

POSSIBLE EVIDENCE FOR IRON SULFATES, IRON SULFIDES, AND ELEMENTAL SULFUR AT GUSEV CRATER, MARS, FROM MER, CRISM, AND ANALOG DATA. R. V. Morris¹, D. W. Ming¹, A. Yen², R. E. Arvidson³, J. Gruener¹, D. Humm⁴, G. Klingelhöfer⁵, S. Murchie⁴, C. Schröder⁵, F. Seelos IV⁴, S. Squyres⁶, S. Wiseman³, M. Wolff⁷, and the MER and CRISM Science Teams. ¹ARES/KR, MASA JSC, Houston, TX 77058, richard.v.morris@nasa.gov. ²Jet Propulsion Laboratory, Pasadena, CA. ³Washington Univ., St. Louis, MO 63130. ⁴Applied Physics Laboratory, Laurel, MD 20723. ⁵Mainz University, Mainz, Germany. ⁶Cornell Univ., Ithaca, NY 14853. ⁷Space Sciences Institute, Brookfield, WI 53045.

Introduction and Background: The Mössbauer (MB) spectrometers on the Mars Exploration Rovers (MER) Spirit (Gusev crater) and Opportunity (Meridiani Planum) have detected 14 Fe-bearing phases, and mineralogical assignments have been made for all except 3 [1-4]. Identified Fe²⁺-bearing phases are olivine, pyroxene, ilmenite, and troilite. Magnetite and chromite are present as mixed Fe²⁺ and Fe³⁺ phases. Identified Fe³⁺ phase are jarosite, hematite, goethite, and nanophase ferric oxide (npOx). Fe⁰ (iron metal) is present as kamacite. Nanophase ferric oxide (npOx) is a generic name for octahedrally coordinated Fe³⁺ alteration products that cannot be otherwise mineralogically assigned on the basis of MER data. On the Earth, npOx would include ferrihydrite, iddingsite, schwertmannite, akaganeite, and superparamagnetic hematite and goethite.

Although a specific assignments can not be made, there are MB constraints on the mineralogical compositions of the remaining 3 Fe-bearing phases. One is a Fe³⁺ sulfate (Fe3Sulfate), but its stoichiometry is not constrained. Another is an npOx-like Fe³⁺ phase (named Fe3D3) that is always associated with jarosite in the Burns formation at Meridiani Planum. The final unidentified phase (Fe?D1) occurs in a Si-rich rock on Home Plate in Gusev crater, and it might be either an Fe²⁺ disulfide (marcasite and/or pyrite) or, alternatively, a phase with tetrahedrally coordinated Fe³⁺.

Four of the 14 Fe-bearing phases have singular or a limited number of occurrences. Chromite occurs only in the Husband Hill rock Assemblée_Gureyere. Fe?D1 occurs only in the rock Fuzzy Smith at Home Plate. Troilite and kamacite occur only in three rocks (interpreted as meteorites) at Meridiani Planum (Barberton, Heat Shield Rock, and Santa Caterina). Fe3Sulfate, occurs in the Columbia Hills and only as subsurface soil that was exposed by the churning action of rover wheels. PasoRobles_Pasadena and DeadSea_Samra are the important exposures studied by MB and the Alpha Particle X-Ray Spectrometer (APXS).

The Fe-bearing phases goethite (Clovis Class rocks in the Columbia Hills) and jarosite (Burns formation) are particularly significant because they, having structural OH, are mineralogical markers for aqueous alteration processes on Mars [1,2]. Other Fe³⁺ bearing altera-

tion products identified by MER that might contain structural OH and/or crystal H₂O and/or hydration H₂O are npOx and Fe3Sulfate. If Fe?D1 is pyrite/marcasite, this phase also implies aqueous processes. Jarosite, Fe3Sulfate, and pyrite/marcasite imply widespread aqueous process under (possibly hydrothermal) acid sulfate conditions. Even npOx, through specific adsorption of sulfate anion (SO₄)⁻² could be a product of acid-sulfate alteration.

The Mars Reconnaissance Orbiter CRISM instrument, a visible, near-IR hyperspectral imager (~0.35 to 4 μm) enables mineralogical examination of Mars with a tool that is sensitive to H₂O and to M-OH (M = Al, Si, Fe, Mg, etc.) at spatial resolution of ~20 m/pixel. We examined a CRISM image of the MER region of Gusev crater (Columbia Hills and plains to the west), looking for spectral evidence of the aqueous process apparent from the MER analyses. We also searched for spectral constraints for the mineralogical composition of our unidentified Fe-bearing phases and the forms of npOx present on Mars.

