1 **Akaganéite and schwertmannite: Spectral properties and geochemical implications**

2 **of their possible presence on Mars**

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4 Janice L. Bishop[1], Enver Murad[2] and M. Darby Dyar[3]

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6 [1]Carl Sagan Center, SETI Institute, 189 Bernardo Ave., Mountain View, CA, 94043, USA

7 [2]Bahnhofstrasse 1, D-95615 Marktredwitz, Germany

8 [3]Mount Holyoke College, Department of Astronomy, South Hadley, MA, 01075, USA.

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20 **Abstract**

21   The ferric oxyhydroxide minerals akaganéite and schwertmannite are associated with

22   acidic environments and iron alteration on Earth and may be present on Mars as well.

23   These minerals have a tunnel structure and are crystallographically related. The extended

24   visible region reflectance spectra of these minerals are characterized by a broad Fe^{3+}

25   electronic transition centered near 0.92 μm, a reflectance maximum near 0.73 μm and a

26   shoulder near 0.59 μm. The near-infrared (NIR) reflectance spectra of each of these

27   minerals are dominated by broad overtones and combinations of the H_2O vibration

28   features. These occur near 1.44-1.48 and 1.98-2.07 μm ($\sim$6750-6950 and 4830-5210 cm^{-1})

29   in akaganéite spectra, while in schwertmannite spectra they occur at 1.44-1.48 and 1.95-

30   2.00 μm ($\sim$6750-6950 and 5005-5190 cm^{-1}). Additional bands due to OH vibrational

31   overtones are found near 1.42 μm ($\sim$7040 cm^{-1}) in akaganéite and schwertmannite spectra

32   and due to OH combination bands in akaganéite spectra at 2.46 μm (4070 cm^{-1}) with

33   weaker components at 2.23-2.42 μm (4134-4492 cm^{-1}). A strong and broad band is

34   observed near 2.8-3.1 μm ($\sim$3300-3600 cm^{-1}) in reflectance and transmittance spectra of

35   akaganéite and schwertmannite due to overlapping OH and H_2O stretching vibrations. H_2O

36   bending vibrations occur near 1620 cm^{-1} ($\sim$6.17 μm) in akaganéite spectra and near 1630

37   cm^{-1} ($\sim$6.13 μm) in schwertmannite spectra with additional bands at lower frequencies due

38   to constrained H_2O molecules. OH bending vibrations occur near 650 and 850 cm^{-1} ($\sim$15.4

39   and 11.8 μm) in akaganéite spectra and near 700 cm^{-1} ($\sim$14.3 μm) in schwertmannite

40   spectra. Sulfate vibrations are observed for schwertmannite as a ν_3 triplet at 1118, 1057

41   and 1038 cm^{-1} ($\sim$8.9, 9.5, and 9.6 μm), ν_1 at 982 cm^{-1} ($\sim$10.2 μm), ν_4 near 690 cm^{-1} ($\sim$14.5

42   μm) and ν_2 at 608 cm^{-1} ($\sim$16.5 μm). Fe-O bonds occur near 410-470 cm^{-1} (μm) for

43   akaganéite and schwertmannite. Both minerals readily absorb H_2O molecules from the

44   environment and adsorb them onto the mineral surfaces and incorporate them into the

45   tunnels. If akaganéite and schwertmannite were present on the surface of Mars they could

46   enable transport of H_2O from the near-surface to the atmosphere as the partial pressure of

47   H_2O varies diurnally.

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Introduction

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51   Akaganéite has recently been identified in a few small (<1 km^2) locations on Mars

52   through visible/near-infrared (VNIR) spectra acquired by the Compact Reconnaissance

53   Imaging Spectrometer for Mars (CRISM) using the bands near 2.0 and 2.46 μm (Carter et al.

54   2014). Schwertmannite is consistent with some Observatoire pour la minéralogy, l'eau, les

55   glaces et l'atmosphère (OMEGA) spectra of Mars (Poulet et al. 2008), although it has broad

56   VNIR spectral features that are not unique to this mineral. Both minerals could be part of

57   the X-ray amorphous phase identified at Gale crater by the MSL (Mars Science Lab) rover

58   (Bish et al. 2013; Blake et al. 2013); however, only akaganéite has been unequivocally

59   identified to date (Ming et al. 2014).

60   Akaganéite and schwertmannite are crystallographically-related ferric minerals that

61   include 0.5 nm^2 tunnels in their structure occupied by anions (Figure 1). Akaganéite has Cl$^-$

62   or F$^-$ in the tunnels (Post and Buchwald 1991; Cornell and Schwertmann 2003; Post et al.

