Presence of beidellites on the Martian surface

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The aluminium rich dioctahedral smectite beidellite is an important indicator mineral for geothermal reservoirs because it is intermediate between the low-grade alteration mineral montmorillonite and higher temperature alteration minerals such as illite or chlorite (Guisseau et al., 2007). Beidellite has been recognised (e.g., Meunier et al., 2000) as an intermediary of the solid-state process of Al for Si substitution during montmorillonite conversion to illite during burial diagensis at temperatures ranging from 100-200 °C. Beidellite can also crystallise where hot (~110-200 °C), essentially Mg-free fluids enter a hydrothermal mineralisation zone, whereas montmorillonite crystallisation may occur with cool (generally <130 °C) surface water contacts (e.g., Yang *et al.*, 2001). Both could form within the same geothermal system, but separately, such that montmorillonite occurs where meteoric water infiltrates nearer the surface and beidellite occurs where hot fluids ascend from deeper geothermal reservoirs.

Analyses of hyperspectral NIR/SWIR orbital data collected by the Martian orbiter based CRISM show many features on the Martian surface that are distinguishable as montmorillonite, beidellite and other Al-rich phyllosilicates (Loizeau et al., 2007; Bishop et al., 2008; Ehlmann et al., 2009). The presence of both montmorillonite and beidellite on Mars indicates a different alteration environment than previously considered (Bishop et al., 2010).

Reflectance spectra were measured at RELAB on either "fluffy" or "compressed" particulates (intended to mimic different surface conditions of Mars) of 10 beidellite and montmorillonite samples (Fig. 1). Samples were sourced from CSIRO Land and Water and the CMS Source Clays Repository. Complete chemical and mineralogical analyses are reported in Bishop et al (2010). The OH combination bands near 2.2 µm are the focus of this study as they should prove useful in the identification of Al-rich phyllosilicates on the surface of Mars. Regardless of the texture, the combination band in spectra of montmorillonite near 2.21 µm (4525 cm^{-1}) shifts towards 2.18 µm (4590 cm^{-1}) in spectra of beidellite, i.e., with increasing total Al content, and specifically with increasing tetrahedral Al. This shift primarily results from the simultaneous loss of intensity of the 2.21 µm band and gain in intensity of the 2.18 µm band as the series evolves from montmorillonite to beidellite.

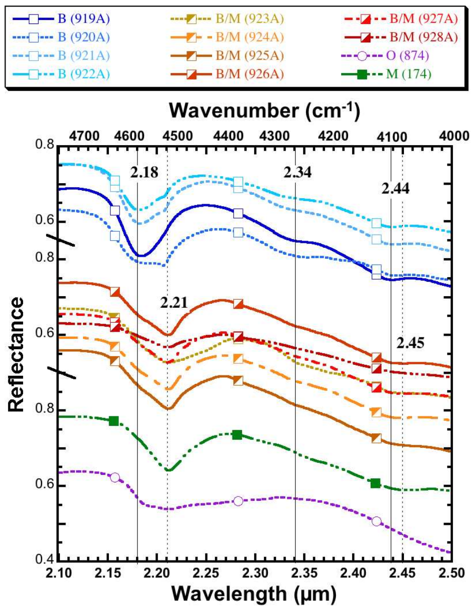

Fig. 1. Reflectance spectra of "fluffy" textured beidellites and beidellite-montmorillonites from 2.1-2.5 µm highlighting the region of OH combination bands. Montmorillonite and opal are shown for comparison and the spectra are offset for clarity. For beidellite the main OH combination band is centred at 2.18 µm (Band 1), while for montmorillonite and opal the main band is centred near 2.21 µm (Band 2). Most samples also have a band near 2.34 µm (Band 3), and 2.44-2.45 (Band 4).

Beidellites: B919 = Delamar; B920 = SBId-1; B921 = SBCa-1; B922 = 3rd Bench; Beidellite-montmorillonites: B/M923 = Cameron; B/M924 = Mt Binjour <0.2 µm; B/M925 = Binjour Plateau 4a <0.1 µm ; B/M926 = Binjour Plateau 4a 0.1-0.2 µm ; B/M 927 = Binjour Plateau 4a 0.2-0.5 µm ; B928 = Binjour Plateau 4a 0.5-2 µm; Montmorillonite: M174 = Jelsovy Potok; Opal: O874. Adapted from Bishop et al. (2010).

