Akaganéite and schwertmannite: Spectral properties and geochemical implications of their possible presence on Mars

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Abstract

The ferric oxyhydroxide minerals akaganéite and schwertmannite are associated with acidic environments and iron alteration on Earth and may be present on Mars as well. These minerals have a tunnel structure and are crystallographically related. The extended visible region reflectance spectra of these minerals are characterized by a broad Fe$^{3+}$ electronic transition centered near 0.92 µm, a reflectance maximum near 0.73 µm and a shoulder near 0.59 µm. The near-infrared (NIR) reflectance spectra of each of these minerals are dominated by broad overtones and combinations of the H$_2$O vibration features. These occur near 1.44-1.48 and 1.98-2.07 µm (~6750-6950 and 4830-5210 cm$^{-1}$) in akaganéite spectra, while in schwertmannite spectra they occur at 1.44-1.48 and 1.95-2.00 µm (~6750-6950 and 5005-5190 cm$^{-1}$). Additional bands due to OH vibrational overtones are found near 1.42 µm (~7040 cm$^{-1}$) in akaganéite and schwertmannite spectra and due to OH combination bands in akaganéite spectra at 2.46 µm (4070 cm$^{-1}$) with weaker components at 2.23-2.42 µm (4134-4492 cm$^{-1}$). A strong and broad band is observed near 2.8-3.1 µm (~3300-3600 cm$^{-1}$) in reflectance and transmittance spectra of akaganéite and schwertmannite due to overlapping OH and H$_2$O stretching vibrations. H$_2$O bending vibrations occur near 1620 cm$^{-1}$ (~6.17 µm) in akaganéite spectra and near 1630 cm$^{-1}$ (~6.13 µm) in schwertmannite spectra with additional bands at lower frequencies due to constrained H$_2$O molecules. OH bending vibrations occur near 650 and 850 cm$^{-1}$ (~15.4 and 11.8 µm) in akaganéite spectra and near 700 cm$^{-1}$ (~14.3 µm) in schwertmannite spectra. Sulfate vibrations are observed for schwertmannite as a $\nu_3$ triplet at 1118, 1057 and 1038 cm$^{-1}$ (~8.9, 9.5, and 9.6 µm), $\nu_1$ at 982 cm$^{-1}$ (~10.2 µm), $\nu_4$ near 690 cm$^{-1}$ (~14.5 µm) and $\nu_2$ at 608 cm$^{-1}$ (~16.5 µm). Fe-O bonds occur near 410-470 cm$^{-1}$ (µm) for akaganéite and schwertmannite. Both minerals readily absorb H$_2$O molecules from the environment and adsorb them onto the mineral surfaces and incorporate them into the tunnels. If akaganéite and schwertmannite were present on the surface of Mars they could enable transport of H$_2$O from the near-surface to the atmosphere as the partial pressure of H$_2$O varies diurnally.
Introduction

Akaganéite has recently been identified in a few small (<1 km²) locations on Mars through visible/near-infrared (VNIR) spectra acquired by the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) using the bands near 2.0 and 2.46 µm (Carter et al. 2014). Schwertmannite is consistent with some Observatoire pour la minéralogy, l’eau, les glaces et l’atmosphère (OMEGA) spectra of Mars (Poulet et al. 2008), although it has broad VNIR spectral features that are not unique to this mineral. Both minerals could be part of the X-ray amorphous phase identified at Gale crater by the MSL (Mars Science Lab) rover (Bish et al. 2013; Blake et al. 2013); however, only akaganéite has been unequivocally identified to date (Ming et al. 2014).

Akaganéite and schwertmannite are crystallographically-related ferric minerals that include 0.5 nm² tunnels in their structure occupied by anions (Figure 1). Akaganéite has Cl⁻ or F⁻ in the tunnels (Post and Buchwald 1991; Cornell and Schwertmann 2003; Post et al. 2003). The structure of schwertmannite is still under debate and it may include SO₄²⁻ and H₂O in the tunnels (Bigham et al. 1994; Fernandez-Martinez et al. 2010) or elsewhere. However the presence of structural sulfate is unquestioned (Loan et al., 2004). Both contain a network of Fe-O and Fe-OH bonds, with the proton on many internal OH groups H-bonded to the Cl⁻ (Song and Boily, 2012) or SO₄²⁻ (Boily et al., 2010) in the tunnels. Adsorbed H₂O is also prevalent for both minerals as evidenced by changes in H₂O stretching and bending band strengths with hydration levels (Boily et al., 2010; Song and Boily, 2012, 2013).

