COMPOSITIONS OF SPHERULES AND ROCK SURFACES AT MERIDIANI.

B. L. Jolliff[1], B. C. Clark[2], D. W. Mittlefehldt[3], R. Gellert[4], and the Athena Science Team, [1]Department of Earth & Planetary Sciences, Washington University, St. Louis, MO 63130; [2]Lockheed Martin Space Systems, POB 179, MS S-8000, Denver, CO 80201; [3]mail code KR, NASA Johnson Space Center, 2101 NASA Parkway, Houston, TX 77058; [4]Department of Physics, CPES, University of Guelph, On N1G 2W1, Canada. (blj@wustl.edu)

Introduction: The Alpha Particle X-ray Spectrometers (APXS) on the Mars Exploration Rovers (MER) have proven extremely valuable for analyzing rocks and soils on the surface of Mars. The precision of their compositional measurements has been shown to be phenomenal through analyses of the compositionally very uniform Meridiani soils [1-4]. Through combined use of the rock abrasion tool (RAT) and the analytical instruments on the in-situ deployment device (IDD), analyses of the interiors of fine-grained and texturally uniform rocks with surfaces ground flat have been made under conditions that are nearly ideal for this mode of analysis [5].

The APXS has also been used frequently to analyze materials whose characteristics, surface morphologies, and sample-detector geometries are less than ideal, but the analyses of which are nonetheless very useful for understanding the makeup of the target materials. Such targets include undisturbed rocks with irregular and sometimes coated surfaces and mixed targets such as soils that include fine-grained components as well as coarse grains and pieces of rocks. Such target materials include the well known hematite-rich concretions, referred to as ‘blueberries’ because of their multispectral color, size, and mode of occurrence [6]. In addition to non-ideal target geometry, such mixed materials also present a heterogeneous target in terms of density. These irregularities violate the assumptions commonly associated with analyses done in the laboratory to achieve the highest possible accuracy. Here we acknowledge the irregularities and we examine the inferences drawn from specific chemical trends obtained on imperfect targets in light of one of the potential pitfalls of natural materials on the surface of Mars, namely thin dust coatings.

Composition of Blueberries: Previous work has focused on the compositional trends associated with mixed soil targets that are rich in spherules [7-9] in order to infer the chemical composition of the spherules. After three years of exploration at Meridiani, Opportunity had analyzed about a dozen such spherule-rich targets using its APXS and its Mössbauer spectrometer, in addition to nearly two dozen measurements on more typical soil. The compositions of the spherule-rich targets spread and form trends on many element-element plots, suggesting control (for those elements) by two dominant components, namely spherules and soil. It is possible to infer the composition of the endmembers from such trends given the rules of mass balance.

Examples of the distribution of compositions among Meridiani materials are shown in Fig. 1. Strongly correlated trends of elements (expressed as oxide concentrations) with Fe_2O_3 concentration extrapolate to high Fe_2O_3, as expected if the spherules are rich in hematite. For elements such as S and Al, trends appear to project to 100% Fe_2O_3 or nearly so, which would be consistent with the spherules being composed purely of hematite. On the other hand, Ca (Fig. 1d) and the minor element Ti (Fig. 2)

