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Spectroscopic Analysis of Allophane and Imogolite Samples with Variable Fe Abundance

for Characterizing the Poorly Crystalline Components on Mars

Revision 1

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20   **Abstract**

21

22   Nanophase materials including silicates, aluminosilicates, and iron oxides are widespread

23   on Mars. These minerals are important because they likely represent a solid-phase record of

24   ancient climatic conditions on the martian surface. Identification and characterization of

25   nanophase compounds is technically challenging due to the small size and poorly ordered nature

26   of these materials, particularly because their chemical compositions can vary widely.

27   This study presents spectra of several synthetic allophane and imogolite samples with a

28   range of chemical compositions that are typical of the natural variability of allophanic materials.

29   These samples were formed under controlled conditions and have been thoroughly characterized

30   in terms of chemical composition and atomic structure.

31   Analyses confirmed that the synthetic materials were allophane and imogolite and were

32   structurally similar to previously studied natural and synthetic examples of these phases. NMR

33   and XAFS data indicated that high-Al proto-imogolite allophanes were similar in structure to

34   imogolite but were less well ordered, and supported the proposed nanoball structures based on

35   rolled octahedral Al sheets. Increasing Si content in allophane produced increasing tetrahedral Al

36   substitution as well as polymerized Si chain structures at Al-Si mole ratios of 1:1, and sheets and

37   possible framework structures at Al-Si mole ratios of 1:2. Fe in allophanes and imogolites

38   substituted exclusively for octahedral Al.

39   Reflectance spectra of the synthetic allophanes and imogolites were comparable to

40   previously analyzed samples. Variations in Fe content of allophane and imogolite resulted in

41   some observable changes in visible/near-infrared (VNIR) reflectance spectra, but these changes

42   were not detectable in emission spectra. Emission spectra of the samples suggest that variations

43   in Al-Si ratio of allophanes should be detectable using remotely sensed data. Because allophanes

44   with different Al-Si ratios typically form in very different environments, this could be significant

45   for interpretation of formation conditions on Mars, with high-Al compositions suggesting

46   possible tephra weathering and high-Si compositions indicating possible formation from thermal

47   waters.

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Introduction

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50   Poorly crystalline aluminosilicates such as allophane and imogolite have been identified

51   on Mars using orbital infrared spectroscopy (Rampe et al. 2012; Weitz et al. 2014; Bishop and

52   Rampe 2016). The presence of these nanophase (np) materials on Mars likely indicates a time

53   when water was intermittent and/or too cold for formation of crystalline clays (Bishop et al.

54   2018). Analysis of Mars Global Surveyor (MGS) Thermal Emission Spectrometer (TES) data

55   (Christensen et al. 2001) provided global maps of regions dominated by basaltic and andesitic or

56   altered terrains (Bandfield et al. 2000; Wyatt and McSween Jr 2002). As spectral libraries of Si-

57   rich alteration products were developed, TES analyses were extended to include more complex

58   components including poorly crystalline Si-rich materials (Michalski et al. 2005; Michalski et al.

59   2006; Rogers and Christensen 2007; Ruff and Christensen 2007; Rampe et al. 2012).

60   Gusev crater contains regions high in Si at Home Plate attributed to opal or hydrated

61   silica (Squyres et al. 2008; Rice et al. 2010; Ruff et al. 2011). Additional observations of

62   amorphous Si on Mars were made from orbit using visible/near-infrared (VNIR) Compact

63   Reconnaissance Imaging Spectrometer for Mars (CRISM) data (Murchie et al. 2009) at Valles

64   Marineris (Milliken et al. 2008), Nili Fossae (Ehlmann et al. 2009), Nili Patera (Skok et al.

65   2010), and Mawrth Vallis (Bishop et al. 2008). The Mars Exploration Rovers (MERs), Spirit and

66   Opportunity, analyzed fine surficial material at Gusev (Spirit) and Meridiani (Opportunity) with

67   many instruments, and the Mössbauer spectrometer detected the presence of nanophase ferric

68   oxides, hydroxides, or oxyhydroxides (np-FeOx) (Klingelhöfer et al. 2004; Morris et al. 2004;

69   Morris et al. 2006a; Morris et al. 2006b). This is consistent with previous VNIR detections of np-

70   FeOx on Mars (Singer 1982; Bell et al. 1990; Morris and Lauer 1990).

71   An X-ray amorphous component was identified by the Chemistry and Mineralogy

72   instrument (CheMin) on board the Mars Science Laboratory (MSL) rover at Gale crater (Blake et

73   al. 2013) that represents ~20-70 wt.% of martian surface material everywhere CheMin has

74   investigated (Blake et al. 2013; Vaniman et al. 2014; Bristow et al. 2018; Morrison et al. 2018).

75   The amorphous component most likely represents a combination of volcanic glass and hydrated

76   amorphous alteration products that are composed primarily of Si, Fe, and S (Ming et al. 2014;

77   Vaniman et al. 2014). Rampe et al. (2012) identified 10-20% allophane and/or amorphous silica

78   at North Acidalia, Solis Planum, Sinus Meridiani, and Aonium-Phrixi using TES data. Bishop

79   and Rampe (2016) found 10-30% allophane (or related phases) in phyllosilicate-rich outcrops at

80   Mawrth Vallis using a combination of TES and CRISM data. The elevated allophane detections

81   in the northern plains (Rampe et al. 2012) could be related to observations of leached basaltic

82   glass in this region (Horgan and Bell 2012). Thus, allophane and imogolite could be a common

83   component of the martian surface where water was present. Further, they may indicate periods of

84   cyclical climate change. Progressive cooling and drying of the surface would result in conditions

85   favorable for amorphous material production, where surface water was not present long enough

86   or conditions were not warm enough to form more long-range ordered clays (Bishop and Rampe

87   2016).

88   Characterization of these materials in the lab is essential for increasing spectral

89   recognition capacities on Mars. Np-aluminosilicates adsorb water readily (Bishop et al. 2013)

90   and can bind with Fe and other species (Baker et al. 2014; Rampe et al. 2016). Understanding the

91   relationship between Al-Si-Fe abundance in poorly crystalline aluminosilicates and their spectral

92   properties will enable future detection of these important materials that encompass up to 70 wt.%

93   of the surface material investigated by Curiosity at Gale crater. The purpose of this study is to

94 characterize several Fe-bearing allophane and imogolite samples with multiple spectroscopic

95 techniques to enable more precise detection and characterization of the poorly crystalline

96 components of the martian regolith.

97

98   **Background**

99   Allophanes are poorly crystalline nanoscale aluminosilicates that are prevalent in soils

100 formed from volcanic ash, where an excess of Si and Al exist in solution (Parfitt 2009). They are

101 frequently found in association with imogolite, most commonly as products of the weathering of

102 volcanic tephra. Allophane imparts unique chemical and physical properties to soils in which it is

103 a predominant mineralogical component, and those properties have implications for the content

104 and retention of phosphate, sulfate, and H_2O in such soils (Rajan 1979; Rampe et al. 2016).

105   Allophane and imogolite exhibit rolled morphologies (Figure 1) with nanometer-scale

106 diameters (Abidin et al. 2007), and therefore lack the long-range ordered orthogonal lattices

107 observed in macroscopically crystalline materials, although imogolite exhibits long-range order

108 in one direction. Allophane and imogolite are difficult to characterize due to their small size and

109 lack of macroscopic crystal ordering; however, research has illuminated much about their

110 structure and formation (Henmi and Wada 1976; Farmer et al. 1980; Abidin et al. 2007; Abidin

111 et al. 2008; Creton et al. 2008b; Creton et al. 2008a; Parfitt 2009; Bishop et al. 2013; Baker et al.

112 2014).

113   Imogolite exhibits nanotubular morphology (Cradwick et al. 1972; Abidin et al. 2007).

114 Nanotubes are typically 2 nm in exterior diameter and the strands may be tens of nanometers in

115 length. These tubes are thought to consist of a rolled gibbsite-like sheet of octahedrally

116   coordinated Al with isolated silicon tetroxide tetrahedra bonded to the tube interior to yield an

117   overall molar Al:Si ratio of 2:1 (Cradwick et al. 1972). Each orthosilicate unit is bonded to three

118   Al atoms and no silica polymerization is observed. Because of its tubular morphology, imogolite

119   has no long-range structure in the cross-tube direction but does possess long-range structure in

120   the along-tube direction. Computer modeling has confirmed this structure and reproduced the X-

121   ray diffractogram of natural imogolite samples (Guimarães et al. 2007; Creton et al. 2008b). In

122   synthesis experiments, imogolite-like aluminogerminates have been observed to evolve from

123   nanospherical allophane-like structures upon aging for periods of >2 weeks (Levard et al. 2010).

124   Due to the lack of long-range crystallographic order, allophanes have been difficult to

125   characterize by X-ray diffraction (Parfitt 2009), and most of the information known about their

126   chemical structures has been determined by methods such as infrared spectroscopy, X-ray

127   absorption spectroscopy (XAS), and nuclear magnetic resonance (NMR), and by computer

128   modeling.

129   Natural allophanes display a continuous variation in Al:Si ratio. High-Al or proto-

130   imogolite allophane exhibits a molar Al:Si ratio of approximately 2:1. Allophanes with higher Si

131   contents have molar Al:Si ratios as low as 0.9 (Parfitt 2009). The lowest Al:Si ratios are found in

132   "stream-deposit" allophanes that precipitate from silica-saturated stream or spring water (Wells

133   et al. 1977; Childs et al. 1990; Parfitt 1990).

134   Proto-imogolite allophane is thought to have a hollow, nanospherical structure that is

135   similar in cross section to the cross-tube structure of imogolite (Figure 1). In the proposed

136   structure, an exterior gibbsite-like sheet of octahedrally coordinated Al is rolled into a nanoball

137   of diameter 3.5–6 nm. Orthosilicate units are bonded to the nanoball interior as in the structure of

138   imogolite. Computer modeling suggests that four to six pores are present in the nanoball

139   structure (Abidin et al. 2007; Creton et al. 2008a). NMR and Fourier transform infrared

140   spectroscopy analyses suggest that high-Si allophanes formed in soil environments have a similar

141   fundamental structure to high-Al allophanes, and that the additional silica is accommodated in a

142   polymerized form in the nanoball interior (Parfitt 1990). In highly Si-enriched "stream deposit"

143   type allophanes, the framework is proposed to be a nanospherical shell of polymerized Si, with a

144   partial or fragmental octahedral Al (Al_O) shell and with some Al substitution in tetrahedral sites

145   (Al_T) (Childs et al. 1990). The tetrahedral Al substitution in these high Si species follows

146   Lowenstein's rule for zeolites where no Al-O-Al linkages are allowed, resulting in a constant

147   Al_T:Si of 1:3 (Childs et al. 1990). An alternative structure for Si-rich allophane based upon a

148   curved kaolinite structure containing a defective tetrahedral sheet was proposed by MacKenzie et

149   al. (1991). At present, no apparent consensus exists on whether high-Si and high-Al forms of

150   allophane represent fundamentally different types of structures, or whether they represent a

151   single fundamental structural type that is progressively modified to accommodate varying Al:Si

152   ratios.

153   Fe-substituted natural and synthetic allophane and imogolite samples have been described

154   and analyzed using a variety of techniques (Kitagawa 1973; Horikawa and Soezima 1977;

155   McBride et al. 1984; Baker and Strawn 2012). These studies found that Fe in allophane and

156   imogolite was spectrally distinct from Fe in Fe oxides, hisingerite and nontronite. Most Fe was

157   substituted for Al in octahedral coordination (Figure 1), although some Fe in natural allophane

158   and imogolite samples may be present as a separate ferrihydrite phase (Baker et al. 2014).

159   Substitution of Fe into the structures of np-aluminosilicates has been reported to affect their

160   morphology (Joussein et al. 2005), as well as the kinetics and end products of their ripening to

161   more crystalline clay minerals (McBride et al. 1984; Farmer et al. 1991; Farmer 1997). Fe-

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162   substituted allophanes may ripen to an Fe-depleted phase plus ferrihydrite (McBride et al. 1984),

163   or they may recrystallize to Fe-bearing clays such as nontronite (Farmer et al. 1991) or

164   ferruginous beidellite (Farmer 1997). The specific conditions that lead Fe-bearing allophane to

165   ripen into various end products are not well understood.

166   The objectives of the present study were: (1) to investigate Fe speciation and

167   coordination state in synthetic allophane and imogolite samples, and (2) to examine how the

168   allophane and imogolite structures are affected by variations in Al:Si and by isomorphic

169   substitution of Fe for Al. We used spectroscopic data and structural modeling to test existing

170   models of allophane structure, to examine the hypothesis that high-Al and high-Si forms of

171   allophane have the same fundamental structure, and to determine whether the presence of

172   isomorphically substituted Fe affects these structures. A further objective was to characterize the

173   reflectance and emission spectra of these materials in support of remote identification of them on

174   Mars and other planetary bodies.

Methods

Materials Synthesis

177   A suite of synthetic Fe-bearing and Fe-free allophane samples was created using the

178   method described by Baker and Strawn (2012) that was modified from Montarges-Pelletier et al.

179   (2005). A solution of 0.1 M $AlCl_3$ was mixed with a sufficient amount of tetraethyl orthosilicate

180   (TEOS) to obtain the desired Al:Si ratio for each allophane sample synthesized (Table 1). Fe-

181   substituted allophanes were produced by mixing 0.1 M $FeCl_3$ with the $AlCl_3$ solution (replacing

182   some of the $AlCl_3$ with $FeCl_3$ in order to maintain constant total volume of 0.1 M chloride

183   solution and correct allophane-forming stoichiometry), to produce the desired Fe content and

184   (Al+Fe):Si ratio. A solution of 0.1 M NaOH was titrated into this mixture under constant stirring

185   in a N_2 purged bottle. Typical synthesis volumes were 250 mL of $AlCl_3$ + $FeCl_3$ and 750 mL of

186   NaOH plus the volume of TEOS needed to obtain the desired Si content. At the end of the

187   titration, the final solution pH was recorded. The resulting suspension of gel in supernatant was

188   stirred for 24 hours, then heated to 95 °C for five days. The suspension was centrifuged to

189   separate the gel, which was placed in dialysis tubing and dialyzed against flowing DI water to a

190   conductivity less than 5 μS/cm. A sample of the centrifuged supernatant was filtered through a

191   0.45 μm filter, acidified, and refrigerated for analysis. A subsample of each synthesized gel was

192   stored frozen. The remainder of each gel was freeze-dried for analysis.

