

**SYNTHETIC (HYDROTHERMAL) HEMATITE-RICH MARS-ANALOG SPHERULES FROM ACID-SULFATE BRINES: IMPLICATIONS FOR FORMATION AND DIAGENESIS OF HEMATITE SPHERULES IN OUTCROPS AT MERIDIANI PLANUM, MARS.** D. C. Golden<sup>1</sup>, D. W. Ming<sup>2</sup>, R. V. Morris<sup>2</sup>, and T. G. Graff<sup>3</sup>. <sup>1</sup>ESCG-Hamilton Sundstrand, Houston, TX; <sup>2</sup>Astromaterials Research and Exploration Science Directorate, NASA Johnson Space Center, Houston, TX ([d.c.golden@nasa.gov](mailto:d.c.golden@nasa.gov)); <sup>3</sup>Arizona State University, Tempe, AZ.

**Introduction:** The Thermal Emission Spectrometer (TES) onboard the Mars Global Surveyor (MGS) orbiter discovered a large area at Meridiani Planum (MP) covered with the Fe-oxide hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) [1,2]. This discovery and favorable landing site characteristics led to selection of MP as the landing site for the Opportunity Mars Exploration Rover (MER) [3]. The Athena science payload onboard the Opportunity rover identified hematite-rich spherules (mean spherule diameter  $\sim 4.2 \pm 0.8$   $\mu$ m) embedded in S-rich outcrop rock and also as lag deposits of whole and broken spherules [4,5,6,7,8,9]. Although the chemical and mineralogical compositions of spherules are not fully constrained, Mössbauer spectrometer (MB) Miniature Thermal Emission Spectrometer (Mini-TES) and chemical analyses from the Alpha Particle X-Ray Spectrometer (APXS) are consistent with a hematite mineralogical composition and an oxide bulk chemical composition consisting of Fe<sub>2</sub>O<sub>3</sub>. MGS-TES, also provides an important constraint that emission from the hematite-rich spherules is dominated by emission along the crystallographic c-axis [1,2,10,11].

The formation of hematite-rich spherules with similar chemical, mineralogical, morphological, and crystallographic properties to the MP spherules is rare on Earth, to date, only two natural analogs have been proposed; one from Utah (Navaho Concretions) and the other from Mauna Kea, Hawaii [12,13]. In this study, we synthesized in the laboratory hematite-rich spherules using conditions that may have existed on Early Mars [14] and compared their properties to those for MP hematite spherules of Mars and the analog spherules from Utah and Mauna Kea in order to assess their relative merit as MP hematite spherule analogs. Such comparisons yield clues to the formation pathway for MP spherules.

**Synthesis of Hematite-Rich Spherules:** Aliquots ( $\sim 15$  mL each) of a solution containing 0.54 M MgSO<sub>4</sub>, 0.3 M Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and 0.5 M FeCl<sub>3</sub> were transferred into 23 mL Teflon-lined steel hydrothermal reaction vessels. The vessels were sealed in ambient air and separately heated at 150 °C for 4, 16, 24, or 72 hours and 200 °C for 24 hours to form products HSDC1 through HSDC5. After cooling to room temperature, supernatants were decanted and reaction products were washed with distilled water to remove soluble salts and then freeze-dried. Mineralogical, chemical, and spectral properties of spherule precipitates were determined by X-ray diffraction analysis (XRD), electron microprobe analysis (EMPA), transmission electron microscopy (TEM), Mössbauer spectroscopy (MB), and thermal emission spectroscopy (TES). We also analyzed several spherical Navaho concretions by these techniques

**Characterization of Hematite-Rich Spherules:** The mineralogy of the precipitates formed from the synthetic brine solutions depended on the temperature (150 or 200 °C) and heating time (4, 16, 24, or 72 h) (Table 1). Hydronium jarosite was the primary phase that formed after 4 h of forced hydrolysis at 150 °C (sample HSDC1). Both hydronium jarosite and hematite formed after a reaction time of 16 h at

150 °C (sample HSDC2). The quantity and XRD crystallite size of the hematite were  $\sim 41\%$  and  $\sim 13$  nm, respectively, from Rietveld analysis. The crystallite size of the hydronium jarosite was smaller ( $\sim 187$  nm) than the size in the 4 hr experiment. With increasing reaction time and temperature, the quantity and crystallite size of the hematite increased to maximum values of  $\sim 87\%$  and  $\sim 44$  nm, respectively, for the 24 h hydrothermal synthesis at 200 °C (sample HSDC5). The quantity and crystallite size of the hydronium jarosite decreased through sample HSDC3 (24 h at 150 °C) with increasing reaction time, where the values were 43% and 91 nm, respectively. Hydronium jarosite was not detected by XRD in samples HSDC4 and HSDC5. The disappearance of hydronium jarosite corresponds to the appearance of hydronium alunite in samples HSDC4 and HSDC5 (Table 1). The quantity and crystallite size of hydronium alunite were  $\sim 13\%$  and 70-80 nm, respectively.

