A new hematite formation mechanism for Mars

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Abstract—The origin of hematite detected in Martian surface materials is commonly attributed to weathering processes or aqueous precipitation. Here, we present a new hematite formation mechanism that requires neither water nor weathering. Glass-rich basalts with Martian meteorite-like chemistry (high FeO, low Al2O3) oxidized at high (700 and 900 °C) temperatures in air and CO2, respectively, form thin (<1 µm) hematite coatings on their outermost surfaces. Hematite is manifested macroscopically by development of magnetism and a gray, metallic sheen on the glass surface and microscopically by Fe enrichment at the glass surface observed in element maps. Visible and near-infrared, thermal infrared, and Raman spectroscopy confirm that the Fe enrichment at the oxidized glass surfaces corresponds to hematite mineralization. Hematite formation on basaltic glass is enabled by a mechanism that induces migration of Fe2+ to the surface of an oxidizing glass and subsequent oxidation to form hematite. A natural example of the hematite formation mechanism is provided by a Hawaiian basalt hosting a gray, metallic sheen that corresponds to a thin hematite coating. Hematite coating development on the Hawaiian basalt demonstrates that Martian meteorite-like FeO contents are not required for hematite coating formation on basalt glass and that such coatings form during initial extrusion of the glassy basalt flows. If gray hematite originating as coatings on glassy basalt flows is an important source of Martian hematite, which is feasible given the predominance of igneous features on Mars, then the requirement of water as an agent of hematite formation is eliminated.

INTRODUCTION

Hematite is a known and important component of Martian surface mineralogy. The visible and near-infrared spectral character of Martian bright, dusty regions is explained by the presence of minor amounts of two forms of hematite. The featureless ferric absorption edge between 0.3–0.7 µm results from nanophase hematite and the weak absorption near 0.86 µm found in some regions on Mars requires subordinate amounts of fine-grained (<10 µm), yet crystalline, red hematite (Morris et al. 1989; Bell et al. 1990; Merenyi et al. 1996). In the thermal infrared, coarse gray hematite (Lane et al. 1999; Christensen et al. 2000b) was detected by the Mars Global Surveyor (MGS) Thermal Emission Spectrometer (TES) in three separate regions on Mars, always as a component of layered, presumably sedimentary, terranes (Christensen et al. 2000b, 2001b). Strong absorptions at 315, 461, and 560 cm−1 observed by TES are characteristic of coarse, gray hematite (Christensen et al. 2000b, 2001b; Lane et al. 2002; Glotch et al. 2004).

The presence and physical character of hematite on Mars is used to assess conditions on the Martian surface responsible for hematite formation. The nanophase, red crystalline, and coarse gray forms of hematite observed on Mars are associated with a variety of different formation mechanisms. Processes involving the alteration and weathering of basaltic materials are the preferred formation mechanisms of the hematite phases present in the bright region dust. One example of such a process is palagonitization of basaltic glass (Morris et al. 1990, 1993, 2000), which can yield both nanophase (amorphous) and fine-grained (crystalline) red hematite. In addition to palagonitic alteration, pedogenic and solfataric alteration of basaltic glasses are all capable of producing nanophase and/or fine-grained red hematite (e.g., Bishop et al. 1998, 2002, 2004; Morris et al. 1990, 1993, 2000; Schiffman et al. 2000, 2002). The preferred formation mechanism proposed by Christensen et al. (2000) for the coarse, gray hematite is precipitation from Fe-rich water (at ambient or hydrothermal temperatures). Glotch et al. (2004), however, argue that the TES-observed hematite signature is...
better explained by hematite resulting from the low-
temperature (~300 °C) transformation of goethite. Glotch et
al. suggest that the goethite precursor could result from
precipitation in water or from aqueous alteration. An
alternative explanation for the gray hematite is that it is
present as a thin coating (Kirkland et al. 2004), but Kirkland
et al. do not discuss or propose a formation mechanism for
such coatings. The involvement of water in the formation of
the gray hematite appears to be supported by the Mars
Exploration Rover (MER) Opportunity observations that
indicate the presence of sulfates and hematite concretions
(Christensen et al. 2004) in an outcrop containing bedforms
originating in flowing water (Herkenhoff et al. 2004).

A previously undescribed hematite formation mechanism
for Mars was suggested by a recent study of the effects of
crystallinity and oxidation on the spectra of Martian basalts
(Minitti et al. 2002). Minitti et al. (2002) oxidized Martian
basaltic samples with a range of glass contents
(crystallinities) in air at 700 °C. For glass-rich samples,
oxidation yielded samples with visible, near-infrared, and
thermal infrared spectra consistent with the presence of
hematite. The hematite signature appeared to originate from a
thin, metallic sheen developed over glassy surfaces. However,
Minitti et al. did not confirm the presence of hematite with
other analyses. The apparent presence of a uniform hematite
coating on the surfaces of oxidized glasses suggested that
hematite could form via oxidation during extrusion of glass-
bearing basaltic flows. In this study, we confirm that
oxidation of basalt glass leads to the formation of a thin,
uniform hematite coating and refine the conditions under
which glass oxidation results in hematite formation with both
natural and additional laboratory samples. The glass
oxidation mechanism of hematite formation acts in a strictly
igneous environment and may provide an important source of
hematite given the widespread occurrence of igneous
materials observed on Mars. The mechanism, which requires
neither chemical weathering nor water, has implications for
the role and importance of water in the formation of hematite
present in Martian surface materials.

