FORMATION OF MARS ANALOG CRYSTALLINE HEMATITE FROM NANOPHASE HEMATITE UNDER LOW TEMPERATURE AQUEOUS CONDITIONS. A. S. Madden[1], M.E. Elwood Madden[1] and V.E. Hamilton[2], [1]School of Geology and Geophysics, University of Oklahoma, 100 E. Boyd, Norman, OK 73019, amadden@ou.edu, [2]Southwest Research Institute, Boulder, CO 80302, hamilton@boulder.swri.edu.

Introduction: Known models of coarsely crystalline hematite formation involve digenesis with liquid water under hydrothermal conditions (>100°C) [1]. Alternative dry mechanisms require high temperature oxidation [2]. However, we have discovered a low temperature mechanism of crystalline hematite formation from aqueous suspensions of hematite nanoparticles.

Here we demonstrate that freeze-thaw cycles and/or cryodesiccation can produce coarse crystalline hematite from hematite nanoparticles, similar to the nanophase iron oxide commonly observed on Mars [3-6]. This mechanism is consistent with hypotheses suggesting mineral assemblages at Meridiani Planum and perhaps other sites on the surface of Mars are indicative of low-temperature aqueous alteration (e.g., [7]).

Crystalline hematite on Mars: Coarse crystalline hematite deposits observed from orbital thermal infrared (TIR) spectra and in situ Mini-TES spectra at Meridiani Planum are found in close association with low temperature alteration and evaporate phases not usually found in hydrothermal environments [8-9]. Lane et al. [10] determined that the spectra of these deposits are consistent with crystallographically orientated hematite. Further investigations by Mars Exploration Rover *Opportunity* confirmed the presence of coarse crystalline hematite [7] and determined that the hematite is found in small (<1- 6 mm diameter) spherules. These have been interpreted to be concretions that eroded out of sulfate-bearing basaltic sediments [7]. Occurrences of crystalline hematite in association with sulfates, evaporite minerals and clays have been also been observed elsewhere, including Valles Marineris and near Aram Chaos (e.g., [11-14]) suggesting these hematite-bearing mineral assemblages also likely formed under low temperature aqueous conditions.

Methods: Synthetic hematite nanoparticles were frozen in a 50 mL centrifuge tube at -4°C and then either thawed at room temperature or cryodesiccated in a Labconco Freezone 6 freeze-dryer for 1 day. Control samples were dried at 328 K. The product material was analyzed with JEOL JSM-880 SEM. TEM imaging was performed in a JEOL 2000FX STEM operated in bright field mode at 200 kV. Thermal infrared emissivity spectra (2000 – 200 cm^{-1} at 2 cm^{-1} sampling/4 cm^{-1} resolution) were acquired using a Nicolet Nexus 470 FTIR spectrometer.

Results: Aqueous nanoparticle suspensions appear bright red and may remain stable as colloidal solutions for periods of several months to years. Frozen then thawed or cryodesiccated samples acquired a granular texture (mm sized grains), deep purple color, and a specular, reflective luster. Gentle grinding of the cryodesiccated material quickly recovers the deep red color. SEM analysis of freeze-thawed and cryodesiccated material demonstrates that grains on the scale of hundreds to thousands of microns exhibit a variety of morphologies, dominated by curved surfaces that appear smooth up to 75,000 magnification. A secondary granular structure is resolved with sizes typically ranging from approximately 50-100 nm at higher magnification.

Hematite nanoparticles deposited as an aqueous suspension on a TEM grid and air-dried at 298K (Fig. 1a) aggregate with their basal surfaces generally oriented on the grid support film due to gravitational settling, but particle rotational orientations within the plane of the image appear mostly random. Additional crystallographic orientation occurs in the cryodesiccated samples (Fig. 1b) and freeze-thawed samples, as indicated by the presence of Moiré fringe patterns which cut across particle aggregates. In order for such fringes to occur across individual crystallites, the building blocks of the aggregate must have common orientations in planes parallel to the image.

The range of spacings observed could be generated by rotating layers of particles that are arranged in sheets of oriented aggregates. While the size of the individual crystallites (~10 nm) matches that of superparamagnetic hematite consistent with reflectivity spectra of the Mars surface [3], the lateral dimensions of the crystallographically oriented domains observed in TEM matches well with the widths of the granular texture observed in SEM (Fig. 1e) as well as the estimated crystallite size for Meridiani Planum hematite as determined by Moessbauer spectroscopy [15].

