



Ambient and cold-temperature infrared spectra and XRD patterns of ammoniated phyllosilicates and carbonaceous chondrite meteorites relevant to Ceres and other solar system bodies

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(Received 02 June 2017; revision accepted 12 March 2018)

Abstract—Mg-phyllosilicate-bearing, dark surface materials on the dwarf planet Ceres have NH₄-bearing materials, indicated by a distinctive 3.06 μm absorption feature. To constrain the identity of the Ceres NH₄-carrier phase(s), we ammoniated ground particulates of candidate materials to compare their spectral properties to infrared data acquired by Dawn's Visible and Infrared (VIR) imaging spectrometer. We treated Mg-, Fe-, and Al-smectite clay minerals; Mg-serpentine; Mg-chlorite; and a suite of carbonaceous meteorites with NH₄-acetate to exchange ammonium. Serpentine and chlorites showed no evidence for ammoniation, as expected due to their lack of exchangeable interlayer sites. Most smectites showed evidence for ammoniation by incorporation of NH₄⁺ into their interlayers, resulting in the appearance of absorptions from 3.02 to 3.08 μm. Meteorite samples tested had weak absorptions between 3.0 and 3.1 μm but showed little clear evidence for enhancement upon ammoniation, likely due to the high proportion of serpentine and other minerals relative to expandable smectite phases or to NH₄⁺ complexing with organics or other constituents. The wavelength position of the smectite NH₄ absorption showed no variation between IR spectra acquired under dry-air purge at 25 °C and under vacuum at 25 °C to –180 °C. Collectively, data from the smectite samples show that the precise center wavelength of the characteristic ~3.05 μm ν₃ absorption in NH₄ is variable and is likely related to the degree of hydrogen bonding of NH₄-H₂O complexes. Comparison with Dawn VIR spectra indicates that the hypothesis of Mg-saponite as the ammonium carrier phase is the simplest explanation for observed data, and that Ceres dark materials may be like Cold Bokkeveld or Tagish Lake but with proportionally more Mg-smectite.

INTRODUCTION

Ammoniated and phyllosilicate-bearing materials were first proposed to explain Ceres's visible/shortwave infrared reflectance spectra observed via telescopes (King et al. 1992). They were then confirmed and globally mapped with the Visible and Infrared (VIR) imaging spectrometer on the Dawn mission (De Sanctis

et al. 2011, 2015; Ammannito et al. 2016). Key infrared absorption features characteristic of dark surface materials on Ceres surface materials are located at ~2.72 μm, indicating Mg-OH-bearing materials, and ~3.06 μm, indicating NH₄-bearing materials (De Sanctis et al. 2015). Their co-occurrence globally makes it likely, but not certain, that ammoniated Mg-phyllosilicates are the carrier of the NH₄ in Ceres's dark

regions, which cover nearly all of the dwarf planet (Ammannito et al. 2016). The most likely candidate is ammoniated Mg-smectite (King et al. 1992).

Ammoniated minerals occur naturally in a variety of geological settings on Earth, including ammoniated alkali feldspars from pegmatites (e.g., Solomon and Rossman 1988), ammonium feldspars like buddingtonite from hydrothermal zones (e.g., Krohn et al. 1993), ammoniated barium feldspars from hydrothermal ores (e.g., Beran et al. 1992), and ammoniated illites and micas, especially from hydrothermal or metamorphic zones near organic-rich rocks (e.g., Sucha et al. 1998; Nieto 2002; Ruiz Cruz and Sanz de Galdeano 2008). In many of these cases, decomposition of organic material supplied the nitrogen for ammonia incorporation in the mineral structure. Additionally, NH_3 gases or NH_4 -bearing fluids of volcanic, hydrothermal, or groundwater origin can exchange with interlayer cations in clay minerals, e.g., smectites, illites, or talc-like stilpnomelane (e.g., Blake 1965). Ammonia has also been observed in meteorites at up to parts per thousand concentrations within select phases (e.g., Pizzarello and Williams 2012).

NH_4 may occur as part of the phyllosilicate mineral lattice (cation substitution), occur in an interlayer site to provide charge balance, or be adsorbed on the mineral surface. Readily available infrared reflectance spectral libraries have ammoniated feldspars, ammoniated salts, and ammoniated Al-phyllosilicates, such as NH_4 -annite and NH_4 -montmorillonite (e.g., Srasra et al. 1994; Bishop et al. 2002; Berg et al. 2016; NASA Keck RELAB database). These have been used in radiative transfer unmixing models to estimate the composition of the Ceres surface (e.g., De Sanctis et al. 2015). Yet, more suitable may be Fe- or Mg-phyllosilicates, which are more typical of meteoritic materials. Spectra from such samples have been previously published (e.g., Russell 1965) and were presented in the original report of ammoniated phyllosilicates on Ceres (King et al. 1992). Yet, spectra of ammoniated Fe-rich and Mg-rich phyllosilicates are not a component of presently existing, publicly available spectral libraries. Additionally, the potential for ammoniation of carbonaceous meteorite materials, a likely source material for the regolith of Ceres (e.g., Prettyman et al. 2017), has not been systematically assessed. Here, we obtain, purify, and ammoniate a variety of Ceres-relevant analog materials, including both phyllosilicates and carbonaceous chondrite meteorites. We then evaluate (1) which phases ammoniate; (2) which ammoniated phases exhibit absorptions with similar positions, widths, and shapes to those observed for Ceres; and (3) if/how the NH_4 -related absorptions change at different temperatures under vacuum. The overarching goals were to refine the

identification of the ammoniated species on Ceres and develop a spectral library suitable for accurate, quantitative radiative transfer models that estimate Ceres's composition.

METHODS

Samples

Phyllosilicates from the smectite, chlorite, and serpentine families were obtained, powdered, checked for additional minerals with FTIR and/or XRD (if needed), purified by settling to diminish the non-phyllosilicate fraction or treated with acetic acid to remove associated carbonate, and sieved to $<150\ \mu\text{m}$ (Table 1). Smectites used included the montmorillonites (dioctahedral Al-smectites) SAz-2 and SWy-3, the nontronites (dioctahedral Fe-smectites) NAu-1 and NAu-2, and the hectorites (trioctahedral Mg,Li-smectites) SHCa-1 and SynH-1. These samples were obtained from the Special Clay and Source Clay collections of the Clay Mineral Society (CMS), and their properties have been detailed in numerous publications (e.g., Keeling et al. 2000; Chipera and Bish 2001; Madejova and Komadel 2001). For saponites (trioctahedral Mg-smectites), we obtained saponite (Sap_IMV) from the IMV company in Nevada, saponite from a mineral dealer (Sap_Baja), and samples of the Griffith saponite (Sap_Grif; Treiman et al. 2014). The saponites are not fully pure, in some cases, so as to ensure sufficient material volume for analysis. For example, the Griffith saponite was extracted from a hand sample of basalt. Pyroxene, feldspar, and small amounts of iron oxides are also present, and so the sample is saponite-enriched material (~30% saponite) but will be referred to as saponite here. Non-swelling phyllosilicates examined were a CMS source clay Mg-chlorite (CCa-2) and Mg-serpentine from Oman (OM12_003, OM12_016), which were characterized in Leask and Ehlmann (2016).

Similarly, particulates of carbonaceous chondrite meteorites were obtained, focusing on CM, CI, and primitive meteorites with spectral properties similar to some asteroids (Takir and Emery 2012). We chose to examine Mighei (CM2), Murray (CM2), Cold Bokkeveld (CM2), Tagish Lake (C2), and Orgueil (CI), representing carbonaceous chondrites with different degrees of aqueous alteration, which were also readily available at tens of milligram quantities needed. As with the phyllosilicates, samples were sieved to $<150\ \mu\text{m}$. In these meteorite types, phyllosilicate phases are the most abundant mineral by bulk, comprising most of the dark matrix material as well as sometimes found in alteration rims around or veins within chondrites. Prior XRD analyses of Mighei, Murray, and Cold Bokkeveld show

Table 1. Samples measured as crushed particulates.

Sample type	Mineral/meteorite type	Sample ID	Reference	Preprocessing
Minerals				
Fe-smectite	Nontronite	NAu-1	Keeling et al. (2000)	
Fe-smectite	Nontronite	NAu-2	Keeling et al. (2000)	
Mg-smectite	Saponite	Sap_IMV	See text	Acid wash
Mg-smectite	Saponite*	Sap_Gr*	Treiman et al. (2014)	Picking from rock vesicles
Mg-smectite	Saponite	Sap_Baja	See text	
Mg,Li-smectite	Hectorite	SHCa-1	Chipera and Bish (2001)	Acid wash
Mg,Li-smectite	Hectorite	SynH-1	Clay Mineral Society	
Mg-Serpentine		OM12_003	Leask and Ehlmann (2016)	Acid wash
Mg-Serpentine		OM12_016	Leask and Ehlmann (2016)	
Mg-chlorite	Ripidolite	CCa-2	Post and Plummer (1972)	
Al-smectite	Montmorillonite	SAz-2	Chipera and Bish (2001)	
Al-smectite	Montmorillonite	SWy-3	Chipera and Bish (2001)	
Meteorites				
Cold Bokkeveld	CM2	Cold Bokkeveld	Zolensky et al. (1993)	
Mighei	CM2	Mighei	Zolensky et al. (1993)	
Murray	CM2	Murray	Zolensky et al. (1993)	
Orgueil	C1	Orgueil	Tomeoka and Buseck (1988)	
Tagish Lake	C2	Tagish Lake	Blinova et al. (2014)	

The Griffith saponite is not a pure sample. A sample of the host rock was provided. Clays were obtained by scraping from interiors of large vesicles; however, there was insufficient sample for the experiment. Consequently, volumes of rock rich in clay-filled vesicles were crushed and included. The sample is ~30% clay and the remainder pyroxene and feldspar.

