Octahedral chemistry of 2:1 clay minerals and hydroxyl band position in the near-infrared.

Application to Mars.

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Abstract

With the arrival of Curiosity on Mars, the MSL has started its ground validation of some of the phyllosilicate characterization carried out with remote sensing near-IR spectroscopy from orbital instruments. However, given the limited range of action of the rover, phyllosilicate identification and characterization will have to rely mainly on orbital near-IR data. Investigation of Earth analogues can greatly assist interpretation of Martian spectra and enable more robust analyses. In this contribution, Mg/Fe-rich clays from submarine hydrothermal origin that had been thoroughly characterized previously were investigated with near-IR reflectance spectroscopy. The clays are mixed-layer glauconite-nontronite, talc-nontronite, talc-saponite and nontronite samples. The hydroxyl bands in the range 2.1-2.35 μm were decomposed into their several individual components to investigate correlations between the octahedral chemistry of the samples and the normalized intensity of several bands. Good correlations were found for the samples of exclusive dioctahedral character (glauconite-nontronite and nontronite), whereas poor or no correlations emerged for the samples with one (talc-nontronite) or two (talc-saponite) trioctahedral layer components, indicating a more complex spectral response. Because these bands analyzed are a combination of the fundamental OH stretching and OH bending vibrations, the response of these fundamental bands to octahedral chemistry was considered. For 2:1 dioctahedral phyllosilicates, Fe and Mg substitution for Al displaces both fundamental bands to lower wavenumbers (longer wavelenghts), so that their effect on the position of the combination band is coherent. In contrast, for trioctahedral clays, Al and Fe$^{3+}$ substitution of octahedral Mg displaces the OH stretching band to lower wavenumber values, and the OH bending band to higher wavenumber values, resulting in partial or total mutual cancelation of their effects. As a result, clays with near-IR spectra indicating Mg-dominated octahedral compositions may in fact contain abundant Fe and some Al substitution. Thus, remote-sensing near-IR mineralogical and chemical identification of clays on Mars appears relatively straightforward for dioctahedral clay minerals but more problematic for trioctahedral clays, for which it may require a more detailed investigation of their near-IR spectra.

Keywords: Infrared observations; Mars; Mineralogy.
Introduction

Recent exploration of Mars using near-infrared (NIR) reflectance spectroscopy has produced one of the most important discoveries in Planetary Science, and one which is generating unabated interest (e.g., Bibring et al., 2006; Vaniman et al., 2014). Data from the MEx/OMEGA (Mars Express Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité) and MRO/CRISM (Mars Reconnaissance Orbiter Compact Reconnaissance Imaging Spectrometer for Mars) instruments have revealed thousands of exposures of phyllosilicate-rich rocks within the Martian crust (Poulet et al., 2005; Murchie et al., 2009; Ehlmann et al., 2011a; Carter et al., 2013). Data from the rover Curiosity have allowed the identification of clay in fluvio-lacustrine materials on the floor of Gale Crater (Vaniman et al., 2014; Bristow et al., 2015), and the rover Opportunity provided information that helped to characterize a clay-bearing suite at Endeavour Crater (Arvidson et al., 2014). Most of the deposits correspond to ancient (Noachian-age, 3.7-4.3 Ga), layered bedrock, most often exposed in impact craters (Ehlmann et al., 2011a; Carter et al., 2013). While geomorphic evidence has long suggested the presence of water on ancient Mars, at least during brief episodes (Carr, 1996), the unambiguous detection of phyllosilicates (Poulet et al., 2005) is the first clear evidence for sustained aqueous activity (Bibring et al., 2005). Furthermore, they seemingly date to the same period when life was forming or beginning to take hold on Earth. Considering that (1) phyllosilicates are among the best materials for preserving evidence of life (Walter & Des Marais, 1993) and (2) microbial activity on Earth promotes phyllosilicate formation (Douglas and Beveridge, 1998) and acts as a modifier of phyllosilicate composition (Cuadros et al., 2013a), Martian clays are very important astrobiological targets. Beyond the possible link to life, Martian clays are important because they provide information about hydrous processes that took place on Mars, such as the water chemistry, water-to-rock ratio, and temperature.

So far, the chemical and mineralogical characterization of Martian phyllosilicates has been mainly based on NIR spectroscopy. The three main features in NIR spectra used for this purpose are the absorption bands at ~1.4 and 2.18-2.35 μm, corresponding to hydroxyl vibrations, and at ~1.9 μm corresponding to molecular water vibrations. There are also vibrations of molecular water of lower intensity in the range 1.41-1.45 μm (Bishop et al., 1994). The hydroxyl bands (~1.4, 2.18-2.35 μm)
change their position depending (mainly) on the chemistry of the octahedral sheet within the phyllosilicate layers (e.g., Bishop et al., 2008). The existence of hydration water (band at ~1.9 μm) is frequently interpreted as indicative of smectite. Other features such as two wide crystal-field absorption bands in the 0.6-1.3 μm region indicate significant Fe content (e.g., Burns, 1993), an obvious band at ~2.4 μm is associated with large Fe and/or Mg content (Michalski et al, 2014) but not exclusively, and doublets or multiplets at the ~1.4 and 2.18-2.35 μm regions are indicative of kaolinite, talc or serpentines, depending on the specific position (Bishop et al., 2002b; Zhang et al., 2006). Saponite, halloysite and sepiolite also display or can display multiplets in these regions (Carter et al., 2013; Robertson and Milliken, 2014), typically less resolved and with less diagnostic value. Carter et al. (2013) have compiled the several clay minerals identified on Mars in the following order of frequency: Fe-Mg phyllosilicates (most of them interpreted as smectite) >> chlorite and corrensite > Al-smectite and Al-mica > kaolin (typically interpreted as kaolinite) > serpentines.

