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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Abstract

Nanophase materials including silicates, aluminosilicates, and iron oxides are widespread on Mars. These minerals are important because they likely represent a solid-phase record of ancient climatic conditions on the martian surface. Identification and characterization of nanophase compounds is technically challenging due to the small size and poorly ordered nature of these materials, particularly because their chemical compositions can vary widely.

This study presents spectra of several synthetic allophane and imogolite samples with a range of chemical compositions that are typical of the natural variability of allophanic materials. These samples were formed under controlled conditions and have been thoroughly characterized in terms of chemical composition and atomic structure.

Analyses confirmed that the synthetic materials were allophane and imogolite and were structurally similar to previously studied natural and synthetic examples of these phases. NMR and XAFS data indicated that high-Al proto-imogolite allophanes were similar in structure to imogolite but were less well ordered, and supported the proposed nanoball structures based on rolled octahedral Al sheets. Increasing Si content in allophane produced increasing tetrahedral Al substitution as well as polymerized Si chain structures at Al-Si mole ratios of 1:1, and sheets and possible framework structures at Al-Si mole ratios of 1:2. Fe in allophanes and imogolites substituted exclusively for octahedral Al.

Reflectance spectra of the synthetic allophanes and imogolites were comparable to previously analyzed samples. Variations in Fe content of allophane and imogolite resulted in some observable changes in visible/near-infrared (VNIR) reflectance spectra, but these changes
were not detectable in emission spectra. Emission spectra of the samples suggest that variations in Al-Si ratio of allophanes should be detectable using remotely sensed data. Because allophanes with different Al-Si ratios typically form in very different environments, this could be significant for interpretation of formation conditions on Mars, with high-Al compositions suggesting possible tephra weathering and high-Si compositions indicating possible formation from thermal waters.
Introduction

Poorly crystalline aluminosilicates such as allophane and imogolite have been identified on Mars using orbital infrared spectroscopy (Rampe et al. 2012; Weitz et al. 2014; Bishop and Rampe 2016). The presence of these nanophase (np) materials on Mars likely indicates a time when water was intermittent and/or too cold for formation of crystalline clays (Bishop et al. 2018). Analysis of Mars Global Surveyor (MGS) Thermal Emission Spectrometer (TES) data (Christensen et al. 2001) provided global maps of regions dominated by basaltic and andesitic or altered terrains (Bandfield et al. 2000; Wyatt and McSween Jr 2002). As spectral libraries of Si-rich alteration products were developed, TES analyses were extended to include more complex components including poorly crystalline Si-rich materials (Michalski et al. 2005; Michalski et al. 2006; Rogers and Christensen 2007; Ruff and Christensen 2007; Rampe et al. 2012).

Gusev crater contains regions high in Si at Home Plate attributed to opal or hydrated silica (Squyres et al. 2008; Rice et al. 2010; Ruff et al. 2011). Additional observations of amorphous Si on Mars were made from orbit using visible/near-infrared (VNIR) Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) data (Murchie et al. 2009) at Valles Marineris (Milliken et al. 2008), Nili Fossae (Ehlmann et al. 2009), Nili Patera (Skok et al. 2010), and Mawrth Vallis (Bishop et al. 2008). The Mars Exploration Rovers (MERs), Spirit and Opportunity, analyzed fine surficial material at Gusev (Spirit) and Meridiani (Opportunity) with many instruments, and the Mössbauer spectrometer detected the presence of nanophase ferric oxides, hydroxides, or oxyhydroxides (np-FeOx) (Klingelhoefer et al. 2004; Morris et al. 2004; Morris et al. 2006a; Morris et al. 2006b). This is consistent with previous VNIR detections of np-FeOx on Mars (Singer 1982; Bell et al. 1990; Morris and Lauer 1990).
An X-ray amorphous component was identified by the Chemistry and Mineralogy instrument (CheMin) on board the Mars Science Laboratory (MSL) rover at Gale crater (Blake et al. 2013) that represents ~20-70 wt.% of martian surface material everywhere CheMin has investigated (Blake et al. 2013; Vaniman et al. 2014; Bristow et al. 2018; Morrison et al. 2018). The amorphous component most likely represents a combination of volcanic glass and hydrated amorphous alteration products that are composed primarily of Si, Fe, and S (Ming et al. 2014; Vaniman et al. 2014). Rampe et al. (2012) identified 10-20% allophane and/or amorphous silica at North Acidalia, Solis Planum, Sinus Meridiani, and Aonium-Phrixi using TES data. Bishop and Rampe (2016) found 10-30% allophane (or related phases) in phyllosilicate-rich outcrops at Mawrth Vallis using a combination of TES and CRISM data. The elevated allophane detections in the northern plains (Rampe et al. 2012) could be related to observations of leached basaltic glass in this region (Horgan and Bell 2012). Thus, allophane and imogolite could be a common component of the martian surface where water was present. Further, they may indicate periods of cyclical climate change. Progressive cooling and drying of the surface would result in conditions favorable for amorphous material production, where surface water was not present long enough or conditions were not warm enough to form more long-range ordered clays (Bishop and Rampe 2016).

Characterization of these materials in the lab is essential for increasing spectral recognition capacities on Mars. Np-aluminosilicates adsorb water readily (Bishop et al. 2013) and can bind with Fe and other species (Baker et al. 2014; Rampe et al. 2016). Understanding the relationship between Al-Si-Fe abundance in poorly crystalline aluminosilicates and their spectral properties will enable future detection of these important materials that encompass up to 70 wt.% of the surface material investigated by Curiosity at Gale crater. The purpose of this study is to
characterize several Fe-bearing allophane and imogolite samples with multiple spectroscopic
techniques to enable more precise detection and characterization of the poorly crystalline
components of the martian regolith.

Background

Allophanes are poorly crystalline nanoscale aluminosilicates that are prevalent in soils formed from volcanic ash, where an excess of Si and Al exist in solution (Parfitt 2009). They are frequently found in association with imogolite, most commonly as products of the weathering of volcanic tephra. Allophane imparts unique chemical and physical properties to soils in which it is a predominant mineralogical component, and those properties have implications for the content and retention of phosphate, sulfate, and H₂O in such soils (Rajan 1979; Rampe et al. 2016).

Allophane and imogolite exhibit rolled morphologies (Figure 1) with nanometer-scale diameters (Abidin et al. 2007), and therefore lack the long-range ordered orthogonal lattices observed in macroscopically crystalline materials, although imogolite exhibits long-range order in one direction. Allophane and imogolite are difficult to characterize due to their small size and lack of macroscopic crystal ordering; however, research has illuminated much about their structure and formation (Henmi and Wada 1976; Farmer et al. 1980; Abidin et al. 2007; Abidin et al. 2008; Creton et al. 2008b; Creton et al. 2008a; Parfitt 2009; Bishop et al. 2013; Baker et al. 2014).

Imogolite exhibits nanotubular morphology (Cradwick et al. 1972; Abidin et al. 2007). Nanotubes are typically 2 nm in exterior diameter and the strands may be tens of nanometers in length. These tubes are thought to consist of a rolled gibbsite-like sheet of octahedrally
coordinated Al with isolated silicon tetroxide tetrahedra bonded to the tube interior to yield an overall molar Al:Si ratio of 2:1 (Cradwick et al. 1972). Each orthosilicate unit is bonded to three Al atoms and no silica polymerization is observed. Because of its tubular morphology, imogolite has no long-range structure in the cross-tube direction but does possess long-range structure in the along-tube direction. Computer modeling has confirmed this structure and reproduced the X-ray diffractogram of natural imogolite samples (Guimarães et al. 2007; Creton et al. 2008b). In synthesis experiments, imogolite-like aluminogerminates have been observed to evolve from nanospherical allophane-like structures upon aging for periods of >2 weeks (Levard et al. 2010).

