

SPECTROSCOPIC LABORATORY EVIDENCE FOR IRON REDUCTION IN PHYLLOSILICATES UNDER LOW PRESSURE CONDITIONS. K.M. Robertson¹ and R.E. Milliken¹. Dept. of Geological Sciences, Brown University, Providence, RI, 02912. kevin_robertson@brown.edu

Introduction: Diagnostic spectral features associated with H₂O and M-OH vibrations in clays [1] have been measured with MRO-CRISM and MEx-OMEGA spectrometers on the surface of Mars [2,3]. Nontronite, saponite, and montmorillonite have been identified based on the position of specific M-OH vibrations occurring near 1.4 μm (stretching overtone) and in the region between 2.1 and 2.7 μm (stretching + bending). Sepiolite has not been identified on Mars, but its near-IR reflectance properties can be very similar to saponite. On Earth, it may be formed under saline and arid conditions or as a secondary alteration mineral in association with serpentine [4], thus it is possible sepiolite could be present on Mars.

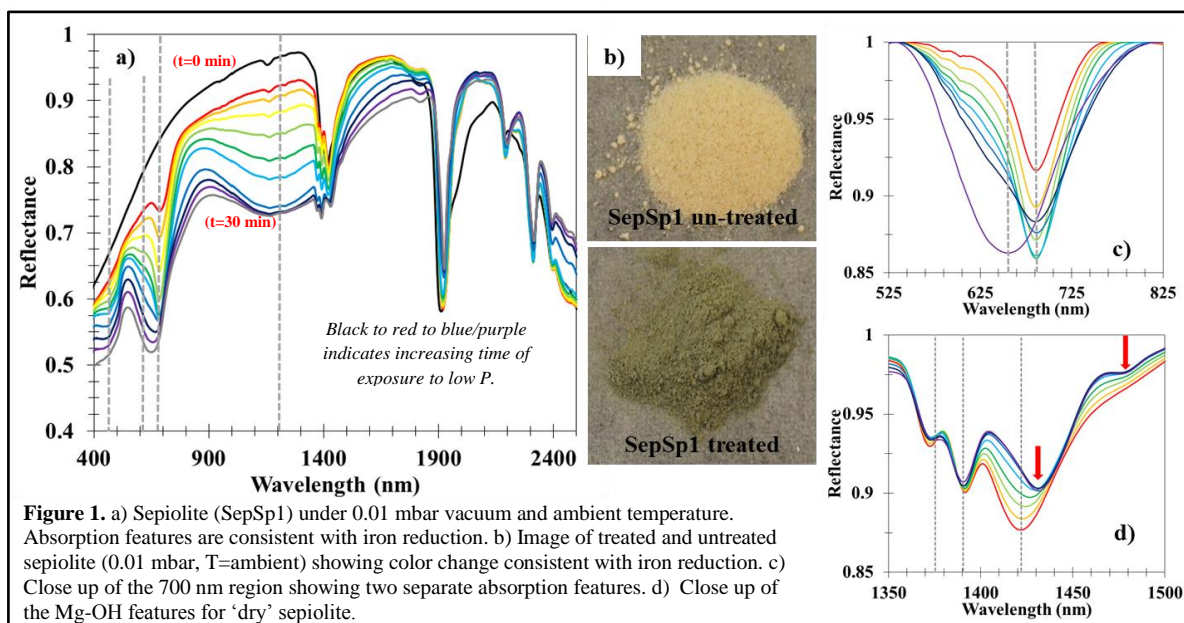
Iron gives rise to strong, broad features at VIS-NIR wavelengths and terrestrial Mg and Al-rich clays often contain trace amounts of iron, and the same is likely true for martian counterparts. Here we report on apparent iron reduction in sepiolite, nontronite, and montmorillonite under variable temperature (-80C – 300C) and pressure (0.01 – 1000 mbar) conditions using visible-near infrared reflectance spectroscopy and discuss its importance for Mars.

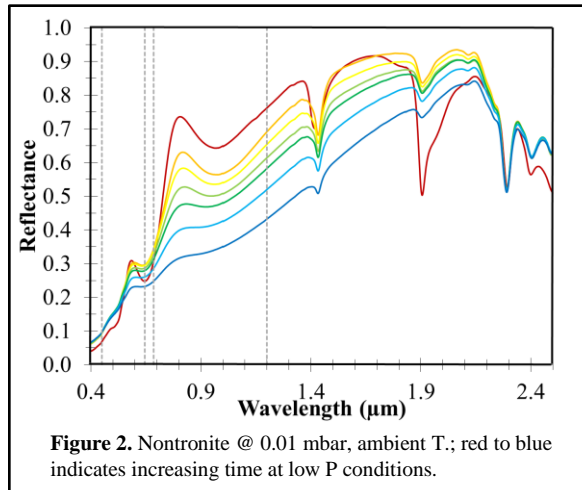
Methods: Sepiolite (SepSp-1), nontronite (NAu-2), Montmorillonite (SAz-2 and SWy-1) were obtained from the clay minerals society. Samples were analyzed with their native exchangeable cations and one aliquot of SWy-1 was exchanged with Fe³⁺ to increase the total iron content. All samples were ground and dry sieved to <45 μm .

VNIR reflectance spectra were measured with an Analytical Spectral Devices (ASD) FieldSpec3 spectrometer and a QTH light source. All

measurements were done *in-situ* using a Linkam THMV350 environmental stage. The chamber was pumped down to 10⁻³ mbar and backfilled with ambient laboratory air using a combination of isolation and bleeder valves connected to a pirani gauge. Temperature was controlled using a combination of a liquid nitrogen cooling system and a heating block to achieve a wide range of temperatures (-150°C – 600°C). Custom designed aluminum sample holders were used to hold a halon white reference and single clay sample under identical environmental conditions. Static experiments were run at 0.01 mbar, 10 mbar and 1000 mbar with temperatures ranging from -80°C to 300°C.

