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Considering the formation of hematite spherules on Mars by freezing aqueous hematite nanoparticle suspensions

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ABSTRACT

The enigmatic and unexpected occurrence of coarse crystalline (gray) hematite spherules at Terra Meridiani on Mars in association with deposits of jarosite-rich sediments fueled a variety of hypotheses to explain their origin. In this study, we tested the hypothesis that freezing of aqueous hematite nanoparticle suspensions, possibly produced from low-temperature weathering of jarosite-bearing deposits, could produce coarse-grained hematite aggregate spherules. We synthesized four hematite nanoparticle suspensions with a range of sizes and morphologies and performed freezing experiments. All sizes of hematite nanoparticles rapidly aggregate during freezing. Regardless of the size or shape of the initial starting material, they rapidly collect into aggregates that are then too big to push in front of a stable advancing ice front, leading to incohesive masses of particles, rather than solid spherules. We also explored the effects of "seed" silicates, a matrix of sand grains, various concentrations of NaCl and $CaCl_2$, and varying the freezing temperature on hematite nanoparticle aggregation. However, none of these factors resulted in mm-scale spherical aggregates. By comparing our measured freezing rates with empirical and theoretical values from the literature, we conclude that the spherules on Mars could not have been produced through the freezing of aqueous hematite nanoparticle suspensions; ice crystallization front instability disrupts the aggregation process and prevents the formation of mm-scale continuous aggregates.

1. Introduction

1.1. The surprising form of coarse crystalline hematite on Mars: spherules

New and surprising observations have emerged at every step as scientists have continued to refine the resolution of analyses used to study hematite on Mars. Earth-based observations of Mars detected the abundant and wide-spread red, dust-borne nanophase hematite that contributes to the distinctive color of Mars (Morris and Lauer, 1990). Later, orbital spacecraft instruments with mapping capabilities such as the Mars Global Surveyor Thermal Emission Spectrometer (MGS TES) discovered significant abundances (~10–60%) of coarse crystalline (gray) hematite in Meridiani Planum, Mars (Christensen et al., 2000). Thermal infrared (TIR) spectra of this crystalline hematite lack an emissivity minimum at 390 cm^{-1} (25.64 µm) (Christensen et al., 2001), indicating that the hematite is crystallographically oriented to provide emission predominantly from crystallographic planes perpendicular to the *c*-axis (Lane et al., 2002). Furthermore, the spectral characteristics and band depths were found to be consistent only with tested materials having grain diameters ~10 µm or larger, more than 1000 times larger than the nanophase ferric oxide in the worldwide dust (Christensen et al., 2000). Based on the stratigraphic relationships of the coarse gray hematite, the favored formation scenario was some type of chemical precipitation involving aqueous fluids (Christensen et al., 2000).

The Mars Exploration Rover (MER) *Opportunity* landed in Meridiani Planum to examine gray crystalline hematite deposits in situ, and discovered that the hematite occurs not as schistose or loose particles, but as mm-scale spherules inferred to be groundwater concretions (Klingelhofer, 2004; Squyres et al., 2004). The surprising occurrence of hematite spherules led to new questions about how such spherules could form and exhibit crystallographic orientation/*c*-axis emission within the geologic and hydrologic

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context of Meridiani Planum. Spherule formation mechanisms and proposed geologic histories need to be consistent with the following three observations, as summarized by Calvin et al. (2008). (1) The spherules occur exclusively in flat-lying, finely layered, sulfate-rich rocks and are associated with eroded lag deposits unrelated to volcanism. (2) The spherules are relatively uniform in size; most seen in MER microscopic imager photographs were a few mm in diameter. (3) Their morphology does not seem to be related to the associated sedimentary structures. The spherule textures plus the spatial occurrence of the spherules in association with sedimentary layers bearing Fe-sulfate minerals such as jarosite (Bibring et al., 2007; McLennan et al., 2005; Sefton-Nash and Catling, 2008; Weitz et al., 2008) prompted additional research to find hematite spherule analogs that could explain both their origin and spectral properties.

The textures of the observed spherules are most consistent with an internal structure consisting of many fine-grained hematite crystallites rather than schistose or mm-scale coarse-grained hematite, regardless of whether the spherules resulted from aqueous diagenesis due to movement of reducing fluids followed by oxidation (e.g., Chan et al., 2004), precipitation in acid saline lakes (e.g., Bowen et al., 2008), hydrothermal alteration of jarosite (e.g., Golden et al., 2008), or recrystallization of an initial Fe-oxyhydroxide or magnetite precursor (e.g., Glotch, 2004). Without necessarily matching the *external* size and texture of the Mars spherules, analogs and theoretical models demonstrated that nanoparticulate hematite aggregates with multiple possible *internal* textures could provide TIR spectra emission dominantly from *c*-axis faces from a nanocrystalline powder aggregate (Glotch, 2004; Glotch et al., 2006; Golden et al., 2008). Thus, spherule formation mechanisms that rely on the aggregation of nanoparticulate hematite from solution present a viable explanation for the origin of the hematite spherules on Mars.

