SPHERULITIC GROWTH OF HEMATITE UNDER HYDROTHERMAL CONDITIONS: INSIGHTS INTO THE GROWTH MECHANISM OF HEMATITE SPHERULES AT MERIDIANI PLANUM, MARS.

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Introduction. Hematite-rich spherules were discovered embedded in sulfate-rich outcrop rock and as lag deposits of whole and broken spherules by the Opportunity rover at Meridiani Planem [1-6]. The Mars Global Surveyor (MGS) Thermal Emission Spectrometer (TES), which has a wider spectral range compared to the Mars Exploration Rover Mini-TES, provided an important constraint that hematite-rich spherules are dominated by emission along the crystallographic *c*-axis [7-10]. We have previously synthesized hematite spherules whose mineralogic, chemical, and crystallographic properties are strikingly similar to those for the hematite-rich spherules at Meridiani Planum [11]. The spherules were synthesized in the laboratory along with hydronium jarosite and minor hydronium alunite from Fe-Al-Mg-S-Cl acid sulfate solutions under hydrothermal conditions. The reaction sequence was (1) precipitation of hydronium jarosite, (2) jarosite dissolution and precipitation of hematite spherules, and (3) precipitation of hydronium alunite upon depletion of hydronium jarosite. The spherules exhibit a radial growth texture with the crystallographic *c*-axis aligned along the radial direction, so that thermal emission spectra have no hematite emissivity minimum at ~390 cm^{-1} similar to the emission spectra returned by MGS TES.

The objective of this paper is to expand on our initial studies [11] to examine the morphological evolution during growth of spherules starting from sub-micrometer crystals to spherules many orders of magnitude in size.

Synthetic Procedure and Analytical Methods: The experimental conditions and the run products for syntheses are described in [11]. Briefly, 15 mL aliquots of a solution containing 0.54 M $MgSO_4$, 0.3 M $Al_2(SO_4)_3 \cdot nH_2O$ (n ~ 18) and 0.5 M $FeCl_3$ were transferred into 23 mL Teflon-lined steel reaction vessels. The vessels were sealed in ambient air and heated at 150ºC for 4-24h or at 200ºC for 24h (forced hydrolysis). Products were washed with distilled water to remove soluble salts and freeze-dried. Freeze-dried precipitates were examined using a JSM 5910LV scanning electron microscope equipped with an IXRF energy dispersive X-ray spectroscopy (EDS) system. Spherules in various stages of evolution were imaged to represent the sequence from sub-micron to about 20 µm.

Spherical Growth Processes. Spherulitic growth is a nonequilibrium process in highly supersaturated solutions, commonly observed in a wide variety of natural and industrial materials [12-15]. Spherule formation is a fundamental crystallization process determined by kinetic parameters which operate under supersaturated conditions and does not depend on the type of material or their crystallographic symmetry. Hematite spherules are composites of smaller subunits of rods or fibers which are radially arranged from the growth point. The growth of spherule starts with random nucleation on a surface of a seed (a foreign particle, bubble, or a crystal of the same material), and then subunits of the spherule nucleate on the seed. Only the nuclei arranged with their c-axes perpendicular to the solid solution interface will penetrate the unstable diffusion layer, due to fast growth of the c-axial direction, protruding into the supersaturated zone as a finger. This process selects the radial growth along the fastest growing direction while the other crystallographic orientations are naturally suppressed because of their slow growth rate.

Spherulitic growth is common in nature, but the factors controlling it were poorly understood until recently [12, 14-16]. There are two growth types for spherules (Fig. 1). Type-1 polycrystalline spherulite structures [17] grow radially outward from a nucleation point, branching intermittently to maintain a space filling character. Growth along directions away from the center is by growth front nucleation (GFN) after a single crystal seed reaches a critical size. Type-2 polycrystalline spherulite structures [17] grow from a fiber-like structure which branches to form secondary fibers forming crystal sheaves, which fan out and close to form a spherical growth pattern, and thereafter grow in a radial fashion by GFN. The phase field theory [14,15] to describe the polycrystalline growth is valid for precipitation from supersaturated solutions, including supercooled melts and supersaturated aqueous solutions. For example, a fluorapatite spherulite has been shown to form from a tree-fractal type branching in an aqueous gel medium, where the growth from a linear seed branches out to assume a spherical shape similar to Type-2 spherules [18,19].