In this study we extend the spectral analyses of akaganéite and schwertmannite across wider spectral ranges, where data are currently available for Mars. The objectives of this
study are i) to present spectral features that can be used for identification of akaganéite and schwertmannite on Mars and ii) to summarize the geochemical conditions that govern the formation and stability of these minerals in order to provide insights into and constraints on the geochemical environments on Mars where these minerals are found. We present the Fe electronic bands in the extended visible region reflectance spectra, and overtones and combination bands of OH and H$_2$O in the near-infrared reflectance spectra for comparison with CRISM spectra of Mars. We present the fundamental OH, H$_2$O and Fe-O vibrations in the mid-infrared (mid-IR) reflectance spectra for comparison with the Thermal Emission Spectrometer (TES) data of Mars. Mid-IR transmittance and attenuated total reflectance (ATR) spectra are also discussed in order to associate structural parameters with the spectral features, although these types of spectra are not comparable to Martian data.

**Background**

**Structural properties of akaganéite and schwertmannite**

Akaganéite, β-FeOOH, is a nanocrystalline ferric oxyhydroxide with high specific surface area and monoclinic structure (Post and Buchwald 1991; Post et al. 2003). The basic structure consists of double chains of edge-shared Fe$^{3+}$-(O,OH) octahedra running parallel to the fourfold symmetrical b-axis (Cornell and Schwertmann, 2003; Ståhl et al., 2003), and are charge-compensated by substitutions of higher-valence cations into the octahedral sites, or by additional H atoms. In early studies Mössbauer spectra run on akaganéite by Murad (1979) identified three distinct Fe$^{3+}$ sites in the structure. Many studies have since addressed the Mössbauer parameters of akaganéite, and more recent
studies suggest two distinct Fe$^{3+}$ sites that require four separate sextets for modeling the low temperature spectra due to the influence of Cl$^-$ on the Fe$^{3+}$ cations (García et al. 2004; Barrero et al. 2006). The two-site Mössbauer model (Figure 2) is consistent with the neutron synchrotron diffraction study of akaganéite structure by Post et al. (2003) who found that the Fe-O bond lengths range in size from 1.94-2.13 Å.

Song and Boily (2012) determined the importance of Cl on the OH bond strength by varying the Cl/Fe ratios in synthetic samples. H$\text{}_2$O has been found to play an important part of akaganéite structure as well. Prominent H$\text{}_2$O bands are observed in spectra of akaganéite collected under dry conditions near 2, 3 and 6 µm (Bishop and Murad, 1996), variable H$\text{}_2$O vapor experiments promote changes in the H$\text{}_2$O bands (Song and Boily 2013) and H$\text{}_2$O contributes significantly to the heat capacity of akaganéite (Snow et al. 2011). The most common morphology of akaganéite nanocrystals is filaments or rods ~0.6 µm long (Musić et al. 2004), and the morphology is dependent on formation conditions, such that longer hydrolysis and aging times produce splitting during crystal growth resulting in ~3.2 µm diameter sheaves (Hu and Chen 2007). The bonding arrangements and positions of the Cl$^-$ and SO$_4^{2-}$ anions of these minerals are shown in Figure 1 for both akaganéite and schwertmannite.

The structure of schwertmannite is similar to that of akaganéite (Bigham et al. 1990), but is disrupted by the larger size of the sulfate anions (Fernandez-Martinez et al. 2010) as shown in Figure 1. Schwertmannite also exhibits high specific surface area and can have a range of OH$^-$ and SO$_4^{2-}$ abundances giving mineral formulas of about Fe$_8$O$_8$(OH)$_{4+6}$(SO$_4$)$_{1-2•n}$H$_2$O (Bigham et al. 1996; Yu et al. 1999; Fernandez-Martinez et al. 2010). Analysis of infrared data under variable hydration levels of schwertmannite and deuterium-exchanged
schwertmannite indicate that the $\text{SO}_4^{2-}$ anion occupies two sites in the structure: one $\text{SO}_4^{2-}$ is bound directly to Fe, while the other is connected via H-bonding (Boily et al. 2010). Fernandez-Martinez et al. (2010) modeled the schwertmannite structure and found best agreement with experimental XRD patterns for a structure having two outer-sphere sulfates H-bonded to OH inside the tunnel, two inner-sphere sulfates bound directly to Fe in the structure and eight $\text{H}_2\text{O}$ molecules per unit cell (Figure 3). The required $\text{H}_2\text{O}$ molecules in the structure are consistent with structural estimates (Bigham et al. 1994; Yu et al. 1999) and infrared experiments (Boily et al., 2010).

