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Constraints on the crystal chemistry of Martian clays from infrared spectroscopy of analogue materials

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1. Abstract

In order to better constrain the mineralogy of Fe-rich clays detected remotely on the Martian surface, we have investigated the structure and geochemistry of a large suite of Fe-rich hydrothermal seafloor clays using a range of techniques, including infrared spectroscopy analogous to the measurements of clays made at Mars by spacecraft. The wavelengths of key spectral absorptions of clays, including the most diagnostic absorption region in Martian data at λ=2.17-2.42 µm varies according to crystal chemical trends and as a function of mixed layering. Here we show how substitution of Mg into Fe-rich clays and Fe into Mg-rich clays affects the spectral character of those materials. We also show that mixed layering is common in our suite of Fe-rich clay samples, and suggest that it may be a common occurrence on Mars.

1. Introduction

Clay minerals detected spectroscopically on Mars hold clues to the planet's geologic history and habitability [1-3]. A large fraction of the clays detected on the Martian surface by infrared techniques have been characterized as Fe/Mg-rich smectites [4-5]. In order to progress beyond this general characterization it is critical to determine precisely how crystal chemical substitutions affect the infrared character of smectitic clays. With this goal in mind, we present the results of an investigation of the mineralogy of Fe-rich clays collected from cores of hydrothermal seafloor sediments in various basins throughout the world.

2. Methods

Thirty-five samples of hydrothermal, Fe-rich clays were well characterized by XRD, Mossbauer spectroscopy, infrared transmission and reflectance spectroscopy, wet chemical analysis, electron microscopy, thermal gravimetry (TG), evolved gas analysis (EGA), and stable isotope geochemistry [6]. Clay formulas were calculated using chemical data corrected for the presence of trace contaminants and Mossbauer results as a guide to FeII and FeIII assignments.

Visible-near infrared reflectance (VNIR) spectra were collected at the KECK/NASA Reflectance Laboratory (RELAB) under both ambient and H_2O-purged conditions. Initially, spectra of each 40-200 mg-sample were collected from 100-12,500 cm^{-1} (0.8-100 µm) at 2 cm^{-1} spectral resolution after stabilizing in H_2O-purged conditions overnight (>12h). To achieve higher spectral resolution of the FeMg-OH spectral absorption located near λ=2.27-2.32 µm, high-resolution (1 nm sampling) data were collected from 2.15-2.4 µm. The precise location of this absorption was identified in continuum-removed spectra of each clay sample and the placement of the feature was compared with various chemical properties of the clays.

3. Results and Implications

The Fe-rich clay samples exhibit spectral absorptions at 1.91 µm attributable to interlayer water, at 2.28-2.32 µm attributable to metal-OH absorptions in the octahedral sheets, and 2.4-2.6 µm attributed to vibrations among metal-OH in the octahedral sheets and bonds between octahedral and tetrahedral sheets [7] (Figure 1). Some of the clays exhibit electronic absorptions centered near 0.6-2 µm related to presence of abundant Fe(III) and Fe(II). Absorptions related to O-H vibrations located near 1.4 µm are present only in samples that appear to be well-ordered based on XRD analysis.

In this abstract, we focus primarily on the nature of the metal-OH absorptions present at 2.28-2.32 µm because these absorptions are the most diagnostic for Martian clays in data returned from the *Observatoire pour l'Eau, les Glaces, la Minéralogie, et l'Activité* (OMEGA) and the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM). One hypothesis is that the position of this band shifts linearly from 2.28 μm in the case of pure nontronite (i.e. Fe-rich) to 2.32 in the case of pure saponite (i.e. Mg-rich) as a function of Fe/Mg ratio in the octahedral sheets of a single phase. Yet, in nature, it appears that true intermediate compositions are uncommon [8,9] unless mixed-layer clays are present [10]. Nearly all of our clay samples show evidence in XRD data for mixed layering [6]. These primarily include interstratification of talc and smectite, and glauconite and smectite; these typically occur as mixed-layers between either two dioctahedral clays or between two trioctahedral clays, but mixed layering between dioctahedral and trioctahedral clays can also occur [6,10].

Figure 2 shows how the metal-OH band shifts in wavelength as a function of composition in the Fe-Mg system. Position "A" marks the location of Al-rich nontronite, which absorbs at the shortest wavelength in this system. Between positions "B" and "C," smectitic clays absorb at an intermediate wavelength and can contain significant amounts of Mg, but in this case, the substitution of Mg occurs because of the presence of talc layers interstratified with the nontronite (dioctahedral-trioctahedral mixed layer clays), rather than the presence of Mg in the nontronite itself. Position "D" marks the location of very Fe-rich nontronites and generally, nontronite that is interstratified with Fe-rich mica (i.e. glauconitic clay). Note that essentially no smectitic clays exhibit absorptions between 2.305 and 2.31 μm. Beginning at 2.31 μm (position "E"), absorptions are due to the presence of abundant talc. These absorptions shift to longer wavelengths, toward position "F" due to the presence of mixed layering with saponitic clay.

4. Conclusions

Fe/Mg-rich smectitic clays on Mars exhibit spectral absorptions in the range of 2.28-2.32 μm that are likely related to the presence of both crystal-chemical substitution in the smectite sheets and the presence of mixed layering. Refinement of these relationships will allow for more detailed interpretation of the mineralogy.

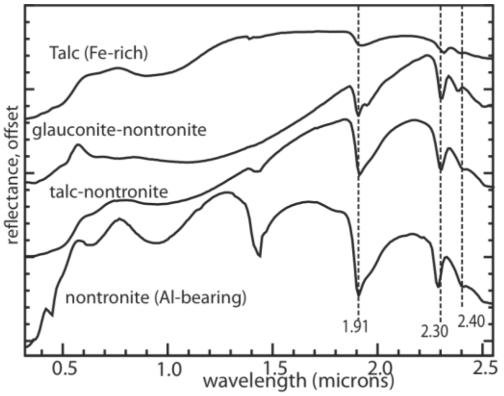

Figure 1: VNIR reflectance spectra of representative samples including talc, nontronite, and mixed-layer smectitic clays.

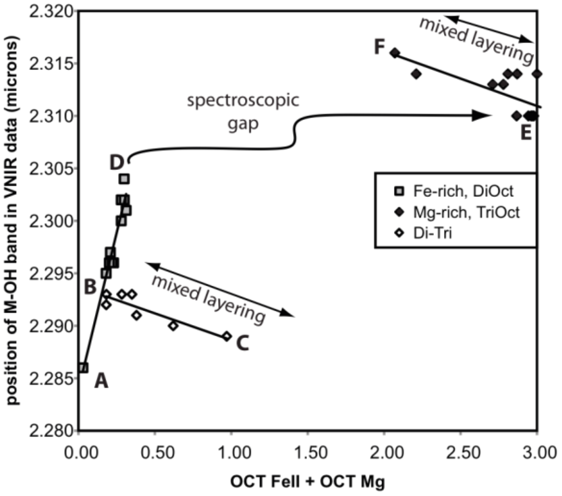

Figure 2: The relationship of metal-OH absorptions to octahedral sheet chemistry.

References

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