193   Under oxygen-free martian conditions, allophanes may form in an environment where Fe

194   is present as Fe^{2+}. Samples were therefore also synthesized using Fe^{2+} by replacing the $FeCl_3$ in

195   the synthesis procedure with $FeCl_2$. These syntheses produced gels that were green in color,

196   suggesting that Fe in them may have remained divalent. However, a color change from green to

197   brown during dialysis and freeze drying suggested that Fe^{2+} in the gel samples began to oxidize

198   rapidly upon exposure to air. Therefore, the only samples that appeared to retain unoxidized Fe

199   were those preserved as frozen gels. As a result, analyses requiring dried samples could not be

200   performed on confirmed Fe(II)-bearing allophanes. Of the following sample analysis techniques,

201   only X-ray absorption spectroscopy permitted analysis of a hydrated gel sample that retained

202   some Fe(II). Previous studies using allophanes synthesized using the same techniques showed

203   that the XAFS spectra of the same samples in both hydrated gel form and as freeze-dried

204   powders yielded identical spectra and modeling results (Baker et al. 2014).

205   A suite of synthetic Fe(III)-bearing and Fe-free imogolite samples was synthesized by Z.

206   Abidin using a previously established method (Abidin et al. 2008). Imogolite suspensions

207   produced using this synthesis were shipped to the University of Idaho where they were freeze-

208   dried for analysis.

209   All synthesized samples were analyzed by X-ray diffractometry (XRD) to confirm that

210   they contained no crystalline materials. In all samples, broad, poorly defined peaks were present

211   at 2θ of 12° and 26°.

Inductively Coupled Plasma Atomic Emission Spectroscopy

213   All supernatant solutions from synthesis experiments were analyzed on a ThermoFisher

214   iCAP Duo inductively-coupled plasma atomic emission spectrometer (ICP-AES) to verify

215   synthesized compositions. Samples were analyzed for Fe, Al and Si. Calibration solutions, a

216   blank and a quality control solution were mixed using 0 ppm, 10 ppm and 50 ppm concentrations

217   of proposed analytes with small additions of HNO_3 and HCl to match preservation methods of

218   supernatants. ICP results were used to calculate the true anhydrous formula of the synthesis

219   products by difference from the composition of the original starting solutions.

Diffuse Reflectance Infrared Spectroscopy

221   Fourier transform infrared (FTIR) spectroscopic analyses were carried out on a Perkin-

222   Elmer System 2000 (Thermo Scientific, Waltham, Massachusetts, USA), using a mixture of 3

223   wt.% sample in optical-grade KBr that was placed into a steel sample cup and analyzed in a

224   diffuse reflectance mounting geometry. Samples were scanned 100 times and the spectra were

225   averaged. Spectra were recorded from 4000 to 600 cm^{-1} using 1 cm^{-1} resolution and processed

226   using the Kubelka-Munk algorithm provided in Perkin Elmer Spectrum 2.0 software. Peak fitting

227   for these spectra was performed in Origin Pro 2019a using the Peak Analyzer tool.

Reflectance Spectroscopy of Bulk, Particulate Samples

229   Bidirectional reflectance spectra were measured of bulk (unmixed with KBr or other

230   compounds), particulate samples from 0.3-2.5 μm under ambient conditions at Brown

231   University's RELAB using a bidirectional VNIR spectrometer relative to Halon and a biconical

232   Nicolet FTIR spectrometer in a controlled, dry environment relative to a rough gold surface as in

233   previous studies (Bishop et al. 2013). The bidirectional spectra were acquired from 0.3 to 2.5 μm

234   at 5 nm spectral sampling. FTIR reflectance spectra were measured under dry conditions from 1-

235   50 μm and then scaled to the bidirectional data near 1.2 μm to create composite, absolute

236   reflectance spectra.

Thermal Emission Spectroscopy of Particulate Samples

238   Thermal emissivity spectra of particulates compressed into pellets were measured at the

239   ASU Mars Space Flight Facility using a modified Nicolet Nexus 670 FTIR interferometric

240   spectrometer. Spectra were measured 270 times over ~4 minutes over the range of 2000 to 200

241   cm^{-1} (5-50 μm) with 2 cm^{-1} spectral sampling as in previous studies (Ruff et al. 1997; Rampe et

242   al. 2012). Pellets were measured in copper sample cups painted black so that they behave as a

243   blackbody and heated to 80 °C before and during data collection. Blackbodies at 70 and 100 °C

244   were measured before sample measurements to calibrate raw data to radiance (Christensen and

245   Harrison 1993).

^{27}Al and ^{29}Si Magic Angle Spinning Nuclear Magnetic Resonance

247   Samples of Fe-free synthetic allophanes and imogolites were analyzed using ^{27}Al and ^{29}Si

248   magic angle spinning (MAS) solid-state nuclear magnetic resonance spectroscopy (NMR) on a

249   Bruker AVANCE 500 MHz spectrometer (Bruker Biospin, Rheinstetten, Germany). Samples

250   were spun at 12.6 kHz and were allowed to run until a signal to noise ratio of greater than 500

251   was achieved. Samples containing Fe were not run due to their paramagnetic nature.

252   **X-Ray Absorption Spectroscopy (XAFS)**

253   Bulk Fe K- edge X-ray absorption near edge spectroscopy (XANES) and extended fine

254   structure spectroscopy (EXAFS) analyses of Fe-bearing samples were performed at beamline 7-3

255   of the Stanford Synchrotron Radiation Laboratory (SSRL). Beamline 7-3 is fed by the SPEAR

256   ring operating with a beam current of 500-495 mA. The X-rays are diverted using a 20 pole 2-

257   tesla wiggler source, then through a vertical collimating mirror into the monochromator. The

258   monochromator for this beamline is two parallel Si(220) crystals with a 6-mm entrance slit. This

259   experimental setup results in a spot size of approximately 3 x 15 mm. A Lytle fluorescent ion

260   chamber detector was used to collect fluorescence measurements over the entire Fe K-edge

261   EXAFS energy range of 6880-7873 eV with an energy step size of 0.35eV. All spectra were

262   collected at 10 K using a liquid He cryostat to prevent beam damage and scanned 4-12 times to

263   increase the signal to noise ratio. Allophane and imogolite samples, in the form of either wet gels

264   or dry powders, were packed into aluminum sample holders 0.7-mm thick and held in place with

265   Kapton tape. No differences are observed between wet gel and dry powder packed mounts of the

266   same synthetic sample (Baker et al. 2014). In general, allophane samples were analyzed as gels

267   and imogolite as dried powders, but for lower-Fe allophanes, the higher Fe concentration in the

268   dried samples yielded improved data in the form of a better signal to noise ratio. The multiple

269   scans were calibrated to an Fe foil, and merged and processed using Athena (Ravel and Newville

270   2005).

271   **FEFF Modeling**

272   The merged spectra were normalized and background subtracted using a cubic spline.

273   The fitting strategy used in this study follows the approach described by Baker and Strawn

274   (2012) and Baker et al. (2014) in previous studies of Fe in clay minerals.

275   Shell fitting of the allophane samples was carried out using the 5-shell allophane nanoball

276   model as well as a 5-shell dioctahedral smectite model, following the modelling philosophy of

277   Baker et al. (2014). A detailed description of these models may be found in that work; the most

278   significant difference between the two is in the Si backscattering shell. Atomic coordinates for

279   the smectite model were taken from Tsipursky and Drits (1984) and coordinates for the nanoball

280   model were taken from a section of the model nanoball described by Creton et al. (2008a). Paths

281   were generated from the atomic coordinates using Atoms (Ravel 2001) and shell fitting was

282   carried out using Artemis (Ravel and Newville 2005).

283   In conducting the fitting, all path lengths were optimized at first, and were then

284   constrained to be equal within that fit. Fe-O3 shell distances were fixed for all models except the

285   1:1 Fe(III) smectite model, where allowing it to float resulted in a better fit. Debye-Waller

286   EXAFS factors were optimized for the first Fe-O1 shell and fixed to be equal to the former for

287   the Fe-Fe, Fe-Al, and Fe-Si backscattering paths. Debye-Waller EXAFS factors were also

288   optimized for the Fe-O2 and then fixed to be equal for the Fe-O3 shell. Octahedral sites were

289   fitted with either Fe or Al, with the total number of Fe-Metal backscatterers constrained to sum

290   to three, resulting in a dioctahedral sheet. Trioctahedral fits, where Fe-metal backscatters sum to

291   6, were attempted for the Fe(II) substituted samples, but no recognizable improvement in the fit

292   was observed. The path length was optimized for the Fe-Si backscattering path, with the number

293   of Si atoms fixed at 2 for the smectite model and 3 for the nanoball model.

294

295   **Results**

296   **Synthetic Allophane**

297   The sample compositions span the range of naturally occurring allophanes from high Si

298   (molar Al:Si 1:2) through halloysite-like (Al:Si 1:1) to proto-imogolite (Al:Si 2:1). These three

299   Al:Si compositions were synthesized with Fe^{3+} isomorphically substituted for 0, 2, 5, and 10

300   mol.% Al in the sample. This yielded 12 samples of allophane with varying compositions and

301   physical properties. Previous synthetic work suggested that the amount of Fe that can substitute

302   in synthetic allophane varies with Si content (Baker et al., 2014). In the present study, however,

303   allophanes at all three Al:Si ratios were successfully synthesized with Fe isomorphically

304   substituted for 10% of Al.

305   Results from ICP-AES analyses of residual Si, Al, and Fe contents in supernatant

306   solutions were used to calculate the true Al:Si ratio and true Fe content of the synthetic samples

307   by difference from the initial solutions (Table 1). The results indicate that the intended Al:Si

308   ratios and Fe contents were achieved. Increased Fe content correlated with slight decreases in

309   bulk Al:Si ratio in the solids, indicating that Fe was substituting for Al in the structure as

310   expected. Also shown in Table 1 are pseudo-cationic formulas for each synthetic allophane

311   composition, calculated from the Al, Fe, and Si contents, to allow for easier comparison of

312   compositional differences between samples.

313   Allophane synthesis was also carried out using Fe(II) rather than Fe(III), to examine

314   whether Fe substitution into allophane is likely under reducing conditions. Allophanes containing

315   10% Fe(II) substituted for Al were successfully synthesized at Al:Si ratios of 1:2 and 2:1, but

316   synthesis at Al:Si of 1:1 was not successful. As noted above, Fe in these samples oxidized

317   rapidly upon exposure to air during processing and freeze-drying. As a result, the only analysis

318   presented here of an allophane still containing residual Fe(II) is of a 2:1 Al:Si sample that was

319   stored as a frozen gel, and analyzed as a gel by XAFS spectroscopy. The results of this analysis

320   are given below.

321   **Visible and Infrared Spectroscopy**

322   Infrared spectra of Fe-free synthetic imogolite and allophane samples (Figures 2-6) show

323   absorption bands that are typical for these materials (Bishop et al. 2013) and provide context for

324   spacecraft observations. Kubelka-Munk transformed spectra of sample-KBr mixtures are shown

325   in Figure 2 and provide the strongest absorptions. Mid-IR emissivity spectra of the pressed pellet

326   samples (Figure 3) are noisier than reflectance spectra, but they are directly comparable to

327   spacecraft data, whereas the reflectance spectra of particulate samples (Figures 4-5) and

328   particularly of KBr-sample mixtures (Figure 2) may differ from remotely sensed spectra. The

329   spectral contrast is relatively low because of the small particle size.

330   Broad H_2O stretching vibrations are observed between 3400 and 3600 cm^{-1}. Imogolite

331   and high-Al allophane both display a broad hydroxyl band near 3535 cm^{-1}, which displays

332   slightly more structure for imogolite than for high-Al allophane, but the two spectra are

333   otherwise similar. This band shifts to lower wavenumber with increasing Si content (Figure 2,

334   vertical solid and dashed lines).

335   The Si-O stretching features at ~950-1050 cm^{-1} can be seen in all samples. Imogolite and

336   high-Al allophane show bands near 935 and 950 cm^{-1}, respectively, that are characteristic of the

337   orthosilicate Si-O-Al stretching vibration in high-Al allophane (Thill 2016); imogolite can

338   display a doublet in this region, but this synthetic sample does not. The 950 cm^{-1} band broadens

339   and shifts to shorter wavelengths with increasing Si content; this likely reflects growth of an

340   additional Si-O-Si absorption feature near 1050 cm^{-1} (Parfitt et al. 1980) that results from

341   increasing abundance of polymerized Si in the allophane structure. Deconvolution of the 800-

342   1350 cm^{-1} region of the diffuse reflectance spectrum of the Fe-free 1:2 Al:Si allophane (Figure 2)

343   yielded a good fit to a primary peak positioned at 1055 cm^{-1} with subsidiary peaks at 893 and

344   1176 cm^{-1} (Figure 6). These shifts in Si-O-Al stretching vibrations are also observable in

345   emissivity spectra (Figure 3). Few differences are observable between the 1:2 and 1:1 allophane

346   compositions in emissivity spectra, except that the Si-O-Si stretching feature near 1045 cm^{-1} is

347   absent or poorly developed in the 1:2 samples but clearly discernable in the higher-Si 1:1

348   samples (Figure 3, dashed line at 1045 cm^{-1}). The Christiansen feature (reflectance minimum or

349   emissivity maximum) is observed near 1215 cm^{-1} for allophane and near 1150 cm^{-1} for imogolite

350   and this shifts slightly towards lower wavenumber with increasing Fe in the imogolite sample

351   (Figure 4, vertical dotted and solid lines and arrow).

352   Al-O-Si deformation and Si-O bending features at ~400-600 cm^{-1} can be resolved in the

353   imogolite spectra (Figure 4). OH out-of-plane bending modes occur near 610 cm^{-1} for allophane

354   and at 595 cm^{-1} for imogolite (Bishop et al. 2013); the 595 cm^{-1} feature is observed in both the

355   imogolite and allophane emissivity spectra shown in Figure 3 but no feature is apparent at 610

356   cm^{-1} (dotted lines). The lack of the OH out-of-plane banding mode in allophane may result from

357   the presence of defects in the structure of proto-imogolite-like compounds, as suggested by the

358   weak Al(IV) and Al(V) peaks observed in NMR. The presence of these compounds or defects

359   may disrupt the short-range order of allophane and degrade its resulting emissivity spectra.