**Spectral features**

**Electronic Excitation bands.** The electronic excitations controlling the extended visible region spectral character of Fe oxyhydroxides are dominated by $\text{Fe}^{3+}$ crystal field theory absorptions and $\text{O}^{2-}$ to $\text{Fe}^{3+}$ charge transfer bands (Burns, 1993). For akaganéite and schwertmannite these include $\text{Fe}^{3+}$ absorptions near 0.43, ~0.6, and ~0.9 μm due to the $^6\text{A}_1$ to $^4\text{E},^4\text{A}_1(^4\text{G}),^6\text{A}_1(^6\text{S})$ to $^4\text{T}_2(^4\text{G})$ and $^6\text{A}_1(^6\text{S})$ to $^4\text{T}_1(^4\text{G})$ transitions, respectively (Sherman et al., 1982; Sherman and Waite, 1985). These give rise to an increasing reflectance slope in the visible region with a shoulder near 0.59 μm and a reflectance maximum near 0.73-0.74 μm. The dominant $\text{Fe}^{3+}$ band in reflectance spectra of akaganéite and schwertmannite is broader than that observed for other ferric oxide-bearing minerals (Morris et al., 1985) due to their nanophase character and multiple Fe sites (Figure 2), and is centered at 0.91-0.92 μm (Figure 4; Bishop and Murad, 1996). Another weak band is present near 0.44 μm (Figure 4).
Visible/near-infrared (VNIR) spectral features. Overtones and combinations of OH and H$_2$O produce features near 1.45, 1.9-2.1, and ~2.46 for akaganéite and near 1.45 and 1.95 µm for schwertmannite (Bishop and Murad, 1996), but a complete understanding of these features was not possible at that time.

Mid-IR spectral features. Transmittance spectra of akaganéite include strong vibrational bands due to H$_2$O stretching near 3484 and 3388 cm$^{-1}$, due to H$_2$O bending near 1628 cm$^{-1}$ and additional vibrations due to O-H and Fe-O bonds near 849, 818, 699, 647 and 488 cm$^{-1}$ (Murad and Bishop, 2000). Related features were observed in ATR and compacted DRIFT spectra (Murad and Bishop 2000).

More recent studies of transmission spectra of akaganéite under low moisture conditions explored the influence of adsorbed H$_2$O on the spectra (Song and Boily 2012; Kozin and Boily 2013; Song and Boily 2013) and discovered variations in the OH and H$_2$O stretching vibrations depending on degree of hydration and proximity to Cl$^-$. Studies have also shown that akaganéite with F$^-$ anions in place of some of the Cl$^-$ in the tunnels results in shifts in the H$_2$O stretching and bending vibrations towards lower frequencies (Cai et al. 2001; Song and Boily 2012).
Formation of akaganéite

Akaganéite is typically formed by hydrolysis of ferric chloride (or less often ferric fluoride) solution at low pH (e.g., Chambaere et al. 1979; Murad 1979; Schwertmann and Cornell 2000; Cai et al. 2001; Song and Boily 2012). FeCl$_3$ hydrolysis forms intermediate hydrated Fe$^{3+}$ molecules [Fe(H$_2$O)$_6$]$^{3+}$ that crystalize as akaganéite, goethite (α-FeOOH) or hematite (α-Fe$_2$O$_3$) (Cai et al., 2001; Parameshwari et al., 2011). Akaganéite formed above pH 3 is generally accompanied by maghemite and goethite that both frequently convert to hematite. Synthesis of akaganéite at elevated pH is facilitated by the presence of Mn (Cai et al., 2001) or dextrose (Parameshwari et al. 2011). Akaganéite can also be formed in corrosive environments containing Fe$^{2+}$ or steel and ferrous chloride, and akaganéite is the sole product when the latter reaction takes place without O$_2$ flow (Rémazeilles and Refait 2007). Akaganéite particles can also be further loaded with Cl$^-$ by reaction in HCl solution (Song and Boily 2012). Akaganéite treated with sulfate were found to be resistant to conversion to hematite upon heating (Musić et al. 2004).