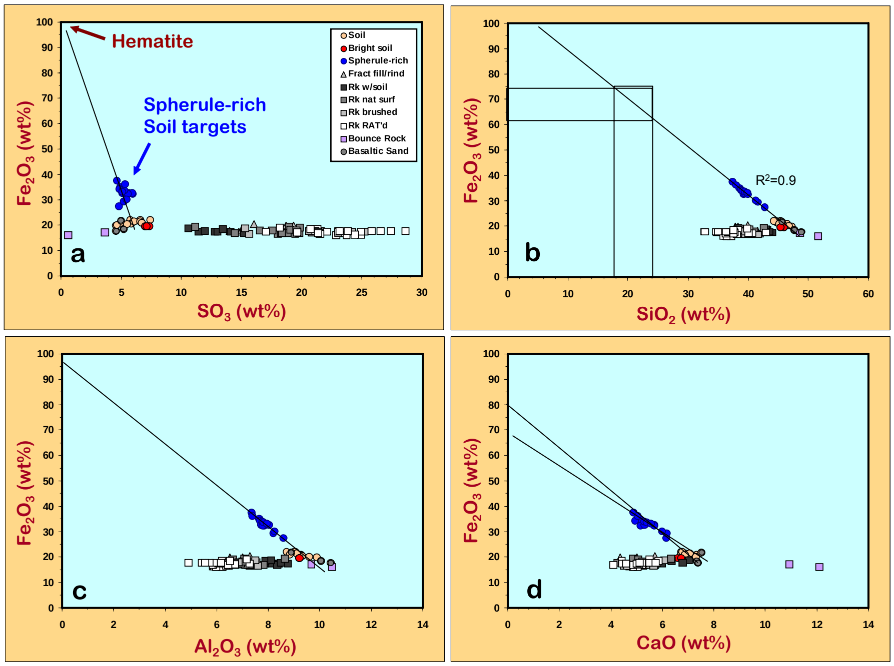

Figure 1. (a) SO_3 vs. Fe_2O_3 suggests the possibility that spherule-rich targets are a mixture of typical soil components and hematite. Likewise for Al_2O_3 (c) and nearly so for SiO_2 (b). However, the trend for CaO vs. Fe_2O_3 (d) does not extrapolate to hematite. Lines in (b) show range of SiO_2 that would be consistent with CaO and non-hematite components.

do not form trends with Fe_2O_3 that extrapolate to hematite; instead these trends extrapolate to values of 60-80% Fe_2O_3 when their concentrations go to zero. The rules of two-component mixing dictate that, unless these elements are dominated by some minor component or are otherwise variable in concentration in the endmembers, the Fe-rich endmember can not be pure hematite. A mass-balance model can be constructed that computes the composition of the spherules at some point along the trend line, and a common approach is to extrapolate the composition to the point at which the concentration of some element goes to zero. Given some assumptions about the composition of the average soil endmember, the average spherule composition by this model is found to be approximately as shown in Table 1 at the point at which the concentration of one or more element(s) is driven to zero or negative. The corresponding Fe_2O_3 concentration at this point is in the range of 58-72 wt.%, with the exact value depending on assumptions of the model.

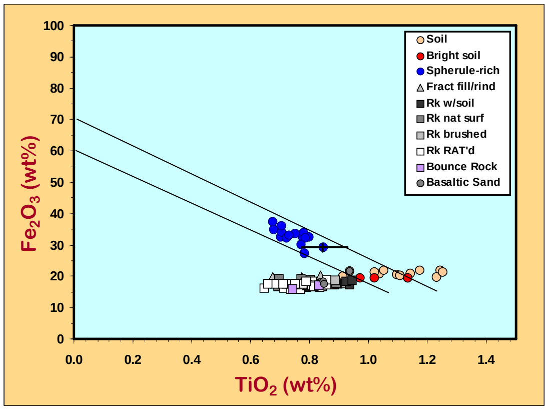

Figure 2. Although the uncertainty for TiO_2 is greater than for CaO, TiO_2 vs. Fe_2O_3 is another example of a trend that does not extrapolate to hematite.

We must consider, however, whether there might be something about the analysis or the target that causes this result other than the composition of the endmembers. A known and potentially significant effect is that of thin coatings on substrates, where the coating is thin enough to transmit the higher-energy X-rays but thick enough to absorb or partially obscure the lower-energy X-rays. Very fine soil grains or dust forming thicknesses of several tenths of a micron to ten microns on a substrate of significantly different composition can have the effect of partially obscuring the substrate differentially according to X-ray energies. A coating on substrate in this range means that the APXS will more effectively 'see' X-rays from the substrate such as those of Cr, Mn, and Fe, but the lower energy X-rays such as from Na, Al, Mg, and Si will reflect mainly the coating material.

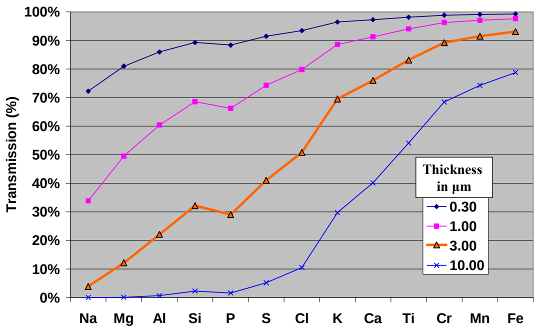

Figure 3. Transmission efficiency of element Kα X-rays through typical soil.