**EXPERIMENTAL TECHNIQUES**

To confirm the formation of a uniform hematite coating
on oxidized basaltic glass, we used basaltic glass samples
synthesized by Minitti et al. (2002). The samples included
glass-rich (85% glass + 15% pigeonite phenocrysts) and fully
glassy basalts with Martian meteorite-like compositions (i.e.,
high FeO, low Al2O3) (Minitti and Rutherford 2000). Minitti
et al. (2002) ground and sieved the glass-rich sample to a 75–
500 μm particle size and the purely glassy sample to a <75 μm
particle size. The samples were subjected to oxidation under
different conditions. Minitti et al. (2002) held the glass-rich
sample at 700 °C in air for 7 days. For this study, we initially
held the fully glassy sample at 350 °C in air for 14 days and,
in a separate experiment, held the same sample at 900 °C in
CO2 for 3 days. We used the pure glass sample in the latter
CO2 experiment only after determining that the 350 °C
experiment had no effect on the chemistry of the sample (see
Results section). The 350 °C experiment was intended to
explore the effects of oxidation at low temperatures and the
CO2-based experiment was conducted in an effort to mimic
oxidation in the Martian atmosphere. Despite using pure CO2,
oxxygen was available in the environment around the sample
due to the reaction CO2 → CO + ½O2. At the temperature of
the experiment, log fO2 of the environment was ~10⁻⁸ (Deines
et al. 1974), corresponding to an oxygen fugacity near the
hematite-magnetite buffer.

**ANALYTICAL TECHNIQUES**

We assessed the chemistry and distribution of elements in
the samples using the JEOL 845 scanning electron
microscope (SEM) at Arizona State University (ASU). Thin
sections of the oxidized glasses were studied via
backscattered electron (BSE) imaging and X-ray mapping.
Images and maps were made with a focused, 15 kV, 0.6–2 nA
beam.

Raman spectroscopy was employed to investigate the
mineralogical nature of the oxidized basalt glasses. We
collected Raman spectra in the Mineral Spectroscopy
Laboratory at the California Institute of Technology using a
Renishaw M1000 Micro Raman spectrometer with a
514.5 nm argon laser operated at 0.5 mW. A double-wedged
quartz depolarizer was used to minimize or eliminate
polarization effects in the Raman spectra. The laser was
focused onto the sample through either 20× or 50× objective
lenses producing 5–8 μm or 3–5 μm spots, respectively.
Collection times varied between 10–240 sec. We also
collected Raman spectra at Arizona State University using a
Jobin-Yvon Triax 550 spectrometer coupled with a Spectra
Physics 2020-5 argon laser. Raman spectra were excited with
the 514.5 nm line of the laser that delivered ~10 mW of power
to the sample surface through a 50× objective lens. We
defocused the laser beam on the sample to a spot size of ~4–
6 μm and collected spectra over three 240-sec intervals. Data
from each interval were added together to produce a final
spectrum. We used combinations of collection time, spot size,
and laser power to prevent degradation or alteration of the
analyzed samples under the laser spot. We selected analysis
conditions guided by the studies of de Faria et al. (1997) and
Shebanova and Lazor (2003), which focused on constraining
proper analysis conditions for Fe oxides and oxyhydroxides.
During the ASU Raman analyses, we monitored the spectra
after each collection interval to ensure no beam-induced
change appeared in the spectra and after both the ASU and
Caltech analyses, the analyzed samples were examined under
reflected light to confirm the absence of laser-induced
damage. Samples of pure phases, including hematite,
maghemite, magnetite, goethite, lepidocrocite, augite, enstatite, and unoxidized basalt glass, were analyzed to obtain Raman spectra for comparison to the experimental samples. Some of the pure phase spectra were collected at ASU or Caltech under the same conditions as the experimental samples and the remaining spectra were collected at Caltech using a red, 780 nm diode laser delivering 0.5 mW to the samples through a 50× objective. Collection times for the spectra obtained with the 780 nm laser lasted 60 sec.

Characterization of the reflectance and emission spectra of the basalt glasses was carried out in order to compare the sample spectra to the remotely sensed spectra of Mars. Visible and near-infrared (VNIR) and mid-infrared spectra were acquired from the unoxidized samples by Minitti et al. (2002) using the Keck/NASA RELAB facility at Brown University. VNIR spectra between 0.32–2.55 μm at a 0.01 μm sampling interval were collected using the bidirectional spectrometer with an incidence angle of 30° and an emergence angle of 0° (Minitti et al. 2002). Mid-infrared spectra were collected using an on-axis, biconical FTIR spectrometer from ~400–5500 cm$^{-1}$ at 4 cm$^{-1}$ intervals with 30° incidence and 30° emergence angles (Minitti et al. 2002). The mid-infrared reflectance spectra of the unoxidized samples were converted to emissivity using Kirchoff’s law ($e = 1 - r$). We collected VNIR spectra of the oxidized samples at the RELAB facility under the same conditions used by Minitti et al. (2002). We also obtained thermal infrared spectra of the oxidized samples between 200–2000 cm$^{-1}$ with 2 cm$^{-1}$ spectral resolution at the Arizona State University Thermal Emission Spectroscopy Laboratory. Each analysis involved 320 scans by the spectrometer to produce an individual spectrum. Multiple spectra of each sample were obtained and averaged together to produce a final spectrum with improved signal-to-noise. The thermal infrared spectral data were also resampled to 10 cm$^{-1}$ spectral resolution for comparison to MGS TES data (Christensen et al. 1992, 2001a).

