

# Transmission infrared spectra (2–25 $\mu\text{m}$ ) of carbonaceous chondrites (CI, CM, CV–CK, CR, C2 ungrouped): Mineralogy, water, and asteroidal processes



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## ABSTRACT

In this work, infrared transmission spectra (2–25  $\mu\text{m}$  range, 5000–400  $\text{cm}^{-1}$ ) of 40 carbonaceous chondrites were analyzed (21 CMs, 5 CVs, 6 CRs, 3 CKs, 3 C2s and 2 CIs). All these meteorite groups are known to have experienced significant aqueous alteration (except the CKs). These IR measurements provide information about the parent body processes experienced, as well as spectra for comparison with observations of Solar System small bodies and possibly with astronomical observations of accretion and debris disks.

This study reveals that each meteorite group appears to have specific signatures in the measured IR spectral range. In the case of the CI and CM groups, results show a variability in the shape of the silicate features that can be related to the evolution of the mineralogy with increasing extent of aqueous alteration extent as described by several authors with other techniques. This evolution of the silicate feature can be seen in the variation in the relative intensities of olivine and phyllosilicate IR features. The variability in the silicate features is correlated with the intensity of an –OH related absorption at 3- $\mu\text{m}$ , which can be used for the classification of the meteorites according to the level of hydration. Interestingly, in the case of CM chondrites, for which the mineralogy is expected to be dominated by phyllosilicates (serpentine mostly), the shape of the silicate absorption resembles that of an amorphous silicate, with a broad and symmetric 10- $\mu\text{m}$  band, unlike terrestrial phyllosilicates.

The CV and CK groups have IR spectra that are dominated by olivine absorption. From this feature, it is possible to determine average Mg numbers for the olivine. For the CVs, the olivine Mg numbers appear to decrease in the order Kaba–Grosnaja–Vigarano–Mokoia–Allende. This trend is likely related to the long duration of metamorphism experienced by these samples and the chemical re-equilibration between chondritic components. In the case of CK chondrites, the inferred bulk Mg# of olivine is 67 ( $\pm 1$ ), and no variation is observed between the three studied samples, which is likely related to their high degree of equilibration.

The 6 CR chondrites show the most variability in their IR spectra, from CM-like spectra in the case of the CR1 Grosvenor Mountains (GRO) 95577 to CV-like spectra for Roberts Massif (RBT) 04133 and Graves Nunataks (GRA) 06100 (one of them being most probably misclassified). Spectra of the remaining CRs show mixtures of various silicate component.

Finally, these spectra can be used for comparison with emission spectra of fine-grained asteroid surfaces and dust-rich cometary tails. In the case of Tempel 1, the only group of CC that matches the observed feature around 10- $\mu\text{m}$  region is the CR group. The spectral comparison shows some striking similarities between CRs and Tempel 1 dust. A genetic link between CR2 and comets is not proven, but mineralogical similarities are suggested from the IR spectra.

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## 1. Introduction

The mineralogy of chondrites is an integrated record of presolar, nebular and asteroidal histories. The complexity of their petrology

is reflected in the menagerie of mineral phases that they contain (Brearley and Jones, 1998; Rubin, 1997). Chondrites are composed of 15 groups out of which 7 belong to the so-called carbonaceous chondrites (CCs) class. CCs share specific compositional characteristics, in particular within the O and Cr isotopes spaces (Clayton and Mayeda, 1999; Warren, 2011a). They are considered as primitive Solar System samples for the similarity of their chemistry

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with the solar photosphere (Barrat et al., 2012). Nevertheless, they all experienced often extensive parent body processing.

The observations of chemical re-equilibration between mineral phases, of re-crystallization and growth of new minerals, as well as thermo-luminescence studies indicate that thermal metamorphism occurred in the parent bodies of all chondrites groups, including CCs (Dodd et al., 1967; McSween, 1977; Guimon et al., 1995). Structural and chemical modifications in the organic matter of CCs have also been observed by Raman and infrared (IR) spectroscopy and attributed to long and short duration metamorphisms (Bouvier et al., 2007; Bonal et al., 2006; Busemann et al., 2007; Cody et al., 2008; Quirico et al., 2011; Orthous-Daunay et al., 2013). The heat source required for metamorphism can be either radiogenic heating by short-lived radionuclides (Grimm and McSween, 1989, 1993), heat deposited during impact and subsequent burial within ejecta blankets (Warren, 2011b), or possibly solar heating for asteroids whose orbital perihelia is close enough to the Sun (Chaumard et al., 2012).

CCs have also interacted with water-rich fluids in their parent body, leading to the hydrolysis of primary constituents and subsequent crystallization of secondary minerals. This process, usually referred to as aqueous alteration, has been described for most CCs groups, including CV, CR, CI and CM (see the review by Brearley (2006) and reference therein). Within these groups, there is variability in the abundances and the nature of the secondary minerals, leading to scales of aqueous alteration (McSween, 1979; Zolensky et al., 1993; Rubin et al., 2007; Rubin and Harju, 2012; Howard et al., 2009, 2010, 2011; Alexander et al., 2013; Takir et al., 2013).

The water responsible for the alteration can be 'preserved' within hydrous minerals and can be retained by these minerals when heated to several hundreds of degrees centigrade. The contribution of CCs as a source for the Earth water has been much debated, for instance from the perspective of hydrogen isotopes (Deloule et al., 1998; Alexander et al., 2012; Bonal et al., 2013).

In this paper, we use IR spectroscopy to try to characterize the amount of water in CCs and to understand the factors controlling the observed diversity in the extent and mineralogy of alteration. This method can relatively rapidly probe both abundances and speciation of water, and provide insights into the mineralogy of the samples (e.g., Osawa et al., 2005; Beck et al., 2010). These transmission spectra are fairly comparable with observational spectra measured from thermally radiating sub-micrometer sized dust particles in cometary or asteroidal environments (Crovisier et al., 1997; Emery et al., 2006; Vernazza et al., 2010; Licandro et al., 2011). They might also provide points of comparison to accretion and debris disks (Morlok et al., 2012; Olofsson et al., 2012).

## 2. Methods

### 2.1. Samples

In this study, chondrites from the CI, CM, CR, CV–CK groups were analyzed. These four groups of meteorites were selected because they show evidence of aqueous alteration as described extensively in the literature. In addition, samples that are classified as C2 ungrouped were also studied. The sample list is given in Table 1.

Two CI chondrites were analyzed, Orgueil and Ivuna. The CM group is the largest CC group, and 21 samples were selected for the present study. Most of them are from the Antarctic Meteorite Collection program. The primary selection criterion was sample availability, but special care was taken to have samples spanning the full range of aqueous alteration as defined by Rubin et al. (2007). Some of the CMs studied have been described as heated

CMs, i.e. having experienced some degree of thermal processing (Akai, 1992; Nakamura, 2005). Fragments of ungrouped C2 chondrites were also selected from Bells, Essebi and Elephant Moraine (EET) 83355. It should be noted that while the recommended classification for Bells and Essebi is C2, they are often considered as CM chondrites (Metzler et al., 1992; Clayton and Mayeda, 1999).

A total of six CR chondrites were chosen for this study, which are Roberts Massif (RBT) 04133, Grosvenor Mountains (GRO) 95577, Pecora Escarpment (PCA) 91082, Graves Nunataks (GRA) 06100, Grosvenor Mountains (GRO) 03116, and LaPaz Icefield (LAP) 02342. Out of these six CR chondrites, two samples have been described as thermally altered, GRO 03116 (Abreu, 2012; Alexander et al., 2013) and GRA 06100 (Abreu and Stanek, 2009; Abreu and Singletary, 2011; Alexander et al., 2013; Schrader et al., 2011). Finally, five CV chondrites were analyzed (Allende, Mokoia, Vigarano, Grosnaja and Kaba). This selection of CVs spans both the so-called oxidized and reduced sub-groups. Because there is a potential connection between the CV and CK groups, samples of 3 CK chondrites were also studied: Allan Hills (ALH) 85002 (CK4), Maralinga and EET 92002 (both CK5s).

