

A NEW HEMATITE FORMATION MECHANISM FOR MARS. Michelle E. Minitti¹, Melissa D. Lane² and Janice L. Bishop³, ¹Center for Meteorite Studies, Arizona State University, Tempe, AZ, 85287-1404 (minitti@asu.edu), ²Planetary Science Institute, 1700 E. Fort Lowell Rd., Suite 106, Tucson, AZ 85719, ³SETI Institute/NASA-ARC, MS 239-4, Moffett Field, CA 94035.

Introduction: Hematite is an important component of Martian surface mineralogy. The visible and near-infrared spectral character of Martian bright regions is explained by the presence of nanophase hematite and subordinate amounts of red, crystalline hematite [e.g., 1]. In the thermal infrared, gray, coarse and crystalline hematite was detected by MGS-TES in three separate regions on Mars, always as a component of layered (sedimentary) terranes [e.g., 2].

The presence and nature of hematite on Mars has been used to assess conditions on the Martian surface responsible for hematite formation. Palagonitization is capable of producing nanophase and red, crystalline hematite [3] and palagonitization implies basalt glass weathering in the presence relatively small amounts of water. The preferred formation mechanism for gray hematite, precipitation from Fe-rich water, implies large bodies of water at multiple sites on Mars [2].

A recent study of Martian basalt spectral properties [4] yielded samples which reveal a new hematite formation mechanism: glass oxidation during extrusion of basaltic flows. This new mechanism, which requires neither chemical weathering nor water, has different implications for the presence of hematite in Martian surface materials.

Laboratory Samples: Glass-rich (85% glass, 15% pigeonite) to fully glassy basalts with Martian meteorite-like compositions (high FeO, low Al₂O₃) were created in the laboratory. The samples were ground to particulates and were then subjected to oxidation under different conditions. The glass-rich sample was oxidized in air at 700 °C for 7 days and the fully glassy sample was oxidized in CO₂ at 900 °C for 3 days. The latter sample was oxidized in CO₂ in an effort to mimic the Martian atmosphere. Oxidation caused transformation of the black, vitreous luster of the glasses to a gray, metallic sheen. The metallic sheen can be removed with gentle abrasion; thus, oxidation created a coating on the glassy surfaces of the basalts.

Analytical: The oxidized basalts were analyzed with multiple techniques to assess the chemistry, mineralogy and spectral properties of the oxidation-induced coatings.

Scanning Electron Microscopy (SEM). Backscattered electron (BSE) images and X-ray maps of the oxidized samples were obtained in a JEOL 845 SEM at Arizona State University. Elemental distributions determined through X-ray mapping reveal that both the air-

and CO₂-oxidized samples exhibit layers of Fe-enriched and Ca-enriched materials at the surfaces of the glasses (Fig. 1). The Fe-rich material is always exterior to Ca-rich material. The thicknesses of the Fe- and Ca-rich layers on the air-oxidized sample are 1.5-2 μm; the thicknesses of the layers on the CO₂-oxidized sample are 0.1-0.6 μm. The Fe- and Ca-rich layers correspond to the coating material on the oxidized glasses.

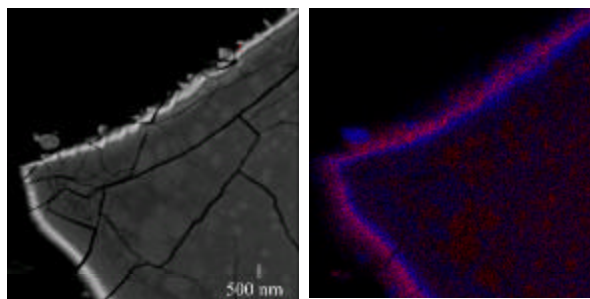


Figure 1: BSE image (left) and elemental map (right) of the air-oxidized basalt glass. The bright rim in the BSE image corresponds to the gray, metallic coating formed on the oxidized glass. The elemental map illustrates that the coating consists of an Fe-rich layer (red) overlying a Ca-rich layer (blue).

Raman Spectroscopy. Raman spectra were obtained from the oxidized glasses using the 514 nm line of an Ar laser. Laser power was maintained at 25 mW and the laser was defocused on the sample surfaces. The spectra were monitored throughout the collection process to ensure that the samples did not undergo transformation under the laser during analysis.

Both the oxidized samples exhibit prominent peaks in their Raman spectra (Fig. 2). The peaks near 220, 240, 287, 398 and 598 cm⁻¹ correspond to peaks exhibited by a gray hematite sample analyzed under the same conditions as the oxidized samples (Fig. 2). The smaller, broad peaks observed in oxidized sample spectra near 325, 480 and 690 cm⁻¹ correspond to broad peaks exhibited by maghemite [5]. The results strongly suggest that the Fe-enrichment at the surface of the oxidized glasses corresponds to hematite and minor maghemite mineralization caused by the oxidation process. Assignment of all peaks to Fe-oxide minerals suggests that the Ca-rich phase is weakly- to non-Raman active, possibly CaO (see Hematite Formation Mechanism section below).