### RESULTS

**Sample Description**

Oxidation in the high-temperature experiments caused significant transformation of the samples. Internally, the glasses are partially devitrified into nm-size pyroxene crystallites (Minitti et al. 2002) or μm-size dendrites. The crystallites formed in the glass oxidized at 700 °C, whereas the dendrites formed in the glass oxidized at 900 °C. Formation of the larger dendrites in the 900 °C experiment is likely due to the higher experiment temperature leading to coarser devitrification products in the glass. Oxidation also caused both high-temperature oxidation products to become magnetic despite the lack of formation of Fe-Ti oxide phenocrysts during the original basalt synthesis experiments. Externally, the black, vitreous luster of the glasses altered to a gray, metallic sheen that can be removed with gentle abrasion. Thus, oxidation created a coating on the glassy surfaces of the basalts oxidized at high temperature. The low-temperature oxidation experiment product did not develop devitrification products, a coating or magnetism, which indicated that the low-temperature experiment did not significantly alter the starting material.

**SEM Analyses**

SEM analyses revealed the chemistry and elemental distributions of the oxidation-induced coatings on the samples. X-ray maps indicated that the samples oxidized both in air and in CO$_2$ at high temperature exhibit layers of Fe and Ca enrichment at the surfaces of the glasses (Figs. 1a and 1b). The Fe-rich layer is always exterior to the Ca-rich layer. The thicknesses of Fe- and Ca-rich layers on the air-oxidized sample range from 1–1.5 μm and the thicknesses of layers on the CO$_2$-oxidized sample range from 0.2–0.7 μm. The Fe-rich layers appear to correspond to bright rims visible in the BSE images of the samples (Figs. 1c and 1d). The CO$_2$-oxidized sample also has a zone of moderate (relative to the outermost Fe layer) Fe enrichment interior to the Fe- and Ca-rich layers. The element distributions in this zone resemble those observed in pyroxene clusters formed by devitrification of the glass. Thus, the moderately Fe-enriched zone is interpreted as pyroxene developed as a near-surface devitrification product. The exact chemical classification of the pyroxene devitrification products was not determined with the SEM data. In contrast to the high-temperature oxidation products, no chemical gradient was developed during the 350 °C oxidation experiment (Fig. 1e). We interpret the lack of chemical gradient development as further evidence (in addition to no devitrification product, coating, or magnetism development) that the low-temperature oxidation step did not meaningfully affect the pure glass sample and that the sample could be used in the 900 °C CO$_2$ oxidation experiment.

**Raman Analyses**

Chemistry alone does not reveal which Fe-rich and Ca-rich phases make up the coatings on the surfaces of the oxidized glasses. Raman analyses were used to determine the mineralogical nature of the Fe-rich and Ca-rich materials. Raman spectra of the air-oxidized samples obtained from both laboratories exhibit peaks near 221, 241, 291, 322, 407, and 610 cm$^{-1}$ and broad peaks near 480, 690, and 1311 cm$^{-1}$ (Fig. 2a). Similarly, Raman spectra of the CO$_2$-oxidized samples exhibit peaks near 223, 240, 290, 405, 491, 604, and 1310 cm$^{-1}$ and a broad peak near 664 cm$^{-1}$ (Fig. 2b). The relative sizes of the peaks vary between the ASU- and Caltech-collected spectra from both the air- and CO$_2$-oxidized samples. However, the consistent appearance of features in both the ASU and Caltech spectra strongly suggest that none
Fig. 1. SEM images of oxidized sample cross sections: a) X-ray element map of air-oxidized sample. Red corresponds to Si, yellow corresponds to Fe; b) X-ray element map of CO$_2$-oxidized sample. Red corresponds to Si, yellow corresponds to Fe; c) BSE image of air-oxidized sample. Bright rim at surface of sample corresponds to zone of Fe enrichment in (a); d) BSE image of CO$_2$-oxidized sample. Bright rim at surface of sample corresponds to zone of Fe enrichment in (b); e) X-ray element map of 350 °C, air-oxidized sample. Red corresponds to Si, yellow corresponds to Fe. Note the lack of Fe-enriched zone at the surfaces of the sample; f) X-ray elemental map of a cross section of a Hawaiian basalt exhibiting a gray, metallic sheen. Purple corresponds to Si, green corresponds to Fe. The Hawaiian basalt exhibits the same Fe enrichment at its surface as the experimentally-oxidized samples.
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Fig. 2. a) Spectra from surfaces of air-oxidized samples collected at Caltech (black) and ASU (gray). The spectra are offset along the intensity axis for clarity; b) spectra from surfaces of CO₂-oxidized samples collected at Caltech (black) and ASU (gray). The spectra are offset along the intensity axis for clarity; c) Raman spectra collected at Caltech from surfaces of air-oxidized (black) and CO₂-oxidized (gray) samples and an unoxidized glass (dashed). The spectra are offset along the intensity axis for clarity. The differences between the oxidized sample spectra and the unoxidized glass spectrum in (c) indicate the occurrence of mineralization at the surfaces of the oxidized samples. The similarities between the spectra in (a) and between the spectra in (b) indicate that both sets of analyses detected the same mineralization. All spectra were excited using a 514.5 nm Ar laser.
of the features is due to analytical conditions. Each coating spectrum differs from the spectrum exhibited by an unoxidized, glassy Hawaiian basalt with broad peaks near 182, 275, 404, 505, 558, 778, and 980 cm\(^{-1}\) (Fig. 2c). The Raman peaks exhibited by the coated surfaces of the experimentally oxidized basalt indicate that the coatings represent mineralization on the oxidized surface of the basalts.

