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Thermal transformations of akaganéite and lepidocrocite to hematite: assessment of possible precursors to Martian crystalline hematite

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Abstract We examine the possibility that crystalline hematite $(\alpha$ -Fe₂O₃) deposits on Mars were derived from the precursor iron oxyhydroxide minerals akaganéite (β -FeOOH) or lepidocrocite (γ -FeOOH) and compare them to an earlier study of goethite (α -FeOOH) and magnetite (Fe₃O₄) precursors. Both the mid-infrared and visible/near infrared spectra of hematite are dependent upon the hematite precursor mineral and the temperature of transformation. Laboratory spectra are compared to spectra from the Mars Global Surveyor Thermal Emission Spectrometer (MGS-TES) and the Mars Exploration Rover (MER) Opportunity Mini-TES and Pancam experiments, allowing us to infer the formation environment of Martian crystalline hematite deposits. Akaganéite and lepidocrocite readily transform to hematite at temperatures of 300 and 500°C, respectively. The visible/ near-infrared and mid-infrared spectra of akaganéitederived hematite are poor matches to data returned from TES, Mini-TES, and Pancam. The spectra of lepidocrocitederived hematite are slightly better fits, but previously published spectra of goethite-derived hematite still represent the best match to MGS and MER spectral data. The experiments demonstrate that hematite precursor mineralogy, temperature of formation, and crystal shape exert a strong control on the hematite spectra.

Keywords Mars · Hematite · Lepidocrocite · Akaganéite · Infrared spectroscopy

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Introduction

Crystalline hematite (α -Fe₂O₃) has been discovered in several localities on Mars, including Meridiani Planum, Aram Chaos, Iani Chaos, Aureum Chaos, and Valles Marineris, using data returned by the Mars Global Surveyor (MGS) Thermal Emission Spectrometer (TES) instrument (Christensen et al. 2000, 2001a, b; Glotch and Christensen 2005; Glotch and Rogers 2007; Weitz et al. 2008). Data returned by the Athena science payload on the Mars Exploration Rover (MER) Opportunity at Meridiani Planum has shown that the crystalline hematite is concentrated in spherules that are eroding from a light-toned sulfate- and silica-rich outcrop (Squyres et al. 2004; McLennan et al. 2005; Glotch et al. 2006a). These spherules have been alternatively interpreted as concretions (Squyres et al. 2004; Chan et al. 2004), volcanic lapilli (McCollom and Hynek 2005), or impact melt spherules (Knauth et al. 2005). In addition, hematite-rich spherules have been produced under hydrothermal conditions in the laboratory with jarosite in the system (Golden et al. in press) suggesting that jarosite may be the Martian hematite precursor. Remote sensing measurements of the other hematite-bearing terrains on Mars indicate that Mg- and Ca-bearing sulfates are also present in association with the hematite (Gendrin et al. 2005; Glotch and Rogers 2007; Noe Dobrea et al. 2008; Weitz et al. 2008).

Initial analyses of the TES hematite spectrum showed that it is dominated by [001] emission (Lane et al. 2002), and this was confirmed by analyses of Mini-TES data (Glotch et al. 2006b; Calvin et al. in press). Previous work also investigated the role of precursor mineralogy and morphology on the visible/near-IR (VNIR) and mid-infrared (MIR) spectral character of hematite by thermally transforming goethite (α -FeOOH) and magnetite (Fe₃O₄) to hematite at various temperatures and examining the subsequent

spectra, transmission electron microscope (TEM) micrographs, X-ray diffraction (XRD) patterns, and Mössbauer spectra of the products (Glotch et al. 2004). That work showed that the MIR emissivity spectrum of hematite derived by the high-temperature oxidation of magnetite is a poor fit to the Martian hematite spectrum, whereas the spectrum of hematite derived by the lower-temperature thermal transformation of goethite provides a good match. Thus, Glotch et al. (2004) concluded that a high-temperature volcanic environment for the formation of crystalline hematite on Mars was unlikely, and that a lower-temperature aqueous environment conducive to the initial formation of goethite was more likely.

Several mineral phases are easily converted to hematite, either through application of mechanical stress and dry heating or through heating in solution at hydrothermal temperatures. These include magnetite, goethite, ferrihydrite (Fe₅HO₈ 4H₂O), schwertmannite $[Fe_{16}O_{16}(OH)_v(SO_4)_z]$ nH_2O], akaganéite (β -FeOOH), lepidocrocite (γ -FeOOH), and jarosite [KFe₃(SO₄)₂(OH)₆] (Cornell and Schwertmann 2003; Golden et al. in press). Amorphous iron oxides/oxyhydroxides or poorly ordered phases such as ferrihydrite are often the first to precipitate in aqueous settings under rapid hydrolysis conditions. These phases are metastable with respect to other iron oxides/oxyhydroxides, and generally age to goethite or another oxyhydroxide. In this work, we expand upon the initial analysis of Glotch et al. (2004)by assessing the thermal transformations of the polymorphs of goethite-lepidocrocite and akaganéite-to hematite and discussing the implications of the results. Understanding the spectral properties of hematite produced from these phases, rather than amorphous or poorly crystalline phases, which are initial precipitates, will provide us with the most information about the potential diagenetic environment that led to the formation of Martian hematite (e.g. McLennan et al. 2005).

