

IDENTIFYING THE PHOSPHATE AND FERRIC SULFATE MINERALS IN THE PASO ROBLES SOILS (GUSEV CRATER, MARS) USING AN INTEGRATED SPECTRAL APPROACH. Melissa D. Lane¹, Janice L. Bishop², M. Darby Dyar³, Mario Parente⁴, Penelope L. King⁵, and Brendt C. Hyde⁵. ¹Planetary Science Institute, Tucson, AZ (*lane@psi.edu*), ²SETI Institute/NASA-Ames Research Center, Mountain View, CA, ³Mount Holyoke College, South Hadley, MA, ⁴Stanford U., Stanford, CA, ⁵Univ. of Western Ontario, Canada.

Introduction: The Mars Exploration Rover (MER) *Spirit* has been exploring Gusev Crater since January 2004 and has been creating typically dark wheel tracks of disturbed soil [1]. Approximately 400 sols into the mission, *Spirit* exposed in its tracks an unusual occurrence of a bright soil high in sulfur and phosphorus and depleted in silicon and aluminum relative to the more typical basaltic Gusev plains soils [2,3]. This bright soil on the northwestern flank of Husband Hill is called “Paso Robles” (hereafter, PR). Preliminary study of this unusual soil by the MER Science Team suggests that the PR soil is rich in sulfate salts (>30 wt. % SO₃) [2,3] and is composed of the following: Fe³⁺-, Mg-, and Ca-sulfates; Ca-phosphate (>5 wt. % P₂O₅); hematite, halite, allophane, and amorphous Si [3,4], with ferric sulfate as an important, dominant new phase.

Using Alpha Particle X-ray Spectrometer (APXS) data [2], we calculate that the bright-toned salt component alone contains ~14% phosphate associated with the 82% sulfate and 4% chloride minerals. Detailed spectroscopic study of these bright deposits has provided some potential ferric sulfate identifications [e.g., 5]; however, a conclusive study has been hampered because phosphate minerals, particularly iron phosphates found in terrestrial gossans have not been widely studied using various spectroscopic techniques, nor are relevant spectra commonly published.

Here we present our current interpretation of the PR bright soil using our library suites of ferric (and other) sulfates and our recently acquired laboratory spectra of ferric (and other) phosphates acquired using visible near-infrared (VNIR) reflectance, thermal infrared (TIR) emissivity, and Mössbauer (MB) spectroscopic techniques. (A more detailed presentation of these phosphate spectra may be found in a companion abstract, this volume [6]).

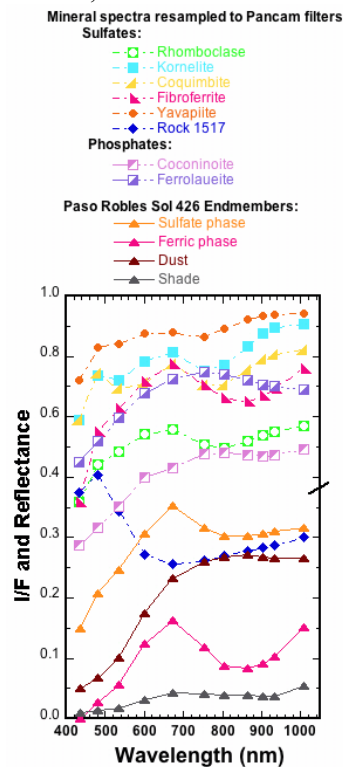
Results: Visible/Near Infrared: Pancam data [7] of the soil tracks at PR were studied using an unmixing clustering technique [8] to provide distinct spectral units (Fig. 1). The spectrum of the “sulfate phase” (the only PR spectrum that will be discussed in detail here) exhibits very unusual spectral characteristics that are unlike typical geologic materials (e.g., a convex upward inflection near 480 nm, a reflectance maximum at ~670 nm, and a minimum near 750-850 nm). The 480-nm behavior is seen in co-

quimbite (Fe³⁺(SO₄)₃ · 9H₂O), kornelite (Fe³⁺(SO₄)₃ · 7H₂O), and rhomboclase ((H₅O₂)⁺Fe³⁺(SO₄)₂ · 2H₂O). Yavapaiite (KFe³⁺(SO₄)₂) and fibroferrite (Fe³⁺(SO₄)(OH) · 5H₂O) exhibit this behavior as well, but to a lesser extent. “Rock 1517” (likely brochantite) exhibits an extreme

480-nm inflection.

