TRANSFORMATION OF IRON(III) OXIDE MINERALS IN MARS-RELEVANT FLUIDS: IMPLICATIONS FOR DIAGENETIC HEMATITE FORMATION. A. L. Knight, K. Mitra, and J. G. Catalano, Department of Earth & Planetary Sciences, Washington University, Saint Louis, MO 63130 USA (alknight@wustl.edu)

**Introduction:** The distinctive reddish hue of the Martian surface is attributed to abundant iron (oxyhydro)oxide minerals. These phases have been identified in numerous rock, soil, sediment, and meteorite samples across Mars [1, 2] and are possible mineralogical indicators of past aqueous and atmospheric conditions on Mars. Hematite (α-Fe₂O₃) is thermodynamically the most stable Fe(III)-oxide mineral on Mars [3]. Most other Fe(III) minerals exist metastably on the Martian surface and can serve as precursor minerals that can undergo diagenetic transformation to stable hematite [4-7]. Hematite has been reported in various locations on Mars including Meridiani Planum and Gale crater [8-10].

The Mars Science Laboratory (MSL) Curiosity rover recently investigated the Vera Rubin Ridge (VRR), a topographically-distinct hematite-bearing sedimentary ridge on Aeolis Mons [11]. VRR yielded strong spectral signatures of red crystalline hematite in Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) [8, 12] images prior to MSL exploration. Detailed *in situ* analysis of the VRR formation by MSL inferred this unit primarily consisted of fine-grained, red and gray (to blue) lacustrine mudstones with thin, parallel stratification. While red hematite is dispersed throughout the VRR bedrock, the decimeter-scale gray to blue zones are dominantly found in the Jura Member [13]. The gray color variation crosscuts strata in the otherwise red-colored VRR, indicating a post-depositional (i.e., diagenetic) origin. Grain-size measurements point towards possible coarsening associated with gray hematite [13, 14]. The abundant iron-related diagenetic features throughout the VRR and the possible correlation between grain-size and spectral reflectance of the hematite could indicate either syn- or post-depositional diagenesis. Gray hematite on Mars has also been found in Sinus Meridiani, Valles Marineris, and Aram Chaos [15].

Unequivocal evidence of diagenesis on the Martian surface has been documented by various orbiter and rover studies [16, 17]. The sediments in Gale crater are lacustrine and have experienced multiple episodes of post-depositional diagenesis. [9, 10, 18]. The chemical composition and nature of the diagenetic fluids that potentially altered the Gale crater sediments, including the VRR, are unclear. Diagenetic fluids that recrystallized pre-existing Fe(III)-bearing phases under ambient to hydrothermal conditions may explain the observed features in the VRR. Coarse-grained gray hematite that cross-cuts strata exposed on the VRR could reflect transformation of precursor Fe(III)-bearing phases (e.g., goethite [5, 19-21], ferrihydrite, akageneite, magnetite [22]) or coarsening of the fine-grained red hematite [22] that is pervasive throughout red units in the VRR as well as the underlying Murray formation.

In this study we explore transformation of goethite and “red” hematite into more crystalline “gray” hematite by plausible Mars-relevant diagenetic fluids. The effect of these diagenetic fluids on the mineralogy and spectral characteristics of the mineral products are investigated. Analyses specifically focused on assessing crystallinity and reflectance properties after aging at elevated temperature in potential diagenetic fluids.

**Methods:** Laboratory experiments were conducted to investigate the transformation of Fe(III) oxide minerals in Mars-relevant fluids at acidic and neutral pH. Goethite (α-FeOOH) and hematite were prepared as starting minerals using standard laboratory preparation techniques [5]. These minerals were dried, ground in a mortar and pestle, and analyzed using X-ray diffraction (XRD) to confirm the mineralogy. Experimental suspensions of 10 mL volume were prepared containing 20 g/L of the respective minerals in 1 M MgSO₄ or MgCl₂ background salt solutions. Sulfate and chloride fluids have been proposed to be the dominant types on Mars [23]. The pH values of the suspensions were set to ~7 or ~3 using small additions of hydrochloric acid and sodium hydroxide. The suspensions were sealed in PTFE-lined bombs (Parr Instrument Co.) and heated in digital convection ovens. The bombs were aged at 98°C and 200°C for ~50 and ~30 days, respectively. Two different temperature conditions were investigated to explore diagenesis at elevated temperature and to accelerate the transformation process.

At the end of the experiments, the bombs were removed from the ovens and allowed to cool before extracting the minerals via syringe filtration using 0.22 μm MCE filters. The filtered minerals were rinsed with ultrapure water and dried by heating in an oven at 70°C for ~1 hour. The washed samples were then analyzed using XRD and VNIR spectroscopy. A portion of the recovered minerals were ground in a mortar and pestle to analyze using XRD. Quantitative mineral abundances were determined via Rietveld refinement using Profex [24]. The remainder was not ground, with the reflectance spectra of the intact minerals acquired using a lab-based Analytical Spectral Devices (ASDs) portable VNIR spectroradiometer.

**Results and Discussion:** The experiments containing goethite as the starting mineral showed
changes in mineralogy at the end of the experiments at both 98 and 200°C (Fig. 1). The 98°C experiments yielded lesser amounts of hematite when starting with goethite compared to the corresponding 200°C studies. This provides a qualitative assessment of the impact of temperature on transformation timescales during diagenesis. As hematite is thermodynamically stable at both temperatures, and thus should be the sole iron oxide present, it indicates that under the fluid conditions studied prolonged heating at elevated temperature is required to drive its formation from a goethite precursor. The experiments at 200°C demonstrated substantial variations in mineralogy with pH and fluid composition. Acidic solutions showed near-quantitative conversion of goethite into hematite in both chloride and sulfate fluids. In contrast, pH 7 solutions yielded only partial transformation to hematite, with a greater extent of conversion in sulfate fluids. These studies indicate that fluid composition affects the rate of iron oxide transformation during diagenesis. It also suggests that other chemical species in aqueous fluids may accelerate diagenetic transformations, motivating future study.

All experiments with “red” hematite showed minor sharpening of hematite peaks in XRD. However, these were still broader than peaks from hematite generated by conversion from goethite, indicating a larger coherent domain size in the latter experiments. The VNIR spectra of thermally-transformed hematite potentially showed changes in reflectivity. However, the volume of minerals recovered from the experiments was inadequate to fill the field of view of the ASD spectrometer, causing artifacts in the data. A detailed relationship between the changes seen in XRD and the reflectance properties of the solid has thus not yet been established. Replicate experiments are being conducted with greater initial mineral mass to permit improved spectral characterization. Additionally, experiments are underway to investigate the transformation of nanophase hematite, ferrihydrite, akaganeite, jarosite, and magnetite in various fluid compositions.

**Conclusion:** The rate of transformation of goethite to hematite is influenced by fluid-type, solution pH, and temperature. The coarsening of fine-grained red hematite to gray hematite may also show similar variations with fluid-type, solution pH, and temperature. Diagenesis in SO4-rich solutions at low pH conditions appear most favorable for driving diagenetic recrystallization to gray hematite. However, further study is necessary to establish the spectral properties of hematite produced under such conditions and recrystallization in alternative fluid compositions needs to be explored.


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**Figure 1:** Final mineral proportions of precipitates obtained by the transformation of goethite to hematite in 10i M MgCl2 and MgSO4 at initial pH 3 and 7 at 98 and 200°C determined via Rietveld refinement.