Table 1. Model Spherule compositions

Model	**1**	**2**	**1**	**2**	**thin-layer**
soil fraction	**0.68**	**0.68**	**0.75**	**0.75**	**model**
SiO_2	23.2	23.7	16.9	17.9	20.9
TiO_2	0.04	0.09	-0.25	-0.17	0.12
Al_2O_3	4.18	4.28	2.77	2.95	4.86
Cr_2O_3	0.00	0.12	-0.12	0.05	0.03
Fe_2O_3	**57.9**	**60.2**	**68.8**	**71.6**	**63.9**
MnO	0.08	0.13	0.00	0.07	0.02
MgO	4.92	4.45	4.24	3.62	4.40
NiO	0.23	0.20	0.27	0.24	nd
CaO	1.52	2.12	0.00	0.88	1.13
Na_2O	2.06	2.02	2.02	1.98	1.44
K_2O	0.16	0.12	0.08	0.02	0.10
P_2O_5	0.74	0.68	0.71	0.63	0.40
SO_3	4.07	1.32	3.61	-0.28	2.31
Cl	0.85	0.53	0.91	0.46	0.21

All Fe listed as Fe_2O_3.

Model 1 uses an average of 16 typical soil compositions as the soil endmember; model 2 uses an average of 3 bright, SO_4-rich soils. Thin layer model (Col. 5) uses X-ray transmission factors [Fig. 3] to model the spherule component as hematite plus a thin layer (3 µm) of soil on pure hematite.

Using a set of X-ray transmission factors calculated from tabulated X-ray absorption coefficients [10; see Fig. 3], we calculated the 'apparent' composition that would be seen by the APXS if the spherules were pure hematite covered by a thin coating of bright (most dust-like) Meridiani soil. Comparing this hypothetical composition to the model spherule compositions shown in Table 1, we find that the hypothetical thin-coating composition calculated for a coating thickness of 3 µm is very similar for most elements. Those that differ the most are Al (high) and Na, P, and Cl (low) (see Table). The real situation is surely more complex, with grains of variable size forming coatings of variable thickness and cover. At ~3 microns, such grains are well below the limit of what can be seen with the MI.

Discussion: The mineralogy of the spherules has been evaluated using other methods, including Pancam VIS-NIR and Mini-TES spectra, and Mössbauer spectra.

Experiments conducted with the Mini-TES, which is sensitive to silicate components and would 'see' through micron-scale coatings, indicate that the spherules are purely hematite [6, 11]. Pancam results indicate that some spherules sitting in soil are coated whereas others are not [12].

Mössbauer spectra, which are sensitive to Fe-bearing mineralogy, also form trends similar to those seen in APXS data for spherule-rich targets [13], with extrapolation to hematite. However, the extrapolation is long and could permit 5-10% pyroxene, especially if the pyroxene contains some Mg. The Mössbauer data have nothing to say about potential Al-silicate components. Perhaps the most compelling argument that the spherules contain a siliciclastic component comes from extrapolation of the trend of areal percentage of spherules in the target, which is independent of X-ray transmission efficiency, vs. measured Fe_2O_3 concentration, as determined by Schneider et al., 2007 [9]. Nonetheless, the point of the calculations involving a potential thin layer of soil/dust is to show that X-ray transmission efficiency could produce an effect that mimics the presence of a siliciclastic component in the spherules similar to that inferred from element-element trends among the spherule-rich soil targets. The abundance of spherules in outcrop targets, as in RAT-grind exposures, is too low (0-3%, average ~1%) to see the effects of spherules on compositional variations in different rock targets.

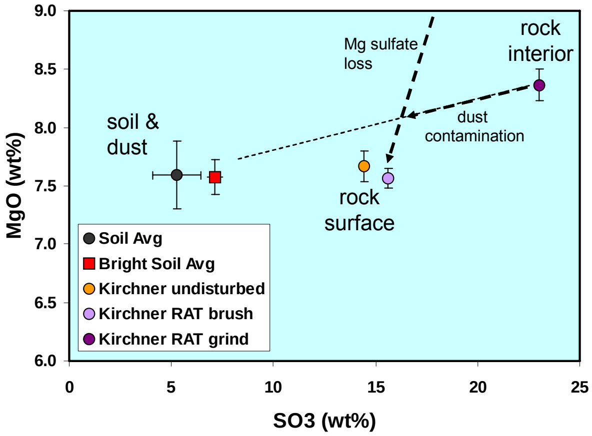

Figure 4. Conceptual representation of potential effects of (1) dust contamination and (2) sulfate loss to produce the rock undisturbed-surface and brushed compositions.