360   Features due to Si-O-Al bending vibrations were observed at 545, 420 and 335 cm^{-1} for

361   allophane and at 495, 415, and 335 cm^{-1} for imogolite by Bishop et al. (2013). Similar bands are

362   observed in this study (Figure 4a, dotted vertical lines).

363   The position of the Si-O-Al stretching band shifts slightly toward lower wavenumbers in

364   the imogolite mid-IR reflectance spectra with increasing Fe (Figure 4a, vertical line and arrow).

365   In contrast, the Si-O-Al bending bands near 495 and 415 cm^{-1} appear to shift towards higher

366   wavenumbers with increasing Fe in these spectra (Figure 4a, vertical line and arrow). The Fe-

367   bearing allophane spectrum includes a doublet band for the Si-O-Al stretching vibration centered

368   near 1025 and 950 cm^{-1} (Figure 4b, vertical solid and dotted lines). These shifts, however, are

369   relatively small and are not observed in thermal-IR emissivity spectra.

370   Reflectance bands for Fe-free allophane and imogolite in the mid-IR range (Figure 4)

371   were also comparable to previous measurements on natural and synthetic allophane and

372   imogolite samples (Bishop et al. 2013; Weitz et al. 2014). The addition of Fe in these materials

373   resulted in overall darkening of the samples (Figure 4). Spectra in the VNIR range (Figure 5)

374   show the development of electronic transition bands from Fe near 0.45 and 0.9 μm (dashed

375   lines). Fe-free allophane spectra display a doublet near 1.38 and 1.40 μm from OH_{2v} (OH

376   stretching overtones), a band at 1.92 μm from $H_2O_{v+\delta}$ (bending and stretching H_2O combination

377   band), and a band at 2.19 μm from $OH_{v+\delta}$ (bending and stretching OH combination band),

378   consistent with previous work (Bishop et al., 2013). Fe-free imogolite has similar bands as

379   allophane, but the doublet from OH_{2v} occurs at 1.37 and 1.39 μm, as reported by Bishop et al.

380   (2013). The addition of Fe to the structures of allophane and imogolite did not significantly

381   affect the position and breadth of the OH and H_2O overtone and combination bands near 1.4, 1.9,

382   and 2.2 μm. However, Fe in the structures of allophane and imogolite appears to increase the

383   intensity of the OH stretching overtone at ~1.37-1.38 μm, such that the band at 1.38 μm becomes

384 more intense than the 1.40 µm band in the spectrum of 1:1 allophane with 10% Fe. A similar

385 effect is observed for the spectrum of imogolite with 5% Fe compared to the Fe-free sample.

386 Subtle broadening of these spectral features is observed for the Fe-enriched samples, but this

387 effect is only barely noted in lab spectra and would not be detectable in remote sensing studies.

388 The addition of Fe to the structures of allophane and imogolite did not significantly affect the

389 position and breadth of the OH and H_2O stretching and bending vibrations at ~1.4, 1.9, and 2.2

390 µm. Fe in the structures of allophane and imogolite appears to increase the intensity of the first

391 OH bending overtone at ~1.38 µm, where, in the spectrum of 1:1 allophane, the band at 1.38 µm

392 becomes more intense than the 1.40 µm band with 10% Fe

393 Addition of Fe(III) to the allophane structure resulted in increased amplitude of the

394 diffuse reflectance bands (Figure 2), although this was less evident in the allophane with 1:1

395 Al:Si than in either the high-Al or high-Si compositions. Substitution of Fe(II) into allophane,

396 however, did not alter the diffuse reflectance spectrum in any observable way, although this

397 could be because Fe in the sample was oxidized during freeze-drying. No obvious Fe-Al-OH or

398 Fe-Fe-OH bands were resolvable in the spectra, even for the highest-Fe samples.

^{27}Al MAS NMR

399

400 The relative abundances of four-coordinate (Al_T), five-coordinate (Al_P) and six-

401 coordinate Al (Al_O) in the allophane structure can be quantified by integration of the peak

402 curves. The peaks are located at ~10, ~36, and ~60 ppm for Al_O, Al_P, and Al_T, respectively

403 (Figure 7). One peak, corresponding to Al_O, is predominant in imogolite. Two distinct peaks are

404 observed in the allophane spectra, corresponding to Al_O and Al_T. Virtually all Al in imogolite is

405 six-coordinate, whereas high-Al "proto-imogolite" allophane contains a small proportion of Al_T

406 (~6%) and Al_P (~3%). The total percentage of tetrahedrally coordinated Al in the structure

407   increases linearly with increasing Si content (Table 1) but is higher in proto-imogolite allophane

408   than in imogolite although the two compounds have the same nominal Al:Si ratio.

409   **^{29}Si MAS NMR**

410   Unlike the large shifts seen in the Al NMR spectra, which correlate to Al coordination

411   number, small shifts seen in the peak differentiation in the Si NMR data are strongly correlated

412   to Si polymerization (Figure 8), and therefore indirectly to the number of Si-Al neighbors in the

413   structure. Imogolites exhibit a spectrum with a well resolved peak at ~79 ppm that arises from

414   the presence of orthosilicate. Proto-imogolite allophanes exhibit a peak in the same location that

415   is broader, suggesting minor polymerization of Si in this sample despite its relatively low Si

416   content. As Si is introduced into the structure, a second, poorly resolved, broad peak develops

417   that is centered between -86 and -90 ppm for the 1:1 Al:Si sample and at ~100 ppm for the 1:2

418   Al:Si sample. This peak dominates the spectrum of the 1:2 Al:Si sample, with only a poorly

419   defined remnant peak remaining near 80 ppm, whereas the two peaks have similar magnitude in

420   the 1:1 Al:Si sample. We interpret the peak between -86 and -90 ppm as arising from Q2 chain

421   silicate structures, whereas the peak near -100 ppm is consistent with Q3 sheet silicate structures.

422   These results suggest that the 1:1 Al:Si allophane contains some orthosilicate tetrahedra as well

423   as some polymerized Si chains, and are consistent with a model for this composition of a proto-

424   imogolite-like structure with additional polymerized Si in its interior. The 1:2 Al:Si sample, by

425   contrast, shows little evidence for orthosilicate tetrahedra and its spectrum is consistent with a

426   phyllosilicate-like structure or a rolled tetrahedral sheet.

427   **XANES and EXAFS spectra**

428   The near-edge X-ray absorption spectra are typical of previous analyses of Fe-substituted

429   allophanes (Baker and Strawn 2012; Baker et al. 2014), except for the Al:Si 2:1, 10% Fe(II)-

430   substituted sample. That sample displays a shift to lower energy of approximately 1 eV in the

431   absorption edge (Figure 9a, arrow), indicating that some Fe(II) remained in the sample; this shift

432   is more easily observable in the first derivative of the spectrum (Figure 9b, arrow). The pre-edge

433   peak is also shifted approximately 0.3 eV lower in energy, to 7113.2 eV. The pre-edge and edge

434   positions for this spectrum suggest that, even in this sample, much of the Fe was oxidized to

435   Fe(III) and only some has been retained as Fe(II). The other Fe(II) substituted sample, at Al:Si of

436   1:2, displays no edge shift to lower energy, indicating the Fe in this sample all oxidized to

437   Fe(III).

438   The XANES data support the conclusion that Fe is isomorphically substituting for Al in

439   octahedral coordination, and that tetrahedral substitution of Fe for Si is not significant in the

440   samples studied. The presence of tetrahedral Fe, or of Fe in (oxyhydr)oxide phases, results in

441   enhanced amplitude of the pre-edge XANES peak (Baker and Strawn 2012; Baker et al. 2014),

442   which is not observed in the spectra presented here (Figure 9).

443   EXAFS spectra and Fourier transformed spectra of the synthetic Fe(III) substituted

444   allophanes and imogolite (Figure 10) are similar to previously published spectra (Baker and

445   Strawn 2012; Baker et al. 2014) but with greater development of the features that are

446   characteristic of Fe-Fe next neighboring atoms. These features include the peaks in the χ

447   spectrum near 5 and 7.25 Å^{-1} and the peak centered near 2.8 Å in the Fourier transformed

448   spectrum. The high-Si allophane sample composition showed weaker development of the Fe-Fe

449   next neighbor features than did higher-Al compositions. Although the sample Al:Si ratios are not

450   exactly the same, this observation is in agreement with that of Baker et al. (2014). The spectrum

451   of the high-Si, Fe(II) substituted allophane shows very little development of the characteristic

452   Fe-Fe features. This spectrum is characteristic of Fe in octahedral coordination but with almost

453   all Fe-Al next neighbors rather than Fe-O-Fe bonds. The spectrum of the high-Al, Fe(II)

454   substituted allophane, by contrast, is very similar to that of the Fe(III) substituted allophane, even

455   though this sample is shown by the XANES spectrum to contain some Fe(II).

EXAFS Modeling

457   Model fits, coordination numbers, path lengths, and Debye-Waller factors for Fe^{3+}

458   substituted samples are summarized in Table 2. Modeled Fe-Fe coordination numbers for Fe(III)

459   substituted samples (Table 2) using the nanoball model are highest with high Al content and

460   lowest in the high-Si sample containing Fe(II). Fe-O1 path lengths exhibit very similar values for

461   all samples, ranging from 1.97 to 1.99. Fe-Fe1 path lengths range from 3.00 to 3.06 Å, while Fe-

462   Al path lengths range from 2.99 to 3.04 Å. Fe-Si path lengths cluster between 3.24 and 3.28 Å.

463   Path lengths do not differ significantly between Fe(II) and Fe(III) substituted samples.

464   Fe-Fe coordination numbers for Fe substituted samples calculated using the smectite

465   model are higher in all cases than those calculated using the nanoball model. Overall patterns

466   among path lengths are similar to the nanoball model. Fe-Fe path lengths range from 3.03 to 3.08

467   Å, and Fe-Al path lengths range from 3.01 to 3.06 Å. Fe-Si path lengths cluster between 3.23 and

468   3.28 Å. Path lengths do not differ significantly between Fe(II) and Fe(III) substituted samples.

469   The Fe-Fe coordination number calculated for the Fe(II) substituted high-Si allophane

470   was much lower than CNs calculated for any other sample. This is consistent with the

471   observation above that typical Fe-Fe next neighbor features are poorly developed in the spectrum

472   of this sample.

473   **Discussion**

474   **Chemical substitution patterns among allophanes and imogolites**

475   Comparison of ^{27}Al NMR data with ICP-AES data (Table 1) shows that the Al_T:Si ratio

476   of higher-Si allophanes stays constant at ~1:3, consistent with naturally occurring high Si

477   allophanes (Childs et al. 1990; Ildefonse et al. 1994). This ratio also follows Loewenstein's rule

478   for zeolites, which states that no Al-O-Al linkages are allowed within the tetrahedral sheet due to

479   charge imbalances (Loewenstein 1954). This represents a tetrahedral Si sheet containing

480   substituted Al_T tetrahedra, with no Al_T tetrahedra sharing edges. This is consistent with the

481   results of ^{29}Si NMR (Figure 8) indicating sheet silicate structures were present in the high-Si

482   allophane. Previous work suggested that natural high-Si allophanes from Silica Springs have a

483   structure that is based on a silicate sheet comparable to that in muscovite mica, rolled into a

484   sphere with an external tetrahedral layer, with an incomplete octahedral sheet in the nanosphere

485   interior (Childs et al. 1990). The results presented here suggest that synthetic high-Si allophanes

486   have a similar structure to naturally occurring ones.

487   The Al_T:Si ratio of high-Al allophane is 0.13, half that of the more Si-rich allophanes.

488   This is in accordance with the ^{29}Si NMR spectrum of this material (Figure 8) which shows that it

489   contains relatively little polymerized silica. This sample does contain more polymerized Si than

490   the imogolite samples, however (Figure 8). It also contains a small proportion of Al_V, whereas

491   imogolite contains very little (Figure 7). These observations from NMR indicate that the proto-

492   imogolite allophanes contain more structural defects than the imogolites that they

493   compositionally resemble. This likely results from the deformations necessary to form a

494   nanosphere, as opposed to a nanotube, from a rolled sheet structure.

495   Previous results from Fe K-edge EXAFS spectroscopy of synthetic allophanes (Baker

496   and Strawn 2012; Baker et al. 2014) found that all Fe present in the samples was in octahedral

497   coordination. They interpreted these results as not supporting the model proposed by Childs et al.

498   (1990) for the structure of higher-Si allophanes because that model calls for incomplete

499   octahedral sheets, and no evidence was found for Fe in other than full octahedral coordination.

500   Incomplete octahedral sheets would be lined along the sheet edges with defect sites occupied by

501   cations that were not in full octahedral coordination. In particles containing only a few hundred

502   octahedral cations (e.g. Creton et al. (2008a)), the cations along the edges of incomplete sheets

503   would represent a significant fraction of total octahedral cations, and would likely be detectable.

504   The present study includes similar observations of Fe coordination but suggests that the previous

505   interpretation by Baker and Strawn (2012) and Baker et al. (2014) was not correct. The ^{29}Si

506   NMR and FTIR results indicate that polymerized Si is present in the high-Si allophane samples,

507   supporting the formation of a phyllosilicate-like structure. Bulk chemistry of the samples

508   indicates that there is not sufficient Al (+ Fe) present in the solid to form a complete octahedral

509   sheet in a nanoball structure based on tetrahedral Si. In addition, the ^{27}Al NMR data for the Al:Si

510   1:2 sample shows that nearly half of the Al present in the samples is in tetrahedral coordination,

511   so the ratio of tetrahedral (Si + Al) to octahedral Al in this sample is approximately 4:1.