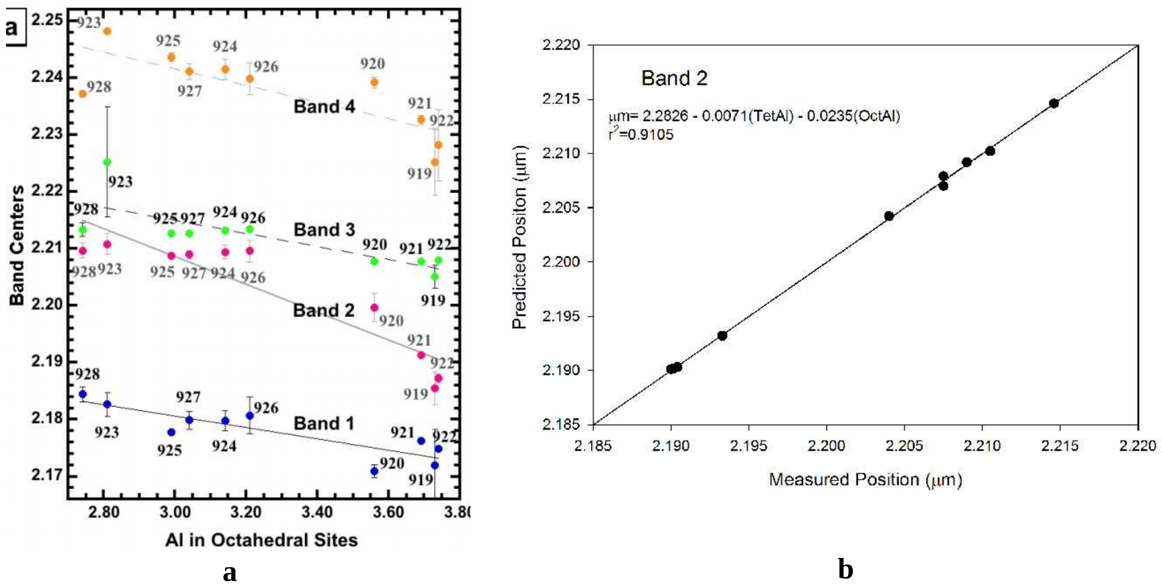

Fig. 2. (a) Effect of octahedral Al content on the positions of NIR Bands 1 – 4. Error bars are from Gaussian fitting of spectra. (b) Predicted values for the wavelength of NIR band 2 from nonlinear regression analyses of tetrahedral and octahedral Al content on the measured NIR positions. Adapted from Bishop et al. (2010).

The four NIR combination bands in the 2.18-2.5 µm region change position as a function of octahedral Al content (Fig. 2A). The greatest shift occurs in the position of band 2 (centred near 2.20-2.21 µm) with varying amounts of Al substitution for Si in the tetrahedral sites. Band 2 also has the greatest area of all four bands (Fig. 1) and increases with increasing tetrahedral Al substitution. The position of band 2 can be predicted with a high degree of accuracy from the structural chemistry (Fig. 2B), providing a sound chemical basis for identification of beidellites, and their differentiation from montmorillonites, in hyperspectral data from Mars.

The spectral differences between beidellites, beidellite-montmorillonites and montmorillonites enable differentiation of these Al-rich smectites in orbital data of Mars with a relatively high degree of confidence. A pure beidellite-type spectrum is observed in an isolated Al phyllosilicates-bearing outcrop in Libya Montes (Fig. 3). Al phyllosilicates are rare in the Libya Montes region, but Fe-rich smectite is common. This beidellite outcrop occurs as a single clay unit amongst basaltic rocks. In contrast, a variety of Al-phyllosilicates are found in the ancient rocks at Mawrth Vallis, including smaller regions having spectral signatures consistent with interstratified beidellite-montmorillonite smectites, as well as large outcrops of Al-phyllosilicates including montmorillonite, beidellite and kaolinite. The Libya Montes spectrum more closely resembles the lab spectra of beidellite, while the Mawrth Vallis spectrum is more consistent with the beidellite-montorillonite lab spectra. The Libya Montes spectrum (Fig. 3B) is a 3X3 pixel spot that was ratioed to a 'background' (spectrally unremarkable) region of the same size in image FRT0000B0CB (Fig. 3A, left). The Mawrth Vallis spectrum (Fig. 3B) is a 10X10 pixel spot from image HRL000043EC (Fig. 3A, right) also ratioed to a nearby background region.

Based on the lower-temperature formation conditions typical of montmorillonite and higher-temperature formation conditions typical of beidellite (e.g. Kloprogge, 2006), detections of these Al-smectites on Mars could act as geothermometers or alteration indicators.