Due to the lack of long-range crystallographic order, allophanes have been difficult to characterize by X-ray diffraction (Parfitt 2009), and most of the information known about their chemical structures has been determined by methods such as infrared spectroscopy, X-ray absorption spectroscopy (XAS), and nuclear magnetic resonance (NMR), and by computer modeling.

Natural allophanes display a continuous variation in Al:Si ratio. High-Al or proto-imogolite allophane exhibits a molar Al:Si ratio of approximately 2:1. Allophanes with higher Si contents have molar Al:Si ratios as low as 0.9 (Parfitt 2009). The lowest Al:Si ratios are found in “stream-deposit” allophanes that precipitate from silica-saturated stream or spring water (Wells et al. 1977; Childs et al. 1990; Parfitt 1990).

Proto-imogolite allophane is thought to have a hollow, nanospherical structure that is similar in cross section to the cross-tube structure of imogolite (Figure 1). In the proposed structure, an exterior gibbsite-like sheet of octahedrally coordinated Al is rolled into a nanoball of diameter 3.5–6 nm. Orthosilicate units are bonded to the nanoball interior as in the structure of imogolite. Computer modeling suggests that four to six pores are present in the nanoball.
structure (Abidin et al. 2007; Creton et al. 2008a). NMR and Fourier transform infrared
spectroscopy analyses suggest that high-Si allophanes formed in soil environments have a similar
fundamental structure to high-Al allophanes, and that the additional silica is accommodated in a
polymerized form in the nanoball interior (Parfitt 1990). In highly Si-enriched “stream deposit”
type allophanes, the framework is proposed to be a nanospherical shell of polymerized Si, with a
partial or fragmental octahedral Al (AlO) shell and with some Al substitution in tetrahedral sites
(AlT) (Childs et al. 1990). The tetrahedral Al substitution in these high Si species follows
Lowenstein’s rule for zeolites where no Al-O-Al linkages are allowed, resulting in a constant
AlT:Si of 1:3 (Childs et al. 1990). An alternative structure for Si-rich allophane based upon a
curved kaolinite structure containing a defective tetrahedral sheet was proposed by MacKenzie et
al. (1991). At present, no apparent consensus exists on whether high-Si and high-Al forms of
allophane represent fundamentally different types of structures, or whether they represent a
single fundamental structural type that is progressively modified to accommodate varying Al:Si
ratios.

Fe-substituted natural and synthetic allophane and imogolite samples have been described
and analyzed using a variety of techniques (Kitagawa 1973; Horikawa and Soezima 1977;
McBride et al. 1984; Baker and Strawn 2012). These studies found that Fe in allophane and
imogolite was spectrally distinct from Fe in Fe oxides, hisingerite and nontronite. Most Fe was
substituted for Al in octahedral coordination (Figure 1), although some Fe in natural allophane
and imogolite samples may be present as a separate ferrihydrite phase (Baker et al. 2014).
Substitution of Fe into the structures of np-aluminosilicates has been reported to affect their
morphology (Joussein et al. 2005), as well as the kinetics and end products of their ripening to
more crystalline clay minerals (McBride et al. 1984; Farmer et al. 1991; Farmer 1997). Fe-
substituted allophanes may ripen to an Fe-depleted phase plus ferrihydrite (McBride et al. 1984),
or they may recrystallize to Fe-bearing clays such as nontronite (Farmer et al. 1991) or
ferruginous beidellite (Farmer 1997). The specific conditions that lead Fe-bearing allophane to
ripen into various end products are not well understood.

The objectives of the present study were: (1) to investigate Fe speciation and
coordination state in synthetic allophane and imogolite samples, and (2) to examine how the
allophane and imogolite structures are affected by variations in Al:Si and by isomorphic
substitution of Fe for Al. We used spectroscopic data and structural modeling to test existing
models of allophane structure, to examine the hypothesis that high-Al and high-Si forms of
allophane have the same fundamental structure, and to determine whether the presence of
isomorphically substituted Fe affects these structures. A further objective was to characterize the
reflectance and emission spectra of these materials in support of remote identification of them on
Mars and other planetary bodies.

Methods

Materials Synthesis

A suite of synthetic Fe-bearing and Fe-free allophane samples was created using the
method described by Baker and Strawn (2012) that was modified from Montarges-Pelletier et al.
(2005). A solution of 0.1 M AlCl₃ was mixed with a sufficient amount of tetraethyl orthosilicate
(TEOS) to obtain the desired Al:Si ratio for each allophane sample synthesized (Table 1). Fe-
substituted allophanes were produced by mixing 0.1 M FeCl₃ with the AlCl₃ solution (replacing
some of the AlCl₃ with FeCl₃ in order to maintain constant total volume of 0.1 M chloride
solution and correct allophane-forming stoichiometry), to produce the desired Fe content and
(Al+Fe):Si ratio. A solution of 0.1 M NaOH was titrated into this mixture under constant stirring in a N₂ purged bottle. Typical synthesis volumes were 250 mL of AlCl₃ + FeCl₃ and 750 mL of NaOH plus the volume of TEOS needed to obtain the desired Si content. At the end of the titration, the final solution pH was recorded. The resulting suspension of gel in supernatant was stirred for 24 hours, then heated to 95 °C for five days. The suspension was centrifuged to separate the gel, which was placed in dialysis tubing and dialyzed against flowing DI water to a conductivity less than 5 µS/cm. A sample of the centrifuged supernatant was filtered through a 0.45 µm filter, acidified, and refrigerated for analysis. A subsample of each synthesized gel was stored frozen. The remainder of each gel was freeze-dried for analysis.

Under oxygen-free martian conditions, allophanes may form in an environment where Fe is present as Fe²⁺. Samples were therefore also synthesized using Fe²⁺ by replacing the FeCl₃ in the synthesis procedure with FeCl₂. These syntheses produced gels that were green in color, suggesting that Fe in them may have remained divalent. However, a color change from green to brown during dialysis and freeze drying suggested that Fe²⁺ in the gel samples began to oxidize rapidly upon exposure to air. Therefore, the only samples that appeared to retain unoxidized Fe were those preserved as frozen gels. As a result, analyses requiring dried samples could not be performed on confirmed Fe(II)-bearing allophanes. Of the following sample analysis techniques, only X-ray absorption spectroscopy permitted analysis of a hydrated gel sample that retained some Fe(II). Previous studies using allophanes synthesized using the same techniques showed that the XAFS spectra of the same samples in both hydrated gel form and as freeze-dried powders yielded identical spectra and modeling results (Baker et al. 2014).

A suite of synthetic Fe(III)-bearing and Fe-free imogolite samples was synthesized by Z. Abidin using a previously established method (Abidin et al. 2008). Imogolite suspensions
produced using this synthesis were shipped to the University of Idaho where they were freeze-
dried for analysis.

All synthesized samples were analyzed by X-ray diffractometry (XRD) to confirm that they contained no crystalline materials. In all samples, broad, poorly defined peaks were present at 2θ of 12° and 26°.

**Inductively Coupled Plasma Atomic Emission Spectroscopy**

All supernatant solutions from synthesis experiments were analyzed on a ThermoFisher iCAP Duo inductively-coupled plasma atomic emission spectrometer (ICP-AES) to verify synthesized compositions. Samples were analyzed for Fe, Al and Si. Calibration solutions, a blank and a quality control solution were mixed using 0 ppm, 10 ppm and 50 ppm concentrations of proposed analytes with small additions of HNO₃ and HCl to match preservation methods of supernatants. ICP results were used to calculate the true anhydrous formula of the synthesis products by difference from the composition of the original starting solutions.