Table 2. XRD peak positions in angstroms of bulk samples before and after ammoniation; those where peak positions did not shift are noted (see text). Full XRD patterns for all samples are available in the supporting information, and example patterns are shown in Fig. 1.

Mineral or meteorite	Sample name	001 peak before ammoniation (Å)	001 peak after ammoniation (Å)	No/reverse peak position shift
Nontronite	NAu-1	15.0	12.6	
Nontronite	NAu-2	14.9	11.6	
Montmorillonite	SAz-2	15.3	12.7	
Montmorillonite	SWy-3	12.6	12.7	x
Hectorite	SHCa-1	15.0	12.3	
Hectorite	SynH-1	14.7	14.7	x
Saponite	Sap_Baja	12.6	12.6	x
Saponite	Sap_Gr	14.9	12.5	
Saponite	Sap_IMV	15.6	12.6	
Chlorite	CCa-2	14.1	14.2	x
Serpentine	OM12-003	7.1	7.1	x
Serpentine	OM12-016	7.3	7.3	x
Cold Bokkeveld	Cold_Bokk	7.2	7.3	x
Mighei	Mighei	7.2	7.2	x
Murray	Murray	7.2	7.2	x
Orgueil	Orgueil	7.5	7.5	x
Tagish Lake	Tagish	11.2–12.5 ^a	12.0	?

^aRange from two samples measured by Blinova et al. (2014); not measured in this study.

75–80 wt% serpentine, with Mg-serpentines dominant in Cold Bokkeveld and Fe-serpentines dominant in Mighei and Murray (Howard et al. 2009). Percent amorphous or smectite clay phases were not reported for these CM chondrites. An XRD pattern of Murray (Pizzarello

et al. 2003) shows serpentine but no smectite, and Zolensky et al. (1993) reported that saponite is rare in Murray. Tagish Lake is a brecciated sample with variable lithologies and thus different mineralogy depending on the fragment, but serpentine and saponite

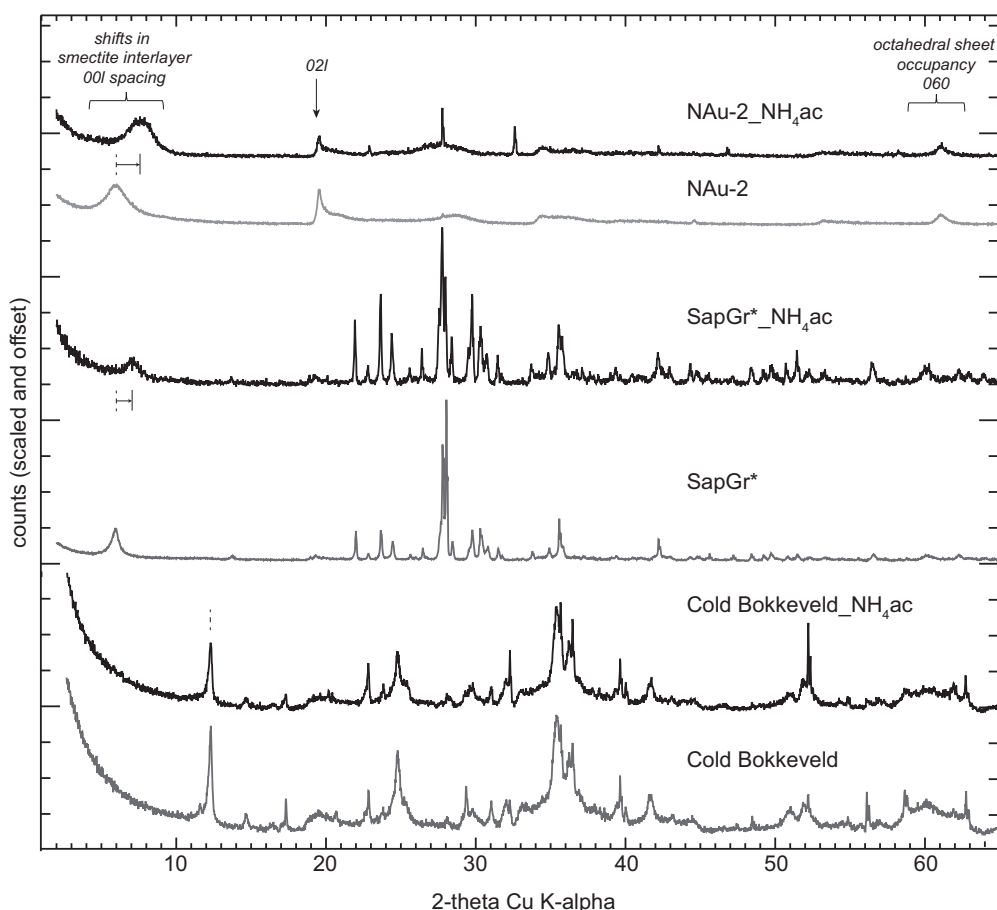


Fig. 1. X-ray diffraction patterns of select smectites and the Cold Bokkeveld meteorite before (thin, gray) and after (thick, black) ammonium acetate treatment. Labeled peaks are due to diffraction planes in the smectite structure. An arrow indicates the 001 peak shift to larger 2θ (smaller layer spacing) after ammoniation. Unlabeled peaks in N Au-2 include NH_4Cl and metal acetates. Unlabeled peaks in Sap-Gr are contaminate silicates (feldspars, pyroxenes). Cold Bokkeveld phases include serpentine, olivine, and magnetite.

are present in ~45–70% abundance in all fragments analyzed (Zolensky et al. 2002; Izawa et al. 2010). Four samples examined by Blinova et al. (2014) “were found to contain abundant clay minerals ... and an amorphous phase” with the matrix dominated by saponite and serpentine. XRD patterns by Izawa et al. (2010) and Blinova et al. (2014) show the basal reflection of a smectite clay in some subsamples. The CI chondrite Orgueil consists of a mixture of serpentine (identified with 7 Å spacing) and saponite (identified by 10–15 Å spacing) in coherent intergrowths with intimately associated Ni- and S-bearing ferrihydroxides (Tomeoka and Buseck 1988).

Ammoniation Procedure

As one potential scenario for ammoniation on Ceres, we assume ammoniation took place by exchange of NH_4^+ in fluids with other interlayer or adsorbed cations.

As mentioned above, NH_4^+ may occur in minerals as (1) an integral part of the lattice (cation substitution), (2) in an interlayer site between stacked layers in phyllosilicate structures, or (3) adsorbed on the mineral surface. Our procedures are designed to examine (2) for select clay minerals and reduce or eliminate the effects of (3) by removal of any NH_4^+ that is merely loosely adsorbed by rinsing treated samples with distilled water prior to performing infrared measurements in dry-air purge and in vacuum. We do not address cation-substituted minerals. Future studies of Ceres spectral analogs may choose to instead focus on (1) or (3).

We use an ammoniation procedure modified from a more complex procedure used in traditional clay mineralogical analyses for determination of cation exchange capacity (Busenberg and Clemency 1973; Borden and Giese 2001). Our samples were submerged in 1 M NH_4 -acetate for 72 h at room temperature. The NH_4 -acetate was then removed via pipetting, and the