### 2.2. Infrared spectroscopy

For each meteorite, 30–50 mg of rock were ground in a dry agate mortar. Out of this mass, 1.0 mg was weighed and mixed with 300 mg of commercial ultrapure KBr powder. This mixture was then compressed to 400 bars in order to obtain a 13 mm diameter pellet of good optical quality. Prior to pellet generation, the KBr powder was heated to 80 °C to minimize terrestrial water contamination. If a more important initial mass of sample might have been preferable (typically 1 g) for representativeness considerations, for sample availability reasons a mass of 30–50 mg was used.

Once made, transmission IR spectra of pellets were measured under a primary vacuum ( $P = 10^{-3}$  mbar) after heating under air at two different temperatures for 2 h, 150 °C and 300 °C. This procedure enables to minimize adsorbed water (but will impact the organic compounds). In the case of the most hydrated samples, cracking of the pellets was observed, presumably due to the release of adsorbed and indigenous water, that resulted in an increase in light scattering as evidenced by the stronger diffuse background of the spectra. However, this effect did not significantly affect the quality of the spectra. Transmission spectra provide information on the absorption properties of the sample. Most of the samples have also been analyzed in reflectance (0.4–2.5  $\mu\text{m}$ ).

Mid-IR spectra were measured with a Bruker V70v spectrometer at the Institut de Planétologie et d'Astrophysique de Grenoble. Spectra were acquired at 2  $\text{cm}^{-1}$  spectral resolution in the 5000–400  $\text{cm}^{-1}$  range (2–25  $\mu\text{m}$ ). Details of the near-IR properties and the reflectance spectra of most of the samples studied can be found in Cloutis et al. (2011a, 2011b, 2012a, 2012b, 2012c, 2012d).

## 3. Results: distinctive characteristics of each group

### 3.1. The IR spectra of silicates in the 2–25 $\mu\text{m}$ range

The 2–25  $\mu\text{m}$  range is dominated by  $\text{SiO}_4$  related vibrations, whether as stretching modes of Si–O within tetrahedron around 10  $\mu\text{m}$ , or as bending modes at higher wavelength. In the case of OH-bearing minerals, additional absorptions are present around 3 and 6  $\mu\text{m}$  due to –OH stretching, X–OH bending and combinations of the two, and at higher wavelengths due to –OH libration (in the 12–16  $\mu\text{m}$  range). Characteristic transmission spectra of terrestrial

**Table 1**

List of samples studied and calculated spectral parameters. Petrologic grade under parenthesis are from Alexander et al. (2013). ALH = Allan Hills, DOM = Dominion Range, EET = Elephant Moraine, GRA = Graves Nunatak, GRO = Grosvenor Range, LEW = Lewis Cliff, MET = Meteorite Hills, MIL = Miller Range, PCA = Pecora Escarpment, QUE = Queen Alexandra Range, WIS = Wisconsin Range.

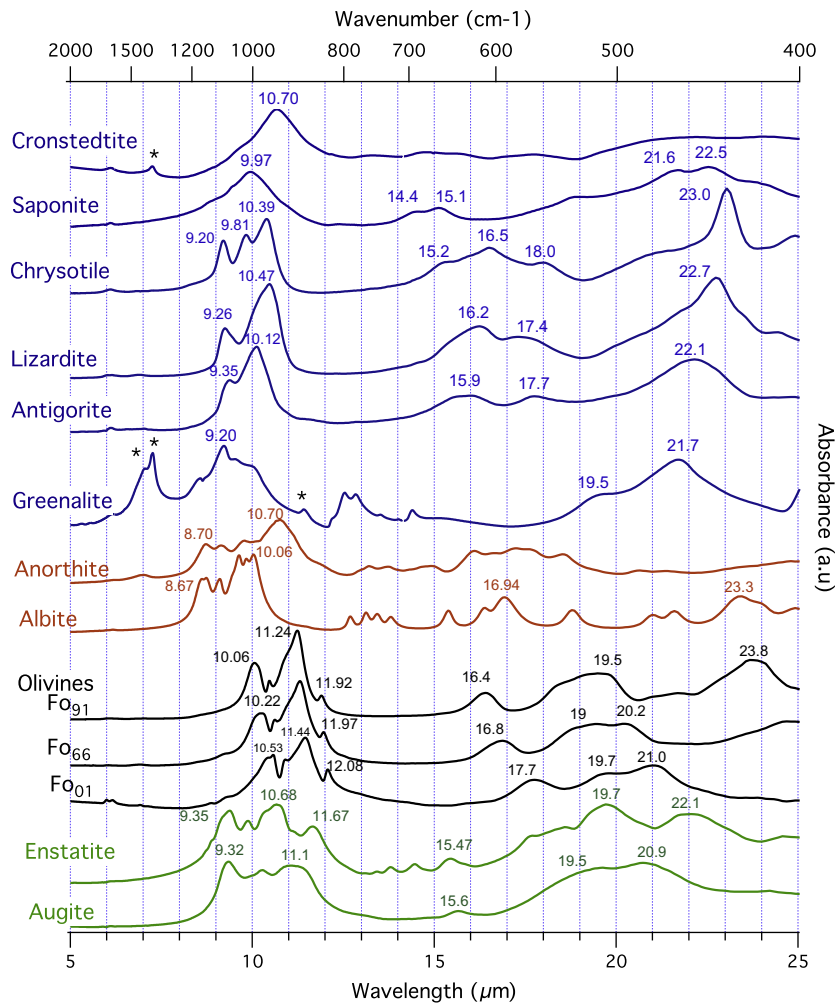
	Group/subtype	Fall/find	Weathering	Petrologic grade	3- $\mu\text{m}$ band intensity (hydration)	11.2 $\mu\text{m}$ feature (olivine)
<b>CI</b>						
Orgueil	CI	Fall	–	1	–	0.585
Ivuna	CI	Fall	–	1	–	1.137
<b>CV</b>						
Allende	CV/Ox	Fall	Fall	3	0.004	1.393
Grosnaja	CV/Ox	Fall	Fall	3	0.013	1.352
Kaba	CV/Ox	Fall	Fall	3	0.006	1.526
Mokoia	CV/Ox	Fall	Fall	3	0.014	1.308
Vigarano	CV/R	Fall	Fall	3	0.013	1.370
<b>CK</b>						
ALH 85002	CK	Find	A	4	0.009	1.158
EET 92002	CK	Find	A/Be	5	0.011	1.156
Maralinga	CK	Find	–	4-an	0.013	1.135
<b>CR</b>						
GRO 03116	CR	Find	B/C	2	0.006	1.050
LAP 02342	CR	Find	A/B	2 (2.5)	0.015	1.025
GRA 06100	CR	Find	B	2	0.017	1.183
GRO 95577	CR	Find	B or B/C	1 (1.3)	0.165	0.555
RBT 04133	CR	Find	B/C	2	–	1.363
PCA 91082	CR	Find	Be	2 (2.3)	0.021	1.048
<b>CM</b>						
<i>Unheated</i>						
ALH 83100	CM	Find	Be	1/2 (1.1)	0.218	0.496
ALH 84029	CM	Find	Ae	2 (1.2)	0.192	0.584
ALH 84044	CM	Find	Ae	2 (1.2)	0.188	0.507
Boriskino	CM	Find	Fall	2	0.101	0.981
DOM 08003	CM	Find	B	2 (1.1)	0.160	0.664
LEW 85311	C2/CM	Find	Be	2 (1.9)	0.068	0.952
LEW 87022	CM	Find	B	2 (1.4)	0.148	0.741
LEW 90500	C2/CM	Find	B	2 (1.6)	0.166	0.700
LON 94101	C2/CM	Find	Be	2 (1.8)	0.122	0.817
MCY 05230	CM	Find	B	2 (1.8)	0.114	0.835
MET 01070	CM	Find	Be	1 (1.0)	0.215	0.500
Niger	C2/CM	Find	Unknown	2	0.083	0.784
QUE 97990	CM	Find	Be	2 (1.7)	0.073	0.953
QUE 99355	CM	Find	B	2 (1.5)	0.128	0.816
Murchison	CM	Fall	W1-2	2 (1.6)	0.114	0.800
Nogoya	CM	Fall	W0	2 (1.1/1.6)	0.137	0.748
<i>Heated</i>						
DOM 03183	CM	Find	B	2 (1.6)	0.105	0.793
EET 96029	C2/CM	Find	A/B	2	0.064	0.982
MIL 07700	CM	Find	A	2	0.052	1.121
PCA 02010	CM	Find	B	2	0.020	1.271
PCA 91008	C2/CM	Find	B	2	0.005	1.239
WIS 91600	C2/CM	Find		2	0.058	0.977
	Type/subtype	Fall/find	Weathering	Petrologic grade	3- $\mu\text{m}$ band intensity (hydration)	11.2 $\mu\text{m}$ feature (olivine)
<b>Ungrouped C2</b>						
Essebi	C2/CM	Fall	–	2 (1.9)	0.062	0.822
Bells	C2/CM	Fall	–	2 (2.1)	0.054	0.970
Tagish Lake	C2	Fall	–	2	0.0605	0.828

silicate minerals are presented in Fig. 1. From the available mineralogical descriptions, these phases are likely components of CCs. Infrared spectra of mineral mixtures in transmission are expected to be roughly linear combinations of individual component spectra, weighted by their modal abundances. Therefore, we only show spectra of components that are expected to be present at more than 10 vol.% in the bulk mineralogy.