**Diffuse Reflectance Infrared Spectroscopy**

Fourier transform infrared (FTIR) spectroscopic analyses were carried out on a Perkin-Elmer System 2000 (Thermo Scientific, Waltham, Massachusetts, USA), using a mixture of 3 wt.% sample in optical-grade KBr that was placed into a steel sample cup and analyzed in a diffuse reflectance mounting geometry. Samples were scanned 100 times and the spectra were averaged. Spectra were recorded from 4000 to 600 cm⁻¹ using 1 cm⁻¹ resolution and processed using the Kubelka-Munk algorithm provided in Perkin Elmer Spectrum 2.0 software. Peak fitting for these spectra was performed in Origin Pro 2019a using the Peak Analyzer tool.

**Reflectance Spectroscopy of Bulk, Particulate Samples**
Bidirectional reflectance spectra were measured of bulk (unmixed with KBr or other compounds), particulate samples from 0.3-2.5 µm under ambient conditions at Brown University’s RELAB using a bidirectional VNIR spectrometer relative to Halon and a biconical Nicolet FTIR spectrometer in a controlled, dry environment relative to a rough gold surface as in previous studies (Bishop et al. 2013). The bidirectional spectra were acquired from 0.3 to 2.5 µm at 5 nm spectral sampling. FTIR reflectance spectra were measured under dry conditions from 1-50 µm and then scaled to the bidirectional data near 1.2 µm to create composite, absolute reflectance spectra.

**Thermal Emission Spectroscopy of Particulate Samples**

Thermal emissivity spectra of particulates compressed into pellets were measured at the ASU Mars Space Flight Facility using a modified Nicolet Nexus 670 FTIR interferometric spectrometer. Spectra were measured 270 times over ~4 minutes over the range of 2000 to 200 cm\(^{-1}\) (5-50 µm) with 2 cm\(^{-1}\) spectral sampling as in previous studies (Ruff et al. 1997; Rampe et al. 2012). Pellets were measured in copper sample cups painted black so that they behave as a blackbody and heated to 80 °C before and during data collection. Blackbodies at 70 and 100 °C were measured before sample measurements to calibrate raw data to radiance (Christensen and Harrison 1993).

**\(^{27}\)Al and \(^{29}\)Si Magic Angle Spinning Nuclear Magnetic Resonance**

Samples of Fe-free synthetic allophanes and imogolites were analyzed using \(^{27}\)Al and \(^{29}\)Si magic angle spinning (MAS) solid-state nuclear magnetic resonance spectroscopy (NMR) on a Bruker AVANCE 500 MHz spectrometer (Bruker Biospin, Rheinstetten, Germany). Samples
were spun at 12.6 kHz and were allowed to run until a signal to noise ratio of greater than 500 was achieved. Samples containing Fe were not run due to their paramagnetic nature.

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

Bulk Fe K-edge X-ray absorption near edge spectroscopy (XANES) and extended fine structure spectroscopy (EXAFS) analyses of Fe-bearing samples were performed at beamline 7-3 of the Stanford Synchrotron Radiation Laboratory (SSRL). Beamline 7-3 is fed by the SPEAR ring operating with a beam current of 500-495 mA. The X-rays are diverted using a 20 pole 2-tesla wiggler source, then through a vertical collimating mirror into the monochromator. The monochromator for this beamline is two parallel Si(220) crystals with a 6-mm entrance slit. This experimental setup results in a spot size of approximately 3 x 15 mm. A Lytle fluorescent ion chamber detector was used to collect fluorescence measurements over the entire Fe K-edge EXAFS energy range of 6880-7873 eV with an energy step size of 0.35eV. All spectra were collected at 10 K using a liquid He cryostat to prevent beam damage and scanned 4-12 times to increase the signal to noise ratio. Allophane and imogolite samples, in the form of either wet gels or dry powders, were packed into aluminum sample holders 0.7-mm thick and held in place with Kapton tape. No differences are observed between wet gel and dry powder packed mounts of the same synthetic sample (Baker et al. 2014). In general, allophane samples were analyzed as gels and imogolite as dried powders, but for lower-Fe allophanes, the higher Fe concentration in the dried samples yielded improved data in the form of a better signal to noise ratio. The multiple scans were calibrated to an Fe foil, and merged and processed using Athena (Ravel and Newville 2005).

**FEFF Modeling**
The merged spectra were normalized and background subtracted using a cubic spline. The fitting strategy used in this study follows the approach described by Baker and Strawn (2012) and Baker et al. (2014) in previous studies of Fe in clay minerals.

Shell fitting of the allophane samples was carried out using the 5-shell allophane nanoball model as well as a 5-shell dioctahedral smectite model, following the modelling philosophy of Baker et al. (2014). A detailed description of these models may be found in that work; the most significant difference between the two is in the Si backscattering shell. Atomic coordinates for the smectite model were taken from Tsipursky and Drits (1984) and coordinates for the nanoball model were taken from a section of the model nanoball described by Creton et al. (2008a). Paths were generated from the atomic coordinates using Atoms (Ravel 2001) and shell fitting was carried out using Artemis (Ravel and Newville 2005).

In conducting the fitting, all path lengths were optimized at first, and were then constrained to be equal within that fit. Fe-O3 shell distances were fixed for all models except the 1:1 Fe(III) smectite model, where allowing it to float resulted in a better fit. Debye-Waller EXAFS factors were optimized for the first Fe-O1 shell and fixed to be equal to the former for the Fe-Fe, Fe-Al, and Fe-Si backscattering paths. Debye-Waller EXAFS factors were also optimized for the Fe-O2 and then fixed to be equal for the Fe-O3 shell. Octahedral sites were fitted with either Fe or Al, with the total number of Fe-Metal backscatterers constrained to sum to three, resulting in a dioctahedral sheet. Trioctahedral fits, where Fe-metal backscatters sum to 6, were attempted for the Fe(II) substituted samples, but no recognizable improvement in the fit was observed. The path length was optimized for the Fe-Si backscattering path, with the number of Si atoms fixed at 2 for the smectite model and 3 for the nanoball model.
Results

Synthetic Allophane

The sample compositions span the range of naturally occurring allophanes from high Si (molar Al:Si 1:2) through halloysite-like (Al:Si 1:1) to proto-imogolite (Al:Si 2:1). These three Al:Si compositions were synthesized with Fe\(^{3+}\) isomorphically substituted for 0, 2, 5, and 10 mol.% Al in the sample. This yielded 12 samples of allophane with varying compositions and physical properties. Previous synthetic work suggested that the amount of Fe that can substitute in synthetic allophane varies with Si content (Baker et al., 2014). In the present study, however, allophanes at all three Al:Si ratios were successfully synthesized with Fe isomorphically substituted for 10% of Al.

Results from ICP-AES analyses of residual Si, Al, and Fe contents in supernatant solutions were used to calculate the true Al:Si ratio and true Fe content of the synthetic samples by difference from the initial solutions (Table 1). The results indicate that the intended Al:Si ratios and Fe contents were achieved. Increased Fe content correlated with slight decreases in bulk Al:Si ratio in the solids, indicating that Fe was substituting for Al in the structure as expected. Also shown in Table 1 are pseudo-cationic formulas for each synthetic allophane composition, calculated from the Al, Fe, and Si contents, to allow for easier comparison of compositional differences between samples.