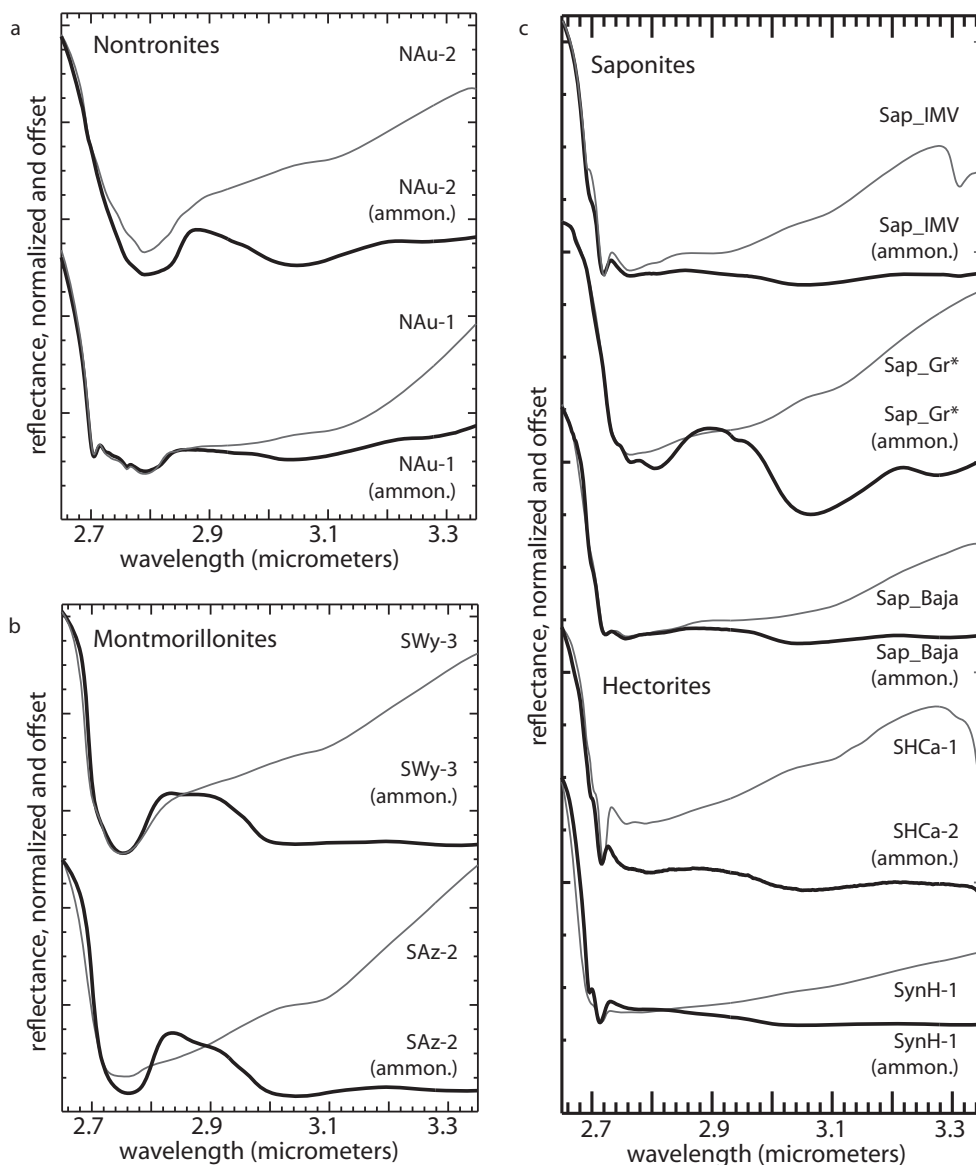


Fig. 2. Room temperature, dry-air purge infrared reflectance spectra of smectites before (thin, gray) and after (thick, black) ammonium acetate treatment for (a) iron smectites, the nontronites NAu-1 and Au-2; (b) aluminum smectites, the montmorillonites SAz-2 and SWy-3; (c) magnesium smectites, the saponites and saponite-bearing materials Sap_IMV, Sap_Gr*, Sap_Baja, and the hectorites, ShCa-1 and SynH-1 (as noted in the text and Table 1, Sap-Gr is $\leq 30\%$ clay mineral with the pyroxene and feldspar comprising the remainder of the sample).

samples were rinsed three to five times with distilled water to remove any residual fluids from ammoniation. Samples were then dried at 300 K, disaggregated, and prepared for measurement. For the ammoniation treatment, we experimented with including an intermediate step with NH_4Cl treatment, as is typical for cation exchange capacity studies (e.g., Busenberg and Clemency 1973). However, we found that this resulted in precipitation of chloride salts in the samples in pilot tests, presumably from cation exchange out of smectite interlayers and their interaction with chlorine

ions. Hence, we modified the procedure to only include the $\text{NH}_4\text{-acetate}$. This is similar to the procedure of Petit et al. (1999), where samples were treated with ammonium acetate, centrifuged, retreated, and then rinsed. A consequence of our $\text{NH}_4\text{-acetate}$ procedure is that some C-H absorptions due to organics may be simultaneously introduced, if these also adsorbed. In searching for the C-H spectral features, these are negligible for most samples, but future users of spectra should consider leaving the $3.35\ \mu\text{m}$ region out of spectral fits or interpolating to remove any absorptions.

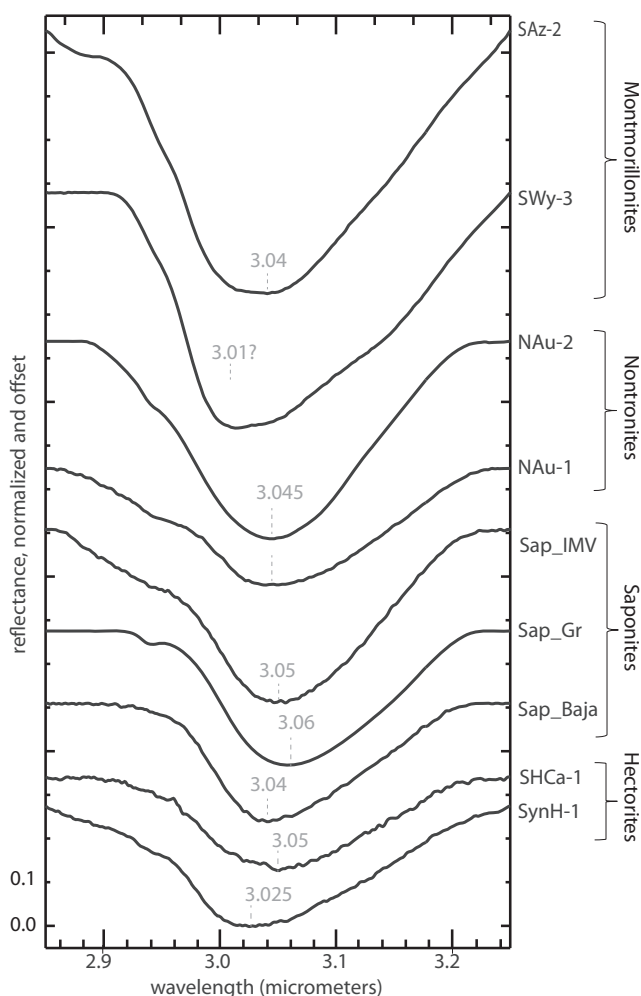


Fig. 3. Room temperature, dry-air purge of the continuum-removed spectra of the NH_4 -stretch region of the ammoniated smectites and smectite-bearing materials from Fig. 1.

Measurements of Diffraction Patterns and Infrared Spectra

All samples were measured in biconical diffuse reflectance mode over 2–25 μm at room temperature and under continuous dry-air purge before and after ammoniation by using an iS50 FTIR instrument equipped with a biconical Pike Technologies AutoDiff accessory. A subset of samples showing signs of ammoniation were then measured under vacuum (base pressure $\sim 3 \times 10^{-5}$ torr) while being cooled from 25 $^\circ\text{C}$ to -180 $^\circ\text{C}$, using a Nicolet 6700 FTIR fitted with a diffuse reflection accessory (Pike Technologies DiffusIR) at a 30° incidence. The sample was placed within a gold-coated sample cup (5 mm inner diameter \times 4 mm deep), which sat tightly fitted in the well of a liquid nitrogen-cooled copper block. The small size of the cup is expected to minimize temperature gradients within the sample. The temperature range chosen covers the range

experienced over all latitudes on Ceres. IR data as well as corresponding visible/near-infrared data (0.4–2.5 μm ; not discussed in the main text) are available in the supporting information.

To determine sample composition and verify the effects of the ammoniation procedure, samples were also measured with X-ray diffraction (XRD). XRD analysis was performed on a Rigaku Smartlab diffractometer using Cu K-alpha radiation and a scintillation detector. Untreated samples were ground in a pestle and mortar, side-packed in sample holders and run between 2 and 65° 2θ , using 0.02° steps at 10 s per step. Smaller quantities of ammoniated materials were ground and top loaded into zero-background silicon sample holders. The samples were spun at 60 rpm during collection from 2 to 65° 2θ , using 0.02° steps at 2 s per step. The XRD data are available in the supporting information.

Based on the results from infrared analyses and ambiguous results from ammoniation of meteorites, select meteorite samples were further processed and interrogated to understand whether smectites were present and responding to cation exchange. To extract clay minerals, previously ammoniated powdered meteorites were placed in plastic vials with 9 mL of deionized (DI) water and sonicated for 1 min. Sonified materials were allowed to settle for 40 min, leaving <2 μm particles in suspension. Suspensions were then pipetted onto zero-background slides and allowed to dry before XRD analysis. After measurement, the slides were treated with ethylene glycol overnight at 60 $^\circ\text{C}$ and run again on the XRD. For Tagish Lake (and CMS standard SAz-2 to verify the procedure) further cation exchange of Mg^{2+} and again NH_4^+ was performed to understand swelling behavior. Materials were scraped off slides onto filter papers inside a Buchner funnel and exposed to three 50 mL aliquots of a 0.1 M solution of MgCl_2 . Each aliquot was left for ~ 10 min before vacuuming off the solution. Extracts were then washed with DI water repeatedly before allowing filters to dry. The dried filters were taped to zero-background slides and X-rayed. The exchange procedure was then repeated using a 0.5 M solution of ammonium acetate, followed by washing, drying, and additional XRD. Low yield from filter papers reduced the quantity of material and quality of patterns; however, shifts in the 001 basal reflection were still observable.

