

THERMAL TRANSFORMATIONS OF LEPIDOCROCITE AND AKAGANÉITE TO HEMATITE: EXAMINATION OF POSSIBLE PRECURSORS TO MARTIAN CRYSTALLINE HEMATITE. T. D. Glotch¹ and M. D. Kraft², ¹Jet Propulsion Laboratory, California Institute of Technology, tglotch@gps.caltech.edu, ²Arizona State University

Introduction: Gray 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 [1-5]. Data returned by the Athena science payload on the Mars Exploration Rover (MER) Opportunity showed that the gray hematite was concentrated in spherules—interpreted as concretions—which are eroding from a light-toned sulfate- and silica-rich outcrop [6-7].

Initial analyses of the TES hematite spectrum showed that it was dominated by [001] emission, and this was confirmed by analyses of Mini-TES data [8-9]. Previous work also investigated the role of precursor mineralogy and morphology on the hematite spectral character by thermally transforming goethite (α -FeOOH) and magnetite (Fe₃O₄) to hematite at various temperatures and examining the subsequent IR spectra in addition to VNIR spectra, TEM photomicrographs, XRD patterns, and Mössbauer spectra [10]. That work showed that the IR 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 was a good match. Thus, [10] concluded that a high-temperature volcanic environment for the formation of gray crystalline hematite on Mars was unlikely, and that a low-temperature aqueous environment conducive to the initial formation of goethite was likely.

In this work, we expand upon the initial analysis of [10] by assessing the thermal transformations of lepidocrocite (γ -FeOOH) and akaganéite (β -FeOOH) to hematite and discussing the implications of the results. Lepidocrocite and akaganéite in nature are often found in association with other iron oxides and oxyhydroxides [11-13], but specific environmental conditions can favor or disfavor their formation. Therefore, if either of these minerals are shown to be a possible precursor to the Martian gray hematite, then 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 [14], a slow rate of Fe³⁺ hydrolysis [15], a low CO₂ fugacity [13, 16], or

the presence of excess Fe²⁺ in solution [11,17-18] all 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 elevated temperatures near 60°C [15].

Samples and Methods:

Lepidocrocite-Precursor Series. The lepidocrocite precursor (LPS2) used in this study is a synthetic yellow-orange powder from Pfizer, Inc. described in previous experimental work [19-20] It is composed of acicular (lath-shaped) crystals with a mean size of 0.03x0.9 μ m. Samples were heated in air to 300°C and 500°C in an Omegalux LMF 3550 furnace for 24 hours and then allowed to cool slowly to room temperature.

Akaganéite-Precursor Series. The akaganéite precursor (AKG1) used in this study is a synthetic precipitate prepared in the manner described by [15]. About 5 g of akaganéite were produced by dissolving 54.06 g FeCl₃•6H₂O in 4L 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°C, 300°C, and 500°C in a furnace for 24 hours and then allowed to cool slowly to room temperature.

Sample Analysis. Mid-Infrared (200-2000 cm⁻¹) thermal emission spectra were acquired on Arizona State University's modified Nicolet Nexus 670 E.S.P. Fourier-Transform Infrared (FTIR) spectrometer. The spectrometer has a CsI beamsplitter and an uncooled deuterated triglycine sulfate (DTGS) detector. Following the method of [10], samples were compressed at 10,000 psi in a Carver hydraulic press into compact pure pellets to increase the contrast of their IR spectra. Samples were heated overnight to 80°C in an oven and were actively heated at the same temperature as spectra were being collected. Each spectrum presented in this work is an average 1000 scans collected on two different dates in 500 scan increments.

Transmission Electron Microscope (TEM) micrographs were acquired on ASU's JOEL 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 spectra were acquired on a Rigaku D/Max-IIB XRD instrument using Cu- K α radiation at 50 kV and 30 mA. Several

authors have investigated the visible/near-IR (VNIR) spectral properties of lepidocrocite and akaganéite and their thermal transformation products [21-22], so these techniques are not employed in this work.

