COMPOSITIONAL CONSTRAINTS ON HEMATITE-RICH SPHERULE (BLUEBERRY) FORMATION AT MERIDIANI PLANUM, MARS.

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Introduction: Meridiani Planum was chosen as the landing site for the Mars Exploration Rover Opportunity partially based on Mars Global Surveyor Thermal Emission Spectrometer data indicating an abundance of hematite [1]. Hematite often forms through processes that involve water, so the site was a promising one to determine whether conditions on Mars were ever suitable for life [1,2]. Opportunity struck pay dirt; it's Miniature Thermal Emission Spectrometer (Mini-TES) and Mössbauer Spectrometer (MB) confirmed the presence of hematite in sulfate-rich sedimentary beds and in lag deposits [3].

Meridiani Planum rocks contain three main components: silicate phases, sulfate and possibly chloride salts, and ferric oxide phases such as hematite [2]. Primary igneous phases are at low abundance [4, 5] despite the basaltic origin of the protoliths. Jarosite, an alkali ferric sulfate, was identified by Mössbauer. Some of the hematite is contained in the spherules, and some resides in finer grains in outcrops [2, 5].

Mössbauer and Mini-TES data indicate that hematite is a dominant constituent of the spherules [5-7]. Panoramic Camera (Pancam) and Microscopic Imager (MI) images of spherule interiors show that hematite is present throughout [2]. The exact composition of the spherules is unknown. Mini-TES only identifies a hematite signature in the spherules; any other constituents have an upper limit of 5-10% [7]. The MB data are consistent with the spherules being composed of only hematite [5].
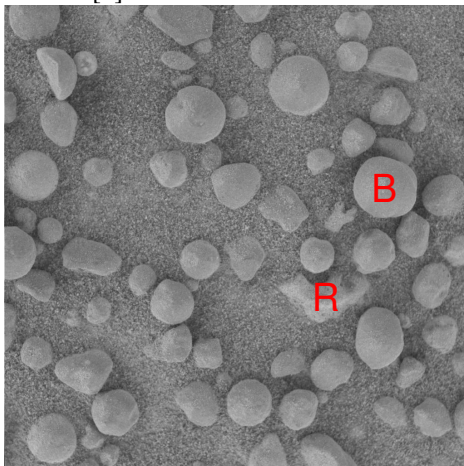

Fig. 1: MI view of undisturbed soil Caviar (sol 369). Blueberries (B) and rock fragments (R) are visible.

The spherules, or "blueberries" are ubiquitous (Fig. 1). Their spherical geometry, uniform spatial distribution, and lack of internal structure lead to the conclusion that they are diagenetic concretions formed in the bedrock in stagnant or slow-moving groundwater [2]. However, the genesis of these concretions remains poorly understood.

Three formation mechanisms are possible for concretions: inclusive, replacive, and displacive. The first would result in a distinct spherule composition compared to the other two. If hematite comprises 40-70% of a spherule, the spherule likely formed by filling in available pore space plus replacing soluble evaporite minerals, a replacive-inclusive mechanism [8]. If correct, included grains are very fine because they cannot be identified in MI images [2, 8]. If hematite comprises more than 70% of a spherule, McLennan et al. [8] suggest that the spherule pushed insoluble siliciclastic material aside as it grew, a displacive mechanism. A lack of disturbances in outcrop layering at spherule boundaries argues against a displacive mechanism [8].

Following [9, 10], we used Alpha Particle X-ray Spectrometer (APXS) data to constrain the spherule formation process. Spherules lie on substrates and cannot be analyzed individually; we can only evaluate average blueberry compositions using mixing models.

Methods: We compared APXS data for spherule-free soils with soils having spherules on the surface for select elements. In the simplest scenario – pure hematite spherules lying atop basaltic soils – element vs. FeO diagrams should show linear mixing relationships. We observe this for Al vs. Fe – a regression line fit to the spherule-rich soils passes through the field of basaltic soils and pure hematite (Fig. 2a). This implies that either the spherules are pure hematite [*e.g.* 5], or that included rocky material has a composition close to a mixing line between basaltic soil and pure hematite. Other element-Fe diagrams show this simple interpretation is incorrect. Thus, a pure replacive model for spherule growth cannot be correct, and the spherules must contain other phases. We determined the fractional area of spherules in MI images of selected soils. Regression of FeO vs. spherule area extrapolates to ~64% FeO (equivalent to ~71% Fe_2O_3) for 100% spherules (Fig. 2b), again suggesting the spherules include non-hematitic material.