63   2003). The structure of schwertmannite is still under debate and it may include SO_4^{2-} and

64   H_2O in the tunnels (Bigham et al. 1994; Fernandez-Martinez et al. 2010) or elsewhere.

65   However the presence of structural sulfate is unquestioned (Loan et al., 2004). Both

66   contain a network of Fe-O and Fe-OH bonds, with the proton on many internal OH groups

67   H-bonded to the Cl$^-$ (Song and Boily, 2012) or SO_4^{2-} (Boily et al., 2010) in the tunnels.

68   Adsorbed H_2O is also prevalent for both minerals as evidenced by changes in H_2O

69   stretching and bending band strengths with hydration levels (Boily et al., 2010; Song and

70   Boily, 2012, 2013).

71   In this study we extend the spectral analyses of akaganéite and schwertmannite across

72   wider spectral ranges, where data are currently available for Mars. The objectives of this

73   study are i) to present spectral features that can be used for identification of akaganéite

74   and schwertmannite on Mars and ii) to summarize the geochemical conditions that govern

75   the formation and stability of these minerals in order to provide insights into and

76   constraints on the geochemical environments on Mars where these minerals are found. We

77   present the Fe electronic bands in the extended visible region reflectance spectra, and

78   overtones and combination bands of OH and H_2O in the near-infrared reflectance spectra

79   for comparison with CRISM spectra of Mars. We present the fundamental OH, H_2O and Fe-O

80   vibrations in the mid-infrared (mid-IR) reflectance spectra for comparision with the

81   Thermal Emission Spectrometer (TES) data of Mars. Mid-IR transmittance and attenuated

82   total reflectance (ATR) spectra are also discussed in order to associate structural

83   parameters with the spectral features, although these types of spectra are not comparable

84   to Martian data.

85

86   **Background**

87   **Structural properties of akaganéite and schwertmannite**

88   Akaganéite, ß-FeOOH, is a nanocrystalline ferric oxyhydroxide with high specific

89   surface area and monoclinic structure (Post and Buchwald 1991; Post et al. 2003). The

90   basic structure consists of double chains of edge-shared Fe^{3+}-(O,OH) octahedra running

91   parallel to the fourfold symmeterical b-axis (Cornell and Schwertmann, 2003; Ståhl et al.,

92   2003), and are charge-compensated by substitutions of higher-valence cations into the

93   octahedral sites, or by additional H atoms. In early studies Mössbauer spectra run on

94   akaganéite by Murad (1979) identified three distinct Fe^{3+} sites in the structure. Many

95   studies have since addressed the Mössbauer parameters of akaganéite, and more recent

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96   studies suggest two distinct Fe^{3+} sites that require four separate sextets for modeling the

97   low temperature spectra due to the influence of Cl^- on the Fe^{3+} cations (García et al. 2004;

98   Barrero et al. 2006). The two-site Mössbauer model (Figure 2) is consistent with the

99   neutron synchrotron diffraction study of akaganéite structure by Post et al. (2003) who

100   found that the Fe-O bond lengths range in size from 1.94-2.13 Å.

101   Song and Boily (2012) determined the importance of Cl on the OH bond strength by

102   varying the Cl/Fe ratios in synthetic samples. H_2O has been found to play an important part

103   of akaganéite structure as well. Prominent H_2O bands are observed in spectra of akaganéite

104   collected under dry conditions near 2, 3 and 6 μm (Bishop and Murad, 1996), variable H_2O

105   vapor experiments promote changes in the H_2O bands (Song and Boily 2013) and H_2O

106   contributes significantly to the heat capacity of akaganéite (Snow et al. 2011). The most

107   common morphology of akaganéite nanocrystals is filaments or rods ~0.6 μm long (Musić

108   et al. 2004), and the morphology is dependent on formation conditions, such that longer

109   hydrolysis and aging times produce splitting during crystal growth resulting in ~3.2 μm

110   diameter sheaves (Hu and Chen 2007). The bonding arrangements and positions of the Cl^-

111   and SO_4^{2-} anions of these minerals are shown in Figure 1 for both akaganéite and

112   schwertmannite.

113   The structure of schwertmannite is similar to that of akaganéite (Bigham et al. 1990),

114   but is disrupted by the larger size of the sulfate anions (Fernandez-Martinez et al. 2010) as

115   shown in Figure 1. Schwertmannite also exhibits high specific surface area and can have a

116   range of OH^- and SO_4^{2-} abundances giving mineral formulas of about $Fe_8O_8(OH)_{4-6}(SO_4)_{1-}$

117   $_2 \bullet nH_2O$ (Bigham et al. 1996; Yu et al. 1999; Fernandez-Martinez et al. 2010). Analysis of

118   infrared data under variable hydration levels of schwertmannite and deuterium-exchanged

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119 schwertmannite indicate that the SO_4^{2-} anion occupies two sites in the structure: one SO_4^{2-}

120 is bound directly to Fe, while the other is connected via H-bonding (Boily et al. 2010).

121 Fernandez-Martinez et al. (2010) modeled the schwertmannite structure and found best

122 agreement with experimental XRD patterns for a structure having two outer-sphere

123 sulfates H-bonded to OH inside the tunnel, two inner-sphere sulfates bound directly to Fe

124 in the structure and eight H_2O molecules per unit cell (Figure 3). The required H_2O

125 molecules in the structure are consistent with structural estimates (Bigham et al. 1994; Yu

126 et al. 1999) and infrared experiments (Boily et al., 2010).

