Hydrous mineralogy of CM and CI chondrites from infrared spectroscopy and their relationship with low albedo asteroids

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Abstract

IR spectroscopy is one of the few techniques that can directly probe water molecules in rocks. This method has been used to characterize the mineralogy of hydrated/hydrous carbonaceous chondrites, and to link known meteorite families with spectroscopic observations of low albedo asteroids. In this paper, we present measurements of the infrared transmission spectra of matrix chunks from 3 CI and 9 CM chondrites. Spectra were measured at ambient conditions and then at different temperatures along a dehydration path toward high-T ($\sim$300 °C) under primary vacuum. At ambient conditions, the 3-μm spectral range is always dominated by adsorbed atmospheric water molecules. Upon moderate ($\sim$100 °C) and high ($\sim$300 °C) heating under low pressure ($P < 10^{-4}$ mbar), adsorbed water and then phyllosilicates interlayer water are removed, revealing a residual absorption band around 3 μm. This band is a characteristic IR feature of the phyllosilicate phases which dominate the mineralogical assemblage of hydrated carbonaceous chondrites. Among the CM chondrites, the high-T spectra reveal a strong variability that appears correlated with the alteration classification scheme of Rubin et al. (2007) and Howard et al. (2009a). The 3-μm band continuously evolves from a broad feature peaking at 3550–3600 cm^{-1} for the weakly altered CMs (Murchison-type) to a sharp asymmetric peak at $\sim$3675 cm^{-1} for the more extensively altered samples (Cold Bokkeveld-type). We attribute this spectral evolution to variations in the chemistry of the phyllosilicate phases from Fe-rich to Mg-rich. On the other hand, the 10-μm spectral region shows a single broad peak which does not compare with known terrestrial serpentine spectra, probably due to high structural disorder of the chondrite phyllosilicate phases. The present work clearly shows that previously published reflectance spectra of chondrites are biased by the presence of adsorbed terrestrial water molecules. Laboratory data collected under dry conditions are needed to reinterpret the chondrite–asteroid connection from the comparison of their 3-μm absorption features.
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1. INTRODUCTION

Carbonaceous chondrites record evidence for the actions of water in the early Solar System. They can contain up to 10 wt.% of H_2O in the form of hydrated, hydroxylated or oxyhydroxylated mineral phases, that were produced

possibly during some nebular stage, but more likely through parent body processes (e.g., Brearley, 2006). The extent of aqueous alteration varies across the different carbonaceous chondrite groups, but is possibly also variable on a given parent body (McSween, 1979). Many workers have focussed on the numerous CM chondrites and tried to identify a mineralogical evolution among the samples. A variety of classification schemes have been discussed based on different petrological, mineralogical and chemical criterion (McSween, 1979; Bunch and Chang, 1980; Burgess et al., 1991; Zolensky et al., 1993; Browning et al., 1996; Rubin et al., 2007; Howard et al., 2009a,b).

Infrared spectroscopy is one of the few techniques that can directly probe protons and then OH and H_2O groups (Farmer, 1974). This technique is widely used in planetary sciences to identify ice and hydrated minerals at the surface of asteroids and planets from solar reflectance spectroscopy (Hiroi et al., 1996, 2001; Rivkin et al., 2000; Jouglet et al., 2007; Milliken and Rivkin, 2009). The diffuse reflectance IR spectra of several carbonaceous chondrites were measured by Miyamoto and Zolensky (1994) to quantify the amount of hydrous minerals they contain. The intensity of the so-called 3-μm band absorption feature is the combination of the stretching v_1 and antistretching v_3 vibration modes of water. This intensity was found to slightly correlate with the total hydrogen content of the samples. However, the connection to the amount of phyllosilicates appeared unclear (Miyamoto and Zolensky, 1994). A major limitation of this study lies in the fact that spectra were measured at ambient conditions. Thus, the amount of adsorbed water is high and potentially dominates the reflectance spectra of the samples (Pommerol et al., 2009). More recently Osawa et al. (2005) tentatively built a taxonomy of carbonaceous chondrites from infrared transmission measurements. Spectra were obtained at ambient conditions and might also be perturbed by a significant amount of adsorbed water.

Here, we report on mid-infrared measurements of the matrices of several CI and CM chondrites in a dry environment allowing the removal of the spectral contribution of adsorbed terrestrial water. Transmission spectra were obtained using an environmental cell than can be heated up to 300 °C and maintained under primary or secondary vacuum. This approach enables to remove weakly bonded water molecules and observe the mineralogical signatures of structural OH and H_2O. An evolution, correlated with the alteration sequence defined by Rubin et al. (2007) is observed among the spectra of CM chondrites. This spectral evolution might correspond to the progressive replacement of the phyllosilicates interlayer cations Fe^{2+} by Mg^{2+} as alteration progresses on the CM parent body. The present work also evidences that under ambient conditions the IR spectra of hydrated matrices are dominated by terrestrial water, hampering a reliable connection between laboratory and asteroid spectra.

2. SAMPLES AND ANALYTICAL METHODS

2.1. Samples

Twelve meteorites having experienced aqueous alteration on their parent bodies were considered in the present work, among which 9 CM and 3 CI chondrites. The selected CM samples span almost the full range of aqueous alteration (from 2.6 to 2.0) as defined by Rubin et al. (2007). They are: Queen Alexandra Range 97990 (QUE 97990, 2.6), Murchison (2.4), Murray (2.4/2.5), Queen Alexandra Range 99355 (QUE 99355, 2.3), Cold Bokkeveld (2.2), Mighei, Boriskino and Nawapali (not studied in Rubin et al., 2007). The CI chondrites Alais, Ivuna and Orgueil were studied as well. Samples were provided by the Museum National d'Histoire Naturelle (Paris, France) and the Johnson Space Center – NASA (Houston, USA).

2.2. Infrared spectroscopy

Infrared spectra were obtained with a BRUKER HYPERION 3000 infrared microscope at the Laboratoire de Planétologie de Grenoble (LPG, France). The IR beam was focused through a 15× objective and the typical size of the spot on the sample was ~50 × 50 μm². Spectra were measured at 4 cm^{-1} spectral resolution with a MCT detector cooled with liquid nitrogen. Particular care was devoted to sample preparation, which is a critical issue in infrared micro-spectroscopy. Samples must be thin (<100 μm) and their surface flat enough, in order to avoid absorption band saturation and scattering artefacts, respectively (Raynal et al., 2000). Matrix chunks were first finely powdered by crushing them between two glass slides. Second, small matrix grains (<100 μm) were selected under a binocular microscope among chondrule fragments (only in CM chondrites) and sulfate or carbonate grains (in CI and CM chondrites). In a first serie of measurements, the matrix grains were crushed between two sapphire windows. The window having the largest amount of sample was kept for analysis. Because of the strong mid-IR absorption of sapphire, these infrared measurements covered only the 4000–1500 cm^{-1} range. In order to gain insights into the Si–O stretch band at ~1000 cm^{-1}, some matrix grains were prepared on KBr windows with the protocol described by Raynal et al. (2000). Matrix grains were first pressed between two glass slides, and transferred by pressing a KBr window onto one of them. The sapphire or KBr windows were finally inserted into an environmental cell, designed and built at LPG. This cell enables temperatures up to 300 °C to be reached under primary or secondary dynamic vacuum (from 10^{-4} down to 10^{-7} mbar). Optical access is permitted from both sides of the cell through ZnS or KBr windows thus enabling measurements in transmission. Samples were progressively heated up to 300 °C with typical steps at 100, 150, 200 °C, and spectra were recorded at each temperature step. Below, we qualify of "high-temperature" the spectra acquired at a temperature of 300 °C.