512   However, Fe K-edge XANES and EXAFS data still indicate that Fe is in octahedral coordination

513   in high-Si allophane samples. Both XANES / EXAFS data and bulk compositional data indicate

514   that Fe is substituting for Al rather than being present in a separate (oxyhydr)oxide phase. This

515   suggests that Fe substituted into the allophane structure may only occupy non-edge sites in the

516   partial octahedral sheets. If Fe can substitute only into limited sections of the allophane structure,

517   this may also explain the previous finding of small Fe clusters in allophanes, even at very low

518   total Fe abundance (Baker and Strawn 2012; Baker et al. 2014). As noted above, Fe-Fe clustering

519   is much less pronounced in the high-Si sample that was synthesized with Fe(II), although the

520   XANES and EXAFS spectra indicate that the Fe in this sample was completely oxidized to

521   Fe(III). However, modeling of the high-Al allophane sample synthesized with Fe(II), which still

522   contained some residual Fe(II) upon XANES and EXAFS analysis, suggests that Fe clustering in

523   this sample is comparable to that in samples synthesized with Fe(III). We hypothesize that this

524   somewhat puzzling difference may have arisen from the different structures of the two

525   endmember allophane types, with Fe clusters being more easily accommodated in the more

526   extensive and fully-formed octahedral sheet of the high-Al allophane.

527   A previous XAFS study (Baker et al. 2014) examined natural and synthetic Fe-bearing

528   imogolites and suggested that Fe in these samples was present at least partly in sorbed form,

529   based on the resemblance of their XANES spectra to those of Fe-sorbed allophane samples.

530   Examination of the XANES spectra of the samples in this study, particularly of the diagnostic

531   pre-edge peaks, (Figure 9), suggests that coordination of Fe in the synthetic imogolite samples is

532   similar to that of Fe in the allophane samples and that all Fe is in octahedral coordination.

533   **Compositional effects on allophane and imogolite spectra**

534   Terrestrial allophanic materials of different composition form in distinctively different

535   environments (Parfitt 2009). Most imogolite and soil allophanes form by weathering of tephra,

536   but allophane-like and imogolite-like materials have also been identified in soils with no obvious

537   volcanic parent material, and variations in soil pH may lead to differences in the Al:Si ratio of

538   allophanes (Yoshinaga and Aomine 1962a; Yoshinaga and Aomine 1962b; Tait et al. 1978;

539   Farmer et al. 1980; Farmer and Fraser 1982; Parfitt and Kimble 1989). Unlike imogolite and

540   proto-imogolite allophanes, naturally occurring high-Si stream-deposit allophanes from New

541   Zealand are deposited by thermal waters that have leached volcanic rocks and associated soils

542   (Wells et al. 1977). If allophanes of different composition can be distinguished by remote

543   sensing, this may aid in interpretation of how allophane deposits formed on Mars.

544   Changes in the mid-IR spectra of allophane due to differences in Si content are distinctive

545   (Figures 2-4). Development of the strong band at 1040 cm^{-1} arises from the polymerization of Si

546   that is also reflected in the NMR spectra of these samples (Figure 8). This band development is

547   apparent in emission spectra of the higher-Si 1:1 and 1:2 allophane samples (Figure 3),

548   suggesting it should be detectable in remotely sensed data. If so, this will be significant in terms

549   of using the presence of allophane to interpret formation conditions on Mars, since detection of

550   high-Si allophanes would suggest formation around thermal features, whereas high-Al

551   allophanes and imogolite would more likely have formed by weathering of tephra.

552   Several features of imogolite and allophane mid-IR reflectance spectra display detectable

553   shifts to higher or lower wavelength with increasing Fe content (Figure 4). The Si-O stretching

554   feature at 1150 cm^{-1} in imogolite is shifted towards longer wavelengths with increasing Fe,

555   although this shift is not observed for the allophanes in our study. Bands at 495 and 415 cm^{-1}

556   shift to shorter wavelengths, and the Si-O-Al stretching vibration becomes a doublet at 950 and

557   1025 cm^{-1} in the high-Fe sample. The shifts observed in mid-IR reflectance spectra were not

558   observed in thermal-IR emissivity spectra, suggesting they may not be detectable in TES data.

559   The Si-O-Al stretching band magnitude for allophanes increased with Fe(III) content in

560   diffuse reflectance spectra (Figure 2). This darkening of the samples was less prominent in the

561   1:1 allophane. A similar darkening was observed in VNIR reflectance spectra (Figure 4).

562   Allophanes containing substituted Fe(II) displayed a similar but less intense increase in

563   absorbance. At shorter wavelengths, increases in Fe content led to subtle broadening of the 1.9

564   μm H_2O combination band and 2.2 μm OH combination band, probably due to the

565   electronegativity of Fe(III) that is broadening the bond strengths.

566   The absence of observable Al-Fe-OH or Fe-Fe-OH bands suggests that detection of Fe in

567   the allophane structure would be limited to higher concentrations than the highest in this study

568   (Al:Fe 9:1). A previous spectroscopic study of Fe in smectites (Neumann et al. 2011) measured

569   Al-Fe-OH bending at 884 cm^{-1} in Wyoming montmorillonite, but only observed Fe-Al-OH and

570   Fe-Fe-OH stretching bands in nontronites. Wyoming montmorillonite contains 2.5 total wt.% Fe

571   with an octahedral Al:Fe ratio of ~7.3 (Schoonheydt et al. 2011) and an ordered distribution of

572   octahedral cations that would maximize the number of Al-Fe cation pairs present in the structure

573   (Vantelon et al. 2003). Previous research has suggested that Fe substituted into allophanes forms

574   small clusters in the octahedral sheet (Baker and Strawn 2012; Baker et al. 2014), which would

575   effectively reduce the number of Fe-Al pairs from the ideal 9:1 suggested by the stoichiometry of

576   the synthetic high-Fe allophane samples, and this may explain why Al-Fe-OH bands were not

577   detected.

578   **Allophane structure**

579   The ^{29}Si NMR data indicate significant differences between high-Al proto-imogolite

580   allophane and high-Si allophane that are consistent with previous observations (Childs et al.

581   1990; Childs et al. 1997; Childs et al. 1999; Parfitt 2009). These data suggest two different

582   allophane structures that arise from variations in Al:Si ratio. Allophanes with high Al contents

583   have an octahedral skeleton with individual orthosilicate tetrahedra attached to its interior. Some

584   additional Si can be accommodated in the high-Al allophane structure through formation of

585   polymerized Si chains. Allophanes with very high Si content are likely structured around a main

586   tetrahedral Si and Al sheet skeleton, with additional Al in octahedral coordination. This could

587   resemble spheroidal halloysite (Joussein et al. 2005), or an aluminous analog of the "ferric

588   kaolinite" structure that has been proposed for hisingerite nanospheres (Eggleton and Tilley

589   1998; Baker and Strawn 2012), although the ^{27}Al NMR peak position is more characteristic of

590   2:1 dioctahedral phyllosilicates (Ildefonse et al. 1994). The high percentage of tetrahedral Al in

591   the Al:Si 1:2 allophane (Table 1), however, indicates that the proportion of tetrahedral to

592   octahedral cations in this sample is approximately 4:1. This very high proportion of cations in

593   tetrahedral coordination indicates that only fragmental octahedral sheets are likely to be present.

594   Deconvolved peaks at 1055 and 1176 cm^{-1} in the infrared spectrum of the high-Si allophane

595   (Figure 6) are similar to peak locations in opal, quartz, and feldspars, suggesting some Si in this

596   sample may be accommodated in an opaline silica-like framework structure.

597   Previous work has suggested that allophanes whose bulk chemistry indicates an

598   intermediate Al:Si ratio consist of a mixture of proto-imogolite allophane with a higher-Si form

599   (Parfitt et al. 1980). However, the highest-Si naturally occurring allophanes are the "stream-

600   deposit" allophanes, which occur in different environments than soil allophanes containing

601   elevated Si. Therefore, it is unclear what composition represents the transition point between the

602   two structures, or whether proto-imogolite and high-Si allophanes should even be considered as

603   the same compound. It has been suggested that naturally occurring material previously identified

604   as high-Al allophane is simply an imogolite precursor, even in samples where imogolite itself

605   has not been identified, possibly due to kinetic limitations (Levard et al. 2012). Further

606   experimental studies of higher-Si allophanes may help elucidate this structural question, and

607   more detailed study of the range of natural allophanes identified as Si-rich, may help determine

608   whether allophane-like materials containing polymerized Si should be treated as a phase distinct

609   from proto-imogolite allophane.

610   Modelling of the Fe substituted allophanes aligns well with the previous results from

611   Baker et al. (2014) in the Fe-O1, Fe-Fe, Fe-Al, and Fe-Si bond path lengths (Table 2). The Fe-O1

612   shell at ~1.99 is consistent with Fe in octahedral coordination. Fe-Fe backscattering distances in

613   the nanoball model show a negative correlation with the addition of Si into the structure, but this

614   correlation is not present in the smectite modeled structure. Differences smaller than 0.02

615   angstrom are typically unresolvable in EXAFS data (Ravel and Newville 2005). In all cases, Fe-

616   Al backscattering paths were slightly shorter than Fe-Fe backscattering paths, likely due to the

617   increased atomic radius of Fe as compared to Al.

618   One of the primary differences in the nanoball and smectite structures at this scale is the

619   Fe-Si backscattering distance. In the nanoball structure, Fe-Si distances should be closer to 3.14.

620   Modeled results show a range of distances from 3.23 to 3.28, much closer to the smectite

621   structure of 3.18 to 3.24 modeled by Baker and Strawn (2014). An allophane model with

622   polyhedral structure that had slightly curved faces rather than a sphere was proposed by Creton

623   et al. (2008). If allophane has such a polyhedral structure, that may explain why the interatomic

624   distances for the Fe-Si backscatterers observed in the present study are comparable to those in

625   flat octahedral sheets rather than to modeled distances in a nanosphere.

626   **Remotely detecting Fe-allophane and Fe-imogolite on Mars**

627   Distinguishing between different X-ray amorphous materials on Mars using remotely

628   sensed IR spectroscopy is difficult because the lack of long-range atomic order results in broader

629   bands than are typical for their crystalline counterparts. Allophane and imogolite have been

630   identified in specific regions on Mars through spectral modeling of TES data (Rampe et al.,

631   2012) and in localized units using both TES models and band positions in CRISM spectra

632   (Bishop and Rampe, 2016). Leached glass and allophane are spectrally similar in the thermal-IR

633   (e.g., Horgan and Bell, 2012), so the identification of regional allophane-bearing deposits on

634   Mars via TES models is not unique. Considering TIR data cannot be used to distinguish between

635   allophane and leached basaltic glass, it is unlikely that the small variations in allophane mid-IR

636   reflectance spectra or imogolite TIR emissivity spectra from the incorporation of Fe into the

637   structure would be observed in TES spectra. The Si/O ratio of X-ray amorphous materials can be

638   distinguished using TES spectra (e.g., Michalski et al., 2005), so imogolite is spectrally distinct

639   from 1:1 and 1:2 allophane, but it may be difficult to distinguish with certainty between

640   amorphous aluminosilicates with similar Si/O ratios (e.g., imogolite and 2:1 allophane).

641   The detection of allophane vs. imogolite is more diagnostic in VNIR reflectance spectra

642   from CRISM because of measurable differences in band positions (Bishop et al., 2013). Bishop

643   and Rampe (2016) identified both allophane and imogolite in Mawrth Vallis based on the small

644   differences in the bands at 1.92-1.93 μm and 2.19-2.20 μm. The incorporation of Fe into

645   allophane and imogolite does not have a significant effect on these bands, so these bands cannot

646   be used to determine whether the allophane and imogolite on Mars contain low levels of Fe.

647   There are variations in the band intensities within the doublet at ~1.4 μm from the incorporation

648   of Fe into the structure of allophane and imogolite, but the band near 1.4 μm is often weak in

649   CRISM spectra due to absorption from other components in the basaltic matrix, so this band also

650   may not demonstrate whether allophane and imogolite on Mars contain Fe. VNIR bands

651   resulting from Fe electronic transitions are present in multiple Fe-bearing minerals (e.g., Morris

652   et al., 1985; Horgan et al., 2014; Bishop et al., 2015), so their presence in CRISM spectra from

653   allophane- or imogolite-bearing terrains may not signify Fe is present in the allophane or

654   imogolite structure, but their absence would indicate that the allophane or imogolite does not

655   have Fe in its structure. A CRISM spectrum from an allophane- and imogolite-bearing unit in

656   Mawrth Vallis presented by Bishop and Rampe (2016; their Figure 1c) does not show a clear

657   band at ~0.9 μm, suggesting that the allophane and imogolite in this unit likely do not contain Fe

658   in their structures.

659   **Implications**

660   The structure of allophane varies with its composition, which in turn is a function of its

661   formation conditions; the structure of imogolite resembles that of high-Al allophanes but is

662   paracrystalline rather than poorly crystalline. Mid- and thermal-infrared spectra of allophanes are

663   useful for distinguishing variations in Si content, and some spectral changes are also observed

664   with varying Fe content in mid-IR reflectance spectra. Infrared spectra of imogolites are distinct

665   from those of allophane, containing more and better-defined spectral bands. Increasing Fe

666   substitution in imogolite produces recognizable broadening and shifts in some of these bands in

667   the VNIR region. Thus, remotely sensed spectra of allophanic materials may contain information

668   regarding the environment of formation and/or deposition of those materials. Although the

669   occurrence of high-Al allophane and imogolite is generally considered to be indicative of early

670   weathering of volcanic tephra, this is not universally true for terrestrial occurrences, and so these

671   materials could potentially also represent weathering of a variety of parent materials under acidic

672   conditions. Distinguishing between these possibilities will be important for characterizing

673   allophane deposits on Mars, where tephra and acidic weathering conditions are both likely to

674   have been important. Identification of high-Si allophane on Mars could potentially be indicative

675   of deposition from thermal waters, and such a finding would be interpreted very differently in

676   terms of the history of martian surface conditions.

677   Fe substitution into the allophane and imogolite structures cause small deviations in the

678   spectra that may not be recognized from orbital data. This emphasizes the importance of

679   returning samples from the martian surface to better characterize the amorphous component and

680   better constrain the environment(s) in which it formed.

681   The existing model of allophane structure is based upon a rolled Al octahedral sheet with

682   attached orthosilicate units, as for imogolite. This structure can accommodate additional Si in its

683   interior by polymerization. However, high-Si allophanes contain far more Si than can be

684   accommodated in the model nanoball interior, spectra of high-Si allophanes indicate that full

685   tetrahedral Si sheets are present, and these materials do not contain enough Al to have full

686   octahedral sheets. Therefore, the materials usually called high-Si allophanes fundamentally differ

687   from high-Al allophanes and may be considered a different material altogether. Future work may

688   elucidate the transition point or range at which the octahedral Al nanoball gives way to the

689   tetrahedral Si nanoball as the fundamental structural unit.

