

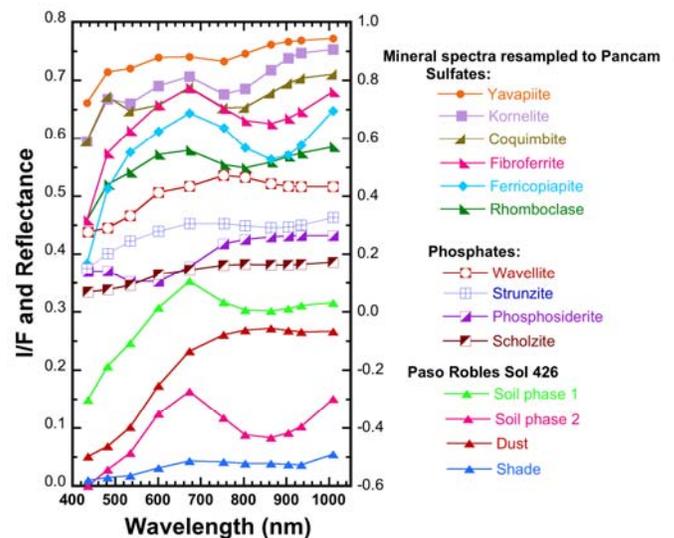
**THE FERRIC SULFATE AND FERRIC PHOSPHATE MINERALS IN THE LIGHT-TONED PASO ROBLES ROVER TRACK SOILS: A MULTI-INSTRUMENT ANALYSIS.** Melissa D. Lane<sup>1</sup>, Janice L. Bishop<sup>2</sup>, M. Darby Dyar<sup>3</sup>, Mario Parente<sup>4</sup>, Penelope L. King<sup>5</sup>, and Brendt C. Hyde<sup>5</sup>. <sup>1</sup>Planetary Science Institute, Tucson, AZ (*lane@psi.edu*), <sup>2</sup>SETI Institute/NASA-Ames Research Center, Mountain View, CA, <sup>3</sup>Mount Holyoke College, South Hadley, MA, <sup>4</sup>Stanford U., Stanford, CA, <sup>5</sup>Univ. of Western Ontario, Canada..

**Introduction:** The Mars Exploration Rover (MER) named *Spirit* has been exploring Gusev Crater since January of 2004 and has been creating typically dark wheel tracks of disturbed soil that mark the rover's course across the surface [1]. Approximately 400 sols into the mission, *Spirit* exposed in its tracks, in addition to the dark soil, 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]. The site of this bright soil is on the northwestern flank of Husband Hill and is called "Paso Robles" (hereafter, PR). Preliminary study of this unusual, bright track soil by the MER Science Team indicated that the bright PR soil is rich in sulfate salts (>30 wt. % SO<sub>3</sub>) and phosphate (>5 wt. % P<sub>2</sub>O<sub>5</sub>) [2,3] and is composed of the following: Fe<sup>3+</sup>-, Mg-, and Ca-sulfates; Ca-phosphate; hematite, halite, allophane, and additional amorphous Si [3,4], with ferric sulfate as an important, dominant new phase.

For the past several years we have focused on investigating the spectral properties of sulfates, and more recently phosphates, in the laboratory using a broad range of spectral techniques including visible-near-infrared reflectance spectroscopy (VNIR), vibrational (thermal infrared, TIR) emission spectroscopy, and Mössbauer (MB) spectroscopy [e.g., 5-13]. These studies have provided well-characterized sample spectra, and work is in progress to continue characterization of the ~370 known sulfate minerals [14] and over 400 phosphate minerals. Included in our comprehensive multi-technique spectral studies are a wide variety of Fe<sup>3+</sup>-sulfates (and other sulfates) that are clearly an important mineral type in the anomalous PR soils. We also include an introductory suite of ferric-bearing phosphate minerals, as well as other phosphates. Here we combine our different spectral databases to make a unified interpretation of comparable data from *Spirit* including data from the Pancam [15], the Mini-TES [16], and the MIMOS II Mössbauer spectrometer [17] to further explore and identify the specific ferric sulfate and phosphate minerals present in these salt-rich soils and better understand the chemistry of Mars.