The identification and characterization of clay minerals on Mars at a global scale will continue relying heavily on NIR remote sensing, as the operation radius of present and future probes is limited. It is then necessary to progress in our ability to read the crystal-chemical character of Martian clays from their NIR spectra, work that can be carried out by careful characterization of Earth analogues and comparison with Martian counterparts. Such is the context of recent studies on kaolinite-smectite mixed-layer (Cuadros and Michalski, 2013), beidellite-montmorillonite series (Bishop et al., 2011), mixtures of Al-rich clays and rhyolitic glass (McKeown et al, 2011), and Fe/Mg-rich clays (Cuadros et al., 2013b). The present contribution uses this same strategy.

Crystal-chemical characteristics of a set of well-characterized Fe/Mg-rich clays of submarine hydrothermal origin (Cuadros et al., 2013b) are correlated with their NIR features in order to gain insights that allow a more accurate identification of Martian clays. Clays of Fe/Mg composition are of great relevance to Mars because they comprise by far the most abundant phyllosilicate detections from orbital observation (Carter et al., 2013).
Materials and methods

Cuadros et al. (2013b) describe in detail the investigated clays, their location of origin and their formation environment. They are from seafloor hydrothermal fields in the Atlantis II Deep (Red Sea), Guaymas Basin (Gulf of California), Grimsey Graben (Tjörnes Fracture Zone; off the Icelandic north coast), East Pacific Rise, and Mid-Atlantic Ridge. They comprise four groups, glauconite-nontronite (G-N) mixed-layer clays, nontronite, talc-nontronite (T-N) and talc-saponite (T-S). Two other samples of terrigenous origin were included for comparison. They are Nontronite 33B, a nontronite product of hydrothermal alteration of the Columbia River Basalt (Manito, Spokane County, Washington, USA), and Nontronite 51, which is in fact a mixture of nontronite (75%) and T-N (95% T, 5% N) from unknown origin and location. Chemical and Mössbauer analyses of these samples, their results and the transformation of the data into the structural formulas of the clays are described by Cuadros et al. (2013b). Here, the octahedral composition of the clays is reported (Table 1).

For the complete description of sample preparation refer to Cuadros et al. (2013b). Before the study described here, samples were ground manually in an agate mortar until a fine, homogeneous powder was obtained. These powders were analyzed using NIR spectroscopy in reflectance mode at RELAB (Reflectance Experiment Laboratory, Brown University, Rhode Island, USA). Two sets of conditions were used: analysis of the 0.33-2.54 μm range at a resolution of 0.01 μm, with an UV-VIS-NIR bidirectional spectrometer; and a more detailed analysis of the region 2.15-2.40 μm at a resolution of 2 cm⁻¹ with a Thermo Nexus 870 FTIR. The second, detailed analysis was not carried out for the specimens labelled POS (Tables 1 and 2) due to lack of sample. The samples were investigated as powder against pressed halon (0.33-2.54 μm) and a brushed gold reference (2.15-2.40 μm), in ambient air atmosphere. In these conditions all samples had their smectite layers hydrated. This is proven because there is a good positive correlation ($R^2 = 0.72$) between hydration water loss (thermogravimetry; water loss < 200 C) and proportion of smectite layers (XRD) in the samples (Cuadros et al., 2013b).
The spectra, consisting of reflectance versus wavelength values, were analyzed using the Grams/AI software package from Thermo Galactic. The bands in the range 2.15-2.40 μm, corresponding to one of the OH absorption bands, were investigated. First the curved background was transformed into a straight, continuum-removed baseline by fitting a quartic or quintic function to the continuum and subtracting it from the spectrum. The spectrum was then deconvolved by Fourier self-deconvolution to locate the position of the absorption maxima (appearing as minima in the reflectance spectra). This procedure decreases bandwidths and resolves overlapping bands.

For each sample, the Fourier self-deconvolution was performed repeatedly using different parameters and the selected result was based on two criteria, (1) the deconvolved spectra had a set of well-resolved maxima that were reproduced consistently in the several calculations and (2) artifact maxima (e.g., those generated on a flat area of the original spectrum) were absent. The number of bands resolved with this technique varied between 1 and 6 (see results section). Finally, the values of the band centers obtained from the deconvolution process were used to model the individual absorption bands by curve-fitting, using Gaussian curves, as suggested for wavelength space (Parente et al., 2011). After a first fit with the band center values from the deconvolution process, the parameters (band positions, widths and heights) were left free to vary. In some cases the position, height or width of one band had to be fixed to avoid producing results with no physical meaning. The fixed parameters were guided by the results from the deconvolution process and by fitting results from similar samples that were more straightforward to model. The areas of the individual bands were normalized to the sums of all areas of the components attributed to OH vibrations. We refer to these values hereafter as normalized bands or normalized intensities.

