SPECTRAL EFFECTS OF DEHYDRATION ON PHYLLOSILICATES; E.A. Bruckenthal and R.B. Singer, Planetary Geosciences Division, Hawaii Institute of Geophysics, 2525 Correa Road, Honolulu, HI 96822

INTROUCTION Six phyllosilicates have been progressively dehydrated under controlled conditions in an effort to study the spectral effects of their dehydration. Justification for the study may be found in both terrestrial and planetary soil science applications. For example, we know through spectroscopic observations of Mars and several asteroids[1,2] that their surfaces contain ubiquitous hydrated silicates. However, due to the anhydrous nature of the extraterrestrial environment, one would not expect these soils to exist in the same hydration states as they do on Earth. Furthermore, spectroscopy provides a tool which probes the internal structures of these clays as they undergo changes. Thus, the spectra obtained at each level of hydration provide information which may be used in future spectroscopic observations of other planets, as well as a data set which complements the existing body of terrestrial soil knowledge.

SAMPLES AND EXPERIMENTAL METHODS Samples were chosen to represent a range of both crystalline and X-ray amorphous soil components. The four crystalline clays include dioctahedral and trioctahedral endmembers of t-o and t-o-t type clays, as well as species characterized by extensive substitutions in their tetrahedral and octahedral layers. Serpentine, $Mg_3Si_2O_5(OH)_4$, represents an endmember (negligible cationic substitution) tricotahedtal t-o clay, while talc, $Mg_3Si_4O_{10}(OH)_2$, is an endmember trioctahedral t-o-t clay. Ca-montmorillonite was chosen as a dioctahedral smectite, while saponite represents the trioctahedral smectite group. Both smectites have the general formula, $(\frac{1}{2} Ca,Na)_{0.7}(Al,Mg,Fe)_4(Si,Al)_8O_{20}(OH)_4 \cdot nH_2O$.

The final two clays studied are Big Island palagonites -- X-ray amorphous, low temperature alteration products of basaltic volcanic glass. The two differ in that the Pahala Ash is more completely weathered, more incipiently crystalline, and significantly more hygroscopic than the Mauna Kea palagonite.

Each clay was ground and dry-sieved to <38 μm, and then equilibrated in a high humidity ($>95\%$) environment. An environment chamber which allows spectrophotometric observations at non-ambient conditions was used in conjunction with a custom-built furnace. Each sample was heated to eight elevated temperatures (120, 160, 200, 250, 300, 400, 600, and 750° C.) in an inert, dry nitrogen atmosphere. Spectra were obtained at room temperature and after heating to each of the aforementioned target temperatures.

BACKGROUND In order to understand the nature of clay dehydration, a brief introduction to the different species of hydration is helpful. The four species of hydration which exist include three forms of adsorbed water and one form of hydroxyl ions.

The first of three types of adsorbed water is found in pores, on surfaces, and around the edges of particulate samples of all clay minerals, regardless of type. It consists of loosely bound H_2O molecules held only by Van der Waals' forces and is called *physically adsorbed water*.

The second and third forms of adsorbed water, found almost exclusively in t-o-t layer clays, refer to those H_2O molecules which are bound more tightly to a clay mineral than physically adsorbed water. Although capable of being removed at low temperatures, these molecules are bound to the basal surfaces of a clay by forces of a more electrostatic nature. This species will be referred to here as *surface-bound water*. Often surface-bound water grades into physically adsorbed water at some distance from the basal surface.

Very similar and difficult to distinguish from surface-bound water are those H_2O molecules bound to cations which have been adsorbed between layers in smectite clays. A distinction must be made between this *cation-bound water* and surface-bound water because researchers have shown that cation-bound water is held much more tightly, and driven off at much higher temperatures, than surface-bound water[3,4].

The final form of hydration consists of those OH molecules which comprise portions of the clay structure through their presence in an octahedral layer. This species of hydration will be referred as *structural hydroxl ions*, and its loss from a clay as dehydroxlation.

INTERPRETATION The plots which follow illustrate spectral changes observed with increasing temperature for three of the six samples investigated. Only those temperatures at which significant changes occurred are shown. Numbers in bold type represent the temperatures associated with each sample.

Talc
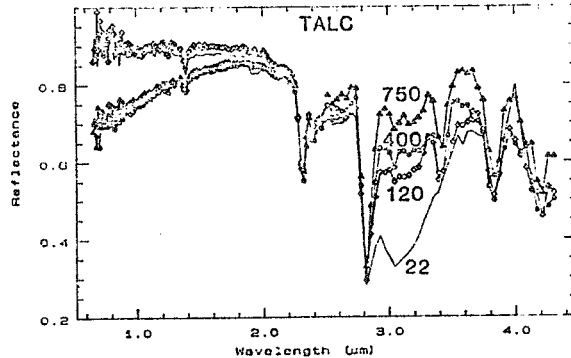
Spectral features to be noted in the room temperature (22° C.) spectrum above include the following: 1) a sharp, 1.4 μm band due to both OH and H_2O 2) a broader 1.9 μm H_2O band 3) a broad, shallow 2.2 μm cation-OH feature 4) very sharp, well-defined 2.3 and 2.4 μm Mg-OH bands 5) a strong OH fundamental near 1.8 μm, and 6) a broad, deep 3.1 μm H_2O absorption. Upon heating to 120°C., physically adsorbed water contributing to the 1.9 and 3.1 μm bands is driven off, dramatically lessening the strength of both features. By 400°, more tightly held water molecules have begun to leave the structure, reducing 1.4 μm band depth, completely eliminating the 1.9 μm band, and further reducing the 3.1 μm band. Limited cationic substitution has attracted surface and/or cation bound water molecules to a few interlayer sights, and sufficient kinetic energy is now available to begin removing them. Most likely some of this water is reincorporated back into the structure to cause the oxidation which is apparent as a slope change between 0.65 and 1.8 μm. Upon heating through 750° C., talc continues losing its most tightly bound H_2O, as shown by the continued decrease in 3.1 μm band strength.