Synthetic Li–Mg–serpentine (chrysotile) was obtained following the method described in Wunder et al. (2009). Initial solid starting-materials, γ-Al_2O_3, Li_2O, synthetic brucite, ($Mg(OH)_2$), or synthetic talc, ($Mg_3Si_4O_{10}(OH)_2$) in the presence of excess water were mixed in the stoichiometric composition of $[(Mg_{44}Li_2Al_2)Si_{32}]O_{80}(OH)_{64}$. Synthesis was performed at 0.4 GPa, 400 °C for 31 days using standard cold-seal hydrothermal vessels.

2.3. Spectra processing

The transmission spectra were converted into absorbance by applying $A = -\log(T/T_0)$, where T_0 is the transmittance without sample and T the transmittance with the sample. In order to compare transmission spectra of samples of different thicknesses, the spectra were normalized. In the case of measurements focusing on the 3 μm band, the maximum absorbance of this broad band was set to 1. Prior to normalization, a spline baseline was calculated and subtracted with control points at 1900, 2000, 2050, 2100, 3750, 3800 and 3900 cm^{-1}. The band full-width at half maximum (FWHM) and barycenter were then calculated. It should be emphasized that scattering effects could not be fully removed, leading to variable uncertainties in the FWHM and barycenter spectral parameters. In the case of acquisition with a KBr window, the spectra are normal-

ized to the absorbance of the Si–O stretching band around 1000 cm^{-1}.

3. RESULTS

3.1. Spectral evolution during dehydration in the 3 μm region

Typical IR spectra of the CI chondrite Orgueil and the CM Boriskino measured in the environmental cell are shown in Figs. 1 and 2. In the case of Orgueil, at room pressure and temperature, a broad feature is observed ranging from 3650 to 3000 cm^{-1} together with a sharp peak at 3700 cm^{-1}. This spectrum is consistent with published transmission measurements (Zaikowski, 1979; Osawa et al., 2001, 2005). Upon heating to 300 °C, the broad feature centered around 3350 cm^{-1} progressively disappears, until only a sharp asymmetric peak dominates the spec-
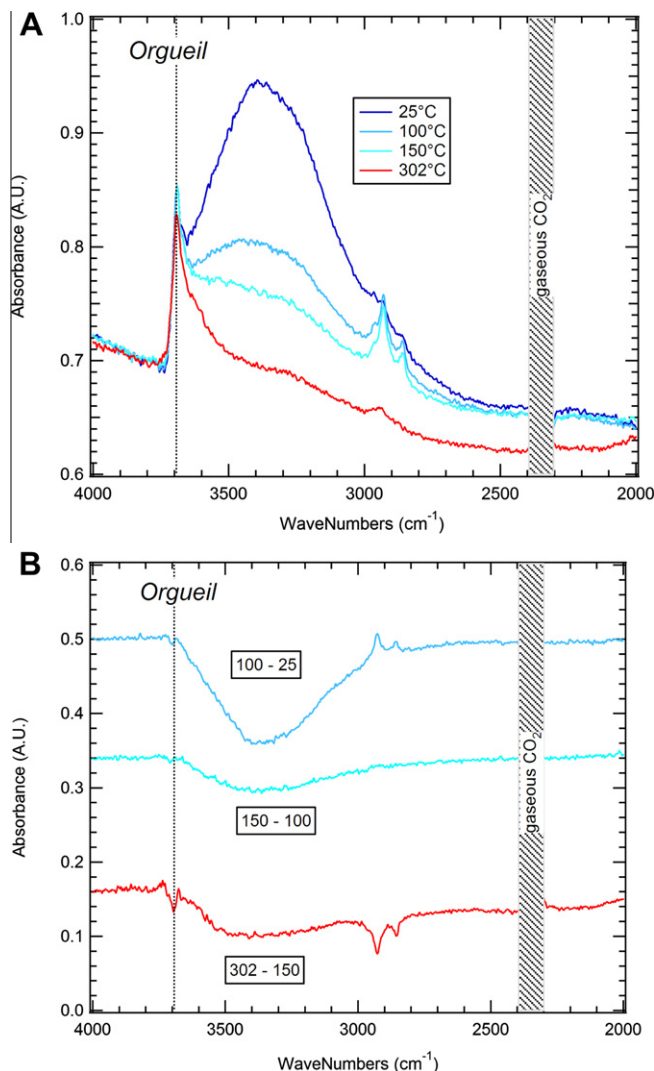

Fig. 1. (A) Transmission spectra (in absorbance) of Orgueil at different temperatures. Spectra were successively measured at increasing temperature steps. At ambient condition, spectra are dominated by the signature of molecular water (adsorbed and interlayer water). The 2300–2400 cm^{-1} spectral feature on all spectra is due to gaseous CO_2. (B) Spectral differences between the measurements of (A) at different temperatures. Spectra are shifted vertically for clarity.
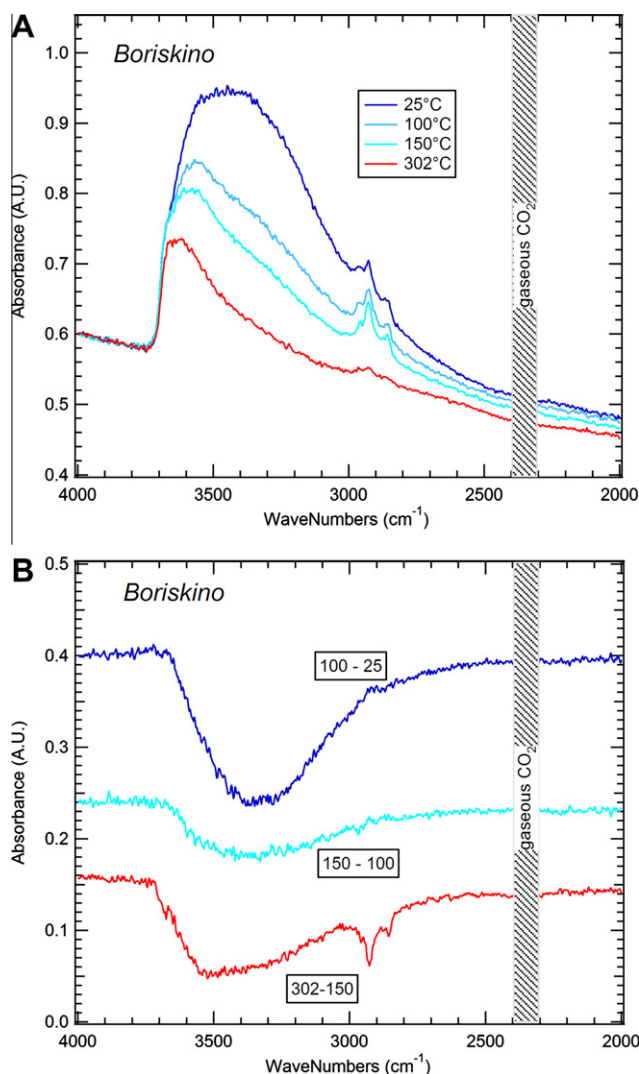
Fig. 2. (A) Transmission spectra (in absorbance) of Boriskino at different temperatures. Spectra were successively measured at increasing temperature steps. At ambient condition, spectra are dominated by the signature of molecular water (adsorbed and interlayer water). (B) Spectral differences between the measurements of (A) at different temperatures. Spectra are shifted vertically for clarity.

trum. This remaining sharp feature at 3670 cm^{-1} is due to the stretching mode of OH groups (Ryskin, 1977), which probes the local cationic environment of the hydroxyl groups in the octahedral layer of the phyllosilicate, with possibly a contribution from tetrahedral cations. In the case of Boroskino (CM), the room temperature spectrum displays a broad asymmetric feature with a maxima between 3350 and 3450 cm^{-1}. Upon heating this feature is progressively reduced toward a broad asymmetric feature centered around 3650 cm^{-1}.