The unusual PR spectral reflectance maximum near 670 nm is not common, but is seen in spectra of several ferric sulfates including coquimbite, kornelite, rhomboclase, fibroferrite, copiapite (Fe²⁺Fe³⁺₄(SO₄)₆(OH)₂ · 20H₂O) (not shown), and ferricopiapite (Fe³⁺,Al,Mg)Fe³⁺₅(SO₄)₆(OH)₂ · 20H₂O) (not shown).

Fig. 1. VNIR spectra of the PR soils and several sulfates and phosphates.



The reflectance minimum that occurs between ~750 and 850 nm is seen in a few ferric sulfates such as coquimbite, kornelite, rhomboclase, and yavapaiite. Comparison of the spectral shapes of the PR bright-track “sulfate phase” soil spectrum to ferric-sulfate spectra suggests that the diagnostic characteristics in the Pancam data are most consistent with coquimbite. Other likely mineral components suggested are kornelite, rhomboclase, yavapaiite, copiapite, ferricopiapite, and/or fibroferrite mixed with darker soil constituents.

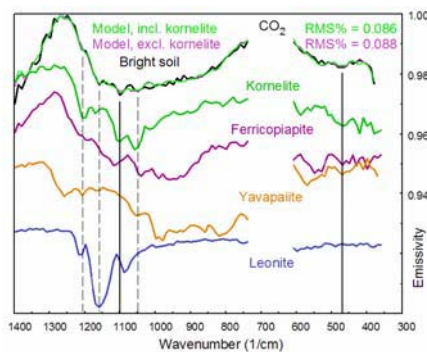
Recently acquired ferric phosphate spectra of coconinoite (Fe³⁺₂Al₂(UO₂)₂(PO₄)₄(SO₄)(OH)₂ · 20H₂O) and ferrolaueite (Fe²⁺Fe³⁺₂(PO₄)₂(OH)₂ · 8H₂O) (Fig. 1) do not show this anomalous spectral behavior and may not contribute significantly to the unusual character of the PR bright-track “sulfate phase” spectrum.

Thermal Infrared: Spectral deconvolution of the Mini-TES [9] bright-soil emissivity spectrum (Fig. 2) was conducted using a linear least-squares algorithm [e.g., 10] and an endmember array that included the dark-track soil, as well as oxide minerals and a diverse suite of Ca-, Mg-, Na-, K-, Fe^{2+} -, and Fe^{3+} -bearing sulfates, including 20 different ferric sulfates. In addition, 7 phosphate minerals were used, including 2 newly acquired phosphates, hotsonite ($\text{Al}_5(\text{PO}_4)(\text{SO}_4)(\text{OH})_{10} \cdot 8\text{H}_2\text{O}$) and ferrolaueite.

Model spectra from 2 deconvolution results are presented (Fig. 2). The two analyses used the same endmember library except for one analysis, the kornelite was removed because MB results (see next section) do not support its presence. Case 1: The best-fit model result showed the bright soil spectrum to contain ~49% dark-track soil. Other principal spectral components included ~13% kornelite, ~11% ferricopiapite/copiapite, ~7% yavapaiite, ~7% leonite ($\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$), and ~4% starkeyite ($\text{Mg}(\text{SO}_4) \cdot 4\text{H}_2\text{O}$). Case 2: The model result was dominated by ~53% dark-track soil, ~15% ferricopiapite/copiapite, ~9% yavapaiite, and ~5% leonite. The minerals yavapaiite and leonite may be a proxy for other minerals because the APXS results suggest that there is a low abundance of K in the PR bright soil. Other ferric sulfates have some spectral features that are similar to the bright PR soil, regardless of not being selected as a dominant phase include coquimbite, parabutlerite, bilinite, and zincobotryogen.

