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2   **Synthesis and characterization of Fe(III)-Fe(II)- Mg- Al smectite solid solutions**

3   **and implications for planetary science**

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1

25   Abstract

26   This study demonstrates the synergies and limits of multiple measurement types

27   for the detection of smectite chemistry and oxidation state on planetary surfaces to

28   infer past geochemical conditions. Smectite clay minerals are common products of

29   water-rock interactions throughout the solar system, and their detection and

30   characterization provides important clues about geochemical conditions and past

31   environments if sufficient information about their composition can be discerned.

32   Here, we synthesize and report on the spectroscopic properties of a suite of smectite

33   samples that span the intermediate compositional range between Fe(II,), Fe(III), Mg,

34   and Al end-member species using bulk chemical analyses, x-ray diffraction, Vis/IR

35   reflectance spectroscopy, UV and green-laser Raman spectroscopy, and Mössbauer

36   spectroscopy. Our data show that smectite composition and the oxidation state of

37   octahedral Fe can be reliably identified in the near infrared on the basis of

38   combination and fundamental metal-OH stretching modes between 2.1-2.9μm,

39   which vary systematically with chemistry. Smectites dominated by Mg or Fe(III)

40   have spectrally distinct fundamental and combinations stretches, whereas Al-rich

41   and Fe(II) rich smectites have similar fundamental minima near 2.76μm, but have

42   distinct combination M-OH features between 2.24 and 2.36μm. We show that with

43   expanded spectral libraries that include intermediate composition smectites and

44   both Fe(III) and Fe(II) oxidation states, more refined characterization of smectites

45   from MIR data is now possible, as the position of the 450cm^{-1} absorption shifts

46   systematically with octahedral Fe content, although detailed analysis is best

47   accomplished in concert with other characterization methods. Our data also

48   provides the first Raman spectral libraries of smectite clays as a function of

49   chemistry, and we demonstrate that Raman spectroscopy at multiple excitation

50   wavelengths, can qualitatively distinguish smectite clays of different structures, and

51   can enhance interpretation by other types of analyses. Our sample set demonstrates

52   how X-ray diffraction can distinguish between dioctahedral and trioctahedral

53   smectites using either the (02,11) or (06,33) peaks, but auxiliary information about

54   chemistry and oxidation state aids in specific identifications. Finally, the

55   temperature-dependent isomer shift and quadrupole splitting in Mössbauer data

56   are insensitive to changes in Fe content but reliability differentiate Fe within the

57   smectite mineral structure.

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60   1. Introduction

61   Smectite clay minerals are among the most common products of water-rock

62   interactions detected throughout the solar system and are key indicators of the

63   geochemistry, oxidation state, and extent of aqueous activity in the environment in

64   which they formed (Gates 2005; Bishop et al. 2008a; Ehlmann et al. 2011; Catalano,

65   2013, Michalski et al. 2015; Gainey et al. 2017, Bristow et al. 2018). Tracing the

66   history of aqueous alteration is a crucial aspect of understanding the formation and

67   evolution of planetary bodies and water reservoirs throughout the solar system.

68   Smectites are 2:1 layer phyllosilicates, comprised of an octahedral sheet between

69   two Si(Al)-O tetrahedral sheets with an expandable interlayer, which contains H_2O

70   and exchangeable cations that balance charge of the overall structure. A generalized

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71   formula is $(Ca,Na)_{0.3-0.5}(Fe,Mg,Al)_{2-3}(Si,Al)_4O_{10}(OH)_2 \bullet nH_2O$. Occupancy of the

72   octahedral sheet is used to classify smectite minerals: trioctahedral smectites have

73   all octahedral sites filled and are dominated by +2 cations; dioctahedral smectites

74   have two of three octahedral sites filled and are dominated by +3 cations. There are

75   a number of major endmember species, including dioctahedral nontronites (Fe(III)-

76   rich), montmorillonites and beidellites (Al-rich), and trioctahedral saponites (Mg or

77   Fe(II)-rich).

78

79   On Mars, smectite-bearing outcrops have been detected on the surface by orbital

80   infrared instruments (Poulet et al. 2005; Bibring et al. 2006; Bishop et al. 2008a;

81   Poulet et al. 2008; Ehlmann et al. 2011; Carter et al. 2013, Ehlmann and Edwards

82   2014), and have also been investigated in-situ by both the MER Opportunity rover

83   (Arvidson et al. 2014; Fox et al. 2016) and the Mars Science Laboratory (MSL)

84   Curiosity rover (Vaniman et al. 2013; Grotzinger et al. 2014; Bristow et al. 2015,

85   2018; Rampe et al. 2017). Fe and Mg-bearing smectites are the most common

86   phyllosilicates detected on Mars, and are found in most exposures of ancient crust,

87   suggesting early conditions conducive to silicate weathering or hydrothermal

88   alteration (Poulet et al. 2005; Bishop et al. 2008a; Ehlmann et al. 2011; Carter et al.

89   2013; Catalano 2013; Ehlmann and Edwards 2014; Michalski et al. 2015). Fe- and

90   Mg-bearing phyllosilicates, including smectites, are also found in carbonaceous

91   chondrite meteorites and detected on other altered solar system bodies such as

92   Ceres, C-class asteroids, and comets (Bunch and Chang 1980; Rivkin et al. 2003,

93   2006; De Sanctis et al. 2015; Ammannito et al. 2016). Due to their ubiquity and

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94   geochemical sensitivity to their formation environment, Fe- and Mg-bearing

95   smectites are a key target material in planetary exploration in seeking to

96   understand the aqueous history of the solar system. Their composition, along with

97   Fe oxidation state, can be indicative of the aqueous conditions that altered the host

98   material to the clay, if the properties can be discerned.

99

100   A wide range of smectites are observed on Earth with aluminous smectites

101   (montmorillonite, beidellite) found most extensively in continental settings because

102   of alteration of the predominantly felsic continental crust (Figure 1). Nontronites

103   and a wide range of intermediate Fe/Mg smectites are observed in oceanic settings

104   and continental settings with basaltic rocks. Smectites formed in subsurface settings

105   contain substantial ferrous (Fe(II)) iron rather than the typical ferric (Fe(III))

106   smectites that form in soils, terrestrial sediments, and on the ocean floor where

107   dissolved O_2 is abundant. The crusts of planetary bodies are generally dominated by

108   rocks of mafic and ultramafic compositions, and most non-terrestrial bodies also

109   lack an oxidizing atmosphere. Indeed, some have postulated the early Martian

110   atmosphere was anoxic and there is widespread evidence for Earth's anoxic early

111   atmosphere (Catling and Moore 2003; Catalano 2013; Sholes et al. 2017).

112   Consequently, Fe/Mg smectites of intermediate composition, containing Fe(II),

113   Fe(III), or mixtures of the two, are expected to be common products forming on

114   such bodies (Guven 1988; Burns 1993).

115

116   A few well-characterized smectite samples from terrestrial deposits, particularly

117   from the Clay Mineral Society Special Clays, have found widespread use as spectral

118   standards for identifying mineral phases on planetary bodies (Michalski et al. 2006;

119   Bishop et al. 2008b; Treiman et al. 2014). The Al smectites (montmorillonites,

120   beidellites) and endmember Fe(III) smectites (nontronites) are well-represented; a

121   relatively limited compositional range of Mg smectites is represented by one

122   common saponite standard. However, there is a large compositional range,

123   representing Fe- and Mg-rich di- and trioctahedral smectites that form from

124   terrestrial alteration, for which there are no common standards (Figure 1). In

125   addition, while Fe(III)-bearing smectites (nontronites and also montmorillonites

126   with moderate Fe contents) are well characterized, smectites containing Fe(II) or

127   mixtures of Fe(II) and Fe(III) are poorly described because they are unstable against

128   oxidation in air(Kohyama et al. 1973; Badaut et al. 1985; Guven 1988; Lajarige et al.

129   1998).

130

131   There has been significant effort to characterize the structural behavior as

132   composition varies along binary axes by synthesizing smectites with controlled

133   compositions and octahedral cation proportions. The Fe(III)-Mg (nontronite-

134   saponite) series is a true solid solution in the absence of Al (Grauby et al. 1994), as is

135   the Fe(III)-Al (nontronite-beidellite) series (Petit et al. 2015). The Al-Mg series

136   (beidellite-saponite) is found to have an immiscibility gap that averages out in bulk

137   measurements due to variability in the molecular structure within a clay particle

138   (Grauby et al. 1993). There have been limited studies of native Fe(II)-bearing

139   smectites, primarily trioctahedral in nature, and the impacts of oxidation on their

140   structures (Chemtob et al. 2015; Chemtob et al. 2017). The substantial body of work

141   on chemically reduced dioctahedral smectites that originally contained Fe(III) are

142   instructive but of uncertain value to the present work, as such transformations

143   result in dihydroxylation, perturbed layer charge, and rearrangement of octahedral

144   cations (Manceau et al., 2000a,b; Hadi et al., 2013) that would not occur in a

145   smectite natively occurring in the ferrous state. Laboratory synthesis studies also

146   constrain physical conditions, such as temperature and pH, that control cation

147   solubility into the smectite structure along binary solutions (Decarreau et al. 2008;

148   Andrieux and Petit 2010).

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150   The ability to determine the conditions in which a smectite mineral formed,

151   including the aqueous geochemistry and oxidation state, and by proxy the potential

152   for habitability, is limited by the ability to accurately identify and measure smectite

153   composition and mineral assemblages. Detailed characterization of the full

154   compositional range of smectite minerals using techniques analogous to those

155   employed in planetary exploration will help improve these capabilities for

156   identification and compositional quantification. Here, we synthesize and report on

157   the spectroscopic properties of a suite of smectite samples that span the

158   intermediate compositional range between Fe, Mg, and Al end-member species,

159   including both Fe(III)- and Fe(II)-dominated samples, using bulk chemical analyses,

160   x-ray diffraction, Vis/IR reflectance spectroscopy, UV and green-laser Raman

161   spectroscopy, and Mössbauer spectroscopy. All spectra and patterns are available in

162   the Supplementary Material.

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164   2. Methods

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166   2.1. Smectite Synthesis

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168   Synthetic smectites were produced at Washington University using a

169   hydrothermal sol-gel method modified from previous studies (Decarreau and

170   Bonnin 1986; Chemtob et al. 2015). Solutions of magnesium, aluminum, iron(III),

171   and iron(II) chlorides as well as sodium silicate were prepared from ultrapure

172   deionized water (>18.2 MΩ cm). These solutions were mixed in stoichiometric

173   proportions corresponding to the target smectite composition. Mg, Al and Fe(II/III)

174   solutions were mixed first as these are acidic in nature, followed by the addition of

175   the alkaline sodium silicate solution. Upon mixing these solutions quickly

176   precipitated a gel, which were then were aged for 24 hours and centrifuged for 30

177   minutes at 16500 RPM in sealed tubes. The supernatant fluid was removed, and the

178   gel was resuspended in ultrapure water and centrifuged again in order to remove

179   excess salt. The gel was again resuspended in ultrapure water and the pH was

180   adjusted to 9 using hydrochloric acid or sodium hydroxide. All steps in syntheses

181   involving Fe(II) were conducted in an anaerobic chamber (Coy Laboratory

182   Products) filled with a 97% N_2/3% H_2 mixture and a catalyst system that

183   decomposes O_2 using the excess hydrogen in the chamber.

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185   After pH adjustment the gel suspensions were placed into PTFE-lined Parr acid

186   digestion vessels and heated in an oven at 200°C for 15 days. To prevent oxidation

187   during heating, the syntheses involving Fe(II) were heated in a vacuum oven

188   backfilled with ultrahigh purity nitrogen gas. After cooling to room temperature, the

189   smectites were immersed in a 0.5 M calcium chloride solution for several hours to

190   Ca-saturate the interlayer via cation exchange, before being washed once more with

191   ultrapure water and dried in a vacuum desiccator. Some of the Fe(III)-bearing

192   samples were incompletely dried, such that during subsequent storage for ~12

193   months, some samples formed minor calcite impurities. These growths were

194   identified by comparing X-Ray diffraction (XRD) patterns collected before and after

195   storage. We attribute the calcite impurities to $CO_2(g)$ taken up by the excess water in

196   the samples reacting with interlayer Ca during gradual dehydration during storage.

197   These calcite impurities were removed by suspending the sample for 30 minutes in

198   a pH 5 sodium acetate-acetic acid solution at 80°C (Ulery and Drees 2008).

199   Following this treatment, the smectites were again Ca saturated, washed and dried.

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201   2.2. Chemical Analysis

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203   Elemental abundances were determined using ~50 mg of each synthetic smectite.

204   These were first gently crushed with an agate mortar and pestle and added to a

205   graphite crucible with 350 mg of lithium metaborate flux. The mixture was fused

206   into a glass bead by heating in a muffle furnace at 1050°C for 15 minutes. The glass

207   beads were dissolved in 40 ml of 10% nitric acid, followed by a 1:100 dilution in 2%

208   nitric acid. The diluted samples were analyzed by inductively coupled plasma

209   optical emission spectroscopy (ICP-OES) using a Perkin Elmer Optima 7300DV

210   instrument.