The high-T (300 °C) spectrum reported here likely probes only the hydroxyl groups, as the water bending mode ν_2 peaking at ~1650 cm^{-1} disappears between 100 and 300 °C (Fig. 3). Therefore, at room conditions, the broad feature centered at 3350 cm^{-1} is due to the presence of terrestrial molecular water. Hydroxyl groups are known to remain stable up to at least 500 °C in the case of phyllosilicates with a tetrahedral–octahedral (T:O) structure layer

(Beaufort et al., 1998) or tetrahedral–octahedral–tetrahedral (T:O:T) (Drits et al., 1998; Kloprogge et al., 2000), as are phyllosilicates in CI and CM chondrites.

In order to characterize the spectral signature of water that is expelled upon heating, we subtracted spectra measured at different temperatures. We simply subtracted the absorbance value measured at a high temperature by the value obtained at a lower temperature. This subtraction reveals that a significant amount of water is released between 25 and 100 °C in the case of Orgueil (CI, Fig. 1B) and Boriskino (CM, Fig. 2B). The spectral signature of water expelled between 25 and 100 °C and that of the water expelled between 150 and 300 °C are significantly different as is clearly seen for Boriskino (Fig. 2B). In the first case, the band appears symmetric and its maximum peaks at 3350 cm^{-1} while in the second it is asymmetric and peaks around 3520 cm^{-1}. The low temperature water fraction (~100 °C) is most likely adsorbed water which is known
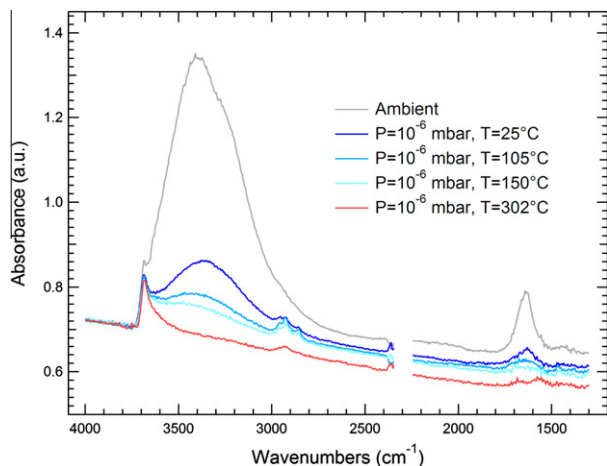
Fig. 3. Transmission spectra of Orgueil obtained during a dehydration experiment, showing both the 3 and 6 μm features. The disappearance of the 6-μm feature upon heating is indicative of H_2O loss. Residual peaks at 300 °C above 6 μm are likely due to the presence of organics.

Fig. 4. High-T (300 °C), low pressure spectra of the CM and CI chondrites. Spectra are shifted vertically for clarity. There is a clear evolution from a Murchison-type to an Orgueil-type spectrum, that appear to be related to the classification of Rubin et al. (2007). The vertical black line corresponds to the absorption maximum of the Orgueil spectra. In the case of multiple measurements of a given sample, the different spectra are presented.

Fig. 5. IR spectra of various serpentine minerals (Salisbury et al., 1991) and Cold Bokkeveld (this study). Spectra are shifted vertically for clarity. The vertical dashed lines correspond to the absorption maximum of antigorite and chrysotile.

to desorb at moderate temperature (<100 °C), while the high-temperature fraction is almost certainly interlayer water within phyllosilicates.

3.2. High-T spectra of CI and CM chondrites in the 3 μm region

The infrared spectra of CM and Orgueil (CI) chondrites measured at 300 °C and under primary vacuum are presented in Fig. 4. Among CM chondrites, two end-member spectral signatures were identified with type samples Murchison and Cold Bokkeveld.

The spectrum of Murchison shows a broad asymmetric feature with a maximum around 3580 cm^{-1}, while the spectrum of Cold Bokkeveld reveals a sharp asymmetric feature with a well-defined peak at 3675 cm^{-1} (Fig. 4). Among CM chondrites, there appears to be a continuous evolution between those two end-members. But some variability within a sample is also encountered (Fig. 4). The spectra of CI chondrites look similar to some of the CM chondrites, in particular Cold Bokkeveld and Nogoya. Although the room temperature spectra might have a contribution from ferrihydrite, it should be negligible at high temperature due to decomposition of this metastable phase (Michel et al., 2007). The 3-μm band is thus likely to be controlled by phyllosilicates only. The strong absorption maximum at 3675 cm^{-1} observed in Cold Bokkeveld like meteorites suggests the presence of Mg-rich serpentines that display sharp OH stretching absorptions in the near-IR spectral region (Ryskin, 1977; Salisbury et al., 1991). Indeed, the strongest absorption of terrestrial lizardite, chrysotile and antigorite are, respectively, found at 3686, 3691 and 3674 cm^{-1} (Salisbury et al., 1991; Post and Borer, 2000). The absorption maximum for the Cold Bokkeveld-type spectra observed at 3675 cm^{-1} most closely corresponds to antigorite (Fig. 5). However, the 10-μm region reveals that the phyllosilicate phases encountered in the CM and CI chondrites
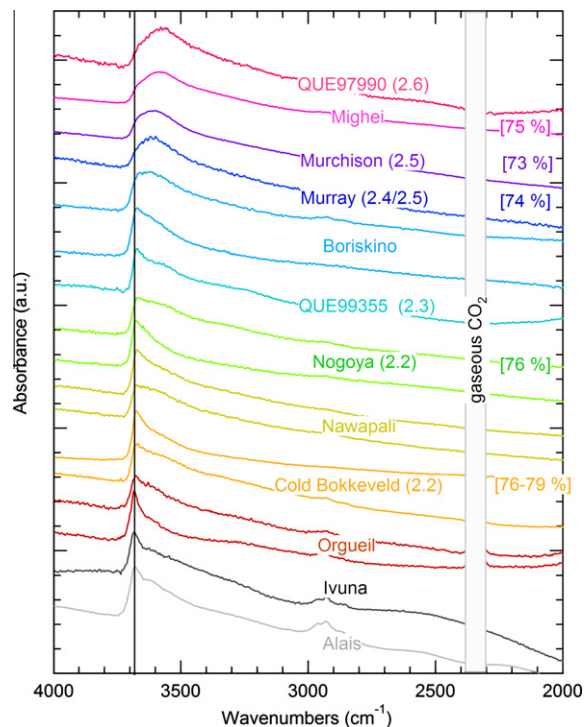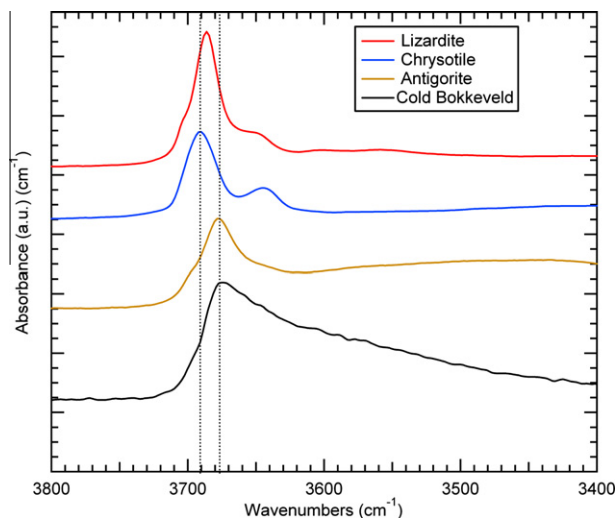
are spectroscopically distinct from commonly encountered terrestrial serpentines (see Section 3.3). Previous TEM and XRD studies show that there is no single poly-type

of serpentine in these samples, hence, we are likely measuring contributions from multiple or highly disordered serpentine phases.