Visible and Infrared Spectroscopy

Spectral characterization of the coatings on the oxidized basalt glasses is important for phase identification and comparison to the spectra of Mars obtained via remote sensing. Comparison of the VNIR spectra of both the air- and CO\(_2\)-oxidized samples before and after oxidation reveals the significant change in spectral character caused by oxidation (Fig. 3). Prior to oxidation, the basalt spectra have positive slopes and weak, broad absorptions near 1.1 and 1.9 \(\mu\)m, consistent with the glassy nature of the basalts. The spectrum of the air-oxidized basalt has an absorption at 0.47 \(\mu\)m, a negative slope from \(-0.74\) to \(-1.4\) \(\mu\)m, and a positive slope at wavelengths longer than \(-1.4\) \(\mu\)m (Fig. 3a). The CO\(_2\)-oxidized sample spectrum also has an absorption at 0.47 \(\mu\)m, but has an overall negative slope at wavelengths longer than 0.65 \(\mu\)m and an absorption near 1 \(\mu\)m (Fig. 3b). The absorption near 1 \(\mu\)m in the CO\(_2\)-oxidized basalt spectrum most likely arises from the pyroxene devitrification products near the surface of the CO\(_2\)-oxidized basalt.

Oxidation also induced changes to the emissivity spectra of the basalts. Before oxidation, both basalt spectra exhibit broad, featureless bands between 800–1200 cm\(^{-1}\) and 400–600 cm\(^{-1}\), diagnostic of the amorphous nature of glass that dominates the modes of the samples (Fig. 4) (Simon and McMahon 1953). The glass-rich sample spectrum (before oxidation in air) has minor pyroxene absorptions between 800–1000 cm\(^{-1}\) due to the pigeonite phenocrysts in the sample (Fig. 4a). After oxidation, the spectrum of the air-oxidized sample displays absorptions near 1230 cm\(^{-1}\) and...
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540 cm$^{-1}$ and a narrowed broad feature between 800–1100 cm$^{-1}$. The spectrum also exhibits a nearly flat, reduced-emissivity section between 200–400 cm$^{-1}$, but it is not possible to assess the degree to which oxidation is responsible for the character of the spectrum between 200–400 cm$^{-1}$ given the lack of data for the unoxidized sample over this spectral range (Fig. 4a). In the spectrum of the CO$_2$-oxidized sample, oxidation transforms the broad features of the unoxidized spectrum to narrower, V-shaped absorptions near 1070 and 466 cm$^{-1}$ (Fig. 4b). Oxidation also introduces minor features into the spectrum of the CO$_2$-oxidized sample near 1200 cm$^{-1}$ and between 800–1000 cm$^{-1}$.

**DISCUSSION**

**Interpretation of the Raman Data**

Comparison of the Raman peak positions obtained from the oxidized basalt coatings to those obtained from known minerals facilitated identification of the phases in the coatings.
(Fig. 5). In the air-oxidized Raman spectrum, peaks near 221, 241, 291, 407, 480, 610, 690, and 1311 cm\(^{-1}\) correspond to peaks exhibited by gray hematite analyzed under the same conditions as the experimental samples (Fig. 5a). A better match to the hematite spectrum is made with the CO\(_2\)-oxidized sample spectrum. Each of the features in the CO\(_2\)-oxidized spectrum is accounted for by features in the gray hematite spectrum (Fig. 5a). Comparison of the oxidized basalt spectra and the spectra of other Fe oxides, Fe oxyhydroxides, and pyroxenes (Figs. 5b–5f) reveals that no other phase provides consistent matches over all of the peak positions to the Raman spectra of the oxidized glasses as hematite does (Fig. 5a). The peak near 670 cm\(^{-1}\) in the magnetite spectrum, however, could account for the relative size of the 690 cm\(^{-1}\) and 664 cm\(^{-1}\) peaks in the air-oxidized and CO\(_2\)-oxidized spectra, respectively. This observation suggests that some fraction of the Fe enrichment on the oxidized glass surfaces is due to the presence of magnetite. It is unclear to what degree magnetite and hematite contribute to the 690/664 cm\(^{-1}\) peaks in the Raman spectra of the oxidized glasses, particularly given the factors that can affect relative peak positions, heights, and breadths (see below).

The relative peak positions, peak heights, and peak breadths differ among the spectra of the air-oxidized sample, the CO\(_2\)-oxidized sample and hematite (Fig. 5a). The peaks exhibited by the experimentally oxidized sample spectra are consistently offset to lower wave numbers relative to the peaks in the hematite spectrum, whereas peak positions among the experimental sample spectra are similar. Relative to the hematite spectrum, the experimentally oxidized sample spectra consistently tend to exhibit stronger peaks near 220, 290, and, in the Caltech-collected spectra, near 690 cm\(^{-1}\) (664 cm\(^{-1}\) for the CO\(_2\)-oxidized sample). The relative peak heights of experimentally oxidized sample spectra differ slightly from one another, primarily in the relative size of the broad peaks near 480 and 690 cm\(^{-1}\) (664 cm\(^{-1}\)). Peak breadth variations are most pronounced between the peaks in the air-oxidized sample spectrum and those in the hematite spectrum. Peaks exhibited by the CO\(_2\)-oxidized sample spectrum are narrow relative to those of the air-oxidized sample spectrum.