Some of the samples contained traces of carbonates (Cuadros et al., 2013b). Carbonates have one band in the range 2.30-2.35 μm that might interfere with our study. Carbonate bands were detectable by small peaks in the mid-IR at ~1400 cm⁻¹ and, in some cases, by small bands or shoulders at ~870 cm⁻¹ (analyses in the mid-IR in reflectance and transmission mode in support of the data presented in this contribution). However, the carbonate bands at 3.4 and 3.9 μm, of lower intensity than the above features, are not observable in any of the samples. The carbonate band at
~2.3 μm, is ~10 times less intense than those at 3.4 and 3.9 μm and thus we can conclude that there is no interference of carbonate vibrations in our study. Other samples contained traces of sulphates, which may produce bands in the region 2.2-2.3 μm. The possibility that these bands were present in our samples was assessed checking for sulphate bands at ~1200 cm⁻¹ in the mid-IR. Only one case showed a mid-IR sulphate band indicating the possibility that there is some sulphate interference. Finally, hydrated silica may have also caused interference in one sample in the range 2.2-2.3 μm, where opal has an intense and wide absorption band. These cases are discussed in the results section.

Results

The NIR spectra displayed variable band depth (i.e., band “height”: distance from baseline to peak), very low for some of them (Va3-382-389, Va3-150-153). There is no obvious reason for this difference. It may be due to the presence of pyrite, hematite or some other phases present in minor amounts (Cuadros et al., 2013b), or it may be caused by some physical characteristic of the clay particles in relation with their origin, such as particle roughness, shape or dimensions. The spectra showed clearly the OH band at ~2.3 μm, indicating their Fe/Mg-rich character, and the molecular water band at ~1.9 μm. However, the OH absorption band at ~1.4 μm had highly variable intensity and is frequently almost imperceptible. All the spectra displayed one or two wide crystal-field absorption bands of different shape and depth in the 0.6-1.3 μm region, indicating the presence of Fe. A composite band in the range 2.35-2.4 μm was present, associated (but not exclusively) with significant Fe and/or Mg content. For the spectra of samples containing talc, the ~2.3 μm band was a doublet, where the two bands were resolved to a variable extent. The proportion of smectite layers in T-N and T-S was one of the factors modifying the resolution of this doublet, generally more resolved in talc-rich samples (see Fig. 1, samples Va22-575-577 and Sea Cliff Dive, with 71% and 27% smectite, respectively). However, crystal-chemical factors of the talc are also an important control on the resolution of this doublet. For example, the specimen with the greatest proportion of talc is 1183-9, a T-S with 98% talc layers, but its doublet is poorly resolved (Fig. 2). This sample has a large octahedral Fe content (0.75 Fe³⁺ and 0.55 Fe²⁺ per O₁₀[OH]₁₂; Cuadros et
al 2013b) and poorly defined hkl XRD peaks, indicative of a crystal lattice with many structural
defects.

The decomposition of the peaks produced a variable number of underlying bands (Figure 2, Table 2). The most intense peaks were readily assigned from the known octahedral composition of the clays. Smaller peaks were more difficult to assign, and we do it here (Table 2) only tentatively. For these difficult assignments we balanced several arguments, such as band assignments in previous studies, octahedral cation abundance in the samples and an approximate progression of increasing wavelength of the $M_2OH$ and $M_3OH$ individual bands by substituting the following cations into the group $Al^{3+} < Fe^{3+} < Mg^{2+} < Fe^{2+}$. In addition, it is possible that the most intense peaks are generated by the overlap of two or more peaks representing different cation groups around the hydroxyls. The analysis below and in the discussion section suggests that the location of individual OH combination bands is controlled by more factors than simply the nature and number of cations surrounding individual OH groups. Unless stated otherwise in the results below, Fe in dioctahedral groups (two metal atoms next to an OH group) is $Fe^{3+}$, whereas Fe in trioctahedral groups (three metal atoms linked to an OH group) is $Fe^{2+}$.

In the G-N samples, there is an intense band at $\sim 2.29 \mu m$ that corresponds to $Fe_2OH$ vibrations and another at $2.31-2.32 \mu m$, generally of lower intensity, that can be assigned to $FeOHMg$ (Table 2). These assignments are in agreement with the octahedral composition of the samples (Table 1). It is more difficult to assign the band at $2.27-2.28 \mu m$ that appears in two samples and the low intensity bands at $\sim 2.36 \mu m$ (Table 2). One possibility is that the $2.27-2.28 \mu m$ band corresponds to $Fe_2OH$ in nontronite layers, as is typically observed (Bishop et al., 2002b), and the band at $\sim 2.29 \mu m$ is the same vibration in the glauconite layers. The obvious difficulty to this interpretation is that there is no correlation between the proportion of nontronite layers and the area of the bands at $2.27-2.28 \mu m$. These bands are probably related to more than one chemical factor. The small band at $\sim 2.36 \mu m$ can be assigned to $Fe^{2+}_3OH$ groups. Mössbauer analysis of three of the G-N samples did not display any $Fe^{2+}$ (Table 1) but it is possible that there is some because the absolute
uncertainty of the integrated areas of doublet peaks determined using Mössbauer spectroscopy was 3-5\% (Cuadros et al., 2013b; each doublet peak representing Fe^{2+} and Fe^{3+} in a specific chemical environment). The actual intensity of the possible Fe^{2+}OH band would not only depend on the amount of Fe^{2+} present but on the cation ordering in the octahedral sheet, especially if Fe^{2+} is in very low concentration. The assignment of the 2.27-2.28 and 2.36 \mu m bands is thus left unresolved.