The spectra presented in Fig. 4 have been ordered based on naked-eye observation that reveals a continuous evolution. Spectra obtained on different matrix chunks for a given sample show that some within sample variation is observed as reported in Fig. 4 (in the case of Orgueil, Boriskino and Nogoya). However, the spectra show that this within sample variation is never as high as the inter-sample variations for the CI and CM we have studied so far. Although we have extracted matrix chunks and thus the petrological context is lost, we propose that this intra-sample variability is due to an heterogeneity in the extent of aqueous alteration, that lead to a spatial heterogeneity in the alteration products at the millimeter scale.

3.3. Si–O stretching vibration modes in the 10 μm region

The 10 μm region of infrared spectra is usually dominated by the Si–O stretching band, strongly controlled by the crystallographic structure. Terrestrial serpentines typically display multiple sharp diagnostic peaks used to distinguish them. The spectra obtained on the CM chondrites Murchison, Cold Bokkeveld and Murray and the 3 CI chondrites are reported in Fig. 6, along with the spectra of several terrestrial phyllosilicates including Mg–serpentines, saponite and cronstedtite. The spectra of the 3 CI chondrites are very similar, with a single unstructured broad feature centered around $1020\ cm^{-1}$. The apparent
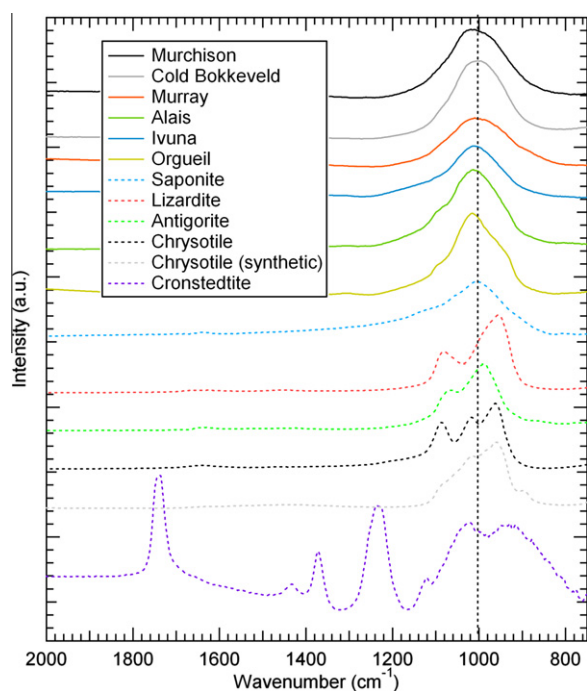

Fig. 6. IR spectra of various serpentine minerals (dotted curves) (Salisbury et al., 1991), Cold Bokkeveld, Murchison, and Murray CM and the three CI (Alais, Ivuna, Orgueil) in the 10 μm region. Spectra are shifted vertically for clarity. The vertical dashed line corresponds to the absorption maximum of saponite.

secondary peak around $1100\ cm^{-1}$ in the spectra of Alais (CI) and Orgueil (CI) can be attributed to the presence of tiny sulfate grains (Salisbury et al., 1991) not separated during sample preparation. The spectra of CM chondrites also display an unstructured band around $1000\ cm^{-1}$ very similar to that observed in CI spectra. This lack of spectral structure in CM chondrites surprisingly does not support the presence of well-known serpentine phases identified by transmission electron microscopic studies (e.g., Lauretta et al., 2000). We also compared spectra measured in of CM and CI chondrites with spectra of synthetic Mg–serpentine (chrysotile) obtained following the method described in Wunder et al. (2009). The 10 μm region of the synthetic serpentine still display three well-defined peaks and does not resembles CM or CI spectra (Fig. 6). It should be noted that any linear mixture of the spectra of terrestrial phyllosilicates displayed in Fig. 6 fails to reproduce the CM and CI chondrite spectra in the 10 μm region. The phyllosilicate phases in CMs, and likely in CIs, appear spectroscopically distinct from the terrestrial serpentines and saponites when considering the 10 μm band as previously noted by Bunch and Chang (1980).

4. DISCUSSION

4.1. Origin of the spectral diversity among CI and CM chondrites

The mineralogy of the phyllosilicates phases in CM and CI chondrites has mostly been studied using transmission electron microscopy (TEM), X-ray diffraction and electron microprobe. In CMs, the dominant phyllosilicates appear to be a serpentine related phase with a $\sim7\,\text{Å}$ spacing (e.g., Tomeoka et al., 1989), in which the Fe–Mg abundance is variable within both the octahedral and tetrahedral sites. Transmission electron microscopy has the advantage to identify the phyllosilicate phases in a petrographical context. But this local mineralogy may not be representative of the bulk sample mineralogy. Because the samples are usually very fine-grained (<100 nm), electron diffraction patterns are difficult to obtain. The identifications of phyllosilicates are thus mainly based on the basal spacing distance measured from high resolution TEM images on well-crystallized grains. In addition to serpentine minerals, using this technique, a menagerie of hydrated and hydroxylated minerals has been described including, chlorite, smectite and brucite. Although there might be continuity in their chemistry, two distinct populations of serpentines are observed in CMs (Tomeoka et al., 1989). An iron-rich phase referred to as cronstedtite, which generally displays platy "long" crystals (>100 nm), as opposed to Mg-rich serpentines which usually present small grain sizes (20 nm). In the case of CIs, the hydrous mineralogy is dominated by a mixture of serpentine and saponite (montmorillonite group smectite), that is found in association with ferrihydrite, a metastable disordered oxyhydroxide (Drits et al., 1993). The 3-μm region in the spectra we obtained on CM chondrites reveals the presence of two end-members, a Murchison-type and a Cold Bokkeveld-type, the latter being quite similar to Orgueil. The Cold Bokkeveld-type spectrum

resembles measurements performed on terrestrial serpentines in the fact that it presents a sharp asymmetric peak around 3670 cm^{-1} (Salisbury et al., 1991; Post and Borer, 2000). In the other hand, the Murchison-type spectra do not correspond to available spectra of terrestrial serpentine minerals in the 3-μm region. These observations suggest either that the phyllosilicate phases either are not serpentine minerals or they are, but, with a distinct crystal chemistry. There is an abundant literature in the case of clay minerals (Madejova et al., 1994; Bishop et al., 2002a, 2002b), but little is known on the effect of the OH bounding cation on the IR spectra of serpentine. Mg-rich serpentines typically display a sharp peak at about 3700 cm^{-1}, but mid-IR spectra of Fe-rich serpentine minerals are poorly documented. As an end-member, we measured IR spectra of terrestrial cronstedtite, under vacuum conditions and moderate temperature (~200 °C). The spectra reveal that H$_2$O-free cronstedtite has a broad absorption band centered around 3200 cm^{-1}, but does not resemble our results for Murchison. However, it does not look like the Murchison spectra, a meteorite which hydrous mineralogy is expected to be dominated by Fe-rich serpentine (Howard et al., 2009a). Therefore, what is usually called "cronstedtite" in the carbonaceous chondrites literature is strictly speaking not a cronstedtite mineral, and the term Fe-rich serpentine should be preferred. The IMA defines cronstedtite as Fe$^{2+}_2$Fe^{3+}(SiFe^{3+})O$_5$(OH)$_4$ hence when first TEM studies identified Fe–Mg serpentine the term cronstedtite should never have been used.