211

212   Structural formulae for the smectites were constructed by taking the molar

213   abundances of each of the cations and normalizing their total positive charge against

214   the twenty-two units of negative charge in the half-unit cell formula. All Ca and Na is

215   assigned to the interlayer. All Si is then assigned to the tetrahedral sheet, as is

216   additional Al to bring the tetrahedral sheet to full occupancy at 4 atoms per half-unit

217   cell. For select Fe(III)-rich samples, Al is insufficient to fill the tetrahedral sheet and

218   Fe(III) is then used to provide full occupancy. The remaining Al, Fe and Mg are then

219   assigned to the octahedral sheet. For the samples containing Fe(II), past syntheses

220   have shown that minor Fe(II) oxidation may occur because of the difficulty in

221   preventing any exposure to air during brief transfers between an anaerobic

222   chamber and vacuum oven. The fraction of iron in the ferrous form [Fe(II)/Total Fe]

223   was determined by digestion of a subsample in 10 g/L ammonium bifluoride

224   followed by complexation of Fe(II) by 1,10-phenanthroline(Tarafder and Thakur

225   2013). The Fe(II) concentration was then determined by measuring the absorbance

226   at 510 nm using an ultraviolet-visible spectrophotometer (Thermo Scientific

227   Evolution 60). These assays were only performed for syntheses involving Fe(II), as

228   the Fe(III) syntheses products at no point were exposed to chemical reductants.

229

230   2.3. X-Ray Diffraction

231

232   Powder XRD patterns were collected on a Bruker D8 Advance diffractometer

233   equipped with a LynxEve XE energy-dispersive strip detector. Samples were gently

234   ground in an agate mortar and pestle and placed into a silicon zero background

235   sample holder for measurement. Samples containing Fe(II) were also enclosed in a

236   air-tight dome to prevent oxidation during measurements, although this produced a

237   large scattering feature between approximately 8° and 18° 2θ. Data were collected

238   using Cu K$_\alpha$ radiation (40 kV, 40 mA) from 3° to 65° 2θ with a 0.015° step size and a

239   0.8 second collection time per step. A continuous scanning data collection mode was

240   employed with the total counts at each data point representing the sum of the

241   counts measured as each of the 192 strips of the detector were swept through the

242   corresponding 2θ position, yielding a total counting time per point of 153.6 s.

243

244   The XRD data were analyzed for both peak positions and lattice parameters, as

245   the asymmetric nature of the turbostratic scattering bands make structural analysis

246   from peak positions alone inaccurate (Moore and Reynolds 1997). The positions of

247   the (001), (02,11) and (06,33) peaks were determined using least squares fitting of

248   a single pseudo-Voigt profile and a linear background. Lattice parameter

249   refinements were conducted using the Profex interface (Doebelin and Kleeberg

250   2015) to BGMN (Bergmann et al. 1998). This employed the approach of Ufer et al.

251   (2004) to simulate the smectite X-ray scattering pattern, with the structure

252   modified to match the compositions determined by sample digestion. The *c* lattice

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253   parameter was obtained through refinement to the (001) feature between 3° and 8°

254   2θ. For the in-sheet lattice parameters, a hexagonal sheet symmetry was assumed,

255   fixing $a = b/\sqrt{3}$. The (02,11) and (06,33) bands were fit separately, from 18° to 21.5°

256   2θ and 57° to 64° 2θ, respectively. b lattice parameters are thus reported for each

257   peak refinement. Corresponding d-spacings associated with diffraction features

258   were then calculated from both the lattice parameters and peak positions for

259   comparison. For the latter, the weighted average wavelength of 1.5418 Å for Cu $K_{\alpha1,2}$

260   radiation was used. This wavelength, along with 1.7903 Å for Co $K_{\alpha1,2}$, was used for

261   peak position conversions between common X-ray tube wavelengths.

262

263   2.4. Visible to Near Infrared Spectroscopy

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265   Visible/near infrared reflectance (VNIR) spectra were acquired at wavelengths from

266   350 to 2500 nanometers and a spectral resolution of 6 nm using an Analytical

267   Spectral Devices (ASD) Fieldspec3 with a 5° field of view and a custom goniometer

268   device at Caltech. The samples were illuminated using a halogen light source placed

269   at a 30° angle, and the fiber optic was positioned normal to the sample surface. The

270   collected samples were calibrated by making measurements relative to a NIST-

271   certified spectralon reflectance standard and correcting for its known properties.

272   The bidirectional reflectances in the Supplementary Materials can thus be

273   considered absolute reflectances. Samples were ground and sieved to particulate

274   sizes less than 120 μm to reduce shadowing effects from larger grains sizes. Fe(II)-

275   bearing samples were measured in a dry Ar atmosphere within an anoxic glovebox.

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277   2.5. Mid-Infrared Spectroscopy

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279   Mid-infrared diffuse reflectance spectra were acquired on a Thermo Scientific

280   Nicolet iS50 transform infrared spectrometer with a 4 cm^{-1} sampling interval and

281   averaged 512 scans. Fe(III)-bearing samples were placed in a dry air-purged sample

282   chamber to acquire diffuse reflectance measurements over 5000-400 cm^{-1} (2-25

283   μm). The system was purged with dry N_2 during measurements of the Fe(II)-bearing

284   samples. The system was calibrated using a rough Al target, which was assumed to

285   have a reflectance of unity. (Any investigations requiring absolute reflectance and

286   utilizing the Supplementary Material should scale MIR to Vis/NIR data values).

287

288   Each sample was also measured using the SensIR Durascope attenuated total

289   reflectance accessory on a Nicolet Magna 860 Fourier transform infrared

290   spectrometer. Powdered samples were pressed against a diamond crystal and

291   spectra were acquired over 4000 - 400 cm^{-1}, (2.5-25 μm) using a KBr beam splitter

292   and an uncooled triglycine sulfate detector with a KBr window. Background

293   calibration spectra were acquired using the diamond crystal alone. All samples were

294   measured in air, as oxidation during the short integration times (<3 minutes) is

295   considered negligible and the sample size required is small.

296

297   2.6. Raman Spectroscopy

298

299   Raman patterns were collected on loosely packed powdered samples on a

300   Renishaw M1000 micro Raman spectrometer using a 532-nm solid state 100 mW

301   laser with a 2400 nm diffraction grating on loosely-packed powdered sample and a

302   spot size of 100 μm. The laser power was attenuated to 10% to avoid ablating the

303   samples, and scans were averaged to improve counting statistics. Spectra were

304   collected between 100 and 4000 cm^{-1} with a 1 cm^{-1} sampling interval. Wavelength

305   accuracy was calibrated using a silicon chip to within 0.5 cm^{-1}. Spectra were

306   background corrected using a cubic spline interpolation. All samples were measured

307   in air. Exposure of the Fe(II) samples was minimized prior to measurement, and

308   oxidation during the <8 minute exposure times is considered minimal. The 532 nm

309   excitation wavelength is equivalent to the Raman spectrometry system planned for

310   the SuperCam instrument designed for the Mars 2020 rover mission (Wiens et al.

311   2017).

312

313   Deep-ultraviolet (DUV) Raman spectra were obtained using MOBIUS (Mineralogy

314   and Organic Based Investigations Using Ultraviolet Spectroscopy), the laboratory

315   prototype for the SHERLOC instrument (Scanning Habitable Environments with

316   Raman and Luminescence for Organics and Chemicals) designed for the Mars 2020

317   rover mission (Beegle et al. 2017). Measurements were done using a 248.58 nm

318   pulsed laser (Photon Systems, Inc) with a focused spot diameter of ~40 μm, an 1800

319   lines/mm diffraction grating and a Horiba Symphony e2v 42-10 CCD liquid nitrogen

320   cooled (−140 °C) detector. Each spectrum was acquired over 30 seconds at a pulse

321   rate of 40 Hz, totaling 1200 pulses. Spectra were collected between over 1024

322   points between ~570 cm^{-1} and ~4200 cm^{-1} with a spectral accuracy of 3.8 cm^{-1}, and

323   wavelengths were calibrated using validating the position of the primary and

324   secondary laser lines at 248.58 and 252.93 nm respectively. For each sample of

325   loosely packed powder, 25 spectra were obtained in a 5x5 array with a spacing of

326   100 μm. Cosmic rays were identified as outliers in the distribution of intensity

327   values in each Raman shift channel and replaced by the value of adjacent points

328   (Uckert et al. 2019). Further processing was done by in-house Python scripts

329   utilizing publicly available packages Numpy, SciPy, and LMFIT (van de Walt et al.,

330   2011; Jones et al., 2001; Newville et al., 2014). Processing included subtraction of a

331   linear baseline by least-squares regression, a recalibration of Raman shift values

332   based on the position of the atmospheric N_2 peak relative to its literature position of

333   2331 cm^{-1}, and subsequent removal of atmospheric N_2 and O_2 peaks by subtraction

334   of a standard atmospheric Raman spectrum acquired on the same spectrometer.

335   The processed spectra were normalized with respect to the N_2 peak amplitude and

336   peak positions, FWHM, and intensities were determined by fitting with gaussian

337   functions.

338

339   2.7. Mössbauer Spectroscopy

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341   Mössbauer spectra were recorded on a spectrometer from SEE Co. operating in

342   the constant acceleration mode in a transmission geometry. Samples were ground in

343   an agate mortar and, depending on the Fe content, 20-60 mg were added to 500 mg

344   boron nitride and mixed in a glass vial to create a homogenous sample (Table S4).

15

345   The resulting mixture was added to a Delrin cup, capped and measured. Spectra

346   were recorded with the temperature maintained using an SVT-400 Dewar from

347   Janis. The quoted isomer shifts are relative to the centroid of the spectrum of a

348   metallic foil of α-Fe at room temperature. Data analysis was performed using the

349   program WMOSS (www.wmoss.org) and quadrupole doublets were fit to Voigt

350   lineshapes.

351

352   3.   Results and Discussion

353

354   3.1. Elemental Abundance of synthesized smectites

355

356   Ten Fe(III)-bearing smectites and six Fe(II)-bearing smectites were synthesized

357   with compositions intermediate to widely used standards (Figure 2). In calculations

358   of structural formulae (Table1), Fe(III) was required to fill the tetrahedral sheet in

359   the two most Fe(III)-rich compositions (samples A and B). Mg content was reduced

360   relative to Fe and Al in each of the final compositions compared to the initial

361   solution, matching observations of other smectite syntheses and suggesting higher

362   Mg solubility than Fe or Al in this system (Chemtob et al. 2015). Octahedral

363   occupancies per half-cell derived from the structural formula (Table 1) indicates

364   that the Fe(III) smectites are generally dioctahedral in nature with the exception of

365   samples G, H, and J, which have formulas suggestive of di-trioctahedral clays. Fe(II)

366   smectite compositions suggest trioctahedral compositions similar to those studied

367   by Chemtob et al. (2015), except for two Al-rich compositions (N and O). Samples K,

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368   L, M and P are consistent with trioctahedral Fe(II)-Mg smectites, sample N is

369   dioctahedral and sample O is a di-trioctahedral smectite. Seven to 15% of the iron in

370   the Fe(II) smectites oxidized during synthesis (Table 1), which is attributed to

371   leakage of small quantities of O_2 into the vacuum oven during synthesis or from

372   leakage into the anaerobic chamber during pre- or post-synthesis treatments.

373

374   3.2. X-Ray Diffraction

375   The XRD patterns (Figure 3) of the synthesized clays confirm that all are

376   smectites, with broad asymmetrical features that are indicative of turbostratic

377   stacking. No other crystalline phases are present except for in sample L, which has

378   <0.4 wt.% quartz (determined by Rietveld refinement) which is attributed to

379   contamination during sample preparation for XRD or present in the sample holder.

380   The (001) diffraction peaks near 6° 2θ (Table 2) correspond to basal layer spacings

381   between 13 and 17 Å (Table 3), consistent with 1 to 3 layers of water in the

382   interlayer. Table 2 also shows the equivalent peak position for each feature if

383   measured by Co K_α radiation, as done onboard the Mars Science Laboratory CheMin

384   XRD instrument. The relatively weak and broad (001) reflections are often observed

385   in XRD patterns of synthetic smectites (Grauby et al. 1993, 1994; Chemtob et al.

386   2015) and indicate small coherent domain sizes, i.e., a small number of stacked

387   layers per crystallite. The peak between 25 to 30° 2θ is primarily the (003)

388   reflection, which like the (001) feature is broad because of the small coherent

389   domain size (Figure 3a). This feature also includes scattering from some water

390   associated with the samples (Morgan and Warren 1938). The remaining features are

391   (hk) peaks associated with X-ray scattering from within the smectite sheet (Brindley

392   and Brown 1980; Moore and Reynolds 1997).

393

394   The (060) d-spacing, typically calculated from the peak position of the (06,33)

395   band near 60° 2θ (Table 3, Figure 3c), is most commonly used to determine unit cell

396   dimensions. This is also typically considered diagnostic of dioctahedral versus

397   trioctahedral structures, although, as our results show, there is overlap in the range

398   of values for these features once the diversity of compositions is considered. The

399   Fe(III) smectites in this study (samples A-J) have (060) d-spacings between 1.520

400   and 1.528 Å based on peak positions. The Fe(II) smectites show a much broader

401   range, from 1.516 to 1.557 Å, consistent with prior work (Chemtob et al. 2015).