In the nontronite group the assignments are in good agreement with the chemistry of the samples. Cy-82-14-5 and 1183-15 have Mg and no Al, and they display Fe_{2}OH (~2.28 \mu m) and FeMgOH (~2.30 \mu m) bands. Cy-82-14-5 also displays a band at 2.329 \mu m possibly due to Mg_{2}OH or Mg_{2}FeOH. Nontronite 33B has low Al and Mg abundances and there are two small bands that can be assigned to Al_{2}OH (2.204 \mu m) and AlFeOH (2.239 \mu m). Alternatively, the latter, may correspond to AlMgOH vibrations.

In the T-N group the main band is in the range 2.280-2.295 \mu m and assigned, in principle, to Fe^{3+}OH, although the range is sufficiently wide to allow further discrimination. There are possible FeMgOH, Mg_{2}FeOH and Mg_{3}OH bands of low intensity in only three of the samples (Table 2) and thus, the significant amount of octahedral Mg in the T-N samples is not accounted for in the band assignment. From their previous study, Cuadros et al. (2013b) concluded that the talc layers in the T-N specimens from submarine hydrothermal sites had nontronite domains, i.e., there is an excess of Fe^{3+} in the talc octahedral sheets. Even in this situation, the scarcity of FeMgOH and Mg_{2}OH vibrations is difficult to explain. Possibly, the main band at 2.280-2.295 \mu m contains FeMgOH vibrations. Finally, Nontronite 51 has bands that could correspond to Al_{2}OH and AlFeOH groups, with the difficulty that no Al was assigned to the octahedral sheet of this sample (Table 1). This discrepancy may be explained by the interference of hydrated silica, as ~9\% silica was identified in this sample (Cuadros et al., 2013b). Opal has a wide NIR band in the range 2.2-2.3 \mu m, modulated to a variable extent into two maxima (McKewon et al., 2011; Ehlmann et al., 2011b), that might be the cause of the low intensity bands at 2.203 and 2.243 \mu m in Nontronite 51 (Table 2).
The T-S group displays the talc Mg$_3$OH doublet at ~2.29 and ~2.31 $\mu$m. Other possible bands are Fe$_2$OH at 2.264-2.283 $\mu$m, where the valence of the Fe atoms is left unspecified. Other small bands can be assigned to AlMgOH and AlFeOH groups, with the difficulty that no or very little Al was assigned to the octahedral sheet of these samples. In one case, Va3-382-389, the band at 2.195 $\mu$m, tentatively assigned to AlMg, could originate from sulphate trace (mirabilite, Na$_2$SO$_4$·10H$_2$O, was identified by Cuadros et al., 2013b). There are also two small bands at 2.352 $\mu$m that could correspond to either Mg$_3$OH or Fe$^{2+}$OH groups (Table 2). If corresponding to Mg$_3$OH, they could be vibrations in saponite layers, rather than in talc layers.

**Discussion**

The above assignments show that the main features of the NIR spectra are consistent with the mineralogy and chemistry of the samples, but there are small bands that cannot be easily reconciled with them. The reasons for this discrepancy can be multiple. First of all, there are some cases of uncertainty due to contamination. Then, clay minerals have a certain degree of chemical heterogeneity between particles. This is true even of single-phase clay minerals. The structural formula is an average composition of all particles. This means that the real clay contains grains or chemical domains with small departures from the average octahedral composition in the structural formula. If the phyllosilicate is a mixed-layer phase, the differences between the average structural formula and the real crystal-chemical domains can become more important, because the octahedral cations are not homogeneously distributed between the different types of layers. Another factor is cation ordering (cation segregation or dispersion, preferred cation pairs or triads), which modifies the relative proportions of metal-OH groups and can considerably affect the relative intensity of the corresponding infrared bands. Still one more factor is the crystal-chemical environment in the octahedral and tetrahedral sheet around the specific cations-OH groups, which can displace the position of the bands. Bishop et al. (2011) provide an example of the effect of the composition of the tetrahedral sheet. Beyond the above, severe differences of hydration state can also modify OH band positions and intensity (Xu et al., 2000). However, modifications generated...
beyond the immediate atoms surrounding OH groups are complex, not always consistent and frequently very small (Bishop et al., 2011; Xu et al., 2000). As indicated above, our study was carried out in approximately constant hydration conditions in which smectite layers were hydrated, thus ruling out effects from very contrasting hydration states. Considering all of the above, it is reasonable to attain a first approximation without including less important variables. Given the complexity of the results, the strategy followed here to further investigate connections between the chemistry and NIR spectra of the studied clays was to look for meaningful correlations that can direct the interpretation of the calculated bands.