We also consider evidence from analogue samples that the precursor for the goethite detected by MB in Clovis Class rocks is an iron sulfide. We suggest that there is some indirect evidence that elemental sulfur might be present to different extents in Clovis Class rocks, the Fe3Sulfate-rich soils, and perhaps even typical (Laguna Class) surface soils.

CRISM Observations: The CRISM image cube (data product FRT00003192_07) includes the Columbia Hills and surrounding plains, including Spirit's landing site. The radiative transfer program DISORT was used to validate the wavelength calibration and to retrieve Lambert Albedos (LA). We used lighting and viewing conditions appropriate for the observations, dust optical depths determined from Pancam observations during the over flight (0.37 at a wavelength of 0.88 μm), and an ice aerosol optical depth of 0.04. Gases modeled included carbon dioxide, carbon monoxide, and water vapor, using historical data generated by Mars Global Surveyor Thermal Emission Spectrometer instrument. The nominal values for DISORT

modeled the data well and allowed retrieval of Lambert albedos from 0.4 to 2.6 μm .

No CRISM Spectral Evidence for M-OH at Gusev: Figure 1 shows CRISM spectra for three surface locations visited by Spirit (El Dorado, and the albedo extremes along the path taken by Spirit from its landing site to the Columbia Hills). Also shown for comparison are spectra derived from a dust devil track and high albedo plains north of the Columbia Hills.

A shallow band may be present near 1.9 μm (Fig. 1a). If it is not a small instrumental or data processing artifact, the feature (an overtone of the H-O-H bending vibration fundamental) plus the broad featured centered near 3.0 μm (data not shown) imply that molecular water is present. From telescopic and laboratory data, [5] estimate 0.5 to 4% H_2O is necessary to account for the 3.0 μm band. As shown in Fig. 1b, there are no detectable spectral features that would indicate the presence of M-OH spectral features.

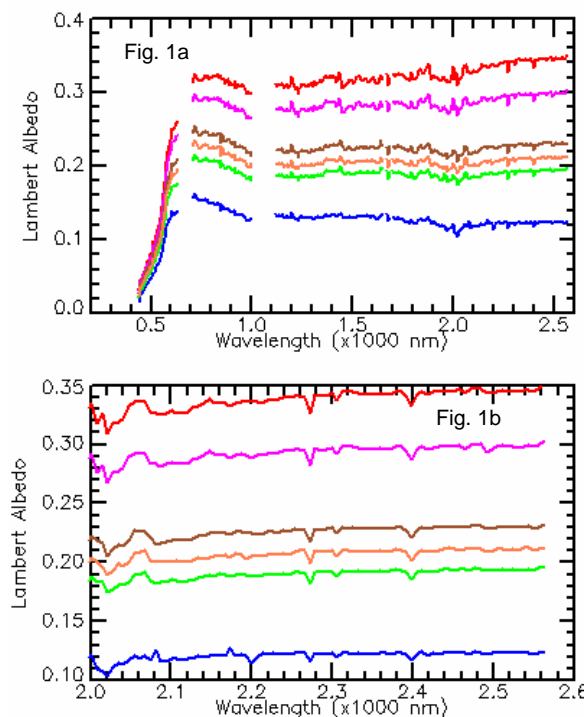


Fig. 1. CRISM Lambert albedo spectra for El Dorado (blue, 39 pixels), dust devil track (green, 49 pixels), Spirit low albedo Plains (coral, 68 pixels), Spirit high albedo Plains (sienna, 68 pixels), and two high albedo regions north of the Columbia Hills (magenta and red, both 121 pixels).

A way to enhance detection limits is to ratio spectra. In Fig. 2 we show a spectrum derived from the Gusev plains west of the Columbia Hills that has a nearly constant albedo (LA \sim 2.0) between 1.0 and 2.6 μm . For purposes of calculating ratios, this spectrum has the advantage that it will not impose spectral slopes between those wavelengths. As shown in Fig. 3, M-OH spectral features are not detected in the ratio spectra.

Our CRISM spectral results for the Gusev plains are in agreement with prior observations of martian bright regions made by OMEGA with respect to the non-detection of M-OH spectral features [6]. Spectral features between 2.0 and 2.6 μm have been detected by OMEGA in certain locales not in Gusev crater, and they are associated with M-OH (e.g., phyllosilicates) and with crystal H_2O (e.g., kieserite) [7-11].