Further informations are obtained by analyzing the 10-μm region of the IR spectra. The spectra we measured in the Si–O stretching region are remarkably similar among the CM and CI chondrites, and remarkably different from terrestrial serpentines. In the case of CI chondrites, the 10-μm region spectrum appears consistent with saponite like phyllosilicates, but not with serpentines, although saponite and serpentine are known to be present in approximately equal proportion in CI chondrites (e.g., Tomeoka and Buseck, 1988). The same conclusion is obtained for CMs, whose mineralogy is dominated by serpentines (Papike, 1997). Two explanations can be proposed to resolve this discrepancy. A first possibility is that TEM studies that are made at the nanometer scale might not be representative of the global phyllosilicate mineralogy. However, bulk meteorite X-ray diffraction studies also suggest that serpentine minerals dominate the hydrous mineralogy of CI and CM chondrites matrices (Bunch and Chang, 1980; Howard et al., 2009a) as well as electron probe micro-analysis (Zolensky et al., 1993; Browning et al., 1996). The second possibility concerns crystallographic order. The lack of long-range ordering might explain the difference between the IR spectra of CM and CI matrices and the considered terrestrial serpentines. Disordered or amorphous silicates are known to exhibit an unstructured band peaking at ~1000 cm^{-1}, while crystalline silicates always exhibit a band with substructures due to crystalline solid-state effects (e.g., Davydov splitting, field correlation effect, LO–TO splitting; Poulet and Mathieu, 1970). The breakdown of long-range crystallographic ordering leads to the optical excitation of numerous vibration modes.

Finally, we interpret from the shape of the 10-μm band that most of phyllosilicates in CI and CM are highly disordered, whatever their chemical composition (i.e., their Fe/Mg ratio). Therefore, terrestrial Mg-rich serpentines (chrysotile, antigorite, lizardite) or almost pure Fe-bearing cronstedtite, cannot be considered as relevant mineralogical analogs of CI and CM phyllosilicates.

4.2. The alteration sequence and the alteration scenario

A number of studies have attempted to characterize the extent of aqueous alteration as were recently reviewed by Howard et al. (2009a). In a pioneering work McSween (1979) remarked that the matrix abundances of CM chondrites show variations that are correlated with a chemical evolution: the meteorites that contain the most matrix were found to be enriched in Mg compared to matrix-poor CM chondrites. From this observation, McSween (1979) suggested that the evolution of Mg/Fe might correspond to an alteration sequence, with a progressive increase of the Mg/Fe ratio of the phyllosilicate phases as the alteration advances.

Recognizing this chemical evolution of the phyllosilicate phases, Browning et al. (1996) tentatively defined a mineralogical alteration index (MAI) from defocused electron microprobe analysis of CM matrices. The MAI is an indicator of the amount of tetrahedral sites occupied by Fe^{3+} within matrix serpentines, a quantity that is expected to decrease as alteration progresses. Calculations of MAI are not straightforward, and require some assumptions.

Mechanisms and processes have been proposed to explain the variability of Mg/Fe in phyllosilicates of CM chondrites. Tomeoka et al. (1989) studied by TEM the petrographical relations between the alteration products. They developed an alteration model in which the different mineral precursors are successively altered, starting by the transformation of Fe/Ni metal into tochilinites [Fe(OH)$_2$(Fe,Ni)S]. Fe-rich matrix olivine subsequently reacts with the fluid to produce Fe-rich serpentines that are usually referred to as cronstedtite. In a following step, chondrule alteration begins which leaches Mg and Si into the fluid that reacts with tochilinite to produce Mg-rich serpentine. As tochilinite hydrolysis continues, more Fe-rich serpentines are produced together with sulfides.

One of the recognized properties of CM alteration is the fact that it is an isochemical process. With the exception of a few fluid mobile elements, major elements concentrations show very minor variations among the group (see Rubin et al. (2007) compilation). Iron is no exception, which suggests a low mobility of the fluid (Howard et al., 2009a).

Our results on CM chondrites indicate a continuous spectral evolution of the 3-μm feature between the end-members Murchison and Cold Bokkeveld types. This evolution appears in agreement with the progressive alteration scheme of Rubin et al. (2007) (Fig. 4). Because serpentine minerals were shown to become enriched in Mg as alteration progresses (Zolensky et al., 1993; Howard et al., 2009a,b) we interpret the spectroscopic evolution to be an effect of the bonding cation on the hydroxyl stretching mode. IR spectra on synthetic serpentine minerals with

various Fe/Mg ratios are required to strictly confirm this interpretation.

Many workers have attempted to define a set of criteria to qualify and/or quantify aqueous alteration (McSween, 1979; Bunch and Chang, 1980; Zolensky et al., 1993; Browning et al., 1996; Rubin et al., 2007; Howard et al., 2009a). This can be quantified on the basis of total phyllosilicate abundance for recovered meteorites but obviously not for asteroids. Here we propose to define a spectroscopic criterion to qualify the degree of aqueous alteration that can be applied both to meteoritic sample measurements, and to infrared observations of asteroids. We focus on the 3-μm region that displays significant variations in our measurements on meteorites and that can be measured on asteroids from reflectance spectroscopy with minor contribution from thermal emission. Asteroid reflectance spectra are obtained by measuring the intensity of the sunlight reflected by an object using Earth-based telescope or onboard IR spectrometer. These spectra typically involve multiple scattering within surface grains and cannot be related in a direct way to laboratory measurements of absorption spectra. However, in the case of absorption bands of moderate intensity (which is the case of the 3-μm band in phyllosilicates) and multiple scattering, the so-called diffuse reflectance spectra is mostly controlled by the imaginary index k, which is directly related to the absorption coefficient by $\alpha = 4\pi k/\lambda$ (where α is the absorption coefficient, k the imaginary index and λ the wavelength). Therefore, band shape (including band maximum position) is expected to have some first order resemblance when comparing a laboratory absorption spectra to a diffuse reflectance spectra. Under some hypothesis, the conversion might even be performed (Hapke, 1993). The band shape can be described by three parameters: the 3-μm band barycenter, the band maximum position, and its full-width at half maximum (FWHM). In order to calculate these parameters, a spline baseline correction (see Section 2.3) is performed on each spectrum before normalization. The barycenter is defined between 3400 and 3700 cm^{-1} as::

$$B_{3400}^{3700} = \frac{\sum_{v=3400}^{v=3700}(A(v) - C(v))v}{\sum_{v=3400}^{v=3700}(A(v) - C(v))}$$

where $A(v)$ is the absorbance at wavenumber v and $C(v)$ is the continuum intensity at the same wavenumber. This band parameter has been previously used to discriminate between different types of hydration on the Martian surface (Pommerol, 2009).

Fig. 7 presents the relationship between our three spectroscopic criteria, and the total phyllosilicate content measured by X-ray diffraction (Howard et al., 2009a). The amount of phyllosilicates can be seen as a first order indicator of the extent of aqueous alteration, and has been shown to correlate with Rubin et al. (2007) classification (Howard et al., 2009b). Our three criteria appear to be related to some degree with the extent of aqueous alteration (Fig. 7). The band maximum position and barycenter increase as alteration progresses, while the 3-μm band narrows and its FWHM becomes smaller. Although the correlations between the spectral parameters and the

amount of phyllosilicates are clear, some variability in the three criteria is present within a given sample. It might be due to sample heterogeneity, and possible optical artifacts due to light scattering (Raynal et al., 2000).