In nature, lepidocrocite and akaganéite are often found in association with other iron oxides and oxyhydroxides (Herbert 1995; Cornell and Schwertmann 2003; Murad and Rojík 2005), but specific environmental conditions can favor or disfavor their formation. Therefore, if either of these minerals is shown to be a possible precursor to the Martian crystalline hematite, specific inferences can be made about the chemical environment on Mars at the time of their formation.

In terrestrial settings, lepidocrocite is often thermodynamically unstable with respect to goethite and jarosite (if sulfate is present in the system). However, several factors can favor the formation of lepidocrocite. The presence of organics (Karathanasis and Thompson 1995), a slow rate of Fe³⁺ hydrolysis (Schwertmann and Cornell 2000), a low CO₂ fugacity (Schwertmann 1985; Murad and Rojík 2005), or the presence of excess Fe²⁺ in solution (Schwertmann and Taylor 1989; Carlson and Schwertmann 1990; Herbert 1995) each favor the precipitation of lepidocrocite rather than goethite. Precipitation of akaganéite, on the other hand, is favored in hydrothermal environments with a high Cl content and temperatures near 60°C (Schwertmann and Cornell 2000). Because a major focus on future Mars exploration is the search for organics or other biosignatures, and analysis of hematite-bearing bedrock on Mars indicated the presence of significant Cl (Rieder et al. 2004), it is important to determine if either of these two oxyhydroxide minerals (from low or high temperature environments) is a reasonable precursor for Martian crystalline hematite.

Background

Remote sensing data

Hematite emissivity spectra $(220-1,400 \text{ cm}^{-1})$ were previously isolated from the TES and Mini-TES data sets using factor analysis and target transformation techniques (Glotch et al. 2004; Glotch and Bandfield 2006). Factor analysis and target transformation can be applied to any data set in which the individual components vary linearly with each other (such as MIR spectral data sets). Details of the techniques are given by Malinowski (1991) and Bandfield et al. (2000, 2002).

A hematite reflectance spectrum (432–1,009 nm) was isolated from Opportunity Pancam data by Farrand et al. (2007) using spectral mixture analysis techniques (Farrand et al. 2006; Adams et al. 1986, 1993) and manual observation of decorrelation-stretched Pancam images (Gillespie et al. 1986). The spectra were calibrated using preflight measurements and converted to I/F, where I is the measured scene radiance and πF is the solar irradiance at the top of the Martian atmosphere (Bell et al. 2004).

Previous spectroscopic analyses of akaganéite and lepidocrocite

Several workers have performed spectroscopic analyses of akaganéite and lepidocrocite in an effort to determine and interpret their VNIR and MIR spectra. Murad and Bishop (2000) summarized many previous MIR spectroscopic investigations of akaganéite, including those by Müller (1967), van der Giessen (1968), Keller (1970), Kauffman and Hazel (1975), Hendel et al. (1981), González-Calbet et al (1981), Kodama (1985), Ishikawa et al. (1986), Raman et al. (1991), and Gotić et al. (1994). In each of these studies, MIR transmittance spectra, usually of akaganéite mixed with KBr and pressed into pellets were presented. Murad and Bishop (2000) showed these measurements to be problematic due to Cl–Br interchange

between the akaganéite and the KBr. Murad and Bishop (2000) performed several spectroscopic analyses of akaganéite, including transmittance with KBr and CsI disks, attenuated total reflectance (ATR), and diffuse reflectance (DRIFTS) measurements.

More recently, Musić et al. (2004) and Zhang et al. (2007) presented MIR transmittance and absorbance spectra of various forms of akaganéite and its thermal decomposition products. Both studies showed that akaganéite generally transforms completely to hematite at temperatures above 300°C. The present study provides the first MIR emissivity spectra of akaganéite that are directly comparable to remote sensing measurements.

Weckler and Lutz (1998) published infrared transmission spectra of FeOOH polymorphs, including akaganéite and lepidocrocite at room and liquid nitrogen temperatures. The spectroscopic features were discussed with respect to proposed crystal structures for each mineral. Bell et al. (1995) also published MIR transmission spectra of lepidocrocite along with other crystalline and nanophase iron oxides/oxyhydroxides, and Gehring and Hofmeister (1994) observed the thermal transformation of lepidocrocite to maghemite using IR and magnetic methods. The thermal transformation of lepidocrocite to maghemite and eventually to hematite was also studied by Morris et al. (1998) using XRD, TEM, and VNIR spectroscopy, who found that essentially pure maghemite was formed at 265 and 223°C for 3 and 300 h heating experiments, respectively. As with akaganéite, the present study provides the first MIR emissivity spectra of lepidocrocite appropriate for comparison with remotely sensed data.