Results:

X-Ray Diffraction. Powder X-ray diffraction spectra that were acquired of the akaganéite and lepidocrocite samples and their thermal transformation products are shown in Figure 1. The relatively narrow lines of the akaganéite sample AKG1 (Figure 1a) indicate that it is well crystalline. The XRD pattern of the sample derived by heating the akaganéite to 500°C (AKGH1-500) indicates that the sample has completely transformed to hematite, and the narrow lines indicate it is well crystalline. An additional XRD pattern of akaganéite heated to 300°C (AKGH1-300) is identical to the AKGH1-500 pattern, indicating that the transformation to hematite was complete at 300°C.

The XRD pattern of the lepidocrocite sample LPS2 (Figure 1b) contains shallow, broad lines, indicating that it is poorly crystalline. Upon heating to 500°C, however, the sample is completely converted to well crystalline hematite.

Transmission Electron Microscopy. TEM micrographs of samples LPS2 and LPSH2-500 and AKG1 and AKGH1-300 are shown in figures 2 and 3. Micrographs of samples LPS2 and LPSH2-500 (Figure 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 [10].

Hematite sample AKGH1-300 and its akaganéite precursor AKG1 (Figure 3) display very different morphologies. The AKG1 crystals are somatoidal and elongated in the [001] direction. Upon heating to 300°C, the bcc anion packing of akaganéite breaks down and rearranges into the hcp packing structure of hematite [12]. The resultant sample is composed of hexagonal and pseudo-hexagonal plates.

Thermal Emission Spectra. Emissivity spectra for the akaganéite thermal transformation series are shown in Figure 4a. After heating to 150°C for 24 hours, the AKGH1-150 spectrum is very similar to the original AKG1 spectrum. Previous work had shown that the thermal transformation process from akaganéite to hematite starts at ~150°C [12], so some change was expected. Factors such as Cl content and excess H₂O within the sample can drive the transformation temperatures higher [12]. Samples AKGH1-300 and AKGH1-500 are very similar, and are representative of well-crystalline hematite. There is a weak feature at ~390 cm⁻¹ indicating that some non-[001] emission is present [8], but much of the emission must be due to the large (001) faces of the hematite crystals.

Thermal emission spectra of the lepidocrocite thermal transformation series are shown in Figure 4b. After heating to 300°C for 24 hours, sample LPSH2-300 displays an infrared spectrum that is a combination of hematite and maghemite. This is consistent with previous studies that show that maghemite is an intermediate product in the thermal transformation of lepidocrocite to hematite [12]. After heating to 500°C for 24 hours, the emissivity spectrum of sample LPSH2-300 is that of pure crystalline hematite. There is only a small kink near 390 cm⁻¹ indicating that most of the emissivity is due to emission from the (001) crystal face.

Discussion and Conclusions: Figure 5 shows Martian crystalline hematite spectra derived from the TES [3] and Mini-TES [23] datasets along with hematite samples derived from lepidocrocite and akaganéite as well as the best-fit goethite-derived hematite from [10]. It is evident that the akaganéite-derived hematite AKGH1-300 is a poor fit to the Martian crystalline hematite in terms of band shape and the relative minimum emissivities between the bands. 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 is seen for the Martian hematite spectrum. This is consistent with other synthetic hematite spectra created at temperatures of 500°C or higher [10]. The best overall fit to the Martian hematite spectra is still the low-temperature goethite-derived hematite spectrum GTSH2-300, discussed by [10].

Lepidocrocite and akaganéite are iron oxyhydroxides that form under specific Eh-pH conditions, and will precipitate from solution under varying circumstances. Like goethite, these minerals can be thermally transformed to hematite, which is observed at Meridiani Planum on Mars. During the lepidocrocite-to-hematite transformation, maghemite forms as an intermediate product. High temperatures (>500°C) are needed to transform lepidocrocite completely to hematite. As discussed by [10], 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 lepidocrocite-to-hematite transformation. The transformation, however, is accompanied by a complete breakdown of the akaganéite crystal structure and the formation of 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. Based on the

current study and previous data [10], it appears to be the case 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 hematite formation processes such as volcanic [24] or impact-related [25], but also precludes aqueous or hydrothermal depositional processes that produce non-acicular hematite crystals.