402   Three of the Fe(II) smectites (K, N, and O) have splittings in the (06,33) peaks that

403   suggest the presence of separate domains of distinct clay compositions intermixed

404   among the layers, which has been observed to occur in previous syntheses of Fe(II)

405   smectites (Chemtob et al. 2015), as well as other smectite compositions (Grauby et

406   al, 1993). The shoulder feature for sample K may indicate an anomalously long d-

407   spacing (~1.58 Å) but the exact origin of this feature is uncertain as the dome used

408   to seal the sample also produce an increase in background scattering near this

409   feature. The splittings in the (06,33) peak for samples N and O are clearer in nature

410   and suggest mixtures of trioctahedral and dioctahedral domains. This parallels a

411   miscibility gap previously reported for the Mg saponite-beidellite series (Grauby et

412   al. 1993), suggesting that Fe(II) saponites also display such a gap as Al content

413   increases. Peak positions of the (02,11) peak similarly show small variation among

18

414   the Fe(III) smectites and much larger variations among the Fe(II) smectites (Table

415   2, Figure 3b). The derived lattice spacing, as calculated from peak refinement,

416   reflects octahedral coordination state (Figure 3d). Dioctahedral sample basal

417   spacings exhibit little dependence on Fe(III) octahedral content (Figure 3e), but tri

418   and di-trioctahedrally coordinated samples demonstrate a more linear trend

419   towards increasing d-spacing with increasing octahedral Fe (both Fe(II) and Fe(III)).

420

421   Lattice parameters were refined for both Fe(III) and Fe(II) smectites using a

422   single smectite structure to model both the (02,11) and (06,33) peaks, and thus

423   obtained one b value from each, even when peak splitting was observed (Table 3).

424   Calculation of the (060) d-spacings from lattice parameters obtains values ~0.004 Å

425   larger than values determined from peak positions (Table 4). This discrepancy is

426   real and results from smectite sheets scattering as 2-dimensional crystals, with peak

427   positions occurring at slightly higher angles in 2θ than the actual (06,33) position

428   (Brindley and Brown 1980; Moore and Reynolds 1997). Lattice parameter

429   refinements of the (02,11) show similar trends in b values as the peak positions.

430   However, the discrepancy between the d-spacing as derived from the peak position

431   and the lattice parameter is an order of magnitude larger in this case, with peak

432   positions underestimating actual d-spacings by 0.04 to 0.07 Å. While this is a long

433   established aspects of the X-ray scattering properties of turbostratic smectites, this

434   is again emphasized here because the (02,11) peak is the primary structural

435   features observable in X-ray diffraction patterns collected by the MSL rover, as the

436   (06,33) peak is outside of the angular range of the instrument.

437

438   3.3. Visible to Near Infrared Spectroscopy

439

440   Spectral features in the Visible to Near Infrared (VNIR) wavelength region are

441   caused by electronic absorptions related to charge transfer and crystal field

442   splitting, as well as the overtones and combinations of the fundamental vibrational

443   modes of the chemical bonds within a mineral structure, such that the wavelength

444   position of absorption features provides characteristic information about the

445   mineral composition (Gates et al. 2017). The reflectance also depends on the

446   particle size and viewing geometry of the samples under investigation. The VNIR

447   reflectances of the synthetic smectite samples exhibit absorptions caused by

448   electronic transitions in Fe(II) and Fe(III), and cation-OH bending and stretching

449   modes between 0.5 and 2.5 μm (Figure 4).

450

451   In the visible and short-wavelength near infrared (0.4-1 μm), Fe crystal field

452   absorptions dominate the spectral shape. Within the Fe(III) samples, overlapping

453   ferric features dominate the spectrum between 0.4 and 1 μm, but vary as a function

454   of Fe content. Fe(III)-bearing samples A-J all have a spectral maximum near 0.76

455   μm. The positive spectral slope from 0.4-0.76μm observed in all Fe(III)-bearing

456   samples is caused by charge transfer bands that are centered in the UV and the

457   broad 0.60μm and 0.96μm absorptions, attributed to electron transitions in the

458   Fe(III) ions in the octahedral structure (Hunt 1977). A narrower feature centered at

459   0.48μm is also an Fe(III) charge transfer absorption (Rossman 1976; Hunt 1977).

460   The 0.96 μm absorption is present in all samples save sample J, which only has 9%

461   octahedral Fe(III). The 0.48 μm absorption is most pronounced in samples with

462   relatively less Fe(III) content, which is consistent with an enhanced charge transfer

463   absorption due to substitution of a 3+ ion into a 2+ crystal site (Burns 1970; Hunt

464   1977). The Fe(II)-bearing samples have a distinctly different spectral shape in the

465   visible and near infrared due to Fe(II) electronic absorptions. Samples K-P have a

466   spectral maximum at 0.5 μm, and very broad absorption features centered around

467   0.72, 0.88-0.92 and 1.11-1.13 μm, attributed to Fe(II) crystal field absorptions (Hunt

468   1977; Bishop et al. 2008c).

469

470   All samples have broad, asymmetrical absorptions centered at 1.91 μm, caused by

471   the combination of bending and stretching modes of H_2O molecules within the

472   mineral structure. The interlayer of smectite clays can accommodate significant

473   molecular substitution, such that ambient humidity affects H_2O absorption into the

474   mineral structure. The depth and structure of the 1.91μm absorption feature is a

475   function of the samples' hydration; a shoulder around 1.97 μm that occurs in some

476   samples indicates the presence of relatively more absorbed water in the interlayer

477   (Bishop et al. 1994). The combination of the symmetric and asymmetric stretch

478   together with the H_2O bending mode occurs at 1.15 μm, and is detectable in the

479   Fe(III)-bearing samples. Sample J, which has the least strong Fe electron features,

480   also shows the second overtone of the H_2O stretching mode at 0.97 μm, which is

481   obscured by the stronger Fe absorptions in the other samples. The 0.97 and 1.15μm

482   absorptions are not apparent in the Fe(II)-bearing samples, likely due to the

21

483   stronger overlapping Fe(II) electronic features. All samples also exhibit a strong

484   absorption centered near 1.41 μm due to the first overtone of the structural OH and

485   H_2O, and a shoulder at 1.46 μm is attributed to a more H_2O saturated interlayer

486   (Bishop et al. 1994). Structure within this absorption is due to overtones of the

487   Metal-OH (M-OH) stretching and bending modes observed at longer wavelengths.

488   Samples H and J and P, with the most octahedral Mg, have a band at 1.395 μm,

489   compared to all other more Fe rich samples which have absorptions centered

490   towards 1.43 μm, consistent with prior work (Madejová et al. 2000).

491

492   The NIR region between 2.1 and 2.5 μm is particularly diagnostic of smectite clay

493   composition as absorptions caused by the combination of the bending and

494   stretching modes of the octahedral cations and hydroxyl molecules occur in this

495   range. The intensities and center positions of these absorptions shift as a function of

496   the relative abundance of Fe(III), Fe(II), Al, and Mg in the octahedral layer (Figure

497   5). Samples with high octahedral Al contents show absorption features in the 2.20-

498   2.25μm range (Figure 5a). In the Fe(III) bearing samples C, D, H and I, shallow and

499   broad absorptions around 2.23μm are combination absorptions attributable to Al-

500   Fe(III)-OH and Al-Mg-OH bending and stretching modes. The Al-related absorptions

501   are more well defined in the Fe(II) bearing samples; a narrow absorption feature

502   shifts from 2.25μm in the most Fe(II) rich samples to 2.23μm in the Fe(II) poor (Mg-

503   rich) samples. Samples O and N, which are the most Al rich samples in the suite, also

504   have well defined Al-Al-OH absorptions at 2.20μm. All of the Fe(III)-bearing samples

505   have distinct absorptions centered at 2.28 μm caused by combination of the Fe(III)$_2$-

506   OH bending and stretching vibrational modes that occur in the mid-infrared (Figure

507   5b) (Madejová et al. 2000; Gates 2005). Samples H and J also have an absorption

508   center at 2.31 μm attributed to the Mg-OH-Mg combination absorption (Grauby et al.

509   1994). Sample K has a dominant absorption at 2.35μm attributed to $Fe(II)_2$-OH

510   combination modes, and the position of this feature shifts to 2.33μm in samples L

511   and M as Fe(II) in the octahedral sheets decreases. Samples N and O lack a defined

512   absorption feature in this wavelength range and have only a shallow shoulder near

513   2.33μm. Sample P has an asymmetric absorption at 2.32, consistent with the low Fe

514   and high Mg octahedral sheet content in this sample.

515

516   The Fe(III)-bearing samples have an absorption band that does not shift

517   significantly as a function of composition at ∼2.39μm. It is most strongly defined in

518   samples J, H, A and B, but is detectable in all of the spectra. This feature is attributed

519   to the combination of cation-OH stretches in the octahedral sheets and the

520   tetrahedral Si-O stretch(Gates 2005). Mg-dominated samples H and J have a

521   narrower, more pronounced absorption compared to the wider features in the more

522   Fe(III) dominated samples. The more aluminous samples, C, D, G, I, N and O,

523   together with all of the Fe(II)-bearing samples, have broad bands with centers

524   shifted towards 2.45μm. In the Fe(II)-bearing samples, this shift is approximately

525   linear as a function of Mg content, although the Fe(III) samples do not show well

526   defined compositional dependence (Fig 5c).

527

528   3.4. Mid-Infrared Spectroscopy

23

529

530   3.4.1.   Attenuated Total Reflectance

531

532   The Attenuated Total Reflectance spectra of the suite of ferruginous smectites are

533 shown in Figure 6, and assignments are made based on previous works. Peaks in the

534 ATR spectra are primarily a function of the absorption coefficient of the material

535 and peaks in the 400-4000 cm^{-1} range are caused by the fundamental molecular

536 vibrational modes. Higher degrees of crystallographic symmetry sharpen peaks,

537 whereas less-ordered structures and overlapping vibrational modes produce broad

538 peaks. Generally, octahedral OH stretching modes occur between 3800-3000 cm^{-1}

539 (2.63-3.33μm) (Figure 6a), and the octahedral OH bending modes, together with the

540 tetrahedral stretching and bending modes, occur between 1200-400 cm^{-1} (8.33-

541 25μm) (Figure 6b).

542

543   All samples have well defined features between 3800-3000 cm^{-1} (2.63-3.33μm)

544 that are caused by H_2O related vibrational modes and cation-OH stretching modes. A

545 shoulder feature that occurs 3220 cm^{-1} (3.1 μm) is the first overtone of the H_2O

546 bending mode that occurs in all samples at 1635cm^{-1} (6.12μm) (Clark et al. 1990;

547 Bishop et al. 1994; Madejová et al. 2002). A broad peak centered around 3390 cm^{-1}

548 (2.94 μm) is attributed outer-sphere H_2O bonding within the interlayer; its strength

549 has been correlated with the hydration levels of the smectite (Bishop et al. 1994;

550 Madejová et al. 1994), and its relative strength among samples measured here also

551 tracks with observed trends in the near-infrared that suggest that some of the

24

552   samples are more hydrated than others. Peak and shoulder features between 3700-

553   3550cm^{-1} (2.70-2.81µm) are attributed to cation-OH stretching modes. Samples A-F

554   have a peak feature, most clearly observed in samples A and B, at 3550cm^{-1}

555   (2.81µm) that is associated with Fe(III)$_2$-OH stretching (Gates 2005). Samples I and J

556   have a well-defined shoulder feature at 3680cm^{-1} (2.71µm) that is ascribed to the

557   Mg$_2$-OH stretching vibration (Grauby et al. 1994). A shoulder at 3630 cm^{-1} (2.75µm)

558   is prominent in almost all of the samples, and is the dominant feature in the Fe(II)-

559   bearing samples (Figure 6a). This is most consistent with features that have been

560   attributed to Al$_2$-OH or Al-M-OH bending modes in other smectite samples (Grauby

561   et al. 1993; Madejová et al. 1994; Gates 2005) and is likely the cause in these

562   samples. The Fe(II)$_2$-OH absorption would be expected at lower wavenumbers

563   (higher wavelengths) than the Fe(III)$_2$-OH absorptions (Gates 2005), but no such

564   feature is observed in the ATR spectra of the Fe(II)-bearing samples, likely due to

565   stronger overlapping H$_2$O features.

566

567   The tetrahedral Si-O stretching and bending modes occur between 400 and 1200

568   cm^{-1} (Figure 6b). In all of the ferruginous smectite samples, the Si-O stretching mode

569   in the tetrahedral sheet occurs around 985 cm^{-1}, and the Si-O-Si bending mode

570   occurs between 415-440cm^{-1} in the Fe(III) bearing samples and 430-460cm^{-1} in the

571   Fe(II) bearing samples. The stretching mode does not demonstrate a significant

572   dependence on composition, but the bending mode moves to longer wavenumbers

573   as Fe content increases in all samples. A band near 485 cm^{-1} attributed to the

574   Fe(III)$_{oct}$-O-Si$_{tet}$ bending mode is apparent in samples with at least 30% Fe(III); the

25

575 shoulder shifts to 510 cm^{-1} in samples C, D, G and I with an increase in Al in the

576 octahedral sheet, implying the presence of an Al-O-Si bending mode(Madejová and

577 Pálková 2017). The feature around 515cm^{-1} in the more aluminous Fe(II)-bearing

578 samples M, N and P is also ascribed to the same Al-O-Si bending mode.

579

580 The fundamental octahedral cation-OH bending modes also occur in the same

581 region as the Si-O fundamental absorptions. An asymmetric band at 680 cm^{-1},

582 present in all of the Fe(III)-bearing samples, is attributed to interactions between

583 the bending of the Fe-O out of plane bend and Si-O vibrations, and in more tri-

584 octahedral samples H and J overlaps the Mg_2-OH bend at 656 cm^{-1} (Grauby et al.