Murad and Bishop (2000), as well as Ryskin (1974), González-Calbet et al. (1981), and Weckler and Lutz (1998), discuss or provide band assignments for lepidocrocite and akaganéite using a variety of methods. We do not reproduce their efforts here. However, it can be generally be stated that features between 2,500 and 3,500 cm⁻¹ are due to OH stretches, those between \sim 600 and 950 cm⁻¹ are due to OH bending modes, and those at <600 cm⁻¹ are OH translational and Fe-O lattice modes (Ryskin 1974; Weckler and Lutz 1998; Murad and Bishop 2000).

Experimental

Sample preparation

The lepidocrocite sample (LPS2) used in this study is a synthetic yellow-orange powder from Pfizer, Inc., described by Morris and Lauer (1981) and Morris et al. (1985). It was provided for use in this study by R. V. Morris. It is composed of acicular (lath-shaped) crystals with a mean size of $0.03 \times 0.9 \ \mu\text{m}^2$. Separate samples were heated in air in an Omegalux LMF 3550 furnace to 300 and 500°C for 24 h and then allowed to cool as the furnace temperature was ramped down over a period of several hours.

The akaganéite sample (AKG1) used in this study is a synthetic precipitate prepared in the manner described by Schwertmann and Cornell (2000). About 5 g of akaganéite were produced by dissolving 54.06 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 4 L distilled water and heating to 40°C for 8 days. The precipitate was collected, washed, and dried. It is composed of somatoidal (spindle-shaped) crystals with a mean crystal size of ~150 nm in the long direction. Portions of the sample were heated in air to 150, 300, and 500°C in a furnace for 24 h and then allowed to cool slowly.

Sample analysis

MIR (200–2,000 cm⁻¹) emission spectra were acquired using Arizona State University's modified Nicolet Nexus 670 E.S.P. FTIR spectrometer. The spectrometer has a CsI beamsplitter and a thermoelectrically stabilized DTGS detector. Samples were compressed at ~69 MPa in a Carver hydraulic press into compact pure pellets to increase the contrast of their emissivity spectra and to avoid scattering due to the finely crystalline nature of the samples. Samples were heated overnight to 80°C in an oven and were actively heated at the same temperature as spectra were being collected. Each emissivity spectrum presented in this work is an average of 1,000 scans collected on two different dates in 500 scan increments. Details of the spectrometer setup, collection, and calibration procedures can be found in Christensen and Harrison (1993) and Ruff et al. (1997).

MIR (400–4,000 cm⁻¹) attenuated total reflectance (ATR) spectra were acquired on Caltech's Nicolet Magna 860 FTIR spectrometer fitted with a SensIR Technologies DuraScope ATR attachment with a type IIA diamond ATR element. The spectrometer was equipped with a KBr beamsplitter and an uncooled DTGS detector with a KBr window. These spectra are comparable to absorption spectra of sample powders dispersed in a KBr pellet. The ATR measurements, however, are acquired by placing a pure powder sample in contact with the ATR element and measuring the light that is totally internally reflected by the element. The measured spectrum displays absorption features related to the fundamental, overtone, and combination vibrational modes of the sample in contact with the element. Details of the ATR technique can be found in Urban (1996).

VNIR reflectance spectra (400–1,100 nm) of the compact pellets were acquired on Caltech's VNIR spectrometer composed of an Oriel tungsten-halogen source shining onto an Acton grating and through a Nicolet Nic-Plan microscope. A total of 100 scans with a 1 s exposure time were referenced to a first-surface mirror for determination of reflectance. Transmission electron microscope (TEM) micrographs were acquired on a JEOL JEM-2010F TEM at ASU's Center for High Resolution Electron Microscopy at a 200 kV potential. Samples were prepared by dispersing a powdered sample in acetone and covering a carbon film-covered grid with the dilute suspension. Powder X-ray diffraction patterns were acquired on a Rigaku D/Max-IIB XRD instrument at Arizona State University using Cu-K α radiation at 50 kV and 30 mA.