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128 **Spectral features**

129 <u>Electronic Excitation bands</u>. The electronic excitations controlling the extended visible

130 region spectral character of Fe oxyhydroxides are dominated by Fe^{3+} crystal field theory

131 absorptions and O^{2-} to Fe^{3+} charge transfer bands (Burns, 1993). For akaganéite and

132 schwertmannite these include Fe^{3+} absorptions near 0.43, ~0.6, and ~0.9 μm due to the $^6A_1$

133 to $^4E,^4A_1(^4G)$, $^6A_1(^6S)$ to $^4T_2(^4G)$ and $^6A_1(^6S)$ to $^4T_1(^4G)$ transitions, respectively (Sherman et

134 al., 1982; Sherman and Waite, 1985). These give rise to an increasing reflectance slope in

135 the visible region with a shoulder near 0.59 μm and a reflectance maximum near 0.73-0.74

136 μm. The dominant Fe^{3+} band in reflectance spectra of akaganéite and schwertmannite is

137 broader than that observed for other ferric oxide-bearing minerals (Morris et al., 1985) due

138 to their nanophase character and multiple Fe sites (Figure 2), and is centered at 0.91-0.92

139 μm (Figure 4; Bishop and Murad, 1996). Another weak band is present near 0.44 μm

140 (Figure 4).

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142   <u>Visible/near-infrared (VNIR) spectral features</u>. Overtones and combinations of OH and

143   H_2O produce features near 1.45, 1.9-2.1, and ~2.46 for akaganéite and near 1.45 and 1.95

144   μm for schwertmannite (Bishop and Murad, 1996), but a complete understanding of these

145   features was not possible at that time.

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147   <u>Mid-IR spectral features</u>. Transmittance spectra of akaganéite include strong

148   vibrational bands due to H_2O stretching near 3484 and 3388 cm^{-1}, due to H_2O bending near

149   1628 cm^{-1} and additional vibrations due to O-H and Fe-O bonds near 849, 818, 699, 647

150   and 488 cm^{-1} (Murad and Bishop, 2000). Related features were observed in ATR and

151   compacted DRIFT spectra (Murad and Bishop 2000).

152   More recent studies of transmission spectra of akaganéite under low moisture

153   conditions explored the influence of adsorbed H_2O on the spectra (Song and Boily 2012;

154   Kozin and Boily 2013; Song and Boily 2013) and discovered variations in the OH and H_2O

155   stretching vibrations depending on degree of hydration and proximity to Cl^-. Studies have

156   also shown that akaganéite with F^- anions in place of some of the Cl^- in the tunnels results

157   in shifts in the H_2O stretching and bending vibrations towards lower frequencies (Cai et al.

158   2001; Song and Boily 2012).

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160   **Formation of akaganéite**

161   Akaganéite is typically formed by hydrolysis of ferric chloride (or less often ferric

162   fluoride) solution at low pH (e.g., Chambaere et al. 1979; Murad 1979; Schwertmann and

163   Cornell 2000; Cai et al. 2001; Song and Boily 2012). $FeCl_3$ hydrolysis forms intermediate

164   hydrated Fe^{3+} molecules $[Fe(H_2O)6]^{3+}$ that crystalize as akaganéite, goethite (α-FeOOH) or

165   hematite (α-Fe_2O_3) (Cai et al., 2001; Parameshwari et al., 2011). Akaganéite formed above

166   pH 3 is generally accompanied by maghemite and goethite that both frequently convert to

167   hematite. Synthesis of akaganéite at elevated pH is facilitated by the presence of Mn (Cai et

168   al., 2001) or dextrose (Parameshwari et al. 2011). Akaganéite can also be formed in

169   corrosive environments containing Fe^{2+} or steel and ferrous chloride, and akaganéite is the

170   sole product when the latter reaction takes place without O_2 flow (Rémazeilles and Refait

171   2007). Akaganéite particles can also be further loaded with Cl^- by reaction in HCl solution

172   (Song and Boily 2012). Akaganéite treated with sulfate were found to be resistant to

173   conversion to hematite upon heating (Musić et al. 2004).

174   Akaganéite is not a common soil mineral on Earth, but does form in Cl-rich

175   environments including brines, marine rusts, and corrosion products (Johnston et al. 1978;

176   Holm et al. 1983; Bibi et al. 2011) and even some iron-rich archaeological sites (Yabuki and

177   Shima 1979; Réguer et al. 2007). Akaganéite has also been found as an alteration phase on

178   some Fe-Ni meteorites found in Antarctica (Buchwald and Clarke 1989) and Ni-bearing

179   phases related to akaganéite have been synthesized. Akaganéite can also be a precursor for

180   nanophase goethite (Regenspurg et al. 2004), hematite (Glotch and Kraft 2008) and

181   magnetite (Ahn et al. 2012). Gradual increase of pH was found to promote OH^- replacement

182   of Cl^- in akaganéite, followed by transformation to goethite and magnetite (Ahn et al. 2012).