Sulfate-rich Sedimentary Rocks of the Burns Formation: The compositions and compositional variations of sulfate-rich rocks of the Burns formation have been well determined by analyses done on the interiors of rocks following RAT grinds [5]. Some 25 such analyses have been done to date. To assess the possibility that rock exteriors are altered relative to interiors, several sets of analyses have been done that include sequential analyses with IDD instruments on the undisturbed rock exterior, a RAT-brushed surface, and an interior surface following a RAT-grind. These sets of analyses show rock exteriors to be significantly depleted of SO_3 relative to the interiors, and variably depleted in Mg, Fe, and Ca. Exteriors appear to have high concentrations of Na, Cl, K, and P relative to rock interiors. One concept involving dust contamination and sulfate loss is illustrated in Fig. 4, and the relationships are shown for representative elements in Fig. 5.

The implications of these variations are significant. The trend indicated in Fig. 4 as dust contamination (or incomplete removal of soil/dust during brushing with the RAT) could also be explained as preferential removal of soft sulfates relative to more resistant siliciclastic components by eolian sand blasting. Loss of sulfate minerals at rock exteriors could represent interaction of highly soluble sulfate minerals with tenuous atmospheric water vapor. Likewise, the enrichment of Na and Cl seems consistent with concentration perhaps by leaching followed by evaporative deposition at the weathering surface. The slight concentration of K and P may be explained by a related observation from Mössbauer data taken on nearby soils, which, without exception, are devoid of jarosite. What may be happening is that jarosite, once exposed at the rock surface, is unstable and with the slightest amount of atmospheric water vapor, hydrolyzes and forms a ferric oxide, which then adsorbs K and P released when jarosite breaks down.

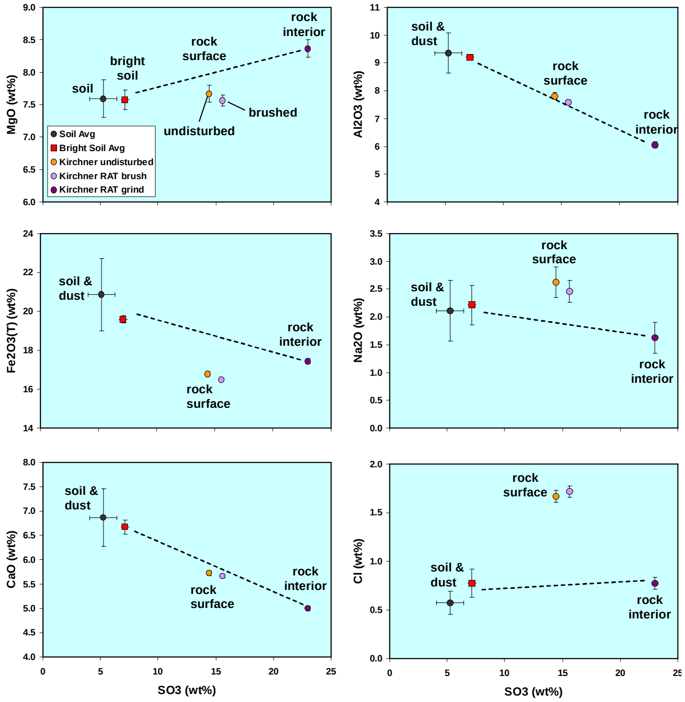

Figure 5. Compositional variations in a natural and RAT-brushed rock surface compared to the rock interior and soil/dust.

Unfortunately, since the Mössbauer spectrometer 'sees' considerably deeper into the rock, coordinated spectra taken on rock surfaces and even on RAT-brushed surfaces cannot be compared directly with the APXS data as long as the rock coatings are thin relative to the depth of penetration of the Mössbauer (hundreds of microns to millimeters). Thus we rely on the APXS data to understand chemical variations at rock surfaces. As with the spherules, however, we must also consider the possible effects of thin layers in causing some of these apparently systematic chemical variations.

Modeling the composition of sulfate-rich outcrop rock with a thin layer of soil or dust provides a straightforward test of the possible effects of differential X-ray transmission efficiency in causing what appear to be systematic compositional variations.

Using the same example as shown in Fig. 5 (Escher_Kirchner, located within Endurance crater and analyzed with the IDD during sols 213-219), we calculated the 'apparent' composition that the APXS would measure if coated with a thin layer of bright, dusty soil. The result is that layers of 2 and 3 micron thicknesses bracket the compositions of many elements as measured on the natural and brushed rock surfaces, and they reproduce the sense of variation from the rock-soil mixing lines shown in the figures (see Fig. 6). Among the major elements most affected are S, Al, and Si. From the X-ray transmission effect along, S is reduced from 23 wt% SO_3 to between 14 and 16 wt.%. Al lies slightly above the mixing line, and Mg, Ca, and Fe fall below it. Only Na, Cl, and perhaps K and P still show systematic enrichment beyond what might be attributed to this effect.