Results

X-ray diffraction

Powder X-ray diffraction spectra were acquired of the original akaganéite and lepidocrocite samples and their thermal transformation products. These are shown in Fig. 1. The narrow lines of the akaganéite sample AKG1 (Fig. 1a) indicate that it is well ordered with few crystal defects. After heating to 150°C, the XRD pattern still displays peaks associated with akaganéite rather than hematite or an intermediate product. The XRD pattern of the sample derived by heating the akaganéite to 300°C (AKGH1-300) indicates that, at this temperature, the sample has completely transformed to hematite, and the narrow lines indicate it is well

Fig. 1 X-ray diffraction patterns for akaganéite, lepidocrocite, and their thermal decomposition products. a Sample AKG1 displays an XRD pattern of pure akaganéite. The XRD pattern of sample AKGH1-150 is very similar to that of AKG1, while the pattern for sample AKGH1-300 is similar to that of pure well-ordered hematite. The XRD pattern of sample AKGH1-500 is identical to that of AKGH1-300 and is not shown. b The XRD pattern of sample LPS2 is similar to that of pure lepidocrocite. The XRD pattern of LPSH2-500 is similar to that of pure well-ordered hematite, while the pattern of sample LPSH2-300 is intermediate between LPS2 and LPSH2-500

ordered. The XRD pattern of the sample heated to 500°C (AKGH1-500) is nearly identical to that of AKGH1-300, indicating that no significant changes in long wavelength order occur within the crystal structure between 300 and 500°C.

The well-defined XRD pattern of the lepidocrocite sample LPS2 indicates that it is well ordered (Fig. 1b), while the pattern of sample LPSH2-300 contains shallow, broad lines, indicating that it is poorly ordered and composed of a mixture of hematite and maghemite. Maghemite is a wellknown intermediate product of the thermal transformation of lepidocrocite to hematite (Cornell and Schwertmann 2003, and references therein). The XRD pattern of sample LPSH2-500 indicates that, upon heating to 500°C, the sample is completely converted by well-ordered hematite.

Transmission electron microscopy

TEM micrographs of samples LPS2, LPSH2-500, AKG1, and AKGH1-300 are shown in Figs. 2 and 3. Micrographs of samples LPS2 and LPSH2-500 (Fig. 2) both show acicular crystals, indicating that the hematite (LPSH2-500) is pseudomorphic after the precursor lepidocrocite (LPS2). The acicular hematite crystals appear similar to those produced by the thermal transformation of acicular goethite to hematite (Glotch et al. 2004).





Fig. 2 TEM micrographs of lepidocrocite and lepidocrocite-derived hematite. **a** Micrograph of lepidocrocite sample LPS2 displaying long, lath-shaped crystals. **b** Upon heating to 500°C, the sample has transformed to hematite, but retains its crystal morphology

Hematite sample AKGH1-300 and its akaganéite precursor AKG1 display very different morphologies (Fig. 3). The AKG1 crystals are somotoidal and elongated in the [001] direction (Cornell and Schwertmann 2003) (Fig. 3a). Upon heating to 300°C, the body-centered cubic (bcc) anion packing of akaganéite breaks down and rearranges into the hexagonal closest packing (hcp) structure of hematite (Cornell and Schwertmann 2003). The resultant crystals are hexagonal and pseudo-hexagonal plates (Fig. 3b).



Fig. 3 TEM micrographs of akaganéite and akaganéite-derived hematite. **a** Micrograph of akaganéite sample AKG1 displaying a somotoidal crystal shape. **b** Upon heating to 300°C, the sample is transformed to hematite and the crystals breakdown and reform as subhexagonal plates

Attenuated total reflectance spectroscopy

Attenuated total reflectance (ATR) spectra for both the akaganéite and lepidocrocite series are shown in Fig. 4. For all spectra, features between 1,900 and 2,400 cm⁻¹ are calibration artifacts that are independent of sample composition. Here, we list the positions of major bands used for identifying the sample, whereas all bands, including minor shoulder features, are listed in Table 1. The akaganéite series samples display systematic changes in spectral character as the Fig. 4 ATR spectra of oxide samples. a Akaganéite AKG1. b AKGH1-150 is very similar to AKG1. c AKGH1-300 is consistent with hematite. d AKGH1-500 is consistent with hematite. e Lepidocrocite LPS2. f LPSH2-300 is partially transformed to hematite and contains maghemite. g LPSH2-500 is fully transformed to hematite



Table 1 ATR and emissivity band locations for samples (in cm^{-1})