Results: Sepiolite (SepSp1) was used extensively in this study because the changes in spectral properties were easily recognizable relative to the other clays (Fig. 1), but all clays examined thus far reveal similar changes in spectral absorptions (though to different extents). Non-clay samples, including opal and jarosite, were also studied but exhibited no changes under the conditions explored here, indicating structural aspects of *clays* are important in driving the observed reactions. In sepiolite, Fe²⁺ - Fe³⁺ charge transfer (~700 nm) and Fe²⁺ and Fe³⁺ electronic transition (~450 nm and ~1200 nm) absorptions developed as the sample was exposed to low-P conditions; these features are similar to those reported in previous nontronite reduction experiments [5]. In the example presented here (0.01 mbar and ambient T) the reaction was completed in less than 30 minutes, which highlights the rapidity of the process. The reaction produces a distinct greenish-grey color in the sample (Fig. 1b) that is limited to the optical surface, similar to previous studies of iron reduction in



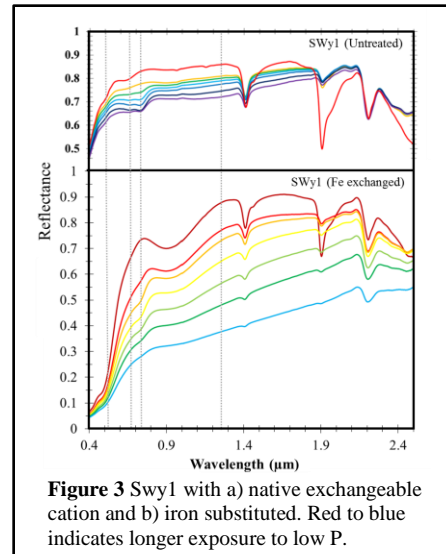


phyllosilicates [6].

A close-up of the ~700 nm feature (Fig. 1c) reveals that there are two distinct features near 685 nm and 645 nm with the latter appearing near the end of the experiment. A close-up of the ~1400 nm region (Fig. 1d) shows the appearance of a 1479 nm feature and a large shift in the 1422 nm feature to 1433 nm. Similar experiments at elevated T (75°C, 100°C, 150°C and 275°C) and low P (0.01mbar) did not significantly affect the time required for the experiment to go to completion whereas, low T experiments (e.g., -25°C and -50°C) slowed the reaction time by an order of magnitude. Increasing the pressure (1000mbar, 10 mbar) resulted in the reaction taking up to 8 days.

Nontronite was measured under ambient T at 0.01 mbar (Fig. 2), resulting in a low albedo positive slope in the VIS region in less than 30 minutes. These effects are similar to those of [7], but in that study nontronite was heated under nitrogen and atmospheric pressure with reaction times ranging from days to months. We suggest the low albedo positive slope observed in nontronite can be attributed to the reduction of Fe³⁺ in the octahedral layer in which Fe²⁺ - Fe³⁺ charge transfer (~700 nm) and Fe²⁺(VI) electronic transition (~1200 nm) bands combine with the broad pre-existing Fe³⁺ bands to produce the observed slope. Samples are also capable of rehydrating and the observed slope persists, suggesting interlayer collapse has not occurred.

The untreated SWy-1 (Fig. 3a) shows minor iron absorption features at expected wavelength ranges. SWy1 contains more Fe³⁺ than SepSp1 (3.3 vs. 1.22 wt% Fe₂O₃, respectively), but the absorption features produced during reduction are not as strong. The observed discrepancy could be related to their respective structures. It has been shown that iron reduction in clays can be a result of H⁺ production through the dissociation of H₂O in their interiors [8]. In smectites, H₂O is found in the interlayer region therefore H⁺ must diffuse through the tetrahedral layers in order to interact with iron in the octahedral layers [9]. In contrast, sepiolite is a hydrous 2:1 phyllosilicate where tetrahedral layers are inverted every three



‘pyroxene’ chains, resulting in a discontinuity in the octahedral sheet and a channel structure where H₂O can behave zeolitically and is directly exposed to octahedral sites [10]. This increased efficiency at H₂O-Fe³⁺ interaction may explain why the resulting octahedral Fe²⁺ (~1200 nm) absorption feature is more pronounced in the sepiolite than in the montmorillonite (SWy-1). Interestingly, the Fe³⁺ exchanged SWy-1 (Fig. 3b), produced results similar to the nontronite, suggesting the process is strongly linked to iron content and not solely to interlayer H₂O.

Conclusions: Results suggest Fe³⁺ in clays can be reduced by lowering P and that such changes are detectable at VIS-NIR wavelengths even when present in trace amounts. This process was shown to occur in three different clays with different structures, suggesting features are not related to interlayer collapse through dehydration. The driving reduction mechanism is still unclear, but one possibility is that interlayer/zeolitic H₂O is split when the samples are exposed to the light source (e.g., UV) under low pO₂ conditions, and resulting H⁺ or H₂ acts to reduce the iron. If so, then this process could occur at the optical surface of Mars. Such reduction and H₂ gas production has been well documented for clays exposed to gamma radiation [8]. These results may provide insight on the coloration and ferrous nature of clay-bearing rocks observed at Yellowknife Bay, which also host possible gas related diagenetic features [11].

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