Discussion: As with the spherules, the real situation on the micron scale at the rock surface is likely to be complex. In some of the other analysis sets, including Yuri_Gagarin (sols 400-405), and Olympia_Ted (sols 679-695), the brushed-rock composition is significantly richer in SO_3 than is the case with Escher_Kirchner; in those cases, the RAT brushing may have been more effective in removing surface soil & dust components. Nonetheless, this example suggests that the effects of differential X-ray transmission efficiency should be considered as a viable contributor to these chemical trends.

Although the model compositions in this exercise lie surprisingly close to the measured compositions, it is still possible that the physical/chemical weathering inferred from the data taken at face value occurs. As shown by [14], Pancam color variations on outcrop surfaces correspond to the extent to which surfaces are exposed to wind-driven abrasion, with vertical surfaces differing from horizontal ones. Color differences may correspond in part to reactions such as the inferred hydrolization of jarosite to form ferric oxide. As with the spherules, further understanding of the possible effects of thin surface coatings should be pursued with laboratory simulations and careful analysis of the data obtained on the surface of Mars.

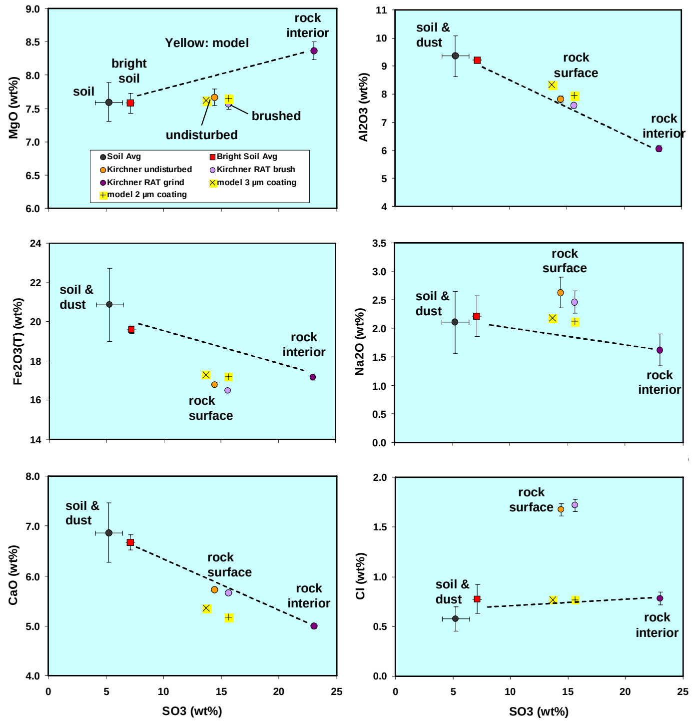

Figure 6. Compositional variations in a natural and RAT-brushed rock surface compared to model compositions (yellow) calculated assuming 2 µm and 3 µm thin layers of soil/dust on rock.

Acknowledgements: The APXS and other instrument teams are thanked, along with the full Engineering and Science teams of the Opportunity Rover for their dedication to MER. Funding for this work was through NASA support of the MER Athena science team. The first author claims sole credit for any computational errors.

References: [1] Rieder et al., 2004, *Science* **306**, 1746-1749; [2] Gellert et al., 2007, *J. Geophys. Res.*, in press; [3] Yen et al., 2005, *Nature* **436**, 49-54; [4] Brückner et al., 2007, this conference; [5] Clark et al. (2005) *EPSL* **240**, 73-94; [6] Calvin et al., 2007, this conference; [7] Jolliff et., 2005, *LPS* **36**, #2269; [8] Jolliff et al., 2007, *LPS* **38,** #2279; [9] Schneider et al., 2007 *LPS* **38**, #1941; [10] XCOM: Photon Cross Sections Database, NIST Standard, Ref. Database 8 (XGAM); [11] Christensen et al., 2004, *Science* **305**, 837-842; [12] Weitz et al., 2006, *J. Geophys. Res.* **111**, S04; [13] Morris et al., 2006, *J. Geophys. Res.* **111**, S15; [14] Farrand et al. (2007), *J. Geophys. Res.*, in press.