Sample	ATR	Emissivity
AKG1	440, 642, 845, 980, 1,612, 3,312	256, 380, 447, 673, 823, 1,053, 1,200, 1,590
AKGH1-150	440, 650, 845, 970, 1,305, 1,418, 1,620, 2,850, 2,930, 3,340, 3,450	253, 380, 450, 671, 826, 1,055, 1,198
AKGH1-300	428, 460, 515, 700, 786, 920, 1,050, 2,950, 3,320, 3,450	308, 330, 378, 446, 468, 554, 580, 910, 1,050
AKGH1-500	430, 455, 515, 690, 789, 918, 1,035, 2,930, 3,350, 3,470	310, 350, 375, 437, 468, 560, 1,060, 1,362
LPS2	464. 500, 596, 750, 895, 1,020, 1,156, 1,436, 1,625, 2,360, 2,857, 3,025, 3,525	268, 360, 474, 505, 590, 740, 1,013
LPSH2-300	428, 520, 615, 690, 1,437, 1,625, 3,300	294, 384, 436, 552, 630
LPSH2-500	428, 513, 695, 920, 1,410, 1,640, 3,400	303, 390, 444, 538, 600

heating temperature increased from 150 to 500°C (Fig. 4a–d). The original akaganéite sample (AKG1) displays strong absorption maxima at 642, 845, 1,612, and 3,312 cm⁻¹. The major features at 1,612 and 3,312 cm⁻¹ represent the H–O– H fundamental bending and stretching modes. The spectrum of AKGH1-150 (Fig. 4b) is similar to that of AKG1 with a few minor differences. There are strong absorptions at 650,

845, 1,418, 1,620, and 3,340 cm⁻¹, and a distinct shoulder feature at \sim 3,450 cm⁻¹ appears. The new feature at \sim 3,450 cm⁻¹ (\sim 2.9 µm) may be the asymmetric (v_3) O-H stretch, which is made visible due to the reduced magnitude of the symmetric O-H stretch as compared to AKG1.

The spectrum of AKGH1-300 (Fig. 4c) is the lowest temperature sample that is consistent with hematite. This

spectrum displays major absorption features at 428 and 515 cm^{-1} with additional minor features at 700, 786, 920, 1,050, and 3,320 cm^{-1} . Note that the bound O-H features are greatly reduced in this spectrum compared to AKG1 and AKGH1-150. The spectrum of AKGH1-500 (Fig. 4d) is similar to that of AKGH1-300. It exhibits major absorption features at 430 and 515 cm⁻¹ with additional minor features at 690, 789, 852, 918, 1,035, and 3,350 cm⁻¹. The features present at 700 and 690 cm⁻¹ in the AKGH1-300 and AKGH1-500 spectra, respectively, are due to tetrahedrally coordinated iron at the crystals' surfaces. These features are indicative of a somewhat incomplete transformation from the akaganéite precursor to hematite and/or a particle size effect due to the finely crystalline nature of these samples (Chernyshova et al. 2007). The bound O-H features of the AKGH1-500 spectrum, while still weak compared to the same features in the AKG1 and AKGH1-150 spectra, are slightly stronger than those seen in the AKGH1-300 spectra. This is counterintuitive and unlikely to be due to structural water within the sample. We hypothesize that this sample has a somewhat higher abundance of bound water on its surface.

The ATR spectra of the lepidocrocite series are displayed in Fig. 4e-g. The spectrum of LPS2 (Fig. 4e) displays absorption features at 464, 500, 596, 750, 895, 1,020, 1,156, 1,436, 1,625, and 3,025 cm⁻¹. The spectrum of LPSH2-300 (Fig. 4f) retains few of the spectral features associated with LPS2. Absorption maxima are present at 428, 520, 690, 1,437, 1,625, and at \sim 3,300 cm⁻¹. Note that the band in the O-H stretching region (\sim 3,300 cm⁻¹) is shifted considerably to higher wavenumbers as compared to LPS2, because the mineral structure has changed. The spectrum of LPSH2-500 (Fig. 4g) is consistent with hematite, with major absorption maxima at 428 and 513 cm⁻¹. Minor absorption maxima are present at 695, 920, and 1,410 cm^{-1} . Additionally, this sample contains bound water as evidenced by the O-H bending and stretching modes at 1,640 and 3,400 cm^{-1} . The presence of the O-H vibrational modes indicates an incomplete transformation from lepidocrocite to hematite. For both LPSH2-300 and LPSH2-500, this conclusion is supported by the presence of minor bands at 690 and 695 cm^{-1} , respectively (Chernyshova et al. 2007).

Visible and near-infrared (VNIR) spectroscopy

VNIR spectra of the lepidocrocite and akaganéite pellets and their thermal transformation products are shown in Fig. 5. The pellet-pressing process significantly reduced the albedo of each sample; so, band intensities were small. However, long integrations (100 scans) allowed for the collection of high-quality spectra.

As seen previously in the XRD patterns and ATR spectra, the heated products of akaganéite and lepidocrocite differ significantly from their precursors. In the VNIR region (Fig. 5), the reflectance spectrum of AKG1 displays absorption bands centered at 500, 660, 800, and 900 nm. The spectrum of AKGH1-150 displays absorption bands at the same wavelengths, although at slightly reduced spectral contrast. The spectra of samples AKGH1-300 and AKGH1-500, however, resemble those of crystalline hematite, with strong absorption bands centered at 670 and 850 nm and a "kink" at ~560 nm (Fig. 5a–d).

