COMPOSITION OF MERIDIANI HEMATITE-RICH SPHERULES: A MASS-BALANCE MIXING-MODEL APPROACH.

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Introduction: One of the great surprises of the Mars Exploration Rovers (MER) mission is the discovery at Meridiani Planum that the surface hematite signature observed from orbit is attributable largely to a surface enrichment of hematite-rich spherules, thought to be concretions, that have weathered out of rocks similar to the underlying sulfate-rich rock formation [1]. A strong hematite signature has been observed by the Mini-TES [2] and by in-situ measurements of spherule-rich targets by the Mössbauer spectrometer (MB) [3] and the alpha-particle X-ray spectrometer (APXS) [4]. The Mini-TES *derived* spectrum of spherule-rich targets on the plains is consistent with nearly pure coarse-grained hematite, with perhaps as little as 5-10 areal % of other components [2]. The occurrence and abundance of the spherules as the bearer of the widespread hematite signature observed by MGS TES over much of Meridiani Planum is significant for global remote sensing, and their occurrence as concretions in the outcrop lithology is significant for the diagenetic history and role of water in the formation of the sedimentary rock formation [5].

Setting: In the outcrop, the spherules make up only 1-2% of the volume of the rocks in which they occur, judging by their abundance in RAT'd surfaces. However, in some locations loose spherules are concentrated in depressions, and on the plains, they are concentrated as a lag deposit because they are hard and relatively resistant to wind abrasion, and too dense to be moved easily by the wind. In RAT'd exposures, cross sections of the spherules appear to be quite homogeneous.

Combined APXS and Mössbauer measurements include the *Berry Bowl* (Sols 46-48) in Eagle Crater and on the Plains at *Jack Russell* (Anatolia trench site, Sol 80), *Fred Ripple* (Sol 91), and *Leah's Choice* (Sol 100). Each of these were targets significantly richer in spherules and rock fragments than typical soil, and the corresponding results reflect very hematite-rich targets (MB) and high concentrations of total Fe (APXS; Fig. 1).

Although each of these occurrences represent mixed targets including soil, spherules, and rock or rock fragments, the targets can be evaluated in terms of the proportions of components using Pancam and microscopic images. The *Berry Bowl* experiment was designed to determine the composition of the spherules by comparing the analysis of a spherule-rich target with an adjacent spherule-free rock surface; however, the experiment was complicated by the presence of a thin layer of soil in the "bowl." Still, the *Berry Bowl* experiment can be modeled as a three-component system. The *Jack Russell* target, which had the highest Fe(total) concentration measured by the APXS, had a co-located microscopic image well-suited for determining the areal proportions of components. This abstract presents a model for determining the composition of the spherules by combining the proportions of components determined from the microscopic image with a mass-balance calculation, showing as an example the results for *Jack Russell*. The same analysis for the *Berry Bowl* target yields similar results for Fe_2O_3. According to the mass-balance model and taking the APXS compositions at face value, the spherules are not pure hematite, but they instead contain a significant fraction (40-50% by weight) of other components.

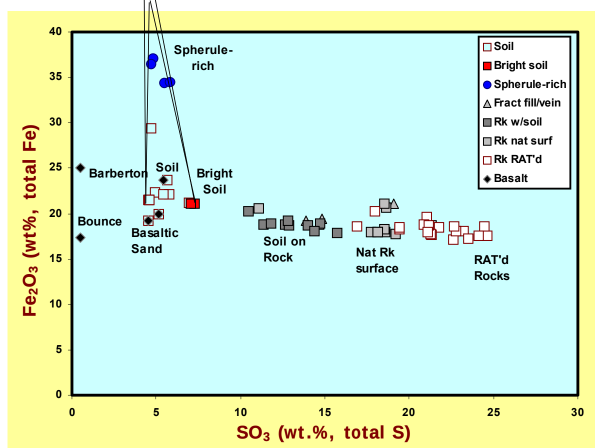

Figure 1. Fe_2O_3(T) vs. SO_3(T), APXS. Lines projecting to high Fe_2O_3 illustrate a 2-component mixing model.

Method: The model presented here involves (1) spatial analysis of the microscopic image of the *Jack Russell* target, (2) conversion of components from area proportions to mass percent using likely component densities, and (3) a compositional mass-balance calculation using the APXS data. Results are presented for a two-component solution (soil-spherules) and a three component solution (soil-spherules-rocks). In the three component model, the rock fragment component can be represented by any mixture of basalt and evaporite rock compositions. The data for Fe(T) as Fe_2O_3 are shown in Figure 1, where the lines represent the concept of two-component mixing. Figure 2 shows just the data for Fe^{3+} as Fe_2O_3, determined from Mössbauer results [3], and illustrates the concept of three-component mixing. The possible solutions indicated are the most plausible ones based on the model described here.