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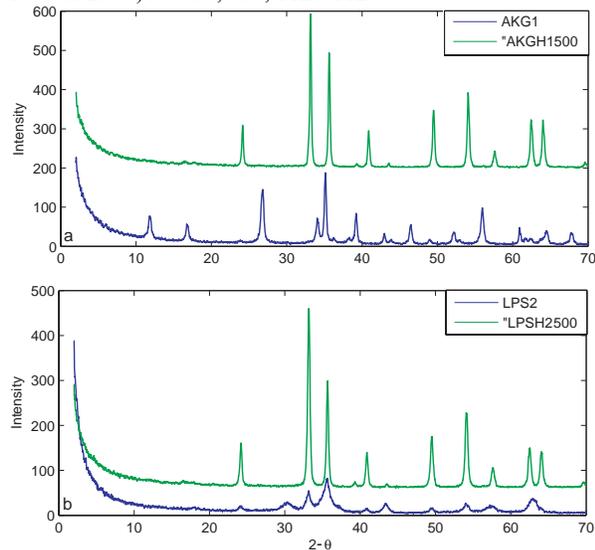


Figure 1. X-ray diffraction patterns for synthetic iron oxide/oxyhydroxide samples. a) Akaganéite AKG1 and akaganéite-derived hematite AKGH1-500 patterns both display sharp lines, indicating that they are well-crystalline. b) The lepidocrocite LPS2 pattern has broad lines indicating that it is poorly crystalline while lepidocrocite-derived hematite LPSH2-500 has sharp lines, indicating that it is well-crystalline.

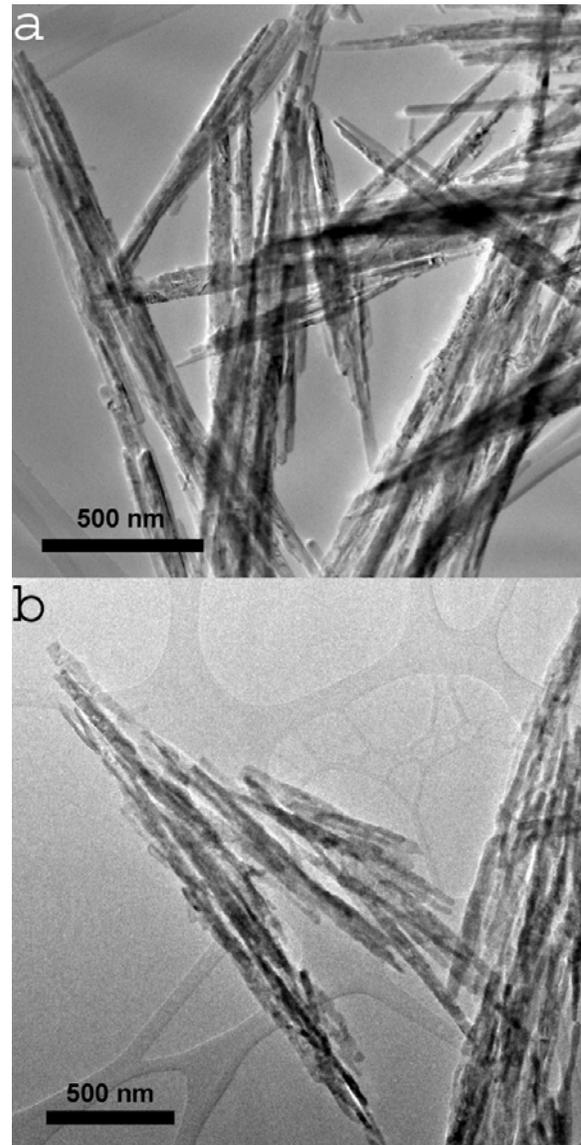


Figure 2. TEM micrographs of a) LPS2 and b) LPSH2-500. Both display the same acicular crystal morphology indicating that the transition from lepidocrocite to hematite was pseudomorphic and topotactic.