The observed variations in peak position, height, and breadth can be explained by minor differences in the chemistry, crystallinity (point or line defects) or grain size of the hematite in the individual samples (e.g., Tuinstra and Koenig 1970; McMillan and Hofmeister 1988; Wang et al. 1998). The ability of minor crystal-chemical differences to influence the expression of peaks in the Raman spectrum of a single mineral is demonstrated by the multiple hematite Raman spectra in Fig. 6. The hematite spectra, obtained from a variety of forms of hematite, exhibit differences in peak occurrence, position, breadth, and relative height. The literature also corroborates the abilities of chemistry, crystallinity, and grain size to influence the expression of Raman peaks in a mineral spectrum. Any of these variables alone or in combination can affect relative peak positions (Wang et al. 1998), suggesting that hematite in the oxidized glass coatings has minor chemical impurities, structural defects, and/or small grain size relative to the analyzed hematite sample. Similarities of peak positions among the experimentally oxidized sample spectra suggest that the glass oxidation process produces hematite that has consistent chemistry and morphology. Deviations from nominal hematite chemistry and stoichiometry (presence of point defects) can also cause changes in relative peak heights (e.g., Tuinstra and Koenig 1970; McMillan and Hofmeister 1988), as can differences between the crystal orientations of the hematite in the coatings relative to the analyzed hematite. Similarities in peak heights among the air- and CO\(_2\)-oxidized sample spectra again suggest that the chemistry and morphology of hematite created in the oxidation process are internally consistent, but different from the analyzed hematite sample. Peak broadening can be attributed to lower degrees of crystallinity (e.g., Tuinstra and Koenig 1970). The narrower peaks exhibited by the CO\(_2\)-oxidized sample spectrum relative to the air-oxidized sample spectrum suggest that the hematite coating of the former sample is better crystallized than that of the latter. The higher degree of crystallinity of the hematite created in the CO\(_2\) oxidation is likely due to the higher temperature of the experiment rather than the oxidation environment, as higher temperatures permit a faster approach to equilibrium. In general, the specific positions and morphologies of the
Raman peaks in the oxidized sample spectra indicate that hematite of varying purity, crystallinity, or grain size is present in the coatings. The minor feature at 325 cm\(^{-1}\) in the air-oxidized sample spectrum appears in neither the hematite nor the CO\(_2\)-oxidized glass spectra (Fig. 5). A potential source of the 325 cm\(^{-1}\) feature is pyroxene, either from the pigeonite phenocrysts formed during crystallization of the sample or from the nm-sized pyroxenes formed by devitrification of the glass during oxidation. Both orthopyroxenes and clinopyroxene exhibit a feature near 330 cm\(^{-1}\) (Fig. 5f). Pyroxenes are also consistent with the broad features in the air-oxidized glass spectrum near 690 cm\(^{-1}\) and in the CO\(_2\)-oxidized glass spectrum near 664 cm\(^{-1}\). A contribution from pyroxene to the 690/664 cm\(^{-1}\) features could lessen the need to appeal to magnetite to explain the relative size of the 690/664 cm\(^{-1}\) features. However, pyroxene devitrification products are present in and nearer to the surface of the CO\(_2\)-oxidized sample, yet its Raman spectrum does not contain the 325 cm\(^{-1}\) feature. Further, neither the air-oxidized nor CO\(_2\)-oxidized sample spectra contain evidence of the large pyroxene feature near 1010 cm\(^{-1}\) (Fig. 5f), which might be expected given the possible expression of the other major pyroxene peaks.

Another possible source of the 325 cm\(^{-1}\) feature is the Ca-rich phase present interior to the hematite. CaO or Ca(OH)\(_2\). Ca-rich phases observed as glass oxidation products in earlier studies (e.g., Cooper et al. 1996; see also Hematite Formation Mechanism section below) are candidates to explain the Ca-rich layer below the hematite layer, but pure, stoichiometric CaO does not have a Raman active mode (G. Wolf, personal communication). If Ca(OH)\(_2\) is the source of the Ca enrichment, the dominance of hematite-related peaks in the Raman spectrum suggests that it is only weakly Raman active. However, if Ca(OH)\(_2\) were responsible for the 325 cm\(^{-1}\) feature, the feature would be expected to appear in the spectrum of the CO\(_2\)-oxidized sample because it also has a Ca-rich layer interior to the hematite layer.

The third possibility is that the 325 cm\(^{-1}\) feature is due to differences in the nature of the glasses in the air- and CO\(_2\)-oxidized samples. Glasses have the potential to exhibit a variety of features (e.g., Fig. 2). It is possible that the air-oxidized glass has a unique Raman signature due to alteration of the glass through formation of the finely distributed, nm-sized pyroxenes and that it differs from the signature of the glass surrounding the larger-scale pyroxene clusters in the CO\(_2\)-oxidized glass. The presence of this feature in the air-oxidized spectrum and its absence in CO\(_2\)-oxidized spectrum does not alter the conclusion that hematite is present at the surface of the oxidized glasses.

Given the feasible explanations for the observed minor variations in peak positions, heights and breadths between the oxidized glass spectra and the hematite spectrum and the overall compelling similarity of Raman features between the oxidized glass spectra and the hematite spectrum, the Raman data clearly indicate that hematite is largely responsible for the Fe enrichment observed at the surfaces of the oxidized glasses.