183   Réguer et al (2009) observed that temperature was primarily responsible for

184   transformation of akaganéite to hematite, while dechlorination largely governed

185   conversion to magnetite.

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187   **Formation of schwertmannite**

188   Synthetic schwertmannite is generally formed at pH ~2.8-4.5 with sulfate

189   concentrations on the order of 1000-3000 mg/L (Bigham et al. 1992; Bigham et al. 1996),

190   while jarosite forms in this pH range at higher sulfate levels (Bigham and Nordstrom 2000)

191   and goethite and ferrihydrite are more stable under more neutral to slightly acidic

192   conditions (Bigham and Murad 1997). Thermodynamic experiments found that

193   schwertmannite formation is favored over ferrihydrite formation across the pH range 2-8

194   for environments containing at least a small amount of sulfate (Majzlan et al. 2004).

195   Formation of schwertmannite is facilitated by *Acidithiobacillus ferrooxidans*, which induces

196   oxidation of Fe^{2+} to Fe^{3+} in solution both in the lab and in natural environments, and

197   *Acidithiobacillus ferrooxidans* thrives in the acidic environments necessary for formation of

198   schwertmannite (Kelly and Wood 2000).

199   Schwertmannite is most commonly found as an alteration product from iron sulfides at

200   mine drainage sites (Bigham et al. 1994; Bigham et al. 1996; Murad and Rojík 2003), but it

201   has also been found in natural streams, e.g. draining from a pyritic schist in the Austrian

202   alps (Schwertmann et al. 1995). Like akaganéite, schwertmannite also starts to form

203   goethite nanoparticles as the pH is increased and SO_4^{2-} anions are replaced by OH^-

204   (Regenspurg et al. 2004).

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Methods

208   The schwertmannite samples studied (Table 1) include both synthetic and natural

209   materials from previous studies (Bigham et al. 1990). The reflectance and Mössbauer

210   spectra of these samples were described by Bishop and Murad (1996). Both akaganéite

211   samples are synthetic and were prepared by hydrolysis of ferric chloride for Mössbauer

212   studies (Murad 1979; Sherman et al. 1982, Table 1). Akaganéite sample JB212 is in the

213   form of a fluffy powder, while JB48 is a dried and crumbled crust. Sample JB212 has greater

214   surface area and is more hydrated than sample JB48. Infrared spectra of akaganéite sample

215   JB212 were presented by Murad and Bishop (2000), and a reflectance spectrum of

216   akaganéite sample JB48 was presented by Bishop and Murad (1996).

217

Measurement of reflectance spectra

219   Reflectance spectra were measured for this study at Brown University's RELAB using a

220   bidirectional VNIR spectrometer under ambient conditions relative to Halon and a

221   biconical Nicolet FTIR spectrometer in a controlled, dry environment relative to a rough

222   gold surface as in previous studies (e.g., Bishop and Murad 2005). The bidirectional spectra

223   were acquired from 0.3 to 2.5 μm at 5 nm spectral sampling. Infrared reflectance spectra

224   were measured with 2 cm^{-1} spectral sampling from 1-50 μm in a dry environment that was

225   purged of H_2O- and CO_2- for 10-12 hours. Composite, absolute reflectance spectra were

226   prepared by scaling the FTIR data to the bidirectional data near 1.2 μm.

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Measurement of transmittance spectra

229   Transmittance spectra were measured using a Nicolet Magna 550 FTIR spectrometer by

230   mixing 1 mg sample with 299 mg KBr to prepare pellets for analysis (Bishop and Murad

231   1996; Murad and Bishop 2000). Because these samples adsorb H_2O rapidly from the air,

232   samples were measured promptly following pellet preparation.

233

234   **Results**

235   **Near-Infrared (NIR) Spectral Properties**

236   The band near 1.45 μm in NIR reflectance spectra of akaganéite and schwertmannite is

237   an overtone of the OH and H_2O stretching vibrations occurring near 2.9-3.1 μm (Figure 4).

238   The band near 1.9-2.1 μm is due to a combination of H_2O vibrations and has a different

239   band center and shape for NIR spectra of akaganéite and schwertmannite and also varies

240   within each sample type. The NIR hydration bands near 1.45 and 1.95 μm are also highly

241   dependent on atmospheric moisture levels (Figures 4-5) and spectra taken under ambient

242   conditions have stronger bands than spectra collected under dehydrated conditions. The

243   H_2O combination band is asymmetric in spectra of both akaganéite and schwertmannite,

244   but is broader in spectra of akaganéite and is centered near 2 μm, while this feature occurs

245   near 1.95 μm in spectra of schwertmannite. Our akaganéite sample JB48 exhibits weaker

246   H_2O bands in general compared to sample JB212; however, the H_2O band strengths

247   increase in spectra of both samples under higher moisture conditions (Figures 4-5).