Montmorillonite
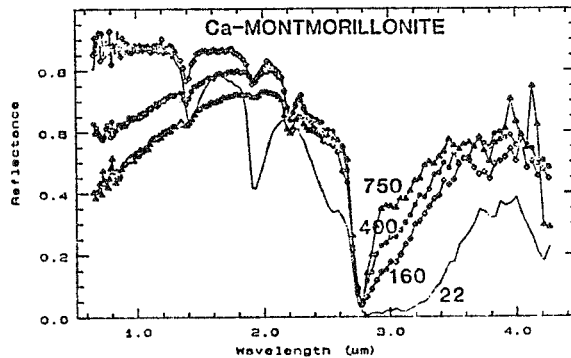
Salient spectral features in the room temperature smectite spectrum include the following: 1) a deep, asymmetric 1.4 μm OH + H_2O band, 2) a deep asymmetric 1.9 μm absorption, 3) a 2.2 μm Al-OH band, and 4) complete saturation in the region between ~2.75 and 3.2 μm, which includes both OH and H_2O fundamentals. As physically adsorbed water is lost through 160°, both the 1.4 μm and 1.9 μm bands decrease in strength, narrow and become more symmetric. This occurs because the molecules which contribute to their absorptions are in more well-defined crystalline sites. When

the water bands decrease in strength, they are less able to mask other absorptions, and the apparent 2.2 μm band increase is due to this effect. At longer wavelengths, both the 2.9 and 3.1 μm H_2O fundamental bands lessen dramatically, eliminating saturation in the 3 μm region. Loss of tightly held, surface-bound water by 400° contributes to a decrease in band strength at 1.4, 1.9, 2.9, and 3.1 μm. Very likely the increased slope between 0.6-1.8 μm is due to cation oxidation by some of this released water. By 750° structural reorganization begins to occur. The 1.4 μm band is now both broad and very weak, suggesting a disruption of sites in which OH is commonly located as well as its loss from the clay. The miniscule 1.9 μm feature indicates that little H_2O remains, a conclusion substantiated by the weak 2.9 and 3.1 μm bands. Incipient structural reorganization is also indicated by a broadening of the 2.2 μm Al-OH absorption.

Palagonite
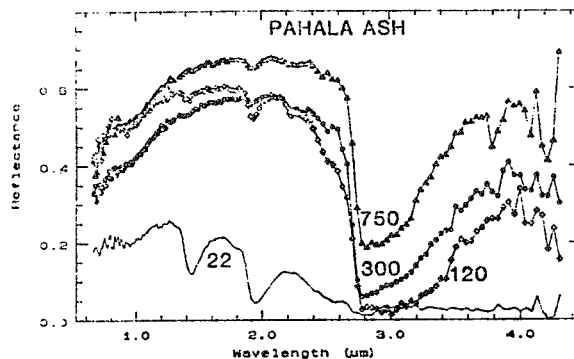
At room temperature the hygroscopic palagonite displays the following four features: 1) a broad Fe^{+2} electronic transition band centered near 1 μm, suggesting the presence of some short range crystalline order, 2) a deep, asymmetric 1.4 μm H_2O + OH band, 3) a deep, asymmetric 1.9 μm H_2O band on which the resolution of a 1.7 μm shoulder feature is evidence for *extreme* hydration, and 4) complete saturation of the 2.7-4.3 μm region. Heating to 120° drives off the most loosely bound water molecules, decreasing the strength of the 1.4 and 1.9 μm features and easing saturation between 3.1-4.3 μm. Lessening these H_2O features enables a previously masked 2.2 μm Al-OH band to be seen. More water, and loosely held OH molecules are driven off by 300°. The lack of a well defined crystalline network eliminates the distinction of *structural* OH ions; hydroxyls are held much less tightly and may be driven off at lower temperatures than in crystalline clays. Removal of some hydroxyls eliminates the 1.4 μm band and lessens the 2.75 μm band. However, the distinct 2.2 μm Al-OH feature indicates that tightly bound hydroxyl ions are still held. By 400° loss of these tightly held hydroxyls begins, indicated by reduction and broadening of the 2.2 μm band and continued reduction of the 2.75 μm band. More H_2O is also lost by this temperature, and lessening 1.9, 2.9, and 3.1 μm bands reflect this change. The trends noted above continue through 750°.

REFERENCES: 1) Feierberg, M.A., Lebofsky, L.A., and H.P. Larson (1981) Spectroscopic evidence for aqueous alteration products on the surfaces of low-albedo asteroids, Geoch. Cosmoch. Acta 45, 971-981. 2) Pimentel, G.C., Forney, P.B., and K.C. Herr (1974) Evidence about hydrate and solid water in the Martian surface from the 1969 Mariner infrared spectrometer, JGR 79, No. 11, 1623-1634. 3) Mackenzie, R.C., The Differential Thermal Investigation of Clays, Mineralogical Society, London, 1957, p. 144-145. 4) Grim, R.E., Clay Mineralogy, 1st ed., McGraw-Hill, New York, 1953, p. 176-177.