The spectrum of LPS2 displays absorption bands at 480, 520, 680, 860, and 910 nm. The spectrum of lepidocrocitederived hematite LPSH2-500 is similar to the akaganéitederived hematite spectra displayed in Fig. 5a, with strong absorption bands centered at 680 and 900 nm. The other product of the lepidocrocite precursor, LPSH2-300, displays a spectrum intermediate between LPS2 and LPSH2-500, with bands centered at 470, 550, 660, and at ~910 nm (Fig. 5e–g). The intermediate nature of the spectrum is consistent with the results of the XRD patterns and mid-infrared ATR spectra.

MIR emission spectroscopy

Emissivity spectra for the akaganéite thermal transformation series are shown in Fig. 6a-d. The AKG1 spectrum exhibits emissivity minima at 256, 380, 447, 673, 823, 1,053, and 1,200 cm⁻¹. After heating to 150°C for 24 h, the AKGH1-150 spectrum (Fig. 6b) still appears similar to the original AKG1 spectrum, with emissivity minima at 253, 380, 450, 671, 826, 1,055, and 1,198 cm⁻¹. Spectra of samples AKGH1-300 and AKGH1-500 (Fig. 6c, d) are very similar, and are representative of well-ordered hematite. The AKGH1-300 spectrum displays emissivity minima at $308, 378, 446, 468, and 553 \text{ cm}^{-1}$. The relatively weak feature at 378 cm^{-1} indicates that some non-[001] emission is present (Lane et al. 2002), but much of the emission must be due to the large (001) faces of the hematite crystals. In addition, the large band centered at 450 cm^{-1} is expressed as a doublet with the two minima at 446 and 468 cm^{-1} . This is likely due to structural inhomogeneity within the sample with individual crystals being either well- or poorly ordered (Chernyshova et al. 2007).

MIR emission spectra of the lepidocrocite transformation series are shown in Fig. 6e–g. The LPS2 spectrum (Fig. 6e) displays emissivity minima at 268, 360, 474, 505, 590, 740, and 1,013 cm⁻¹. After heating to 300°C for 24 h, sample LPSH2-300 (Fig. 6f) displays an infrared spectrum that is consistent with a combination of hematite and maghemite (e.g. Sidhu, 1988), with emissivity minima at 295, 360, 384, 436, 552, and 630 cm⁻¹. This is consistent with previous studies that show that maghemite is an intermediate product in the thermal transformation of lepidocrocite to hematite (Cornell and Schwertmann 2003). Fig. 5 VNIR spectra (400– 1,100 nm) of akaganéite, lepidocrocite, and their thermal transformation products. a Akaganéite AKG1. b The spectrum of AKGH1-150 displays all the same spectral features that AKG1 displays, but at reduced contrast. c AKGH1-300 is consistent with hematite. d AKGH1-500 is consistent with hematite. e Lepidocrocite LPS2. f The LPSH2-300 is intermediate between lepidocrocite and hematite. g LPSH2-500 is consistent with hematite



A spectrum of synthetic maghemite is shown in Fig. 6h for comparison. After heating to 500°C for 24 h, the emissivity spectrum of sample LPSH2-500 (Fig. 6g) is equivalent to that of crystalline hematite. The spectrum displays emissivity minima at 303, 390, 444, and 538 cm⁻¹. There is only a small feature near 390 cm⁻¹ indicating that the (001) crystal faces are responsible for most of the observed emission (Glotch et al. 2006b). Finally, the 538 cm⁻¹ band is broadened toward higher frequency, with a shoulder feature at ~600 cm⁻¹, consistent with broadening observed for other hematite samples created at high temperatures (Glotch et al. 2004).

None of the emissivity spectra exhibit a feature near 690–700 cm⁻¹ that was observed in the ATR spectra of AKGH1-300, AKGH1-500, LPSH2-300, and LPSH2-500. This is consistent with the interpretation of the feature as a surface vibrational mode due to the presence of tetrahedrally coordinated iron (Chernyshova et al. 2007). While ATR spectra are sensitive to the top 2–5 μ m of a sample,

emissivity spectra are sensitive to depths of $\sim 100-200 \ \mu m$. Therefore, it should be expected that this mode is more readily observable in the surface-sensitive ATR spectra.