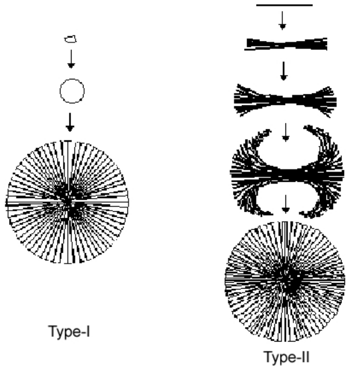

Figure 1: The two growth types for spherules (adopted from Granasy et al. 2004). Type 1 starts from a single nucleus and grows radially outwards to assume a spherical shape. Type 2 nucleus is an elongated particle which branches off from both ends to give intermediate shapes to finally end up in a spherule.

It has been proposed that anions affect the shape of Fe-oxide particles and that chloride ions promote the spherical shape [20]. However, spherule growth is effected by a number of factors including anions (e.g., Cl^-, SO_4^{2-}), supersaturation, extent of hydrolysis (determined by acidity), viscosity of the medium (affects diffusion of ions), and impurities (e.g., Al) [21]. The formation of the radial fibers which are the growth units of Type-2 spherules may be controlled by the preferential adsorption of sulfate anions on specific crystal faces [22].

Synthetic Hematite Morphology, Size, and Crystallographic Fabric. The morphology of the initial stages of our synthetic hematite spherule formation is shown in Figure 2. Spherule appears to start as an elongated shape (< 2 μm in size) and then it evolves through the morphological changes described above for the Type-2 spherulitic growth (Figs. 2b-e). The formation of Type-1 spherules are straight forward starting from a single nucleus to grow radially outwards to form the final spherule (e.g., Fig. 2f). Morphological features resulting from spherulitic growth are also observed in some Meridiani spherules (e.g., Fig. 3).

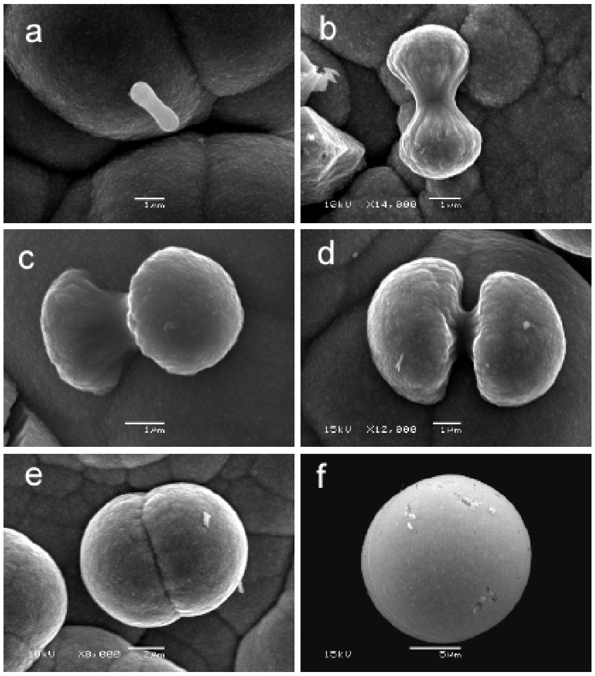

Figure 2: Growth of type II spherules where growth nucleation produces an elongated form (3a) whose ends branch out to form a sheaf-like shape (3b). Further growth of these sheaves enlarge into two hemispheres (3b,c), which coalesces to form a spherule (3d,e). The seam where the two hemispheres seal is seen in 3e, and is not visible in some mature spherules (e.g., 3f) making it impossible to tell whether the spherule in (3f) is a type 1 or 2 process.

The spherical shape, radial growth pattern, and crystallographic orientation (*c*-axis parallel to radial growth direction) of our synthetic hematite particles [11] are specific characterizing parameters that are not commonly reported in the literature for hematite [e.g., 23]. Until now, the only other known occurrence of hematite spherules is spherules discovered in sulfatetic tephra near the top of Mauna Kea, Hawaii [24]. High-resolution TEM work has not been done to document the *c*-axis orientation for the Mauna Kea spherules.