The most important factor determining OH band positions is the nature of the cations immediately surrounding OH groups, and thus the analysis was focused on them. Several correlations between normalized NIR band areas and relative proportions of octahedral cations were attempted (Figures 3 and 4). First of all, the bands in the spectra were divided into two groups, those from dioctahedral and those from trioctahedral environments. As, typically, trioctahedral clays (i.e., with large Mg + Fe$^{2+}$ content) have the maximum absorption of the investigated band at 2.3 μm or higher wavelength and dioctahedral clays (major Al and Fe$^{3+}$) below this value, a regression of the normalized area above and below 2.3 μm versus the ratio (Al+Fe$^{3+}$/Al+Fe$^{3+}$+Mg+Fe$^{2+}$) should produce a meaningful correlation. Such is the case for the dioctahedral clays, G-N and nontronites (Figure 3, top row). The G-N and nontronite samples were plotted both separately and together to test whether they would follow a similar trend (Figure 3, top row). They can be considered to fall within the same trend, although the correlation values are lower in the combined plot than in the independent plots. Interestingly, the submarine nontronites appear to be marginally closer to the trend of the G-N samples than Nontronite 33B, which might be due to the greater Mg content of G-N and submarine nontronite specimens (Nontronite 33B is of terrestrial origin). The nontronites are slightly off the trend of the G-N samples probably because the former do not have Fe$^{2+}$, as the latter do. For the samples with one or two trioctahedral layer components, T-N and T-S, the correlations are not meaningful (Figure 4, top row).
Secondly, a simplified approach was followed, focused on the main cations only, Fe and Mg. The normalized intensity of the \((\text{Fe}^{3+})_2\text{OH}\) band versus the ratio \((\text{Fe}^{3+} / \text{Mg})\) produces a good correlation for G-N and nontronite samples (Figure 3, middle row). Because in this analysis Fe\(^{2+}\) is not considered, the G-N and nontronite specimens come closer into the same trend (Figure 3, panel G-N, Nont). The T-N samples show a meaningful correlation with this approach, although this correlation arises mainly from the one data point in the bottom, left corner (Figure 4, T-N in the middle row). The T-S samples do not produce a meaningful correlation (Figure 4, middle row, right).

Finally, the complementary approach was followed, plotting the normalized area of the main Mg band (FeOHMg for the G-N, nontronite and T-N groups; the two talc Mg\(_3\)OH bands for the T-S group; all versus Mg / Mg+Fe\(^{3+}\); Table 2). Again, the dioctahedral samples develop meaningful correlations (Figure 3, bottom row) but T-N and T-S samples do not (Figure 4, bottom row). It can be argued that the analysis of T-S samples that do not use Fe\(^{2+}\), as in the two bottom T-S plots of Figure 4, is incorrect, because octahedral Fe\(^{2+}\) is as abundant as Fe\(^{3+}\) in these samples (Table 1). However, using Fe\(^{2+}\) did not improve results (Figure 4, top T-S plot). Overall, the best correlations for the dioctahedral samples are those considering Mg, rather than Fe. Based on these observations, it is probably a good strategy to use the cation with the second greatest octahedral concentration, rather than the most abundant, to investigate the contribution to IR absorption of the several bands. The reason is because there is greater probability for the second most abundant cation to generate one single band, which decreases the error in the band identification and quantification. The most abundant cation has a greater probability to contribute to several bands, resulting in larger uncertainty in the identification and calculations.

From the above analysis, it appears that Fe/Mg-rich clays of a dioctahedral nature generate NIR bands in the 2.1-2.35 \(\mu\)m region that can be correlated well with their octahedral chemistry, although details regarding the intensity and position of these bands may not match the octahedral composition. Reasons for these differences have been suggested above. Mixed-layer clays with
one or two trioctahedral components, however, do not produce 2.1-2.35 μm NIR bands that can be correlated with their octahedral chemistry. Clays from the T-N group produce some trends that may be useful, but the T-S samples do not. The possible reason for this different behaviour between dioctahedral and trioctahedral clays is discussed below. A structural complication exists for the T-N samples indicated by Cuadros et al. (2013b), consisting in the fact that talc layers have nontronite domains within their octahedral sheet. This can cause irregularities in the distribution of the cations and the types of metal groups they produce around hydroxyls, because dioctahedral Fe-rich domains are present in trioctahedral Mg-rich sheets.

The nature of the two OH bands in the NIR spectrum at ~1.4 and 2.18-2.35 μm has been determined as corresponding to the first overtone of the fundamental OH stretching band and a combination of the OH stretching and bending bands, respectively (e.g., Bishop et al., 2002b), both in the mid-IR. This can be shown by compiling and averaging values of the center of OH stretching and bending bands for different cation groups, calculating the position of the corresponding overtone and combination bands and comparing them with experimental values (Table 3). The first overtone of the OH stretching vibration does not appear exactly at twice the value of the fundamental band, but slightly below, due to the anharmonic character of the OH vibration. The approximate value of 1.96 was used here for the calculation of the first overtone, following Bishop et al., (2002b). The combination of bending and stretching vibrations is calculated as the sum of the wavenumbers of both vibrations. The agreement between the calculated and experimental values is very good (Table 3).

Thus, the position of the combination band at 2.1-2.35 μm in the NIR is controlled by the position of the OH stretching and bending bands in the mid-IR. For dioctahedral clays, substitution of Mg or Fe for Al displaces the position of OH bands, both stretching and bending, towards lower wavenumbers (Figure 5, Table 3). Thus the displacements of the stretching and bending bands are in the same direction and, when the wavenumber values are added, both contribute to modify the position of the combination NIR band in the same direction. In trioctahedral phyllosilicates,
however, the opposite is true. Substitution of Al or Fe$^{3+}$ for Mg in the octahedral sheet displaces the stretching and bending OH mid-IR bands in opposite directions (Figure 5, Table 3). As a result, the contribution of both vibrations to the combination band in the NIR displaces its position in the opposite direction, partially or totally cancelling each other. This is probably the reason why there is such a poor correlation between octahedral chemistry and the relative intensity of individual NIR components in the samples with trioctahedral layers.