As seen in Fig. 1, the spectral differences in the 8–12  $\mu\text{m}$  region mean that it is quite straightforward to identify the major mineral phases that are present. The mafic silicates olivine, pyroxene and feldspars all have clearly identifiable spectral signatures. These signatures are to first order controlled by crystal structure rather than by crystal chemistry as exemplified by the spectra of olivine with various compositions presented in Fig. 1.

Serpentines is a mineral group of 1:1 trioctahedral layer silicates with three common polymorphs, chrysotile, antigorite and lizardite. As seen in Fig. 1, they have distinct structures in their 8–12  $\mu\text{m}$  band complex and can be readily identified by IR spectroscopy.

The IR spectra obtained for our meteorite samples are presented in Figs. 2–6. The measured spectra are on powdered fragments of meteorites and therefore provide information on the bulk meteorite mineralogies. They represent an average of the respective contribution of the constituents present in chondrites (matrix, chondrules, calcium–aluminum inclusions). It is apparent from these figures that each group presents very specific signatures in the 2–25  $\mu\text{m}$  spectral region. This variability will be described in the next sections and linked to sample mineralogy.



**Fig. 1.** Transmission IR spectra (absorbance) of selected silicates and phyllosilicates. Spectra are from [Salisbury et al. \(1991\)](#), except for greenalite (from Porth Arthur locality) and cronstedtite (Kisbanya, Romania) that were measured in this study. The stars in the greenalite and cronstedtite spectra mark peaks that are due to carbonates.

### 3.2. CV and CK chondrites

The five spectra of the CV chondrites analyzed are shown in [Fig. 2](#). When compared to the other CCs groups, the spectra obtained for the CV chondrites are remarkably homogeneous. The  $\text{SiO}_4$  stretching region (from 8 to 12  $\mu\text{m}$ ) shows sharp absorption peaks that reflect the dominance of olivine in their mineralogy. The positions of the doublet peaks at 11.3 and 10.0  $\mu\text{m}$  are indicative of forsteritic olivine ( $\text{Fo} > 50$ ) ([Burns and Huggins, 1972](#)).

On top of this general homogeneity of CV spectra, subtle variations are present in the  $\text{SiO}_4$  stretching region, for example in the width of the 10.0  $\mu\text{m}$  feature ([Fig. 2](#)). At around 20  $\mu\text{m}$ , there is a clear evolution from a single peak to a doublet, in the order Kaba, Grosnaja, Vigarano, Mokoia and Allende. These variations might be related to an evolution in the chemistry of olivine during thermal metamorphism ([Bonal et al., 2006](#)) or aqueous alteration ([McSween, 1977](#)). By using the calibration of [Burns and Huggins \(1972\)](#) it is possible to infer the bulk composition of olivine in CV chondrites using the position of the band located at around 16–17  $\mu\text{m}$ . Doing so, the olivine in Kaba is almost pure forsterite ( $\text{Fo} > 98$ ), while the amount of Fe increases in the order Grosnaja ( $\text{Fo}_{87}$ ), Vigarano ( $\text{Fo}_{83}$ ), Mokoia ( $\text{Fo}_{76}$ ) and finally Allende ( $\text{Fo}_{74}$ ). This evolution appears to be in reasonable agreement with the petrologic types determined by [Bonal et al. \(2006\)](#) where Kaba is defined as 3.1, Mokoia and Grosnaja as 3.6 and Allende as  $>3.6$ . The sole exception is Vigarano, which is classified as 3.1–3.4 (due

to uncertainties in the Raman measurements), but this discrepancy might be related to the fact that Vigarano is a reduced CV chondrite, while the other samples are classified as oxidized CV chondrites. There are compositional differences between oxidized and reduced CVs ([Krot et al., 1995](#)), the pre-metamorphic composition might have differed, and the oxidized and reduced CVs might not belong to the same isochemical metamorphic sequence.

The three studied CKs show infrared spectra that are somewhat similar to those of CVs, with a maximum of absorption around 11.3  $\mu\text{m}$  that is indicative of the dominance of olivine. This olivine has a typical composition of  $\text{Fo}_{67}$  using the calibration of [Burns and Huggins \(1972\)](#). This is in a very good agreement with measurements of matrix olivines from CK chondrites ([Chaumard et al., 2012](#)) that exhibit a range of compositions from  $\text{Fo}_{64}$  to  $\text{Fo}_{70}$ . The matrix abundances in CKs are high ( $>75\%$ ), and therefore the signature of matrix olivine's will dominate their transmission spectra. Although the various studied CKs belong to distinct petrological types (two CK4s and one CK5), their transmission spectra are similar, and so are the inferred bulk Mg# of their olivine. This is likely related to the high degree of equilibration of CK chondrites.

### 3.3. CR chondrites

The spectra of the CR chondrites are shown in [Fig. 3](#) in the 5–25  $\mu\text{m}$  range. They display significant variability. CV-like spectra were obtained from RBT 04133 and GRA 06100, while for GRO

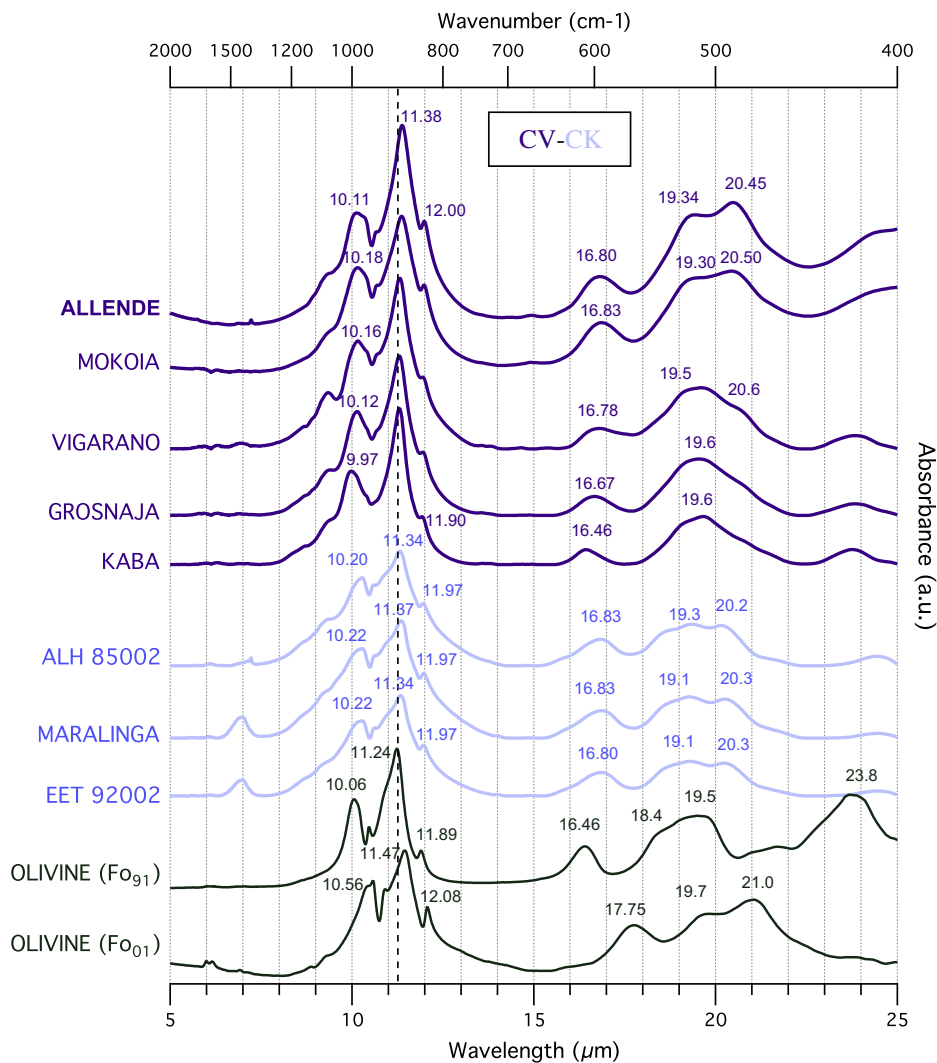


Fig. 2. Transmission IR spectra of CV and CK meteorites. ALH = Allan Hills; EET = Elephant Moraine.

