



Research paper

Identification of iron in Earth analogues of Martian phyllosilicates using visible reflectance spectroscopy: Spectral derivatives and color parameters

Manuel Sánchez-Marañón^{a,*}, Javier Cuadros^b, Joseph R. Michalski^c, Manuel Melgosa^d, Vesselin Dekov^e

^a Department of Soil Science and Chemical Agriculture, University of Granada, 18071 Granada, Spain

^b Department of Earth Sciences, Natural History Museum, Cromwell Road, London SW7 5BD, UK

^c Department of Earth Sciences & Laboratory for Space Research, The University of Hong Kong, Hong Kong, China

^d Department of Optics, University of Granada, 18071 Granada, Spain

^e Department of Marine Resources and Energy, Tokyo University of Marine Science and Technology, 4-5-7 Konan, Minato-ku, Tokyo 108-8477, Japan

ARTICLE INFO

Keywords:

Color
Fe content
Mars
Phyllosilicates
Visible spectral range

ABSTRACT

A range of phyllosilicate compositions have been detected spectroscopically on Mars, but the largest fraction by far corresponds to clay minerals rich in Fe and Mg. Given that most of our understanding of Martian clays comes from remote sensing data, it is critically important to explore the details of how compositional variation affects spectral features of phyllosilicates. The greatest efforts have focused so far on near-infrared (NIR) spectroscopy. Recently, ambiguities have been detected in the NIR spectra of 2:1 phyllosilicates with intermediate Fe–Mg content that preclude mineral and chemical discrimination. Such ambiguities highlight the relevance of exploring the visible spectral range as a complementary tool to characterize Martian phyllosilicates precisely. This article reports the investigation of laboratory reflectance spectra (330–800 nm) from 34 Earth analogues of Martian phyllosilicates with a wide range of Mg–Fe composition, including nontronite, celadonite and saponite end-members, as well as interstratified glauconite-nontronite, talc-nontronite, and talc-saponite. The spectra indicated the presence of Fe(III) by absorption modulations and a decrease in total reflectance, especially in samples with tetrahedral Fe(III). Absorption bands at 370 and 420 nm were diagnostic of octahedrally and tetrahedrally coordinated Fe(III), respectively. Band amplitudes in the second derivative of the Kubelka-Munk function correlated positively with Fe(III) content ($R^2 > 0.8$). Standard color analyses of the visible reflectance spectra under the CIE illuminant D65 indicated that the CIELAB color parameter a^*_{10} was positively correlated with tetrahedral Fe(III), b^*_{10} was positively correlated with octahedral Fe(III), and L^*_{10} was negatively correlated with Fe(III) in both structural sites. Because Fe(II) was in relatively low amount, it did not provide clear spectral evidence. Multiple regression models using the amplitude of the diagnostic absorption bands predicted well absolute Fe content in the phyllosilicates ($R^2 = 0.89$) and the ratio Fe/(Fe + Mg + Al) ($R^2 = 0.84$). CIELAB color parameters improved the prediction of total Fe ($R^2 = 0.92$) and the ratio Fe/(Fe + Mg + Al) ($R^2 = 0.93$). Application of these analyses to Martian data has challenges set by Fe oxide dust coating and spatial and spectral resolution. However, these results mark an avenue to develop testable tools using visible-wavelength spectral data from both satellite and lander probes to help establishing Fe content and mineral identification of Martian phyllosilicates.

1. Introduction

Clay minerals formed by alteration of mafic rocks have variable amounts of Fe whose determination is important for their mineralogical and chemical characterization. Reflectance spectroscopy is a technique increasingly used because it allows remote-sensing identification and characterization of mineral deposits both on Earth and in planetary

bodies, including ferromagnesian phyllosilicates (Blewett et al., 1995; Moroz et al., 2000; Fan et al., 2012; Carter et al., 2013; Schäfer et al., 2016). Particularly, the near-infrared range (NIR) has been used with tremendous success in Mars exploration, where abundant phyllosilicate deposits have been identified. Very succinctly, phyllosilicates are identified and characterized with NIR spectroscopy using mainly the following absorption bands: one at 1.9 μm , indicating the existence of

* Corresponding author.

E-mail address: msm@ugr.es (M. Sánchez-Marañón).