Akaganéite is not a common soil mineral on Earth, but does form in Cl-rich environments including brines, marine rusts, and corrosion products (Johnston et al. 1978; Holm et al. 1983; Bibi et al. 2011) and even some iron-rich archaeological sites (Yabuki and Shima 1979; Réguer et al. 2007). Akaganéite has also been found as an alteration phase on some Fe-Ni meteorites found in Antarctica (Buchwald and Clarke 1989) and Ni-bearing phases related to akaganéite have been synthesized. Akaganéite can also be a precursor for nanophase goethite (Regenspurg et al. 2004), hematite (Glotch and Kraft 2008) and magnetite (Ahn et al. 2012). Gradual increase of pH was found to promote OH$^-$ replacement of Cl$^-$ in akaganéite, followed by transformation to goethite and magnetite (Ahn et al. 2012).
Réguer et al (2009) observed that temperature was primarily responsible for transformation of akaganéite to hematite, while dechlorination largely governed conversion to magnetite.

**Formation of schwertmannite**

Synthetic schwertmannite is generally formed at pH ~2.8-4.5 with sulfate concentrations on the order of 1000-3000 mg/L (Bigham et al. 1992; Bigham et al. 1996), while jarosite forms in this pH range at higher sulfate levels (Bigham and Nordstrom 2000) and goethite and ferrihydrite are more stable under more neutral to slightly acidic conditions (Bigham and Murad 1997). Thermodynamic experiments found that schwertmannite formation is favored over ferrihydrite formation across the pH range 2-8 for environments containing at least a small amount of sulfate (Majzlan et al. 2004).

Formation of schwertmannite is facilitated by *Acidithiobacillus ferrooxidans*, which induces oxidation of Fe$^{2+}$ to Fe$^{3+}$ in solution both in the lab and in natural environments, and *Acidithiobacillus ferrooxidans* thrives in the acidic environments necessary for formation of schwertmannite (Kelly and Wood 2000).

Schwertmannite is most commonly found as an alteration product from iron sulfides at mine drainage sites (Bigham et al. 1994; Bigham et al. 1996; Murad and Rojík 2003), but it has also been found in natural streams, e.g. draining from a pyritic schist in the Austrian alps (Schwertmann et al. 1995). Like akaganéite, schwertmannite also starts to form goethite nanoparticles as the pH is increased and SO$_4^{2-}$ anions are replaced by OH$^-$(Regenspurg et al. 2004).
Methods

The schwertmannite samples studied (Table 1) include both synthetic and natural materials from previous studies (Bigham et al. 1990). The reflectance and Mössbauer spectra of these samples were described by Bishop and Murad (1996). Both akaganéite samples are synthetic and were prepared by hydrolysis of ferric chloride for Mössbauer studies (Murad 1979; Sherman et al. 1982, Table 1). Akaganéite sample JB212 is in the form of a fluffy powder, while JB48 is a dried and crumbled crust. Sample JB212 has greater surface area and is more hydrated than sample JB48. Infrared spectra of akaganéite sample JB212 were presented by Murad and Bishop (2000), and a reflectance spectrum of akaganéite sample JB48 was presented by Bishop and Murad (1996).

Measurement of reflectance spectra

Reflectance spectra were measured for this study at Brown University’s RELAB using a bidirectional VNIR spectrometer under ambient conditions relative to Halon and a biconical Nicolet FTIR spectrometer in a controlled, dry environment relative to a rough gold surface as in previous studies (e.g., Bishop and Murad 2005). The bidirectional spectra were acquired from 0.3 to 2.5 µm at 5 nm spectral sampling. Infrared reflectance spectra were measured with 2 cm⁻¹ spectral sampling from 1-50 µm in a dry environment that was purged of H₂O- and CO₂- for 10-12 hours. Composite, absolute reflectance spectra were prepared by scaling the FTIR data to the bidirectional data near 1.2 µm.

Measurement of transmittance spectra
Transmittance spectra were measured using a Nicolet Magna 550 FTIR spectrometer by mixing 1 mg sample with 299 mg KBr to prepare pellets for analysis (Bishop and Murad 1996; Murad and Bishop 2000). Because these samples adsorb H₂O rapidly from the air, samples were measured promptly following pellet preparation.