585 1994; Frost and Kloprogge 2000b; Gates 2005). The Fe(II)-bearing samples have

586 less well defined features in this region than the Fe(III)-bearing samples, but have a

587 very broad plateau between 658-570cm^{-1} caused by overlapping Mg_2-OH, Fe(II)-

588 Fe(III)-OH and Fe(II)$_2$-OH bending modes that are not well distinguished. The

589 Fe(III)-bearing samples also exhibit a pair of bands at 815-817 and 870 cm^{-1} that are

590 attributed to the Fe(III)$_2$-OH and the Fe(III)-Al-OH bends (Grauby et al. 1994; Gates

591 2005; Andrieux and Petit 2010). The 817 cm^{-1} band is only apparent in samples A-E

592 and disappears with decreasing Fe. The Fe-Al-OH bend is also detectable in the

593 Fe(II) bearing samples, although it has reduced spectral contrast.

594

595   3.4.2. Diffuse Infrared Reflectance

596

597   Similar to reflectance spectra in the visible and near infrared, mid-infrared

598   reflectance spectra depend on both the real and imaginary component of the

599   complex index of refraction. However, while the real component is relatively

600   constant from the visible out to about 5-6 μm such that spectra in the visible to near

601   infrared are practically a function of only the variation in the imaginary component,

602   both the real and imaginary components vary significantly through the infrared

603   region, causing both reflectance minima and maxima that are telling of the

604   mineralogy. Spectral features between ~4000 and 100 cm^{-1} (2.5-25 μm) are caused

605   by the fundamental bending and stretching modes of hydroxyl bonds in the

606   octahedral sheets and silicate structures in the tetrahedral sheets, as well as

607   molecular water within the structure (Figure 7).

608

609   As in the ATR spectra, the presence of interlayer and adsorbed H_2O causes the

610   deep, broad absorptions centered at 2.94μm (3400cm^{-1}) and 3.12μm (3200cm^{-1})

611   (Clark et al. 1990; Bishop et al. 1994). The depth of this feature is dependent on the

612   abundance of water molecules within the interlayer. Superimposed on the

613   fundamental H_2O stretches are the narrower stretching modes of the cations bound

614   to the hydroxyl molecules within the octahedral sheets (Figure 7a). In the Fe(III)

615   samples, absorption minima shift from ~2.79 to 2.75μm with decreasing Fe(III)

616   content (Figure 7b). All samples except for H and J have the deepest metal-OH

617   stretching minimum between 2.80-2.82μm (3560-3540cm^{-1}), consistent with Fe(III)

618   being the controlling cation in the octahedral sheets. The Fe(III)$_2$-OH stretch occurs

619   at 2.80μm (3560 cm^{-1}) (Madejová et al. 1994) and is most prominent in samples A

620   and B. Samples C, D, E and F have band minima shifted approximately linearly

621   towards 2.75μm (3635 cm^{-1}) due to the presence of aluminum and the Al$_2$-OH

622   stretching mode. Samples H and J, having the least Fe(III) within the octahedral

623   sheets, show distinct, narrow minima at 2.721μm (3674 cm^{-1}), which are attributed

624   to the Mg-OH-Mg stretching modes. As with the Fe(III)-bearing samples, the minima

625   of the Fe(II)-bearing samples also shift linearly to longer wavelengths and shorter

626   wavenumbers with increasing Fe(II) from 2.72-2.76μm (3680-3624cm^{-1}) (Figure

627   7b).

628

629   The mid-infrared region between 100 and 1200 cm^{-1} contains information about

630   both the octahedral and tetrahedral sheets, as both the fundamental bending modes

631   of the octahedral cation-OH bonds and the bending and stretching modes of the Si-O

632   bonds in the tetrahedral sheet occur in this range (Figure 8). Features are similar to

633   those observed in the ATR spectra, although the band positions are shifted, and as

634   the reflectance is sensitive to both the absorption and scattering coefficients, display

635   features related to changes in both the real and imaginary component of the index of

636   refraction. All samples have a strong peak centered between 1030-1045cm^{-1} that is

637   attributed to the fundamental Si-O stretch. The position of this feature does not

638   demonstrate a clear trend as a function of composition in the Fe(III)-bearing

639   samples, but does shift to larger wavenumbers in the more aluminous Fe(II)-bearing

640   samples (Figure 8d). A peak around 455 cm^{-1}, which ranges from 410 to 480 cm^{-1}

641   with decreasing Fe, is attributed to the Si-O bending mode (Frost and Kloprogge

642   2000b) (Figure 8b). The dioctahedral samples A, B, C, D, E, F, and G all have

643   secondary peaks between 490-510cm^{-1}; samples A and B in particular have the most

644   distinct secondary peaks centered at 500 cm^{-1}, attributed to the Fe(III)$_{tet}$-O-Si

645   bending modes, due to Fe substitution into the tetrahedral sheet (Frost and

646   Kloprogge 2000b; Madejová and Pálková 2017). The secondary peaks in the other

647   dioctahedral samples are weaker relative to the tetrahedral Fe(III) as they are

648   caused by out of plane Fe-O bend, between the tetrahedral and octahedral sheets.

649   The trioctahedrally-coordinated samples, particularly H and J, typically show only a

650   single Si-O bending peak, but have a pronounced shoulder near 530 cm^{-1} attributed

651   to the Mg-O out of plane bending mode (Gates et al. 2017). Samples N and O in the

652   Fe(II)-bearing samples appear double peaked in this spectral region, consistent with

653   the peak splitting of the (06,33) peak in the XRD indicating multiple clay domains,

654   i.e., a partial trioctahedral and dioctahedral nature.

655

656   The fundamental bending modes of the octahedral cation-OH bonds occur

657   between 600 and 1000 cm^{-1}. All of the Fe(III)-bearing samples have a broad band

658   near 845cm^{-1} that does not manifest in the Fe(II)-bearing samples. This bending

659   feature is assigned to Fe(III)$_2$-OH in the dioctahedral samples and Fe-Mg-OH in the

660   trioctahedral Fe(III)-bearing samples (Keeling et al. 2000; Gates 2005). The peak

661   center shifts to shorter wavenumbers as the Mg content of the samples increase and

662   the Fe content decreases (Figure 8c). Samples A-D also have a have a shallow, broad

663   peak near 906 cm^{-1} which is attributed to the Al-OH-Fe(III) bending mode (Andrieux

664   and Petit 2010).

665

666   Samples A – G have a low-intensity, very broad plateau between 745-802 cm^{-1}

667   caused by overlapping contributions of OH bending modes and tetrahedral Si

668   vibrations (Gates 2005). The shoulders are better resolved as a function of

669   increasing Fe content; the bands associated with the feature are the Fe-Al-OH and

670   Fe-Mg-OH bends, which are broadened by lattice deformations caused by irregular

671   cation substitution (Grauby et al. 1994; Gates 2005; Andrieux and Petit 2010).

672   All samples save O and N exhibit a weak Fe-O out of plane bending mode between

673   octahedral Fe and Al and the bridging oxygen that contributes to an asymmetrical,

674   broad peak around 687cm^{-1} (Grauby et al. 1994; Gates 2005). This feature overlaps

675   with the Mg-Mg-OH bend that occurs closer to 630cm^{-1}, which is most apparent in

676   samples H, J.

677

678   3.5. Raman Spectroscopy

679

680   Raman spectroscopy probes the vibrational modes within the mineral structure,

681   similar to IR spectroscopy methods, but not all bond structures are active in both

682   the IR and Raman, so the two methods are frequently complementary. Like IR

683   measurements, Raman spectroscopy is useful for identifying the stretching and

684   bending modes of the octahedral M-OH interactions and the tetrahedral silicate

685   structure. Smectite clays do not generally have strong Raman responses, due to the

686   low crystallinity and small grain sizes that characterize clay minerals. In particular,

687   the Fe(II)-bearing samples in this study have lower measured intensities and

688   greater photoluminescence effects that obscure features relative to the Fe(III)-

689   bearing samples.

690

691   3.5.1. 532nm Green Raman

692

693   The Raman spectra produced using the 532nm excitation laser are shown in

694   Figure 9. Most of the Raman peaks between 100 and 1100 cm^{-1} contain information

695   about the tetrahedral bonds (Figure 9b). All of the samples have a peak near 185 cm^{-}

696   ^{1}. It is sharply defined in the Fe(III) bearing samples and sample P, and is detectable

697   but weaker in samples with increasing Fe(II) content. There is not a significant

698   positional change as a function of composition (Figure 9d). Similar peaks near

699   187cm^{-1} observed in other nontronites were ascribed to an octahedral asymmetric

700   Fe(III)$_{oct}$-O$_{tet}$ stretching vibration (Frost and Kloprogge 2000a).

701

702   A pair of bands at 245 and 280 cm^{-1} occur in all of the Fe(III)-bearing samples

703   (Figure 9b). In Fe(III)-rich samples, both peaks are evident, and the 245 cm^{-1} peak is

704   better resolved, whereas in the trioctahedral sample J only the 280 cm^{-1} peak is

705   detected. The intensity and FWHM of the 245 cm^{-1} peak decreases as Mg content

706   increases. In the Fe(II)-bearing samples, peaks around 255cm^{-1} are poorly resolved

707   in samples O and M, but the signal intensity in all of the Fe(II)-bearing clays make

708   identification challenging. These features are attributed to a lattice deformation

709   between the non-bridging oxygen atoms within the tetrahedral structure and the

710   octahedral OH molecules (Frost and Kloprogge 2000a).

31

711

712   Peaks observed in the Fe(III) samples at 360, 465, and 676-687 cm^{-1} (Figure 9b) are

713   all associated with vibrational modes of the SiO_4 unit (Frost and Kloprogge 2000a).

714   The peak at 465 cm^{-1} can be resolved in all samples, although it is much weaker in

715   the Fe(II)-bearing samples due overlapping features at higher Raman shift, and does

716   not show a compositional dependence. The 465cm^{-1}feature is attributed to the Si-O

717   bending mode in the tetrahedral sheets. The $\sim$680cm^{-1} feature in shifts in position

718   from longer to shorter wavenumbers as a function of decreasing Fe(III) content, and

719   occurs only as a weak shoulder in the Fe(II) bearing samples except in sample P

720   where it is well resolved. The 680cm^{-1} is attributed to Fe(III)-Si-O bending modes

721   between the octahedral and tetrahedral sheets.

722

723   Samples J and H have a sharply defined peak at 432cm^{-1} that is much weaker in the

724   rest of the Fe(III)-bearing samples and is not well resolved in the Fe(II)-bearing

725   samples (Figure 9b). It is plausible that this is a Mg-related feature, i.e. Mg-O or Mg-

726   OH, given that these two samples tend to exhibit Mg-related features in the IR that

727   are not observed in the other more Fe-rich samples. There is also a broad

728   absorption near 510cm^{-1} that is detected in all of the Fe(III)-bearing samples except

729   J, and is best defined in the aluminous-Fe(III) bearing samples. Its presence cannot

730   be confirmed in the Fe(II)-bearing samples due to a very broad peak around 600cm^{-}

731   ^{1}, which is the strongest feature in these samples. Weaker peaks around 600 cm^{-1}

732   are also detected in most of the Fe(III) bearing samples. The peak position of the

733   600cm^{-1} peak shifts to shorter wavenumbers with increasing Fe content, although

734   the trend is weak, and there is not a systematic variation in the 510cm^{-1} band

735   position as a function of composition. Due to the compositional dependencies, both

736   of these feature may be related to Fe and Al within the crystal structure (Bishop and

737   Murad 2004; Wang et al. 2015).

738

739   The octahedral bonds in phyllosilicates are weaker Raman scatters than the

740   tetrahedral silicate structures (Wang et al. 2015). Between 800-1000cm^{-1} there is

741   very low signal to noise and very broad features that are tentatively attributed to M-

742   OH bending modes (Bishop and Murad 2004) (Figure 9b). In samples A-F, there is a

743   shoulder feature near 885cm^{-1}, and in samples D, E and F the hump center shifts

744   towards 920cm^{-1}. Samples K-O also have very weak, broad features centered near

745   920cm^{-1}. These features may be consistent with the Al-Fe(III)-OH and Al-Al-OH

746   bending modes, respectively (Bishop and Murad 2004). The signal to noise is

747   insufficient to positively identify other features, as laser interference patterns,

748   particularly apparent in J and H, are on a similar intensity scale (Figure 9b).

749

750   The metal-OH stretching modes show a distinct compositional trend, and occur

751   between Raman shifts of 3500-3700 cm^{-1} as broad envelopes of overlapping peaks

752   (Figure 9c). Broader peaks caused by the Al-FeOH and Fe-FeOH stretches occur at

753   3630 and 3570 cm^{-1}, respectively, and are detected to varying degrees in all samples

754   except sample J. Sample P is the only Fe(II) bearing samples with detectable

755   stretching modes due to significant photoluminescence that dominated much of the

756   spectral range in the rest of the samples. Sample P has an overall shape consistent

33

757   with the Mg-rich samples H and J with the Mg-OH related shoulder at 3685 cm^{-1},

758   although the spectral contrast is reduced compared to the Fe(III)-bearing samples. A

759   low, broad hump centered at 3400 cm^{-1} in most of the samples is attributed to an

760   H$_2$O stretching mode, consistent with a hydrated interlayer, and is particularly

761   apparent in samples H, I, J and K (de Ligny et al.,2013).