248   Akaganéite spectra also include an asymmetric OH combination band near 2.46 μm with

249   multiple shoulders at shorter wavelengths (Figure 4). Schwertmannite spectra include a

250   broad shoulder near 2.54 μm (Figure 4) that is similar to features in this spectral region

251   that are frequently observed in spectra of hydrated sulfates and other minerals. This

252   feature is weakened as the environment becomes drier. Specific OH combination bands

253   cannot be resolved for schwertmannite in these spectra, likely because of a distribution of

254   OH vibrational energies and diffuse band positions.

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256   **Mid-IR Spectral Properties**

257   Reflectance and transmittance spectra are shown for the OH and H_2O stretching region

258   in Figure 6. A broad band is observed near 3 μm in the reflectance spectra for both

259   akaganéite and schwertmannite. Spectra of the natural schwertmannite exhibit weak bands

260   at 3620 and 3692 cm^{-1} that are not observed for the synthetic sample. These could be

261   related to the overtone band observed in the natural schwertmannite spectra at 7062 cm^{-1}

262   (Figure 5). Reflectance spectra of akaganéite sample JB212 acquired first in the mid-IR

263   region contain a band near 3642 cm^{-1} that disappears after the sample is heated by the NIR

264   beam and is not present in mid-IR spectra of this sample collected again following

265   measurement of the NIR spectra (Figure 6). This suggests that the 3642 cm^{-1} band is due to

266   H_2O that is readily removed by heating. Differences are observed between the reflectance

267   and transmittance spectra due to the increased scattering of the reflectance spectra. The

268   reflectance spectra were measured of loose particulate samples, while the transmittance

269   and DRIFT spectra were measured of compressed powders.

270   The H_2O bands occur from ~1430 to 1635 cm^{-1} and are stronger in reflectance spectra

271   of loose, particulate samples of akaganéite and schwertmannite (R_JB212, R_JB130,

272   R_JB131 in Figure 7). In contrast, the OH and Fe-O bands occur at lower frequencies (longer

273   wavelengths) and these features are stronger in spectra of compressed samples (DRIFT

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274   JB212, R JB48). This effect is due to scattering of the mineral grains and is commonly

275   observed in the mid-IR region (Salisbury et al. 1991).

276   Several SO_4^{2-} vibrations are observed weakly in the reflectance spectra (Figure 7) and

277   more strongly in the transmittance spectra of schwertmannite (Figure 8) as seen for sulfate

278   minerals in previous studies (e.g. Ross 1974; Lane 2007). The ν_3 vibration occurs as a

279   triplet at 1118, 1057 and 1038 cm^{-1}, the ν_1 vibration at 982 cm^{-1}, and the ν_2 vibration at 608

280   cm^{-1}, similar to those observed by Boily et al. (2010). Another broad band centered at 696

281   to 702 cm^{-1} in our spectra is likely a combination of the ν_4 SO_4^{2-} vibration and the OH

282   bending (OHδ) vibration. Deuterium exchange experiments by Boily et al. (2010) showed

283   that this band decreased in intensity and shifted towards lower wavenumbers as OH

284   decreased in the system. They observed OHδ at 712 cm^{-1}. Assuming a band center of OHδ at

285   712 cm^{-1} in our spectra as well suggests that the ν_4 SO_4^{2-} vibration likely occurs ~690 cm^{-1}.

286   Fe-O vibrations are observed at 426 cm^{-1} in transmittance spectra of akaganéite and at

287   414-420 cm^{-1} in the transmittance spectra of schwertmannite (Figure 8). The Fe-O band

288   occurs near 470 cm^{-1} for both akaganéite and schwertmannite in reflectance spectra

289   (Figure 7). The asymmetric shape of the Fe-O bands implies the presence of more than one

290   type of Fe-O bond, which is consistent with observations from Mössbauer spectroscopy

291   (Murad 1979) and XRD (Post et al. 2003) as illustrated in Figure 2. Views of the akaganéite

292   and schwertmannite structures along the z-axis (Figure 9) show how some Fe-O bonds are

293   more influenced by the presence of anions than others in these structures. The Cl/Fe ratio

294   in akaganéite is much higher than the S/Fe ratio in schwertmannite due to the elevated

295   number of Cl$^-$ anions present in the akaganéite structure (Figure 9).