RESULTS

Phyllosilicate Sample Patterns and Spectra After Ammoniation

X-ray diffraction data show that many smectite clay samples changed their interlayer spacing upon

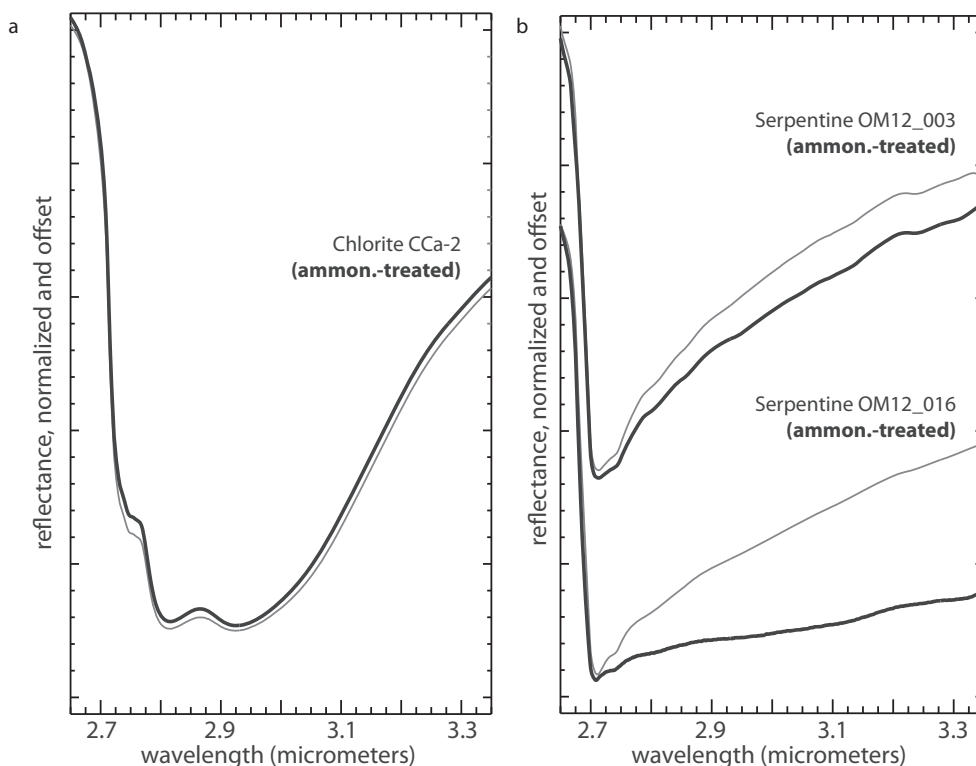


Fig. 4. Room temperature, dry-air purge infrared reflectance spectra before (thin, gray) and after (thick, black) ammonium acetate treatment for (a) the Mg-chlorite CCa-2 and (b) the Mg-serpentines, OM12_003 and OM12_016.

ammoniation at room temperature and ambient relative humidity of $\sim 50\%$. NH_4^+ insertion into the interlayer of smectite clays causes the basal reflection (001) to shift to larger 2θ , i.e., smaller layer spacing (Table 2). For example, in the NAu-2 and Sap-Gr smectite materials, the 001 peak shifts from ~ 15 angstroms (\AA) in the untreated sample to $11.5\text{--}12.5$ \AA in the treated sample (Fig. 1). Additional sharp XRD peaks that appear only in the ammoniated NAu-2 are NH_4Cl and metal acetates. The latter may be the dark precipitate observed visually upon ammoniation of the nontronite sample. The decrease in interlayer spacing indicates that, as desired, NH_4^+ ions are being incorporated into the smectite structure rather than the larger $\text{NH}_4\text{-acetate}$ molecule. The NH_4^+ ion, like K^+ and to a lesser extent Na^+ , has a low enthalpy of hydration (-307 , -321 , and -405 kJ mol^{-1} , respectively) compared with other common metal cations that typically occupy the interlayer like Ca^{2+} (-1592 kJ mol^{-1}) or Mg^{2+} (-1922 kJ mol^{-1}) (e.g., Barshad 1950; Pironon et al. 2003). Thus, the replacement of more typical metal cations in the interlayer with NH_4^+ reduces the retention of interlayer H_2O at the same relative humidity. This is an effect similar to that observed for K^+ ion in saponite (Suquet et al. 1975) and previously observed for ammoniation of Na-saturated montmorillonite (Gautier et al. 2010). The

loss of interlayer water upon ammoniation causes the interlayer spacing to decrease. Two smectites, SWy-3 and Sap_Baja, already had relatively collapsed smectite interlayers (12.6 \AA) prior to ammonium acetate treatment, probably because of Na^+ in the interlayer in their natural state, and their basal spacing did not significantly change (Table 2). Synthetic hectorite had fairly swollen interlayers (14.7 \AA) but its spacing likewise did not change.

IR spectroscopic data exhibit new absorptions at the expected position of ~ 3.05 μm (Fig. 2), the ν_3 absorption (e.g., Russell 1965; Petit et al. 1998), also showing most smectite minerals readily ammoniated at room temperature. The nontronites developed absorptions at 3.045 μm (Figs. 2a and 3). The montmorillonite SAz-2 developed an absorption at 3.04 μm (Figs. 2b and 3). The montmorillonite SWy-3 developed a deep absorption (Fig. 2b), but the continuum-removed band depth center at room temperature is near 3.01 μm , close to the location expected for bound H_2O , making the interpretation of this absorption ambiguous. All Mg-smectite materials showed absorptions between 3.03 and 3.06 μm near the expected positions for NH_4 (Figs. 2c and 3).

As anticipated, serpentine and chlorite samples did not ammoniate. Unlike smectites, these phyllosilicates lack an interlayer for hosting species with positive

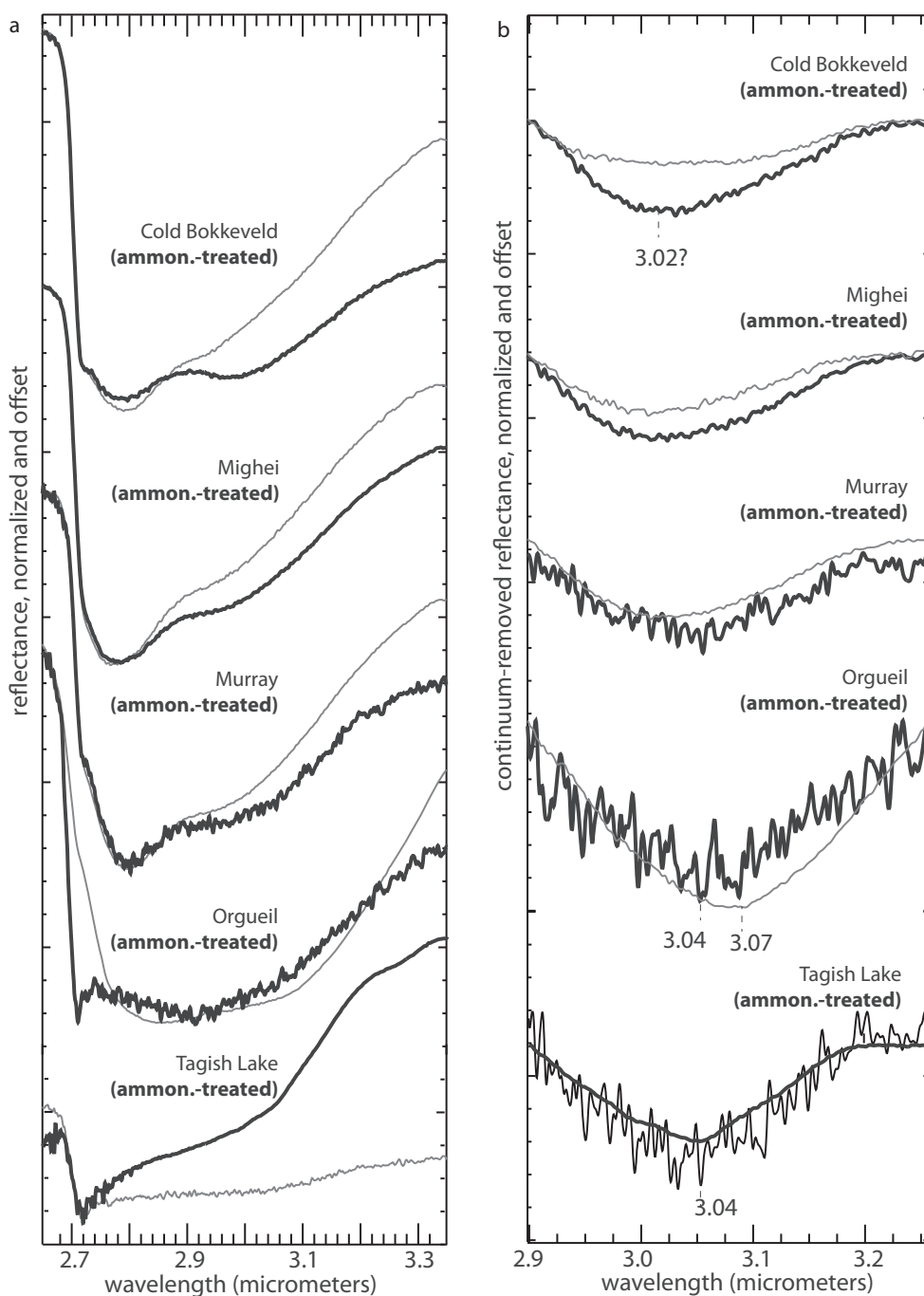


Fig. 5. a) Room temperature, dry-air purge infrared reflectance spectra of carbonaceous chondrite meteorites before (thin, gray) and after (thick, black) ammonium acetate treatment. b) Continuum removed.

charge. No evidence for loosely bound (e.g., adsorbed) NH_4^+ was seen in serpentine or chlorite spectra (Fig. 4). The basal reflection did not shift in XRD patterns (Table 2). The sole effect—also true for the smectites—is that the samples became darker and lower contrast, likely due to aggregation of some of the finer particulates after a wet-dry cycle to make larger particles, thus darkening the sample.

