COMPOSITION AND FORMATION OF THE "PASO ROBLES" CLASS SOILS AT GUSEV CRATER.

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Introduction: Light-toned, subsurface soil deposits (Figure 1) have been excavated by the Mars Exploration Rover (MER) Spirit in six distinct locations along its traverse across the Columbia Hills of Gusev Crater. Samples at two of these sites have been analyzed in detail by the Mössbauer (MB) and Alpha Particle X-ray Spectrometers (APXS), providing information on iron mineralogy and elemental chemistry, respectively. These soils are referred to as "Paso Robles" class deposits.
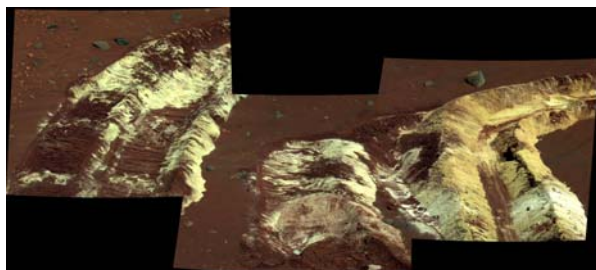

Figure 1: False color Pancam mosaic of the "Tyrone" area, an example of a "Paso Robles" class soil.

APXS and MB data: The most relevant APXS and MB data sets on these soils were collected at the original Paso Robles location on the north side of Husband Hill and at the Dead Sea location in the inner basin.

Mössbauer Results: The MB data are dominated by a narrow doublet indicative of a ferric iron phase (Figure 2). The two measurements at Paso Robles which are separated by ~1 meter have approximately a factor of 4 difference in the amount of hematite. The measurement at the Dead Sea location has the least amount of contamination from typical basaltic soils and slightly different MB parameters than the measurements at Paso Robles.

APXS Results: The sulfur content of the Paso Robles class soils (30 to 35 wt% SO_3) is the highest of all measurements made by the rovers, including Meridiani outcrop rocks. The elemental composition of these deposits is distinct from typical soils and exhibits significant variability. Measurements of nearby samples at the same site show differences of greater than 20% in at least half of the measured elements. Between the two sites, there is greater than 50% variability in over half the elements.
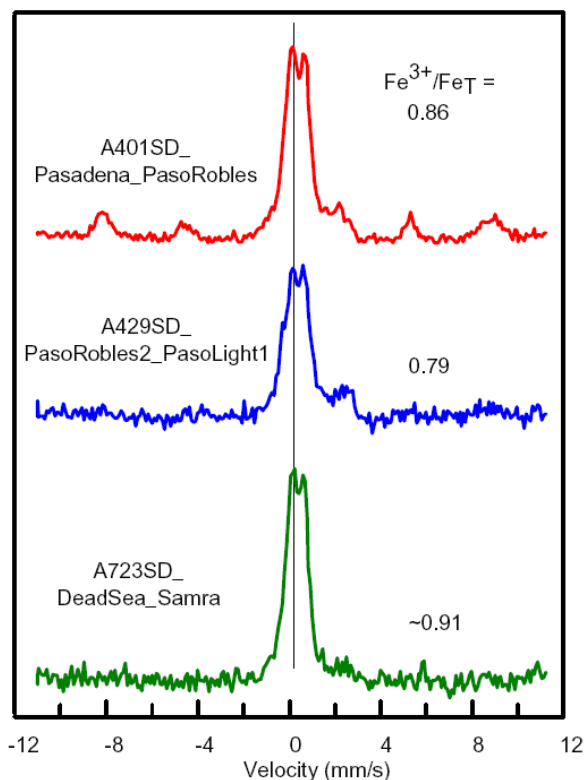

Figure 2: Ferric iron dominates the Mössbauer spectra, and associations with sulfur in the APXS data indicate the presence of one or more ferric sulfates.

Signatures of Local Rocks: Chemical signatures of nearby rocks are evident in these unique soil deposits. The most obvious indicator is the significantly elevated phosphorous content at the Paso Robles site (4.7 and 5.6 wt% P_2O_5), which is found amidst the Wishstone and Watchtower class rocks. Members of this rock class have measured phosphate levels of up to 5.2% P_2O_5, the highest of all rocks measured by MER. In contrast, the soil measurements at the Dead Sea site, which are not surrounded by phosphate-rich rocks, have only 0.5 wt% P_2O_5 (Figure 3). A possible additional indicator of local rock chemistry includes an unusually low Cr abundance in one measurement at the Paso Robles site, again consistent with Wishstone and Watchtower class materials. The enhanced Mg and Ni of Algonquin class rocks [1] may be present in one of the nearby Dead Sea measurement.
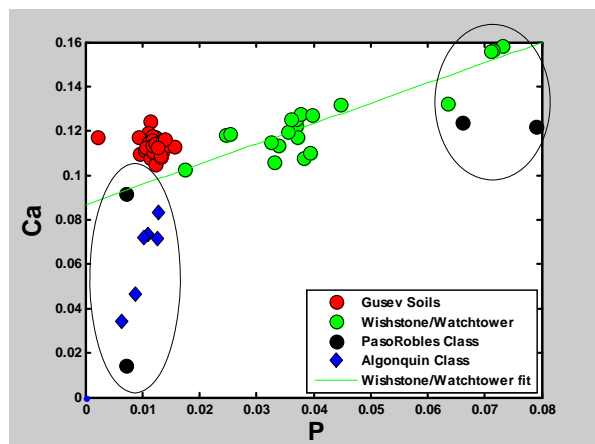
Figure 3: For elements which are readily mobilized in solution, the compositions of Paso Robles class soils are more similar to nearby rocks than to other deposits within its own soil class.