Results

Near-Infrared (NIR) Spectral Properties

The band near 1.45 µm in NIR reflectance spectra of akaganéite and schwertmannite is an overtone of the OH and H₂O stretching vibrations occurring near 2.9-3.1 µm (Figure 4). The band near 1.9-2.1 µm is due to a combination of H₂O vibrations and has a different band center and shape for NIR spectra of akaganéite and schwertmannite and also varies within each sample type. The NIR hydration bands near 1.45 and 1.95 µm are also highly dependent on atmospheric moisture levels (Figures 4-5) and spectra taken under ambient conditions have stronger bands than spectra collected under dehydrated conditions. The H₂O combination band is asymmetric in spectra of both akaganéite and schwertmannite, but is broader in spectra of akaganéite and is centered near 2 µm, while this feature occurs near 1.95 µm in spectra of schwertmannite. Our akaganéite sample JB48 exhibits weaker H₂O bands in general compared to sample JB212; however, the H₂O band strengths increase in spectra of both samples under higher moisture conditions (Figures 4-5). Akaganéite spectra also include an asymmetric OH combination band near 2.46 µm with multiple shoulders at shorter wavelengths (Figure 4). Schwertmannite spectra include a broad shoulder near 2.54 µm (Figure 4) that is similar to features in this spectral region that are frequently observed in spectra of hydrated sulfates and other minerals.
feature is weakened as the environment becomes drier. Specific OH combination bands
cannot be resolved for schwertmannite in these spectra, likely because of a distribution of
OH vibrational energies and diffuse band positions.

Mid-IR Spectral Properties

Reflectance and transmittance spectra are shown for the OH and H₂O stretching region in Figure 6. A broad band is observed near 3 μm in the reflectance spectra for both akaganéite and schwertmannite. Spectra of the natural schwertmannite exhibit weak bands at 3620 and 3692 cm⁻¹ that are not observed for the synthetic sample. These could be related to the overtone band observed in the natural schwertmannite spectra at 7062 cm⁻¹ (Figure 5). Reflectance spectra of akaganéite sample JB212 acquired first in the mid-IR region contain a band near 3642 cm⁻¹ that disappears after the sample is heated by the NIR beam and is not present in mid-IR spectra of this sample collected again following measurement of the NIR spectra (Figure 6). This suggests that the 3642 cm⁻¹ band is due to H₂O that is readily removed by heating. Differences are observed between the reflectance and transmittance spectra due to the increased scattering of the reflectance spectra. The reflectance spectra were measured of loose particulate samples, while the transmittance and DRIFT spectra were measured of compressed powders.

The H₂O bands occur from ~1430 to 1635 cm⁻¹ and are stronger in reflectance spectra of loose, particulate samples of akaganéite and schwertmannite (R_JB212, R_JB130, R_JB131 in Figure 7). In contrast, the OH and Fe-O bands occur at lower frequencies (longer wavelengths) and these features are stronger in spectra of compressed samples (DRIFT
JB212, R JB48). This effect is due to scattering of the mineral grains and is commonly observed in the mid-IR region (Salisbury et al. 1991).

Several SO$_4^{2-}$ vibrations are observed weakly in the reflectance spectra (Figure 7) and more strongly in the transmittance spectra of schwertmannite (Figure 8) as seen for sulfate minerals in previous studies (e.g. Ross 1974; Lane 2007). The $\nu_3$ vibration occurs as a triplet at 1118, 1057 and 1038 cm$^{-1}$, the $\nu_1$ vibration at 982 cm$^{-1}$, and the $\nu_2$ vibration at 608 cm$^{-1}$, similar to those observed by Boily et al. (2010). Another broad band centered at 696 to 702 cm$^{-1}$ in our spectra is likely a combination of the $\nu_4$ SO$_4^{2-}$ vibration and the OH bending (OH$\delta$) vibration. Deuterium exchange experiments by Boily et al. (2010) showed that this band decreased in intensity and shifted towards lower wavenumbers as OH decreased in the system. They observed OH$\delta$ at 712 cm$^{-1}$. Assuming a band center of OH$\delta$ at 712 cm$^{-1}$ in our spectra as well suggests that the $\nu_4$ SO$_4^{2-}$ vibration likely occurs $\sim$690 cm$^{-1}$.

