Spectroscopic evidence for hydrous iron sulfate in the Martian soil

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[1] Despite in situ analyses by several landers, the composition of the Martian soil remains unclear. Recently, constituent minerals in the soil have been proposed from thermal emissivity and Mössbauer spectroscopic data from Mars. These data were interpreted to show spectral evidence for carbonate and an unspecified mineral containing bound water, as well as olivine. Here we present an alternative interpretation, suggesting that these spectral features can be satisfied by a single type of mineral, namely hydrous iron sulfates. Acidic waters necessary for production of hydrous iron sulfates would preclude carbonate formation and indicate a dramatically different chemical environment on Mars, in which olivine would be highly unstable and unlikely to survive soil formation, regardless of its presence in the rocks. Hydrous iron sulfates are efflorescent salts and may be rusting agents in the Martian soils.


1. Introduction

[2] Sulfates are likely to be present in the Martian soil as indicated by the sulfur measured at the Viking, Mars Pathfinder (MPF), and Mars Exploration Rover (MER) landing sites (~5–10 wt % SO 3 ) [Toulin et al., 1977; Foley et al., 2003; Squyres et al., 2004; Gellert et al., 2004] and the oxidizing conditions on Mars. Telescopic and orbital observations of Mars tentatively identified sulfate [e.g., Blaney and McCord, 1995; Pollack et al., 1990; Bandfield, 2002; Cooper and Mustard, 2002], possibly associated with bound water [e.g., Hauk et al., 1973; Murchie et al., 1993]. Two recent Mars missions provided additional evidence for sulfate on Mars. The Mars Express OMEGA team reported that kieserite (MgSO 4 ·H 2 O) was identified in Valles Marineris [Bibring et al., 2004] and the MER Mössbauer team identified jarosite (K 2 Fe 3+ (SO 4 ) 2 (OH) 6 ) within the bedrock exposed in Eagle crater at the Opportunity site in Meridiani Planum [Klingelhofer et al., 2004].

2. Laboratory Samples and Analytical Techniques

[3] Spectral analysis of Miniature Thermal Emission Spectrometer (Mini-TES) data from the MER Spirit in Gusev Crater suggested that the soil is composed of fine-grained silicate with additional constituents of an unspecified mineral containing bound water and a carbonate [Christensen et al., 2004]. The carbonate was inferred from two emissivity minima at ~1580 and 1390 cm −1 and the intervening convex upward shape (Figure 1a)–an overall spectral character that resembles a laboratory carbonate/silicate mixture [Bandfield et al., 2003]. The bound water mineralogy was inferred from the emissivity maximum at ~1630 cm −1 (Figure 1a). These interpretations were based on a similar spectrum and interpretation using orbital Mars Global Surveyor Thermal Emission Spectrometer (TES) data of medium-to-high-albedo soil (Figure 1a) [Bandfield et al., 2003]. Spectral similarity indicates that the Martian soil is globally mixed and broadly of similar composition.

[4] However, here we suggest that hydrous iron sulfates (HISs) exhibit a spectral shape that closely matches the TES and Mini-TES data over the 1200 to 1700 cm −1 range (Figure 1a) and could account for the carbonate and bound water features discussed above. We will show that the presence of HISs in the Martian soil is consistent with all wavelengths of spectroscopic data from Mars, including TES, Mini-TES, extended-visible (Imager for MPF (IMP) and MER Pancam), and MER Mössbauer spectra.
Figure 1. (a) Two Martian soil spectra compared to szomolnokite and ferricopiapite. Hatched area represents Mars’ atmospheric CO₂ band. Two vertical solid lines and one dashed line demarcate the carbonate and bound water features, respectively, reported by Bandfield et al. [2003] and Christensen et al. [2004]. (b) Emissivity spectra of <63-µm HIS subfractions. The well-defined doublet disappears (or is severely muted) in both spectra.

conditions. These data were spliced at 1.13 µm to off-axis biconical reflectance data (measured relative to gold) using a Nicolet FT-IR spectrometer under purged atmospheric conditions.