Hematite spherules and hydronium jarosite contain approximating 4 wt % and 22 wt % water as inferred from EMPA totals less than 100%. This suggests that Fe-rich-spherules are hydrohematite. The high H<sub>2</sub>O content is also evident in the TES spectra (not shown).

The hematite-rich spherules exhibit a radial growth pattern consisting of fibrous hematite with the c-axis of particles aligned along the elongation direction of the hematite fibers (i.e., elongated along the [001] direction, TEM data not shown). A manifestation of this relationship is the absence of an emissivity minimum near 390 cm<sup>-1</sup> (Table 2). This feature is also absent in hematite with a platy morphology [10]. Comparison of the synthetic spherules with natural analogs show that the synthetic and Mauna Kea spherules are more similar to MP hematite spherules, than the Navaho concretions, which are goethite plus  $\alpha$ -quartz (Table 2).

**Implications for Hematite Spherule Formation at Meridiani Planum:** The synthetic hematite spherules have many characteristics in common with the MP hematite spherules, including hematite mineralogy, spherical morphology, association with jarosite, and absence of a hematite emissivity minimum near 390 cm<sup>-1</sup>, an important characteristic determined for MP hematite from Martian orbit [2]. There is however, a key difference: Meridiani hematite spherules are larger than our synthetic products. It is possible that we could form larger synthetic spherules, similar to the size of MP spherules, through a synthetic system that would continuously supply the starting solution composition over a sufficient length of time. The results of this study support the conclusions of [15] that the spherules at MP are diagenetic hematitic concretions that appear to have formed fairly rapidly under near isotropic fluid flow conditions by the breakdown of jarosite during basin recharge. However, our experiments and the Mauna Kea spherules [13] suggest that hydrothermal systems may be necessary for hematite spherule formation. Such crystallographically oriented spherulitic growth can form by growth front nucleation [16], where preferential growth along hematite [001] direction is a

result of inhibited growth along other directions due to strong bidentate  $\text{SO}_4^{2-}$  adsorption [17]. From this work, we infer that the hematite spherules in MP Mars may have formed under mild hydrothermal conditions when warm solutions moved through the Meridiani sediments, possibly from acid-sulfate groundwater heated by a near surface magmatic heat source.

**References:** [1] Christensen P.R. *et al.* (2000) *JGR*, 105, 9623-9642. [2] Christensen P.R. *et al.* (2001) *JGR*, 106, 23823-23871. [3] Golombek, M.P. *et al.* (2003) *JGR*, 108, 8072. doi:10.1029/2003JE002074. [4] Squyres S.W. *et al.* (2004) *Science* 306, 1731-1733. [5] Squyres S.W. *et al.* (2006) *JGR*, 111, E12S12, doi: 10.1029/2006JE002771. [6] Christensen P.R. *et al.* (2004) *Science* 306, 1733-1739. [7] Klingelhofer G. *et al.* (2004) *Science*, 306, 1740-1745. [8] Herkenhoff *et al.* (2004) *Science*, 306, 1723-1726. [9] Morris *et al.* (2006) *JGR* 111, E12S15, doi: 10.1029/2006JE002791. [10] Lane, M.D. *et al.* (2002) *JGR*, 107, 5126. [11] Glotch *et al.* (2006), *JGR* 111, E12S03, doi 10.1029/2005JE002672. [12] Chan M.A. *et al.* (2004) *Nature* 429, 731-734. [13] Morris, R.V. *et al.* (2005) *EPSL*. 240, 168-178. [14] Golden *et al.* (2007) *LPSC XXXVIII*, Abstract # 2257 CD-ROM. [15] McLennan S.M. *et al.* (2005) *EPSL* 240, 95-121. [16] Granacy, L. *et al.* (2007) *Physics Review Letters*, 98, 10.1103/PhysRevLett.98.035703. [17] Sugimoto, T. and Wang, Y. (1998) *J. Colloid Interface Sci.*, 207, 137-149.

Table 1. Formation conditions and analyses of synthetic hematite spherules.