Meteorite Patterns and Spectra After Ammoniation

Meteorite spectra from Murray, Mighei, and Tagish Lake showed no appreciable changes upon ammoniation (Fig. 5). Mighei and Murray have weak absorptions between 3.02 and 3.05 μm that did not change in strength. Tagish Lake has a 3.05 μm absorption that did not change in strength. Orgueil

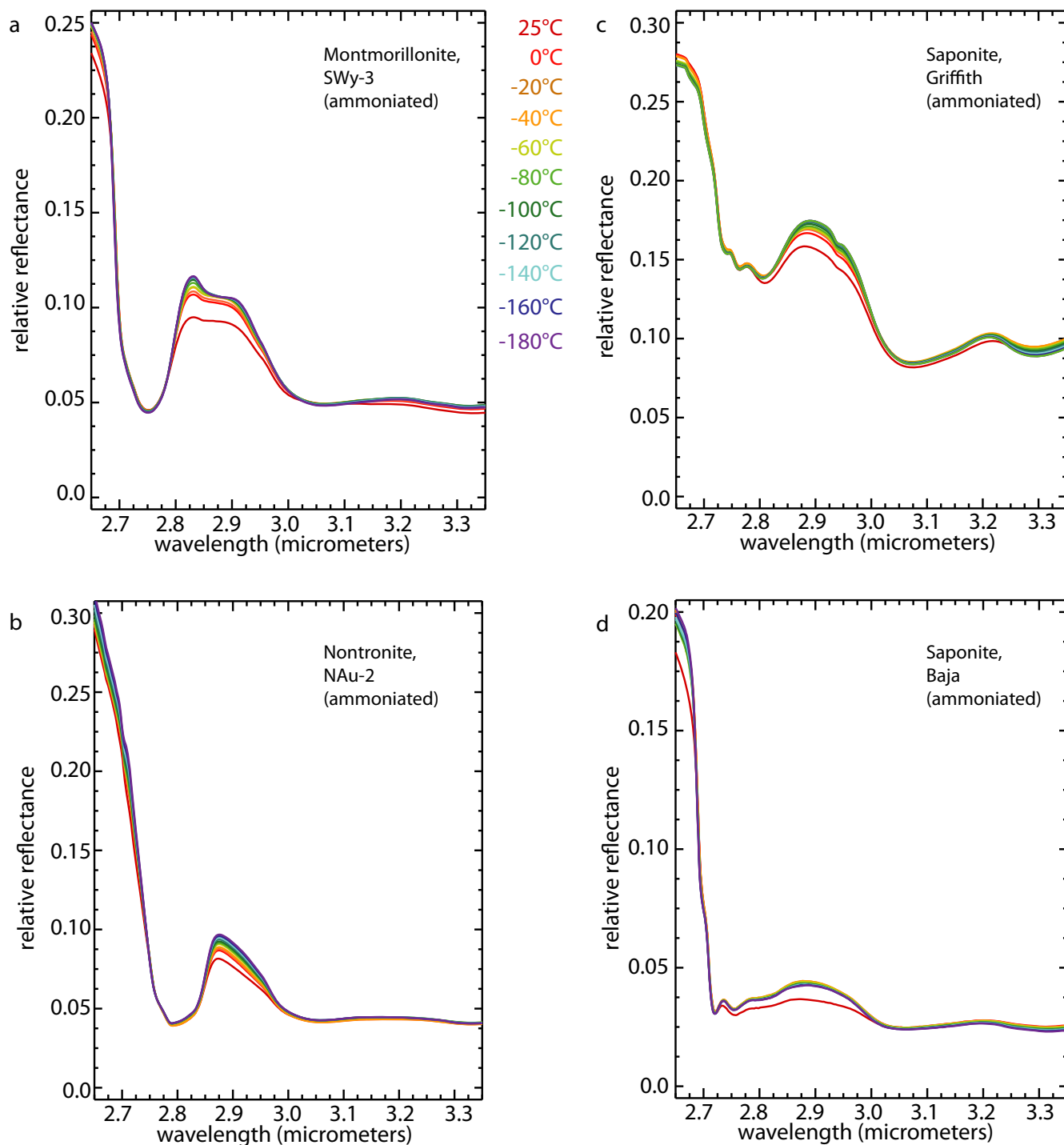


Fig. 6. Infrared reflectance spectra under vacuum of the select ammoniated smectite samples, acquired as a function of temperature. a) Montmorillonite, SWy-3; (b) nontronite, NAu-2; (c) saponite-bearing materials from Griffith, CA; and (d) saponite from Baja, Mexico. (Color figure can be viewed at wileyonlinelibrary.com.)

spectra changed by developing a more pronounced absorption near 2.72 μm (Fig. 5), perhaps because more bound water was driven off following post-ammoniation drying, and a 3.4 μm absorption became apparent

(perhaps due to C-H; spectra are in supporting information), but the ν_3 absorption at wavelengths typical of NH_4 was not observed. The Cold Bokkeveld sample did develop a deeper absorption between 3.0

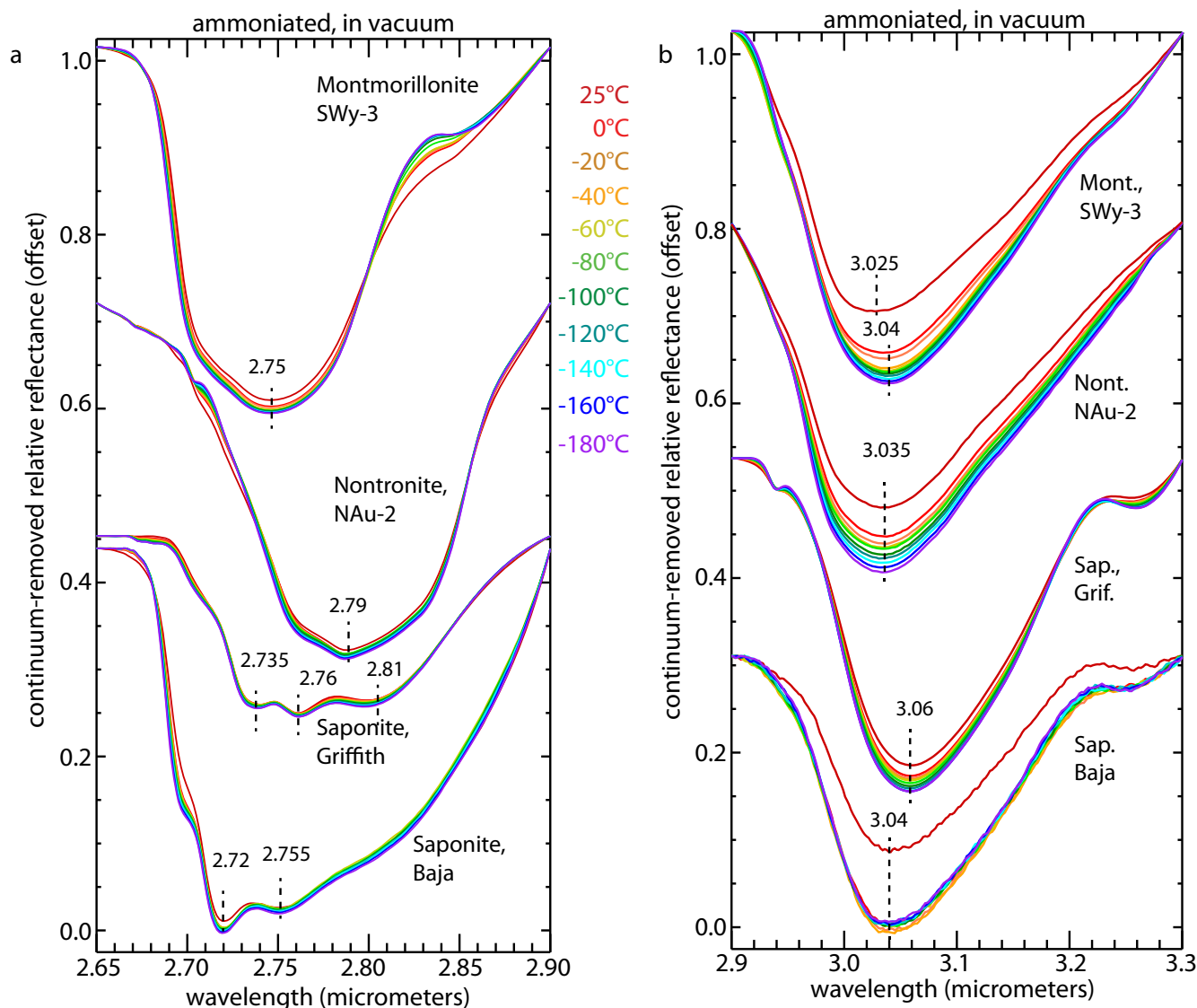


Fig. 7. Continuum-removed infrared spectra of ammoniated phyllosilicates acquired under vacuum at different temperatures, shown for spectral ranges focusing on (a) the metal-OH vibrations and (b) the NH_4^+ vibrations near 3 μm . Spectra are from the samples in Fig. 6. (Color figure can be viewed at wileyonlinelibrary.com.)

and 3.1 μm , which might be attributed to ammoniation (Fig. 5). However, analysis of XRD patterns showed that the sample had peaks in counting data at 7 \AA and other 2θ values consistent with serpentine and no evidence of a smectite. The peaks did not shift upon ammoniation (Fig. 1).

Effects of Cold and Vacuum on Infrared Spectra of Ammoniated Materials

A subset of the materials that showed evidence for ammoniation, Cold Bokkeveld, and Tagish Lake were examined under vacuum at cold temperatures to understand if the position and properties of the NH_4^+

absorption—or any other absorptions near the expected NH_4 absorption position—shifted with temperature. Analyses of spectra acquired from 25 $^{\circ}\text{C}$ to -180 $^{\circ}\text{C}$ show little to no change for either the NH_4^+ absorptions or the metal-OH absorptions (Fig. 6). The continuum-removed positions of saponites under vacuum and cold temperatures are the same as those under dry-air purge at room temperature (Fig. 7; Table 3). The continuum position of nontronite NAu-2 shifted by 0.01 μm , although this small shift is near the limit of our ability to resolve the center location of the relatively broad band. The montmorillonite sample SWy-3 clearly exhibits a band shift to longer wavelengths as the spectra are acquired at colder

Table 3. Positions of the NH_4 -related absorption feature in smectites and meteorite samples under dry-air purge at room temperature, under vacuum at room temperature, and under cold vacuum.