The XRD analyses (not shown) confirm the identities of the ferricopiapite and szomolnokite and show no evidence of impurities above the detection limits. VNIR spectroscopy is sensitive to carbonate due to overtones/combinations of the fundamental molecular vibrations [Gaffey et al., 1993]. Carbonate in these samples (that might cause the thermal IR spectral features in question) would produce features near 3.5 and 4 µm. These features were not observed, confirming the XRD results¹. Mössbauer measurements provide information regarding iron states. We found our ferricopiapite \( \sim(\text{Fe}^{3+},\text{Al},\text{Mg})\text{Fe}^{3+} \text{SO}_4\text{d(OH)}_2 \cdot 20 \text{H}_2\text{O} \) to contain exclusively ferric iron and our szomolnokite sample to be dominated by ferrous iron \( \sim\text{Fe}^{2+}_{0.9}\text{Fe}^{3+}_{0.1}\text{SO}_4 \cdot \text{H}_2\text{O} \).

3.2. Thermal IR

EMissivity spectra were obtained at Arizona State University using a modified Nicolet FT-IR spectrometer with a continuously scrubbed atmosphere. Spectra of the HIS hand samples at ~50°C were acquired over 160 scans at 2 cm⁻¹ sampling. The powders were maintained at 50°C with a sample-cup heater during 270 scans.

3. Results

3.1. Sample Purity

The XRD analyses (not shown) confirm the identities of the ferricopiapite and szomolnokite and show no evidence of impurities above the detection limits. VNIR spectroscopy is sensitive to carbonate due to overtones/combinations of the fundamental molecular vibrations [Gaffey et al., 1993]. Carbonate in these samples (that might cause the thermal IR spectral features in question) would produce features near 3.5 and 4 µm. These features were not observed, confirming the XRD results¹. Mössbauer measurements provide information regarding iron states. We found our ferricopiapite \( \sim(\text{Fe}^{3+},\text{Al},\text{Mg})\text{Fe}^{3+} \text{SO}_4\text{d(OH)}_2 \cdot 20 \text{H}_2\text{O} \) to contain exclusively ferric iron and our szomolnokite sample to be dominated by ferrous iron \( \sim\text{Fe}^{2+}_{0.9}\text{Fe}^{3+}_{0.1}\text{SO}_4 \cdot \text{H}_2\text{O} \).

3.3. VNIR

VNR spectra can discriminate between Fe²⁺ and Fe³⁺. Ferricopiapite exhibits a 0.5 to 0.7-µm ferric absorption edge and a strong Fe³⁺ absorption at ~0.87 µm, whereas the szomolnokite exhibits a strong absorption at ~0.94 µm, consistent with the dominance of Fe²⁺ (Figure 2a). Figure 2b shows spectra of the Martian soil measured by IMP (S. Murchie et al., New insights into the geology of the Mars Pathfinder landing site from spectral and morphologic analysis of the IMP 12-color super panorama, submitted to Icarus, 2003) and Pancam [Bell et al., 2003, 2004; Morris et al., 2004] and a mixture spectrum containing 10% szomolnokite, convolved to Pancam (and similar IMP) filters. The similar spectral shape of IMP and Pancam data suggests that the Martian soil is broadly homogeneous, in agreement with the thermal data. Figure 2b demonstrates that a mixture including an HIS component is consistent with the observed extended-visible Martian soil spectra.