The TIR emissivity spectrum of cryodesiccated hematite nanoparticle aggregates is shown in Figure 2 along with emissivity spectra of Martian hematite acquired by the Thermal Emission Spectrometer (TES) instrument on the Mars Global Surveyor spacecraft [8], Mini-TES spectra collected in situ at Meridiani Planum, and an oriented laboratory hematite [10]. A distinguishing characteristic of TIR spectra acquired perpendicular to the c-axis of oriented hematite (in the laboratory and on Mars) is the lack of a small emission minimum at ~390 cm^{-1} [10]. The spectrum of our cryodesiccated hematite also lacks this spectral feature, indicating that we are observing dominantly the basal planes of a crystallographically oriented hematite sample. Controls dried at 328 K in air formed coarse specular grains that range up to several mm in size, but did not produce the same morphologies observed at the nanoscale.

Conclusions: These results provide a novel low temperature mechanism by which coarse crystalline hematite may have formed from nanophase iron oxides in aqueous systems on Mars. Freezing likely results in aggregation and alignment of hematite nanoparticles in two dimensions, with further alignment of macroscale crystallites oriented along their basal surfaces during the advance of a freezing front under confined freezing conditions. During air drying of the controls, particles remain rotationally disordered relative to each other as the solution dries. While spherules were not directly produced through freezing of nanoparticle solutions, this work suggests that similar crystallographically ordered aggregation processes may have contributed to the formation of spherules.

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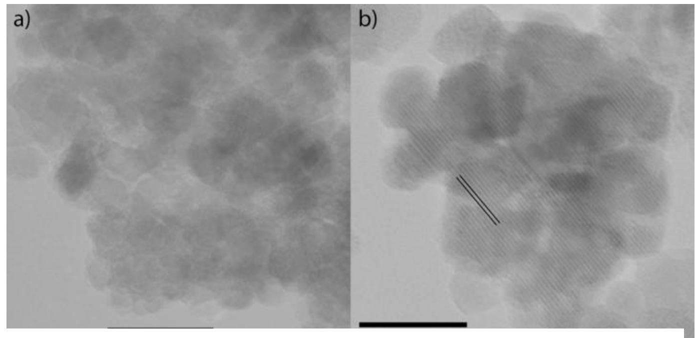

Figure 1. Transmission electron micrographs of aqueous hematite nanoparticle suspension before (a) and after (b) cryodesiccation. The scale bar is 20 nm. Fringes in (b) can be seen to cut across individual particles, suggesting crystallographic orientation of individual nanoparticles to form stacked crystallites; an example is highlighted in black.

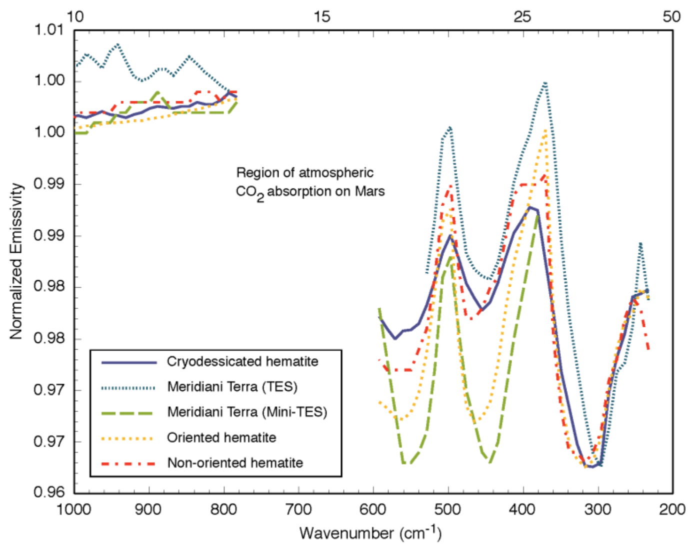

Figure 2. Thermal emission spectrum of cryodesiccated hematite plotted with the average TES and Mini-TES spectrum from Meridiani Planum [8,9] and the spectrum of a c-axis-oriented sample of hematite [10]. Laboratory data are resampled and normalized to the resolution and spectral contrast of the TES spectrum to facilitate comparison. Data in the region of Mars' atmospheric CO_2 absorption (825 - 508 cm^{-1}) are omitted from the TES spectrum for clarity.