Sample	Abs. center (μm), 25 °C, dry-air purge	Abs. center (μm), 25 °C, vacuum	Abs. center (μm), -180 °C, vacuum
Montmorillonite (SWy-3)	3.01	3.025	3.04
Nontronite (NAu-2)	3.045	3.035	3.035
Saponite, Griffith	3.06	3.06	3.06
Saponite, Baja	3.04	3.04	3.04
Cold Bokkeveld	3.025	3.09	3.09
Tagish Lake	3.09	3.09	3.09

temperatures. Interestingly, montmorillonite and nontronite also exhibit greater variability in band depth over the temperature range, becoming deeper at colder temperatures (Fig. 7b). For Cold Bokkeveld, the new absorption at 3.025 μm persists but its wavelength position shifts markedly to 3.09 μm after pump down to vacuum. The 3.09 μm band deepens for colder temperatures (Fig. 8; Table 3). Tagish Lake also exhibits a 3.09 μm band, though this was present both before and after ammoniation and does not shift position with pump down to vacuum or with temperature (Fig. 9).

DISCUSSION

Effects of Ammoniation on XRD Patterns and IR Spectra of Phyllosilicates and Meteorites

Nonexpanding phyllosilicates—serpentine and chlorites—showed no effects from treatment with ammonium acetate. This is consistent with the expected behavior given that serpentine layers are charge neutral and do not have interlayer sites, and chlorites are charge neutral and have a nonexchangeable $\text{Mg}(\text{OH}_2)$ interlayer (for discussion of structures, see Bishop et al. 2008). There is also no evidence in infrared spectra for adsorbed NH_4^+ , indicating that our procedures successfully removed any excess surface NH_4^+ by rinsing the treated materials.

A surprising result was that none of the carbonaceous chondrite samples were clearly ammoniated to produce infrared features similar to those of smectite clays (and Ceres) nor showed XRD peak shifts. One simple explanation could be that smectite is present only in small amounts. That most carbonaceous chondrites showed no ammoniation after treatment is consistent with serpentine

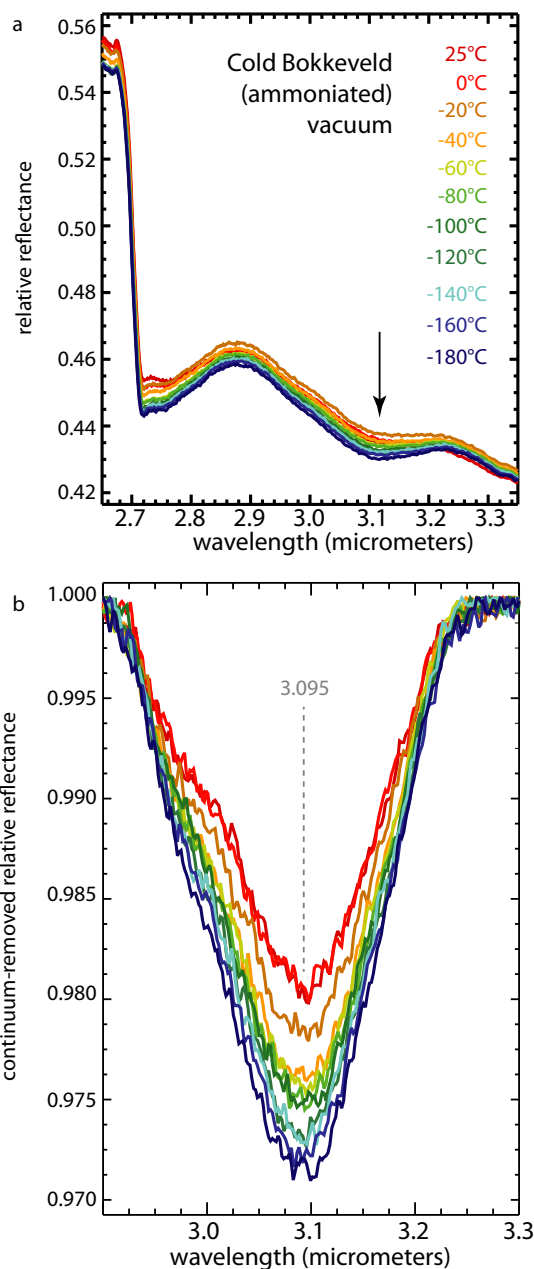


Fig. 8. a) Infrared reflectance spectra acquired under vacuum at multiple temperatures of a possibly ammoniated (see text) carbonaceous chondrite Cold Bokkeveld, acquired as a function of temperature. The arrow indicates the absorption that may be caused by NH_4 . b) continuum removed near 3.1 μm . (Color figure can be viewed at wileyonlinelibrary.com.)

being the dominant (or only) phyllosilicate species in CM carbonaceous chondrites like Mighei, Murray, and Cold Bokkeveld (e.g., Zolensky et al. 1993), and as indicated by our XRD data. However, in Orgueil (trace smectite) and Tagish Lake (minor to major smectite), where saponite has been reported and we detected smectite in XRD data, other factors might be responsible. For example, the small

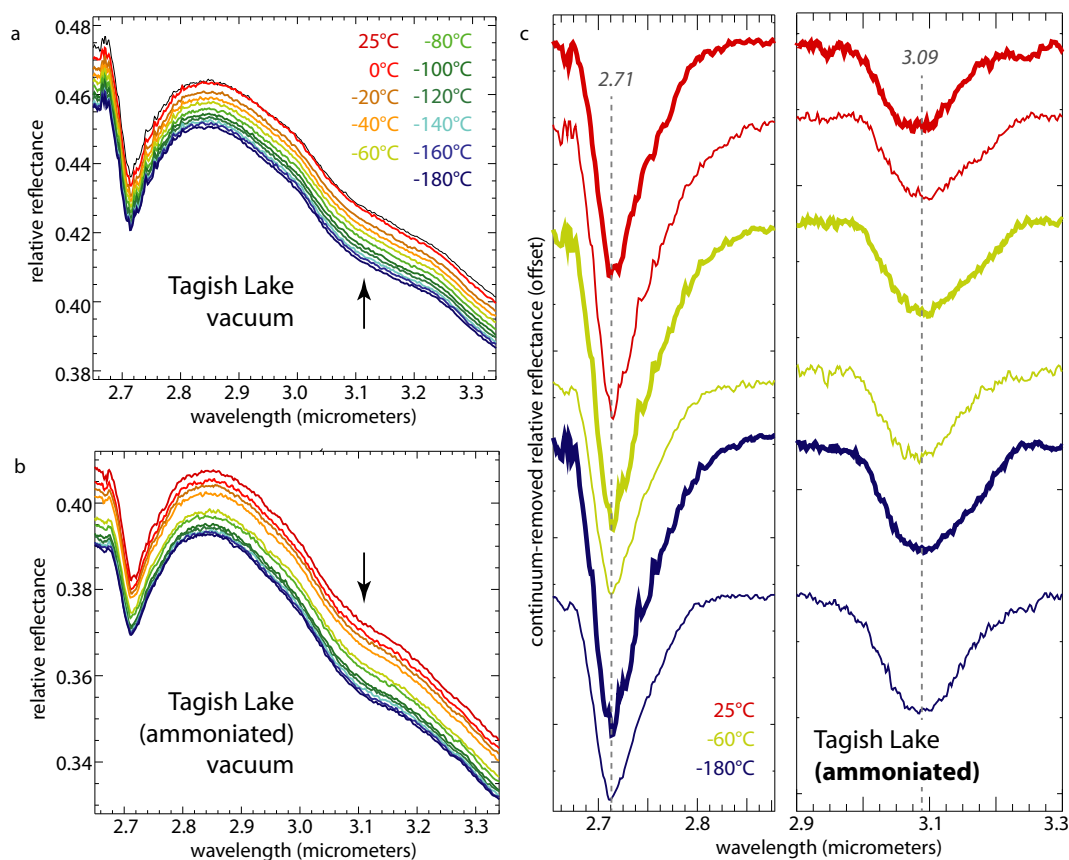


Fig. 9. Infrared reflectance spectra acquired under vacuum at multiple temperatures of a carbonaceous chondrite Tagish Lake, acquired (a) before and (b) after ammoniation. c) Select temperature ranges of the metal-OH and NH_4 stretch region are shown for spectra before (thin line) and after (thick line) ammoniation. (Color figure can be viewed at wileyonlinelibrary.com.)

length scales of ordered stacks of smectite layers with intercalated organic carbon compounds (Garvie and Buseck 2007) may inhibit NH_4^+ uptake, or NH_4^+ may complex with other organic, metal, or salt species intimately mixed in the clay matrix (e.g., Carroll 1959).

To determine whether the smectites from Orgueil and Tagish Lake were capable of exchanging cations, we first isolated only the clay-sized ($<2 \mu\text{m}$) fraction (see Methods) from bulk samples. The expected swelling behavior was observed after treating the meteorite clay-sized fraction with ethylene glycol (Fig. 10; Table 4), thus confirming the presence of smectite. For Tagish Lake, Mg^{2+} exchange and exchange back to NH_4^+ was performed, and the 001 basal layer spacing increased and decreased as expected in this smectite isolate (Fig. 10). (Small sample sizes and their adherence to filter papers precluded further tests on the smectite fractions.) Although we observe cation exchange in smectitic meteoritic materials, we note that the size-separation procedure, which involves sonication and suspension in DI water, may promote disruption of clay-matrix aggregates and probably selects for materials that have the least intimate association with

materials that may hinder cation exchange. We also note that although cation exchange clearly takes place in extracted smectites, we do not know if their cation exchange capacity is of the same order as clay mineral standards. Our experiments do not allow us to rule out the possibility that the extracts have fewer exchangeable sites because of occlusion or intercalation of organics.