762

763   3.5.2.   248nm Deep-UV Raman

764

765   The DUV Raman spectra of the synthetic smectites (Figure 10a) begin at 800cm^{-1}

766   due to the use of an edge filter to suppress a second laser emission line at 700 cm^{-1}

767   (252.9 nm). Therefore, any lattice modes of tetrahedral SiO$_4$ unit or octahedral M-

768   OH bending modes between 100-800cm^{-1} are not recorded. Every sample has a

769   broad (FWHM of 120-300 cm^{-1}) peak feature at approximately 1065cm^{-1}, attributed

770   to a Si-O stretching mode (Figure 10c). This peak varies between about 1055 and

771   1070cm^{-1}; although the Fe(III)-bearing samples do not demonstrate a clear

772   compositional trend, the Fe(II)-bearing samples show a shift to longer wavelengths

773   with increasing octahedral iron content. The presence of Fe in the samples also had

774   a marked impact on the measured Raman intensity of this Si-O stretch; a clear trend

775   is seen in the integrated peak intensity (after normalization to an internal standard,

776   the atmospheric N$_2$ signal), which decreased with increasing Fe content (Figure

777   10d). This is not unexpected, as smectites are known to have UV absorption bands

778   that are highly dependent on the concentration of octahedral Fe, particularly at

779   ~250 nm, very close to the laser excitation wavelength (Chen *et al.*, 1979). However,

780   both samples J and O show less intensity than the trend would predict for Fe-poor

781   smectite. The intensity of sample P is also compromised by a strong Raman

782   reflectance peak near 1075cm^{-1} caused by minor calcite contamination that formed

783   after synthesis.

784

785   The Metal-OH stretching modes show demonstrable compositional trends (Figure

786   10b, 10e), and unlike in the Green Raman spectra, the Fe(II) bearing smectite

787   spectra are not photoluminescence dominated, such that stretching modes can be

788   detected. Samples J, P, O and N have a broad, multi-modal peak between 3300 and

789   3700 cm^{-1} consistent with the stretching mode of interlayer H_2O. These samples also

790   have distinct shoulders or superimposed peaks around 3660 and 3700cm^{-1}, which,

791   although shifted, are attributed to Mg and Al-OH stretching modes. Fe(III)-bearing

792   samples A-I, and Fe(II)-bearing samples K, L and M all have low intensity peaks that

793   vary between 3560 and 3620cm^{-1} with no systematic dependence on Fe or Al

794   content. This feature is attributed to Fe-OH stretching, although there is not a clear

795   distinction between Fe(III) and Fe(II) bonds.

796

797   A minor peak is observed at ~1600 cm^{-1} in all samples, although the intensity

798   relative to the 1050cm^{-1} peak varies widely and shows non-systematic

799   compositional trends (Figure 10a). This peak is not easily assigned, as few studies

800   for which Raman spectra are reported for smectites and other clay minerals have

801   considered the 1400-3000 cm^{-1} region (Frost and Kloprogge 2000; Wang et al.

802   2015). The peak occurs in the same frequency range as either an H_2O bending mode

803   or the C=C stretching mode (Ferrari and Robertson 2001; Bishop and Murad 2004;

804   Socrates 2004), e.g., the 'G' band of carbonaceous material (Schopf et al. 2005;

805   Quirico et al. 2009). As the H_2O content does not show large variation in the IR or

806   Green Raman measurements, we tentatively assign the strongest $\sim1600cm^{-1}$ peaks

807   to a possible organic contaminant, which may have been picked up during handling.

808   Although a corresponding peak is not definitively observed under 532 nm excitation

809   in samples other than P, N and M, selective detection of carbon-rich contaminants

810   using 248 nm excitation can be attributed to resonant enhancement of C=C

811   vibrations associated with π-π^* absorption in the UV(Asher and Johnson 1984;

812   Beegle et al. 2015; Sapers et al. 2019). Previous studies using the same UV Raman

813   instrument have shown that the resonant Raman scattering from certain carbon-

814   rich compounds, such as polycyclic aromatics, can be detected at concentrations as

815   low as 0.1 ppm within mineral matrices (Abbey et al. 2017).

816

817   3.6. Mössbauer Spectroscopy

818

819   The significant difference in isomer shift between ferrous and ferric iron make

820   Mössbauer spectroscopy a useful technique to determine iron oxidation state. In

821   general, a Mössbauer spectrum will display a quadrupole doublet for each type of

822   coordination environment. The center of the two lines, the isomer shift, is

823   dependent on various factors of which oxidation state and coordination geometry

824   are most important in clays. In addition to the isomer shift, information about the

825   electric field gradient can be gleaned from the quadrupole splitting (ΔE_Q), which can

826   be used to distinguish different coordination environments.

827

828   Mössbauer data were collected on 11 out of 16 species (Figure 11). Data

829   collection of samples G-J and P was hampered by the low concentrations of iron,

830   especially because samples were not synthesized using [57]Fe doped material. The

831   Mössbauer spectra collected for samples A-F show either an unresolved quadrupole

832   doublet or quadrupole doublets with a small quadrupole splitting (Figure 11a). The

833   small quadrupole splitting for these samples is characteristic of high-spin Fe(III) in

834   an octahedral coordination environment. Although the spectra of A-F are broad,

835   they can be fit well with a single quadrupole doublet with isomer shifts between

836   0.34 and 0.36 mm s^{-1} (Table 5). These isomer shifts are characteristic of octahedral

837   Fe(III) sites (Burns, 1994) and within the range of Fe(III) smectites (0.33-0.37 mm s^{-1}

838   ) (Murad and Schwertmann 1984; Treiman et al. 2014). No ferrous material is

839   present based on the absence of quadrupole doublets with an isomer shift above 1.0

840   mm s^{-1} (Chemtob et al. 2015). For sample A, an improved fit was obtained with a

841   small tetrahedral site Fe component (7.5%), resulting in an isomer shift of 0.25 and

842   quadrupole splitting of 1.50, but the large overlap between peaks also produced

843   high uncertainty.

844

845   The Mössbauer spectra collected for K-O show a quadrupole doublet centered

846   between 1.10 and 1.15 mm s^{-1} characteristic for octahedral Fe(II) and a smaller

847   broad unresolved quadrupole doublet due to Fe(III) (Figure 10b, Table 5). Most

848   spectra of K-O can be fit with well with a single quadrupole doublet with linewidths

849   between 0.4-0.5 mm s^{-1}. The high isomer shifts observed (>1 mm s^{-1}) are

850   characteristic of octahedral Fe(II) sites and are comparable to those observed for

851   similar Fe(II) smectites (Chemtob et al. 2015). Although the spectra recorded by our

852   other techniques show distinct difference upon changing the iron ratio, the

853   quadrupole splitting and isomer shifts (Table 5, and Figure 10c, 10d) do not show

854   any consistent variation with increasing or decreasing Fe content. The absence of

855   any systematic variation with Fe content is consistent with Mössbauer observations

856   made for the jarosite family (McCollom et al. 2014) and for Fe(II) smectites by

857   Chemtob *et al* 2015.

858

859   Fitting the areas of the doublets yields Fe(II)/Fe(III) ratios in close agreement

860   with those determined by other techniques (Table 5). The ratios of samples K and L

861   deviate more, which is likely due to oxidation during storage or the handling

862   process of these samples. The Fe(II) ratio measured in sample K decreased between

863   subsequent measurements before and after the sample was handled in air (Figure

864   S1). Due to the oxidation, the ratios only represent a lower bound on the Fe(II)

865   content at the time of synthesis.

866

867   As Mössbauer spectra of Fe phases typically have temperature dependent effects

868   and the temperature of sample measurement can vary under planetary conditions,

869   we investigated the temperature dependency on the isomer shift two samples,

870   Fe(III)-bearing sample A and Fe(II)-bearing K. Spectra were recorded between 80 and

871   320 K (Figure 12). In line with work on octahedral Fe(III) by *e.g.* DeGraven and Alboom

872   (1991),the isomer shift of both samples exhibits a dramatic decrease of 0.14 mm s^{-1} upon

873   cooling the samples from 320 to 80K (Table 6). The difference of 0.1 mm s^{-1} between

874   293 K and 80 K is the same that observed for certain nontronites (Murad et al. 1987). No

875   additional hyperfine features were resolved at lower temperatures and therefore the other

876   samples were collected at room temperature, which is also consistent with previous

877   studies (Chemtob et al., 2015, McCollom et al., 2014, Morris et al., 2006).

878

879   4.   Implications for planetary remote sensing and in-situ exploration

880

881   This study demonstrates the synergies and limits of multiple measurement types

882   for the detection of smectite chemistry and oxidation state on planetary surfaces to

883   infer past geochemical conditions. Reflectance spectroscopy has previously been

884   shown to detect alteration minerals, including smectite clays, at levels ~10% in

885   natural mineral assemblages (Ehlmann et al. 2012; Greenberger et al. 2012). We

886   demonstrate that smectite composition and the dominant oxidation state of Fe in

887   the octahedral state can be identified in the near infrared on the basis of their metal-

888   OH vibrational modes. The 2.0-3μm region is particularly useful. The fundamental

889   M-OH stretching modes between 2.6-2.9μm vary systematically with chemistry, and

890   the metal-OH minimum wavelength increases for smectites with Mg, Al, Fe(II) and

891   Fe(III) respectively. Smectites dominated by Mg or Fe(III) are spectrally distinct,

892   whereas Al-rich and Fe(II) rich smectites both have minima near 2.76 (Figure 7).

893   This absorption has been interpreted to represent Al phyllosilicates in Ceres bright

894   spots (De Sanctis et al. 2016), but our study shows that the spectral pattern would

895   also be consistent with the presence of Fe(II) smectites. Use of multiple wavelength

896   regions in the NIR can yield unique solutions, if overtone and combination

897   absorptions are present in remotely sensed data. The ~2.24 µm absorption tracks

898   Mg substitution well, and the M-OH feature near 2.32 is diagnostic of Fe(III) vs.

899   Fe(II), shifting considerably with Mg substitution in Fe(II) smectites only (Figure 5).

900   This multiple wavelength approach extends previous analyses of the 2.3 µm's

901   variation with octahedral sheet occupancy and iron content (Michalski et al., 2015).

902   The overtone and fundamental H_2O stretches at 1.9 and 3µm provide additional

903   information on the degree of hydration in smectites. The visible wavelength region

904   can provide qualitative auxiliary information about Fe oxidation, but the electronic

905   absorptions observed between 0.4-1 µm are not unique to smectite clays, so the M-

906   OH features are more diagnostic of smectite speciation, particularly in mineral

907   assemblages.

908

909   As instrument builders consider implementation approaches, spatial and spectral

910   resolution, as well as signal-to-noise (SNR), are key considerations to enable

911   discrimination of the diagnostic absorptions. Many NIR reflectance spectrometers,

912   such as the Mars Express/OMEGA, MRO/CRISM, Dawn/VIR, Osiris-Rex/OVIRS and

913   Cassini/VIMS, are sensitive from ~1-4/5µm with sufficient spectral resolution to

914   distinguish the features discussed above, and provide global views of planetary

915   surfaces at relatively large pixel footprints between tens and hundreds of meters

916   square. Higher spatial resolution, of course, allows mineral identifications to be

917   better associated with particular strata or geomorphic features, improving geologic

918   interpretations and providing further constraints on alteration environments.

919   Detailed analysis of spectral variation on the hand-sample scale (mm-cm) is

920   particularly useful to identify alteration textures and spatial patterns, all of which

921   provide key context in understanding the alteration environment. Such fine

922   resolution VNIR spectral analysis will be employed for the first time on Mars

923   onboard the Mars-2020 rover by the SuperCam instrument (Wiens et al. 2017) and

924   on the Exo-Mars rover by Ma_MISS (De Sanctis et al. 2017) and micrOmega (Bibring

925   et al. 2017).

926

927   In the mid-infrared, the silicate stretching and bending modes active in smectite

928   clays are common to other silicates as well, and the M-OH bending modes are

929   discernable but overlap and combine, making direct identification of a particular

930   smectite species challenging, particularly if the measurement is of a bulk mineral

931   assemblage. Michalski et al. (2005) demonstrated how the Si-O and M-O bends

932   changed in character between dioctahedral and trioctahedral smectites. Here we

933   demonstrate that the 450 cm^{-1} absorption systematically varies in position with

934   octahedral Fe(III) and Fe(II) content, although other information from the VNIR (or

935   Mössbauer in-situ) must be brought to bear to determine the oxidation state and the

936   the relationship between absorption position and Fe content (Figure 8b). The Mars

937   Global Surveyor Thermal Emission Spectrometer (TES) and Mars Exploration Rover

938   Mini-TES thermal emission instruments in orbit around and on the surface of Mars,

939   respectively, have been used with this multi-instrument approach to conduct

41

940   surveys with other orbiting or payload elements specifically characterizing smectite

941   minerals and alteration phases (Michalski et al. 2006, 2010; Ruff and Christensen

942   2007). OTES on Osiris-REX, along with OVIRS, is also characterizing the

943   phyllosilicates on the asteroid Bennu (Hamilton et al., 2019). With our expanded

944   spectral libraries, more refined characterization of smectites from MIR data is now

945   possible.

946

947   Raman spectroscopy is a new addition to planetary science instrumentation, and

948   is opening new avenues for in-situ remote mineralogical analysis of planetary

949   surfaces, as well as the detection of organic components. The green Raman

950   SuperCam Raman system is designed to obtain patterns from several meters distant

951   to the target from on the mast of the Mars 2020 rover (Wiens et al. 2017), and the

952   deep-UV Raman SHERLOC system will interrogate rock surfaces on the micrometer

953   scale from its position on the Mars 2020 rover arm (Beegle et al. 2017). Our data

954   provides the first Raman spectral libraries as a function of their chemistry (Figure 9,

955   10). Precise identification of smectite clays, and clay minerals in general, will likely

956   be a challenge in natural mineral assemblages due to the generally low Raman

957   intensities inherent to clay minerals and sensitivity to complex lattice variation.