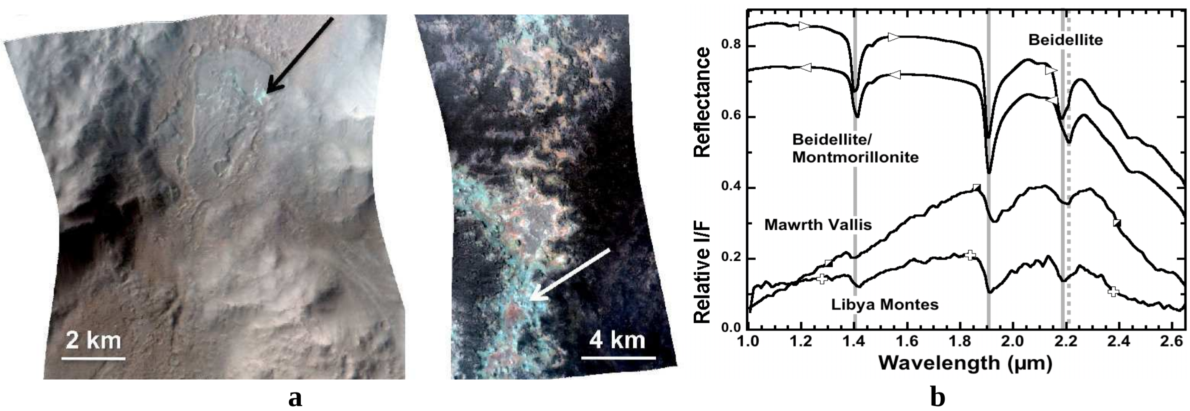

Fig. 3. (a) Evidence of outcrops of beidellite (arrows) in CRISM images (left) from Libya Montes and (right) from Mawrth Vallis. (b) Relative CRISM I/F spectra from 1-2.65 μm of beidellite outcrops in Libya Montes and Mawrth Vallis (lower two spectra) compared with lab reflectance spectra of beidellite (B921A) and a beidellitic montmorillonite (B927A). Adapted from Bishop et al. (2010).

References

Bishop JL, Noe Dobrea EZ, McKeown NK, Parente M, Ehlmann BL, Michalski JR, Milliken RE, Poulet F, Swayze GA, Mustard JF, Murchie SL & Bibring JP (2008) Phyllosilicate diversity and past aqueous activity revealed at Mawrth Vallis, Mars. *Science*, **321**, pp. 830-833.

Bishop JL, Gates WP, Makarewicz HD, McKeown NK, Hiroi T. (2010) Reflectance spectroscopy of beidellites and their importance for Mars. *Clays and Clay Minerals.* Submitted May 2010.

Ehlmann BL, Mustard JF, Swayze GA, Clark RN, Bishop JL, Poulet F, Marais DJD, Roach LH, Milliken RE, Wray JJ, Barnouin-Jha O & Murchie SL (2009) Identification of hydrated silicate minerals on Mars using MRO-CRISM: Geologic context near Nili Fossae and implications for aqueous alteration. *J. Geophys. Res.*, **114**,

Guisseau D, Mas PP, Beaufort D, Girard JP, Inoue A, Sanjuan B, Petit S, Lens A & Genter A (2007) Sigificance of the depth-related transition montmorillonite-beidellite in the Bouillante geothermal field (Guadeloupe, Lesser Antilles). *American Mineralogist*, **92**, 1800-1813

Kloprogge, J. T. (2006) Spectroscopic studies of synthetic and natural beidellites: A review *Applied Clay Science*, **31**, 165-179.

Loizeau D, Mangold N, Poulet F, Bibring JP, Gendrin A, Ansan V, Gomez C, Gondet B, Langevin Y, Masson P & Neukum G (2007) Phyllosilicates in the Mawrth Vallis region of Mars. *Journal of Geophysical Research*, **112**,

Meunier A, Lanson B & Beaufort D (2000) Vermiculitization of smectite interfaces and illite layer growth as a possible dual model for illite-smectite illitization in diagenetic environments: a synthesis *Clay Minerals*, **35**, 573-586

Yang K, Browne PL, Huntington JF & Walshe JL (2001) Characterising the hydrothermal alteration of the Broadlands-Ohaaki geothermal system, New Zealand, using short-wave infrared spectroscopy. *Journal of Volcanology and Geothermal Research*, **106**, 53-65

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