**Results:** *Visible/Near Infrared Reflectance Spectroscopy:* Pancam data [18] of the soil tracks at PR (sols 400 and 426) were studied using a clustering technique [19]. Clustering via statistical analyses of the Pancam scenes of the PR tracks provided four

common endmembers including "soil phase 1", "soil phase 2", "dust", and "shade". The spectra of these four regional endmembers are shown in Fig. 1. The bright, sulfate-rich spectrum ("soil phase 1") exhibits very unusual, diagnostic spectral characteristics for typical geologic materials (e.g., a convex upward feature near 480 nm, a reflectance maximum at ~670 nm, and a minimum near 800-850 nm). Fig. 1 also shows the VNIR spectra of several Fe<sup>3+</sup>-sulfates from our spectral library that share the unusual spectral properties of the sulfate-bearing "soil phase 1". The bright-soil Pancam spectrum is not spectrally unique to any single ferric sulfate alone, because these pure mineral endmember spectra are too bright and are not an exact spectral shape match. However, the unusual Pancam spectrum indicates the strong likelihood of containing certain ferric sulfate minerals and enables us to rule out some sulfates such as jarosite.



**Figure 1.** VNIR spectra of the PR bright-soil components. Green spectrum represents the sulfate-bearing phase. For comparison, reflectance spectra of several ferric sulfates and some phosphates are shown.

For example, the convex-upward shape of a VNIR spectrum at ~480 nm is extremely unusual; Fig. 1 shows that this behavior is seen in coquimbite and kornelite. Yavapaiite, fibroferrite, rhomboclase, and ferricopiapite exhibit this behavior as well, but to a lesser extent.

In contrast, most ferric oxide-bearing minerals exhibit a reflectance maximum near 700-800 nm and a reflectance minimum between 850-950 nm [e.g., 20, 21]. The unusual PR spectral reflectance maximum near 670 nm is not common, but is seen in spectra of several ferric sulfates including coquimbite, kornelite, fibroferrite, ferricopiapite, and rhomboclase.

The reflectance minimum that occurs between ~800 and 850 nm is seen in a few ferric sulfates such as fibroferrite and ferricopiapite. For other ferric sulfates and ferric oxides, this band occurs at shorter or longer wavelengths and is less similar to the character of the PR bright soil spectrum.

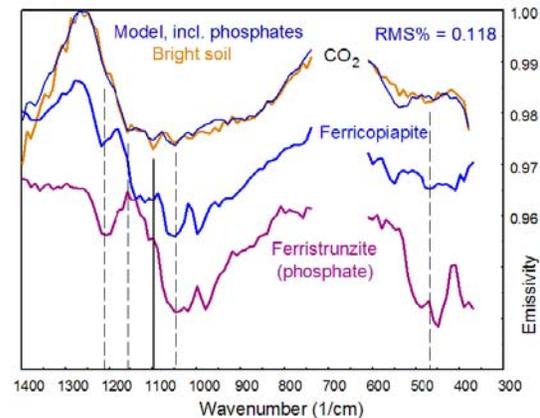
Comparison of the spectral shapes of the PR bright-track soil spectra to many laboratory ferric-sulfate spectra suggests that the diagnostic spectral characteristics in the Pancam data are similar to coquimbite, kornelite, yavapaiite, rhomboclase, fibroferrite, and ferricopiapite. However, the Pancam data along with the other spectral data sets (to be presented next) are most consistent with ferricopiapite mixed with darker host soil constituents.

Our laboratory studies of sulfates have progressed farther than our phosphate studies. A few initial phosphate VNIR spectra are shown in Fig. 1, including those for wavellite, strunzite, phosphosiderite, and scholzite. Examination of the phosphosiderite spectrum and others not shown suggest that perhaps the 480-nm band seen in the PR spectrum could be attributed to the phosphate component of the bright soil or related to a transition metal like Mn (although it also could be attributed to a ferric sulfate mineral as discussed above). We are continuing our phosphate studies with the hope of identifying the specific phosphate component mineral in the bright PR soils.

*Vibrational (Thermal) Emission and Alpha-Particle-X-ray Spectroscopy:* The Mini-TES bright soil spectrum (sol 404) (Fig. 2) shows a pronounced local emissivity maximum at 1650  $\text{cm}^{-1}$  that is indicative of structural water in the minerals present (e.g., they are hydrated). From the Pancam images and spectra (discussed above) and the navigational camera images from the rover (not shown), it is clear that the bright Martian tracks also contain a contribution of the dark soil; hence, for the spectral deconvolution, the dark-track soil spectrum (from sols 400 and 403) (Fig. 2) was included as an endmember.

