

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

INTRODUCTION It is known 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. Therefore, six phyllosilicates have been progressively dehydrated under controlled conditions in an effort to study the spectral effects of their dehydration. The spectra obtained at each level of hydration provide information which may be used in future spectroscopic observations of other planets.

SAMPLES AND EXPERIMENTAL METHODS Samples were chosen to represent a range of both crystalline and X-ray amorphous soil components. Serpentine, talc, Ca-montmorillonite and saponite, represent 1:1 and 2:1 layer clays and di- and trioctahedral smectites, respectively. Two X-ray amorphous ferric oxides (palagonites) formed in semi-arid environments on the Big Island of Hawaii comprise the non-crystalline samples studied.

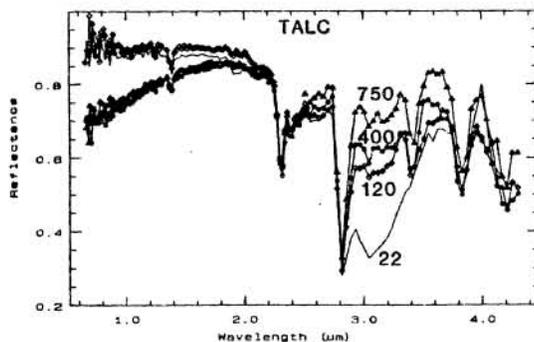
Each clay was ground and dry-sieved to $<38 \mu\text{m}$, and then equilibrated in a high humidity ($>95\%$) environment. An environment chamber which allows spectrophotometric observations at non-ambient conditions was used in conjunction with a custom-built furnace. Spectra were obtained in an inert,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

SPECIES OF HYDRATION In order to understand the nature of clay dehydration, a brief introduction to the different species of hydration is helpful.

Adsorbed Water The first of three types 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 interlayer sites of 2:1 layer clays, consist of H_2O molecules bound more tightly to a clay mineral than physically adsorbed water. One form, referred to here as *surface-bound water*, is attached to the basal clay surfaces, while the other form, *cation-bound water*, is bound to cations adsorbed between the layers in smectite clays. A distinction must be made between these two forms of adsorbed 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}.

Hydroxyl Groups The final form of hydration consists of OH molecules which comprise portions of the clay structure through their presence in an octahedral layer. These molecules are called *structural hydroxyl ions*, and their loss from a clay is dehydroxylation.

INTERPRETATION 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 22° C. spectrum at left include the following: 1) a sharp, 1.4 μm OH + H_2O band, 2) a broad 1.9 μm H_2O band, 3) a shallow 2.2 μm cation-OH feature 4) very sharp 2.3 and 2.4 μm Mg-OH bands, 5) a strong OH fundamental at 2.8 μm , and 6) broad, deep H_2O absorptions between 2.9 and 3.1 μm . Upon heating to 120°C., physically adsorbed water is driven off, lessening the strength of the 1.4 and $\sim 3 \mu\text{m}$ features. By 400°, more tightly held water molecules begin to leave the structure, reducing 1.4 and $\sim 3 \mu\text{m}$ features, and eliminating the 1.9 μm band, and further reducing the 3.1 μm band. The slope change between 0.65 and 1.8 μm is likely

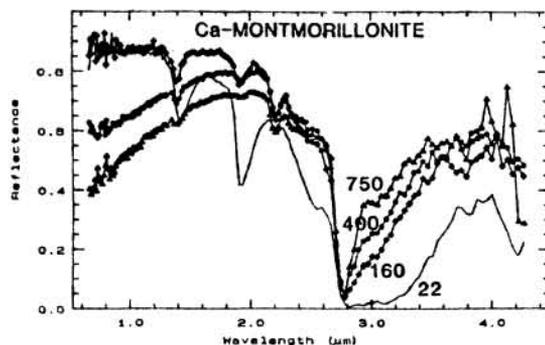
a result of cation oxidation by some of this released water. Upon heating through 750° C., talc continues losing its most tightly bound H_2O , as shown by the continued decrease in 3.1 μm band strength.