958   However, the M-OH stretching modes between 3000-4000cm^{-1} in both Green and

959   Deep UV Raman data sets will useful for identifying phyllosilicates and qualitatively

960   judging their composition. In both Raman excitation modes, it is possible in some

961   cases to detect the Fe(III), Al, and Mg-OH stretching modes, although intensity

962   decreases significantly as Fe content increases. The M-OH bending modes and

42

963   silicate features between 400-1000cm^{-1} require high signal to noise to be

964   distinguished, and are likely to be overlapping with more crystalline phases in

965   natural mineral assemblages that would mask phyllosilicate detection.

966   Photoluminescence, which is frequently much stronger than Raman signal, is also a

967   likely obstacle in identifying mineral assemblages on planetary surfaces; Fe(II)

968   bearing smectites are apparently more susceptible to photoluminescence when

969   using a 532nm excitation laser than DUV (Figure 10). Carrying more than one

970   excitation laser, as the Mars 2020 rover is planning, may help mitigate

971   photoluminescence concerns, as switching wavelengths can reduce the effect for a

972   given material. Thus, Raman is best used in concert with other approaches for

973   characterization smectite-bearing mineral assemblages.

974

975   In-situ XRD analyses offer the most quantitative means to measure the absolute

976   abundance of smectite clays and their coordination (Figure 3). The Chemistry and

977   Mineralogy Analyzer instrument (CheMin), an X-Ray diffractometer onboard the

978   Mars Science Laboratory rover Curiosity, has demonstrated the common occurrence

979   of smectite clays in the sedimentary deposits within Gale Crater (Vaniman et al.

980   2013; Bristow et al. 2018). Notably, our sample set of synthetic smectites have peak

981   positions, as corrected for measurements using Co Ka radiation (Table 2), that cover

982   the full range of observations of martian smectites in Gale crater (Vaniman et al.

983   2013; Treiman et al. 2014; Bristow et al. 2018). This demonstrates that, potentially,

984   the compositions of the data set presented here is representative of the martian

985   samples, and that all martian observations can be consistent with the presence of a

986   single smectite, and that mixtures of dioctahedral and trioctahedral phases are not

987   required to describe the features observed (e.g., Bristow et al., 2018). The CheMin

988   instrument requires the use of the position of the (02,11) peak to calculate the

989   octahedral site occupancy of smectites measured in Gale Crater, Mars, as the (06,33)

990   peak occurs outside the diffraction range. Our results demonstrate that it is critical

991   to recognize that peak positions of the (02,11) bands produce substantial systematic

992   errors if used to obtain lattice parameters of smectites. Use of the (06,33) band peak

993   positions, widely employed in terrestrial studies of clays but inaccessible by the

994   ChemMin instrument on MSL, yields an order of magnitude smaller systematic

995   error. Thus, as with prior investigations, our study shows the value of incorporating

996   the (06,33) peak into instrument diffraction ranges in order to best distinguish

997   dioctahedral and trioctahedral smectites. In most laboratory settings, clay mineral

998   fractions are separated from the rest of the sample, making measurements more

999   straightforward, but martian samples are measured in bulk, which can further

1000   obfuscate precise analysis and calculation of lattice parameters. Consequently,

1001   identifications of specific phyllosilicate phases are most easily made when applying

1002   secondary information. On the Curiosity rover, this is water release temperature

1003   from Evolved Gas Analysis with the SAM instrument (Bristow et al. 2015). VNIR,

1004   MIR and Mössbauer are also highly synergistic because they provide information on

1005   the Fe oxidation state that XRD alone cannot.

1006

1007   Mössbauer spectra can aid in confirming detections of smectite minerals using

1008   the measured isomer shifts and patterns in quadrupole splittings. Particularly,

44

1009   Mössbauer measurements provide a quantitative and highly sensitive means to

1010   determine Fe(II)/Fe(III) ratios better all other analysis techniques discussed here,

1011   but do not demonstrate uniquely identifying patterns that distinguish smectites of

1012   varying quantitative Fe content from one another. Consequently, Mössbauer

1013   spectroscopy is best utilized in conjunction with other in-situ approaches to

1014   examine alteration mineralogy. The Mössbauer parameters reported here, derived

1015   from room temperature measurements, can be used in direct comparison to extra-

1016   terrestrial Mössbauer measurements, despite overall ambient temperature

1017   differences between the library and in-situ measurements (Morris et. al., 2006). The

1018   temperature dependence derives from the temperature gradient between the

1019   sample and source, which while highlighting hyperfine structures, renders

1020   comparisons to measurements under different temperature gradient conditions ill-

1021   posed. However, Mössbauer measurements made in extra-terrestrial settings, such

1022   as by the Mars Exploration Rovers, have kept both the source and samples

1023   (planetary surfaces) at the same ambient temperature. Our measurements also have

1024   a negligible temperature difference between source and sample measured at room

1025   temperature, so we thus mitigate the temperature dependencies of the derived

1026   parameters, creating a database for application to determination of smectite

1027   presence and Fe.

1028

1029   Collectively, the data presented here are foundational for the study of smectite clays

1030   across the solar system. The ability to determine the coordination, crystal chemistry,

1031   and oxidation state will enable new insights into the geological and environmental

1032   evolution of planetary bodies.

1033

1034

1035   5. Acknowledgements

1041

1042

1043   6. References

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1406   Tables
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1408   Table 1. Calculated molecular formulas of synthetic intermediate smectite samples.

Sample	Calculated Formula	Octahedral Occupancy	%Fe(II)^a
A	$Ca_{0.37}Na_{0.10}[Fe^{III}_{1.68}Mg_{0.40}][Si_{3.32}Al_{0.51}Fe^{III}_{0.17}]O_{10}(OH)_2$	2.08	-
B	$Ca_{0.28}[Fe^{III}_{1.54}Mg_{0.64}][Si_{3.55}Al_{0.39}Fe^{III}_{0.06}]O_{10}(OH)_2$	2.18	-
C	$Ca_{0.35}Na_{0.22}[Fe^{III}_{1.24}Mg_{0.37}Al_{0.39}][Si_{3.43}Al_{0.57}]O_{10}(OH)_2$	2.00	-
D	$Ca_{0.35}Na_{0.23}[Fe^{III}_{1.04}Mg_{0.46}Al_{0.53}][Si_{3.44}Al_{0.56}]O_{10}(OH)_2$	2.03	-
E	$Ca_{0.40}[Fe^{III}_{1.06}Mg_{0.93}Al_{0.15}][Si_{3.70}Al_{0.30}]O_{10}(OH)_2$	2.14	-
F	$Ca_{0.35}Na_{0.07}[Fe^{III}_{0.96}Mg_{0.84}Al_{0.29}][Si_{3.80}Al_{0.20}]O_{10}(OH)_2$	2.09	-
G	$Ca_{0.24}[Fe^{III}_{0.69}Mg_{1.12}Al_{0.52}][Si_{3.66}Al_{0.34}]O_{10}(OH)_2$	2.33	-
H	$Ca_{0.39}[Fe^{III}_{0.68}Mg_{1.75}Al_{0.02}][Si_{3.60}Al_{0.40}]O_{10}(OH)_2$	2.45	-
I	$Ca_{0.31}Na_{0.28}[Fe^{III}_{0.57}Mg_{0.92}Al_{0.63}][Si_{3.67}Al_{0.33}]O_{10}(OH)_2$	2.12	-

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J	$Ca_{0.37}[Fe^{III}_{0.27}Mg_{2.31}Al_{0.08}][Si_{3.60}Al_{0.40}]O_{10}(OH)_2$	2.66	-
K	$Ca_{0.23}[Fe^{II}_{2.23}Fe^{III}_{0.28}Al_{0.26}Mg_{0.12}][Si_{3.51}Al_{0.49}]O_{10}(OH)_2$	2.89	89.0
L	$Ca_{0.30}[Fe^{II}_{1.43}Fe^{III}_{0.23}Al_{0.40}Mg_{0.66}][Si_{3.55}Al_{0.45}]O_{10}(OH)_2$	2.72	86.0
M	$Ca_{0.29}Na_{0.05}[Fe^{II}_{1.50}Fe^{III}_{0.11}Al_{0.29}Mg_{0.92}][Si_{3.46}Al_{0.54}]O_{10}(OH)_2$	2.81	93.1
N	$Ca_{0.27}Na_{0.08}[Fe^{II}_{0.80}Fe^{III}_{0.09}Al_{1.29}Mg_{0.10}][Si_{3.54}Al_{0.46}]O_{10}(OH)_2$	2.28	90.0
O	$Ca_{0.28}Na_{0.12}[Fe^{II}_{0.64}Fe^{III}_{0.11}Al_{1.08}Mg_{0.50}][Si_{3.56}Al_{0.44}]O_{10}(OH)_2$	2.34	85.4
P	$Ca_{0.29}Na_{0.06}[Fe^{II}_{0.69}Fe^{III}_{0.11}Al_{0.35}Mg_{1.57}][Si_{3.57}Al_{0.43}]O_{10}(OH)_2$	2.72	86.6

1409   [a] Mol.% of total iron occurring as Fe(II); only measured for syntheses involving
1410   iron(II) chloride.
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1432   Table 2. Measured peak positions of diagnostic diffraction features of the synthetic
1433   smectites using Cu Kα and their calculated corresponding positions for
1434   measurements using Co Kα radiation.

Sample	°2θ Cu Kα			°2θ Co Kα		
	(001)	(02,11)	(06,33)	(001)	(02,11)	(06,33)
A	6.00(8)[a]	19.61(1)	60.856(8)	6.97	22.81	72.04
B	6.29(2)	19.71(1)	60.93(1)	7.30	22.93	72.14
C	5.99(8)	19.63(1)	60.800(9)	6.96	22.83	71.97
D	6.31(3)	19.64(1)	60.87(1)	7.33	22.84	72.06
E	6.04(6)	19.76(2)	60.843(8)	7.01	22.98	72.02
F	6.06(4)	19.71(1)	60.806(8)	7.04	22.93	71.98
G	6.10(1)	19.68(1)	60.86(2)	7.08	22.89	72.05
H	6.13(1)	19.63(1)	60.718(6)	7.12	22.83	71.87
I	6.51(2)	19.72(1)	60.807(9)	7.56	22.94	71.98
J	6.37(2)	19.50(1)	60.584(4)	7.40	22.68	71.70

K	5.36(5)	19.21(3)	59.37(2)[b]	6.22	22.35	70.20
L	5.2(1)	19.28(1)	60.019(8)	6.10	22.42	71.00
M	5.46(6)	19.32(2)	60.096(7)	6.34	22.47	71.10
N	5.7(1)	19.89(1)	61.13(4)[b]	6.63	23.13	72.38
O	5.6(1)	19.81(2)	60.84(3)[b]	6.51	23.04	72.01
P	5.7(9)	19.50(2)	60.42(1)	6.62	22.68	71.51

1435   [a] Numbers in parentheses represent fitting uncertainties in the last digit.
1436   b Peaks consist of doublets but fitted as single feature. When modeled as doublets,
1437   contain peaks at 58.32(14)° and 59.61(5)° for K, 60.42(12)° and 61.86(10)° for N,
1438   and 60.29(12)° and 61.65(18)° for O.
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1458   Table 3. Comparison between d-spacings as derived from the fitted lattice
1459   parameters and as calculated from observed peak positions.

Sample	$d_{(001)}$ (Å)		$d_{(02,11)}$ (Å)		$d_{(06,33)}$ (Å)	
	Lattice	Peak	Lattice	Peak	Lattice	Peak
A	14.9	14.7	4.57	4.53	1.526	1.522
B	14.2	14.0	4.55	4.50	1.524	1.520
C	14.6	14.7	4.58	4.52	1.528	1.523
D	14.0	14.0	4.57	4.52	1.526	1.522
E	14.8	14.6	4.56	4.49	1.527	1.522
F	14.7	14.6	4.57	4.50	1.528	1.523
G	14.7	14.5	4.57	4.51	1.526	1.522
H	14.6	14.4	4.58	4.52	1.530	1.525
I	14.0	13.6	4.56	4.50	1.528	1.523
J	13.0	13.9	4.60	4.55	1.533	1.528
K	16.5	16.5	4.66	4.62	1.552	1.557[a]
L	16.8	16.8	4.64	4.60	1.545	1.541
M	16.1	16.2	4.63	4.59	1.543	1.540

N	15.4	15.5	4.53	4.46	1.520	1.516 [a]
O	15.5	15.8	4.55	4.48	1.525	1.523 [a]
P	15.4	15.5	4.60	4.55	1.536	1.532

1460 [a] Determined from position when fitting with a single peak. Fitting (06,33) bands as
1461 a double yield d-spacings of 1.582 Å and 1.551 Å for K, 1.532 Å and 1.500 Å for N,
1462 and 1.535 Å and 1.504 Å for O.
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1486 Table 4. Lattice parameters derived from refinement to individual peaks assuming
1487 hexagonal sheet symmetry.

Sample	c (Å)	b (Å), (02,11)	b (Å), (06,33)
A	14.87(12) [a]	9.146(7)	9.158(10)
B	14.18(3)	9.103(7)	9.147(11)
C	14.57(23)	9.150(8)	9.168(2)
D	14.04(18)	9.130(7)	9.154(5)
E	14.79(33)	9.122(7)	9.161(4)
F	14.72(21)	9.134(6)	9.167(5)
G	14.70(3)	9.135(3)	9.154(3)
H	14.61(19)	9.156(4)	9.179(2)
I	13.95(43)	9.126(9)	9.169(2)
J	13.02(16)	9.194(3)	9.197(2)
K	16.52(9)	9.329(4)	9.310(17)
L	16.80(12)	9.274(6)	9.268(3)
M	16.11(11)	9.252(10)	9.259(41)
N	15.39(10)	9.063(29)	9.119(15)

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O	15.46(14)	9.102(13)	9.149(6)
P	15.35(12)	9.192(9)	9.217(2)

1488 ^{a} Numbers in parentheses represent fitting uncertainties in the last digit.