03116, PCA 91082 and LAP 02342 the 10  $\mu\text{m}$  band controlled by  $\text{SiO}_4$  stretching modes has a more complex structure, probably due to a mixture of olivine and enstatite as identified by the 11.2  $\mu\text{m}$  and 9.3  $\mu\text{m}$  features.

In the case of the CR1 GRO 95577, the spectrum reveals a quite distinct mineralogy with respect to studied CR2 chondrites. The  $\text{SiO}_4$  stretching feature at around 10  $\mu\text{m}$  is similar to that measured in the heavily altered CM and CI chondrites, with a single saponite-like feature. However, the bending region does not match saponite.

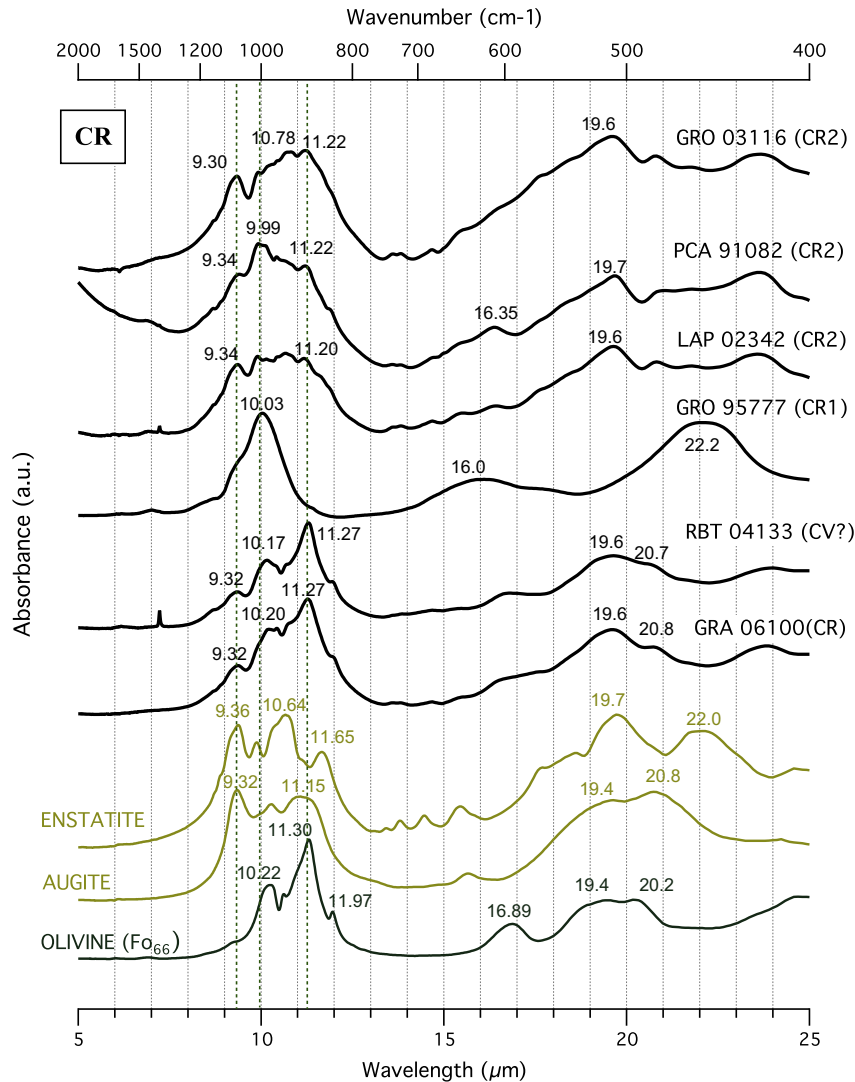
### 3.4. CM chondrites

CM chondrites typically have a relatively narrow peak in the  $\text{SiO}_4$  stretching region, with a maximum of absorption at around 10.0  $\mu\text{m}$  (Fig. 4). Although abundant serpentines have been described in CM chondrites (Tomeoka and Buseck, 1988; Zolensky et al., 1997; Lauretta et al., 2000; Howard et al., 2009), the 10  $\mu\text{m}$  feature of the measured CMs does not resemble to a highly crystalline serpentine-like feature, but rather resembles that of saponite (Fig. 1). Significant spectral variability is observed within the studied CMs, which can be understood in the light of the aqueous alteration scheme described by Rubin et al. (2007). The most heavily altered samples present a single “saponite-like” 10- $\mu\text{m}$  feature similar to that observed for CI chondrites. This is the case of

Meteorite Hills (MET) 01070, classified as 2.0 by Rubin et al. (2007). The spectra of saponite matches the 10- $\mu\text{m}$  feature of heavily altered CM, however bending modes of the later (at higher wavelengths) are clearly distinct from those observed in saponite. With decreasing degree of aqueous alteration, the growth of a second peak at 11.2  $\mu\text{m}$  is observed and can be explained by an increase in the abundance of olivine within the samples. The spectra of Queen Alexandra Range (QUE) 97990 or Miller Range (MIL) 07700 are examples of CM chondrites displaying a clear “olivine shoulder” in the  $\text{SiO}_4$  stretching region. The growth of the 11.2  $\mu\text{m}$  peak is concomitant with the appearance of features at 16.5 and 19.5  $\mu\text{m}$ . This confirms the attribution to forsteritic olivine (Fig. 1) and, therefore, the existence of a relation between the mineralogy derived from IR and the aqueous alteration extent as defined by Rubin et al. (2007) using petrological criteria (alteration of chondrules, chemistry of PCP, etc.).

### 3.5. Unusual CM chondrites, and ungrouped C2

The spectra of “unusual” CM chondrites can be seen in Fig. 5, together with spectra of ungrouped C2 chondrites. A large diversity occurs within this sample suite. In the case of Wisconsin Range (WIS) 91600, the spectrum appears similar to that of weakly altered CM chondrites. However, in the most extreme case, PCA



**Fig. 3.** Transmission IR spectra of CR chondrites from this study. GRO = Grosvenor Mountains, LAP = LaPaz Icefield, PCA = Pecora Escarpment, RBT = Robert Massif, GRA = Graves Nunataks. The top three samples show a complex structure, while the spectra of the CR1 GRO 95777 resembles CM spectra, and the spectra of RBT 04133 and GRA 06100 resembles CV spectra. RBT 04133 has been suggested to be a CV (Davidson et al., 2009), while GRA 06100 is thought to have been heated (Abreu and Stanek, 2009; Alexander et al., 2013).

02010, the 10.0  $\mu\text{m}$  saponite-like feature is absent, and the signature of olivine dominates the spectrum, similarly to what is observed for CV chondrites. In the case of PCA 91008, the structure of the  $\text{SiO}_4$  stretching is more complex, showing a mixture of olivine and probably pyroxene features.

The spectra of C2 chondrites are dominated by a saponite-like feature at about 10.0  $\mu\text{m}$  and share similarities with CM chondrites. The CM Niger appears to show similarities with the ungrouped C2s. Small olivine signatures are detected at 11.2  $\mu\text{m}$  with increasing intensity in the order Niger–Essebi–Bells.