An additional puzzle is the deepening of a 3.02–3.09 μm absorption in Cold Bokkeveld—which has negligible smectite—after the ammoniation procedure. This absorption was not present in previously measured spectra of Cold Bokkeveld at cold temperatures (Takir et al. 2013). Speculatively, it is possible that amorphous, poorly crystalline phases may be taking up NH_4^+ , as observed by Bishop et al. (2002) for tephros. Similarly, we might be observing evidence for organic- NH_4^+ complexes as these have already been identified at ppt to ppm concentrations in insoluble organic matter in carbonaceous chondrites (Pizzarello and Williams 2012).

Considering the results collectively, lack of expression of an IR absorption of NH_4^+ incorporation in smectite in bulk Tagish Lake and Orgueil where smectites are present may be due to either (1)

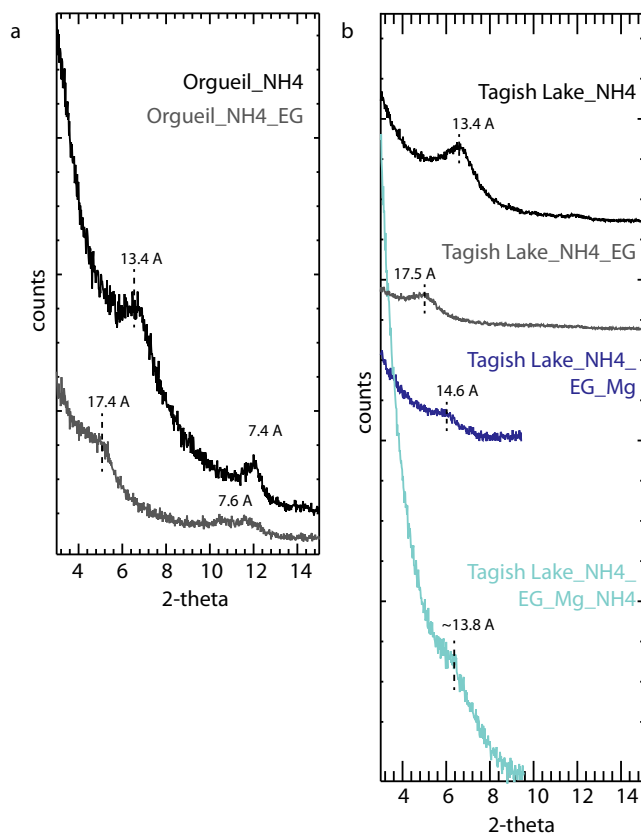


Fig. 10. Ammoniated portions of (a) Orgueil and (b) Tagish Lake were processed to isolate the smectite fraction by settling. Smectite fractions were then treated stepwise to establish whether meteorite exchanged interlayer materials (see Methods). Sample was lost during filtration at each step. Consequently, the last patterns of Tagish Lake have low signal and 2θ portions dominated by the pattern of the filter paper were removed. (Color figure can be viewed at wileyonlinelibrary.com.)

proportionally low smectite clay fractions in these particular subsamples so that the expression of the absorption is not discernible; (2) inhibition of NH_4^+ uptake in smectite and preferred complexing of the NH_4^+ with something else in the meteorite bulk sample, perhaps by organics; or (3) no change in 3.01–3.1 μm absorption because the meteorites already had interlayer NH_4^+ in its smectite clays. Cause (3) is speculative but is permitted by the data from Tagish Lake. An initial cation exchange, monitoring the fluid chemistry, would be required to test. The Tagish Lake sample had a 001 basal reflection position consistent with an NH_4^+ (or K^+) and a 3.05 μm IR absorption at the beginning of the experiment. The 3.05 μm IR absorption makes Tagish Lake similar to Ceres-like asteroids seen telescopically (Takir and Emery 2012). Future studies are certainly required to assess whether smectites in carbonaceous chondrites are ammoniated. Detailed, multitechnique characterization of meteorite

Table 4. XRD peak positions of the isolated clay fraction in angstroms of before and after ammoniation.

Sample	Treatment	001 peak (\AA)
Orgueil	Ammoniated	13.4
	Ammoniated, then ethylene glycolated	17.4
Tagish Lake	Ammoniated	13.4
	Ammoniated, then ethylene glycolated	17.5
	Ammoniated, then ethylene glycolated, then Mg^{2+} exchanged	14.6
	Ammoniated, then ethylene glycolated, then Mg^{2+} exchanged, then ammoniated	13.8

phyllosilicate mineralogy before any ammoniation treatment as well as later measurements to quantify ammonium uptake and responsible phase are warranted. If large enough meteorite samples can be analyzed destructively, a portion of sample can be crushed; purified to remove non-smectite materials; treated with a wide array of solutions; and then examined with multiple microscopic techniques, including IR spectroscopy.

Though the meteorite samples are puzzling, the XRD and infrared data of the smectite clay samples do clearly provide key information on phyllosilicate species that uptake ammonia. As expected based on the results of prior studies, most of our smectite samples did ammoniate. The NH_4 absorption at 3.05 μm appearing in the smectites arises from the ν_3 stretching vibration (e.g., Russell 1965; Petit et al. 1998). The observed positions of our absorptions are consistent with those reported for NH_4 -bearing phases broadly (3.01–3.08 μm ; Berg et al. 2016) and smectites specifically (3.04–3.06 μm ; Chourabi and Fripiat 1981; Petit et al. 1998; Bishop et al. 2002). Though not the focus of this study, the ν_4 bending vibration at 6.94 μm is also infrared-active, and many additional overtone and combination absorptions are generated at shorter wavelengths (Fig. 11). We also observe an 3.30 μm absorption, as also noted by prior workers (Mortland et al. 1963; Russell 1965; Chourabi and Fripiat 1981; Bishop et al. 2002). Bishop et al. (2002) suggested that these may be due to amine salts. Chourabi and Fripiat (1981) hypothesized that this absorption is due to distortion of the NH_4 tetrahedra by interactions with oxygens in an tetrahedral sheet with high charge due to M^{3+} substitution (e.g., Al^{3+} , Fe^{3+}). Alternatively, Mortland et al. (1963) instead explained the 3.30 and 3.54 μm absorptions, which co-occur in both their and our data sets, as resulting from differences in the hydrogen bonding environment within the smectite interlayer.

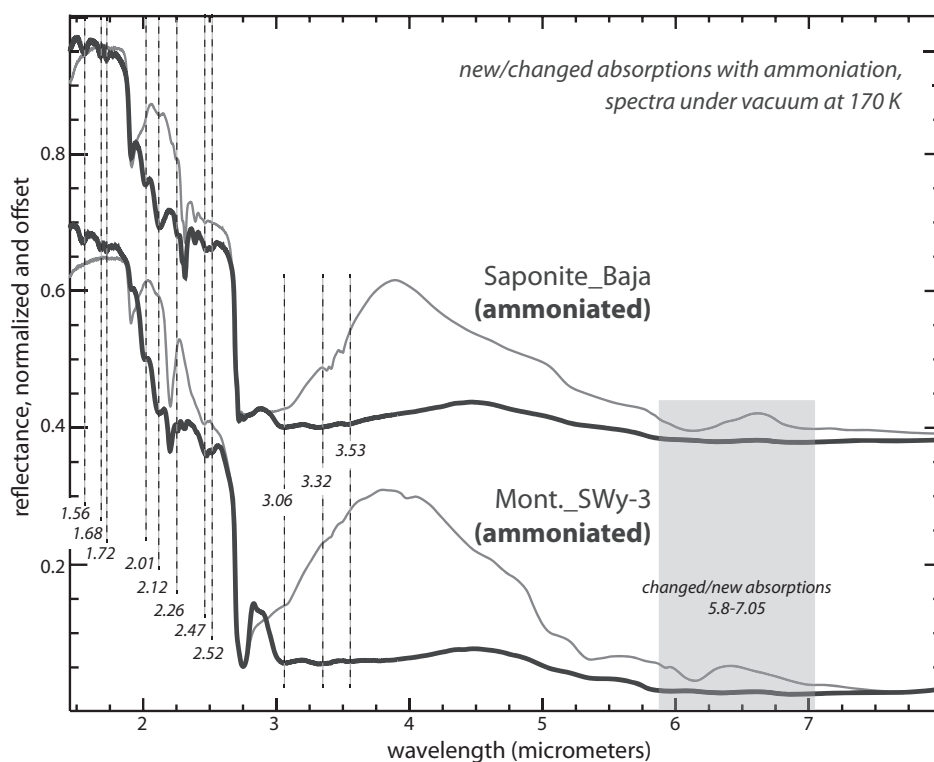


Fig. 11. Select ammoniated smectites, all acquired under vacuum at 170 K, shown over the full wavelength range: the Griffith sample with saponite and the SWy-3 montmorillonite sample. Absorptions that appeared following ammoniation are shown with dashed lines. (Color figure can be viewed at wileyonlinelibrary.com.)

Changes in the exact minimum position of the $\sim 3.05 \mu\text{m}$ absorption are related to changes in the charge/bonding environment in the interlayer. As with other prior studies on the topic (e.g., Chourabi and Fripiat 1981), no systematic variation in the $\text{NH}_4^+ \nu_3$ overtone position has been observed, by us or others, that might be related to the tetrahedral layer charge or dioctahedral versus trioctahedral nature of the samples (Mortland et al. 1963; Russell 1965). We cannot confirm or refute the speculation that degree of NH_4^+ hydrogen bonding with oxygen in the octahedral layers may determine band position (Suquet et al. 1975; Gautier et al. 2010). Changes in hydrogen bonding might also explain changes of positions for the absorptions of montmorillonite and for Cold Bokkeveld with temperature. However, as Zhang et al. (2007) reported, absorption band strengths and positions for hydrous phases can change at low temperatures even when there is no change in the quantity of volatiles present as a result of changes in dipole interactions and thus material optical constants. Here, bands appear to become stronger with colder temperatures, uncoupled with band narrowing. $\text{NH}_4\text{-H}_2\text{O}$ interactions at low temperature warrant further laboratory study as they are important for interpretation of spectra from Ceres and may be important for outer solar system bodies.