For Cases 1 and 2 only 1.2% and 4.2% phosphate, respectively, were indicated—far less than present in the bright PR soil. This effect may be due to the lack of sufficient phosphates in the endmember library.

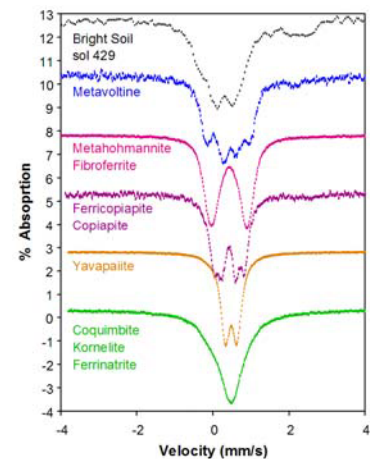
Fig. 2: TIR spectra of the PR bright soil, 2 deconvolution results, and several selected sulfate minerals.



Mössbauer: The PR dark soil MB data (sols 426-427) indicate dominantly Fe^{2+} (70% of the total Fe); sols 401-403 (dark and light soil) (not shown) and 429A (light, Fig. 3) are Fe^{3+} -rich (87 and 82%, respectively). The Fe^{3+} doublets are best resolved in the 429A spectrum from the light soil, where they have $\delta = 0.40$ - 0.42 mm/s and $\Delta = 0.36$ and 0.93

mm/s. There are numerous ferric sulfates with similar parameters. For the $\Delta = 0.36$ mm/s doublet, the most likely matches that are also consistent with those found by Pancam or Mini-TES would be ferricopiapite and/or yavapaiite, which have doublets with $\Delta = 0.36$ - 0.40 and 0.31 mm/s. Other possibilities from the MB data include krausite and metavoltine. The doublet with $\Delta = 0.93$ mm/s also is similar to a large group of ferric sulfates, but its best matches are to metahohmannite ($\Delta = 0.94$ mm/s), butlerite/ parabutlerite ($\Delta = 0.96$ - 0.97 mm/s) and/or fibroferrite ($\Delta = 0.96$ mm/s). Kornelite and coquimbite, which fall at $\Delta = 0.06$ - 0.15 and 0.11 mm/s, respectively, are not a good match (but the errors on the MER data may be significant, although they are as-yet unquantified).

Fig. 3: MB spectra of PR bright soil and several sulfate minerals for comparison.



Comparison of the MB parameters to the PR data suggest that a possible phosphate candidate is strunzite or another phosphate with similar structure. Strunzite was not yet measured in VNIR or TIR.

Future Work: Additional ferric phosphates, (e.g., strengite and phosphosiderite) will be acquired and shared between the spectroscopy labs. These Fe^{3+} phosphates occur in terrestrial soils and gossans and may help satisfy the discrepancies of the Paso Robles soil analyses between the different spectral techniques.

References: [1] Yen, A. S. et al. (2005) *Nature*, 436, 49-54. [2] Gellert, R. et al. (2006) *JGR*, 111, E02S05. [3] Ming, D. W. et al. (2006) *JGR*, 111, E02S12. [4] Morris, R. V. et al. (2006) *JGR*, 111, E02S13. [5] Lane, M. D. et al. (2006) *AGU*, 87(52), abstr. P44A-03. [6] Lane, M. D., Dyar, M. D., and Bishop, J. L. (2007) *this volume*. [7] Bell, J. F. III et al. (2006) *JGR*, 111, E02S03. [8] Parente, M. (2007) *this volume*. [9] Christensen et al. (2003) *JGR*, 108, 8064. [10] Ramsey, M. S. and Christensen, P. R. (1998) *JGR*, 103, 577-596. [11] Klingelhöfer, G. et al. (2003) *JGR*, 108.