If the spherules grew inclusively, chemical data should reflect a compositional component of the included grains. We tested several models of possible included "rock" compositions, only two of which are discussed. Model 1 is average Meridiani outcrop rock interior normalized to eliminate SO_3 and Cl. Model 2 is average outcrop rock interior corrected to remove probable soluble salts – Na- and Mg-chlorides, jarosite, and Mg- and Ca-sulfates. Model 2 was constrained by the average MB-determined mineralogy of outcrop rock interiors. The model compositions, and mixing lines with hematite, are shown in Fig. 2c.

Discussion and Conclusions: None of our models can easily explain the spherule-rich soil data. For a small rocky component contained in blueberries, the mixing models are not sufficiently different from mixing pure hematite to significantly change mixing vectors for many elements (Fig. 2c); all tested models can explain the Al-Fe trend. Potentially Ca-Fe is the most diagnostic because the spherule data plot below a pure hematite-basaltic soil mixing line. Inclusion of ~30% insoluble rock (low in Ca due to $CaSO_4$ loss) in hematite spherules can adequately explain the spherule soil data (Fig. 2d). However, the insoluble rock is high in SiO_2, and results in no match for the Si-Fe trend.

We are left with two possibilities. The first is that there is an included rock component in the blueberries, but that it is unlike those tested in our models. We tested the most plausible rock compositions based on our knowledge of Meridiani materials; other models would be increasingly *ad hoc*.

The second is that there is no rock component [*cf.* 5]. In this case, the blueberries formed replacively or displacively and are composed of pure hematite. This leaves unexplained discrepancies between the CaO content of spherule soils and mixtures of basaltic soil and pure hematite (Fig. 2d), and the fractional area of spherules vs. FeO content that extrapolates to ~71% Fe_2O_3 for 100% spherules (Fig. 2b). These discrepancies might be explained by dust or chemical coatings on the blueberries [11], but the data seem inconsistent with this. A dust coating would shift the compositions above a hematite-soil mixing line, but the CaO data lie below this (Fig. 2d). Lighter elements, such as Al_2O_3, should be more susceptible to dust contamination, yet the Al_2O_3 data fit the hematite-soil mixing model very well (Fig. 2a).

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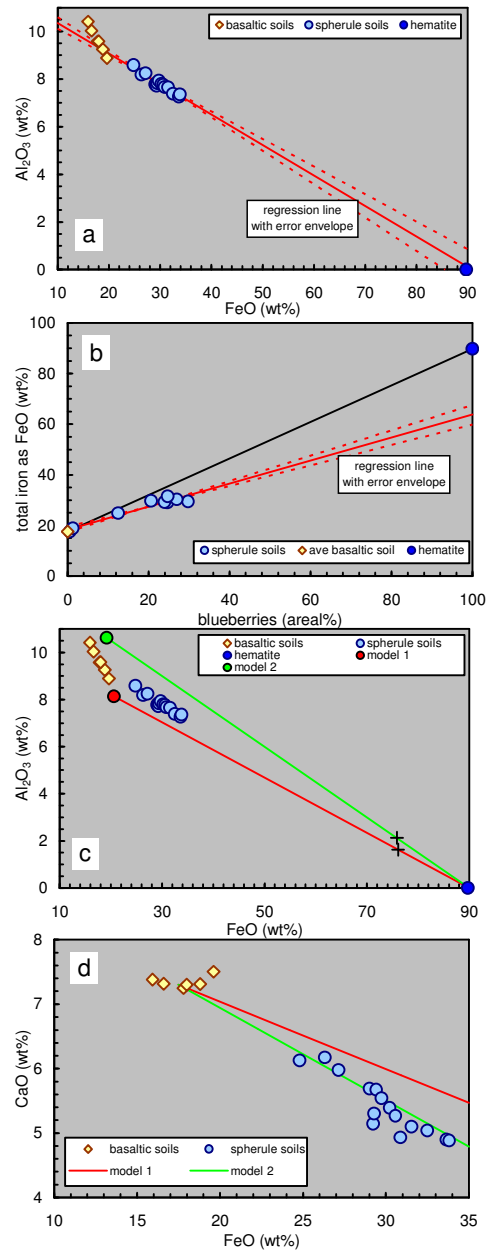
Fig. 1: (a) Regression of spherule soils for Al-Fe passes through pure hematite and basaltic soils. (b) Regression of spherule soils for FeO-% blueberries implies spherules are not pure hematite. (c) Two model "rock" compositions for possible material included in hematite spherules, and mixing lines with hematite; plus signs are mixtures of 20% "rock" and 80% hematite. (d) Model 2 can fit the CaO vs. FeO trend for spherule soils.