample of nontronite and montmorillonite showed significant color change. Nontronite samples changed from yellow-green to shades of reddish brown. Montmorillonite samples transitioned from gray to shades of orange.

Weighing the heated samples showed there was an average of about 25% mass loss, most likely due to the loss of interlayer water, as it has been shown to be lost at lower temperatures than is structural water [6].

XRD spectra taken of nontronite samples heated to low temperatures (T < 750°C) showed that the 001 peak had disappeared, consistent with the loss of interlayer water, but all other peaks were still intact. There was also very little difference in the spectra of samples heated in air and those heated in CO_2, indicating the CO_2 atmosphere had little, if any, effect on the transformation process.

The XRD spectra of samples heated to intermediate temperatures (800°C < T < 1000°C) showed low intensity, broad peaks. These are evidence of a complex mixture of secondary nanocrystalline phases.

The sharp, well-defined peaks in the XRD spectra of samples heated to high temperatures (T > 1100°C) indicate the sample has melted and recrystallized into new phases (Figure 1). New phases such as hematite, cristoballite and sillimanite were identified.

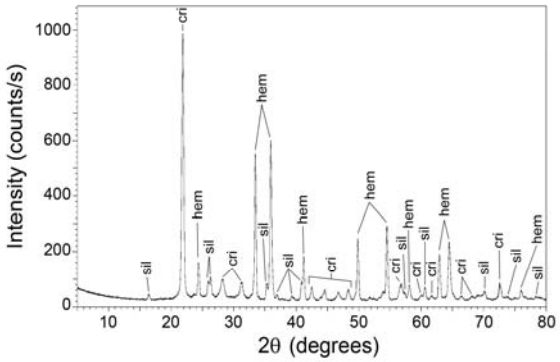

Figure 1: *XRD of a sample of nontronite heated to 1130°C. The identifying peaks of the new phases that formed have been marked (hem: hematite, sil: sillimanite, and cri: crystoballite).*

Unlike the nontronite spectrum, the 001 peak was still intact in the XRD of low-temperature samples of montmorillonite, as were many of the other identifying peaks of montmorillonite, indicating montmorillonite is possibly more resistant to heat than nontronite.

XRD spectra of samples heated to high temperatures (T = 1130°C) showed evidence of the formation of both secondary phases as well as amorphous glass, indicated by a large "hump" feature at low 2θ values (~ 22°) (Figure 2). Secondary phases that were identified include sillimanite and cristoballite.

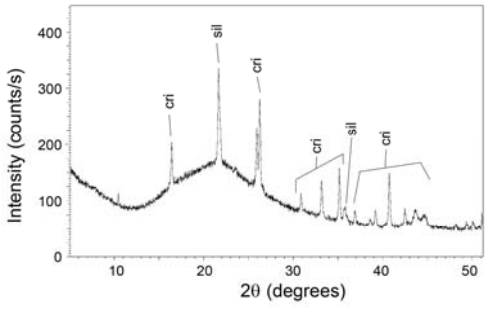

Figure 2: *XRD of a sample of montmorillonite heated to 1130°C. The identifying peaks of the new phases formed are marked (sil: sillimanite; cri: cristoballite).*

Near infrared (NIR) reflectance spectra were taken of each sample. Figure 3 shows the NIR reflectance spectra of an untreated sample of nontronite compared to several heated samples. At T = 475°C and 630°C, the 1.4 µm band corresponding to the structural hydroxyl in the clay has disappeared. This correlates with the fact that structural OH^- is lost at temperatures above ~300°C [8]. However, the 1.9 µm hydration band is still visible. This is most likely the result of the nontronite being destroyed locally so that interlayer water can still be present [6]. The 2.3 µm band has not completely disappeared, but instead has flattened into a plateau rather than a distinct peak. After temperatures have reached ~800°C, the spectra become featureless in this range indicating the structure of nontronite has been completely destroyed.

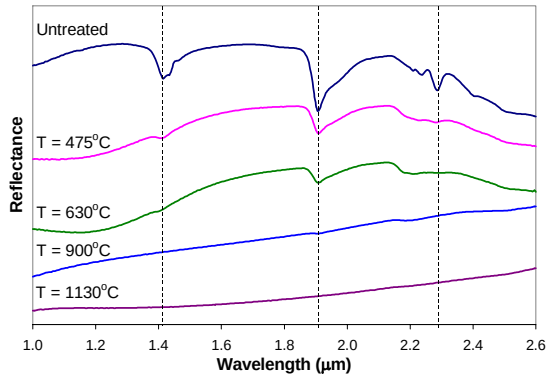

Figure 3: *NIR spectra of samples of heated nontronite.*

Figure 4 shows the NIR spectra of several heated samples of montmorillonite. The same trends can be seen: the hydration band is still intact at low temperatures and the spectra are featureless after ~800°C. Also, the 2.2µm band has also flattened into a plateau shape.

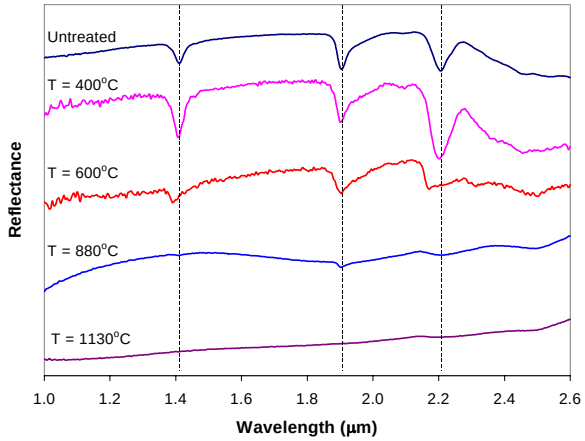

Figure 4: *NIR spectra of samples of heated montmorillonite Spectra of 400°C and 600°C samples were provided by Dan Ostrowski.*

Implications for Mars:

If clays were indeed the first minerals on the surface of Mars, then they would have been in an environment of daily volcanic eruptions and continuous impacts. They would have inevitably come into contact with lava flows and been pulverized by the heat and pressure generated by constant impacts. The high temperatures from these events, especially volcanism, would have easily transformed these clays into secondary phases. This process has been reproduced and analyzed in the lab. If impact-induced hydrothermal processes formed the clays seen in crater ejecta on Mars, their spectral signature would be identical to that of untreated clays. This is not the case. Their spectra are more similar to that of the heated clays, especially the plateau shape of the 2.3 µm band in the low-temperature samples. This indicates they were pre-existing and altered by the heat of the impact.

Conclusions:

Heat is the substantial factor in the transformation of clays. Clays are affected even at low temperatures (~350°C) by the loss of interlayer water and color change. Clays transform into secondary phases, such as hematite, sillimanite, and cristoballite, at temperatures above ~1100°C. The clays seen in crater ejecta on Mars could not have been formed by impact-induced hydrothermal systems but existed pre-impact because their spectra are not identical to that of untreated clays but rather they are more similar to that of altered clays.

Future work:

Further analysis of the heated samples includes Raman spectroscopy to detect any amorphous phases that may have been formed at low temperatures. Also, we plan to investigate the spectra of these samples in other regions such as the mid-infrared range. We also intend to continue this work using other clay minerals.

Acknowledgments:

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References:

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