Although synthetic, Mauna Kea, and Meridiani Planum hematite particles are all spherical in shape, the Meridiani Planum spherules are a factor of ~40 to 400 times larger in diameter than our synthetic spherules. We suggest that several of the factors discussed above account for possible differences in size. Specifically, higher temperatures improve kinetics and, more importantly, the much longer formation time (years versus hours) [e.g., 25] inferred for Meridiani Planum spherules is consistent with larger spherules. Our spherules were formed in only a few hours from a limited Fe^{3+} source, whereas, the Meridiani spherules may have formed over a period up to 1000 Mars years in a continuous flux of Fe^{3+} from dissolving jarosite. It is possible that the larger spherules grew as a result of growth over a longer time span assuming that a source of Fe^{3+} (e.g., jarosite dissolution or Fe^{2+} oxidation) was available for diffusion to the growth zone of the hematite spherule during the growth.

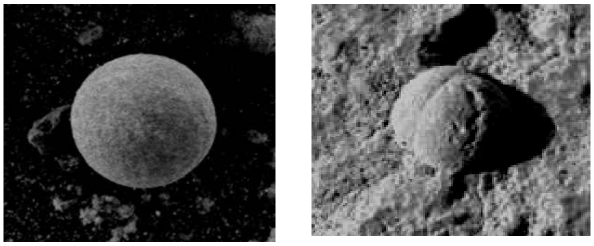

Figure 3. Two meridian spherules with a midseam corresponding to Type II growth (right) and one which has no obvious seam (left) (MER-Data). The latter could either be type 1 or 2 growth process (see text). Spherule size is ~ 4 mm.

Conclusion: The hematite spherules synthesized by hydrothermal treatment of acid-sulfate brines containing Fe^{3+} were similar in all aspects except size to those of Meridiani Planum. The synthetic spherules exhibited both Type-1 and Type-2 polycrystalline spherulite growth processes. Morphological features resulting from spherulitic growth (e.g., Type 2) are also observed in some Meridiani Spherules.. Therefore, by analogy the morphological evolution of laboratory synthesized hematite spherules must be similar to that of the Meridiani Planum spherules and that they also must have formed by a similar process.

References: [1] Squyres, S.W., et al. (2004) *Science*, **306**, 1698-1703. [2] Squyres, S.W., et al. (2006) *JGR* **111**, E12S12, doi:10.1029/2006JE002771. [3] Christensen, P.R., et al., (2004) *Science*, **306**, 1733-1739. [4] Klingelhöfer, G., et al., (2004) *Science*, **306**, 1740-1745. [5] Herkenhoff, K.E et al., *Science*, **306**, 1723-1726. [6] Morris, R.V., et al., (2006) *JGR* **111**, E12S15, doi:10.1029/2006JE002791. [7] Christensen, P.R, et al., (2000JGR 105, 9623-9642. [8] Christensen, P.R., et al. (2001) *JGR*, **106**, 23,823-23,871. [9] Lane, M.D, *et al*., (2002) *JGR*, **107**, 5126, doi: 10.1029/2001JE001832. [10] Glotch, T. D, et al., (2006) *JGR*, **111**, E12S03, doi:10.1029/2005JE002672. [11] Golden, D.C., et al., (2008) *Am. Min*., **93**, 1201-1214. [12] Magill, J.H. (2001) *J. Mat. Sci*., **36**, 3143-3164. [13] Smith, R.K., et al.,(2001) *Am. Min*., **86,** 589-600. [14] Granasy, L., et al., (2004a) *Mat. Res. Soc. Proc*. JJ4.5. [15] Granasy, L., et al., (2004b) *Nat. Mat.,* **3**, 645-650. [16] Granasy, L., et al., (2007) *Phys. Rev. Lett*., **98**, 10.1103/PhysRevLett.98.035703. [17] Granasy, L., et al., (2005 *Phys. Rev. E*, **72**, 10.1103/PhysRevE.72.011605. [18] Busch, S., et al., (1999) *Euro. J. Inorg. Chem*. **10**, 1643-1653. [19] Colfen, H. and Antonietti, M. (2005) *Ange. Chim. Int*., **44**, 5576-5591. [20] Kandori, K., et al., (2000) *Phys. Chem. & Chem. Phys*., **2**, 3293-3299. [21] Matijevic, E., and P. Scheiner (1978) *J. Coll. Interf. Sci*., **63**, 509-524. [22] Sugimoto, T., and Wang, Y. (1998) *J. Coll. Inter. Sci*., **207**, 137-149. [23] Cornell, R. and Schwertmann, U. (1996) *The Iron Oxides: Structure, Properties, Reactions, Occurrences, and Uses*. VHC, New York. [24] Morris, R.V., et al., (2005) *EPSL*, **240**, 168-178. [25] McLennan, S.M., et al. (2005) EPSL, **240**, 95-121.