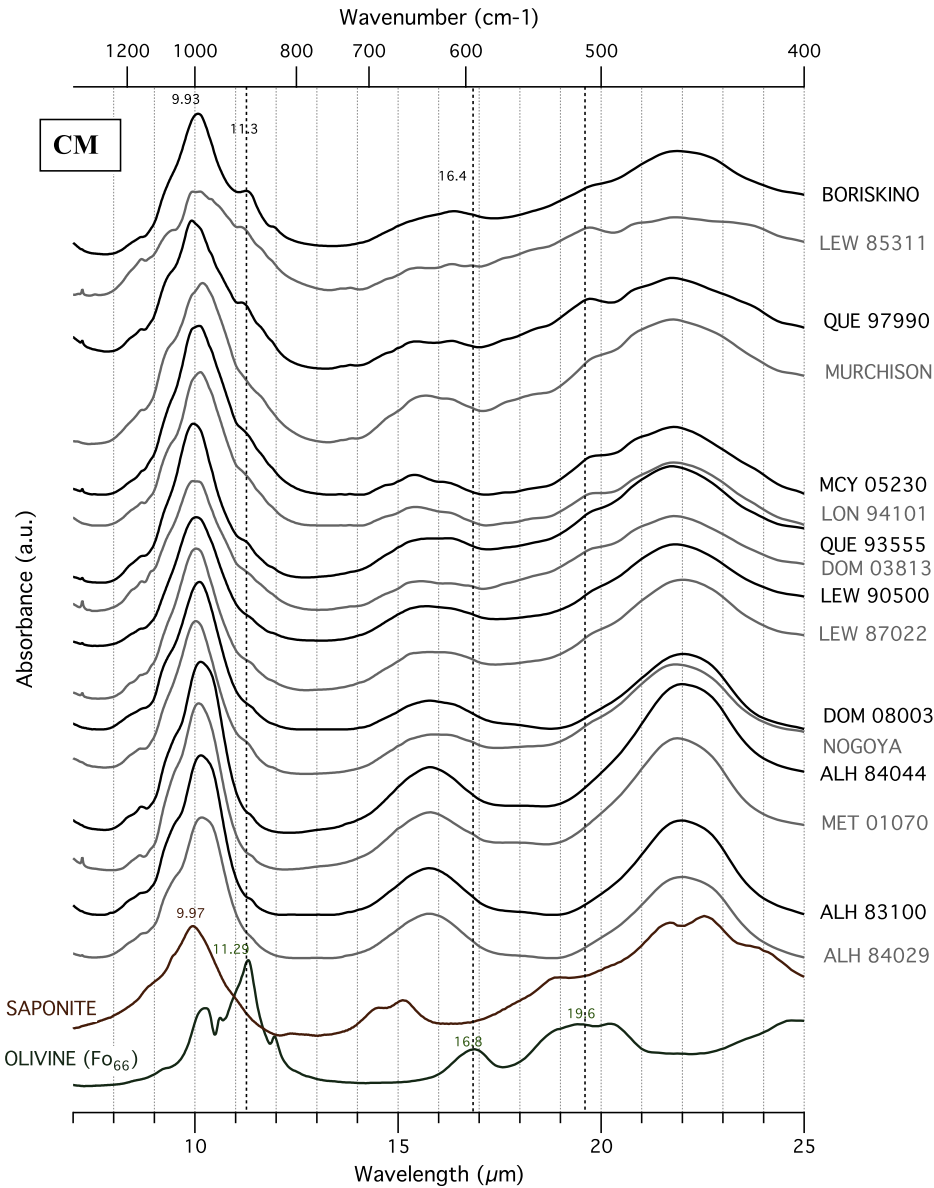
### 3.6. CI chondrites

The transmission spectra of Ivuna and Orgueil, two CI chondrites, are presented in Fig. 6. They are compared to spectra of the heavily altered GRO 95777 (CR1) and the heavily altered CM MET 01070 (CM2.0) chondrites. This comparison reveals that the phyllosilicates constituting the CIs are distinct from those of CMs since the maximum of absorption of the  $\text{SiO}_4$  stretching is located at 9.9  $\mu\text{m}$ , which is slightly lower than that of CMs and the CR1. In addition, a doublet around 22–23  $\mu\text{m}$  is present for

both CIs rather than a single peak as seen for CMs and the CR1. The shape and position of the stretching and bending modes of the two CIs point to the presence of saponite in both meteorites, which has been described in various studies (Tomeoka and Buseck, 1988; Zolensky et al., 1993; Brearley and Jones, 1998).

Another specific property of the CI chondrite spectra is the presence of a peak at around 8.5  $\mu\text{m}$ . This peak can be explained by the presence of sulfates in these samples, which are likely of terrestrial origin (Gounelle and Zolensky, 2001).

Finally, the spectra of the two CI chondrites are not identical. CI chondrites are breccias, presenting heterogeneous clasts, and heterogeneities have been seen among the four CI chondrites (Morlok et al., 2006). The major difference found here between the two CIs studied is the presence of a well-identified peak at 11.2  $\mu\text{m}$  in the spectra of Ivuna, that we interpret to be due to the presence of a small amount of olivine. This is in agreement with the different degree of aqueous alteration seen by these two samples that was previously suggested based on carbonates compositions (Endress and Bischoff, 1996). However, bulk H contents of Ivuna and Orgueil reported by Alexander et al. (2012) are almost identical, and due to the brecciated nature of CIs, sampling issues cannot be ruled out.



**Fig. 4.** Transmission IR spectra of CM chondrites. From bottom to top, note the growth of absorptions peaks at 11.2, 16.7 and 19.5 μm due to olivine. PCA = Pecora Escarpment, MIL = Miller Range, DOM = Dominion Range, LEW = Lewis Cliff, ALH = Allan Hills, MET = Meteorite Hills, QUE = Queen Alexandra Range, MCY = MacKay Glacier, LON = Lonewolf Nunataks.

**4. Quantifying the level of hydration**

Because a given secondary mineralogy is controlled by a multiplicity of factors (P, T, fO<sub>2</sub>, pH, pE, rock/fluid ratio, etc.) that potentially vary between and within parent bodies, ordering meteorites according to their degree of aqueous alteration is a difficult task. The approach followed here is to quantify aqueous alteration by the amount of H<sub>2</sub>O and –OH contained by a sample, following Howard et al. (2009, 2010, 2011) and Howard and Alexander (2013) who measured the proportion of phyllosilicates in CI, CM and CV chondrites using powder X-ray diffraction (XRD).

Infrared transmission spectra of CCs makes it possible to measure directly –OH groups from their absorption at around 3-μm (from 3700 to 3000 cm<sup>-1</sup> in Fig. 7). This feature has been used previously to quantify water abundances in planetary materials both by absorption and by reflectance spectroscopy (Milliken and Mustard, 2005; Pommerol et al., 2009; Lafay et al., 2012). Here we used the spectra measured at 300 °C to avoid any contamination by adsorbed or mesoporic water. This precludes the use of this