Spectral deconvolution of the bright-soil spectrum (Fig. 2) was conducted using a linear least-squares algorithm [e.g., 22] and an endmember array that included the dark-track soil, as well as various particle sizes of a diverse suite of oxide, sulfate, and phosphate minerals.

The deconvolution result (Fig. 2) achieved an RMS of 0.118%. The result showed the Mini-TES



**Figure 2.** Mini-TES spectra of bright and dark track soils and the modeled fit (RMS=0.118%) to the bright-PR soil spectrum. Also shown are ferricopiapite and ferrostrunzite that exhibit some band positions similar to the bright soil. Spectra are offset for clarity.

bright soil spectrum to contain ~60% dark-track soil. The remainder of the spectral components included ferric sulfates at ~20%, including ~16% ferricopiapite and ~4% fine-grained coquimbite; ~8% Mg-bearing sulfate (kainite, polyhalite, and leonite); and ~3% Ca-bearing sulfate (fine-grained anhydrite and polyhalite). Nanophase hematite was indicated at ~4% and phosphate at ~6%. Of that total phosphate, ~3% was attributed to ferrostrunzite.

Ferricopiapite is selected as a major PR soil component because its spectrum has emissivity features at 1210, 1047, and 466  $\text{cm}^{-1}$ , similar to the bright PR soil spectrum (Fig. 2). The additional bands in the PR spectrum within the sulfate and phosphate  $\nu_3$  regions (~1250-1050  $\text{cm}^{-1}$  and ~1100-1000  $\text{cm}^{-1}$ , respectively [12, 23] suggest that more than ferricopiapite is present in the salt fraction as is supported by the additional minerals returned by the deconvolution result. When compared to the bright soil spectrum, other ferric sulfates have some spectral features that are similar to the bright PR soil regardless of not being selected as a dominant phase with the deconvolution technique (including coquimbite, parabutlerite, bilinite, and zincobotryogen). The primary phosphate selected was ferrostrunzite. However, we have only begun to study a wide range of phosphate minerals, so perhaps the true present phosphate was not available in the end-member set of spectra.

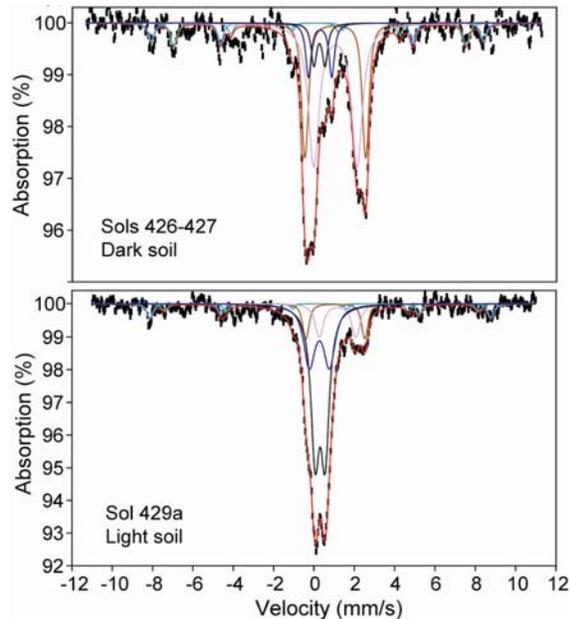
The APXS data [2] may be used to provide some constraints for fitting potential salts in the PR soils to the VNIR, TIR, and MB spectra. For PR Light (as named by the MER APXS team) we calculate that sulfates, phosphates, and halides make up ~82%, 14%, and ~4 mole % of the salts, respectively, from APXS

data. This is remarkably similar to the deconvolution result that, when the dark-track soil component is removed, the deconvolution-derived salt component is represented by ~84% total sulfate and ~16% total phosphate (halide isn't identified as a separate phase because it cannot be directly detected in the wavelength region of the Martian data, although the sulfate kainite contains Cl).