690   **Acknowledgments**

695

696   **References**

697   Abidin, Z., Matsue, N. and Henmi, T. (2007) Differential formation of allophane and imogolite:

698   experimental and molecular orbital study, Journal of Computer-Aided Materials Design

699   14, 1, 5-18.

700   Abidin, Z., Matsue, N. and Henmi, T. (2008) A new method for nano tube imogolite synthesis,

701   Japanese Journal of Applied Physics 47, 6S, 5079.

702   Baker, L.L. and Strawn, D.G. (2012) Fe K-edge XAFS spectra of phyllosilicates of varying

703   crystallinity, Physics and Chemistry of Minerals 39, 8, 675-684.

704   Baker, L.L., Nickerson, R.D. and Strawn, D.G. (2014) XAFS study of Fe-substituted allophane

705   and imogolite, Clays and Clay Minerals 62, 1, 20-34.

706   Bandfield, J.L., Hamilton, V.E. and Christensen, P.R. (2000) A global view of Martian surface

707   compositions from MGS-TES, Science 287, 5458, 1626-1630.

708   Bell, J.F., McCord, T.B. and Owensby, P.D. (1990) Observational evidence of crystalline iron

709   oxides on Mars, Journal of Geophysical Research: Solid Earth 95, B9, 14447-14461.

710   Bishop, J.L. and Rampe, E.B. (2016) Evidence for a changing Martian climate from the

711   mineralogy at Mawrth Vallis, Earth and Planetary Science Letters 448, 42-48.

712   Bishop, J.L., Rampe, E.B., Bish, D.L., Abidin, Z., Baker, L.L., Matsue, N. and Henmi, T. (2013)

713   Spectral and hydration properties of allophane and imogolite, Clays and Clay Minerals

714   61, 1, 57-74.

715   Bishop, J.L., Fairén, A.G., Michalski, J.R., Gago-Duport, L., Baker, L.L., Velbel, M.A., Gross,

716   C. and Rampe, E.B. (2018) Surface clay formation during short-term warmer and wetter

717   conditions on a largely cold ancient Mars, Nature Astronomy 2, 206-213.

718   Bishop, J.L., Dobrea, E.Z.N., McKeown, N.K., Mario Parente, Ehlmann, B.L., Michalski, J.R.,

719   Milliken, R.E., Poulet, F., Swayze, G.A., Mustard, J.F., Murchie, S.L. and Bibring, J.-P.

720   (2008) Phyllosilicate diversity and past aqueous activity revealed at Mawrth Vallis, Mars,

721   Science 321, 830-833.

722   Blake, D.F., Morris, R., Kocurek, G., Morrison, S., Downs, R., Bish, D., Ming, D., Edgett, K.,

723   Rubin, D. and Goetz, W. (2013) Curiosity at Gale crater, Mars: Characterization and

724   analysis of the Rocknest sand shadow, Science 341, 6153, 1239505.

725   Bristow, T.F., Rampe, E.B., Achilles, C.N., Blake, D.F., Chipera, S.J., Craig, P., Crisp, J.A., Des

726   Marais, D.J., Downs, R.T., Gellert, R., Grotzinger, J.P., Gupta, S., Hazen, R.M., Horgan,

727   B., Hogancamp, J.V., Mangold, N., Mahaffy, P.R., McAdam, A.C., Ming, D.W.,

728   Morookian, J.M., Morris, R.V., Morrison, S.M., Treiman, A.H., Vaniman, D.T.,

729   Vasavada, A.R. and Yen, A.S. (2018) Clay mineral diversity and abundance in

730   sedimentary rocks of Gale crater, Mars, Science Advances 4, 6, eaar3330.

731   Childs, C., Inoue, K., Seyama, H., Soma, M., Theng, B. and Yuan, G. (1997) X-ray

732   photoelectron spectroscopic characterization of Silica Springs allophane, Clay Minerals

733   32, 4, 565-572.

734   Childs, C.W., Parfitt, R.L. and Newman, R.H. (1990) Structural studies of Silica Springs

735   allophane, Clay Minerals 25, 3, 329-341.

736   Childs, C.W., Hayashi, S. and Newman, R.H. (1999) Five-coordinate aluminum in allophane,

737   Clays and Clay Minerals 47, 1, 64-69.

738   Christensen, P.R. and Harrison, S.T. (1993) Thermal infrared emission spectroscopy of natural

739   surfaces: Application to desert varnish coatings on rocks, Journal of Geophysical

740   Research: Solid Earth 98, B11, 19819-19834.

741   Christensen, P.R., Bandfield, J.L., Hamilton, V.E., Ruff, S.W., Kieffer, H.H., Titus, T.N., Malin,

742   M.C., Morris, R.V., Lane, M.D. and Clark, R. (2001) Mars Global Surveyor Thermal

743   Emission Spectrometer experiment: investigation description and surface science results,

744   Journal of Geophysical Research: Planets 106, E10, 23823-23871.

745   Cradwick, P.D.G., Farmer, V.C., Russell, J.D., Masson, C.R., Wada, K. and Yoshinaga, N.

746   (1972) Imogolite, a hydrated aluminum silicate of tubular structure, Nature Physical

747   Science 240, 187-189.

748   Creton, B., Bougeard, D., Smirnov, K.S., Guilment, J. and Poncelet, O.G. (2008a) Structural

749   model and computer modeling study of allophane, Journal of Physical Chemistry C 112,

750   2, 358-364.

751   Creton, B., Bougeard, D., Smirnov, K.S., Guilment, J. and Poncelet, O. (2008b) Molecular

752   dynamics study of hydrated imogolite. 1. Vibrational dynamics of the nanotube, The

753   Journal of Physical Chemistry C 112, 27, 10013-10020.

754   Eggleton, R.A. and Tilley, D.B. (1998) Hisingerite; a ferric kaolin mineral with curved

755   morphology, Clays and Clay Minerals 46, 4, 400-413.

756   Ehlmann, B.L., Mustard, J.F., Swayze, G.A., Clark, R.N., Bishop, J.L., Poulet, F., Des Marais,

757   D.J., Roach, L.H., Milliken, R.E., Wray, J.J., Barnouin-Jha, O. and Murchie, S.L. (2009)

758   Identification of hydrated silicate minerals on Mars using MRO-CRISM: Geologic

759   context near Nili Fossae and implications for aqueous alteration, J. Geophys. Res. 114,

760   E00D08.

761   Farmer, V. (1997) Conversion of ferruginous allophanes to ferruginous beidellites at 95° under

762   alkaline conditions with alternating oxidation and reduction, Clays and Clay Minerals 45,

763   4, 591-597.

764   Farmer, V., Krishnamurti, G. and Huang, P. (1991) Synthetic allophane and layer-silicate

765   formation in SiO 2-Al 2 O 3-FeO-Fe 2 O 3-MgO-H 2 O systems at 23 C and 89 C in a

766   calcareous environment, Clays and Clay Minerals 39, 561-570.

767   Farmer, V.C. and Fraser, A.R. (1982) Chemical and colloidal stability of sols in the Al2O3-

768   Fe2O3-SiO2-H2O system: their role in podzolization, Journal of Soil Science 33, 4, 737-

769   742.

770   Farmer, V.C., Russell, J.D. and Berrow, M.L. (1980) Imogolite and proto-imogolite allophane in

771   spodic horizons: Evidence for a mobile aluminium silicate in podzol formation Journal of

772   Soil Science 31, 4, 673-684.

773   Guimarães, L., Enyashin, A.N., Frenzel, J., Heine, T., Duarte, H.A. and Seifert, G. (2007)

774   Imogolite nanotubes: stability, electronic, and mechanical properties, ACS Nano 1, 4,

775   362-368.

776   Henmi, T. and Wada, K. (1976) Morphology and composition of allophane, American

777   Mineralogist 61, 5-6, 379-390.

778   Horgan, B. and Bell, J.F. (2012) Widespread weathered glass on the surface of Mars, Geology

779   40, 5, 391-394.

780   Horikawa, Y. and Soezima, H. (1977) State analysis of iron in allophanic clays II: Iron L-

781   emission band spectra from allophanic clays and hisingerite by the use of an X-ray

782   microanalyzer, Clay Science 5, 2, 97-102.

783   Ildefonse, P., Kirkpatrick, R.J., Montez, B., Calas, G., Flank, A.M. and Lagarde, P. (1994) 27 Al

784   MAS NMR and aluminum X-ray absorption near edge structure study of imogolite and

785   allophanes, Clays and Clay Minerals 42, 3, 276-287.

786 Joussein, E., Petit, S., Churchman, J., Theng, B., Righi, D. and Delvaux, B. (2005) Halloysite

787   clay minerals -- a review, Clay Minerals 40, 4, 383-426.

788 Kitagawa, Y. (1973) Substitution of aluminum by iron in allophane, Clay Science 4, 4, 151-154.

789 Klingelhöfer, G., Morris, R.V., Bernhardt, B., Schröder, C., Rodionov, D.S., de Souza, P.A.,

790   Yen, A., Gellert, R., Evlanov, E.N., Zubkov, B., Foh, J., Bonnes, U., Kankeleit, E.,

791   Gütlich, P., Ming, D.W., Renz, F., Wdowiak, T., Squyres, S.W. and Arvidson, R.E.

792   (2004) Jarosite and Hematite at Meridiani Planum from Opportunity's Mössbauer

793   Spectrometer, Science 306, 5702, 1740.

794 Levard, C., Doelsch, E., Basile-Doelsch, I., Abidin, Z., Miche, H., Masion, A., Rose, J.,

795   Borschneck, D. and Bottero, J.Y. (2012) Structure and distribution of allophanes,

796   imogolite and proto-imogolite in volcanic soils, Geoderma 183–184, 100-108.

797 Levard, C., Rose, J., Thill, A., Masion, A., Doelsch, E., Maillet, P., Spalla, O., Olivi, L.,

798   Cognigni, A., Ziarelli, F. and Bottero, J.Y. (2010) Formation and growth mechanisms of

799   imogolite-like aluminogermanate nanotubes, Chemistry of Materials 22, 8, 2466-2473.

800 Loewenstein, W. (1954) The distribution of aluminum in the tetrahedra of silicates and

801   aluminates, American Mineralogist: Journal of Earth and Planetary Materials 39, 1-2, 92-

802   96.

803 MacKenzie, K.J.D., Bowden, M.E. and Meinhold, R.H. (1991) The structure and thermal

804   transformations of allophanes studied by 29 Si and 27 Al high resolution solid-state

805   NMR, Clays and Clay Minerals 39, 4, 337-346.

806 McBride, M.B., Farmer, V.C., Russell, J.D., Tait, J.M. and Goodman, B.A. (1984) Iron

807   substitution in aluminosilicate sols synthesized at low pH, Clay Minerals 19, 1, 1-8.

808 Michalski, J.R., Kraft, M.D., Sharp, T.G. and Christensen, P.R. (2006) Effects of chemical

809   weathering on infrared spectra of Columbia River Basalt and spectral interpretations of

810   martian alteration, Earth and Planetary Science Letters 248, 3, 822-829.

811 Michalski, J.R., Kraft, M.D., Sharp, T.G., Williams, L.B. and Christensen, P.R. (2005)

812   Mineralogical constraints on the high-silica martian surface component observed by TES,

813   Icarus 174, 1, 161-177.

814 Milliken, R.E., Swayze, G.A., Arvidson, R.E., Bishop, J.L., Clark, R.N., Ehlmann, B.L., Green,

815   R.O., Grotzinger, J.P., Morris, R.V., Murchie, S.L., Mustard, J.F. and Weitz, C. (2008)

816   Opaline silica in young deposits on Mars, Geology 36, 11, 847-850.

817 Ming, D.W., Archer, P.D., Glavin, D.P., Eigenbrode, J.L., Franz, H.B., Sutter, B., Brunner, A.E.,

818   Stern, J.C., Freissinet, C., McAdam, A.C., Mahaffy, P.R., Cabane, M., Coll, P.,

819   Campbell, J.L., Atreya, S.K., Niles, P.B., Bell, J.F., Bish, D.L., Brinckerhoff, W.B.,

820   Buch, A., Conrad, P.G., Des Marais, D.J., Ehlmann, B.L., Fairén, A.G., Farley, K.,

821   Flesch, G.J., Francois, P., Gellert, R., Grant, J.A., Grotzinger, J.P., Gupta, S., Herkenhoff,

822   K.E., Hurowitz, J.A., Leshin, L.A., Lewis, K.W., McLennan, S.M., Miller, K.E.,

823   Moersch, J., Morris, R.V., Navarro-González, R., Pavlov, A.A., Perrett, G.M., Pradler, I.,

824   Squyres, S.W., Summons, R.E., Steele, A., Stolper, E.M., Sumner, D.Y., Szopa, C.,

825   Teinturier, S., Trainer, M.G., Treiman, A.H., Vaniman, D.T., Vasavada, A.R., Webster,

826   C.R., Wray, J.J. and Yingst, R.A. (2014) Volatile and Organic Compositions of

827   Sedimentary Rocks in Yellowknife Bay, Gale Crater, Mars, Science 343, 6169, 1245267.

828 Montarges-Pelletier, E., Bogenez, S., Pelletier, M., Razafitianamaharavo, A., Ghanbaja, J.,

829   Lartiges, B. and Michot, L. (2005) Synthetic allophane-like particles: textural properties,

830   Colloids and Surfaces A: Physicochemical and Engineering Aspects 255, 1-3, 1-10.

831   Morris, R.V. and Lauer, H.V. (1990) Matrix effects for reflectivity spectra of dispersed

832   nanophase (superparamagnetic) hematite with application to Martian spectral data,

833   Journal of Geophysical Research: Solid Earth 95, B4, 5101-5109.

834   Morris, R.V., Klingelhöfer, G., Bernhardt, B., Schröder, C., Rodionov, D.S., de Souza, P.A.,

835   Yen, A., Gellert, R., Evlanov, E.N., Foh, J., Kankeleit, E., Gütlich, P., Ming, D.W., Renz,

836   F., Wdowiak, T., Squyres, S.W. and Arvidson, R.E. (2004) Mineralogy at Gusev Crater

837   from the Mössbauer Spectrometer on the Spirit Rover, Science 305, 5685, 833.