Allophane synthesis was also carried out using Fe(II) rather than Fe(III), to examine whether Fe substitution into allophane is likely under reducing conditions. Allophanes containing 10% Fe(II) substituted for Al were successfully synthesized at Al:Si ratios of 1:2 and 2:1, but synthesis at Al:Si of 1:1 was not successful. As noted above, Fe in these samples oxidized
rapidly upon exposure to air during processing and freeze-drying. As a result, the only analysis
presented here of an allophane still containing residual Fe(II) is of a 2:1 Al:Si sample that was
stored as a frozen gel, and analyzed as a gel by XAFS spectroscopy. The results of this analysis
are given below.

**Visible and Infrared Spectroscopy**

Infrared spectra of Fe-free synthetic imogolite and allophane samples (Figures 2-6) show
absorption bands that are typical for these materials (Bishop et al. 2013) and provide context for
spacecraft observations. Kubelka-Munk transformed spectra of sample-KBr mixtures are shown
in Figure 2 and provide the strongest absorptions. Mid-IR emissivity spectra of the pressed pellet
samples (Figure 3) are noisier than reflectance spectra, but they are directly comparable to
spacecraft data, whereas the reflectance spectra of particulate samples (Figures 4-5) and
particularly of KBr-sample mixtures (Figure 2) may differ from remotely sensed spectra. The
spectral contrast is relatively low because of the small particle size.

Broad H$_2$O stretching vibrations are observed between 3400 and 3600 cm$^{-1}$. Imogolite
and high-Al allophane both display a broad hydroxyl band near 3535 cm$^{-1}$, which displays
slightly more structure for imogolite than for high-Al allophane, but the two spectra are
otherwise similar. This band shifts to lower wavenumber with increasing Si content (Figure 2,
vertical solid and dashed lines).

The Si-O stretching features at ~950-1050 cm$^{-1}$ can be seen in all samples. Imogolite and
high-Al allophane show bands near 935 and 950 cm$^{-1}$, respectively, that are characteristic of the
orthosilicate Si-O-Al stretching vibration in high-Al allophane (Thill 2016); imogolite can
display a doublet in this region, but this synthetic sample does not. The 950 cm$^{-1}$ band broadens
and shifts to shorter wavelengths with increasing Si content; this likely reflects growth of an
additional Si-O-Si absorption feature near 1050 cm\(^{-1}\) (Parfitt et al. 1980) that results from
increasing abundance of polymerized Si in the allophane structure. Deconvolution of the 800-
1350 cm\(^{-1}\) region of the diffuse reflectance spectrum of the Fe-free 1:2 Al:Si allophane (Figure 2)
yielded a good fit to a primary peak positioned at 1055 cm\(^{-1}\) with subsidiary peaks at 893 and
1176 cm\(^{-1}\) (Figure 6). These shifts in Si-O-Al stretching vibrations are also observable in
emissivity spectra (Figure 3). Few differences are observable between the 1:2 and 1:1 allophane
compositions in emissivity spectra, except that the Si-O-Si stretching feature near 1045 cm\(^{-1}\) is
absent or poorly developed in the 1:2 samples but clearly discernable in the higher-Si 1:1
samples (Figure 3, dashed line at 1045 cm\(^{-1}\)). The Christiansen feature (reflectance minimum or
emissivity maximum) is observed near 1215 cm\(^{-1}\) for allophane and near 1150 cm\(^{-1}\) for imogolite
and this shifts slightly towards lower wavenumber with increasing Fe in the imogolite sample
(Figure 4, vertical dotted and solid lines and arrow).

Al-O-Si deformation and Si-O bending features at ~400-600 cm\(^{-1}\) can be resolved in the
imogolite spectra (Figure 4). OH out-of-plane bending modes occur near 610 cm\(^{-1}\) for allophane
and at 595 cm\(^{-1}\) for imogolite (Bishop et al. 2013); the 595 cm\(^{-1}\) feature is observed in both the
imogolite and allophane emissivity spectra shown in Figure 3 but no feature is apparent at 610
cm\(^{-1}\) (dotted lines). The lack of the OH out-of-plane banding mode in allophane may result from
the presence of defects in the structure of proto-imogolite-like compounds, as suggested by the
weak Al(IV) and Al(V) peaks observed in NMR. The presence of these compounds or defects
may disrupt the short-range order of allophane and degrade its resulting emissivity spectra.
Features due to Si-O-Al bending vibrations were observed at 545, 420 and 335 cm\(^{-1}\) for
allophane and at 495, 415, and 335 cm$^{-1}$ for imogolite by Bishop et al. (2013). Similar bands are
observed in this study (Figure 4a, dotted vertical lines).

The position of the Si-O-Al stretching band shifts slightly toward lower wavenumbers in
the imogolite mid-IR reflectance spectra with increasing Fe (Figure 4a, vertical line and arrow).
In contrast, the Si-O-Al bending bands near 495 and 415 cm$^{-1}$ appear to shift towards higher
wavenumbers with increasing Fe in these spectra (Figure 4a, vertical line and arrow). The Fe-
bearing allophane spectrum includes a doublet band for the Si-O-Al stretching vibration centered
near 1025 and 950 cm$^{-1}$ (Figure 4b, vertical solid and dotted lines). These shifts, however, are
relatively small and are not observed in thermal-IR emissivity spectra.

Reflectance bands for Fe-free allophane and imogolite in the mid-IR range (Figure 4)
were also comparable to previous measurements on natural and synthetic allophane and
imogolite samples (Bishop et al. 2013; Weitz et al. 2014). The addition of Fe in these materials
resulted in overall darkening of the samples (Figure 4). Spectra in the VNIR range (Figure 5)
show the development of electronic transition bands from Fe near 0.45 and 0.9 µm (dashed
lines). Fe-free allophane spectra display a doublet near 1.38 and 1.40 µm from OH$_2$ (OH
stretching overtones), a band at 1.92 µm from H$_2$O$_{v+δ}$ (bending and stretching H$_2$O combination
band), and a band at 2.19 µm from OH$_{v+δ}$ (bending and stretching OH combination band),
consistent with previous work (Bishop et al., 2013). Fe-free imogolite has similar bands as
allophane, but the doublet from OH$_{2v}$ occurs at 1.37 and 1.39 µm, as reported by Bishop et al.
(2013). The addition of Fe to the structures of allophane and imogolite did not significantly
affect the position and breadth of the OH and H$_2$O overtone and combination bands near 1.4, 1.9,
and 2.2 µm. However, Fe in the structures of allophane and imogolite appears to increase the
intensity of the OH stretching overtone at ~1.37-1.38 µm, such that the band at 1.38 µm becomes
more intense than the 1.40 µm band in the spectrum of 1:1 allophane with 10% Fe. A similar
effect is observed for the spectrum of imogolite with 5% Fe compared to the Fe-free sample.
Subtle broadening of these spectral features is observed for the Fe-enriched samples, but this
effect is only barely noted in lab spectra and would not be detectable in remote sensing studies.
The addition of Fe to the structures of allophane and imogolite did not significantly affect the
position and breadth of the OH and H$_2$O stretching and bending vibrations at ~1.4, 1.9, and 2.2
µm. Fe in the structures of allophane and imogolite appears to increase the intensity of the first
OH bending overtone at ~1.38 µm, where, in the spectrum of 1:1 allophane, the band at 1.38 µm
becomes more intense than the 1.40 µm band with 10% Fe

Addition of Fe(III) to the allophane structure resulted in increased amplitude of the
diffuse reflectance bands (Figure 2), although this was less evident in the allophane with 1:1
Al:Si than in either the high-Al or high-Si compositions. Substitution of Fe(II) into allophane,
however, did not alter the diffuse reflectance spectrum in any observable way, although this
could be because Fe in the sample was oxidized during freeze-drying. No obvious Fe-Al-OH or
Fe-Fe-OH bands were resolvable in the spectra, even for the highest-Fe samples.