**Implications**

The analysis performed here probably cannot be carried out on Martian orbital spectra because they may be too noisy to allow decomposition with sufficient detail. However, this analysis produces information of great interest for their interpretation. The normalized intensity of individual components of the NIR OH combination band of dioctahedral 2:1 phyllosilicates is correlated with the chemistry of the octahedral sheet to such an extent that it should allow a good prediction of the octahedral composition based on the overall band center, as shown by Michalski et al. (2014) for the samples studied here. The two fundamental vibrations combining to produce the NIR combination band, OH stretching and OH bending, both in the mid-IR region, have their position modified by the octahedral chemistry in a consistent and constructive way, resulting in a well-developed trend between chemistry and band location. This correlation should be exploited in the analysis of 2:1 dioctahedral phyllosilicates on Mars. Moreover, kaolinite, although a 1:1 clay mineral, could also be included in this type of analysis because (1) the position of its OH combination band falls within the same trend as that of the 2:1 dioctahedral clays, (2) some octahedral substitution is possible in kaolinite, and (3) kaolinite-smectite mixed-layer, which has octahedral sheets of intermediate composition, is also present on Mars (Cuadros and Michalski, 2013).

Alterations to the trend between octahedral chemistry and position of the OH combination band in the 2.18-2.35 μm range for dioctahedral phyllosilicates may arise due to different cation distributions. Random distribution, cation segregation, cation dispersion, existence of preferred pairs and of excluded pairs, all of them produce distributions of individual OH absorption bands.
with different relative intensities, which affects the position of the overall band. Octahedral cation
distribution is worth investigating on Mars because cation ordering is probably related to the
environment and mechanism of the phyllosilicate formation.

In trioctahedral 2:1 phyllosilicates, however, it is problematic to assess their octahedral
composition solely from the location of the OH combination band at ~2.3 μm because the two
corresponding fundamental bands are displaced in the opposite direction by the same octahedral
substitutions. The result is a null or inconsistent effect of such substitutions on the band position.
Thus, on Mars, spectra that are interpreted as saponite may in fact correspond to phyllosilicates
with significant Fe$^{3+}$ or Fe$^{2+}$ octahedral substitution (Figure 6), with or without mixed-layer phases.

Interestingly, the clay investigated by Curiosity at the floor of Gale Crater is an Fe-rich saponite
(Vaniman et al., 2014; Bristow et al., 2015). Based on our conclusions, it might be difficult to relate
NIR and chemical data for clays of this or similar crystal-chemistry. In order to avoid the uncertainty
generated by this situation, it is advisable to investigate also the first overtone of the stretching OH
vibration at ~1.4 μm. In this band, the position is only controlled by the displacements of one
fundamental vibration. Unfortunately, there are several problems with the analysis of this band. In
the first place, the 1.4 μm band has a reduced response to clay chemistry (total range of variation
of 0.023 μm in Table 3, as opposed to a 0.148 μm range for the OH combination band). In the
second place, this band has frequently low intensity, as observed in clays from Earth (Figure 1)
and Mars (Arvidson et al., 2014). The reasons for this low intensity are unclear so far, but may be
related to crystal-chemical order. Loss of hydration water alone, as suggested by Arvidson et al.
(2014), is not a possible reason because this band is generated by structural OH groups (the
molecular water component in the range 1.41-1.45 has a limited contribution as shown by Bishop
et al., 1994). However, if the above problems can be overcome, the 1.4 μm band can be a useful
tool to investigate the chemistry of trioctahedral clays. First, the general trioctahedral character of
the clay can be ascertained from the position of the combination OH band at ~2.3 μm. Second, one
can search for displacements of the 1.4 μm towards higher frequency (lower wavenumber, Figure
Further investigation of the crystal-chemical controls on the position and intensity of the 1.4 μm band will help characterization of Martian clays.

Acknowledgements

We thank J. Scholten, A. Kraetschell, J. Broda, J. Alt, P. Lonsdale, R. Hekinian, S. Petersen and M. Davydov for providing the studied samples, and T. Hiroi for measurement of the NIR spectra. The study was funded by the IEF Marie Curie program of the EC (Hydro-Mars project). Two anonymous referees are thanked for their comments that helped to improve this contribution.
References


Table 1. Octahedral composition of the studied samples (Cuadros et al., 2013b). The mineral phases and percent of smectite (Di- and Tri-sm are dioctahedral and trioctahedral smectite) are added for reference. G-N: glauconite-nontronite mixed-layer; N: nontronite; T-N: talc-nontronite mixed-layer; T-S: talc-saponite mixed-layer.

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<th>% Tri-sm</th>
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Table 2. Position, relative area (normalized to 1) and possible assignment of the components resulting from the curve fitting calculations of NIR spectra. The nature of the samples (type column) and % smectite layers are included for reference. In some cases two possible assignments are proposed. Question marks indicate tentative assignments or open questions.