296

297   **Discussion**

298   **Akaganéite NIR band assignments**

299   NIR band assignments were made for akaganéite based on calculations of the expected

300   vibrations of combination bands resulting from the individual stretching and bending

301   modes in the infrared region (Table 2). The frequencies selected were determined from the

302   band positions in Figures 4-8 and also from IR experiments on akaganéite under different

303   hydration and anion conditions (Murad and Bishop 2000; Cai et al. 2001; Song and Boily

304   2012; Song and Boily 2013). H_2O and OH stretching (ν) vibrations should have distinct but

305   related frequencies; because the stretching vibrations overlap giving a broad envelope of

306   vibrations, these were estimated. To check the H_2O_ν vibrational frequencies selected, we

307   measured the H_2O $_{2\nu}$ (stretching overtone) frequencies near 6700-7050 cm^{-1} ($\sim$1.42-1.48

308   μm) and calculated the H_2O_ν values using methods developed for phyllosilicate spectral

309   features (Bishop et al. 2002; Petit et al. 2004). The refined method developed by Petit et al.

310   (2004) was applied here such that the overtone vibration is equal to the fundamental

311   vibration plus an anharmonicity constant of 85.6 cm^{-1} that was determined experimentally

312   for talc and tested successfully by Bishop et al. (2011) for beidellite:

313         $F(H_2O_{2\nu}) = 2X [F(H_2O_\nu) +85.6$ $cm^{-1}]$, where F is the frequency of the vibration in

314   wavenumbers.

315   The NIR band at 2.46 μm is attributed to the OH combination stretching plus out-of-

316   plane bending vibration ($OH_{\nu+\delta}$) for OH groups that are associated with Cl^- ($\sim$3410+650 =

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317   4060 cm^{-1}). The OH combination bands at 2.42 μm are attributed to isolated OH groups

318   with in-plane bending vibrations (~3508+800 = 4308 cm^{-1}), and the bands at 2.32 μm arise

319   from isolated OH groups with out-of-plane bending modes (~3508+623 = 4131 cm^{-1}). The

320   latter bands near 2.32 and 2.42 μm appear as weak shoulders on the strong 2.46 μm band.

321   Spectra of some akaganéites (e.g., JB48) show an additional weak band or shoulder near

322   2.23 μm that can be explained as a combination of stretching and bending vibrations for OH

323   groups H-bonded to H_2O (~3642+850 = 4492 cm^{-1}). The calculated $OH_{\nu+\delta}$ bands compared

324   well with the measured band positions at 4070, 4302, 4134, and 4492 cm^{-1}. This could

325   indicate the presence of OH$^-$-rich, Cl$^-$-poor nanoparticles that begin to form with increasing

326   pH (Ahn et al. 2012).

327   Similarly, the expected H_2O combination band ($H_2O_{\nu+\delta}$) frequencies for akaganéite

328   were calculated by summing the IR stretching and bending mode frequencies (Table 2).

329   The broad $H_2O_{\nu+\delta}$ band is composed of at least three separate components: H_2O influenced

330   by Cl$^-$ (3413+1430 = 4843 cm^{-1} or ~2.06 μm), H_2O constrained in the tunnels (3473+1523

331   = 4996 cm^{-1} or ~2.00 μm), and isolated H_2O adsorbed on the outer surfaces of the structure

332   (3508+1617 = 5125 cm^{-1} or ~1.95 μm). These calculated NIR $H_2O_{\nu+\delta}$ bands compare well

333   with features observed in the NIR spectra at 4830, 4980, and 5040 cm^{-1}. Spectra of one

334   akaganéite sample (JB48) also include another set of H_2O vibrations that could reflect

335   partial alteration of this sample. This fourth $H_2O_{\nu+\delta}$ band occurs near 1.92 μm and is

336   assigned as a combination of H_2O_ν at 3562 cm^{-1} and H_2O_δ at 1635 cm^{-1} to give a calculated

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337    $H_2O_{\nu+\delta}$ band of 5197 cm^{-1}, which compares well with the measured value of 5210 cm^{-1} for

338   the spectra of this sample (Figures 3, 4, 5).

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340   **Schwertmannite NIR band assignments**

341   NIR band assignments were made for schwertmannite based on calculations of the

342   expected vibrations of the combination band resulting from the individual stretching and

343   bending modes in the infrared region (Table 2). The frequencies selected were determined

344   from the band positions in Figures 4-8 and also from IR experiments on schwertmannite

345   under different hydration conditions (Bishop and Murad 1996; Boily et al. 2010). The

346   broad $H_2O_{\nu+\delta}$ band is likely composed of several components. These are more difficult to

347   calculate for schwertmannite than for akaganéite because the H_2O_δ vibration has several

348   components including many weak shoulders and thus the exact band centers cannot be

349   determined. Several approximate $H_2O_{\nu+\delta}$ band calculations were performed in order to

350   provide an estimate of what is occurring. Less-constrained H_2O such as isolated H_2O

351   molecules adsorbed on the outer surfaces of the structure can be represented by

352   3528+1665 = 5193 cm^{-1} or ~1.93 μm, while H_2O constrained in the tunnels could be

353   3483+1635 = 5118 cm^{-1} or ~1.95 μm. The H_2O molecules H-bonded to sulfate groups in the

354   tunnels would be further constrained and could have bands expressed by 3483+1523 =

355   5006 cm^{-1} or ~2.00 μm and 3413+1430 = 4843 cm^{-1} or ~2.06 μm.