$^{27}$Al MAS NMR

The relative abundances of four-coordinate (Al$_T$), five-coordinate (Al$_P$) and six-
coordinate Al (Al$_O$) in the allophane structure can be quantified by integration of the peak
curves. The peaks are located at ~10, ~36, and ~60 ppm for Al$_O$, Al$_P$, and Al$_T$, respectively
(Figure 7). One peak, corresponding to Al$_O$, is predominant in imogolite. Two distinct peaks are
observed in the allophane spectra, corresponding to Al$_O$ and Al$_T$. Virtually all Al in imogolite is
six-coordinate, whereas high-Al “proto-imogolite” allophane contains a small proportion of Al$_T$
(~6%) and Al$_P$ (~3%). The total percentage of tetrahedrally coordinated Al in the structure
increases linearly with increasing Si content (Table 1) but is higher in proto-imogolite allophane than in imogolite although the two compounds have the same nominal Al:Si ratio.

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

Unlike the large shifts seen in the Al NMR spectra, which correlate to Al coordination number, small shifts seen in the peak differentiation in the Si NMR data are strongly correlated to Si polymerization (Figure 8), and therefore indirectly to the number of Si-Al neighbors in the structure. Imogolites exhibit a spectrum with a well resolved peak at ~79 ppm that arises from the presence of orthosilicate. Proto-imogolite allophanes exhibit a peak in the same location that is broader, suggesting minor polymerization of Si in this sample despite its relatively low Si content. As Si is introduced into the structure, a second, poorly resolved, broad peak develops that is centered between -86 and -90 ppm for the 1:1 Al:Si sample and at ~100 ppm for the 1:2 Al:Si sample. This peak dominates the spectrum of the 1:2 Al:Si sample, with only a poorly defined remnant peak remaining near 80 ppm, whereas the two peaks have similar magnitude in the 1:1 Al:Si sample. We interpret the peak between -86 and -90 ppm as arising from Q2 chain silicate structures, whereas the peak near -100 ppm is consistent with Q3 sheet silicate structures.

These results suggest that the 1:1 Al:Si allophane contains some orthosilicate tetrahedra as well as some polymerized Si chains, and are consistent with a model for this composition of a proto-imogolite-like structure with additional polymerized Si in its interior. The 1:2 Al:Si sample, by contrast, shows little evidence for orthosilicate tetrahedra and its spectrum is consistent with a phyllosilicate-like structure or a rolled tetrahedral sheet.

**XANES and EXAFS spectra**
The near-edge X-ray absorption spectra are typical of previous analyses of Fe-substituted allophanes (Baker and Strawn 2012; Baker et al. 2014), except for the Al:Si 2:1, 10% Fe(II)-substituted sample. That sample displays a shift to lower energy of approximately 1 eV in the absorption edge (Figure 9a, arrow), indicating that some Fe(II) remained in the sample; this shift is more easily observable in the first derivative of the spectrum (Figure 9b, arrow). The pre-edge peak is also shifted approximately 0.3 eV lower in energy, to 7113.2 eV. The pre-edge and edge positions for this spectrum suggest that, even in this sample, much of the Fe was oxidized to Fe(III) and only some has been retained as Fe(II). The other Fe(II) substituted sample, at Al:Si of 1:2, displays no edge shift to lower energy, indicating the Fe in this sample all oxidized to Fe(III).

The XANES data support the conclusion that Fe is isomorphically substituting for Al in octahedral coordination, and that tetrahedral substitution of Fe for Si is not significant in the samples studied. The presence of tetrahedral Fe, or of Fe in (oxyhydr)oxide phases, results in enhanced amplitude of the pre-edge XANES peak (Baker and Strawn 2012; Baker et al. 2014), which is not observed in the spectra presented here (Figure 9).

EXAFS spectra and Fourier transformed spectra of the synthetic Fe(III) substituted allophanes and imogolite (Figure 10) are similar to previously published spectra (Baker and Strawn 2012; Baker et al. 2014) but with greater development of the features that are characteristic of Fe-Fe next neighboring atoms. These features include the peaks in the $\chi$ spectrum near 5 and 7.25 Å$^{-1}$ and the peak centered near 2.8 Å in the Fourier transformed spectrum. The high-Si allophane sample composition showed weaker development of the Fe-Fe next neighbor features than did higher-Al compositions. Although the sample Al:Si ratios are not exactly the same, this observation is in agreement with that of Baker et al. (2014). The spectrum...
of the high-Si, Fe(II) substituted allophane shows very little development of the characteristic Fe-Fe features. This spectrum is characteristic of Fe in octahedral coordination but with almost all Fe-Al next neighbors rather than Fe-O-Fe bonds. The spectrum of the high-Al, Fe(II) substituted allophane, by contrast, is very similar to that of the Fe(III) substituted allophane, even though this sample is shown by the XANES spectrum to contain some Fe(II).

EXAFS Modeling

Model fits, coordination numbers, path lengths, and Debye-Waller factors for Fe$^{3+}$ substituted samples are summarized in Table 2. Modeled Fe-Fe coordination numbers for Fe(III) substituted samples (Table 2) using the nanoball model are highest with high Al content and lowest in the high-Si sample containing Fe(II). Fe-O1 path lengths exhibit very similar values for all samples, ranging from 1.97 to 1.99. Fe-Fe1 path lengths range from 3.00 to 3.06 Å, while Fe-Al path lengths range from 2.99 to 3.04 Å. Fe-Si path lengths cluster between 3.24 and 3.28 Å. Path lengths do not differ significantly between Fe(II) and Fe(III) substituted samples.

Fe-Fe coordination numbers for Fe substituted samples calculated using the smectite model are higher in all cases than those calculated using the nanoball model. Overall patterns among path lengths are similar to the nanoball model. Fe-Fe path lengths range from 3.03 to 3.08 Å, and Fe-Al path lengths range from 3.01 to 3.06 Å. Fe-Si path lengths cluster between 3.23 and 3.28 Å. Path lengths do not differ significantly between Fe(II) and Fe(III) substituted samples.

The Fe-Fe coordination number calculated for the Fe(II) substituted high-Si allophane was much lower than CNs calculated for any other sample. This is consistent with the observation above that typical Fe-Fe next neighbor features are poorly developed in the spectrum of this sample.
Discussion

Chemical substitution patterns among allophanes and imogolites

Comparison of $^{27}$Al NMR data with ICP-AES data (Table 1) shows that the Al$_T$:Si ratio of higher-Si allophanes stays constant at ~1:3, consistent with naturally occurring high Si allophanes (Childs et al. 1990; Ildefonse et al. 1994). This ratio also follows Loewenstein’s rule for zeolites, which states that no Al-O-Al linkages are allowed within the tetrahedral sheet due to charge imbalances (Loewenstein 1954). This represents a tetrahedral Si sheet containing substituted Al$_T$ tetrahedra, with no Al$_T$ tetrahedra sharing edges. This is consistent with the results of $^{29}$Si NMR (Figure 8) indicating sheet silicate structures were present in the high-Si allophane. Previous work suggested that natural high-Si allophanes from Silica Springs have a structure that is based on a silicate sheet comparable to that in muscovite mica, rolled into a sphere with an external tetrahedral layer, with an incomplete octahedral sheet in the nanosphere interior (Childs et al. 1990). The results presented here suggest that synthetic high-Si allophanes have a similar structure to naturally occurring ones.