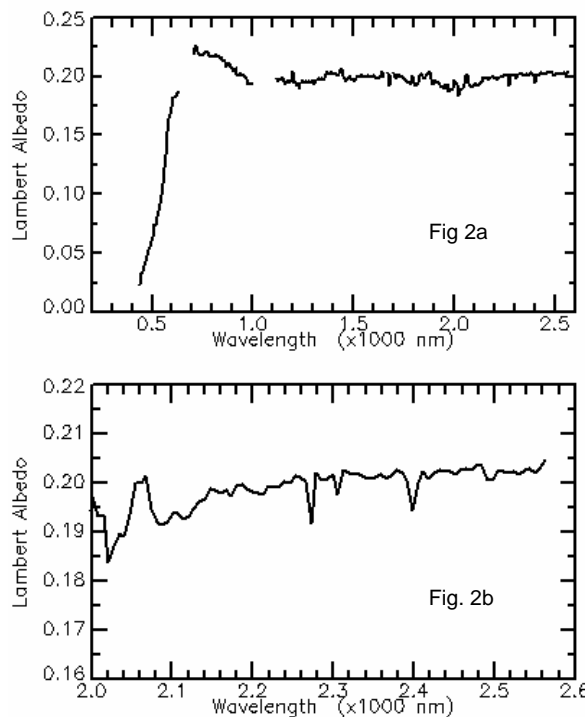


Fig. 2. CRISM Lambert albedo spectra for the Gusev plains west of the Columbia Hills (\sim 2000 pixels) that have LA \sim 2.0 between 1.0 and 2.6 μm .

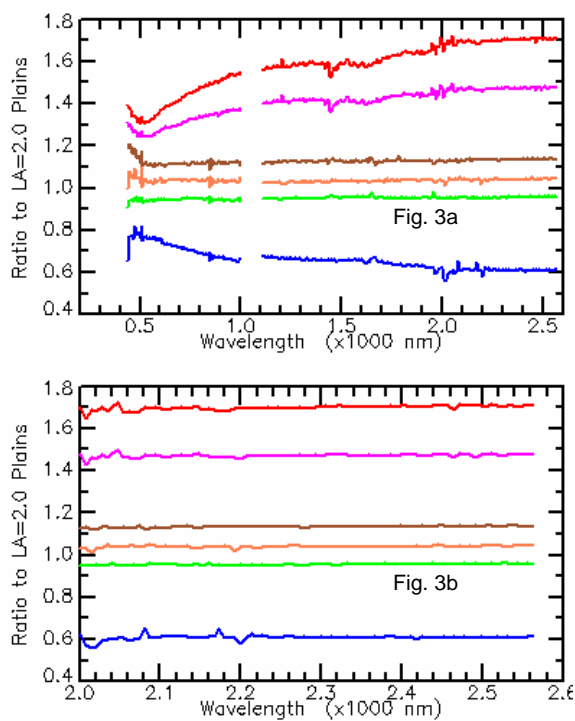


Fig. 3. Ratio of CRISM spectra in Fig. 1 to spectrum of Gusev plains in Fig. 2.

MER Laguna Class soil [1] is the surface target for the CRISM spectra discussed above. Its Fe mineralogical composition from MB is olivine, pyroxene, magnetite, nanophase ferric npOx, and minor hematite. npOx is the Fe^{3+} weathering product, and its abundance is lowest in dark soils like El Dorado and highest in bright, fine-grained soils like Desert_Gobi [1]. The concentration of npOx which is the product of the total Fe concentration as measured by APXS and the percentage of Fe associated with npOx as determined by MB, correlates with the concentration of S [1,2,12], implying Fe^{3+} and S (as sulfate) might be associated in the same compound. Alternatively, formation of npOx and accumulation of S may be coupled through some weathering process that does not involve significant formation of S-bearing npOx.

As discussed above, the CRISM spectra do not give use any evidence for S speciation in Laguna Class soil. It cannot be excluded that the S is present at least in part as elemental sulfur. A sample of hydrothermal elemental sulfur we obtained from Kilauea Volcano has high albedo, is spectrally neutral between ~ 0.4 and $2.6 \mu\text{m}$, and would be difficult to detect in the presence of npOx. The weak $1.9 \mu\text{m}$ band seems to limit npOx to its more anhydrous forms (e.g., nanophase Hm or Gt). Significant contributions to martian npOx from

ferrihydrate, schwertmannite, and/or akaganeite are not favored.

MER and Analog Evidence for Sulfide Precursors in Clovis Class Rocks: Clovis Class rocks are goethite-bearing rocks located on Husband Hill. [13] propose that the occurrence of goethite (as opposed to Fe-sulfates like jarosite) in Clovis Class rocks suggests that the invading acidic solutions were mostly neutralized by basalt dissolution. We suggest that it is also possible that the source of the sulfur was Fe-sulfide (perhaps pyrrhotite, Fe_{1-x}S) disseminated within the rock. Interaction of the sulfide with H_2O solutions and/or vapors formed acid-sulfate alteration agents. Goethite formed as a product of pyrrhotite alteration and from acid sulfate alteration of the silicate portion of the rock. An advantage to this process is that the alteration can occur at low water to rock ratios, minimizing leaching of soluble elements.