APXS data also may be used to determine the possible sulfate types. We examined the elements Fe, Mg, Ca, and Na + K because these cations make up the most common sulfate minerals (and other minerals). Al is omitted from this list because it is a major constituent of silicates. We treat the alkali elements, Na and K, together because they commonly substitute for each other. Fe is the most abundant cation in PR Light ( $\text{Fe}/(\text{Fe}+\text{Mg}+\text{Ca}+\text{Na}+\text{K}) = 42\%$ ) and is much more abundant than in the 2 dark PR soils considered (33 and 36%). The Fe could be hosted in silicates and oxides; however, the VNIR and TIR data suggest that those minerals are modeled readily by the PR dark-track soil. Therefore, it is highly probable that the Fe is dominant in sulfates. It is also likely that some of the ferric iron is hosted in ferric phosphate, as was indicated by the TIR spectral deconvolution.

In addition, Ca and  $\text{Ca}/(\text{Fe}+\text{Mg}+\text{Ca}+\text{Na}+\text{K})$  are enriched in PR Light, suggesting that Ca-bearing sulfates may be an important constituent; although only negligible anhydrite (2.6%) and polyhalite (<1%) were derived from the TIR deconvolution analysis. The APXS data also may be used to rule out certain sulfate minerals. Because the abundance of Na + K is low, it is unlikely that those elements are hosted in sulfates (e.g., leonite, kainite, and polyhalite, even though these minerals were indicated by the TIR emissivity data deconvolution). Interestingly, our deconvolution results did not return any simple Mg-sulfates; however, several Mg-bearing sulfates were identified (ferricopiapite, leonite, kainite, and polyhalite).

**Mössbauer Spectroscopy:** The PR dark soil MB data (sols 426-427) show dominantly  $\text{Fe}^{2+}$  (70% of the total Fe). The data from sol 429A (light) are  $\text{Fe}^{3+}$ -rich (82%) (Fig. 3). Parameters similar to olivine are found in both dark and light soils ( $\delta = 1.15\text{-}1.17$  mm/s and  $\Delta = 2.93\text{-}3.03$  mm/s). A second  $\text{Fe}^{2+}$  doublet ( $\delta = 1.16\text{-}1.31$  mm/s and  $\Delta = 1.84\text{-}2.18$  mm/s) is present in all spectra studied, and probably represents a mixture of pyroxene in the soil and/or  $\text{Fe}^{2+}$  in a hydrous sulfate. The  $\text{Fe}^{3+}$  doublets in the 429A light soil spectrum have  $\delta = 0.40\text{-}0.42$  mm/s and  $\Delta = 0.36$  and  $0.93$  mm/s. We have studied a large suite of sulfate and phosphate samples, and comparison of the laboratory Mössbauer parameters to the PR salt-bearing spectra show that there are numerous ferric sulfates and ferric phosphates



**Figure 3:** Mössbauer data for bright and dark PR soils. Sextets representing magnetite (parameters are indistinguishable within errors) are shown in light aqua.  $\text{Fe}^{2+}$  doublets are shown in brown, while  $\text{Fe}^{3+}$  doublets are black and dark blue. The sum of all component peaks is shown in red. Data are plotted as error bars based on counting statistics.

with similar parameters (Fig. 4). The sulfate and phosphate parameters tend to be similar because the mineral structures of both mineral classes are based on a tetrahedral anion ( $\text{SO}_4$  and  $\text{PO}_4$ , respectively). For the  $\Delta = 0.36$  mm/s doublet, the most likely ferric sulfate match that is also consistent with the analyses of Pancam and Mini-TES data would be ferricopiapite, which has doublets with  $\Delta = 0.36\text{-}0.40$  mm/s. The ferric phosphate, ferristrunzite, also has similar parameters to the 0.36 mm/s doublet and was also suggested by the deconvolution of the Mini-TES data. Other possibilities from the MB data include the ferric sulfates metavoltine, halotrichite (not shown), yavapaiite, and krausite and the ferric phosphates ferristrunzite, lipscomite, and perhaps strengite. 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 ( $\Delta = 0.96\text{-}0.97$  mm/s), fibroferrite ( $\Delta = 0.96$  mm/s), and possibly ferricopiapite. The best fit by the phosphates is by ferristrunzite; again this mineral selection is consistent with the thermal emissivity deconvolution.

**Discussion:** The spectroscopic methods used herein all point to a sulfate assemblage in the PR bright soil that is dominated by ferricopiapite or a