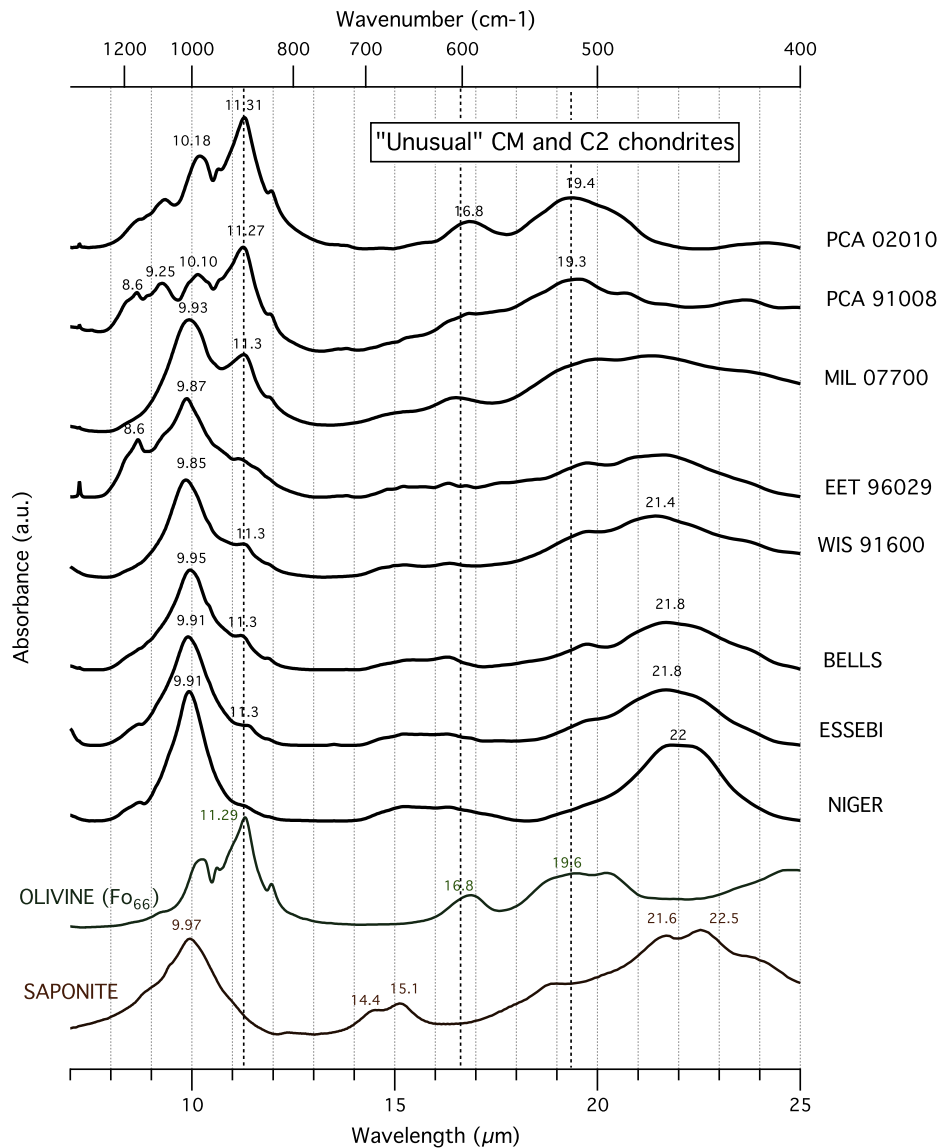
classification for CI chondrites because they contain abundant iron hydroxydes (Bland et al., 2004; Beck et al., 2012) that decompose below 300 °C (Montes-Hernandez et al., submitted for publication).

Two spectral criteria were developed for this purpose. The first is the integrated intensity of the 3-μm band, normalized to that of the SiO<sub>4</sub> tetrahedron band. The normalization to the SiO<sub>4</sub> band removes any variability in absorbance due to small variations in the thickness of the pellet. This criterion is calculated as follows:

$$C_{3\mu/10\mu} = \frac{\int_{2.65}^{2.85} \text{absorbance}(\lambda) d\lambda}{\int_{7.7}^{14.3} \text{absorbance}(\lambda) d\lambda} \tag{1}$$

The second criterion is a mineralogical indicator of the relative abundance of olivine with respect to phyllosilicates, by using the intensity of the 11.2-μm olivine SiO<sub>4</sub> tetrahedron stretching band. It is written:

$$C_{11.2\mu} = \frac{\int_{11.15}^{11.25} \text{absorbance}(\lambda) d\lambda}{\int_{10.94}^{10.98} \text{absorbance}(\lambda) d\lambda} \tag{2}$$



**Fig. 5.** Transmission spectra of heated CM chondrites and ungrouped carbonaceous chondrites. PCA = Pecora Escarpment, LEW = Lewis Cliff, EET = Elephant Moraine, WIS = Wisconsin Range.

Fig. 8 shows the relation between these two criteria and reveals a trend for CM and C2-ung, that is expected in a model where olivine is progressively replaced by (–OH)–bearing phases through aqueous alteration, or where phyllosilicates are replaced by olivine upon thermal metamorphism.

Fig. 8 separates the various meteorites according to their content of hydrous phases. It appears to be in reasonable agreement with the Rubin et al. (2007) scale, the most altered sample MET 01070 being identified as (–OH)–rich and almost devoid of olivine, while with decreasing aqueous alteration degree (Rubin et al., 2007) samples evolve toward the bottom right side of the diagram (less –OH and more olivine).

Various aqueous alteration schemes have been proposed to describe petrological variations amongst CM chondrites. Here, the suggestion of Howard et al. (2009) is followed, which defines the extent of aqueous alteration by the proportion of phyllosilicates in a given meteorite. The integrated intensity of the –OH band at 3- $\mu\text{m}$  ( $C_{3\mu/10\mu}$ ) provides a direct proxy for the abundances of –OH groups and therefore of phyllosilicates. Together with the  $\text{SiO}_4$  silicate criteria defined previously ( $C_{11.2\mu}$ ), it is possible to

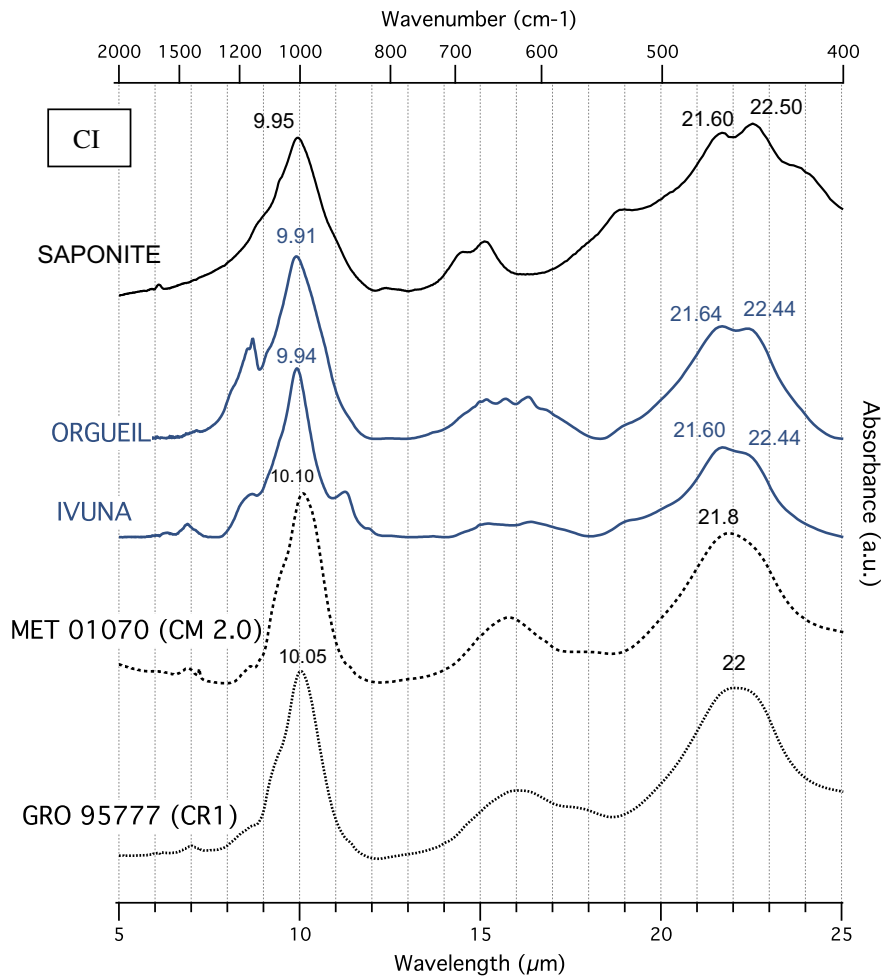
order CCs according to their aqueous alteration extent. When these two criteria are plotted against each other, a continuous evolution from CV chondrites to CM chondrites is observed (Fig. 8). The most aqueously altered CM samples are MET 01070 and ALH 83100, while the less hydrated “unheated” CMs are QUE 97990 and MIL 07700. In addition, the 3- $\mu\text{m}$  band also shows a fair correlation with the petrological scale defined by Alexander et al. (2013) as well as the –OH/ $\text{H}_2\text{O}$  hydrogen contents derived by Alexander et al. (2012, 2013).

## 5. Discussion

### 5.1. CM and CI chondrites: which phyllosilicates?

CM chondrites are the most abundant CCs and an extensive literature exists on the composition of their phyllosilicates. According to numerous studies, the dominant phases belong to the serpentine group, typically a mixture of Fe-rich cronstedtite and Mg-rich serpentine (see Brearley, 2006). However, from our





**Fig. 6.** Transmission IR spectra of CI chondrites compared to those of a heavily altered CM chondrite (Meteorite Hills 01070) and a heavily altered CR chondrites (Grosvenor Range 95777). Petrological scale for Meteorite Hills 01070 is from [Rubin et al. \(2007\)](#).

observations, none of the standard serpentine phases have an IR spectra that matches that of CM chondrites.