<https://doi.org/10.1016/j.clay.2018.08.016>

Received 19 May 2018; Received in revised form 16 August 2018; Accepted 20 August 2018

Available online 05 September 2018

0169-1317/ Crown Copyright © 2018 Published by Elsevier B.V. All rights reserved.

hydration water (a typical feature of fine-grained phyllosilicates), and bands of variable position around 1.4 μm and between 2.18 and 2.35 μm , corresponding to hydroxyl vibrations that change frequency depending on the crystal-chemical environment of hydroxyl groups in the phyllosilicates (Bishop et al., 2008a). In addition, hydration water also contributes a component to the 1.4 μm band (Bishop et al., 1994). So far, remote-sensing identification of the Martian phyllosilicates is based mainly on the comparison between spectra of phyllosilicate end-members from libraries and Martian spectra. The shortcomings of such an approach are obvious, because it can be expected that Martian phyllosilicates will frequently have complex, intermediate compositions or appear in polyminerally mixtures. Efforts are being carried out to increase our ability to characterize Martian phyllosilicate phases with a wider or more complex range of chemical and structural features (Milliken et al., 2010; McKeown et al., 2011; Cuadros and Michalski, 2013).

In particular, correlations between the octahedral chemistry and the position and intensity of NIR hydroxyl bands have been carefully investigated in the Mg–Fe compositional range, including nontronite and interstratified glauconite-nontronite, talc-nontronite, and talc-saponite (Michalski et al., 2015; Cuadros et al., 2016). Authors concluded that substitution of both Fe(III) for Al and that of divalent cations for trivalent cations in dioctahedral phyllosilicates clearly displace the vibration of hydroxyl bands to longer wavelengths, but that no band modification accompanies Fe(III) substitution for Mg in trioctahedral clays, which means that Fe detection and phyllosilicate identification with NIR is unreliable in this latter case. Further, Fe–Mg phyllosilicates with a mixed dioctahedral and trioctahedral composition (talc-nontronite, saponite-nontronite) cannot be distinguished from nontronite. It is then desirable to develop complementary analyses that may help to discriminate chemistry and mineralogy where NIR cannot.

In the visible spectral region there are also diagnostic features of the presence of Fe in minerals, which have been explained using the crystal field theory (Burns, 1993). In particular, Sherman and Vergo (1988) provided detailed absorption band assignments of electronic transitions to assist interpretation of spectra from nontronites and other Fe-containing smectites. Their visible spectra were dominated by the crystal field transitions of Fe(III) in octahedral coordination sites such as the $2[{}^6A_{1g}] \rightarrow 2[{}^4T_{1g}]$ transition, that produces an absorption band near $22,000\text{ cm}^{-1}$ (455 nm), attributed to electron-pair excitation of magnetically coupled Fe(III). Other important octahedral Fe(III) transitions found by Sherman and Vergo (1988) were ${}^6A_{1g} \rightarrow {}^4T_{2g}$ and ${}^6A_{1g} \rightarrow {}^4E_g$, producing, respectively, bands at $15,500\text{ cm}^{-1}$ (645 nm) and $27,000\text{ cm}^{-1}$ (370 nm). In addition, an absorption band around $23,000\text{ cm}^{-1}$ (435 nm) was assigned to the ${}^6A_1 \rightarrow {}^4E, {}^4A_1$ single-electron transition of tetrahedrally coordinated Fe(III). In this case, the electronic transition is Laporte-allowed, which means a much greater absorption coefficient than for transitions of octahedrally coordinated Fe(III). One more band described by Sherman and Vergo (1988) was that at $14,000\text{--}15,000\text{ cm}^{-1}$ (666–714 nm) in a saponite and a montmorillonite, that they assigned to intervalence charge transfer $\text{Fe(II)} + \text{Fe(III)} \rightarrow \text{Fe(III)} + \text{Fe(II)}$. Intervalence charge transfer has also been described near $13,700\text{ cm}^{-1}$ (730 nm) in the spectrum of a reduced nontronite (Lear and Stucki, 1987). The high intensity of the 435 nm band of tetrahedrally coordinated Fe(III) is illustrated by the fact that the existence of such absorption band made a saponite dark brown rather than green, as expected for a mixed-valent saponite with Fe(II) and Fe(III) in octahedral coordination (Sherman and Vergo, 1988). Indeed, color in minerals is mainly controlled by absorptions in the visible wavelength range, although is also modified by other factors such as particle size and surface roughness (Burns, 1993; Sánchez-Marañón et al., 2004).