Fe-O vibrations are observed at 426 cm$^{-1}$ in transmittance spectra of akaganéite and at 414-420 cm$^{-1}$ in the transmittance spectra of schwertmannite (Figure 8). The Fe-O band occurs near 470 cm$^{-1}$ for both akaganéite and schwertmannite in reflectance spectra (Figure 7). The asymmetric shape of the Fe-O bands implies the presence of more than one type of Fe-O bond, which is consistent with observations from Mössbauer spectroscopy (Murad 1979) and XRD (Post et al. 2003) as illustrated in Figure 2. Views of the akaganéite and schwertmannite structures along the z-axis (Figure 9) show how some Fe-O bonds are more influenced by the presence of anions than others in these structures. The Cl/Fe ratio in akaganéite is much higher than the S/Fe ratio in schwertmannite due to the elevated number of Cl$^{-}$/anions present in the akaganéite structure (Figure 9).
Akaganéite NIR band assignments

NIR band assignments were made for akaganéite based on calculations of the expected vibrations of combination bands resulting from the individual stretching and bending modes in the infrared region (Table 2). The frequencies selected were determined from the band positions in Figures 4-8 and also from IR experiments on akaganéite under different hydration and anion conditions (Murad and Bishop 2000; Cai et al. 2001; Song and Boily 2012; Song and Boily 2013). H$_2$O and OH stretching ($\nu$) vibrations should have distinct but related frequencies; because the stretching vibrations overlap giving a broad envelope of vibrations, these were estimated. To check the H$_2$O$_{\nu}$ vibrational frequencies selected, we measured the H$_2$O$_{2\nu}$ (stretching overtone) frequencies near 6700-7050 cm$^{-1}$ (~1.42-1.48 µm) and calculated the H$_2$O$_{\nu}$ values using methods developed for phyllosilicate spectral features (Bishop et al. 2002; Petit et al. 2004). The refined method developed by Petit et al. (2004) was applied here such that the overtone vibration is equal to the fundamental vibration plus an anharmonicity constant of 85.6 cm$^{-1}$ that was determined experimentally for talc and tested successfully by Bishop et al. (2011) for beidellite:

\[ F(H_2O_{2\nu}) = 2X [F(H_2O_{\nu}) + 85.6 \text{ cm}^{-1}] \]

where F is the frequency of the vibration in wavenumbers.

The NIR band at 2.46 µm is attributed to the OH combination stretching plus out-of-plane bending vibration (OH$_{\nu+\delta}$) for OH groups that are associated with Cl· (~3410+650 =
The OH combination bands at 2.42 µm are attributed to isolated OH groups with in-plane bending vibrations (~3508+800 = 4308 cm⁻¹), and the bands at 2.32 µm arise from isolated OH groups with out-of-plane bending modes (~3508+623 = 4131 cm⁻¹). The latter bands near 2.32 and 2.42 µm appear as weak shoulders on the strong 2.46 µm band.

Spectra of some akaganéites (e.g., JB48) show an additional weak band or shoulder near 2.23 µm that can be explained as a combination of stretching and bending vibrations for OH groups H-bonded to H₂O (~3642+850 = 4492 cm⁻¹). The calculated OH
\[ \nu + \delta \]
bands compared well with the measured band positions at 4070, 4302, 4134, and 4492 cm⁻¹. This could indicate the presence of OH⁻-rich, Cl⁻-poor nanoparticles that begin to form with increasing pH (Ahn et al. 2012).

Similarly, the expected H₂O combination band (H₂O\[ \nu + \delta \]) frequencies for akaganéite were calculated by summing the IR stretching and bending mode frequencies (Table 2). The broad H₂O\[ \nu + \delta \] band is composed of at least three separate components: H₂O influenced by Cl⁻ (3413+1430 = 4843 cm⁻¹ or ~2.06 µm), H₂O constrained in the tunnels (3473+1523 = 4996 cm⁻¹ or ~2.00 µm), and isolated H₂O adsorbed on the outer surfaces of the structure (3508+1617 = 5125 cm⁻¹ or ~1.95 µm). These calculated NIR H₂O\[ \nu + \delta \] bands compare well with features observed in the NIR spectra at 4830, 4980, and 5040 cm⁻¹. Spectra of one akaganéite sample (JB48) also include another set of H₂O vibrations that could reflect partial alteration of this sample. This fourth H₂O\[ \nu + \delta \] band occurs near 1.92 µm and is assigned as a combination of H₂O\[ \nu \] at 3562 cm⁻¹ and H₂O\[ \delta \] at 1635 cm⁻¹ to give a calculated
H$_2$O$_{\nu+\delta}$ band of 5197 cm$^{-1}$, which compares well with the measured value of 5210 cm$^{-1}$ for the spectra of this sample (Figures 3, 4, 5).