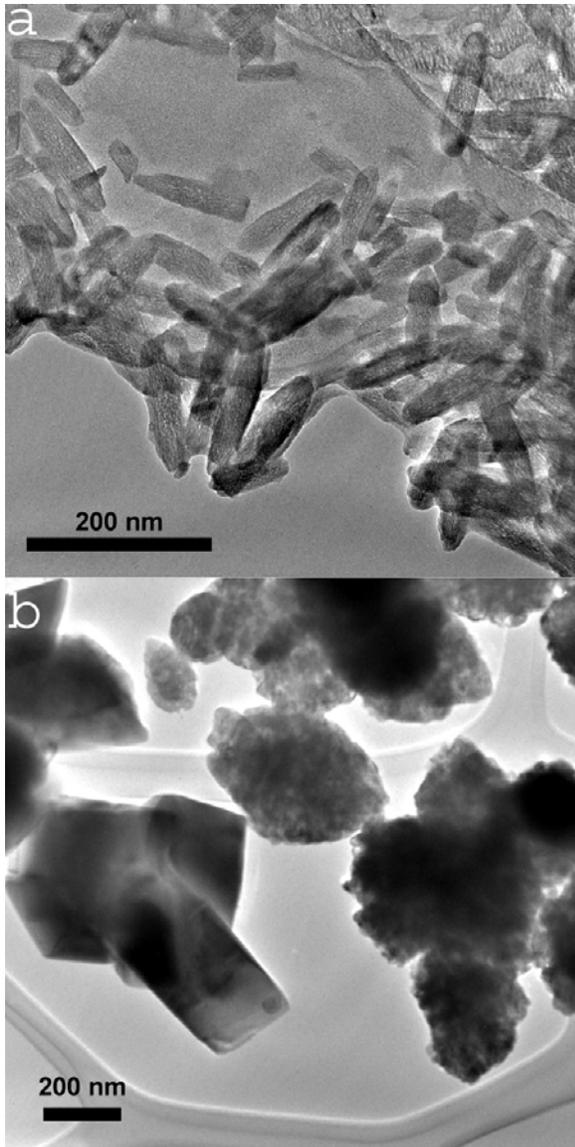


Figure 3. TEM micrographs of a) AKG1 and b) AKGH1-300. Upon heating to 300°C, the crystal structure of AKG1 completely breaks down and reforms hexagonal and pseudo hexagonal hematite plates.

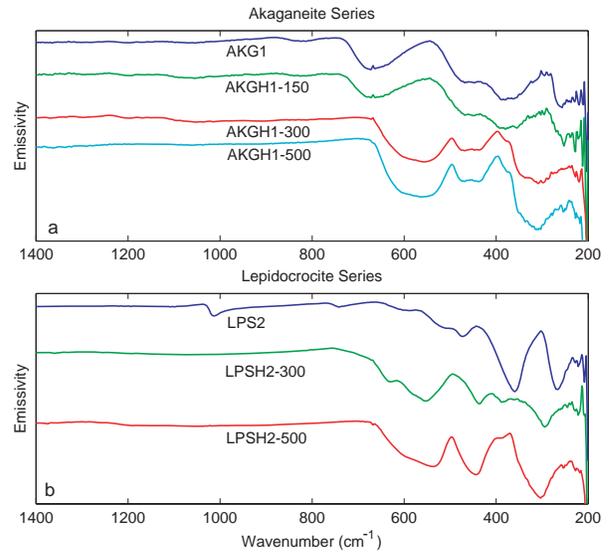


Figure 4. a) Akaganéite AKG-1 and its thermal transformation products. The sample is completely converted to hematite at 300°C. b) Lepidocrocite LPS2 and its thermal transformation products. Upon heating to 300°C, the sample is a mixture of hematite and maghemite. The sample is completely converted to hematite at 500°C.

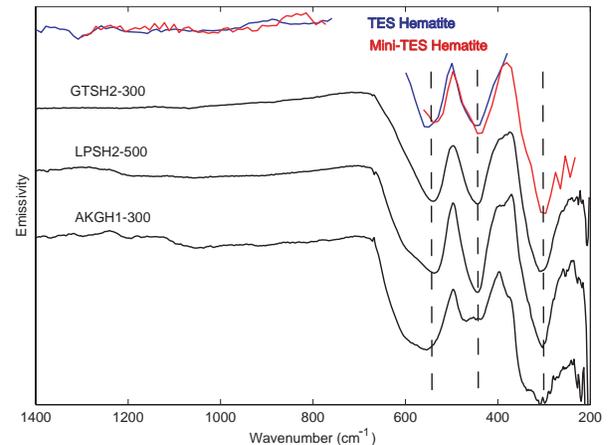


Figure 5. TES and Mini-TES hematite spectra compared to hematite derived from goethite [10], lepidocrocite, and akaganéite. Lepidocrocite-derived hematite is a better match to the Martian spectra than akaganéite-derived hematite, but goethite-derived hematite is still the best match.