16

356   The additional shoulder feature near 2.54 µm (3940 cm^{-1}) is inconsistent with OH

357   combination bands and is observed to vary in shape and intensity with changing moisture

358   levels. This feature is attributed to H_2O molecules in the schwertmannite structure but the

359   exact band assignment has not yet been made.

360

361   **Implications for Mars**

362   Akaganéite and schwertmannite may be present on Mars as part of the nanophase

363   component that is thought to contain Fe, Cl and S (Ming et al. 2014). These minerals are

364   found in acidic environments where oxidation of iron-rich fluids has taken place. Although

365   they are fairly rare on Earth, they could be more common on Mars. Schwertmannite was

366   predicted to be present on Mars as part of gossans or iron sulfide oxidation products

367   (Burns 1994). Schwertmannite is consistent with Martian spectra features at Terra

368   Meridiani (Poulet et al. 2008) but its unique identification will likely be difficult because it

369   exhibits broad NIR spectral bands and broad XRD peaks. Spectral features characteristic of

370   schwertmannite that could be used for its detection on Mars include broad bands near 1.45

371   and 1.95 µm, a reflectance maximum near 2.15 µm, a decrease in reflectance from 2.15-2.5

372   µm, and a shoulder near 2.54 µm (Figure 4). Akaganéite could be detected on Mars using

373   broad NIR spectral features at 1.45 and 2.0 µm, a reflectance maximum near 2.2 µm, and a

374   band at 2.46 µm that may have shoulders near 2.32 and 2.42 µm (Figure 4, Table 2).

375   Cl has been found in the soil at all Martian landing sites (e.g. Clark and Van Hart 1981;

376   Gellert et al. 2006; Ming et al. 2014), chlorides are thought to be present in some northern

377   bright regions (Osterloo et al. 2010), and perchlorates have been found at the Phoenix

378   landing sites (Hecht et al. 2009) and at the Rocknest site at Gale crater (Leshin et al. 2013).

17

379   Features consistent with akaganéite have been identified recently using NIR spectra of

380   Mars in a few small outcrops at Robert Sharp, Gale and Antoniadi craters by Carter et al.

381   (2014). Akaganéite was also identified on Mars by Ming et al. (2014) using XRD data of

382   samples collected at the John Klein and Cumberland Hill drill holes at Yellowknife Bay in

383   Gale Crater. Although these occurrences of akaganéite represent low abundances and

384   isolated outcrops, akaganéite may be commonly present on Mars as part of the Cl

385   mineralogy.

386   The presence of akaganéite on Mars would indicate a hydrothermal environment with

387   temperatures near 60 °C, low pH, excess Cl^- and limited SO_4^{2-} (Schwertmann and Cornell

388   2000). Akaganéite converts to nanophase hematite at 300 °C (Glotch and Kraft 2008) that

389   is inconsistent with the grey hematite at Meridiani Planum (Christensen et al. 2001), but

390   could be consistent with the nanophase hematite observed as a component of the soil at

391   Gusev Crater and Meridiani Planum by the Mini Mössbauer instrument (Morris et al.

392   2006b; Morris et al. 2006a). The presence of schwertmannite on Mars would reflect a low

393   pH environment with moderate sulfate concentrations (Bigham et al. 1996).

394   Schwertmannite formation on Earth is facilitated by *Acidithiobacillus ferrooxidans* (Kelly

395   and Wood 2000), but it can also form inorganically. The presence of akaganéite or

396   schwertmannite in the Martian surface soil today would imply that since their formation

397   little modification of the surface has taken place through aqueous or thermal alteration that

398   would convert these minerals to nanophase hematite.

399

400   **Acknowledgments**

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626   Figure Captions

627

628   Figure 1 Structural models of akaganéite and schwertmannite based on refinements from

629   Post et al. (2003) and Fernandez-Martinez et al. (2010), respectively. O and OH anions are

630   shown in red, Fe cations in orange, H cations in blue, Cl⁻ ions in green and SO_4^{2-} ions in

631   yellow. The positions of H were not refined in the structure for schwertmannite so they

632   cannot be shown. H_2O molecules are also located in the tunnels and adsorbed on the

633   mineral surfaces but are not included in these diagrams as their positions are not yet

634   refined.

635

636   Figure 2 Akaganéite structural models showing the two Fe sites with O anions in red, Fe

637   cations in orange, and H cations in blue. Both Fe sites are distorted, with Fe-(O, OH)

638   distances ranging from 1.94 to 2.11 Å for Fe1 and from 1.98 to 2.13 Å for Fe2 (Post et al.

639   2003). The mean Fe-(O, OH) distances are 2.01 and 2.05 Å for Fe1 and Fe2, respectively.

640   Because the Fe2 site is slightly larger than the Fe1 site, the quadrupole splitting of the

641   corresponding doublet in the Mössbauer spectrum should also be slightly higher.