Like talc, serpentine does not have the extensive cationic substitutions which result in interlayer adsorption of molecules. Correspondingly, the serpentine spectra show identical spectral trends. Mauna Kea palagonite spectra are also quite similar. In this case, however, the paucity of tightly held water is due to the lack of a well-defined crystalline network.

DEHYDRATION OF PHYLLOSILICATES

Bruckenthal, E.A. and Singer, R.B.

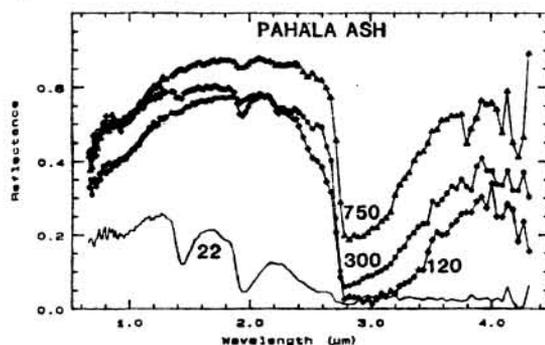
Like talc, serpentine does not have the extensive cationic substitutions which result in inter-layer adsorption of molecules. Correspondingly, the serpentine spectra show identical spectral trends. Mauna Kea palagonite spectra are also quite similar. In this case, however, the paucity of tightly held water is due to the lack of a well-defined crystalline network.



Montmorillonite Spectral features at left include the following: 1) and 2) deep, asymmetric 1.4 and 1.9 μm bands, 3) a 2.2 μm Al-OH band, and 4) complete saturation in the $\sim 2.75 - 3.2 \mu\text{m}$ region, which includes both OH and H_2O fundamentals. As physically adsorbed water is lost through 160°, and more tightly bound water through 400°, 1.4, 1.9 and $\sim 3 \mu\text{m}$ 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. As this occurs they are less able to mask other absorptions, and the apparent 2.2 μm band increase is due to this effect. The increased slope between 0.6

and 1.8 μm is due to cation oxidation by some of this released water. By 750° structural reorganization begins to occur. The 1.4 and 2.2 μm bands are 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.

Because of its structural similarity to the montmorillonite, the saponite demonstrated nearly identical spectral behavior.



Palagonite At room temperature the following four features are observed: 1) a broad Fe^{+2} band centered near 1 μm , implying short range crystalline order, 2) and 3) deep, asymmetric 1.4 and 1.9 μm bands, and 4) complete saturation of the 2.7-4.3 μm region. Heating to 120° drives off loosely bound water, decreasing the the 1.4 and 1.9 μm features, easing saturation between 3.1-4.3 μm , and unmasking a 2.2 μm Al-OH band. More water, and some OH molecules are driven off by 300°. Since a well-defined crystalline network is lacking, structural hydroxyls are driven off at much lower temperatures than in crystalline clays, eliminating the 1.4 and lessening the 2.8 μm bands. By 400°

(not shown) loss of more H_2O and tightly held OH occurs, weakening the 1.9, 2.2, and 2.8 μm bands. Loss of these species continues through 750°, but by this temperature the palagonite begins to redevelop some crystallinity. Fe^{+2} and H_2O bands at ~ 1 and 1.9 μm deepen, and an Al-OH band reappears near 2.2 μm , shortward of where one was lost previously. Thus, upon heating, this sample first loses, then regains its incipient crystallinity. The other five samples show differing amounts of dehydration and dehydroxylation, but none show any evidence of recrystallization.

DATA ANALYSIS The 1.4 and 1.9 bands, and the entire $\sim 3 \mu\text{m}$ feature have been analyzed with regard to depth, area, width, and asymmetry at each of the nine temperatures. Additionally, Dr. James Gooding of Johnson Space Center has performed differential scanning calorimetry on all the samples, yielding the amount of $\text{H}_2\text{O} + \text{OH}$ remaining in the clay structures at each temperature. Band depth and area are found to vary in non-linear, though regular ways with extent of hydration. Width and asymmetry cannot be correlated with extent of hydration, but are related more directly to degree of sample crystallinity and orientation of hydrated species within the clay structure.

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.

ACKNOWLEDGEMENTS The authors wish to thank Jim Gooding for his many contributions. This work was supported by NASA grant NSG 7590.