1.2. Motivation: nanoparticle assembly through freezing

Freeze/thaw cycles can generate landscape-modifying physical forces. Such cycles have been shown to transport boulders across Death Valley on Earth (Norris et al., 2014). "Frost heave" results from thermomolecular pressure: water kept in a liquid state below its bulk freezing temperature in capillaries, fractures, and pores migrates in response to temperature gradients, then crystallizes upon reaching a colder area; this crystallization drives further mass transport and ice crystallization (e.g., Dash, 1989; Derjaguin and Churaev, 1978; Murton et al., 2006).

In this work, we explored the hypothesis that freezing of aqueous solutions containing nanoparticulate hematite could lead to the formation of mm-scale spherules. This hypothesis was motivated by the following lines of evidence.

(1) We previously demonstrated that linear and curved mm-scale dark (gray) aggregates could be formed by freezing aqueous hematite nanoparticle suspensions and thermal infrared spectra of these aggregate powders contained the unique spectral signature indicative of coarse-crystalline gray hematite measured from Meridiani Planum (Madden et al., 2010).
(2) Aqueous suspensions of nanoparticulate iron oxides form directly during alteration of jarosite (e.g., Barron et al., 2006; Elwood Madden et al., 2012; Golden et al., 2008). The presence of aqueous fluids as well as observations of current surface conditions implies those solutions could also freeze.
(3) Microscale spherules have been shown to form during freeze-concentration of nanoparticle suspensions (e.g., Im and Park, 2002).

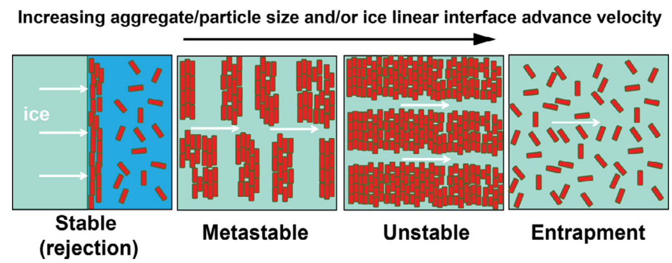

Fig. 1. Changes in texture of aggregates formed by an ice crystallization growth front as a function of particle or aggregate size and the linear advance velocity of ice crystallization. Linear advance velocity is in the direction of the arrows. Schematic based on Deville (2008).

(4) Low-temperature weathering and freezing/thawing processes may have been important during the evolution of the Mars surface (e.g., Michalski et al., 2013; Niles and Michalski, 2009).

Although it is clear that ice crystallization has the potential to physically reorganize solid materials, particulates suspended in the solution are excluded from the crystallizing ice only under certain conditions. Experimental (Corte, 1962; Körber et al., 1985; Rowell and Dillon, 1972; Spannuth et al., 2011), theoretical (Casses and Azouni-Aidi, 1994; Gilpin, 1980, 1979; Rempel and Worster, 2001, 1999), or combined theoretical and experimental studies (e.g., Elliott and Peppin, 2011; Peppin et al., 2007; Rempel, 2012) investigating the freezing of solutions containing a range of colloidal materials including latex spheres, common sedimentary silicates, clays, oxides, silica, alumina, etc. have afforded several general observations. Particle exclusion from the crystallizing ice front is a sensitive function of both the particle size and the velocity of the advancing ice front. Smaller sizes and lower ice crystallization/interface velocity favor the stable advance of the crystallizing ice with complete exclusion of particles. As particle size increases (perhaps increasing due to aggregation) and/or interface velocity increases, a critical point is reached at which particles begin to be intermittently trapped within the ice (unstable). Continued increases in particle/aggregate size and/or interface velocity lead to parallel tracks of pure ice and ice with trapped particles (metastable), followed by complete particle entrapment/engulfment (Fig. 1) (Deville et al., 2009).

Several researchers have demonstrated the utility of quantitative freezing interface velocity/particle size relationships to create organized structures built by particle aggregation (Deville, 2008; Deville et al., 2009, 2007; Zhang et al., 2005). In most cases, unstable and metastable conditions are generated to create columns and interlocking pore networks. Controlling aggregates to form more complex shapes remains challenging, because a number of interfacial forces and mass/heat fluxes determine the shape of the interface (Lock, 1990; Rempel, 2012). Aggregates can be shaped in part by confining/defining the geometry of the freezing. Im and Park (2002) froze suspensions of latex microspheres, producing planar, curved, and spherical aggregates. Flat and curved aggregates were produced by freezing particles trapped near the edges of the freezing interface, while spherical structures were produced in the center of the freezing solution as the ice crystallization trapped remaining particle/liquid droplets by approaching from all directions. However, spherical aggregates formed by Im and Park (2002) were all $<10\,\mu m$ in diameter, presumably at least in part due to a relatively small freezing cell with a low solution volume. Our research aims to experimentally investigate the freezing of hematite nanoparticle suspensions to identify variables such as hematite particle size, morphology, and concentration, ice crystallization linear advance velocity (as related to temperature), the