Comparison to Ceres Spectra

Ammoniated saponite spectra from this study match the position and width of the Ceres $3.06 \mu\text{m}$ feature (Fig. 12), consistent with the interpretations of King et al. (1992) and De Sanctis et al. (2015) that this is the likely carrier phase of ammonium on the Ceres surface. Importantly, select smectites (e.g., Sap_Baja) also possess a strong $2.72 \mu\text{m}$ Mg-OH stretch absorption, even when ammoniated. This means that a single phase could generate both features on Ceres. On Ceres, the $2.72 \mu\text{m}$ absorption is two to three times stronger than the $3.06 \mu\text{m}$ absorption. In our smectite samples, the $2.72 \mu\text{m}$ absorption is the same strength (Sap-Gr) or four times stronger (Sap_Baja), suggesting properties not dissimilar to Ceres; but further details of ammonium uptake need to be studied to constrain the causes of the relative band strengths. Serpentine minerals can also contribute to the $2.72 \mu\text{m}$ band. The positions observed for Ceres are more consistent with the Fe-bearing, Mg-serpentine in Cold Bokkeveld materials than the nearly pure Mg-serpentine endmember mineral we used.

The NH_4 -related absorptions observed in most smectite samples at 3.30 and $3.54 \mu\text{m}$ may also contribute to some of the observed complexity of Ceres spectra in the

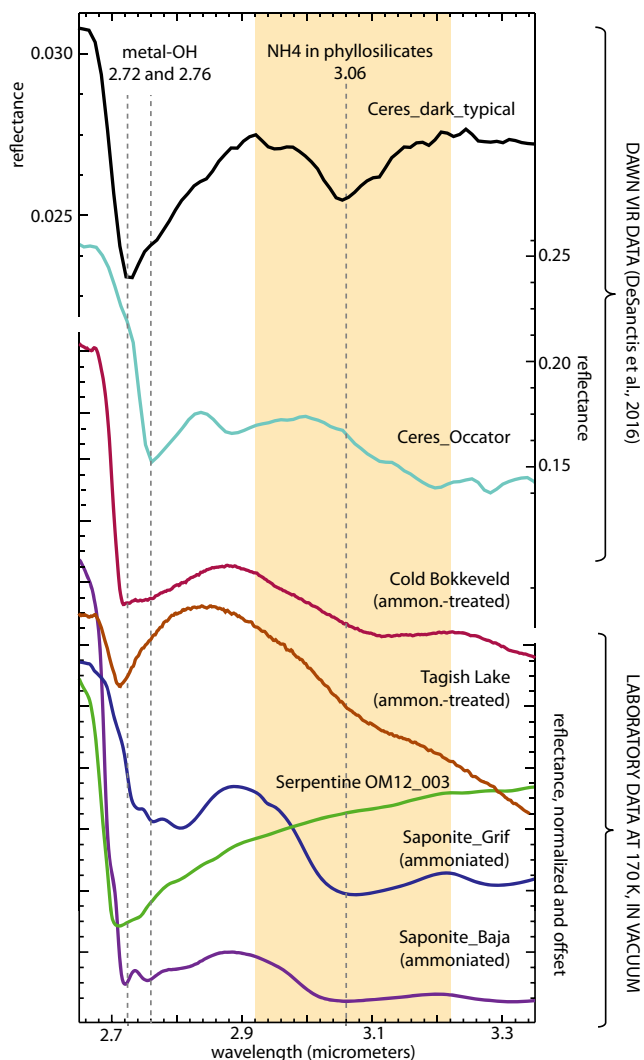


Fig. 12. Spectra from Ceres (De Sanctis et al. 2016) compared to ammoniated samples measured under vacuum at 170 K. The orange-shaded region denotes the width of the 3.06 μm absorption on Ceres. (Color figure can be viewed at wileyonlinelibrary.com.)

3.3–3.5 μm region, a complicated spectral wavelength range where organics and carbonates also have absorptions. The shorter wavelength ($<3 \mu\text{m}$) NH_4^+ absorptions from overtones and combinations of ammonium are not typically observed in Ceres's dark regions, though these can be obscured by other constituent dark minerals.

While other combinations of ammoniated phases and Mg-phyllosilicates may be permitted, ammoniated saponite is the simplest explanation for the observed spectral features in Ceres's dark material. Interestingly, the CI and CM materials did not ammoniate, in spite of their saponite content, suggesting that the Ceres dark materials are not exactly similar to our five meteorites. This result is consistent with elemental composition

data which also show differences between Ceres average composition and carbonaceous chondrites (Prettyman et al. 2017). But nonetheless, the spectral properties of Cold Bokkeveld and Tagish Lake (and to some extent Orgueil) are similar to Ceres dark material. Thus, materials like carbonaceous chondrites but more enriched in saponite are probably good first-order analogs for Ceres dark material.

None of the materials in our study shared the characteristics of the Ceres bright spots. This is consistent with the bright spots being relatively more enriched in NH_4 salts and Na carbonates (De Sanctis et al. 2016). We took care to avoid the generation of such salts by fluid–rock interactions in the presence of ammonium in this study, though early trials by ammoniation with NH_4Cl solutions did lead to salts.

Though the band position and width of saponite is a clear match, the ammoniated smectite spectra in our study show a lowered continuum reflectance relative to the initial particulates (Fig. 2) that makes them less Ceres-like in overall shape after ammoniation. This is likely because some of the particulates in the $<150 \mu\text{m}$ samples clumped after the wet–dry cycling, leading to a coarsening of the effective particle size of the mixtures. On Ceres, there would be comminution from meteorite impacts and finer surface material. We avoided the additional grinding because prior workers advised it could disrupt hydrogen bonds in interlayers (e.g., Suquet et al. 1975), but gentle separation seems warranted in future work to obtain Ceres-like endmember spectra of appropriate particle size. Additionally, were we to repeat the study, we might first try to exchange all interlayers of all samples (phyllosilicate and meteorite) to a specific cation, dry fully, and only then do ammoniation to avoid any effects due to the type of pre-existing interlayer cation and prior amount of interlayer water. We would also conduct further measurements to quantify ammonium uptake/cation sites available.

CONCLUSIONS

The Al-, Fe-, and Mg-smectite clay mineral samples treated with NH_4 -acetate in solution at room temperature readily acquired an infrared absorption at 3.01–3.06 μm due to ammonium ion substitution in the clay interlayer, and XRD data showed that the spacing of the clay interlayer decreased. As expected, phyllosilicates lacking an exchangeable interlayer like serpentines and chlorite did not exhibit this absorption upon treatment nor did their 001 peaks shift.

We also attempted to ammoniate a suite of carbonaceous chondrites, ranging from CM chondrites rich in serpentine to CI and C2 chondrites with appreciable saponite, using the same procedures.

Surprisingly, none of the meteorites exhibited a strengthened $\sim 3.05 \mu\text{m}$ absorption after treatment; some samples did show a $3.09 \mu\text{m}$ absorption (Cold Bokkeveld); other samples showed a weak $3.05 \mu\text{m}$ absorption both before and after treatment (Tagish Lake). The NH_4^+ absorption may have been too weak to discern due to relatively low abundances of smectite in the meteorites, though smectite was present in Orgueil (trace) and Tagish Lake (minor to major). Cation exchange of the NH_4^+ may have been inhibited by the small size of smectite crystallites intimately associated with matrix materials (organic and amorphous gels); occupation of interlayer sites with organics; and/or complexing of NH_4^+ with other organics, salts, or metal oxides in the matrix rather than smectite. For Tagish Lake, more speculatively, smectites may have already been ammoniated. Future detailed studies of meteorite phyllosilicates are required to discriminate between these possibilities. The meteorite clay fraction did, when separated from other meteoritic materials, show XRD evidence for interlayer cation exchange upon various treatments.

At low temperatures relevant to Ceres and under vacuum, the infrared spectra of the smectite clays mostly retain the same absorption band position observed at room temperature, and NH_4^+ absorptions sometimes become stronger. At both room temperature and cold temperatures to 90K, ammoniated saponite exhibits $3.04\text{--}3.06 \mu\text{m}$ absorptions similar to that found on Ceres. Consequently, the presence of ammoniated Mg-smectite appears to be the simplest explanation for the absorption observed in Ceres's dark material.

Acknowledgments—We appreciate the work of Stephanie Meursing in acquiring the XRD data. Thanks to Allan Treiman for providing the Griffith saponite, Mark Raven for providing the nontronites, Dave Rachford for providing the IMV saponite, and Christopher Herd for providing the Tagish Lake sample. Thanks to John Beckett for facilitating use of meteorites in the Caltech collection. Robert Hodyss gratefully acknowledges funding from the NASA Astrobiology Institute (Icy Worlds). Bethany Ehlmann thanks the Dawn project for welcoming her as an affiliate and partially supporting this work. Thanks to Janice Bishop, an anonymous reviewer, Hap McSween, and Tim Jull for comments that improved this manuscript.

Editorial Handling—Dr. Hap McSween

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SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article:

Data S1. Visible to infrared spectra and XRD patterns of samples are available at <MAPS site TBD> as both text files and ENVI spectral library files.