There is widespread use of the visible spectral range in the identification and quantification of Fe oxides, oxy-hydroxides, and hydroxysulfates by examining the shape of diffuse-reflectance spectra (Bishop and Murad, 1996), analyzing the position and intensity of the crystal

field bands (Sánchez-Marañón et al., 2015), and calculating color parameters (Scheinost and Schwertmann, 1999; Torrent and Barrón, 2002; Sellitto et al., 2009). The successful application of visible spectroscopy to Fe oxides and oxy-hydroxides, with structural similarities to phyllosilicates, suggests that the same approach is viable for the latter. Indeed, the absorption bands of octahedral Fe(III) in nontronite have similar wavelengths to those of the ferric oxides and oxy-hydroxides (Sherman and Waite, 1985; Scheinost et al., 1998). One may expect color to be a diagnostic and quantifiable feature of the amount and position of Fe(III) in phyllosilicates.

The reliability of visible spectroscopy and colorimetric methods to investigate Fe in phyllosilicates is finding confirmation. A plethora of research articles on the mineralogy of planetary materials and Earth analogs has addressed the interpretation of extended visible-region spectra (400–1,000 nm), although most of these were concerned with finding a set of spectral indices of chemical and mineralogical composition without colorimetric meaning (Morris et al., 2000; Farrand et al., 2008; Schäfer et al., 2016). Further to this, the chromophore effect of Fe structurally bound in clay minerals, which reduces their brightness (Musiel et al., 2008), is well-known, and a number of studies have proved the merit of colorimetry in identifying the presence of Fe in phyllosilicates with minor and trace contents. Quantitative analyses of the color of clays using a standard observer and a standard illuminant in the CIELAB color space (CIE, 2004), showed inverse correlations ($P < .001$) of the Fe content with L^*_{10} (lightness) and $h_{ab,10}$ (hue-angle), as well as positive correlations with a^*_{10} and b^*_{10} (chromatic coordinates) in talc (Soriano et al., 1998; Soriano et al., 2002) and kaolinite (Gámiz et al., 2005; Gámiz et al., 2011; Bouzidi et al., 2014).

The objective of the current study was to analyze the visible-region reflectance spectra of 2:1 phyllosilicates with a wide range of chemical composition and complex structural features, from nontronite and glauconite to talc and saponite, both end-member and interstratified phases, in order to evaluate their Fe content using crystal-field band positions and color parameters. The results of this study are of particular interest for investigation of phyllosilicates on Mars, as they may provide alternative and complementary evidence to remote-sensing NIR and chemical and mineralogical techniques in landers.

2. Samples and methods

Thirty four samples were investigated, consisting of the following end-member and interstratified phyllosilicates: nontronite, celadonite, saponite, glauconite-nontronite, talc-nontronite, and talc-saponite (Table 1). Four samples are of continental origin (Glauconite 97, Nontronite 33B, Nontronite 51, and CRB 03–026; hereinafter named continental samples), whereas the rest originated in submarine hydrothermal fields. Their specific origin, determination and discussion of their mineralogy, chemical composition, and crystal-chemical structure are in Cuadros et al. (2013). Their results are summarized in Table 1. The samples cover a range of Mg–Fe chemical composition in the mineral series talc/saponite (Mg-rich) to celadonite/nontronite/glauconite (Fe-rich). They were investigated as proxies for the Mg/Fe-rich smectitic phyllosilicates found on Mars (Michalski et al., 2015; Cuadros et al., 2016). Some of the samples contain two or more phyllosilicate phases, both end-members and interstratified phases (e.g., sample M64/1 139GTV-5E [Turtle pits] contains three talc-saponite phases and one saponite end-member). While all tetrahedral Fe (Fe tet in Table 1) is Fe(III), octahedral Fe can be Fe(III) and Fe(II).

The clay samples were ground manually in an agate mortar during 10 min until a fine, homogeneous powder was obtained. Approximately 100 mg of each sample were prepared as a loose powder in a 1-cm diameter sample cup under ambient air atmosphere. The spectral reflectance factor from each sample was recorded using a bi-directional spectrometer at Reflectance Experiment Laboratory (RELAB, Brown University, Rhode Island, U.S.A.) in the 330–2,540 nm range at a resolution of 10 nm. The bi-directional reflectance factor is defined as the

Download English Version:

<https://daneshyari.com/en/article/11007144>

Download Persian Version:

<https://daneshyari.com/article/11007144>

[Daneshyari.com](https://daneshyari.com)