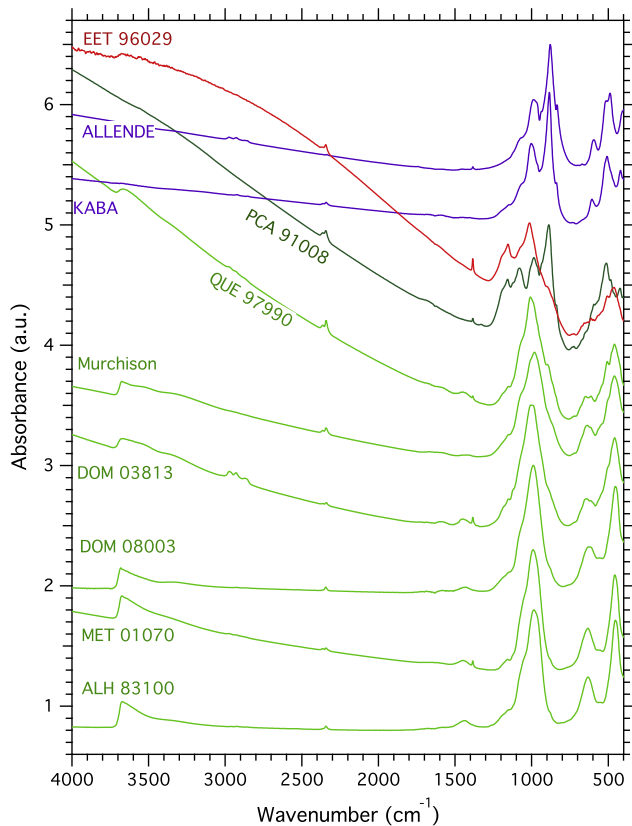
The chemical composition of matrix phyllosilicates has often been inferred from electron probe analysis of thin sections, but the presence of finely disseminated sulfides and Fe-oxides precludes a direct measurement within the volume probed by the electron beam. Analyses are usually excessively rich in Fe with regard to a serpentine or smectite composition, and a trend is typically observed toward the Fe apex in the Fe–Mg–Si triangular diagram (see for instance [McSween, 1979](#) or [Zolensky et al., 1993](#)). Transmission electron microscopy (TEM) can provide clues to the mineralogy of matrix phyllosilicates providing petrographical information at a scale that is able to distinguish phyllosilicates from other matrix constituents. Many phyllosilicates have been reported in CM chondrites and debated in the literature. An incomplete list includes: chrysotile, cronstedtite (Fe-rich serpentine), septechlorite ([Bunch and Chang, 1980](#)), greenalite ([Barber, 1981](#)), lizardite ([Akai and Kanno, 1986](#)), chlorite ([Zolensky et al., 1993](#)) and vermiculite ([Zolensky et al., 1993](#)).

It is difficult to determine the modal mineralogy of CM chondrites and the respective amount of the various silicates observed from TEM and electron probe studies. Important insights about mineral abundances were gained from the detailed analysis of XRD diffraction spectra by [Bland et al. \(2004\)](#) and [Howard et al. \(2009, 2011\)](#). The XRD spectra of a series of CCs reveals that a combination of fine-grained and more crystalline serpentine can account for 70–80 vol.% of CM2 chondrites. From the comparison

with TEM studies, [Howard et al. \(2009\)](#) attribute the fine-grained component to Mg-serpentine and the more poorly crystalline material to cronstedtite.

The IR transmission spectra of CM chondrites obtained here can provide information on the bulk mineralogy of these samples and therefore the nature of phyllosilicates. When compared to the spectra in the 5–25  $\mu\text{m}$  region, it is clear that “typical” terrestrial serpentine has a complex 10  $\mu\text{m}$  band that does not match the observations of CMs chondrites, and the Fe-rich serpentine cronstedtite, which was measured in a previous study ([Beck et al., 2010](#)) does not match this feature either. Two possible explanations can be invoked for this apparent discrepancy. The first one is that the apparent broadening and “simplification” of the IR spectra is due to the very low crystallinity of serpentine (a few unit cells typically), the lack of long range order impacting the infrared spectra. However, according to [Howard et al. \(2009\)](#), more than half of CM2 serpentines are well crystalline and show fine XRD peaks. It is important to note that most TEM studies reveal that the mixing between phases is intimate, i.e. at the nm scale, which might impact the IR spectra.

A second possibility is the effect of cation substitutions in the serpentines. For the two series talc/saponite and serpentine/7  $\text{\AA}$ -chlorites the coupled Al–Si and Mg–Al substitutions induce a broadening of the Si–O and –OH feature ([Farmer, 1974](#)). CM2 serpentines are likely highly substituted by  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  in both the tetrahedral and octahedral sites. Such substitutions will have an impact on the infrared spectra and might result in saponite-like features.



**Fig. 7.** Transmission spectra of various carbonaceous chondrites, including the 3- $\mu\text{m}$  spectral region ( $3700\text{--}3000\text{ cm}^{-1}$ ). PCA = Pecora Escarpment, MIL = Miller Range, DOM = Dominion Range, ALH = Allan Hills, MET = Meteorite Hills, QUE = Queen Alexandra Range, EET = Elephant Moraine.

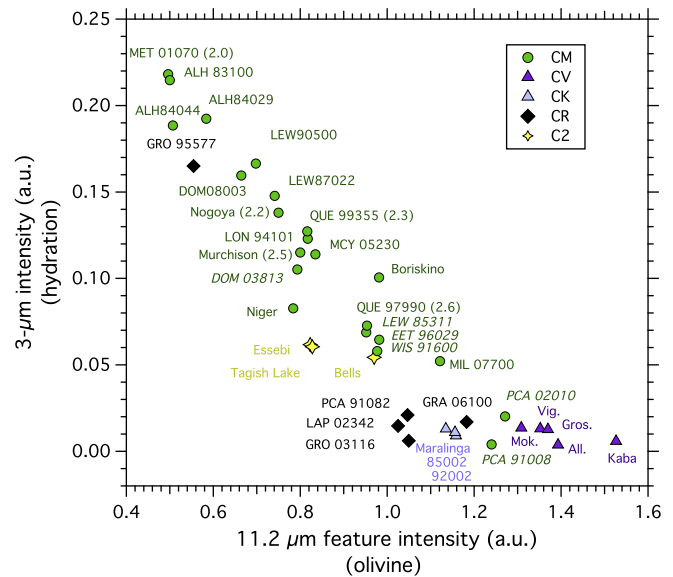
## 5.2. The extent of aqueous alteration

### 5.2.1. Aqueous alteration of CM

The CM chondrites analyzed here reveal the heterogeneity within the group in their contents of hydrated minerals, as has previously been demonstrated by several workers (McSween, 1979; Zolensky et al., 1993; Rubin et al., 2007; Howard et al., 2009, 2011; Alexander et al., 2013). The advantage of the present IR analysis is that it is possible to build bulk mineralogical criteria that are expected to depend linearly with the amount of water/OH present in the sample.

In this respect, the proportion of phyllosilicates relative to olivine varies significantly within our sample suite from olivine-rich to olivine-free CM chondrites (Fig. 4). Because this study is performed on bulk rock samples, part of these variations can be related to different proportions of matrix with respect to chondrules across the meteorite suite. The fine-grained matrix is much more easily affected by aqueous alteration. In the case of the weakly altered CMs, the matrix is rich in hydrated minerals while chondrules are typically poor in secondary products (Rubin et al., 2007). In heavily altered CMs, chondrules are almost totally transformed to secondary products (Rubin et al., 2007). In the present study, in the case of the highly altered CMs, no signature of olivine can be seen in the silicate IR features. Such an observation also suggests that all silicates (within chondrules and matrix) have been transformed into phyllosilicates within these samples.