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1515   Table 5. Isomer shift and quadrupole splitting of the Fe-rich smectite samples.

Smectite	Fe^{II} δ (mm s^{-1})	Fe^{II} ΔE_Q (mm s^{-1})	Fe^{III} δ (mm s^{-1})	Fe^{III} ΔE_Q (mm s^{-1})	Fe^{II}/Fe^{III}
A	--	--	0.35 ± 0.02	0.61 ± 0.01	0
B	--	--	0.35 ± 0.02	0.61 ± 0.01	0
C	--	--	0.36 ± 0.02	0.64 ± 0.01	0
D	--	--	0.36 ± 0.02	0.67 ± 0.01	0
E	--	--	0.34 ± 0.02	0.59 ± 0.01	0
F	--	--	0.35 ± 0.02	0.60 ± 0.01	0
K	1.11 ± 0.02	2.53 ± 0.01	0.40 ± 0.02	0.77 ± 0.01	77.2
L	1.13 ± 0.02	2.59 ± 0.01	0.42 ± 0.02	0.61 ± 0.01	72.1
M	1.16 ± 0.02	2.54 ± 0.01	0.44 ± 0.02	0.58 ± 0.01	91.8

N	1.13 ± 0.02	2.63 ± 0.01	0.40 ± 0.02	0.55 ± 0.01	85.1
O	1.13 ± 0.02	2.61 ± 0.01	0.39 ± 0.02	0.55 ± 0.01	88.8

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1519 Table 6. Variation in the isomer shift in samples A and K as temperature is adjusted.
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Temperature (K)	δ (mm s^{-1}) – Sample A	δ (mm s^{-1}) – Sample K
80	0.46 ± 0.01	1.26 ± 0.01
120	0.44 ± 0.01	1.24 ± 0.01
160	0.43 ± 0.01	1.22 ± 0.01
200	0.41 ± 0.01	-
240	0.39 ± 0.01	-
280	0.37 ± 0.01	-
293	0.35 ± 0.01	-
310	0.35 ± 0.01	1.15 ± 0.01
320	0.33 ± 0.01	1.13 ± 0.01

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1528 Figure Captions
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1530 Figure 1: Terrestrial continental and marine smectite clay minerals span a wide

1531 range of bulk compositions [references 1-24]. Common smectite spectral standard

1532 samples are highlighted as open circles; Fe in these standards is predominantly in

1533 the 3+ oxidation state.

1534

1535 Figure 2. Ternary diagrams showing the compositions of 16 synthetic ferruginous

1536 smectite samples investigated in this study. The full structural composition is shown

1537   in the left diagram, whereas the right diagram shows the composition of the

1538   octahedral sheet only. Fe(III)-bearing samples are shown in brown circles. Fe(II)-

1539   bearing samples are shown in blue-green diamonds. Colors trend from light to dark

1540   with increasing octahedral Fe content. Colors are kept consistent in following

1541   figures. Small squares show the compositions of Clay Mineral society standards

1542   NAu-1, NAu-2, Ng-1, SWa-1, Sap-Ca1, SWy-1, SAz-1, STx-1b, SCa-3, SBId-1 that are

1543   frequently used as spectroscopic standards (Van Olphen et al., 1979, Post, 1984,

1544   Gates 2005, Gailhanou et al., 2012, Castellina et al., 2017).

1545

1546   Figure 3. (a) XRD patterns of the synthetic smectite samples. No background

1547   subtraction is performed to avoid aliasing broad features. (b) Peak positions of the

1548   (02,11) peaks and (c) of the 060 peak shift to smaller angles with decreasing Fe(III)

1549   content. (d) The calculated b-axis spacing based on fitting the (02, 11) peak with

1550   respect to octahedral occupancy; vertical lines delineate approximate distinctions

1551   between di, di-tri, and tri-octahedral structures. (e) Dioctahedral samples show little

1552   dependence of the d-spacing on octahedral iron content, although the trioctahedral

1553   Fe(II)-bearing samples show a more linear trend (trend lines fit only to the

1554   dioctahedral and trioctahedral samples, respectively).

1555

1556   Figure 4. Visible to near infrared reflectance spectra of (a) Fe(III) bearing smectite

1557   samples and (b) Fe(II) bearing smectite samples. (c) Continuum removed

1558   absorption features between 2.1 and 2.5 μm for all samples with wavelengths of

1559   overtones and combination absorptions from the literature indicated as detailed in

1560   the text.

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1562   Figure 5. Trends in the position and intensity of metal-OH combination absorptions.

1563   Larger data points indicate greater relative band depth of the absorption, from 0.01-

1564   0.34, and are relative across panels. a) Position of ~2.24μm absorptions as a

1565   function of octahedral magnesium. Absorptions at shorter wavelengths (~2.235μm)

1566   are attributed to Al-Mg-OH combination bands, whereas absorptions at longer

1567   wavelengths (~2.25μm) are attributed to Al-Fe(II)-OH combination bands. The

1568   samples with the highest Fe(III) content have low Al content and therefore have

1569   negligible Al-M-OH absorptions. Trend line is fit to both Fe(II) and Fe(III) bearing

1570   samples that have a measurable absorption. b) Position of the ~2.3 μm absorption

1571   as a function of octahedral Fe content. $Fe(II)_2$-OH combination modes trend towards

1572   2.36μm whereas $Fe(III)_2$-OH combination modes trend towards 2.29 μm. Mg-M-OH

1573   combinations trend towards 2.31 μm. c) Position of the ~2.45μm absorption as a

1574   function of octahedral Mg content. This feature is broad and shallow in the Fe(III)-

1575   bearing samples, without a significant trend, but the Fe(II)-bearing samples

1576   demonstrate a linear trend towards shorter wavelengths with increasing octahedral

1577   Mg content.

1578

1579   Figure 6. Attenuated Total Reflectance (ATR) spectra of the synthetic ferruginous

1580   smectite suite. (a) The hydroxyl bending modes and (b) the hydroxyl and

1581   tetrahedral stretching modes. Peak attributions are described in the text. The peak

1582   at ~850cm^{-1} in the shaded box is attributed to calcite contamination in sample P.

1583

1584   Figure 7. (a) Mid-infrared Diffuse Reflectance spectra of the M-OH stretching modes

1585   of the sample suite. The deep broad feature around 3μm is caused by the

1586   fundamental H_2O stretching mode, and the narrower absorptions superimposed are

1587   the M-OH absorptions. (b) The position of the M-OH absorption as a function of

1588   octahedral iron content. The minima of both sample sets shifts to longer

1589   wavelengths with increasing octahedral iron, but the Fe(II) and Fe(III) bearings

1590   samples are offset from each other.

1591

1592   Figure 8: (a) Mid-infrared Diffuse Reflectance spectra of the silicate bending and

1593   stretching and M-OH bending modes, scaled and offset to emphasize features. A

1594   peak attributed to calcite contamination in sample P is indicated by the translucent

1595   box. Other peak attributions are discussed in the text. (b) The position of the Si-O

1596   bend between 430-480cm^{-1} is dependent on octahedral Fe content, with decreasing

1597   iron shifting the peak position to longer wavenumbers. Fe(II) bearing samples are

1598   offset to longer wavenumbers than Fe(III)-bearing samples. (c)The Fe(III) samples

1599   show a Fe(III)$_2$-OH bending mode around 845 cm^{-1} that shifts in position as a

1600   function of octahedral iron. M-OH bending modes are much more subdued in the

1601   Fe(II) samples, although the Fe-OH and Mg-OH bends around 650 cm^{-1} are apparent

1602   in all samples. (d) The position of the Si-O stretch does not shift as a function of

1603   composition in the Fe(III)-bearing samples, but increasing Al content in the Fe(II)-

1604   bearings samples does shift this mode to larger wavenumbers. The trend line is only

1605   fit to the Fe(II) samples.

1606

1607   Figure 9. (a)Raman patterns obtained using a 532nm excitation laser. (b) Raman

1608   shifts between 100-1200 cm^{-1} highlight silicate stretching and bending modes and

1609   overlapping metal-OH bends. (c) Metal-OH stretching modes occur between 3000-

1610   4000cm^{-1}. Labeled features are discussed in the text.

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1612   Figure 10: (a) Raman spectra obtained using a 248.6 nm excitation laser from 700-

1613   4000cm^{-1}, and (b) the M-OH stretching region from 3000-4000cm^{-1}. (c) The Si-O

1614   stretching mode is detected around 1060cm^{-1} and (d) the normalized signal

1615   intensity decreases as Fe content increases, due to increased UV absorption. (e) The

1616   peak and shoulder positions of the Fe(II), Fe(III), Al and Mg-OH stretching modes

1617   shift as a function of composition.

1618

1619   Figure 11: Mössbauer spectra for (a) Fe(II)-bearing smectite samples A-F at room

1620   temperature and (b) of Fe(II)-bearing smectite samples K-O. The Isomer Shifts are

1621   shown as diamonds and the quadrupole splitting ΔE_Q is shown as circles for the (c)

1622   Fe(II)-bearing samples and (d) Fe(II)-bearing samples.

1623   Figure 12. The Isomer shift is temperature dependent. (a) Mössbauer spectra of 'A'

1624   collected from 80 to 320 K with 40 K intervals in black and the fit in red. The spectra

1625   are referenced to the centroid of the spectrum of a α-Fe foil at room temperature.

1626   (b) The isomer shift of A decreases as a function of increasing temperature. (c)