**Schwertmannite NIR band assignments**

NIR band assignments were made for schwertmannite based on calculations of the expected vibrations of the combination band resulting from the individual stretching and bending modes in the infrared region (Table 2). The frequencies selected were determined from the band positions in Figures 4-8 and also from IR experiments on schwertmannite under different hydration conditions (Bishop and Murad 1996; Boily et al. 2010). The broad H$_2$O$_{\nu+\delta}$ band is likely composed of several components. These are more difficult to calculate for schwertmannite than for akaganéite because the H$_2$O$_{\delta}$ vibration has several components including many weak shoulders and thus the exact band centers cannot be determined. Several approximate H$_2$O$_{\nu+\delta}$ band calculations were performed in order to provide an estimate of what is occurring. Less-constrained H$_2$O such as isolated H$_2$O molecules adsorbed on the outer surfaces of the structure can be represented by $3483+1635 = 5118$ cm$^{-1}$ or $\sim$1.95 $\mu$m. The H$_2$O molecules H-bonded to sulfate groups in the tunnels would be further constrained and could have bands expressed by $3483+1523 = 5006$ cm$^{-1}$ or $\sim$2.00 $\mu$m and $3413+1430 = 4843$ cm$^{-1}$ or $\sim$2.06 $\mu$m.
The additional shoulder feature near 2.54 µm (3940 cm⁻¹) is inconsistent with OH combination bands and is observed to vary in shape and intensity with changing moisture levels. This feature is attributed to H₂O molecules in the schwertmannite structure but the exact band assignment has not yet been made.

**Implications for Mars**

Akaganéite and schwertmannite may be present on Mars as part of the nanophase component that is thought to contain Fe, Cl and S (Ming et al. 2014). These minerals are found in acidic environments where oxidation of iron-rich fluids has taken place. Although they are fairly rare on Earth, they could be more common on Mars. Schwertmannite was predicted to be present on Mars as part of gossans or iron sulfide oxidation products (Burns 1994). Schwertmannite is consistent with Martian spectra features at Terra Meridiani (Poulet et al. 2008) but its unique identification will likely be difficult because it exhibits broad NIR spectral bands and broad XRD peaks. Spectral features characteristic of schwertmannite that could be used for its detection on Mars include broad bands near 1.45 and 1.95 µm, a reflectance maximum near 2.15 µm, a decrease in reflectance from 2.15-2.5 µm, and a shoulder near 2.54 µm (Figure 4). Akaganéite could be detected on Mars using broad NIR spectral features at 1.45 and 2.0 µm, a reflectance maximum near 2.2 µm, and a band at 2.46 µm that may have shoulders near 2.32 and 2.42 µm (Figure 4, Table 2).

Cl has been found in the soil at all Martian landing sites (e.g. Clark and Van Hart 1981; Gellert et al. 2006; Ming et al. 2014), chlorides are thought to be present in some northern bright regions (Osterloo et al. 2010), and perchlorates have been found at the Phoenix landing sites (Hecht et al. 2009) and at the Rocknest site at Gale crater (Leshin et al. 2013).
Features consistent with akaganéite have been identified recently using NIR spectra of Mars in a few small outcrops at Robert Sharp, Gale and Antoniadi craters by Carter et al. (2014). Akaganéite was also identified on Mars by Ming et al. (2014) using XRD data of samples collected at the John Klein and Cumberland Hill drill holes at Yellowknife Bay in Gale Crater. Although these occurrences of akaganéite represent low abundances and isolated outcrops, akaganéite may be commonly present on Mars as part of the Cl mineralogy.

The presence of akaganéite on Mars would indicate a hydrothermal environment with temperatures near 60 °C, low pH, excess Cl⁻ and limited SO₄²⁻ (Schwertmann and Cornell 2000). Akaganéite converts to nanophase hematite at 300 °C (Glotch and Kraft 2008) that is inconsistent with the grey hematite at Meridiani Planum (Christensen et al. 2001), but could be consistent with the nanophase hematite observed as a component of the soil at Gusev Crater and Meridiani Planum by the Mini Mössbauer instrument (Morris et al. 2006b; Morris et al. 2006a). The presence of schwertmannite on Mars would reflect a low pH environment with moderate sulfate concentrations (Bigham et al. 1996). Schwertmannite formation on Earth is facilitated by Acidithiobacillus ferrooxidans (Kelly and Wood 2000), but it can also form inorganically. The presence of akaganéite or schwertmannite in the Martian surface soil today would imply that since their formation little modification of the surface has taken place through aqueous or thermal alteration that would convert these minerals to nanophase hematite.