Discussion

Figure 7 shows a comparison of the VNIR spectra of hematite samples AKGH1-500 and LPSH2-500 with the Pancam spectrum of the hematite-rich spherules observed at Meridiani Planum (Bell et al. 2004; Farrand et al. 2007). The Pancam hematite spectrum in Fig. 7a is displayed as I/F. Laboratory spectra are resampled to Pancam spectral resolution and displayed in reflectance. Several similarities are immediately apparent, including the steep "red" slope to short wavelengths, absorption features at ~800–900 nm, and a "kink" in the slope at 500–550 nm. The Martian hematite spectrum, however, has a deeper spectral feature at 900 nm relative to the surrounding

Fig. 6 MIR emissivity spectra of the akaganéite and lepidocrocite series. a Akaganéite AKG1. b AKGH1-150 is spectrally similar to the original akaganéite sample. c AKGH1-300 is consistent with hematite. d AKGH1-500 is consistent with hematite. e Lepidocrocite LPS2. f LPSH2-300 is consistent with a mixture of maghemite and hematite. g LPSH2-500 is consistent with hematite. h Synthetic maghemite ISK1 for comparison to LPSH2-300 (f)



Wavelength (nm)

Fig. 7 Comparison of laboratory hematite spectra to Pancam spectrum of hematite spherules. a AKGH1-500 and LPSH2-500 resampled to Pancam spectral resolution. The y axis for the Pancam spectrum is on the left. The *y* axis for the laboratory spectra is on the right. b The same spectra, with their continua removed. LPSH2-500 looks most similar to the Martian hematite, but both LPSH2-500 and AKGH1-500 display several spectral features not present in the Martian hematite spectrum. Spectra are offset for clarity



points. Although it appears that the Martian hematite spectrum also has a shallower red spectral slope than the laboratory spectra, they cannot be reliably compared due to the differences in spectral contrast. Martian hematite deposits at Meridiani Planum and other regions are often referred to as "gray hematite." As the presence of the red slope makes clear, the hematite-rich spherules at Meridiani Planum are not truly gray, as might be expected for terrestrial hydrothermal or metamorphic specularite deposits. A gray hematite spectrum would be flat over the VNIR spectral region.

To enhance the spectral features for a more detailed comparison between the laboratory and Martian hematite spectra, all spectra were continuum-corrected using a background removal algorithm in the OMNIC ESP software (Fig. 7b). Following Clark and Roush (1984), the continua were divided into rather than subtracted from the original spectra to preserve band positions. Two major differences between the Martian and laboratory hematite spectra are apparent. First, the Martian hematite spectrum has a reflectance maximum at 680 nm where the laboratory spectra exhibit small minima. Second, the position of the short wavelength minimum is shifted from 535 nm in the laboratory spectra to 482 nm in the Martian spectrum. Qualitatively, the LPSH2-500 spectrum is a slightly better match to the Martian hematite than the AKGH1-500 spectrum, mainly due to its deeper 900 nm absorption feature.

Figure 8 shows Martian crystalline hematite spectra derived from the TES (Glotch and Christensen 2005) and Mini-TES (Glotch and Bandfield 2006) datasets along with the hematite samples derived from lepidocrocite and aka-ganéite and the best-fit goethite-derived hematite (GTSH2-300) from Glotch et al. (2004). It is evident that the aka-ganéite-derived hematite AKGH1-300 is a poor fit to the

Martian crystalline hematite in terms of band shape and the relative band depths. The lepidocrocite-derived hematite LPSH2-500 spectrum is a better fit to the Martian hematite spectra in terms of band position and the relative minimum emissivities between the bands. However, the band centered at 540 cm⁻¹ is broader than that seen for the Martian hematite spectrum. This is consistent with other synthetic hematite spectra created at temperatures of 500°C or higher (Glotch et al. 2004). The best overall fit to the Martian hematite spectra is still the low-temperature goethite-derived hematite spectrum GTSH2-300, discussed by Glotch et al. (2004).

In interpreting the MIR and VNIR data, the differing particle sizes of the Martian spherules and the laboratory samples must be taken into account. Individual crystals of the akaganéite and lepidocrocite precursors are of the order of ~ 100 nm in size. The Martian spherules, on the other hand, tend to be several millimeters in diameter. As shown in this work (Figs. 6, 8) and in Glotch et al. (2004), pressing the sample powders into compact pellets results in MIR spectra comparable to those of coarse particulates with no appreciable scattering features usually observed in the spectra of fines. On the other hand, VNIR spectra of the pellets display steep red slopes; so, the pressing does not result in coarse gray hematite. Currently, we cannot determine if the Martian spherules are composed of a conglomeration of finer crystals. However, the fact that the spectrum shows a red slope (Fig. 7; Farrand et al. 2007) suggests that this might be the case. While dust coatings on the spherules might add some red spectral character to the spherule spectrum, the deep absorption feature at 900 nm and the sharp kink at \sim 540 nm are indicative of red crystalline hematite.