An example of pyrrhotite alteration under low water to rocks ratios is shown in Fig 4. The XRD powder pattern of naturally occurring pyrrhotite measured on the same day it was powdered (blue spectrum) shows the characteristic pattern of pyrrhotite plus quartz, chlorite, and biotite impurities. The XRD powder pattern of a powder prepared in 1982 and measured in 2007 shows that the pyrrhotite has completely altered to goethite, hydronium jarosite, and elemental sulfur. Between 1982 and 2007, the sample was maintained at ambient laboratory conditions so that the only source of H_2O was atmospheric water vapor.

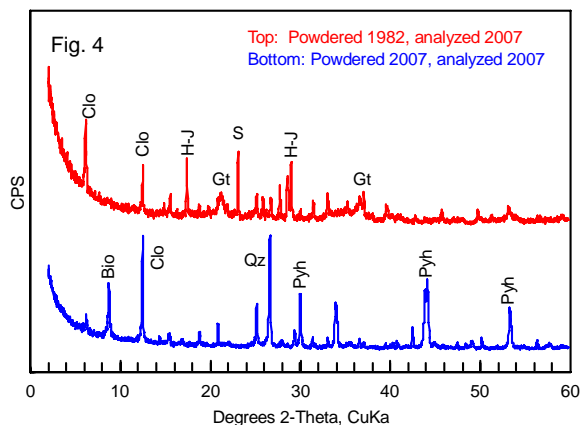


Fig. 4. Powder X-diffraction pattern for a freshly ground powder of pyrrhotite (blue) and for a powder prepared in 1982 (red) and allowed to set in laboratory air. Pyh= pyrrhotite, Qz= quartz, Clo= chlorite, Bio= biotite, Gt= goethite, H-J= hydronium jarosite, and S= elemental sulfur.

MER Evidence for Hydrothermal Sulfides and Elemental Sulfur at Home Plate: The Home Plate area of the Columbia Hills is considered to have a volcanic origin [4]. The presence of a rock (Fuzzy Smith) with a possible pyrite/marcasite assemblage [4] and S-rich soil (DeadSea_Samra) [14] suggest a magmatic hydrothermal system with a high proportion of SO₂. Under hydrothermal conditions, SO₂ can (with H₂O) disproportionate to form elemental sulfur and H₂SO₄ [e.g., 15]. Thus, it possible that elemental S is (or was) present in association with the S-rich deposits in the Columbia Hills.

Summary: The rock Fuzzy Smith is the only sample analyzed to date that has possible mineralogical evidence for indigenous Fe-sulfide. Fe sulfide is implicated as a possible precursor for goethite in Clovis Class Rocks. Elemental S could be widespread on the martian surface as a minor component in association with Laguna Class (basaltic) soil and as a significant component in association with S-rich soil (i.e., Paso Robles Class soil). Close association of sulfides and elemental sulfur with unaltered rock provides a pathway for acid sulfate alteration at low water to rock ratios with minimal element loss (and passive enrichment) by leaching processes.

References: [1] Morris *et al.* (2006), *JGR*, 111, E02S13, doi:10.1029/2005JE002584. [2] Morris *et al.* (2006) *JGR*, 111, E12S15, doi:10.1029/2006JE002791. [3] Clark *et al.* (2007), *JGR*, in press. [4] Squyres *et al.* (2007), *Science*, in press. [5] Yen *et al.* (1998), *JGR*, 103, 11,125. [6] Bibring *et al.* (2006). *Science*, 312, 400. [7] Bibring *et al.* (2005), *Science*, 307, 1576. [8] Gendrin *et al.* (2005), *Science*, 307, 1587. [9] Langevin *et al.* (2005), *Science*, 307, 1591. [10] Arvidson *et al.* (2005), *Science*, 307, 1591. [11] Poulet *et al.* (2005), *Nature*, 438, 623. [12] Yen *et al.* (2005) *Nature*, 436/7, doi:10.1038/nature03637. [13] Ming *et al.* (2005), *JGR*, 111, E02S12, doi:10.1029/2005JE002560. [14] Yen *et al.* (2007), *LPSC38*, Abs#2030. [15] Kusakabe *et al.* (2000), *J. Volc. Geoth. Res.*, 97, 287.