<p>| Sample      | Type | % Sm | Pos | Area | Assign | Pos | Area | Assign | Pos | Area | Assign | Pos | Area | Assign | Pos | Area | Assign | Pos | Area | Assign | Pos | Area | Assign |
|-------------|------|------|-----|------|--------|-----|------|--------|-----|------|--------|-----|------|--------|-----|------|--------|-----|------|--------|-----|------|--------|-----|------|--------|
| Va22-1144-1145 | G-N  | 68   | 2.299 | 0.497 | Fe₂      | 2.312 | 0.429 | FeMg     | 2.361 | 0.073 | Fe₃(+2) |
| Va22-612-614   | G-N  | 59   | 2.295 | 0.804 | Fe₂      | 2.318 | 0.105 | FeMg     | 2.358 | 0.090 | Fe₃(+2) |
| Va22-588-591   | G-N  | 56   | 2.295 | 0.792 | Fe₂      | 2.318 | 0.111 | FeMg     | 2.359 | 0.097 | Fe₃(+2) |
| Va22-603-604   | G-N  | 50   | 2.295 | 0.777 | Fe₂      | 2.318 | 0.108 | FeMg     | 2.362 | 0.115 | Fe₃(+2) |
| Va22-1145-1146 | G-N  | 47   | 2.281 | 0.082 | Fe₂      | (sm?) | 2.297 | 0.426 | Fe₂      | (glc?) | 2.313 | 0.527 | FeMg | 2.364 | 0.047 | Fe₃(+2) |
| Va22-586-587   | G-N  | 39   | 2.294 | 0.826 | Fe₂      | 2.318 | 0.087 | FeMg     | 2.361 | 0.087 | Fe₃(+2) |
| Va22-639-640   | G-N  | 33   | 2.272 | 0.147 | Fe₂      | (sm?) | 2.295 | 0.530 | Fe₂      | (glc?) | 2.316 | 0.229 | FeMg | 2.356 | 0.094 | Fe₃(+2) |
| Va22-1030-1034 | G-N  | 23   | 2.298 | 0.595 | Fe₂      | 2.319 | 0.166 | FeMg     | 2.358 | 0.238 | Fe₃(+2) |
| 1183-15       | N    | 100  | 2.286 | 0.230 | Fe₂      (+3) | 2.304 | 0.770 | FeMg     |        |        |        |
| Cy-82-14-S    | N    | 100  | 2.283 | 0.151 | Fe₂      (+3) | 2.302 | 0.826 | FeMg     | 2.329 | 0.023 | Mg₃ / Mg₂Fe |
| Nontronite 33B | N    | 100  | 2.204 | 0.015 | Al₂      | 2.239 | 0.005 | AlFe     | 2.286 | 0.980 | Fe₂(+3) |
| Va3-150-153   | T-N  | 80   | 2.280 | 1.000 | Fe₂      (+3) |        |        |        |        |        |        |
| Nontronite 51 | T-N  | 76   | 2.203 | 0.008 | Al₂?     | 2.243 | 0.057 | AlFe?    | 2.287 | 0.849 | Fe₂(+3) |
| Va22-471-475  | T-N  | 75   | 2.295 | 0.949 | Fe₂      (+3) | 2.316 | 0.051 | FeMg / Mg₃ | 2.354 | 0.006 | Mg₃ / Fe₃(+2) |
| Va22-575-577  | T-N  | 71   | 2.292 | 1.000 | Fe₂      (+3) |        |        |        |        |        |        |
| Va22-583-586  | T-N  | 69   | 2.292 | 0.986 | Fe₂      (+3) | 2.324 | 0.014 | Mg₃ / Mg₂Fe |
| CHN-290-292   | T-N  | 68   | 2.292 | 1.000 | Fe₂      (+3) |        |        |        |        |        |        |</p>
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sm: smectite; glc: glauconite.
Table 3. Experimental and calculated values of the location of several OH bands in the mid- and near-infrared. The location of the fundamental stretching and bending bands are used to calculate those of the first stretching overtone and the bending plus stretching combination.

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<td>876&lt;sup&gt;f&lt;/sup&gt;</td>
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<td>MgFeOH</td>
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<td>2.700</td>
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<td>1.428</td>
<td>775&lt;sup&gt;f&lt;/sup&gt;</td>
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<td>2.815</td>
<td>6964</td>
<td>1.436</td>
<td>820&lt;sup&gt;f&lt;/sup&gt;</td>
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<td>2.714</td>
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<td>1.385</td>
<td>664&lt;sup&gt;l&lt;/sup&gt;</td>
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<td>737&lt;sup&gt;l&lt;/sup&gt;</td>
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<td>1.400</td>
<td>646&lt;sup&gt;l&lt;/sup&gt;</td>
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<td>1.409</td>
<td>646&lt;sup&gt;l&lt;/sup&gt;</td>
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<sup>a</sup> Wavenumber of stretching overtone = Wavenumber of stretching × 1.96.
<sup>b</sup> Wavenumber = wavenumber of stretching + wavenumber of bending.
<sup>c</sup> Averaged from values in Madejová et al. (1994) using the individual decomposed bands, and Bishop et al. (2002a) using the overall bands in Al-rich smectites.
<sup>d</sup> Averaged from values in Bishop et al. (2011).
<sup>e</sup> Range from Bishop et al. (2011).
<sup>f</sup> Averaged from values in Bishop et al. (2002a).
<sup>g</sup> Range from Bishop et al. (2002b).
<sup>h</sup> Averaged from values in Madejová et al. (1994; excluding AlMgOH-assigned band at 3684 cm<sup>-1</sup>), Fialips et al. (2002), Zviagina et al. (2004), Dainyak et al. (2006).
Averaged from values in Madejová et al. (1994), Fialips et al. (2002), Zviagina et al. (2004).

