

SPECTRAL PROPERTIES OF DECCAN PALAEOOLS, INDIA: IMPLICATIONS FOR THERMALLY ALTERED PHYLLOSILICATES ON MARS.

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Introduction:

The exact origin of the phyllosilicates identified on Mars by MEx/OMEGA and MRO/CRISM [1-3] is still a topic of debate. Current theories suggest they are the result of liquid water activity and were formed during Mars' Noachian period [4] while others propose more recent processes such as hydrothermal systems resulting from meteorite impacts [5].

To fully understand phyllosilicate formation on Mars, it is beneficial to study analog deposits on Earth. One attractive candidate for martian smectites is the Deccan Palaeosols in western India. These bole beds have been the primary focus of several studies investigating palaeoenvironments on Earth [6]. While most theories agree these bole beds formed from the weathering of volcanic material [7], it has also been suggested that the original material was heated by subsequent volcanic flows [6].

This study focuses on the spectral properties of the Deccan Palaeosols, compares them to known mineral phases, and attempts to link terrestrial alteration processes with those that occurred on Mars.

Samples and Analytical Methods:

Eleven samples, labeled A-I, were first analyzed by X-ray diffraction (XRD). Each sample's reflectance spectrum was then recorded using an FTIR in the near-infrared (NIR) region (1.0-2.5 μm) and mid-infrared (MIR) region (5-15 μm). NIR spectra were recorded after the sample sat on a hotplate at 150°C under a flow of dry N₂ for two hours to remove any adsorbed water. Spectra were normalized and offset for clarity.

Results:

The samples were grouped according to their color: red, yellow, or green. There were seven red samples, two yellow and two green samples.

XRD analysis indicated that the samples are mixtures of phyllosilicates and iron oxides (Fig. 1), based on their interlayer 001 peak at 2θ between 6-10°. Green samples are composed mainly of nontronite and celadonite; red samples contain nontronite and hematite; yellow samples showed strong evidence for vermiculite and minor montmorillonite.

NIR spectra of the samples are mostly dominated by smectite signatures, i.e. hydration bands at 1.4 and 1.9 μm and metal-OH bands in the 2.2-2.4 μm region (Fig. 2). Spectra of green and yellow samples have bands in the 1.0-1.2 μm and 2.35-2.37 μm regions indicating the presence of Fe²⁺ [8] as well as a band at

2.29, indicating Fe³⁺. This supports the XRD data showing the green and yellow samples contain nontronite (Fe³⁺), vermiculite (Fe²⁺) and celadonite (Fe²⁺/Fe³⁺). Spectra of red samples showed a band at 2.21 μm indicating Al and a weak band at 2.29 μm region indicating small amounts of Fe³⁺ [8].

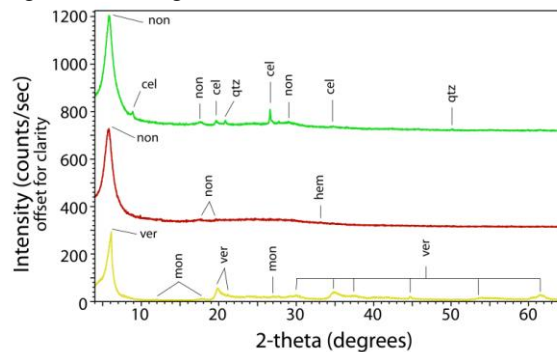


Figure 1: XRD analysis of samples B (green), G (red) and EG (yellow). Abbr.: non = nontronite; cel = celadonite; qtz = quartz; hem = hematite; mon = montmorillonite; ver = vermiculite.

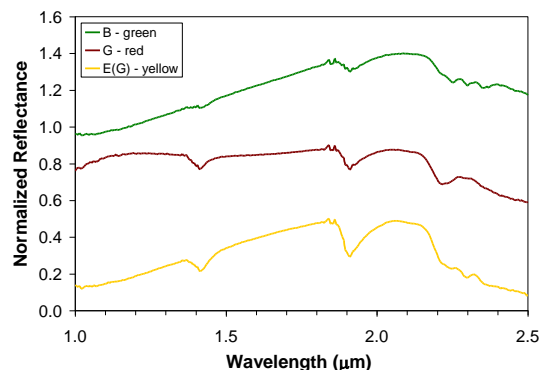


Figure 2: NIR reflectance spectra of samples B (green), G (red) and EG (yellow).

The NIR spectra of our Deccan samples were compared to those of heated nontronite and montmorillonite samples (Fig. 3) [9]. Although XRD data suggested nontronite, the overall spectrum of Sample G (red) resembles montmorillonite heated to 600°C. However, the position of the 1.4 μm band more closely matches that in the sample of untreated montmorillonite. This suggests the Deccan sample is a mixture of thermally altered and unaltered montmorillonite and nontronite. There is only a weak band at 2.29 μm as in the untreated nontronite spectrum, indicating any Fe³⁺ in the smectite of the red Deccan sample is overshadowed by the Al. Although they have no significant signal in the NIR

range [9], Fe^{3+} -oxides are most likely responsible for the sample's red color.

Figure 4 shows the MIR spectra of a green, red and yellow Deccan sample. All three spectra show bands at 6.1 and 8.5 μm representative of H_2O bending and SiO_2 , respectively [8], and are similar to MIR spectra of smectites [8, 9]. The spectrum of Sample B (green) has features at 5.4, 5.6, and 12.6 μm which are not present in the red and yellow spectra. These bands indicate the presence of thermal alteration products [9].