Elemental Sulfur? With over 30 wt% SO_3, it is reasonable to assess whether any of these soils may contain elemental sulfur. The Samra measurement in the Dead Sea region has the greatest concentration of sulfur (35 wt% SO_3) and the lowest abundance of measured cations (7 wt% as oxides) when Si and Fe are excluded. Assuming a 5% contamination from basaltic soils in this measurement based upon the olivine and pyroxene in the MB data and the amount of K in the APXS results, a charge balance calculation indicates that all of the sulfur can be accommodated in a Mg-sulfate (12% with Mg:S = 1:1) and a ferric sulfate (39% with Fe:S ~ 2:3). The primary remaining constituent of this sample would be 40% silica. The derived molar Fe-S ratio is consistent with a ferric sulfate of the form $Fe_2(SO_4)_3 \cdot nH_2O$.

Based upon the interpretation of the combined data from the MER instruments, Paso Robles class soils are believed to be hydrated. An attempt to derive the actual level of hydration from the Pu scattering peaks in the APXS data is in progress [2]. Hydration of many sulfates occurs both as H_2O and OH^- groups, the latter of which provides a negative charge. If OH^- is abundant in the ferric sulfate(s), the Fe-S ratio could be larger. Figure 4 shows the relationship between Fe in the ferric sulfate phase as determined by MB and S measured by APXS. The apparent ratio of Fe:S in this plot is approximately 3:2; however, this result assumes that other sulfates are present in equal quantities in each of the measurements. This situation seems improbable and thus the Fe:S ratio is not uniquely constrained, but this illustrates the possibility of an Fe:S ratio larger than 2:3. For larger Fe:S ratios, charge balance could be maintained if the excess sulfur (~10 mole% if Fe:S = 3:2) were in native form.
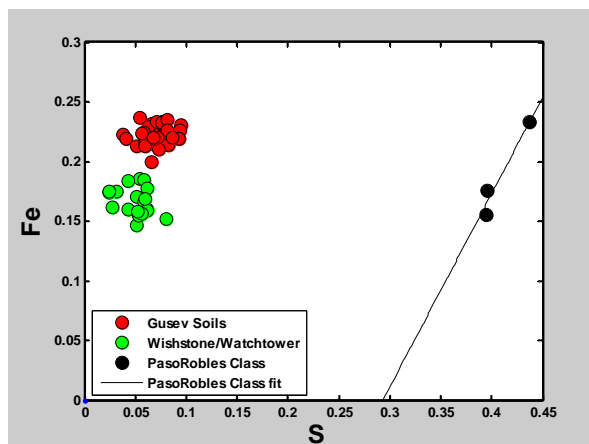

Figure 4: Fe-S trend in Paso Robles class soils accounting for only the ferric sulfate phase identified in the MB data.

Similar calculations with the other Paso Robles class soil analyses are less constrained due to the absence of MB data in one case and substantially greater basaltic soil contamination in the remaining two. In all measured samples, Fe^{3+} and Mg-sulfates are likely, Ca-sulfates are possible but not necessary (Ca-phosphates are more likely), and excess silica is present.

Formation Processes: The apparent signature of the nearby rocks in the Paso Robles class soil deposits is a strong indicator that these materials are precipitates from aqueous solution or volcanic vapors which mobilized these elements. The presence of ferric sulfates suggests that these fluids and/or vapors were oxidized and rich in sulfuric acid (pH < 1) [3, 4]. The differences in the MB parameters (possibly due to hydration state differences or cation substitutions) and in the elemental chemistry between the two locations indicate that these aqueous processes were localized.

The observed compositional variability over short length scales suggests that these precipitates are derived from solutions with low water-to-rock ratios. Reworking of initial, more homogenous, deposits through impact gardening cannot be ruled out, but given cm-scale differences, redistribution of these materials through aolian processes is unlikely.

The mineral assemblages suggested by the APXS and MB data are consistent with efflorescent salt accumulations from acid weathering [5]. The possibility of elemental sulfur, however, would indicate that hydrothermal and/or fumarolic activity is a more likely origin for Paso Robles class soils.

References: [1] Mittlefehldt, D. W. et al. (2006) *LPSC,* XXXVII, #1505. [2] Mallett, C. L. et al. (2006), *X-ray Spec, 35,* 329-337. [3] Ming, D. W. et al. (2006) *JGR, 111,* E02S12. [4] Morris, R. V. et al. (2006) *JGR, 111,* E02S13. [5] Joeckel, R. M. et al. (2004), *Chem. Geol., 215,* 433-452.