3.4. Mössbauer

Mössbauer (MB) spectra of ferricopiapite and szomolnokite are shown in Figure 3, with the first MB soil spectrum acquired at Gusev [Klingelhöfer et al., 2004] and the HISs römerite (ideally \( \sim\text{Fe}^{2+}_{0.9}\text{Fe}^{3+}_{0.1}\text{SO}_4 \cdot 14\text{H}_2\text{O} \); our results show \( \sim\text{Fe}^{2+}_{0.4}\text{Fe}^{3+}_{0.6}\text{SO}_4 \cdot 14\text{H}_2\text{O} \) for comparison. Spectra of olivine (forsterite, Mg₁₈Fe₀₅SiO₄) and...
jarosite are included. As shown in Figure 3, Fe2+-bearing sulfates have spectra that closely resemble, and may be confused with olivine, a mineral that was proposed for the interpretation of the MB soil (and rock) data [Morris et al., 2004; Klingelhofer et al., 2004]. The MER Fe3+ features (~0.8 mm/s) are inconsistent with jarosite or olivine, but are very similar to Fe3+ in HIS. It is important to note that the contributions to MB spectra from silicates would be muted because they contain significantly fewer iron atoms per mole (1/10 to 1/3 as much) relative to the HIS phases.

4. Discussion

[16] Comparison of TES and Mini-TES soil spectra to those of a large suite of sulfate minerals suggests that the global Martian soil may contain HISs. Not only can HIS minerals account for the above-mentioned carbonate and bound water thermal emission features, but also HISs can account for both the purported olivine features in the MB soil data and fit the other MB soil features. (We wish to emphasize that the olivine in the rocks at the MER site and identified in outcrops elsewhere on Mars [e.g., Hoefen et al., 2003; Hamilton and Christensen, 2004] is not being questioned. We suggest that chemical weathering of rock to form soil destroys the chemically fragile olivine, hence, it would not survive to become a soil component. This interpretation is supported by the presence of alteration rinds on the Gusev rocks that show possible olivine casts, indicating that olivine has weathered away [McSween et al., 2004].) Additionally, HIS provides a good fit to the extended-visible soil spectra from IMP and Pancam.

[17] Terrestrials HISs form in the presence of acidic water. Low-pH waters can form HISs by oxidation of volcanogenic iron sulfide minerals or by the mobilization of iron from mafic rocks and subsequent combination with sulfur in the acid derived from volcanic H2S and H2SO4 aerosols [e.g., Burns, 1987; Bigham and Nordstrom, 2000]. Accessory sulfide minerals that could have been the precursors to the HISs are present in Martian meteorites [McSween, 1985] and volcanic materials are ubiquitous. On Mars oxidative chemical weathering could have occurred under cold to hydrothermal conditions. Even with minimal water on the surface of Mars, HISs could have been produced according to the acid-fog model that describes direct volcanic aerosol/basalt interaction or interaction of basalt with an acid produced by mixing volcanic gases with water vapor or with transient surface water [Settle, 1979; Banin et al., 1997].

[18] The low-pH geologic setting appropriate for the genesis of HISs would preclude the formation of carbonate in a similar environment and would be an aggressive chemical-weathering environment for olivine. Dissolution of olivine would introduce Mg into solution and contribute to the production of Mg sulfate [Tosca et al., 2004]. Perhaps the Mg sulfate identified in Valles Marineris [Bibring et al., 2004] is an indicator that chemical weathering of olivine has occurred on Mars.

[19] A recent chemical-weathering study of synthesized Mars-like basalts [Tosca et al., 2004] produced HISs when exposed to acidic solutions. Acidic conditions were likely on Mars as a necessary condition for the formation of HISs.
jarosite identified at the MER Meridiani Planum landing site. This laboratory result lends support to our interpretation that HfSs are present in the Martian soil.

[20] Although the discussion presented in this work is focused on only two HfSs, ferricopiapite and szomolnokite that represent a range of iron and hydration states, there are many HfSs that we are researching (e.g., copiapite, fibroferrite, melanterite, ro¨merite, voltaite, sideronatrite, botryogen, metavolinite, etc.). At this time we are not identifying a specific chemistry of HfS, but rather are suggesting the presence of HfSs as a type of mineral in the global Martian soil that also may be a crusting agent.

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