642

643   Figure 3 Views of the schwertmannite structure along the y- and z-directions showing the

644   two inner-sphere and two outer-sphere sulfates with O anions in red, Fe cations in orange,

645   and SO_4^{2-} ions in yellow.

646

647   Figure 4 VNIR reflectance spectra of akaganéite and schwertmannite samples measured

648   under ambient (patterned lines) and dehydrated (solid lines) conditions. The Fe^{3+}

25

649   electronic transitions are marked by dashed lines, and the OH and H_2O vibrational

650   overtones and combination bands are marked by solid lines.

651

652   Figure 5 NIR reflectance spectra of akaganéite and schwertmannite from 3800 to 7300 cm^{-1}

653   showing the influence of variable hydration levels on the H_2O and OH overtone and

654   combination bands.

655

656   Figure 6 IR reflectance and transmittance spectra from 3000 to 7200 cm^{-1} in the region of

657   overlapping H_2O and OH stretching vibrations.

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659   Figure 7 Mid-IR spectra from 400-2000 cm^{-1} illustrating differences in spectral character

660   for transmittance and reflectance spectra and for compacted samples (DRIFT JB212 and R

661   JB48) compared to loose particulate samples (R JB212, RJB130, R JB131). This region

662   features H_2O bending bands (solid lines) at ~1430-1635 cm^{-1}, OH bending modes (dotted

663   lines) from ~550-900 cm^{-1} and Fe-O absorptions near 410-470 cm^{-1}.

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665   Figure 8 Transmittance and ATR spectra of akaganéite and schwertmannite from 400-1500

666   cm^{-1}. Akaganéite OH in-plane bending vibrations at ~840 cm^{-1} and out-of-plane bending

667   vibrations near 650 cm^{-1} are marked by dotted lines. Schwertmannite OH vibrations near

668   700 and 600 cm^{-1} are marked by dashed lines. The Fe-O vibrations are marked with

669   patterned lines. The SO_4^{2-} ν_1 vibration at 982 cm^{-1} and the ν_3 triplet at ~1030-1120 cm^{-1} are

670   marked by solid lines.

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672 Figure 9 Views of the akaganéite and schwertmannite structures along the z-axis direction

673 showing the positions of Cl$^-$ (green) and SO$_4^{2-}$ (yellow) anions with respect to the Fe

674 (orange) cations and O or OH (red) anions. Because the positions of the OH anions in

675 schwertmannite have not been refined, the H$^+$ cations in that mineral are not shown.

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677   Table 1 Origin of akaganéite and schwertmannite samples in this study

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Sample ID	other ID	mineral	formation	reference
JB48		akaganéite	synthetic	Sherman et al. (1982)
JB212		akaganéite	synthetic, hydrolysis of $FeCl_3$	Murad (1979)
JB131	Z510b	schwertmannite	synthetic, pH 2.9	Bigham et al. (1990)
JB130	Bt-4	schwertmannite	Glenn's run, Belmont Co., Ohio, pH 3.2	Bigham et al. (1990)

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689   Table 2 Band assignments for spectral features
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	measured $H_2O\ 2\nu$ (cm^{-1})	calculated $H_2O\ \nu$ (cm^{-1})	measured $H_2O\ \delta$ (cm^{-1})	calculated $H_2O\ \nu+\delta$ (cm^{-1})	calculated $H_2O\ \nu+\delta$ (μm)	measured $H_2O\ \nu+\delta$ (cm^{-1})
Akaganéite						
(JB48)	7038	3562	1635	5197	1.92	5210
(JB212)	6930	3508	1617	5125	1.95	5040
(JB212)	6860	3473	1523	4996	2.00	4980
(JB212)	6740	3413	1430	4843	2.06	4830

	measured OH ν (cm^{-1})	measured in-plane OH δ (cm^{-1})	measured out-of-plane OH δ (cm^{-1})	calculated OH $\nu+\delta$ (cm^{-1})	calculated OH $\nu+\delta$ (μm)	measured OH $\nu+\delta$ (cm^{-1})
Akaganéite						
OH⋯Cl⁻	3410		650	4060	2.46	4070
OH isolated	3508	800		4308	2.32	4302
OH isolated	3508		623	4131	2.42	4134
OH⋯H2O	3642	850		4492	2.23	4492

	measured $H_2O\ 2\nu$ (cm^{-1})	calculated $H_2O\ \nu$ (cm^{-1})	measured $H_2O\ \delta$ (cm^{-1})	calculated $H_2O\ \nu+\delta$ (cm^{-1})	calculated $H_2O\ \nu+\delta$ (μm)	measured $H_2O\ \nu+\delta$ (cm^{-1})
Schwertmannite						
	6970	3528	1665	5193	1.93	5190
	6880	3483	1635	5118	1.95	5120
	6880	3483	1523	5006	2.00	5005
	6740	3413	1430	4843	2.06	

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