**Interpretation of the Visible and Infrared Spectroscopy Data**

The VNIR data can be interpreted in light of the demonstrated presence of hematite in the experimental sample coatings. Both oxidized glass spectra have low reflectivity, which is particularly notable for the CO\(_2\)-oxidized sample spectrum because it originates from a <75 µm particulate sample (Fig. 3) and fine-grained samples tend to yield bright, not dark, spectra. Low reflectivity is consistent with VNIR spectra of gray hematite (e.g., Hunt et al. 1971; Morris et al. 1985; Lane et al. 2002). Both spectra also exhibit an absorption near 0.47 µm. The position of this feature corresponds to an electronic Fe\(^{3+}\) transition in hematite (Burns 1993). A distinct absorption at 0.47 µm is not observed in the VNIR spectrum of pure hematite because the band is typically saturated. The feature does appear in the spectra of samples with minor amounts of hematite dispersed in a scattering matrix (Morris and Lauer 1990). The low reflectivities of the oxidized glass spectra are also consistent with the presence of magnetite in the sample coatings. The VNIR spectrum of magnetite is largely featureless (e.g., Hunt et al. 1971; Morris et al. 1985), making its positive identification in the oxidized glass spectra difficult. Magnetite can exhibit a small reflectivity maximum between 0.73–0.81 µm (Morris et al. 1985). However, the position of this maximum falls at longer wavelengths than the reflectivity maxima observed in the coating spectra. The negative spectral slope at wavelengths >0.65 µm in the CO\(_2\)-oxidized spectrum is consistent with the presence of a thin, Fe\(^{3+}\)-bearing coating over a basalt substrate (Singer and McCord 1979; Fischer and Pieters 1993), though not specifically a hematite coating. The lack of a negative spectral slope across all wavelengths >0.74 µm in the air-oxidized sample spectrum may be because the coating is optically thin in the VNIR and/or the coarse particle size of the bulk sample limits scattering.

In the thermal infrared, despite the definitive evidence of hematite in the oxidation-induced coatings, gray hematite-related features like those detected by TES are not apparent in the spectra (Figs. 4 and 7a). The exceptions are the local emissivity maximum at 497 cm\(^{-1}\) and the absorption near 540 cm\(^{-1}\) in the spectrum of the air-oxidized sample (Figs. 4a and 7a). The emissivity maximum falls at effectively the same position as the maximum exhibited by gray hematite near 500 cm\(^{-1}\). The position of the absorption is consistent with the gray hematite feature near 560 cm\(^{-1}\) (Fig. 7a). Assignment of the 497 cm\(^{-1}\) emissivity maximum and the 540 cm\(^{-1}\) feature to hematite is further supported by...
comparison of the air-oxidized sample spectrum to a TES spectrum from a surface in Meridiani Planum exhibiting both TES basalt and hematite features (Christensen et al. 2001b). Data between 500–800 cm$^{-1}$ are omitted due to interference from the Martian CO$_2$ atmosphere. The dashed spectrum is the thermal infrared emission spectrum of coarse-grained, gray hematite. The depths of the hematite absorption features are scaled for comparison to the other spectra. The TES and hematite spectra are shifted along the emissivity axis for clarity. All spectra have 10 cm$^{-1}$ spectral resolution; b) comparison of the air-oxidized (black) and CO$_2$-oxidized (gray) sample spectra to the spectrum of magnetite (dashed). The positions of absorptions and emissivity maxima in the magnetite spectrum are not observed in the oxidized glass spectra.

Fig. 7. a) Comparison of hematite signatures in laboratory and natural samples. The black spectrum is the thermal infrared emission spectrum of the air-oxidized sample. The gray spectrum is a TES spectrum from a surface in Meridiani Planum exhibiting both TES basalt and hematite signatures (Christensen et al. 2001b). Data between 500–800 cm$^{-1}$ are omitted due to interference from the Martian CO$_2$ atmosphere. The dashed spectrum is the thermal infrared emission spectrum of coarse-grained, gray hematite. The depths of the hematite absorption features are scaled for comparison to the other spectra. The TES and hematite spectra are shifted along the emissivity axis for clarity. All spectra have 10 cm$^{-1}$ spectral resolution; b) comparison of the air-oxidized (black) and CO$_2$-oxidized (gray) sample spectra to the spectrum of magnetite (dashed). The positions of absorptions and emissivity maxima in the magnetite spectrum are not observed in the oxidized glass spectra.

A well-understood mechanism exists to explain the formation of hematite on the surface of basalt glass in oxidizing conditions. Cooper et al. (1996) determined that oxidizing conditions induce a coupled migration of divalent cations and charge within an oxidizing glass. The process is initiated by the reaction of Fe$^{2+}$ at the glass surface with atmospheric oxygen. Atmospheric oxygen removes electrons from Fe$^{2+}$ cations in the glass and the resulting oxygen anions react with either Fe, Ca, or Mg on the glass surface to form oxides. This reaction has three products: the newly created...
oxide, Fe$^{3+}$ cations in the glass, and a cation vacancy in the glass, created by removal of the cation to form the new oxide. The oxidation process proceeds by migration of Fe$^{3+}$ and cation vacancies to the interior of the glass, with the migration of Fe$^{3+}$ accommodated by effectively transferring positive charge from an oxidized Fe cation to an unoxidized neighbor in the glass interior (Fe$^{3+}$ shifts its positive charge, or a “hole,” to a neighboring Fe$^{2+}$). As positive charge and cation vacancies migrate inward, mass and charge balance in the glass are maintained by the outward migration of Fe$^{2+}$, Ca$^{2+}$, or Mg$^{2+}$ cations. The divalent cations that reach the surface of the oxidizing glass can then become involved in oxide-producing reactions. As a result, Fe, Ca, and Mg oxides are observed as surficial products of glass oxidation (Cook et al. 1990; Cooper et al. 1996).