Averaged from values in Bishop et al. (2002a), Fialips et al. (2002).

Averaged from Bishop et al. (2002b) and Di Leo and Cuadros (2003) from saponite, and Petit et al. (2004) from talc.

Averaged saponite values from Kloprogge and Frost (2001), Grauby et al. (1994), Bishop et al. (2008).


Values for talc from Zhang et al. (2006).

Averaged from several values of talc and talc-saponite from Cuadros et al. (2008), Petit et al. (2004), Wilkins and Ito (1967).

From Petit et al. (2004).

Averaged from talc values in Petit et al. (2004), Wilkins and Ito (1967), and from smectite values in Neumann et al. (2011).

From Neumann et al. (2011).

From Petit et al. (2004).
Figures

Figure 1. Near-infrared spectra representative of the several groups of samples investigated. T-S: talc-saponite mixed-layer; T-N: talc-nontronite; N: nontronite; G-N: glauconite-nontronite.

Figure 2. Results of band decomposition for two of the samples. The band on the far right is not part of the OH system. The grey, smooth line is the overall modeled spectrum, which coincides exactly with some of the individual bands in some areas. T-S: talc-saponite mixed-layer.

Figure 3. Correlations between the normalized intensities of individual decomposed NIR bands and octahedral cation ratios. The top row uses all bands and all cations. The other two rows focus the analysis on the main bands and most abundant cations. Nontronite (N) and glauconite-nontronite (G-N) bands are plotted together in the right-hand side panels. The dash lines are for regressions including Nontronite 33B, a non-marine specimen. The solid lines include only the marine samples.

Figure 4. Correlations between the normalized intensities of individual decomposed NIR bands and octahedral cation ratios. As in Figure 3, the top row uses all bands and all cations; whereas the other two rows focus the analysis on the main bands and most abundant cations. Talc and saponite have a Mg$_3$OH component at $\sim$2.29 $\mu$m (Table 2), which was computed with the bands above 2.30 $\mu$m. T-N: talc-nontronite mixed-layer; T-S: talc-saponite.

Figure 5. Effect of cation substitution on OH band location. Sketch indicating how the increasing proportion of the several octahedral cations modifies the position of the OH stretching (left) and bending vibrations (right) in dioctahedral and trioctahedral 2:1 clays. Arrows indicate the direction.
of change produced by each cation. The length of the arrows is an indication of the extent of the change. For dioctahedral phyllosilicates, the cations produce changes of the position of OH stretching and bending vibrations in the same direction. In trioctahedral clays Mg, Al and Fe(III) produce changes in the opposite direction in OH stretching and bending vibrations.

Figure 6. Comparison of the ~2.31 μm band of one of the saponites in the CRISM library and three of our samples, corresponding to T-S (talc-smectite) of variable smectite and octahedral Fe contents. LASA51 (or SapCa-1) has reported octahedral compositions in the ranges 2.61-2.87 Mg, 0.03-0.09 Fe, 0.00-0.15 Al per O₁₀(OH)₂ (Post, 1984; Malla and Komarneni, 1993); Sea Cliff Dive has 0.05 octahedral Fe(III) and 0.29 Fe(II); Logatchev-2 has 0.10 Fe(III); 1183-9 has 0.75 Fe(III) and 0.55 Fe(II). See Table 1 for complete octahedral compositions.
Wavenumber (cm\(^{-1}\))

Reflectance

Wavelength (\(\mu\text{m}\))

Figure 2
Figure 3

Graphs showing the relationship between the fraction of NIR area below 2.3 μm and the ratio of octahedral Fe to total Mg-Al for G-N and Nont samples. The R² values range from 0.63 to 0.95.

Graphs also show the relative area of the main Fe band and Mg band for G-N and Nont samples, with R² values ranging from 0.80 to 0.95.
Figure 4

- **T-N**
  - Fraction NIR area below 2.3 μm
    - $R^2 = 0.52$
  - Oct Fe$^{3+}$ + Al / Oct Fe$_{tot}$ + Mg + Al

- **T-S**
  - Fraction NIR area below 2.3 μm
    - $R^2 = 0.06$
  - Oct Fe$^{3+}$ + Al / Oct Fe$_{tot}$ + Mg + Al

- **T-N**
  - Relative area of main Fe band
    - $R^2 = 0.70$
  - Oct Fe$^{3+}$ / Oct Fe$^{3+}$ + Mg

- **T-S**
  - Relative area of main Fe band
    - $R^2 = 0.04$
  - Oct Fe$^{3+}$ / Oct Fe$^{3+}$ + Mg

- **T-N**
  - Relative area of main Mg band(s)
    - $R^2 = 0.43$
  - Oct Mg / Oct Fe$^{3+}$ + Mg

- **T-S**
  - Relative area of main Mg band(s)
    - $R^2 = 0.04$
  - Oct Mg / Oct Fe$^{3+}$ + Mg
Fig. 5
FIGURE 6

- CRISM library saponite (LASA51)
- T-S (27% S)
  - Sea Cliff Dive
  - 0.34 OCT Fe
- T-S (11% S)
  - Logatchev
  - 0.10 OCT Fe
- T-S (2% S)
  - 1183-9
  - 1.3 OCT Fe