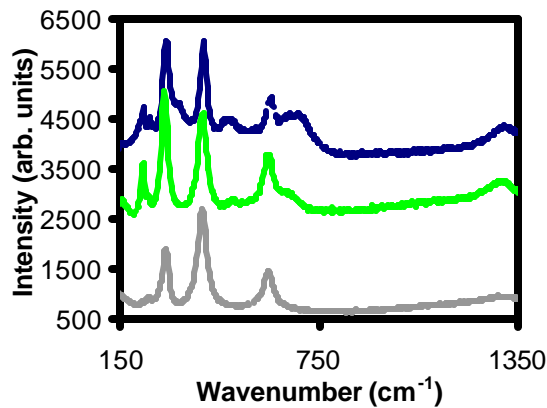


Figure 2: Raman spectra from the air-oxidized (blue) and CO₂-oxidized (green) basalt glasses in comparison to a spectrum of gray hematite (gray).

Infrared Spectroscopy. The visible and near-infrared spectrum of the air-oxidized sample (Fig. 3a) exhibits a relatively featureless ferric absorption edge between 0.3-0.7 μm , similar to that of the Martian dust spectrum. The ferric absorption edge is consistent with the hematite coating on the oxidized glass. In the emissivity spectra, however, the signature of hematite (expressed as $<600\text{ cm}^{-1}$) is not strongly expressed (Fig 3b). The lack of hematite-related features, with the exception of the absorption near 540 cm^{-1} in the spectrum of the air-oxidized sample, is likely due to the thinness of the hematite coatings relative to the wavelength of mid-infrared radiation.

Hematite Formation Mechanism: A well-understood mechanism exists to explain the formation of hematite on the surface of basalt glass in oxidizing conditions. Cooper et al. [6] determined that oxidizing conditions induce migration of divalent cations (Fe, Ca, Mg) toward the surface of oxidizing glass. The divalent cations pile up at the glass surface and eventually form oxide phases. Basalt glasses studied by [6] formed MgO and CaO on their oxidized surfaces. The dominance of Fe-oxides on surfaces of Martian oxidized glasses is likely dictated by the Fe-rich nature of the glasses.

Is it possible for this formation process to act in geologically feasible conditions? The gray, metallic sheen frequently observed on newly extruded Hawaiian basalt flows is an apparent analog to the hematite coatings on the experimental basalts. Elemental maps (not shown) of the metallic sheen on a Hawaiian basalt indicate that the sheen corresponds to Fe- and Ca-rich layers in the same geometry as those observed on the experimental samples (Fig. 1). The Hawaiian sheen also exhibits broad, weak Raman peaks at 325, 480 and 702 cm^{-1} that correspond to the positions of Raman peaks

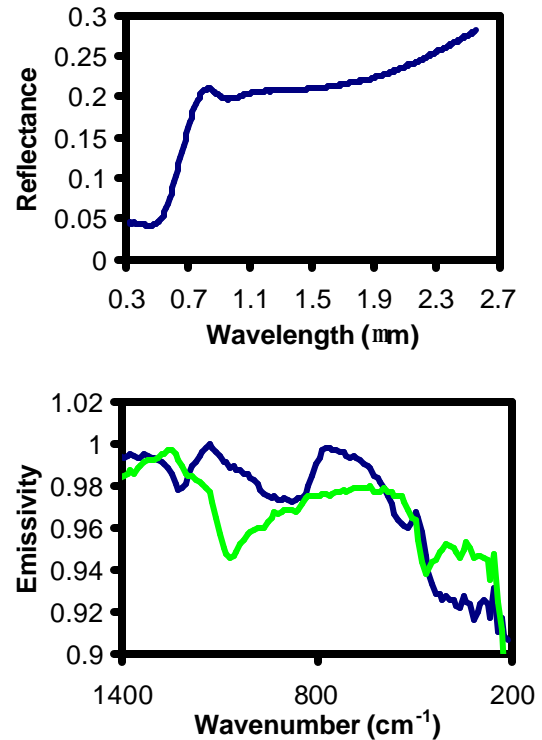


Figure 3: a) Reflectance and b) emissivity spectra of air-oxidized (blue) and CO₂-oxidized (green) basaltic glasses.

exhibited by maghemite. The Hawaiian sample indicates that it is possible to develop Fe-oxide mineralization on glassy basalts during extrusion.

Conclusions and Implications: Laboratory samples and a terrestrial analog suggest that hematite can form on Martian basalts during extrusion. Given the widespread occurrence of volcanic materials on Mars, hematite originating from oxidation of glassy basalt flows is potentially abundant on Mars. Coatings from oxidized basalt glasses could be weathered off and contribute hematite (and maghemite?) to Martian dust. Also, if hematite-coated flows were buried and underwent metamorphism, the hematite coatings could potentially coarsen and obtain spectral characters comparable to that of TES-observed hematite. Geomorphic evidence, however, argues against an igneous origin of the TES-observed hematite deposits [e.g. 2]. Overall, if hematite formed on glassy basalt flows is an important source of Martian hematite, the need to rely on water-related processes of hematite formation is lessened.

References: [1] Morris R.V. et al. (1989) *JGR*, 94, 2760-2778. [2] Christensen P.R. et al. (2001) *JGR*, 106, 23873-23885. [3] Morris R.V. et al. (2000) *JGR*, 105, 1757-1817. [4] Minitti M.E. et al. (2001) *JGR*, 107, 10.1029, 2001JE001518. [5] de Faria, D.L.A. et al. (1997) *J. Raman Spectr.*, 28, 873-878. [6] Cooper R.F. et al. (1996) *GCA*, 60, 3253-3265.