In order to visualize the full dataset in a 2D space, the band barycenter is plotted against the FWHM in Fig. 8. This figure reveals a common evolution of these two criteria: the FWHM decreases as the barycenter shifts to higher frequencies. The least altered sample according to the Rubin et al. (2007) or Howard et al. (2009a) classifications are on the lower-right end of the diagram (QUE 97990), while the heavily altered sample Nogoya is located on the upper left side. According to this diagram, the CM chondrites aqueous alteration sequence is (for increasing alteration): Cold Bokkeveld (2.2), Niger, Nogoya (2.2), Boriskino, Nawapali, Murray (2.4/2.5), Murchison (2.5), QUE 97990 (2.6) and QUE 99355 (2.3). With the exception of QUE 99355, there is a general agreement between our relative alteration degree and the classification of Rubin et al. (2007). In our classification of Fig. 8, QUE 99355 appears to be less altered than expected from Rubin et al. (2007) classification. However, naked-eye spectral comparison in Fig. 4 appears to show that QUE 99355 is intermediate between Nogoya and Murray, and then in agreement with Rubin et al. (2007). A possible explanation of the discrepancy when using our two spectral criterions is that they might be sensitive to small interference artifact presents in the IR spectra of QUE 99355 (Fig. 4) that are due to multiple light reflection on between the samples flat surfaces.

The diagram presented in Fig. 8 might still be quite helpful in trying to classify the extent of aqueous alteration from IR spectroscopy. Note that the technique is easy to implement and measurements are very fast and relatively cheap.

4.3. The CI–CM connection

Based on IR spectroscopy, two important observations can be made: the measurements show diversity within a given sample and there appears to be a continuous evolution from the heavily altered CI Orgueil toward the more weakly altered CM chondrites (Murchison-like) (Fig. 4). The intra-sample heterogeneity was observed in most samples for which measurements were duplicated, including the CI Orgueil and the CM Cold Bokkeveld. This heterogeneity might be explained by the mm-size chemical heterogeneities prior to alteration, or by a spatial heterogeneity of alteration for a given sample, but also by a combination of the two. Alteration has been observed to be heterogeneous in CMs, and the presence of alteration veins has been used to argue for a parent body process. In the case of Cold Bokkeveld, the rock was described as a breccia that contains clasts of various alteration degrees (Metzler et al., 1992). Our measurements were performed on random matrix chunks, and a similar study in a petrological context (i.e., *in situ*) might help in understanding the heterogeneity of the hydrous mineralogy. It is interesting to note that by XRD Cold Bokkeveld is the only CM yet analyzed to show significant inter sample heterogeneity.
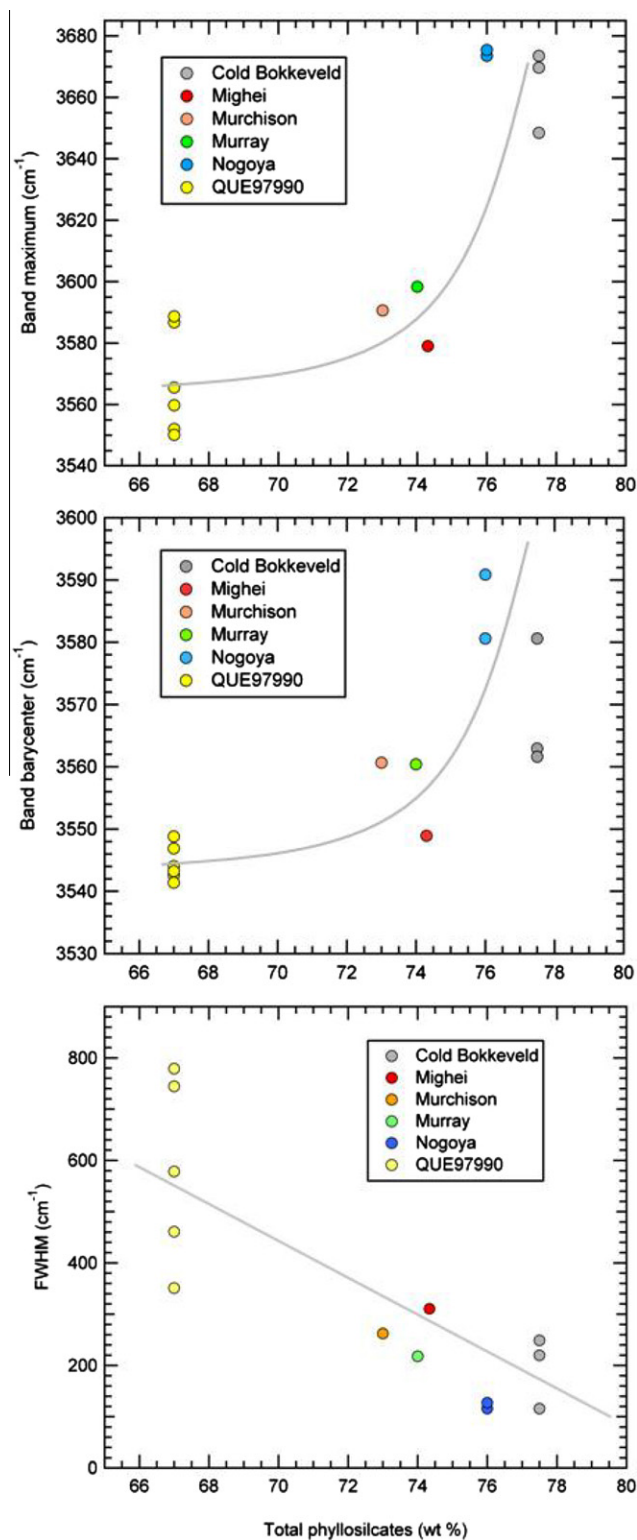
Fig. 7. 3-µm Band maximum, band barycenter and FWHM (full-width half maximum) as a function of the total phyllosilicates content as measured by X-ray (Howard et al., 2009a,b). The black curves are quides for the eye.

The continuous evolution between CM and CI previously raised the question of the genetic link between the two chondrite groups. From mass balance calculation

Zanda et al. (2006, 2009) suggested that the oxygen isotope systematic and volatile content variability can be explained by a mixture between three components and they suggest a
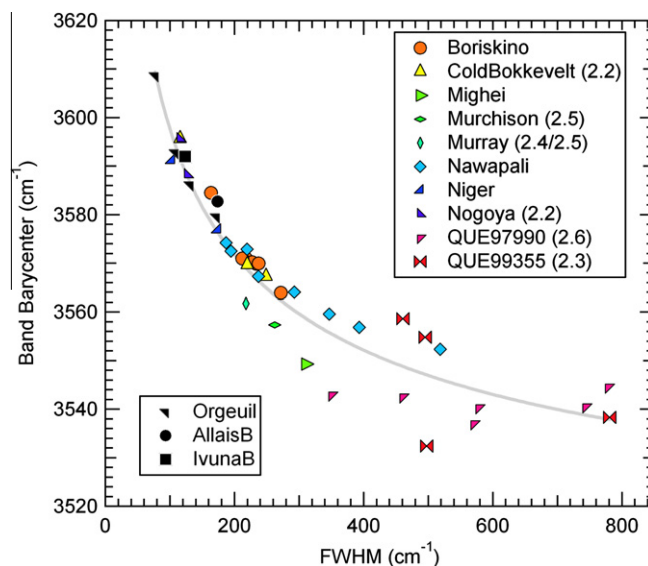
Fig. 8. 3-μm Band barycenter as a function of its FWHM for the different CM and CI chondrites samples. The black curve is a second order polynomial regression to the dataset.

chemical continuity among carbonaceous chondrites. On the contrary, H isotopic compositions of CM and CI chondrites matrix measured by Eiler and Kitchen (2004), tend to indicate a different protolith or fluid composition for CM and CI meteorites. Although the fluids might have been different in term of hydrogen isotopes, the alteration products appear to be quite similar between highly altered CM and CI which means that the mineralogical processes were likely similar.