The distribution of products resulting from cation migration is dictated by a combination of the mobility and concentration of the cations and the temperature of oxidation. In the experiments of this study, the Fe oxide (hematite) is consistently exterior to the Ca oxide and there is no observed Mg oxide development on the sample surfaces. This distribution requires more efficient Fe migration than Ca migration (and in turn, Mg migration). Experiments of Cooper et al. (1996) and Cook and Cooper (2000) illustrate that at sufficiently high FeO concentrations (>1.9 wt%) and temperatures (700 °C), Fe migration is favored over Ca and Mg migration. The temperature of the experiments in this study (700 and 900 °C) are high enough to favor Fe migration and the FeO concentration of the basalt glasses (~19.5 wt%), a result of their Martian meteorite-like nature, is well above the minimum FeO concentration. FeO is also present in much greater concentration than either CaO (~9 wt%) or MgO (5–7 wt%) in the glasses, further favoring its migration during oxidation relative to the other two cations. The higher concentration of CaO relative to MgO in the glasses is consistent with the presence of a Ca-enriched layer and the absence of an Mg-enriched layer near the surface of the oxidized glasses. The behaviors of divalent cations in response to temperature and concentration support the observed distribution of Fe, Ca, and Mg at the surfaces of the oxidized glasses. The high temperatures of the experiments and the high concentration of Fe combine to facilitate hematite formation on the surfaces of the oxidized glasses.

The lack of chemical gradient development observed in the product of the 350 °C experiment (Fig. 1e) suggests that high oxidation temperatures are necessary to induce cation migration and, ultimately, hematite coating formation. Thus, hematite coating formation is not expected on already emplaced glass-rich basalt flows exposed to moderately elevated temperature environments such as reheating during nearby magma emplacement or nearby hydrothermal activity. Rather, the high temperatures necessary to induce hematite coating formation are expected to exist only during initial extrusion of glass-rich basalt flows.

**Terrestrial Analog for Process**

While laboratory studies provide a formation mechanism for hematite coatings on basalt glasses and suggest that such coatings would form during basalt extrusion, is it possible for the process to act in geologically relevant conditions? We studied the gray, metallic sheen commonly observed on newly extruded Hawaiian basalt flows as an apparent analogue to the hematite coatings on the experimental basalts. Our Hawaiian basalt was collected from cooling pahoehoe films in October 2001 (K. Hibbitts, personal communication) and we subjected it to the same suite of SEM and Raman analyses used to study the experimentally oxidized basalts. Elemental maps of the metallic sheen on the Hawaiian basalt indicate that the sheen corresponds to Fe- and Ca-rich layers in the same geometry as those observed on the experimentally oxidized basalts (Fig. 1f). The Fe- and Ca-rich layers range in thickness from 0.5–0.7 µm. The presence of the Fe- and Ca-enriched layers at the surface of a naturally emplaced glass-rich basalt suggests that the process active in the experimentally oxidized basalts is also active in naturally oxidized basalts.

Raman analyses further indicate that the experimentally oxidized samples capture a natural hematite formation process. Initial Raman analysis of the surface of the Hawaiian basalt led to alteration of the gray, metallic sheen under the laser as evidenced by fluorescence and nearly featureless Raman spectra. Substituting a 20× objective for the 50× objective expanded the area over which the laser power was distributed and eliminated the occurrence of alteration. The resulting Raman spectrum of the Hawaiian sheen exhibits peaks near 216, 285, and 400 cm$^{-1}$ and broad peaks near 650 and 1300 cm$^{-1}$ which correspond to the positions of Raman peaks exhibited by hematite (Fig. 8) and the experimentally oxidized basalt glasses (Fig. 5). A portion of the peaks in the Raman spectrum of the unoxidized glassy bottom of the Hawaiian sample (Fig. 2c) occur at positions similar to those of peaks in the Raman spectrum of the sheen. However, we favor assignment of peaks exhibited by the sheen to hematite primarily because the broad peak near 1300 cm$^{-1}$ corresponds to a peak resulting from the antiferromagnetic nature of hematite (de Faria et al. 1997), which makes the peak diagnostic of hematite. Confirmation that the Fe enrichment at the surface of the Hawaiian basalt is hematite fully demonstrates that the oxidation experiments reproduce a naturally occurring process and supports the deduction that hematite coatings can form on the surfaces of glassy basalts during extrusion. The Hawaiian basalt also demonstrates that high, Martian meteorite-like concentrations of FeO in a basalt glass are not required for hematite formation.