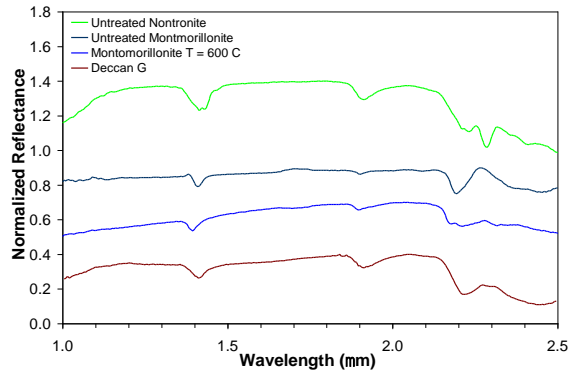


Figure 3: NIR spectra of Deccan G (red) sample compared to nontronite and montmorillonite samples.

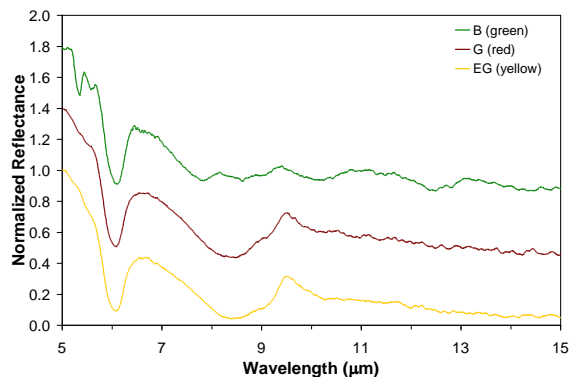


Figure 4: MIR reflectance spectra of Samples B (green), G (red) and EG (yellow).

Figure 5 shows the MIR spectra of Deccan B (green) compared to that of heated montmorillonite and nontronite samples. The bands at 8.75, 10.2, and 11.4 μm are similar to the heated montmorillonite spectrum, while the double band between 5 and 6 μm is similar to the heated nontronite spectrum.

To characterize the temperature at which the Deccan soils were heated, we heated our samples in 100°C increments starting at 300°C and systematically recorded their NIR and MIR spectra. We supposed that the palaeotemperature would correspond approximately to the last temperature before we observed a change in their spectral properties (decreased band depth, different continuum, etc. [9]). We found that the Deccan soils were heated to temperatures between 400 and 500°C.

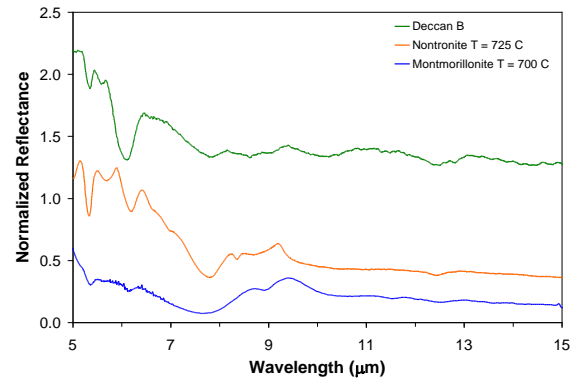


Figure 5: MIR reflectance spectra of Deccan samples compared to nontronite and montmorillonite samples heated to around 700°C.

Discussion and Conclusions:

Previous studies show that the red Deccan samples contained slightly higher concentrations of Fe^{3+} and Al^{3+} [10]. Our NIR spectra confirm the presence of Al but the absence of strong Fe^{3+} bands suggests the Fe^{3+} is in iron oxide phases which have no signature in the NIR region [9]. Iron oxides would also explain the samples' red color and are confirmed by XRD analysis showing hematite in the sample. Spectra of green and yellow samples, however, indicate the presence of $\text{Fe}^{2+}/\text{Fe}^{3+}$ -bearing smectites (e.g. celadonite and vermiculite).

The samples' reflectance spectra were compared to those of thermally altered nontronite and montmorillonite and similarities to both spectra were identified. The bands at 5.4, 5.6 and 12.6 μm in the MIR spectra of the green sample have been attributed to sillimanite and cristobalite, resulting from thermal alteration [9]. This confirms that the Deccan soils contain various unaltered and altered phyllosilicates, suggesting that they were altered by heating after their formation.

The Deccan Palaeosols are thus good analogs for heated phyllosilicates on Mars. By comparing the spectral properties of naturally heated phyllosilicates, like the Deccan palaeosols, to remote sensing observations of Mars our results will help distinguish between unaffected and thermally altered phyllosilicates. This will provide insights into the processes and timescales of the phyllosilicates formation on the martian surface.

References: [1] Poulet, F., et al., (2005) *Nature* 481, 623-627. [2] Bishop, J., et al., (2008) *Science* 321, 830-833. [3] Mustard, J., et al., (2007) *JGR* 112(E08S03). [4] Chevrier, V., et al., (2007) *Nature* 448, 60-63. [5] Fairen, A., et al., (2010) *PNAS* doi: 10.1073/pnas.1002889107. [6] Ghosh, P., et al., (2006) *Palaeogeography, Palaeoclimatology, Palaeoecology* 242, 90-109. [7] Wilkins, A., et al., (1994) Wiley Eastern Ltd, New Delhi, 217-232. [8] Bishop, J., et al., (2008) *Clay Minerals* 43, 35-54. [9] Gavin, P., and Chevrier, V., (2010) *Icarus*, 208, 721-734. [10] Widdowson, M., et al., (1997) *Geol. Soc. Spl. Pub.*, 120, 269-281.