4.4. The CM chondrite/asteroid connection

C-type asteroids are the most abundant asteroids in the main belt and display spectral features that suggest a relationship with carbonaceous chondrites (Jones et al., 1990). In particular, C-type asteroids have a low albedo and some of them exhibit an IR absorption around 3-μm (Jones et al., 1990; Lebofsky et al., 1990). These asteroids have been tentatively connected to specific meteorite groups by comparing observed solar reflectance spectra to laboratory measurements.

The spectra obtained at low pressure and moderate temperature in the present work reveal that terrestrial adsorbed water significantly perturbs the IR signature at 3 μm. In the case of Murchison (CM), the spectrum at ambient conditions is dominated by a broad peak centered at $\sim$3300 cm^{-1} (2.95 μm), while the spectra recorded in "dry" atmospheric conditions show an asymmetric peak centered at $\sim$3670 cm^{-1} (2.72 μm) with a broad long wavelength wing (Fig. 9). It is extremely likely that the signature of adsorbed water is strongly present in all laboratory reflectance spectra measured at ambient conditions (Pommerol et al., 2009) and thus most previously published measurements of terrestrial minerals and chondrite infrared spectra are likely biased for asteroid comparison. At the surface of asteroids, only minute amounts of adsorbed water can be expected. In order to obtain valid analogs of infrared reflec-
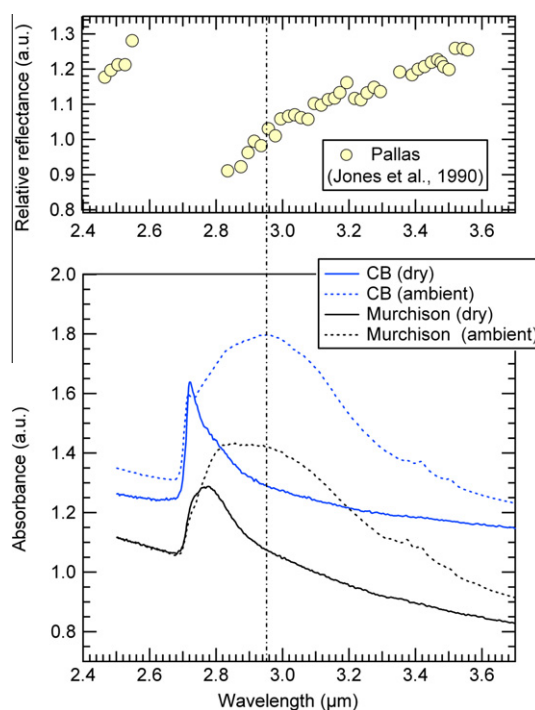

Fig. 9. IR transmission spectra (in absorbance) of Murchison and Cold Bokkeveld (CB) at ambient and dry ($T = 300$ °C, primary vacuum) conditions. The reflectance spectrum of Pallas (Jones et al., 1990) is also presented for comparison.

tance spectra for altered parent bodies (e.g., CM, CI), meteorite reflectance spectra acquired in dry vacuum conditions are required.

Pallas is a large low albedo asteroid on which a 3-μm feature was observed (Jones et al., 1990). We will not discuss here the nature of Pallas surface material, but rather use its reflectance spectrum as an illustration of the 3-μm band

problem. Fig. 9 presents the spectrum of Pallas (2) together with our measurements of Murchison and Cold Bokkeveld both in ambient and dry conditions. The comparison between the ambient meteorite spectra and the Pallas observation displays a clear incompatibility in band position and shape, despite the limited spectral coverage of the asteroid spectrum. However, when adsorbed water molecules are removed, the absorption maximum is shifted toward lower wavelengths and the two CMs spectra appear to be possible candidates for interpreting Pallas surface material reflectance spectra. However, asteroids observations in the 2.6–2.8 μm range are requisite for a detailed comparison of band position and shape with chondrite spectra.

5. CONCLUSION

We have measured the near-infrared spectra of CM and CI carbonaceous chondrites, under ambient and dry conditions. Adsorbed water strongly dominates the 3-μm region in the spectra measured under ambient conditions. When adsorbed water is removed by moderate heating under vacuum, the OH absorption band is clearly observed and we show that it displays a continuous spectral evolution between samples. We qualify this 3-μm band spectral evolution by mean of spectroscopic criteria (band barycenter, position of the maximum and FWHM), which appear to be correlated to the extent of aqueous alteration as defined by Rubin et al. (2007) and Howard et al. (2009a) from independent methods. We propose that our spectroscopic criteria reflect the evolution of the chemistry of the phyllosilicates phase from magnesian to ferrous as alteration processes. In the future, synthetic serpentines with chemistry analogous to that of chondrites are needed to characterize the effects of the tetrahedral and octahedral cations on the infrared spectra, and possibly to use the near-IR spectra of chondrites to quantify their chemical changes induced by alteration.

Previously published infrared spectra of carbonaceous chondrites were measured under ambient conditions. Similarly to our transmission spectra under similar conditions, those reflectance measurements are very likely perturbed by adsorbed water, especially in the 3 μm spectral range. Therefore reflectance spectra of carbonaceous chondrites in "dry conditions" are strongly needed in order to have valid analog measurements for direct comparison with published asteroid reflectance spectra and future spectral observations of 21 Lutetia by the VIRTIS instrument aboard the Rosetta spacecraft.

REFERENCES

Beaufort D., Cassagnabere A., Petit S., Lanson B., Berger G., Lacharpagne J. C. and Johansen H. (1998) Kaolinite-to-dickite reaction in sandstone reservoirs. *Clay Miner.* **33**, 297–316.

Bishop J., Madejova J., Komadel P. and Froschl H. (2002a) The influence of structural Fe, Al and Mg on the infrared OH bands in spectra of dioctahedral smectites. *Clay Miner.* **37**, 607–616.

Bishop J., Murad E. and Dyar M. D. (2002b) The influence of octahedral and tetrahedral cation substitution on the structure of smectites and serpentines as observed through infrared spectroscopy. *Clay Miner.* **37**, 617–628.

Brearley A. J. (2006) The action of water. In *Meteorites and the Early Solar System II* (eds. R. P. Bonzel, D. S. Lauretta and H. Y. McSween Jr.). The University of Arizona Science Series, Tuczon.

Browning L. B., McSween H. Y. and Zolensky M. E. (1996) Correlated alteration effects in CM carbonaceous chondrites. *Geochim. Cosmochim. Acta* **60**, 2621–2633.

Bunch T. E. and Chang S. (1980) Carbonaceous chondrites. II: Carbonaceous chondrite phyllosilicates and light element geochemistry as indicators of parent body processes and surface conditions. *Geochim. Cosmochim. Acta* **44**, 1543–1577.

Burgess R., Wright I. P. and Pillinger C. T. (1991) Determination of sulfur-bearing components in C1 and C2 carbonaceous chondrites by stepped combustion. *Meteoritics* **26**, 55–64.

Drits V. A., Lindgreen H., Salyn A. L., Ylagan R. and McCarty D. K. (1998) Semiquantitative determination of trans-vacant and cis-vacant 2: 1 layers in illites and illite-smectites by thermal analysis and X-ray diffraction. *Am. Miner.* **83**, 1188–1198.

Drits V. A., Sakharov B. A., Salyn A. L. and Manceau A. (1993) Structural model for ferrihydrite. *Clay Miner.* **28**, 185–207.

Eiler J. M. and Kitchen N. (2004) Hydrogen isotope evidence for the origin and evolution of the carbonaceous chondrites. *Geochim. Cosmochim. Acta* **68**, 1395–1411.

Farmer V. C. (1974) *The Infrared Spectra of Minerals*. London, p. 539.