**CONCLUSIONS AND IMPLICATIONS**

Glass-rich basalts with Martian meteorite-based chemistry (high FeO, low Al$_2$O$_3$) oxidized at high (700 and
900 °C) temperatures in air and CO2, respectively, form thin (<1 µm) hematite coatings on the outermost surfaces of the glasses. Hematite is manifested macroscopically by development of magnetism and a gray, metallic sheen on the glass surface and microscopically by Fe enrichment at the glass surface observed in element maps. Raman analyses confirm that the Fe enrichment at the surfaces of the oxidized glasses corresponds to hematite, and some possible magnetite, mineralization. Glass-rich basalt oxidized at lower temperatures (350 °C) does not develop any evidence of hematite formation. Thus, hematite formation is concluded to occur only at high temperatures, likely during extrusion and emplacement of glass-rich basalt. Hematite formation on basaltic glass is enabled by an oxidation mechanism that induces migration of divalent cations, most notably Fe2+, to the surface of an oxidizing glass (e.g., Cooper et al. 1996). Once concentrated at the surface of an oxidizing basalt glass, the Fe2+ cations can be oxidized and form hematite. A terrestrial “proof of concept” is provided by Hawaiian basalt with a gray, metallic sheen that corresponds to a thin hematite coating. Hematite coating development on a Hawaiian basalt with 10–11 wt% FeO demonstrates that Martian meteorite-like FeO contents (~19 wt% FeO; Minitti and Rutherford 2000) are not required for a basalt glass to form a hematite coating and that such coatings indeed form during extrusion.

The experimentally oxidized basalt glasses and the Hawaiian basalt analogue strongly suggest that hematite can form on Martian basalts during extrusion whether they are like those observed by TES or like Martian meteorite basalts. Concentrations of FeO extrapolated from mineralogies of the TES basalt determined through linear deconvolution of the TES surface type 1 spectrum (Christensen et al. 2000a; Bandfield et al. 2000) range between 5–15 wt% FeO (McSween et al. 2003). This range of TES basalt FeO contents overlaps the FeO content of the Hawaiian basalt of this study suggesting that TES basalt contains adequate amounts of FeO for hematite coating formation. Concentrations of FeO in rocks measured on the Martian surface by Mars Pathfinder (e.g., Foley et al. 2003) and MER (Gellert et al. 2004) are also sufficient to have facilitated hematite coating formation, if those rocks or their counterparts at the respective landing sites were glass-bearing igneous rocks.

If hematite coatings formed by oxidation during basalt extrusion are present on the Martian surface, their detectability by Mars remote sensing instruments varies with wavelength. In the VNIR, the spectral range and resolution capabilities of current (OMEGA; Bibring et al. 2004) and future (CRISM; Murchie et al. 2002) instruments are sufficient to distinguish differences between the spectra of hematite-coated glassy basalts and their unoxidized counterparts (Fig. 3). Further, the distinction could be observed from either coarse or fine particle size materials (Fig. 3). However, the relatively subtle features associated with the hematite coating (low reflectivity, absorption near 0.47 µm, negative spectral slope across a portion of wavelengths >0.74 µm) could also be assigned to other Fe3+-bearing materials, making unique detection of hematite-coated basalts like those of this study difficult. Recognition of hematite-coated basalts could also be hindered by the presence of bright dust (Morris et al. 1989). If VNIR spectra like those of the oxidized samples in Fig. 3 were obtained from Mars, imaging data that reveal the geologic context of the source of the spectra and/or albedo data might enable positive identification of hematite coated basalts. In the thermal infrared, the oxidized sample spectra (Fig. 4) have the same spectral range and resolution as TES data, illustrating that detection of hematite coatings is possible with TES. The coating crystallinity and thickness and corresponding subtlety (or lack) of features in the thermal infrared, however, makes hematite coating detection even more challenging than in the VNIR. The oxidized spectra suggest that a hematite coating must have a minimum thickness of ~1 µm to yield features diagnostic of hematite in the thermal infrared (Fig. 4a). Because the combined Raman and thermal infrared data of this study suggest that hematite crystallinity and particle size influence the strength of the hematite signature in the thermal infrared, thinner coatings might require some form of metamorphism to coarsen and/or recrystallize the hematite in the coatings to enable detection.

Despite challenges associated with its unique detection, hematite originating from oxidation of glassy basalt flows is potentially abundant on Mars given the widespread occurrence of volcanic materials on the Martian surface (Mouginis-Mark et al. 1992; Bandfield et al. 2000). Hematite coatings formed on oxidized, glassy basalt flows easily could be physically weathered off and contribute to the red hematite observed in the Martian soil. Hematite
coatings like those in this study do not yield a thermal infrared signature like that of the gray hematite detected by TES. Additionally, the recent apparent evidence for the role of water in the formation of hematite and its associated deposits at the Meridiani landing site (e.g., Christensen et al. 2004; Herkenhoff et al. 2004) seems to discount the possibility that the Meridiani hematite represents a hematite coating produced during extrusion of a glassy basalt flow. Given similar, water-related sedimentary origins proposed for the hematite-associated materials in Aram Chaos and Valles Marineris (Nedell et al. 1987; Christensen et al. 2001b; Glotch and Christensen 2003; Weitz et al. 2003), it may also be unlikely that hematite-coated basalts like those in this study are the source of the hematite signature in these regions. However, formation of the gray hematite in Aram Chaos and Valles Marineris by glassy basalt flow oxidation during extrusion should not be discounted as these sites are studied further. If gray hematite originating as coatings on glassy basalt flows is an important source of Martian hematite, as may well have been the case in other areas of Mars, it removes the requirement of water as an initial alteration agent of Martian crustal materials. The new hematite formation mechanism presented here should be taken into consideration when assessing the nature and source of the hematite component of Martian surface materials and the role of water as a necessary agent in hematite formation.

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