838   Morris, R.V., Klingelhöfer, G., Schröder, C., Rodionov, D.S., Yen, A., Ming, D.W., de Souza

839   Jr., P.A., Fleischer, I., Wdowiak, T., Gellert, R., Bernhardt, B., Evlanov, E.N., Zubkov,

840   B., Foh, J., Bonnes, U., Kankeleit, E., Gütlich, P., Renz, F., Squyres, S.W. and Arvidson,

841   R.E. (2006a) Mössbauer mineralogy of rock, soil, and dust at Gusev crater, Mars: Spirit's

842   journey through weakly altered olivine basalt on the plains and pervasively altered basalt

843   in the Columbia Hills, Journal of Geophysical Research: Planets 111, E2.

844   Morris, R.V., Klingelhöfer, G., Schröder, C., Rodionov, D.S., Yen, A., Ming, D.W., de Souza,

845   P.A., Wdowiak, T., Fleischer, I., Gellert, R., Bernhardt, B., Bonnes, U., Cohen, B.A.,

846   Evlanov, E.N., Foh, J., Gütlich, P., Kankeleit, E., McCoy, T., Mittlefehldt, D.W., Renz,

847   F., Schmidt, M.E., Zubkov, B., Squyres, S.W. and Arvidson, R.E. (2006b) Mössbauer

848   mineralogy of rock, soil, and dust at Meridiani Planum, Mars: Opportunity's journey

849   across sulfate-rich outcrop, basaltic sand and dust, and hematite lag deposits, Journal of

850   Geophysical Research: Planets 111, E12, n/a-n/a.

851   Morrison, S.M., Downs, R.T., Blake, D.F., Vaniman, D.T., Ming, D.W., Hazen, R.M., Treiman,

852   A.H., Achilles, C.N., Yen, A.S., Morris, R.V., Rampe, E.B., Bristow, T.F., Chipera, S.J.,

853   Sarrazin, P.C., Gellert, R., Fendrich, K.V., Morookian, J.M., Farmer, J.D., Des Marais,

854   D.J. and Craig, P.I. (2018) Crystal chemistry of martian minerals from Bradbury Landing

855   through Naukluft Plateau, Gale crater, Mars, American Mineralogist 103, 6, 857-871.

856   Murchie, S.L., Mustard, J.F., Ehlmann, B.L., Milliken, R.E., Bishop, J.L., McKeown, N.K., Noe

857   Dobrea, E.Z., Seelos, F.P., Buczkowski, D.L., Wiseman, S.M., Arvidson, R.E., Wray,

858   J.J., Swayze, G., Clark, R.N., Des Marais, D.J., McEwen, A.S. and Bibring, J.-P. (2009)

859   A synthesis of Martian aqueous mineralogy after 1 Mars year of observations from the

860   Mars Reconnaissance Orbiter, Journal of Geophysical Research-Planets 114, E00D06.

861   Neumann, A., Petit, S. and Hofstetter, T.B. (2011) Evaluation of redox-active iron sites in

862   smectites using middle and near infrared spectroscopy, Geochimica et Cosmochimica

863   Acta 75, 9, 2336-2355.

864   Parfitt, R. (1990) Allophane in New Zealand-a review, Soil Research 28, 3, 343-360.

865   Parfitt, R.L. (2009) Allophane and imogolite: role in soil biogeochemical processes, Clay

866   Minerals 44, 1, 135-155.

867   Parfitt, R.L. and Kimble, J.M. (1989) Conditions for Formation of Allophane in Soils, Soil

868   Science Society of America Journal 53, 3, 971-977.

869   Parfitt, R.L., Furkert, R.J. and Henmi, T. (1980) Identification and structure of two types of

870   allophane from volcanic ash soils and tephra, Clays and Clay Minerals 28, 5, 328-334.

871   Rajan, S.S.S. (1979) Adsorption and Desorption of Sulfate and Charge Relationships in

872   Allophanic Clays1, Soil Science Society of America Journal 43, 1, 65-69.

873   Rampe, E., Kraft, M., Sharp, T., Golden, D., Ming, D. and Christensen, P. (2012) Allophane

874   detection on Mars with Thermal Emission Spectrometer data and implications for

875   regional-scale chemical weathering processes, Geology 40, 11, 995-998.

876   Rampe, E.B., Morris, R., V., Archer, P.D., Agresti, D.G. and Ming, D.W. (2016) Recognizing

877   sulfate and phosphate complexes chemisorbed onto nanophase weathering products on

878   Mars using in-situ and remote observations. American Mineralogist. 101: 678 p.

879   Ravel, B. (2001) ATOMS: crystallography for the X-ray absorption spectroscopist, Journal of

880   Synchrotron Radiation 8, 314-316.

881   Ravel, B. and Newville, M. (2005) ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-

882   ray absorption spectroscopy using IFEFFIT, Journal of Synchrotron Radiation 12, 4, 537-

883   541.

884   Rice, M.S., Bell, J.F., Cloutis, E.A., Wang, A., Ruff, S.W., Craig, M.A., Bailey, D.T., Johnson,

885   J.R., de Souza, P.A. and Farrand, W.H. (2010) Silica-rich deposits and hydrated minerals

886   at Gusev Crater, Mars: Vis-NIR spectral characterization and regional mapping, Icarus

887   205, 2, 375-395.

888   Rogers, A.D. and Christensen, P.R. (2007) Surface mineralogy of Martian low-albedo regions

889   from MGS-TES data: Implications for upper crustal evolution and surface alteration,

890   Journal of Geophysical Research: Planets 112, E1.

891   Ruff, S.W. and Christensen, P. (2007) Basaltic andesite, altered basalt, and a TES-based search

892   for smectite clay minerals on Mars, Geophysical research letters 34, 10.

893   Ruff, S.W., Christensen, P.R., Barbera, P.W. and Anderson, D.L. (1997) Quantitative thermal

894   emission spectroscopy of minerals: A laboratory technique for measurement and

895   calibration, Journal of Geophysical Research: Solid Earth 102, B7, 14899-14913.

896   Ruff, S.W., Farmer, J.D., Calvin, W.M., Herkenhoff, K.E., Johnson, J.R., Morris, R.V., Rice,

897   M.S., Arvidson, R.E., Bell III, J.F., Christensen, P.R. and Squyres, S.W. (2011)

898   Characteristics, distribution, origin, and significance of opaline silica observed by the

899   Spirit rover in Gusev crater, Mars, Journal of Geophysical Research: Planets 116, E7.

900 Schoonheydt, R.A., Johnston, C.T., Brigatti, M.F. and Mottana, A. (2011) The surface properties

901   of clay minerals, In Layered Mineral Structures and their Application in Advanced

902   TechnologiesEd., pp. 0, Mineralogical Society of Great Britain and Ireland.

903 Singer, R.B. (1982) Spectral evidence for the mineralogy of high-albedo soils and dust on Mars,

904   Journal of Geophysical Research: Solid Earth 87, B12, 10159-10168.

905 Skok, J.R., Mustard, J.F., Ehlmann, B.L., Milliken, R.E. and Murchie, S.L. (2010) Silica deposits

906   in the Nili Patera caldera on the Syrtis Major volcanic complex on Mars, Nature

907   Geoscience 3, 838.

908 Squyres, S.W., Arvidson, R.E., Ruff, S., Gellert, R., Morris, R.V., Ming, D.W., Crumpler, L.,

909   Farmer, J.D., Marais, D.J.D., Yen, A., McLennan, S.M., Calvin, W., Bell, J.F., Clark,

910   B.C., Wang, A., McCoy, T.J., Schmidt, M.E. and de Souza, P.A. (2008) Detection of

911   Silica-Rich Deposits on Mars, Science 320, 5879, 1063.

912 Tait, J., Yoshinaga, N. and Mitchell, B. (1978) The occurrence of imogolite in some Scottish

913   soils, Soil Science and Plant Nutrition 24, 1, 145-151.

914 Thill, A. (2016) Characterisation of imogolite by microscopic and spectroscopic methods, In

915   Developments in Clay Science. Yuan, P., Thill, A. and Bergaya, F., Ed., pp. 223-253,

916   Elsevier.

917 Tsipursky, S.I. and Drits, V.A. (1984) The distribution of octahedral cations in the 2:1 layers of

918   dioctahedral smectites studied by oblique-texture electron diffraction, Clay Minerals 19,

919   2, 177-193.

920   Vaniman, D.T., Bish, D.L., Ming, D.W., Bristow, T.F., Morris, R.V., Blake, D.F., Chipera, S.J.,

921   Morrison, S.M., Treiman, A.H., Rampe, E.B., Rice, M., Achilles, C.N., Grotzinger, J.P.,

922   McLennan, S.M., Williams, J., Bell, J.F., Newsom, H.E., Downs, R.T., Maurice, S.,

923   Sarrazin, P., Yen, A.S., Morookian, J.M., Farmer, J.D., Stack, K., Milliken, R.E.,

924   Ehlmann, B.L., Sumner, D.Y., Berger, G., Crisp, J.A., Hurowitz, J.A., Anderson, R., Des

925   Marais, D.J., Stolper, E.M., Edgett, K.S., Gupta, S. and Spanovich, N. (2014) Mineralogy

926   of a Mudstone at Yellowknife Bay, Gale Crater, Mars, Science 343, 6169, 1243480.

927   Vantelon, D., Montarges-Pelletier, E., Michot, L.J., Pelletier, M., Thomas, F. and Briois, V.

928   (2003) Iron distribution in the octahedral sheet of dioctahedral smectites. An Fe K-edge

929   X-ray absorption spectroscopy study, Physics and Chemistry of Minerals 30, 1, 44-53.

930   Weitz, C.M., Bishop, J.L., Baker, L.L. and Berman, D.C. (2014) Fresh exposures of hydrous Fe-

931   bearing amorphous silicates on Mars, Geophysical Research Letters 41, 24, 8744-8751.

932   Wells, N., Childs, C. and Downes, C. (1977) Silica Springs, Tongariro National Park, New

933   Zealand—analyses of the spring water and characterisation of the alumino-silicate

934   deposit, Geochimica et cosmochimica acta 41, 10, 1497-1506.

935   Wyatt, M.B. and McSween Jr, H.Y. (2002) Spectral evidence for weathered basalt as an

936   alternative to andesite in the northern lowlands of Mars, Nature 417, 263.

937   Yoshinaga, N. and Aomine, S. (1962a) Imogolite in some Ando soils, Soil Science and Plant

938   Nutrition 8, 3, 22-29.

939   Yoshinaga, N. and Aomine, S. (1962b) Allophane in Some Ando Soils, Soil Science and Plant

940   Nutrition 8, 2, 6-13.

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944 **Figure Captions**

945 Figure 1: Schematic cross-section of a high-Al allophane nanoball with Fe present in octahedral

946 substitution for an Al atom.

947 Figure 2: Kubelka-Munk transformed diffuse reflectance mid-IR spectra for synthetic allophanes

948 and imogolite of varying Fe content mixed with KBr. Vertical solid and dashed lines at 950,

949 1050, 3400, and 3500 cm^{-1} indicate the respective locations of characteristic OH-stretching and

950 Si-O-Al bending features in imogolite and high-Si allophane as discussed in the text.

951 Figure 3: Thermal-IR emissivity spectra for Fe-free and Fe-bearing synthetic allophanes and

952 imogolite. Solid and dashed lines at 1045, 950, 935, 590, 556, 538, 495, and 484 cm^{-1} indicate

953 the locations of characteristic spectral features discussed in the text.

954 Figure 4: a. Mid-IR reflectance spectra for selected synthetic allophanes and imogolite. Solid and

955 dashed vertical lines indicate the locations of characteristic spectral features, and arrows indicate

956 the direction of band shifts with increasing Fe content, as discussed in the text. b. Expanded

957 section of Figure 4a from the gray box.

958 Figure 5: a. VNIR reflectance spectra of selected synthetic allophanes and imogolites with

959 varying Fe abundances. Dashed lines indicate electronic transition bands that develop as Fe

960 content increases; dotted and solid lines indicate band centers that shift as Fe content changes. b.

961 Expanded section of Figure 5a from the grey box. Spectra are offset for clarity.

962 Figure 6: Peak fitting of Fe-free, high Si allophane sample showing deconvolved peaks at 893,

963 1055, and 1175 cm^{-1}.

964   Figure 7. ^{27}Al Magic angle spinning nuclear magnetic resonance spectra for Fe-free allophanes

965   and imogolite. Spectra have been vertically offset for clarity.

966   Figure 8. ^{29}Si Magic angle spinning nuclear magnetic resonance spectra for Fe-free allophanes

967   and imogolite. Spectra have been vertically offset for clarity.

968   Figure 9: a. XANES spectra and b. first derivative spectra of Fe-bearing allophanes and

969   imogolite. Spectra have been vertically offset for clarity. Arrows indicate location of feature

970   discussed in the text.

971   Figure 10: a. EXAFS chi spectra and b. Fourier transformed spectra of Fe-bearing allophanes and

972   imogolite. Spectra have been vertically offset for clarity. Dashed curves show fits to Fe-bearing

973   allophane spectra using the montmorillonite 5-shell model.

974   Table 1. Synthesized allophane nominal and measured compositions. A pseudo-cationic formula is given for each sample assuming
975   sufficient O to coordinate the Al, Fe, and Si present. The presence of hydroxyl is indicated but total water in the samples was not
976   determined.