The Al$_T$:Si ratio of high-Al allophane is 0.13, half that of the more Si-rich allophanes. This is in accordance with the $^{29}$Si NMR spectrum of this material (Figure 8) which shows that it contains relatively little polymerized silica. This sample does contain more polymerized Si than the imogolite samples, however (Figure 8). It also contains a small proportion of Alv, whereas imogolite contains very little (Figure 7). These observations from NMR indicate that the proto-imogolite allophanes contain more structural defects than the imogolites that they compositionally resemble. This likely results from the deformations necessary to form a nanosphere, as opposed to a nanotube, from a rolled sheet structure.
Previous results from Fe K-edge EXAFS spectroscopy of synthetic allophanes (Baker and Strawn 2012; Baker et al. 2014) found that all Fe present in the samples was in octahedral coordination. They interpreted these results as not supporting the model proposed by Childs et al. (1990) for the structure of higher-Si allophanes because that model calls for incomplete octahedral sheets, and no evidence was found for Fe in other than full octahedral coordination. Incomplete octahedral sheets would be lined along the sheet edges with defect sites occupied by cations that were not in full octahedral coordination. In particles containing only a few hundred octahedral cations (e.g. Creton et al. (2008a)), the cations along the edges of incomplete sheets would represent a significant fraction of total octahedral cations, and would likely be detectable.

The present study includes similar observations of Fe coordination but suggests that the previous interpretation by Baker and Strawn (2012) and Baker et al. (2014) was not correct. The $^{29}\text{Si}$ NMR and FTIR results indicate that polymerized Si is present in the high-Si allophane samples, supporting the formation of a phyllosilicate-like structure. Bulk chemistry of the samples indicates that there is not sufficient Al (+ Fe) present in the solid to form a complete octahedral sheet in a nanoball structure based on tetrahedral Si. In addition, the $^{27}\text{Al}$ NMR data for the Al:Si 1:2 sample shows that nearly half of the Al present in the samples is in tetrahedral coordination, so the ratio of tetrahedral (Si + Al) to octahedral Al in this sample is approximately 4:1.

However, Fe K-edge XANES and EXAFS data still indicate that Fe is in octahedral coordination in high-Si allophane samples. Both XANES / EXAFS data and bulk compositional data indicate that Fe is substituting for Al rather than being present in a separate (oxyhydr)oxide phase. This suggests that Fe substituted into the allophane structure may only occupy non-edge sites in the partial octahedral sheets. If Fe can substitute only into limited sections of the allophane structure, this may also explain the previous finding of small Fe clusters in allophanes, even at very low
total Fe abundance (Baker and Strawn 2012; Baker et al. 2014). As noted above, Fe-Fe clustering is much less pronounced in the high-Si sample that was synthesized with Fe(II), although the XANES and EXAFS spectra indicate that the Fe in this sample was completely oxidized to Fe(III). However, modeling of the high-Al allophane sample synthesized with Fe(II), which still contained some residual Fe(II) upon XANES and EXAFS analysis, suggests that Fe clustering in this sample is comparable to that in samples synthesized with Fe(III). We hypothesize that this somewhat puzzling difference may have arisen from the different structures of the two endmember allophane types, with Fe clusters being more easily accommodated in the more extensive and fully-formed octahedral sheet of the high-Al allophane.

A previous XAFS study (Baker et al. 2014) examined natural and synthetic Fe-bearing imogolites and suggested that Fe in these samples was present at least partly in sorbed form, based on the resemblance of their XANES spectra to those of Fe-sorbed allophane samples. Examination of the XANES spectra of the samples in this study, particularly of the diagnostic pre-edge peaks, (Figure 9), suggests that coordination of Fe in the synthetic imogolite samples is similar to that of Fe in the allophane samples and that all Fe is in octahedral coordination.

**Compositional effects on allophane and imogolite spectra**

Terrestrial allophanic materials of different composition form in distinctively different environments (Parfitt 2009). Most imogolite and soil allophanes form by weathering of tephra, but allophane-like and imogolite-like materials have also been identified in soils with no obvious volcanic parent material, and variations in soil pH may lead to differences in the Al:Si ratio of allophanes (Yoshinaga and Aomine 1962a; Yoshinaga and Aomine 1962b; Tait et al. 1978; Farmer et al. 1980; Farmer and Fraser 1982; Parfitt and Kimble 1989). Unlike imogolite and proto-imogolite allophanes, naturally occurring high-Si stream-deposit allophanes from New
Zealand are deposited by thermal waters that have leached volcanic rocks and associated soils (Wells et al. 1977). If allophanes of different composition can be distinguished by remote sensing, this may aid in interpretation of how allophane deposits formed on Mars.

Changes in the mid-IR spectra of allophane due to differences in Si content are distinctive (Figures 2-4). Development of the strong band at 1040 cm$^{-1}$ arises from the polymerization of Si that is also reflected in the NMR spectra of these samples (Figure 8). This band development is apparent in emission spectra of the higher-Si 1:1 and 1:2 allophane samples (Figure 3), suggesting it should be detectable in remotely sensed data. If so, this will be significant in terms of using the presence of allophane to interpret formation conditions on Mars, since detection of high-Si allophanes would suggest formation around thermal features, whereas high-Al allophanes and imogolite would more likely have formed by weathering of tephra.

Several features of imogolite and allophane mid-IR reflectance spectra display detectable shifts to higher or lower wavelength with increasing Fe content (Figure 4). The Si-O stretching feature at 1150 cm$^{-1}$ in imogolite is shifted towards longer wavelengths with increasing Fe, although this shift is not observed for the allophanes in our study. Bands at 495 and 415 cm$^{-1}$ shift to shorter wavelengths, and the Si-O-Al stretching vibration becomes a doublet at 950 and 1025 cm$^{-1}$ in the high-Fe sample. The shifts observed in mid-IR reflectance spectra were not observed in thermal-IR emissivity spectra, suggesting they may not be detectable in TES data.

The Si-O-Al stretching band magnitude for allophanes increased with Fe(III) content in diffuse reflectance spectra (Figure 2). This darkening of the samples was less prominent in the 1:1 allophane. A similar darkening was observed in VNIR reflectance spectra (Figure 4). Allophanes containing substituted Fe(II) displayed a similar but less intense increase in absorbance. At shorter wavelengths, increases in Fe content led to subtle broadening of the 1.9
µm H₂O combination band and 2.2 µm OH combination band, probably due to the
electronegativity of Fe(III) that is broadening the bond strengths.

The absence of observable Al-Fe-OH or Fe-Fe-OH bands suggests that detection of Fe in
the allophane structure would be limited to higher concentrations than the highest in this study
(Al:Fe 9:1). A previous spectroscopic study of Fe in smectites (Neumann et al. 2011) measured
Al-Fe-OH bending at 884 cm⁻¹ in Wyoming montmorillonite, but only observed Fe-Al-OH and
Fe-Fe-OH stretching bands in nontronites. Wyoming montmorillonite contains 2.5 total wt.% Fe
with an octahedral Al:Fe ratio of ~7.3 (Schoonheydt et al. 2011) and an ordered distribution of
octahedral cations that would maximize the number of Al-Fe cation pairs present in the structure
(Vantelon et al. 2003). Previous research has suggested that Fe substituted into allophanes forms
small clusters in the octahedral sheet (Baker and Strawn 2012; Baker et al. 2014), which would
effectively reduce the number of Fe-Al pairs from the ideal 9:1 suggested by the stoichiometry of
the synthetic high-Fe allophane samples, and this may explain why Al-Fe-OH bands were not
detected.

