CONDITIONS FAVORING THE FORMATION OF MARTIAN "BLUEBERRIES" BY FREEZING AQUEOUS HEMATITE SUSPENSIONS.

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Introduction: The Opportunity Mars Exploration Rover (MER) found small spherules of gray, crystalline hematite in the Meridiani Planum region of Mars [1]. Although several terrestrial analogues share similarities with the Martian hematite spherules, none of them can adequately explain all the characteristics of the spherules, such as their mineralogy, internal structure, shape, size and distinctive thermal infrared spectral properties [1,2].

Previous studies demonstrated that coarse crystalline hematite spectrally similar to the hematite of the spherules can form through a freeze-thaw cycle and also through sublimation of frozen aqueous suspensions of hematite, although these experiments did not produce spherules [3]. However, previous theoretical and experimental research suggests at low freezing rates, the crystallizing ice front should reject the particles and force them into the center, potentially creating spherules [4-6]. This study investigates how synthetic hematite particles of various sizes and shapes in aqueous solution aggregate as the solution freezes and the particles are rejected or entrapped by the ice.

Methods: We synthesized hematite nanoparticles with average diameters of ~10-200 nm using the methods of [7]. Freezing with and without hematite or salt was performed in cylindrical-conical tubes or beakers with various volumes at temperatures from 243K to 269K. In selected experiments, we used thermocouples linked with LabVIEW to measure and record the temperature of solutions as freezing progressed. Then we calculated an average linear freezing ice-solution interface velocity by dividing the radius of the container by the freezing time. We examined and photographed the frozen hematite suspensions with a stereomicroscope to see whether or not the hematite particles were rejected by the crystallizing ice front, as well as the size and shape of the aggregates. We extracted samples for analysis by Scanning Electron Microscopy both before and after freeze-drying.

Results and discussion: Linear freezing rate decreased continuously with decreasing temperature, except in the highest temperature experiments that correspond to the slowest freezing rate. Additions of NaCl (0.01 and 0.1 M) had little effect, whereas $CaCl_2$ increased freezing velocity from 4 to 5 microns/s due to freezing point depression. Changes in the concentration of hematite in the solutions did not have a significant effect on the magnitude of the freezing interface velocity. Variations in size (~10-200 nm) or particle concentrations led to average interface velocities that varied by less than a factor of two.

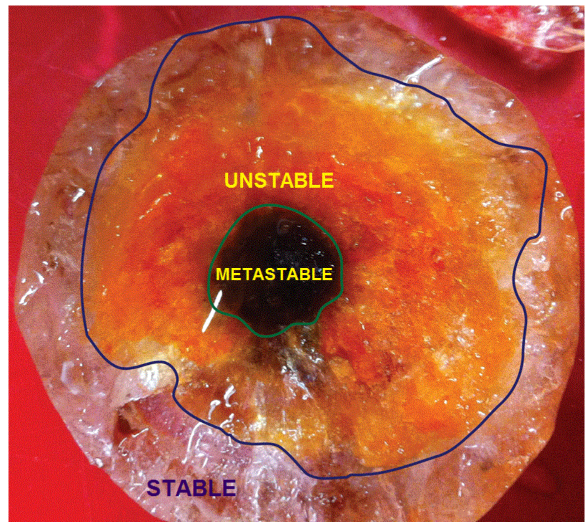

Figure 1. Cross-section through frozen hematite solution, showing where the freezing interface was stable, metastable, and unstable.

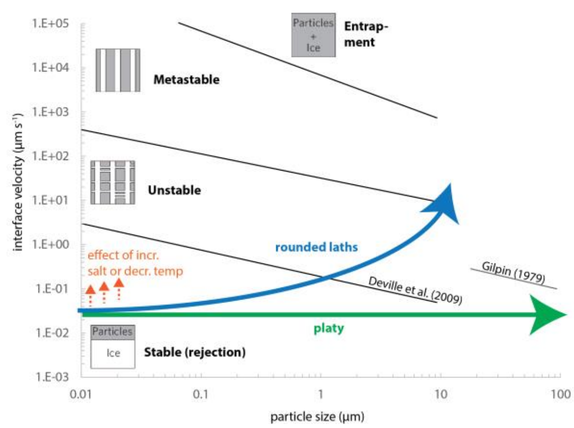

Figure 2. Relationships between particle/ aggregate size, ice crystallization interface velocity, and texture. Boundary lines were determined by empirical and theoretical considerations [5-6].