977

Sample	Nominal compositions (mol ratios)			Actual compositions (mol ratios)			Al coordination (%)			Formula
	(Al+Fe):Si	Fe(III):Al	Fe(II):Al	Al:Si	Fe:Al	(Al+Fe):Si	Al_T	Al_P	Al_O	
100516-2:1	2	0	0	2.02	0	2.02	6.2	3.1	90.5	$Al_2O_3 \, SiO_2 \, (OH)_n$
121916-2:1	2	0.02	0	1.97	0.0204	2.01	-	-	-	$Al_{1.97}Fe_{0.04}O_3 \, SiO_2 \, (OH)_n$
011917-2:1	2	0.05	0	1.91	0.0526	2.02	-	-	-	$Al_{1.91}Fe_{0.1}O_3 \, SiO_2 \, (OH)_n$
013117-2:1	2	0.1	0	1.82	0.111	2.02	-	-	-	$Al_{1.82}Fe_{0.22}O_3 \, SiO_2 \, (OH)_n$
030917-2:1	2	0	0.1	1.81	0.111	2.02	-	-	-	$Al_{1.81}Fe_{0.22}O_3 \, SiO_2 \, (OH)_n$
101716-1:1	1	0	0	1.02	0	1.02	27.9	3.6	68.5	$Al_2O_3 \, (SiO_2)_2 \, (OH)_n$
103116-1:1	1	0.02	0	1.02	0.0203	1.05	-	-	-	$Al_{2.04}Fe_{0.04}O_3 \, (SiO_2)_2 \, (OH)_n$
110716-1:1	1	0.05	0	1.01	0.0524	1.06	-	-	-	$Al_{2.02}Fe_{0.1}O_3 \, (SiO_2)_2 \, (OH)_n$
111416-1:1	1	0.1	0	0.95	0.111	1.05	-	-	-	$Al_{1.9}Fe_{0.22}O_3 \, (SiO_2)_2 \, (OH)_n$
102416-1:2	0.5	0	0	0.50	0	0.50	42.3	n.d.	57.7	$Al_2O_3 \, (SiO_2)_4 \, (OH)_n$
121116-1:2	0.5	0.02	0	0.52	0.0204	0.53	-	-	-	$Al_{2.08}Fe_{0.04}O_3 \, (SiO_2)_4 \, (OH)_n$
112816-1:2	0.5	0.05	0	0.50	0.0526	0.53	-	-	-	$Al_{2.0}Fe_{0.21}O_3 \, (SiO_2)_4 \, (OH)_n$
120416-1:2	0.5	0.1	0	0.48	0.111	0.53	-	-	-	$Al_{1.92}Fe_{0.44}O_3 \, (SiO_2)_4 \, (OH)_n$
040117-1:2	0.5	0	0.1	-	-	-	-	-	-	-

978   - not analyzed

979   n.d. not detected

980

981

982

983   Table 2. Fitting results for allophane samples. CN: coordination number. R: interatomic distance (Å). σ^2: Debye-Waller factor (Å^2).

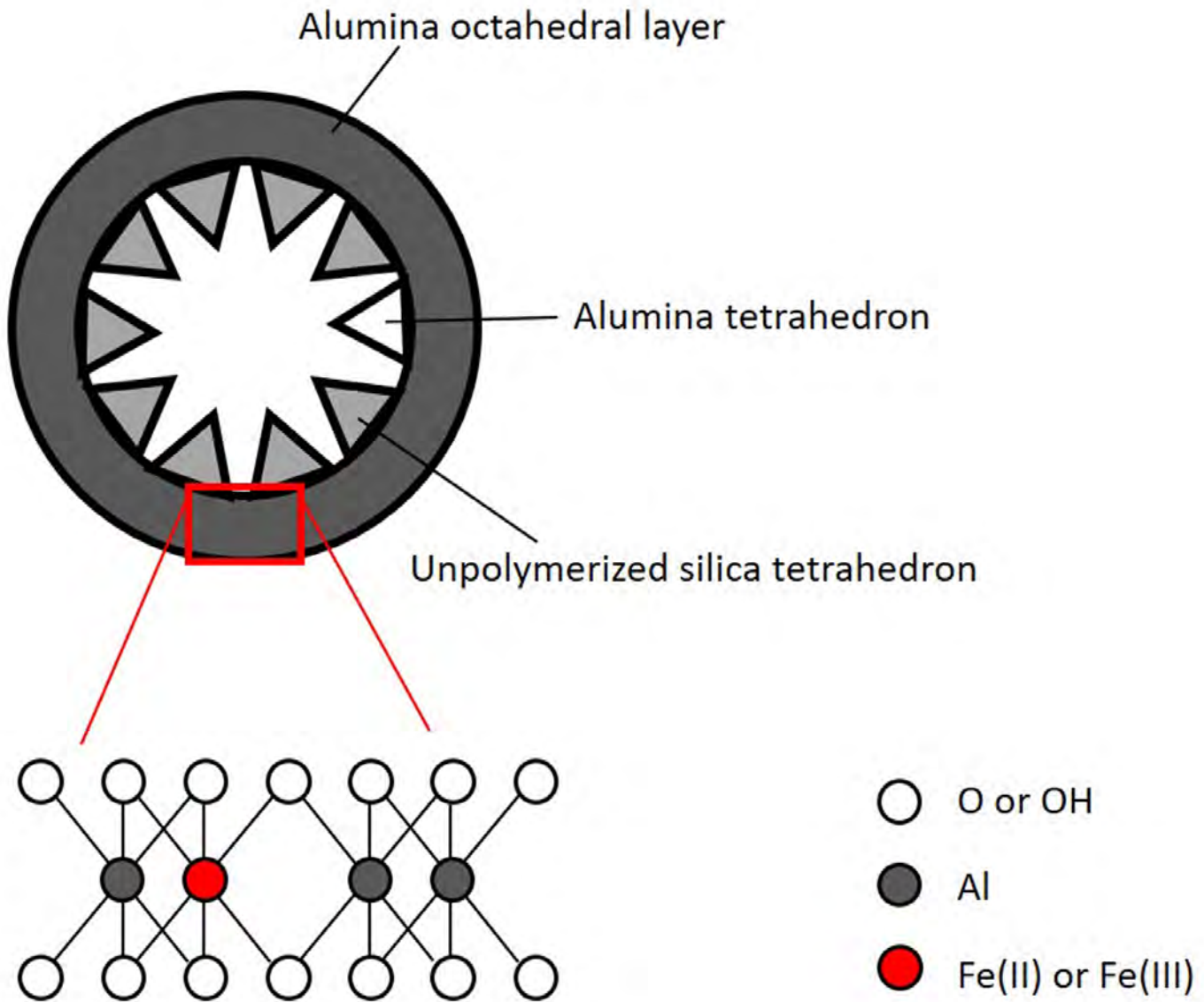|	Nanoball Model															
	120416-1:2 Al:Si 1:2 10% Fe(III)			111416-1:1 Al:Si 1:1 10% Fe(III)			013117-2:1 Al:Si 2:1 10% Fe(III)			040117-1:2 Al:Si 1:2 10% Fe(II)*			030917-2:1 Al:Si 2:1 10% Fe(II)**		
	E0		-3.043	E0		-3.787	E0		-4.111	E0		-1.554	E0		-4.776
Path	R factor		0.004	R factor		0.011	R factor		0.007	R factor		0.011	R factor		0.011
	CN	R	σ^2	CN	R	σ^2	CN	R	σ^2	CN	R	σ^2	CN	R	σ^2
Fe-O1	6	1.99	0.006	6	1.99	0.006	6	1.97	0.008	6	1.99	0.009	6	1.99	0.007
Fe-Fe	1.96	3.06	0.006	1.63	3.03	0.006	1.67	3.00	0.008	1.50	3.06	0.009	0.58	3.01	0.007
Fe-Al	1.04	3.04	0.006	1.37	3.01	0.006	1.33	2.99	0.008	1.50	3.01	0.009	2.42	3.02	0.007
Fe-Si	3	3.28	0.006	3	3.28	0.006	3	3.24	0.008	3	3.26	0.009	3	3.27	0.007
Fe-O2	6	3.79	0.030	6	3.76	0.023	6	3.75	0.022	6	3.68	0.040	6	3.72	0.019
Fe-O3	3	3.98	0.030	3	3.98	0.023	3	3.98	0.022	3	3.98	0.040	3	3.98	0.019
	Smectite Model															
	120416-1:2 Al:Si 1:2 10% Fe(III)			111416-1:1 Al:Si 1:1 10% Fe(III)			013117-2:1 Al:Si 2:1 10% Fe(III)			040117-1:2 Al:Si 1:2 10% Fe(II)*			030917-2:1 Al:Si 2:1 10% Fe(II)**		
	E0		-2.325	E0		-2.498	E0		-3.255	E0		0.364	E0		-3.968
Path	R factor		0.005	R factor		0.006	R factor		0.008	R factor		0.012	R factor		0.011
	CN	R	σ^2	CN	R	σ^2	CN	R	σ^2	CN	R	σ^2	CN	R	σ^2
Fe-O1	6	1.99	0.006	6	1.99	0.006	6	1.97	0.008	6	2.00	0.010	6	1.99	0.007
Fe-Fe	2.01	3.05	0.006	2.22	3.06	0.006	2.10	3.03	0.008	2.22	3.08	0.010	0.95	3.03	0.007
Fe-Al	0.99	3.01	0.006	0.78	3.06	0.006	0.90	3.04	0.008	0.78	3.02	0.010	2.05	3.02	0.007
Fe-Si	2	3.28	0.006	2	3.26	0.006	2	3.23	0.008	2	3.23	0.010	2	3.28	0.007
Fe-O2	1	3.51	0.052	1	3.50	0.018	1	3.34	0.029	1	3.38	0.028	1	3.39	0.029
Fe-O3	6	3.70	0.052	6	3.79	0.018	6	3.70	0.029	6	3.70	0.028	6	3.70	0.029

984   *Although this sample was synthesized using Fe(II), XAFS results indicated that most or all Fe in it was oxidized to Fe(III) prior to analysis, as
985   discussed in the text.

986   ** This sample was synthesized using Fe(II); XAFS results indicated that some Fe in it was oxidized to Fe(III) prior to analysis, as discussed in
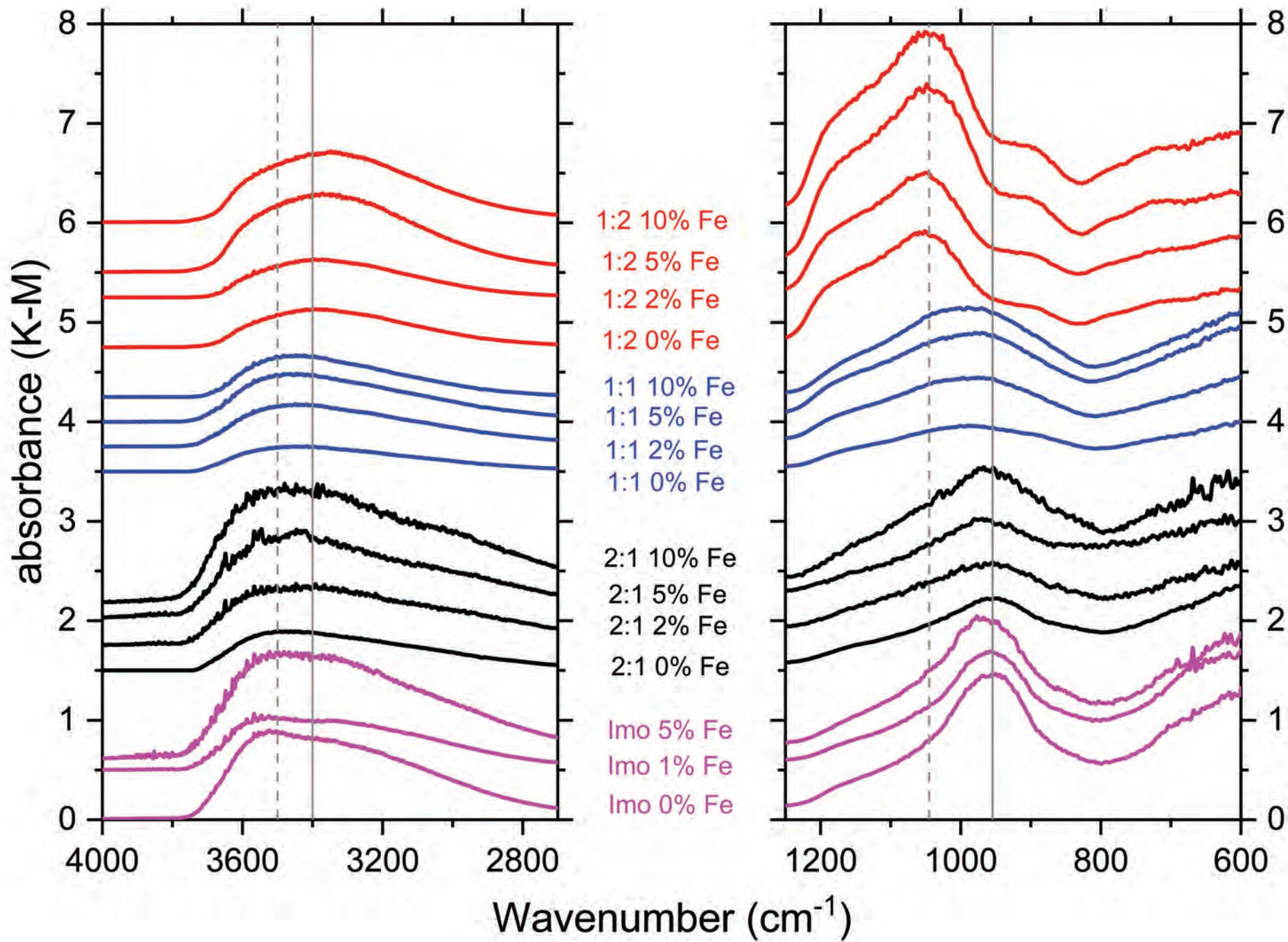987   the text.