Allophane structure

The ²⁹Si NMR data indicate significant differences between high-Al proto-imogolite
allophane and high-Si allophane that are consistent with previous observations (Childs et al.
1990; Childs et al. 1997; Childs et al. 1999; Parfitt 2009). These data suggest two different
allophane structures that arise from variations in Al:Si ratio. Allophanes with high Al contents
have an octahedral skeleton with individual orthosilicate tetrahedra attached to its interior. Some
additional Si can be accommodated in the high-Al allophane structure through formation of
polymerized Si chains. Allophanes with very high Si content are likely structured around a main
tetrahedral Si and Al sheet skeleton, with additional Al in octahedral coordination. This could
resemble spheroidal halloysite (Joussein et al. 2005), or an aluminous analog of the “ferric
kaolinite” structure that has been proposed for hisingerite nanospheres (Eggleton and Tilley
1998; Baker and Strawn 2012), although the $^{27}$Al NMR peak position is more characteristic of
2:1 dioctahedral phyllosilicates (Ildefonse et al. 1994). The high percentage of tetrahedral Al in
the Al:Si 1:2 allophane (Table 1), however, indicates that the proportion of tetrahedral to
octahedral cations in this sample is approximately 4:1. This very high proportion of cations in
tetrahedral coordination indicates that only fragmental octahedral sheets are likely to be present.

Deconvolved peaks at 1055 and 1176 cm$^{-1}$ in the infrared spectrum of the high-Si allophane
(Figure 6) are similar to peak locations in opal, quartz, and feldspars, suggesting some Si in this
sample may be accommodated in an opaline silica-like framework structure.

Previous work has suggested that allophanes whose bulk chemistry indicates an
intermediate Al:Si ratio consist of a mixture of proto-imogolite allophane with a higher-Si form
(Parfitt et al. 1980). However, the highest-Si naturally occurring allophanes are the “stream-deposit” allophanes, which occur in different environments than soil allophanes containing
elevated Si. Therefore, it is unclear what composition represents the transition point between the
two structures, or whether proto-imogolite and high-Si allophanes should even be considered as
the same compound. It has been suggested that naturally occurring material previously identified
as high-Al allophane is simply an imogolite precursor, even in samples where imogolite itself
has not been identified, possibly due to kinetic limitations (Levard et al. 2012). Further
experimental studies of higher-Si allophanes may help elucidate this structural question, and
more detailed study of the range of natural allophanes identified as Si-rich, may help determine
whether allophane-like materials containing polymerized Si should be treated as a phase distinct
from proto-imogolite allophane.
Modelling of the Fe substituted allophanes aligns well with the previous results from Baker et al. (2014) in the Fe-O1, Fe-Fe, Fe-Al, and Fe-Si bond path lengths (Table 2). The Fe-O1 shell at ~1.99 is consistent with Fe in octahedral coordination. Fe-Fe backscattering distances in the nanoball model show a negative correlation with the addition of Si into the structure, but this correlation is not present in the smectite modeled structure. Differences smaller than 0.02 angstrom are typically unresolvable in EXAFS data (Ravel and Newville 2005). In all cases, Fe-Al backscattering paths were slightly shorter than Fe-Fe backscattering paths, likely due to the increased atomic radius of Fe as compared to Al.

One of the primary differences in the nanoball and smectite structures at this scale is the Fe-Si backscattering distance. In the nanoball structure, Fe-Si distances should be closer to 3.14. Modeled results show a range of distances from 3.23 to 3.28, much closer to the smectite structure of 3.18 to 3.24 modeled by Baker and Strawn (2014). An allophane model with polyhedral structure that had slightly curved faces rather than a sphere was proposed by Creton et al. (2008). If allophane has such a polyhedral structure, that may explain why the interatomic distances for the Fe-Si backscatterers observed in the present study are comparable to those in flat octahedral sheets rather than to modeled distances in a nanosphere.

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

Distinguishing between different X-ray amorphous materials on Mars using remotely sensed IR spectroscopy is difficult because the lack of long-range atomic order results in broader bands than are typical for their crystalline counterparts. Allophane and imogolite have been identified in specific regions on Mars through spectral modeling of TES data (Rampe et al., 2012) and in localized units using both TES models and band positions in CRISM spectra (Bishop and Rampe, 2016). Leached glass and allophane are spectrally similar in the thermal-IR
(e.g., Horgan and Bell, 2012), so the identification of regional allophane-bearing deposits on Mars via TES models is not unique. Considering TIR data cannot be used to distinguish between allophane and leached basaltic glass, it is unlikely that the small variations in allophane mid-IR reflectance spectra or imogolite TIR emissivity spectra from the incorporation of Fe into the structure would be observed in TES spectra. The Si/O ratio of X-ray amorphous materials can be distinguished using TES spectra (e.g., Michalski et al., 2005), so imogolite is spectrally distinct from 1:1 and 1:2 allophane, but it may be difficult to distinguish with certainty between amorphous aluminosilicates with similar Si/O ratios (e.g., imogolite and 2:1 allophane).

The detection of allophane vs. imogolite is more diagnostic in VNIR reflectance spectra from CRISM because of measurable differences in band positions (Bishop et al., 2013). Bishop and Rampe (2016) identified both allophane and imogolite in Mawrth Vallis based on the small differences in the bands at 1.92-1.93 µm and 2.19-2.20 µm. The incorporation of Fe into allophane and imogolite does not have a significant effect on these bands, so these bands cannot be used to determine whether the allophane and imogolite on Mars contain low levels of Fe. There are variations in the band intensities within the doublet at ~1.4 µm from the incorporation of Fe into the structure of allophane and imogolite, but the band near 1.4 µm is often weak in CRISM spectra due to absorption from other components in the basaltic matrix, so this band also may not demonstrate whether allophane and imogolite on Mars contain Fe. VNIR bands resulting from Fe electronic transitions are present in multiple Fe-bearing minerals (e.g., Morris et al., 1985; Horgan et al., 2014; Bishop et al., 2015), so their presence in CRISM spectra from allophane- or imogolite-bearing terrains may not signify Fe is present in the allophane or imogolite structure, but their absence would indicate that the allophane or imogolite does not have Fe in its structure. A CRISM spectrum from an allophane- and imogolite-bearing unit in
Mawrth Vallis presented by Bishop and Rampe (2016; their Figure 1c) does not show a clear band at ~0.9 µm, suggesting that the allophane and imogolite in this unit likely do not contain Fe in their structures.

**Implications**

The structure of allophane varies with its composition, which in turn is a function of its formation conditions; the structure of imogolite resembles that of high-Al allophanes but is paracrystalline rather than poorly crystalline. Mid- and thermal-infrared spectra of allophanes are useful for distinguishing variations in Si content, and some spectral changes are also observed with varying Fe content in mid-IR reflectance spectra. Infrared spectra of imogolites are distinct from those of allophane, containing more and better-defined spectral bands. Increasing Fe substitution in imogolite produces recognizable broadening and shifts in some of these bands in the VNIR region. Thus, remotely sensed spectra of allophanic materials may contain information regarding the environment of formation and/or deposition of those materials. Although the occurrence of high-Al allophane and imogolite is generally considered to be indicative of early weathering of volcanic tephra, this is not universally true for terrestrial occurrences, and so these materials could potentially also represent weathering of a variety of parent materials under acidic conditions. Distinguishing between these possibilities will be important for characterizing allophane deposits on Mars, where tephra and acidic weathering conditions are both likely to have been important. Identification of high-Si allophane on Mars could potentially be indicative of deposition from thermal waters, and such a finding would be interpreted very differently in terms of the history of martian surface conditions.

Fe substitution into the allophane and imogolite structures cause small deviations in the spectra that may not be recognized from orbital data. This emphasizes the importance of
returning samples from the martian surface to better characterize the amorphous component and
better constrain the environment(s) in which it formed.