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References


Holm, N.G., Dowler M.J., Wadsten T., and Arrhenius G. (1983) β-FeOOH · Cl₈ (akaganéite) and Fe₁₋ₓO (wüstite) in hot brine from the Atlantis II Deep (Red Sea) and the uptake of amino acids by synthetic β-FeOOH · Cl₈. Geochimica et Cosmochimica Acta, 47, 1465-1470.


Figure Captions

Figure 1 Structural models of akaganéite and schwertmannite based on refinements from Post et al. (2003) and Fernandez-Martinez et al. (2010), respectively. O and OH anions are shown in red, Fe cations in orange, H cations in blue, Cl- ions in green and SO₄²⁻ ions in yellow. The positions of H were not refined in the structure for schwertmannite so they cannot be shown. H₂O molecules are also located in the tunnels and adsorbed on the mineral surfaces but are not included in these diagrams as their positions are not yet refined.

Figure 2 Akaganéite structural models showing the two Fe sites with O anions in red, Fe cations in orange, and H cations in blue. Both Fe sites are distorted, with Fe-(O, OH) distances ranging from 1.94 to 2.11 Å for Fe1 and from 1.98 to 2.13 Å for Fe2 (Post et al. 2003). The mean Fe-(O, OH) distances are 2.01 and 2.05 Å for Fe1 and Fe2, respectively. Because the Fe2 site is slightly larger than the Fe1 site, the quadrupole splitting of the corresponding doublet in the Mössbauer spectrum should also be slightly higher.

Figure 3 Views of the schwertmannite structure along the y- and z-directions showing the two inner-sphere and two outer-sphere sulfates with O anions in red, Fe cations in orange, and SO₄²⁻ ions in yellow.

Figure 4 VNIR reflectance spectra of akaganéite and schwertmannite samples measured under ambient (patterned lines) and dehydrated (solid lines) conditions. The Fe³⁺

25
electronic transitions are marked by dashed lines, and the OH and H$_2$O vibrational
overtones and combination bands are marked by solid lines.

Figure 5 NIR reflectance spectra of akaganéite and schwertmannite from 3800 to 7300 cm$^{-1}$
showing the influence of variable hydration levels on the H$_2$O and OH overtone and
combination bands.

Figure 6 IR reflectance and transmittance spectra from 3000 to 7200 cm$^{-1}$ in the region of
overlapping H$_2$O and OH stretching vibrations.

Figure 7 Mid-IR spectra from 400-2000 cm$^{-1}$ illustrating differences in spectral character
for transmittance and reflectance spectra and for compacted samples (DRIFT JB212 and R
JB48) compared to loose particulate samples (R JB212, RJB130, R JB131). This region
features H$_2$O bending bands (solid lines) at $\sim$1430-1635 cm$^{-1}$, OH bending modes (dotted
lines) from $\sim$550-900 cm$^{-1}$ and Fe-O absorptions near 410-470 cm$^{-1}$.

Figure 8 Transmittance and ATR spectra of akaganéite and schwertmannite from 400-1500
cm$^{-1}$. Akaganéite OH in-plane bending vibrations at $\sim$840 cm$^{-1}$ and out-of-plane bending
vibrations near 650 cm$^{-1}$ are marked by dotted lines. Schwertmannite OH vibrations near
700 and 600 cm$^{-1}$ are marked by dashed lines. The Fe-O vibrations are marked with
patterned lines. The $SO_4^{2-}$ $\nu_1$ vibration at 982 cm$^{-1}$ and the $\nu_3$ triplet at $\sim$1030-1120 cm$^{-1}$ are
marked by solid lines.
Figure 9 Views of the akaganéite and schwertmannite structures along the z-axis direction showing the positions of Cl\(^{-}\) (green) and SO\(_4^{2-}\) (yellow) anions with respect to the Fe (orange) cations and O or OH (red) anions. Because the positions of the OH anions in schwertmannite have not been refined, the H\(^{+}\) cations in that mineral are not shown.
Table 1 Origin of akaganéite and schwertmannite samples in this study

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Table 2 Band assignments for spectral features

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