Sample	HSDC1	HSDC2	HSDC3	HSDC4	HSDC5
Time (h)	4	16	24	72	24
T (°C)	150	150	150	150	200
Phases	HJ	HJ>Hm	Hm>HJ	Hm>HA	Hm>HA
FWHM	--	0.65	0.64	0.46	0.19
EMPA Chemistry (%)					
Phase	HJ	Hm	Hm	Hm	Hm
Al <sub>2</sub> O <sub>3</sub>	5.3	0.84	0.61	0.62	0.61
Fe <sub>2</sub> O <sub>3</sub>	44.0	88.6	89.4	91.6	94.5
SO <sub>3</sub>	34.1	3.7	3.6	3.0	1.7
Total*	84.2	93.4	93.8	95.4	97.0

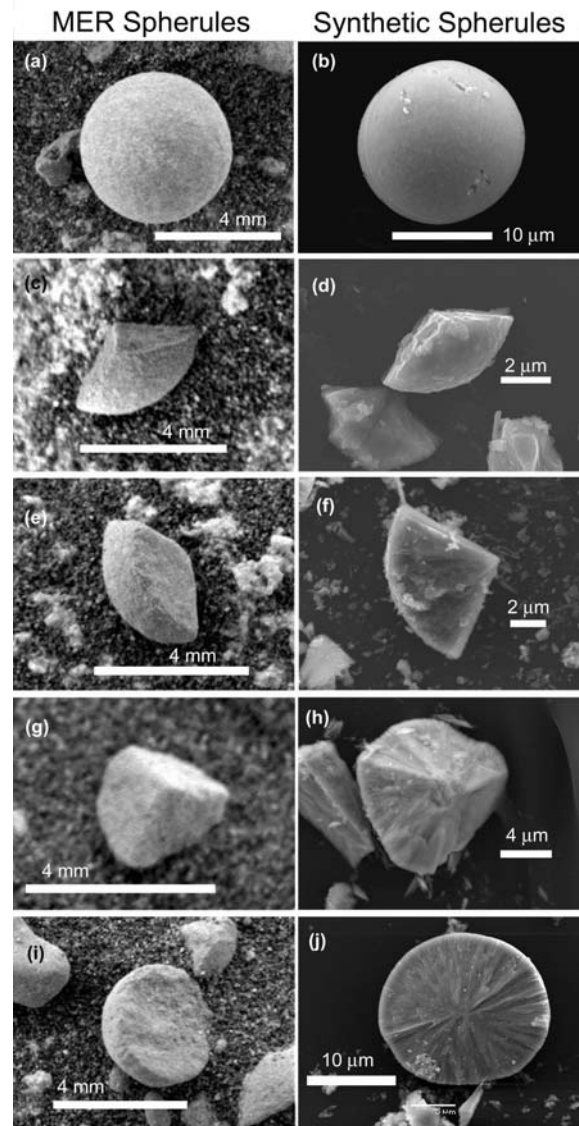
\*Includes trace components not reported here. HJ = hydronium jarosite, Hm = hematite, HA = hydronium alunite

Table 2. Comparison of properties of Navho Concretions, synthetic spherules (this study), Mauna Kea spherules, and Meridiani Planum spherules.

Property	Navaho Concretions	Synthetic Spherules§	Mauna Kea spherules†	MP spherules‡
Size	mm-cm*	5-20 µm	10-100 µm	~4.2 mm#
Fe <sub>2</sub> O <sub>3</sub> (wt %)	~35*	88-95	82-97	60-99
Fe-mineral	Goethite§	Hematite	Hematite	Hematite
Association	Qtz*	J+A	J+A	Sulfates (J)
Texture	Concentric	Radial	Radial	Radial
Fracture	Irregular§	Radial	Radial	Radial
TIR-emiss /C	No Hm§	yes	unknown	yes
TIR 1650 cm <sup>-1</sup>	No Hm§	yes	unknown	ND
Environment	Not acid sulfate*	Acid-sulfate	Acid-sulfate	Acid-sulfate

\*[12]; § this study; † [13]; ‡ [5]; # [15]; || [9]; Qtz = quartz, J = jarosite, and A = alunite.

Figure 1. Comparison of morphology of whole and broken spherules from MER MI images of hematite spherules from Meridiani Planum (a, c, e, g, and i) and SEM images of synthetic hematite spherules (b, d, f, h, and j). Fracture surface textures in both sets of spherules are consistent with a spherulitic (radial) growth.



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