Hapke B. (1993) *Theory of Reflectance and Emittance Spectroscopy*. Cambridge University Press, Cambridge.

Hiroi T., Zolensky M. E., Pieters C. M. and Lipschutz M. E. (1996) Thermal metamorphism of the C, G, B, and F asteroids seen from the 0.7 micron, 3 micron and UV absorption strengths in comparison with carbonaceous chondrites. *Meteorit. Planet. Sci.* **31**, 321–327.

Hiroi T., Zolensky M. E. and Pieters C. M. (2001) The Tagish lake meteorite: a possible sample from a D-type asteroid. *Science* **293**, 2234–2236.

Howard K. T., Benedix G. K., Bland P. A. and Cressey G. (2009a) Modal mineralogy of CM2 chondrites by X-ray diffraction (PSD-XRD). Part 1: Total phyllosilicate abundance and the degree of aqueous alteration. *Geochim. Cosmochim. Acta* **73**, 4576–4589.

Howard K. T., Benedix G. K., Bland P. A. and Cressey G. (2009b) PSD-XRD modal mineralogy of CM chondrites spanning the complete petrographic range. In: *72nd Annual Meeting of the Meteoritical-Society*, Nancy, France.

Jones T. D., Lebofsky L. A., Lewis J. S. and Marley M. S. (1990) The composition and origin of the C, P, and D asteroids-water as a tracer of thermal evolution in the outer belt. *Icarus* **88**, 172–192.

Jouglet D., Poulet F., Milliken R. E., Mustard J. F., Bibring J. P., Langevin Y., Gondet B. and Gomez C. (2007) Hydration state

of the Martian surface as seen by Mars Express OMEGA: 1. Analysis of the 3 mu m hydration feature. *J. Geophys. Res. (Planets)* **112**, E08S06, doi:10.1029/2006JE002846.

Kloprogge J. T., Frost R. L. and Hickey L. (2000) Infrared emission spectroscopic study of the dehydroxylation of some hectorites. *Thermochim. Acta* **345**, 145–156.

Lauretta D. S., Hua X. and Buseck P. R. (2000) Mineralogy of fine-grained rims in the ALH 81002 CM chondrite. *Geochim. Cosmochim. Acta* **64**, 3263–3273.

Lebofsky L. A., Jones T. D., Owensby P. D., Feierberg M. A. and Consolmagno G. J. (1990) The nature of low-albedo asteroids from 3-μm multi-color photometry. *Icarus* **83**, 16–26.

Madejova J., Komadel P. and Cicel B. (1994) Infrared study of octaedral site populations in smectites. *Clay Miner.* **29**, 319–326.

McSween H. Y. (1979) Alteration in CM carbonaceous chondrites inferred from modal and chemical variations in matrix. *Geochim. Cosmochim. Acta* **43**, 1761–1770.

Metzler K., Bischoff A. and Stoeffler D. (1992) Accretionary dust mantles in CM chondrites – evidence for solar nebula processes. *Geochim. Cosmochim. Acta* **56**, 2873–2897.

Michel F. M., Ehm L., Liu G., Han W. Q., Antao S. M., Chupas P. J., Lee P. L., Knorr K., Eulert H., Kim J., Grey C. P., Celestian A. J., Gillow J., Schoonen M. A. A., Strongin D. R. and Parise J. B. (2007) Similarities in 2-and 6-line ferrihydrite based on pair distribution function analysis of X-ray total scattering. *Chem. Mater.* **19**, 1489–1496.

Milliken R. E. and Rivkin A. S. (2009) Brucite and carbonate assemblages from altered olivine-rich materials on Ceres. *Nat. Geosci.* **2**, 258–261.

Miyamoto M. and Zolensky M. E. (1994) Infrared diffuse reflectance spectra of carbonaceous chondrites: amount of hydrous minerals. *Meteoritics* **29**, 849–853.

Osawa T., Kagi H. and Nagao K. (2001) Mid-infrared transmission spectra of individual Antartic micrometeorites and carbonaceous chondrites. *Antarct. Meteorit. Res.* **14**, 71–88.

Osawa T., Kagi H., Nakamura T. and Noguchi T. (2005) Infrared spectroscopic taxonomy for carbonaceous chondrites from speciation of hydrous components. *Meteorit. Planet. Sci.* **40**, 71–86.

Papike J. J. (1997) *Planetary Materials*. Mineralogical Society of America, Washington.

Pommerol A., Schmitt B., Beck P. and Brissaud O. (2009) Water sorption on Martian regolith analogs: thermodynamics and near-infrared reflectance spectroscopy. *Icarus* **204**, 114–136.

Pommerol A. (2009) *Hydratation minérale à la surface de Mars: caractérisation spectroscopique, thermodynamique et application à la télédétection*. Ph.D. thesis.

Post J. L. and Borer L. (2000) High-resolution infrared spectra, physical properties, and micromorphology of serpentines. *Appl. Clay Sci.* **16**, 73–85.

Poulet H. and Mathieu J. P. (1970) *Spectres de vibration et symétrie des cristaux*. Gordon & Breach, New York.

Raynal P. I., Quirico E., Borg J., Deboffle D., Dumas P., d'Hendecourt L., Bibring J. P. and Langevin Y. (2000) Synchrotron infrared microscopy of micron-sized extraterrestrial grains. In: *International Conference on Mars Exploration Program and Sample Return Missions*. Pergamon, Elsevier Science Ltd., Paris, France.

Rivkin A. S., Howell E. S., Lebofsky L. A., Clark B. E. and Britt D. T. (2000) The nature of M-class asteroids from 3-mu m observations. *Icarus* **145**, 351–368.

Rubin A. E., Trigo-Rodríguez J. M., Huber H. and Wasson J. T. (2007) Progressive aqueous alteration of CM carbonaceous chondrites. *Geochim. Cosmochim. Acta* **71**, 2361–2382.

Ryskin A. S. (1977) The vibrations of protons in minerals: hydroxyl, water and ammonium. In: *Infrared Spectra of Minerals*. Mineralogical Society of Great Britain & Ireland.

Salisbury J. W., Walter L. S., Vergo N. and D'Aria D. (1991) *Infrared (2.1–25 μm) Spectra of Minerals*. Johns Hopkins University Press, Baltimore.

Tomeoka K. and Buseck P. R. (1988) Matrix mineralogu of the Orgueil CI carbonaceous chondrite. *Geochim. Cosmochim. Acta* **52**, 1627–1640.

Tomeoka K., McSween, Jr., H. Y. and Buseck P. R. (1989) Mineralogical alteration of CM carbonaceous chondrites: a review. *Antarct. Meteorit. Res.* **2**, 221.

Wunder B., Deschamps F., Watenphul A., Guillot S., Meixner A., Romer R. L. and Wirth R. (2009) The effect of chrysotile nanotubes on the serpentine–fluid Li isotopic fractionation. *Contrib. Mineral. Petro.* **159**, 781–790.

Zaikowski A. (1979) Infrared-spectra of the Orgueil (C-1) chondrite and serpentine minerals. *Geochim. Cosmochim. Acta* **43**, 943–945.

Zanda B., Hewins R. H., Bourot-Denise M., Bland P. A. and Albarede F. (2006) Formation of solar nebula reservoirs by mixing chondritic components. *Earth Planet. Sci. Lett.* **248**, 650–660.

Zanda B., Le Guillou C. and Hewins R. H. (2009) The relationship between chondrules and matrix in chondrites. In: *72nd Annual Meeting of the Meteoritical-Society*, Nancy, France.

Zolensky M., Barrett R. and Browning L. (1993) Mineralogy and composition of matrix and chondrule rims in carbonaceous chondrites. *Geochim. Cosmochim. Acta* **57**, 3123–3148.

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