Figure 3 shows the *Jack Russell* target. Spherules range from about 1 to 4 mm diameter and, along with spherule fragments, take up some 15 to 30 % of the area of the scene. Fine soil makes up 60% of the scene and the total of spherules plus rock fragments is 40%. By comparison to similar targets that have Pancam multi-

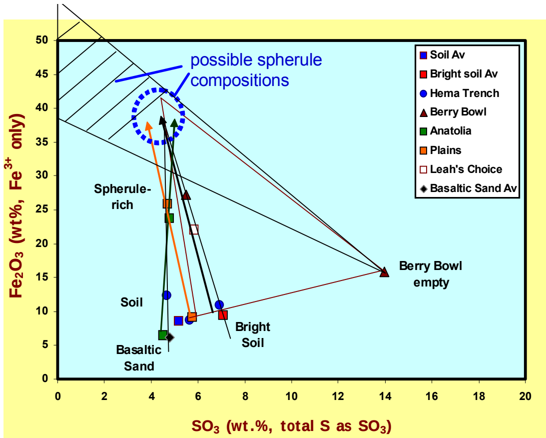

Figure 2. Fe_2O_3 [Fe^{3+}/Fe(T), MB × Fe_2O_3(T), APXS] showing selected compositions and graphical representation of three-component mixing model.

spectral coverage, the rock fragments consist of both the evaporite outcrop lithology and basalt [6].

The distribution of spherules within the field of view of the in-situ instruments is a potential source of error. The APXS working diameter is 2.5 cm, but most of the signal comes from a somewhat smaller area than this. Taking five ~1.5 cm diameter circles and subsampling the 20% distribution shown in Fig. 3b gives an average of 21± 2% coverage.

The mass-balance equation for three components is:

$$C_{sph}\times mf_{sph} + C_{rk}\times mf_{rk} + C_{soil}\times mf_{soil} = C_{mix}$$

where C is the concentration (wt%) of an element, *mf* is the mass fraction of the component, and *sph*=spherule, *rk*=rock, and *mix*=*Jack Russell*. Rearranging the equation allows solving for C_{sph}:

$$C_{sph} = (C_{mix} - (C_{rk}\times mf_{rk} + C_{soil}\times mf_{soil})) / mf_{sph}$$

The conversion from area (assume area=vol) to mass fraction assumes densities of 1.5 g/cc for soil, 2.5 g/cc for rock, and 4.4 g/cc for spherules.

Results and Discussion: Taking the APXS results at face value, the concentration of Fe_2O_3 in the spherules may be calculated using proportions of components constrained by the microscopic image (Fig. 3). Results are shown in the table below.

Table. Mass-balance mixing model results for *Jack Russell*

Case	model	area, sph	mf, sph	Fe_2O_3 sph	Evap:Bas
1	2-Comp	15 vol%	0.341	54 wt%	
2	2-Comp	20 vol%	0.423	45 wt%	
3	2-Comp	30 vol%	0.527	36 wt%	
4	3-Comp	15 vol%	0.302	60 wt%	1:1.3
5	3-Comp	20 vol%	0.386	48 wt%	1:1
6	3-Comp	30 vol%	0.534	37 wt%	2:1

The ratio of evaporite to basalt in the rock component can be varied, but is constrained by the need to prevent negative S concentrations in the spherule composition, e.g., Case 4.

Note that more area coverage by spherules corresponds to lower spherule Fe_2O_3 content.

There are several important caveats. One is that the target is heterogeneous and involves several mm of topography, thus violating the ideal conditions for the APXS measurement. Also, the effective sampling depth varies as a function of X-ray energy (on the order of 10 µm at the low-energy range and 50 µm at high-energy, e.g., Fe [4]). Thus if the spherules in the *Jack Russell* target have dust coatings on the order of 10-40 µm thick, the spherule composition would not have been measured directly. Lab measurements on heterogeneous targets with simulated mass and Z distribution such as those measured on Mars will help to constrain potential sources of measurement error. The potential effects of coatings on spherule and fragment surfaces are allayed somewhat by the observation of Pancam multispectral data that spherules perched on the soil and exposed to wind abrasion are less likely to be coated [6].

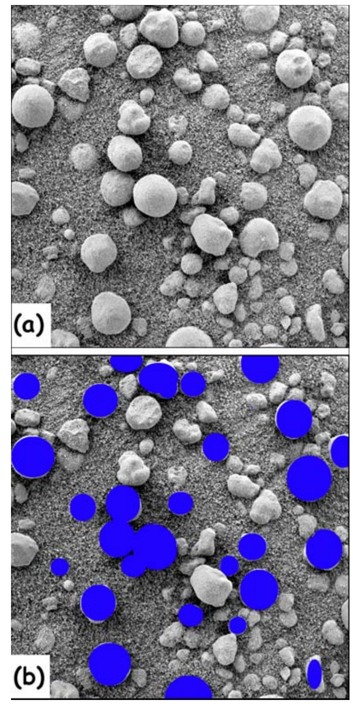

Figure 3. Jack Russell, sol 80 MI ~3 cm across. In (b), blue covers 20 % of the area.

The mass-balance model indicates, in addition to Fe_2O_3, significant FeO (Fe^{2+}) in the spherules (9-11 wt%), and this is not consistent with Mössbauer data. Here, the *Berry Bowl* experiment provides a constraint. In the *Berry Bowl*, spherules make up some 25-30% of the area, and a three-component mass-balance model indicates spherule Fe_2O_3 concentrations of 42-47 wt%, but only 3-4 wt% FeO. In the case of *Jack Russell*, the non-Fe_2O_3 component has a basaltic composition, but depleted in CaO, whereas in the model for the *Berry Bowl*, the non-Fe_2O_3 component of the spherules is enriched in silica and other oxides relative to FeO.

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References: [1] Squyres et al., *Science* **305**, 2004; [2] Christensen et al., *Science* **305**, 2004; [3] Klingelhöfer et al., *Science* **305**, 2004; [4] Gellert et al., *Science* **305**, 2004; [5] McLennan et al., *LPS* **36**, this vol., 2005 [6] Weitz et al., *LPS* **36**, this vol., 2005.