Most experiments revealed similar ice-hematite and aggregate textures. The frozen hematite solutions all had the same basic structure of a clear outer rim, an orange inner layer, and a concentrated core (Figure 1).

The clear outer rim is the area where the freezing interface was stable and the ice front rejected the hematite particles. The orange inner rim is where the ice crystallization front was unstable and some particles were trapped in the ice [5]. The concentrated core is where we found the largest hematite aggregates. Textures in this area include increasingly large aggregates aligned in radial linear columns separated by ice and a hematite-free central spot. These textures indicate a mixture of instability, metastability, and entrapment [5] which resulted from increased ice crystallization front velocity in this area (Figure 3). Freeze-drying these experimental products led to a loose powder consisting of nano- to micro-scale aggregates having maximum diameters of hundreds of microns.

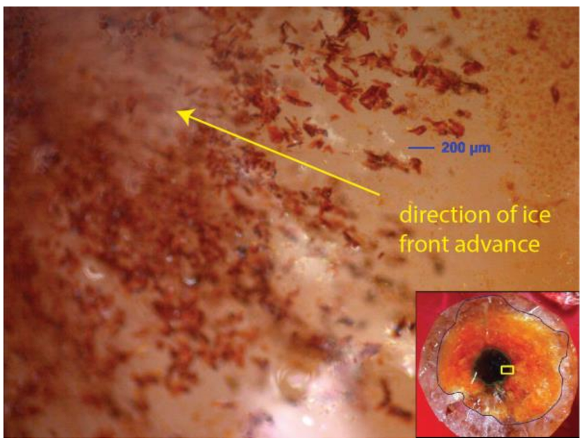

Figure 3. Example of hematite aggregate organization due to instabilities in the crystallizing ice front, indicating the interface velocity was too high to form millimeter-scale solid aggregates.

Experiments with the smallest (~10 nm) plate-shaped particles maintained the most stable ice-solution interface crystallization conditions. In some experiments with these particles, we observed clear ice down to the dense center core, where aggregates up to millimeters in size form. No spherules were produced; instead aggregates typically had smooth, curved surfaces.

These experiments demonstrate conditions favorable for the formation of stable hematite aggregates of millimeter size. In agreement with previous theoretical and experimental evidence [5,6], the smallest particles should be the most readily excluded. Low ice-solution interfacial velocities are required (Figure 2) to produce larger ice-free aggregates of hematite, as would be needed to produce millimeter-scale spherules such that those observed on Mars. This is consistent with our experimental observations, as larger plate-shaped particles do not form millimeter-scale aggregates by freezing. On the other hand, differences between textures formed in platy and rounded laths of similar sizes demonstrate that the morphology is important. Spatially and temporally resolved data with the more equant particles indicates that freezing rate increases dramatically with time, consistent with the textural observations (Figure 2). In order to reach millimeter scale aggregates, experiments with ~10 nm platy hematite necessarily maintain much slower ice-solution interfacial velocities. In addition to particle size and morphology, conditions that favor slower ice-solution interface velocities include higher freezing temperatures and lower salinity solutions.

These experiments suggest that hematite "blueberry" formation by aggregation of nanoparticle suspensions would be favored by conditions that maintain low ice-solution interface velocities, nanometer-scale particles, and platy morphologies. Our further experiments will explore methods to achieve slower ice crystallization. Additionally, we plan to perform thermal emission spectroscopic analyses with samples of ranging hematite particle size, shape, and aggregate textures. Although the Martian spherules exhibit distinctive features in MER Mini-TES infrared spectra, their internal structure is poorly constrained by existing data. Our spectral analyses will help constrain the range of particle characteristics that generate spectra similar to Martian spherules. Texture/spectra relationships contribute to the development of conceptual models that can fully explain the formation and properties of hematite spherules.

References: [1] Calvin W. M. et al. (2008) *J. Geophys. Res.-Planets,* 113(E12). [2] Lane M.D. et al. (2002) *J. Geophys. Res.*, 107(E12), 5126, [3] Im S. H. and Park O. O. (2002) *Appl. Phys. Lett.*, 80(22), 4133-4135. [4] Madden A. S. et al. (2010) *Earth Planet. Sci. Lett.*, 298, 377-384. [5] Deville et al. (2009) *Nat. Mater.*, 8, 966-972. [6] Gilpin R.R. (1980) *J. Coll. Sci.*, 74, 44-63. [7] Schwertmann R.M. and Cornell U. (2000) *Iron oxides in the Laboratory*.

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