FIG 1
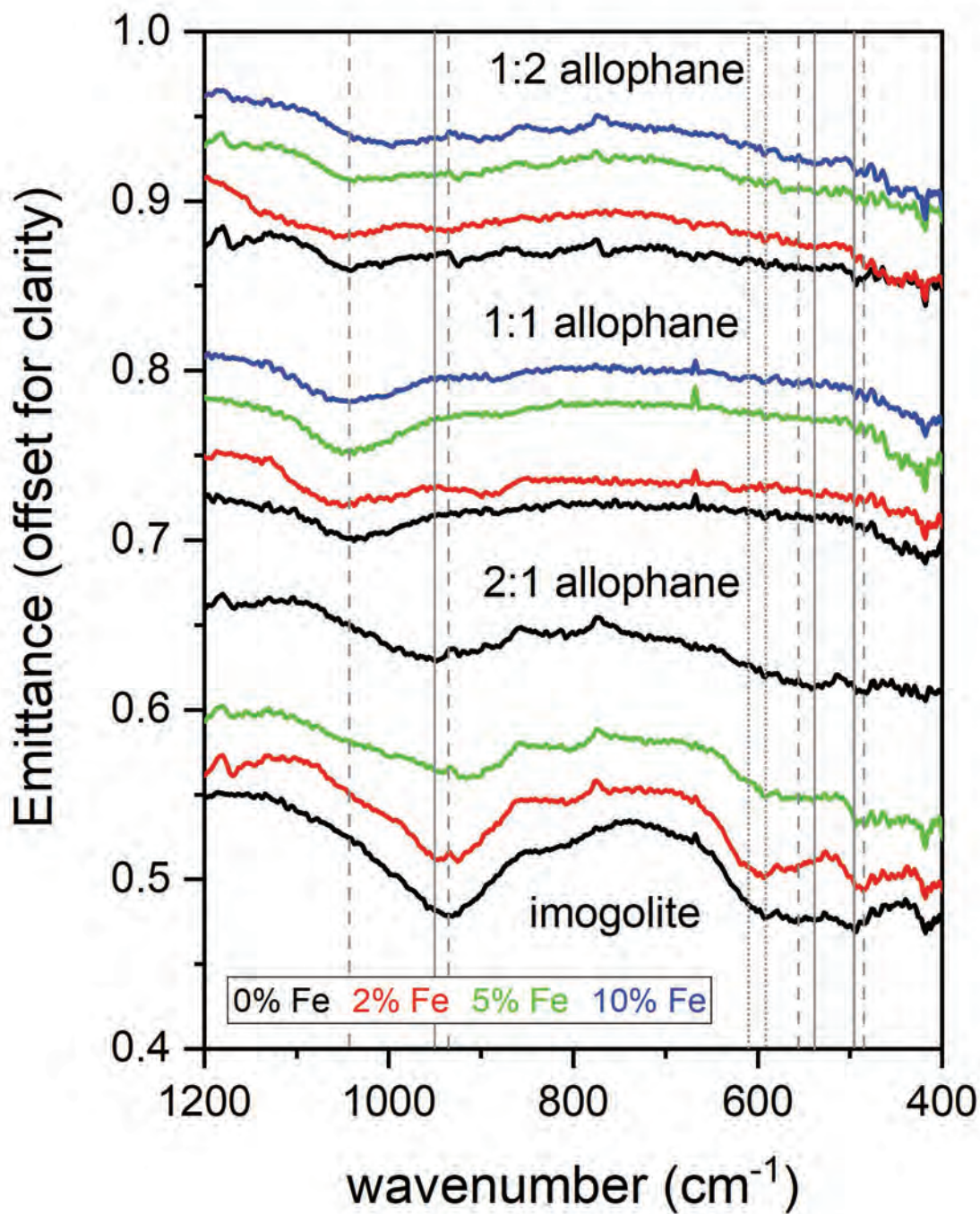
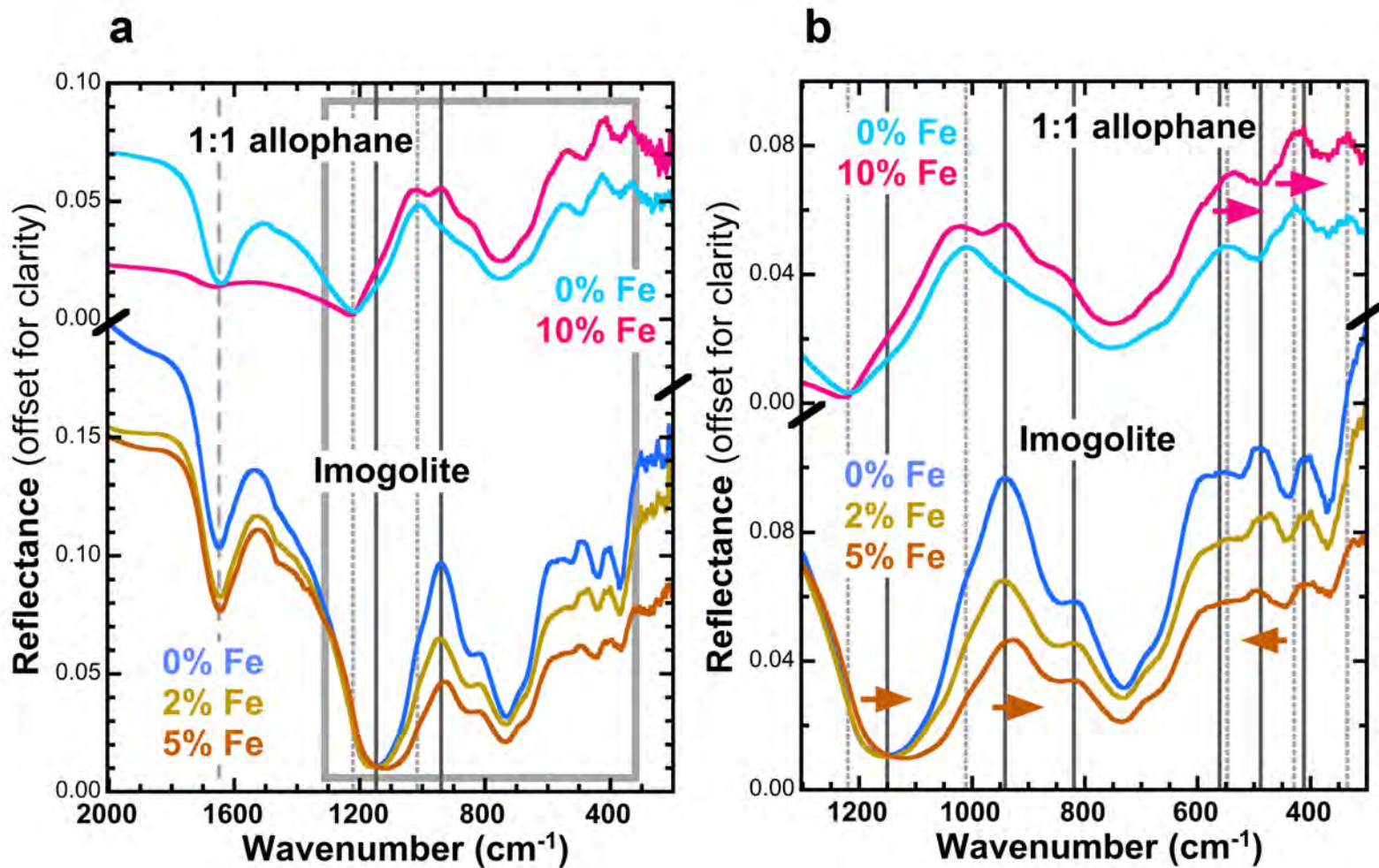Cross Section of Fe-Substituted Proto-Imogolite Allophane

Fig 2

FIG 3

FIG 4

Fig 5

FIG 6

102416-1:2
Fe-free high-Si allophane
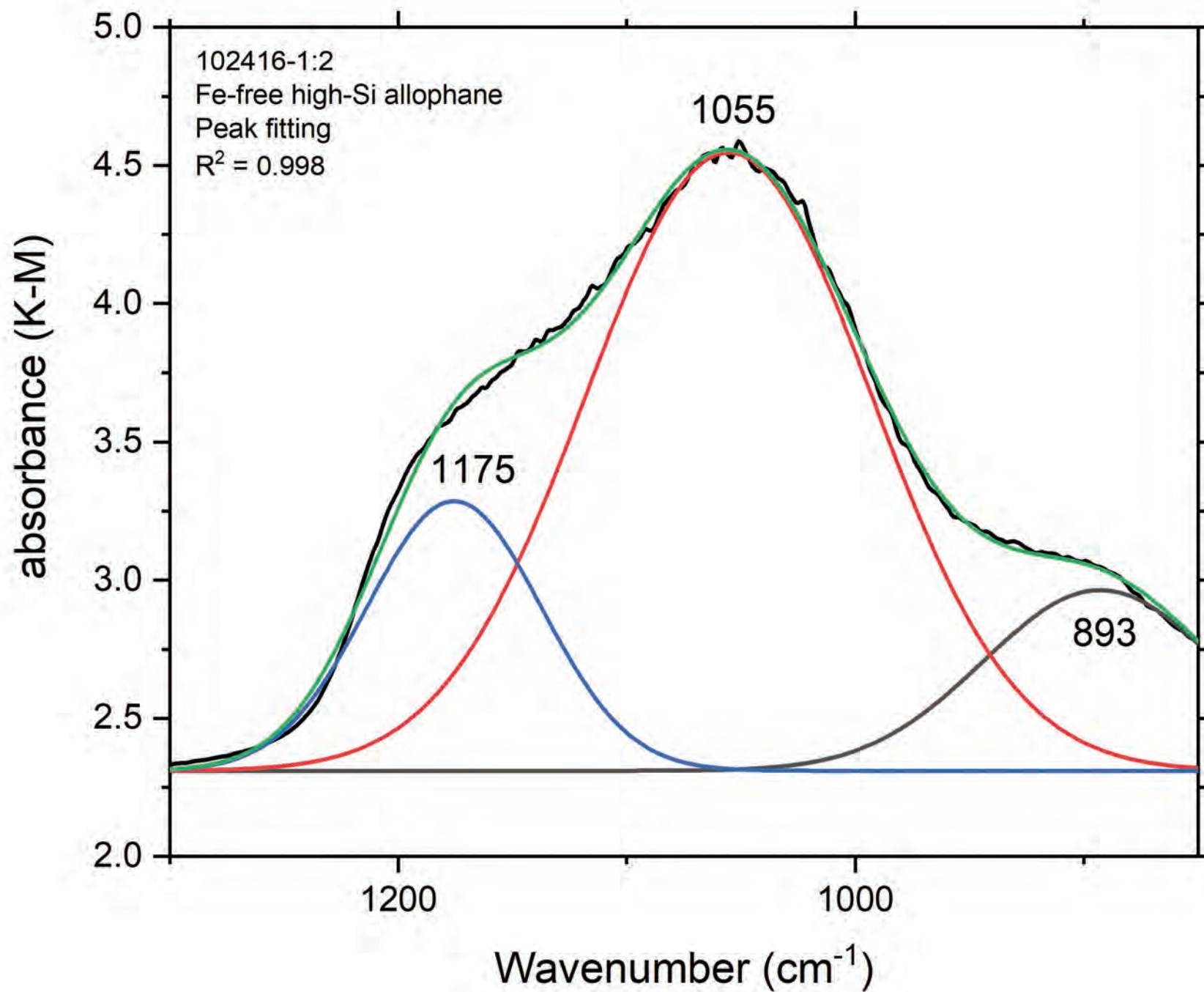Peak fitting
$R^2 = 0.998$

1055

1175

893

absorbance (K-M)

Wavenumber (cm^{-1})
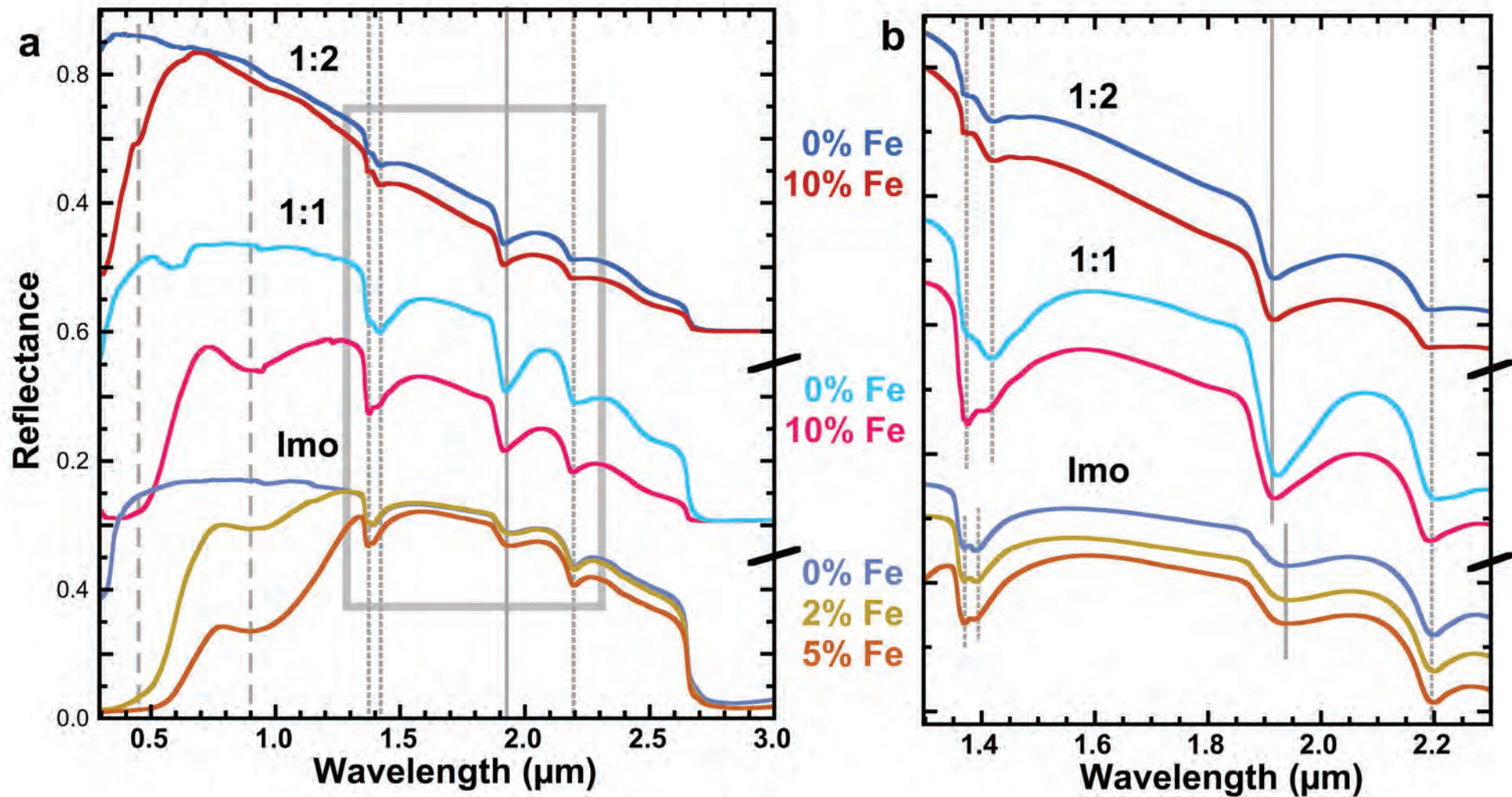
FIG 7

^{27}Al NMR Spectra

FIG 8

^{29}Si NMR Spectra

FIG 9

FIG 10