The existing model of allophane structure is based upon a rolled Al octahedral sheet with
attached orthosilicate units, as for imogolite. This structure can accommodate additional Si in its
interior by polymerization. However, high-Si allophanes contain far more Si than can be
accommodated in the model nanoball interior, spectra of high-Si allophanes indicate that full
tetrahedral Si sheets are present, and these materials do not contain enough Al to have full
octahedral sheets. Therefore, the materials usually called high-Si allophanes fundamentally differ
from high-Al allophanes and may be considered a different material altogether. Future work may
elucidate the transition point or range at which the octahedral Al nanoball gives way to the
tetrahedral Si nanoball as the fundamental structural unit.

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Figure Captions

Figure 1: Schematic cross-section of a high-Al allophane nanoball with Fe present in octahedral substitution for an Al atom.

Figure 2: Kubelka-Munk transformed diffuse reflectance mid-IR spectra for synthetic allophanes and imogolite of varying Fe content mixed with KBr. Vertical solid and dashed lines at 950, 1050, 3400, and 3500 cm$^{-1}$ indicate the respective locations of characteristic OH-stretching and Si-O-Al bending features in imogolite and high-Si allophane as discussed in the text.

Figure 3: Thermal-IR emissivity spectra for Fe-free and Fe-bearing synthetic allophanes and imogolite. Solid and dashed lines at 1045, 950, 935, 590, 556, 538, 495, and 484 cm$^{-1}$ indicate the locations of characteristic spectral features discussed in the text.

Figure 4: a. Mid-IR reflectance spectra for selected synthetic allophanes and imogolite. Solid and dashed vertical lines indicate the locations of characteristic spectral features, and arrows indicate the direction of band shifts with increasing Fe content, as discussed in the text. b. Expanded section of Figure 4a from the gray box.

Figure 5: a. VNIR reflectance spectra of selected synthetic allophanes and imogolites with varying Fe abundances. Dashed lines indicate electronic transition bands that develop as Fe content increases; dotted and solid lines indicate band centers that shift as Fe content changes. b. Expanded section of Figure 5a from the grey box. Spectra are offset for clarity.

Figure 6: Peak fitting of Fe-free, high Si allophane sample showing deconvolved peaks at 893, 1055, and 1175 cm$^{-1}$. 
Figure 7. $^{27}\text{Al}$ Magic angle spinning nuclear magnetic resonance spectra for Fe-free allophanes and imogolite. Spectra have been vertically offset for clarity.

Figure 8. $^{29}\text{Si}$ Magic angle spinning nuclear magnetic resonance spectra for Fe-free allophanes and imogolite. Spectra have been vertically offset for clarity.

Figure 9: a. XANES spectra and b. first derivative spectra of Fe-bearing allophanes and imogolite. Spectra have been vertically offset for clarity. Arrows indicate location of feature discussed in the text.

Figure 10: a. EXAFS chi spectra and b. Fourier transformed spectra of Fe-bearing allophanes and imogolite. Spectra have been vertically offset for clarity. Dashed curves show fits to Fe-bearing allophane spectra using the montmorillonite 5-shell model.
Table 1. Synthesized allophane nominal and measured compositions. A pseudo-cationic formula is given for each sample assuming sufficient O to coordinate the Al, Fe, and Si present. The presence of hydroxyl is indicated but total water in the samples was not determined.

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<th>Sample</th>
<th>Nominal compositions (mol ratios)</th>
<th>Actual compositions (mol ratios)</th>
<th>Al coordination (%)</th>
<th>Formula</th>
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<td>1.82 0.111 2.02</td>
<td>- - -</td>
<td>Al(<em>{1.82})Fe(</em>{0.22})O(_3) SiO(_2)(OH)(_n)</td>
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<tr>
<td>030917-2:1</td>
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<td>1.81 0.111 2.02</td>
<td>- - -</td>
<td>Al(<em>{1.81})Fe(</em>{0.22})O(_3) SiO(_2)(OH)(_n)</td>
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<td>1.02 0 1.02</td>
<td>27.9 3.6 68.5</td>
<td>Al(_2)O(_3)(SiO(_2))(_2)(OH)(_n)</td>
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<tr>
<td>103116-1:1</td>
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<td>1.02 0.0203 1.05</td>
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<tr>
<td>110716-1:1</td>
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<td>1.01 0.0524 1.06</td>
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<td>0.95 0.111 1.05</td>
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<td>0.50 0 0.50</td>
<td>42.3 n.d. 57.7</td>
<td>Al(_2)O(_3)(SiO(_2))(_4)(OH)(_n)</td>
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<td>121116-1:2</td>
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<td>0.52 0.0204 0.53</td>
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<td>Al(<em>{2.08})Fe(</em>{0.04})O(_3)(SiO(_2))(_4)(OH)(_n)</td>
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<td>112816-1:2</td>
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<td>0.50 0.0526 0.53</td>
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<td>Al(<em>{2.0})Fe(</em>{0.2})O(_3)(SiO(_2))(_4)(OH)(_n)</td>
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<td>Al(<em>{1.92})Fe(</em>{0.44})O(_3)(SiO(_2))(_4)(OH)(_n)</td>
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<td>- - -</td>
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- not analyzed
n.d. not detected
Table 2. Fitting results for allophane samples. CN: coordination number. R: interatomic distance (Å). $\sigma^2$: Debye-Waller factor (Å$^2$).

<table>
<thead>
<tr>
<th>Path</th>
<th>120416-1:2</th>
<th>111416-1:1</th>
<th>013117-2:1</th>
<th>040117-1:2</th>
<th>030917-2:1</th>
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<td>Al:Si 1:2 10% Fe(III)</td>
<td>Al:Si 1:1 10% Fe(III)</td>
<td>Al:Si 2:1 10% Fe(III)</td>
<td>Al:Si 1:2 10% Fe(III)*</td>
<td>Al:Si 2:1 10% Fe(III)**</td>
</tr>
<tr>
<td>CN</td>
<td>R</td>
<td>$\sigma^2$</td>
<td>CN</td>
<td>R</td>
<td>$\sigma^2$</td>
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<td>Fe-O1</td>
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<td>0.006</td>
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<td>3.98</td>
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</tbody>
</table>

Smectite Model

<table>
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<th>Path</th>
<th>120416-1:2</th>
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<td></td>
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<td>Al:Si 1:2 10% Fe(III)*</td>
<td>Al:Si 2:1 10% Fe(III)**</td>
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<tr>
<td>CN</td>
<td>R</td>
<td>$\sigma^2$</td>
<td>CN</td>
<td>R</td>
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<tr>
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<td>3.01</td>
<td>0.006</td>
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<td>3.70</td>
<td>0.052</td>
<td>6</td>
<td>3.79</td>
</tr>
</tbody>
</table>

*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 discussed in the text.

** 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 the text.
FIG 1

Cross Section of Fe-Substituted Proto-Imogolite Allophane

- Alumina octahedral layer
- Alumina tetrahedron
- Unpolymerized silica tetrahedron

- ○ O or OH
- □ Al
- ○ Fe(II) or Fe(III)
Fig 2

A graph showing the absorbance (K-M) over the wavenumber (cm\(^{-1}\)) for different iron concentrations. The y-axis represents absorbance ranging from 0 to 8, and the x-axis represents wavenumber ranging from 4000 to 600 cm\(^{-1}\). Each line represents a different concentration of iron, indicated by the labels on the right side of the graph.
FIG 3

Emittance (offset for clarity)

1:2 allophane
1:1 allophane
2:1 allophane
imogolite

0% Fe  2% Fe  5% Fe  10% Fe

wavenumber (cm⁻¹)
FIG 6

Fe-free high-Si allophane
Peak fitting
$R^2 = 0.998$

Absorbance (K-M)

Wavenumber (cm$^{-1}$)