1627   Mössbauer spectra of sample K collected from 80 to 293 K. (d). The isomer shift of K

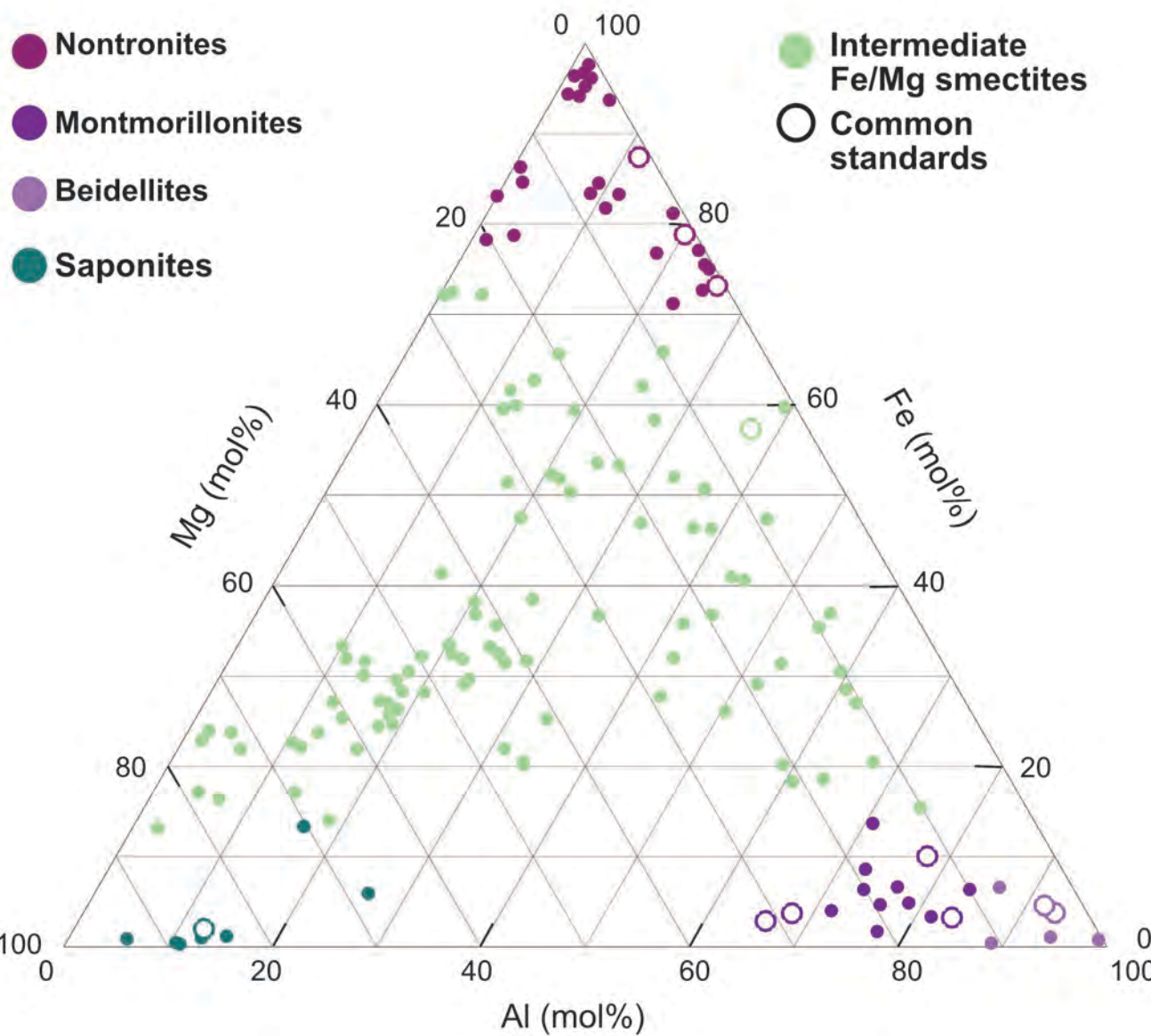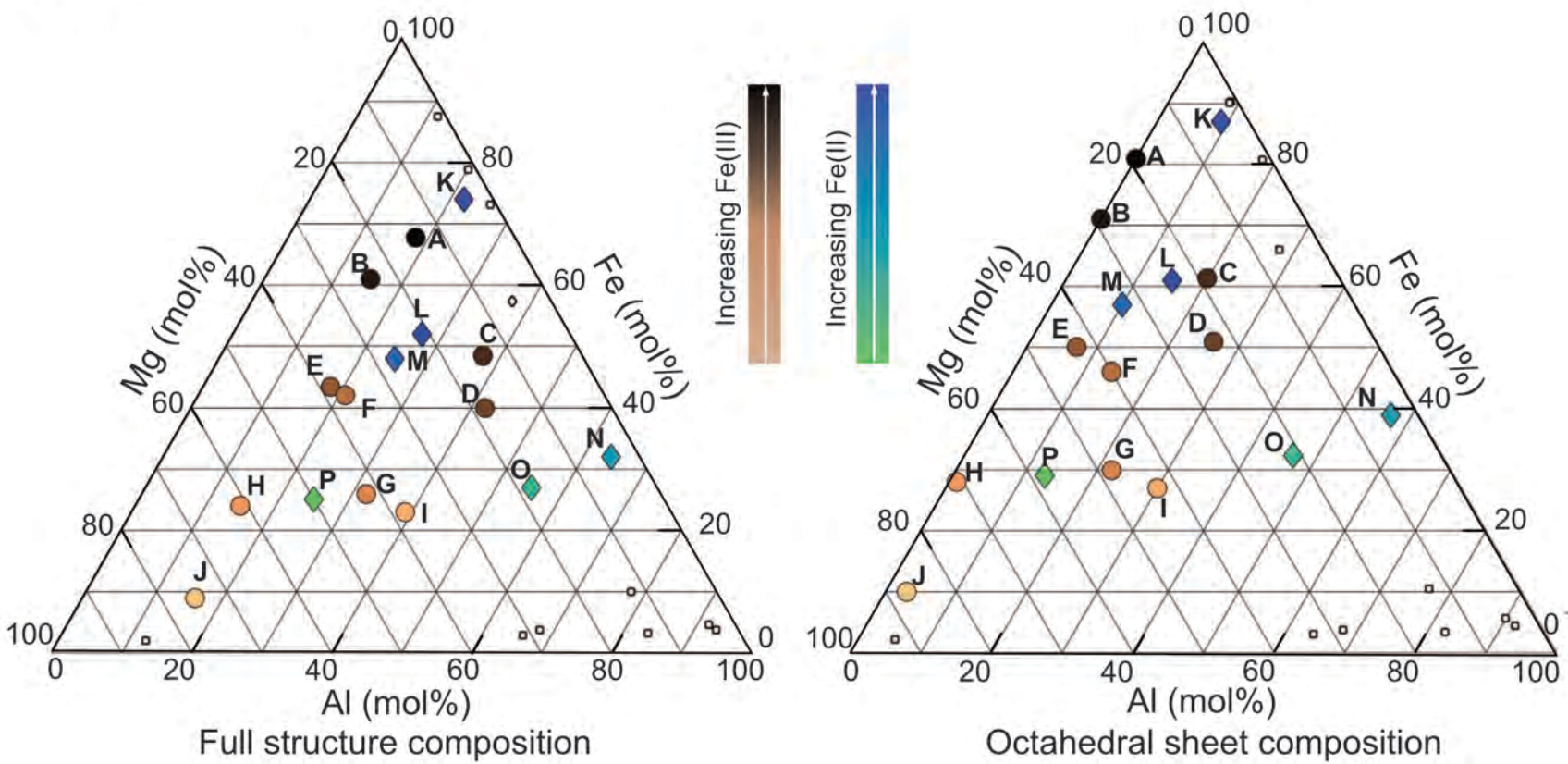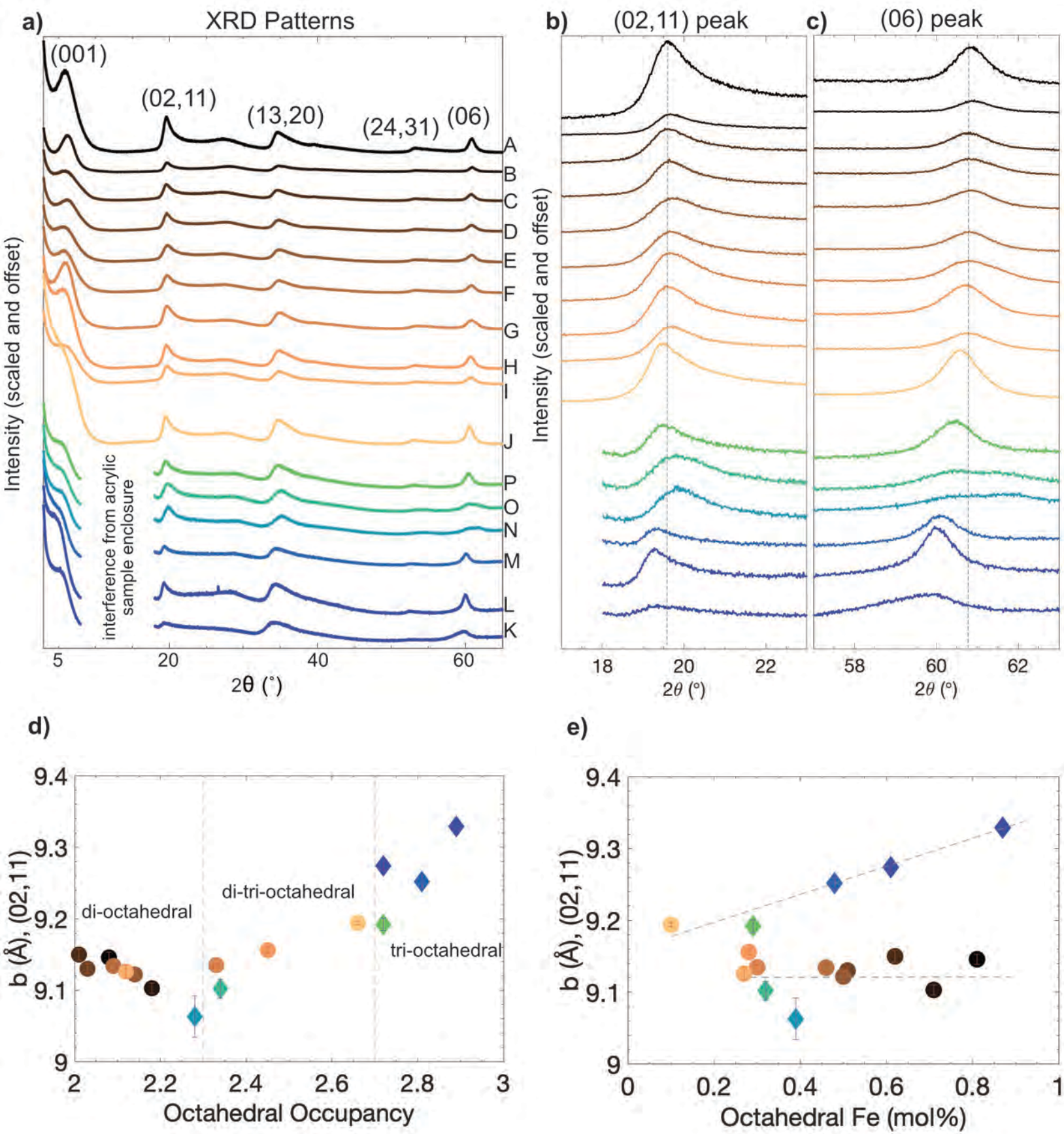1628   decreases as temperature increases.
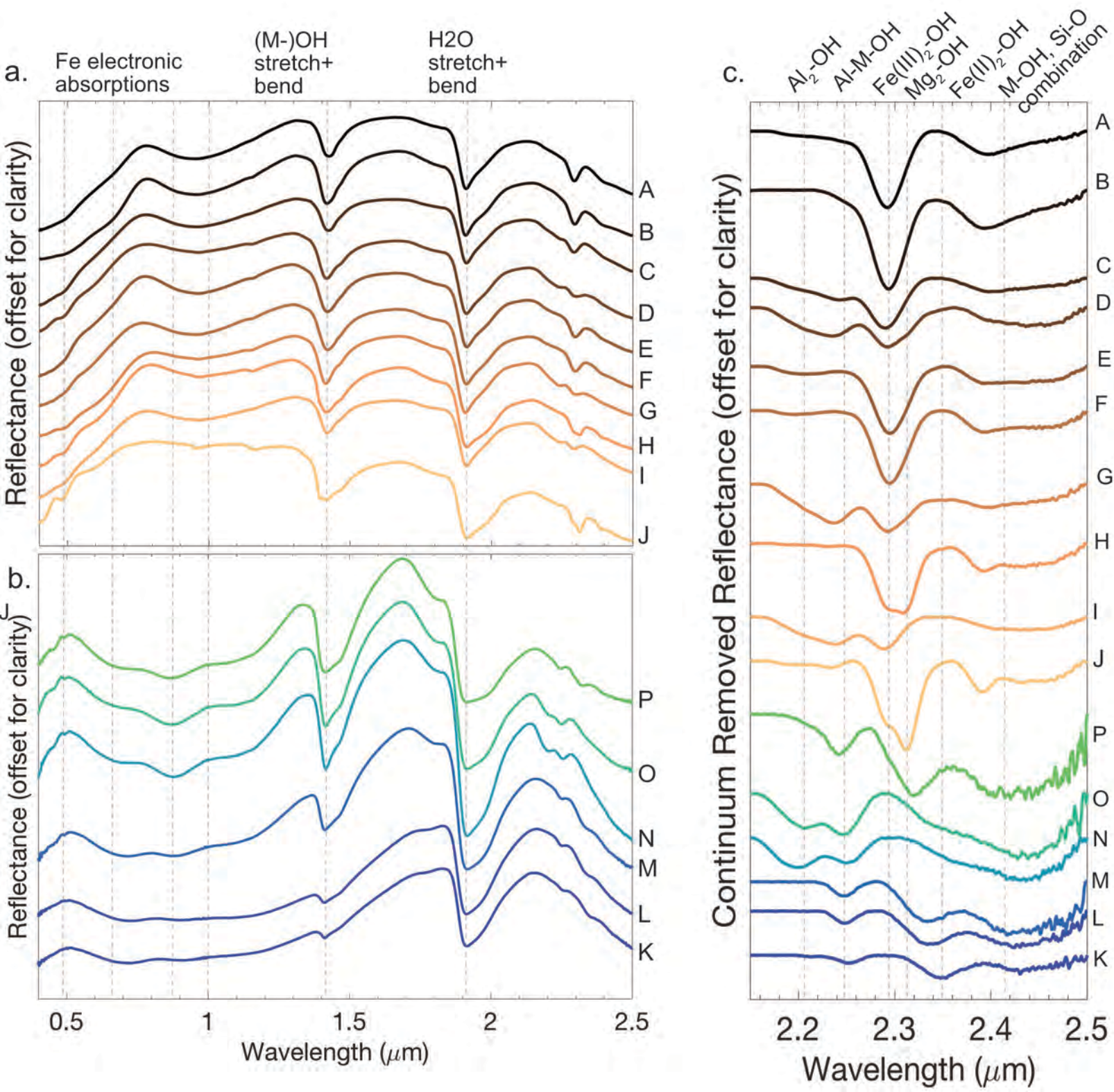
Figure 1

Figure 2

Full structure composition

Octahedral sheet composition

Figure 3.

a) XRD Patterns

(001) (02,11) (13,20) (24,31) (06)

interference from acrylic sample enclosure

2θ (°)

b) (02,11) peak

c) (06) peak

d)

di-octahedral   di-tri-octahedral

tri-octahedral

e)

Figure 4

a. Fe electronic absorptions (M-)OH stretch+ bend H2O stretch+ bend

c. Al$_2$-OH Al-M-OH Fe(III)$_2$-OH Mg$_2$-OH Fe(II)$_2$-OH M-OH, Si-O combination

Figure 5

Figure 6

Figure 7

a)

Reflectance (scaled and offset)

Fe(III)-OH

Mg-OH

H_2O stretch

Fe(II)-OH

A
B
C
D
E
F
G
H
I
J
P
O
N
M
L
K

Wavelength (μm)

b)

Absorption position

Fe(III)-bearing

Fe(II)-bearing

Fe (mol %)

Figure 8

Figure 9

a) Silicate stretching and bending, M-OH bending modes | M-OH stretching modes

b) 185 245 280 360 432 465 510 600 680 884 920

c) 3450 3575 3684

Scaled Counts (offset for clarity)

Raman Shift (cm^{-1})

photoluminescence interference

Figure 10

a)

Si-O stretch   N₂ interference   M-OH stretches

b)   M-OH stretches

A, B, C, D, E, F, G, H, I, J, P, O, N, M, L, K

Intensity (scaled and offset)

Raman shift (cm⁻¹)

c) Si-O stretch

d) Si-O stretch intensity

e) M-OH stretches

Wavenumber Position

Normalized Intensity

Wavenumber position

Octahedral Fe (mol%)

Figure 11

Figure 12