Lepidocrocite and akaganéite are iron oxyhydroxides that form under specific Eh-pH conditions, and will precip-

Fig. 8 TES (Glotch et al. 2004) and Mini-TES (Glotch and Bandfield 2006) hematite spectra compared to hematite derived from goethite, lepidocrocite, and akaganéite. Lepidocrocitederived hematite is a better match to the Martian spectra than akaganéite-derived hematite, but goethite-derived hematite is still the best match. Spectra are offset for clarity



itate from solution under varying circumstances. Like goethite, these minerals can be thermally transformed to hematite, a mineral that is observed at Meridiani Planum on Mars. During the lepidocrocite-to-hematite transformation, maghemite forms as an intermediate product. High temperatures of 370–600°C are needed to transform lepidocrocite completely to hematite depending on the origin and foreign cation content (Cornell and Schwertmann 2003). As discussed by Glotch et al. (2004), spectra of hematite formed at high temperatures are inconsistent with the Martian hematite spectra.

The akaganéite-to-hematite transformation takes place at much lower temperatures (<300°C) than the lepidocrociteto-hematite transformation. The transformation, however, is accompanied by a complete breakdown of the akaganéite crystal structure and the formation of hexagonal and pseudo-hexagonal hematite plates. The resulting hematite spectrum is a poor match in terms of band shapes and relative band minimum emissivities to the Martian hematite spectra.

Low-temperature, goethite-derived hematite still appears to be the best spectral match to the Martian crystalline hematite, although a high-temperature lepidocrocite-tohematite mechanism cannot be completely ruled out. This latter mechanism, however, is not favored. Based on the current study and previous data (Glotch et al. 2004), it appears that both a low-temperature formation and an acicular crystal morphology are required to produce a spectrum that is an acceptable match to the Martian crystalline hematite. This precludes high-temperature volcanic (McCollom and Hynek 2005) or impact-related (Knauth et al. 2005) hematite formation processes, and also precludes those aqueous or hydrothermal depositional processes that produce nonacicular hematite crystals.

Fine crystals of iron oxides/oxyhydroxides, including hematite, are generally thermodynamically unstable with respect to coarse-grained hematite; so, over time, original finely crystalline precipitates would be expected to "age" to coarse hematite through a process called Ostwald ripening (Langmuir 1971; Cornell and Schwertmann 2003). Acicular hematite crystals have been precipitated from solution at high pH at ~80°C (Schwertmann et al. 1968). Since an acicular crystal morphology appears to be required to match the Martian hematite spectra, a natural coarsening of originally precipitated fine-grained acicular hematite could also be a valid mechanism to produce the Martian coarsely crystalline hematite.

Conclusions

We have performed heating experiments on lepidocrocite and akaganéite to assess the possibility that either of these minerals were precursors to the crystalline hematite spherules observed at Meridiani Planum Mars. TEM micrographs of the lepidocrocite, akaganéite, and their heated by-products show that lepidocrocite keeps its acicular crystal shape as it is transformed to hematite. By contrast, somatoidal akaganéite crystals breakdown and reform as hexagonal and pseudo-hexagonal crystals upon their transformation to hematite, which is consistent with previous studies (Cornell and Schwertmann 2003). Attenuated total reflectance spectra show that structural and/or surface-bound water from the oxyhydroxide precursors is still present in the hematite crystal structures, even when heated to 500°C. We hypothesize that hydration bands observed in the ATR spectra of samples LPSH2-500 and AKGH1-500 are mainly due to surface-bound water rather than structural water remaining in the hematite crystals.

VNIR and MIR emissivity spectra were acquired and compared to Pancam, Mini-TES, and MGS-TES hematite spectra. In general, lepidocrocite-derived hematite is a better spectral match to Pancam VNIR and TES and Mini-TES MIR data than akaganéite-derived hematite. However, lowtemperature goethite-derived hematite (Glotch et al. 2004) still provides the best match to the TES and Mini-TES hematite spectra.

The apparent likelihood of a goethite precursor to the Martian crystalline hematite is informative of the initial formation environment. Goethite precipitation is favored over hematite in aqueous environments with temperatures below 37°C and at slightly higher pH levels. At higher temperatures and lower pH levels, hematite precipitation is favored. Goethite precipitation is favored over akaganéite at temperatures below 60°C and in a solution with low levels of Cl and F. Finally, goethite precipitation would be favored over lepidocrocite in environments with low levels of Fe²⁺ and organics in solution.

Like the goethite-derived hematite described by Glotch et al. (2004), the lepidocrocite-derived hematite crystals are acicular in shape. The akaganéite-derived hematite crystals, on the other hand, are hexagonal or pseudo-hexagonal plates, and provide a poor match to the Martian hematite spectra. The goethite-, lepidocrocite-, and akaganéitederived hematite MIR spectra are all dominated by [001] emission as are the hematite spectra of the Martian spherules (Lane et al. 2002; Glotch et al. 2004; Glotch and Bandfield 2006), but the akaganéite-derived hematite spectra are clearly an inferior match to the Martian hematite spectra. These results and those of Glotch et al. (2004) indicate that both temperature of formation and crystal shape play a strong role in the IR spectrum of hematite.

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