A number of factors might be responsible for the variations in the extent of aqueous alteration. Temperature, pH, Eh, and fluid/rock ratio are interdependent parameters that will affect the kinetics of mineral hydrolysis and the nature of the secondary products. Two lines of evidence suggest that the fluid-to-rock ratios were not



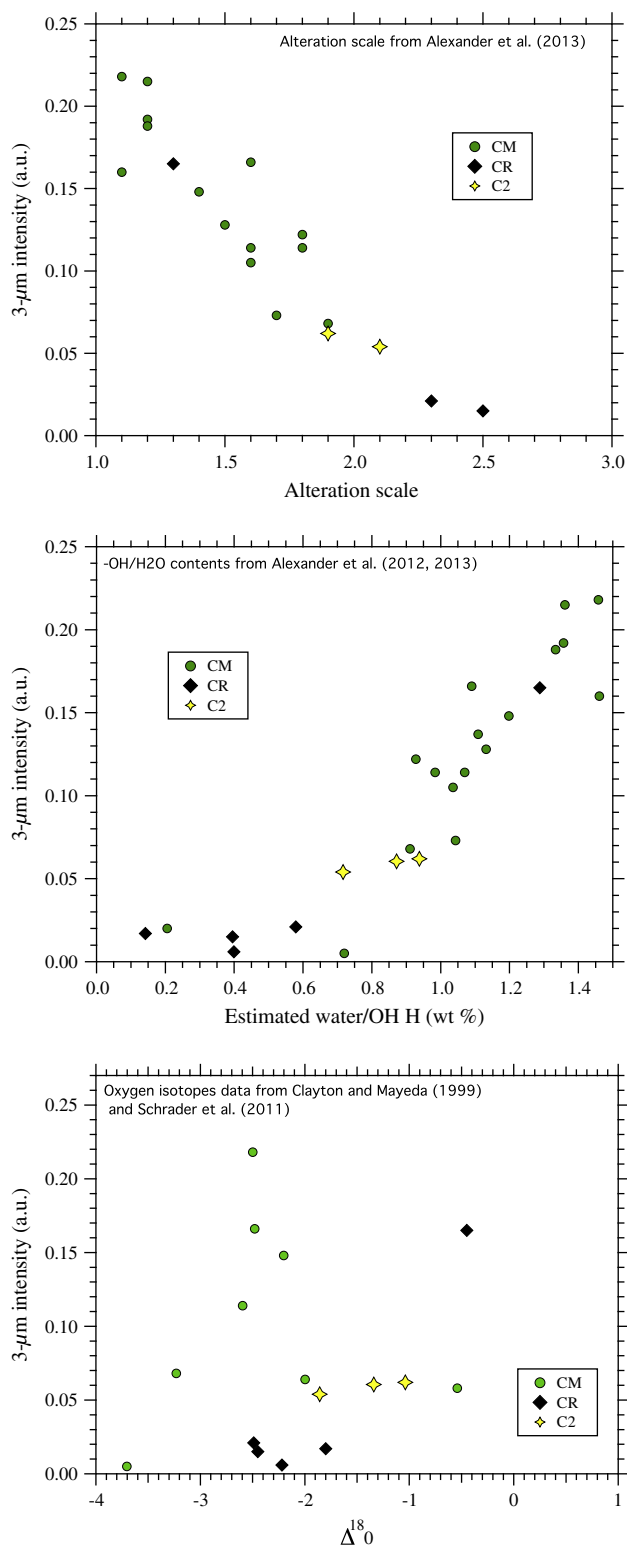
**Fig. 8.** Classification of carbonaceous chondrites based on the spectral criterion described in this study. The trend is related to variations in the modal abundance of phyllosilicates relative to olivine. ALH = Allan Hills, DOM = Dominion Range, EET = Elephant Moraine, GRA = Graves Nunatak, GRO = Grosvenor Range, LEW = Lewis Cliff, MET = Meteorite Hills, MIL = Miller Range, PCA = Pecora Escarpment, QUE = Queen Alexandra Range, WIS = Wisconsin Range. The sample labeled 85002 and 92002 are the CK chondrites ALH 85002 and EET 92002, respectively. The CM chondrites whose names are in *italic* have been identified as heated. When available, petrologic subtypes from Rubin et al. (2007) are given.

very high during aqueous alteration of CM chondrites. First, this process was shown to be isochemical for all major elements (McSween, 1979; Rubin et al., 2007), and that no significant leaching of elements occurred. In addition, the absence of a correlation between bulk oxygen isotopes and water-abundance in the CM and CI groups suggests that water did not buffer the bulk oxygen isotope composition and that the fluid-to-rock ratios were likely not too high (Alexander et al., 2013). However, more complex models can be proposed to describe the oxygen isotopes systematic (Young et al., 1999; Benedix et al., 2003). For some samples analyzed here, the oxygen isotopes compositions are available, but there was no obvious correlation found between these compositions and the aqueous alteration extent determined in this work (Fig. 9).

A low fluid–rock ratio might imply that fluid availability could have played a role in controlling the present amount of water in CM. Still other factors might be responsible for the variability observed. Rubin and Harju (2012) proposed that shock-related brecciation controlled the extent of aqueous alteration by creating porosity and facilitating fluid circulation. This model stems from the observation that the most altered CM chondrites display significant textural orientation of chondrules. However, shock wave experiments reveal that in order to create preferred orientation by impacts, peak shock pressures above 10 GPa are needed and the effect of shock will be more likely to compact pores rather than to create them (Tomeoka et al., 1999). Still, shock wave experiments are limited by their small duration (Gillet and Goresy, 2013) and therefore the thickness of the shock-front, and it cannot be excluded that an appropriate set of impact speed and size might create both porosity and texturing.

### 5.2.2. Aqueous alteration of CRs

The intensity of the 3- $\mu\text{m}$  band in the CM chondrites spectra compared to the intensities in that CR2 chondrite spectra indicates that the CR2s are weakly altered with respect to CM2. Although their matrices all show signatures at 3  $\mu\text{m}$  (as previously observed by



**Fig. 9.** Comparison of the  $3\text{-}\mu\text{m}$  band intensity with the petrological scale from Alexander et al. (2013) and the estimated  $\text{-OH/H}_2\text{O}$  hydrogen content (Alexander et al., 2012, 2013). Also shown is the relation with  $\Delta^{18}\text{O}$  from Clayton and Mayeda (1999) and Schrader et al. (2011).

Bonal et al., 2013), in the case of bulk rock measurements, the intensity of the  $3\text{-}\mu\text{m}$  band is much smaller than for the measured CM2s.

In the case of the CR1, GRO 95577, the  $3\text{-}\mu\text{m}$  band intensity is much stronger than for the CR2s, and the structure of the  $\text{SiO}_4$

bands is quite similar to those observed for CM and CI chondrites. GRO 95577 was initially classified as a C2 chondrite, but its petrology and oxygen isotopic composition made it a member of the CR clan (Clayton and Mayeda, 1999; Weisberg and Prinz, 2000). In addition, the matrix/chondrule/opaque phase modal abundances and chemistry are remarkably similar to those in Renazzo (Perronnet et al., 2006; Weisberg and Huber, 2007). However, all silicates appear to have been altered to secondary products (Perronnet et al., 2006; Weisberg and Huber, 2007), which is entirely consistent with IR observations. From its IR spectrum alone it would not be possible to distinguish GRO 95577 from a heavily altered CM or a CI. Indeed, the  $10\text{-}\mu\text{m}$  silicate stretching feature shows a thin asymmetric peak with a maximum around  $10.0\text{ }\mu\text{m}$  that resembles that of saponite. According to Perronnet et al. (2006), chondrules were altered to serpentine phases (Fe-rich antigorite) as well as matrix silicates. The composition found for chondrule phyllosilicates by Weisberg and Huber (2007) is intermediate between saponite and serpentine. Still, when observed in the infrared, GRO 95577 phyllosilicates resemble saponite, possibly because of their poor crystallinity as suggested previously for CMs (Beck et al., 2010).

### 5.2.3. Aqueous alteration of CVs

Aqueous alteration has been reported in CV chondrites by several authors (Hashimoto and Grossman, 1987; Keller and Buseck, 1991; Brearley, 1997; Krot et al., 1997). Matrix, chondrules and even CAIs have all been at least partially altered to secondary products, including ( $\text{-OH}$ )-bearing phases. Nevertheless, the proportions of secondary phases are likely low, considering the low abundance of hydrogen measured in CV chondrites typically below 0.5 wt% (Clarke et al., 1971; Alexander et al., 2012; Montes-Hernandez et al., submitted for publication).

As expected, the infrared spectra of CV chondrites reveal that their mineralogy is largely dominated by olivine. There is evidence of aqueous alteration based on the presence of  $3\text{ }\mu\text{m}$  features in the spectra, but because they are quite faint terrestrial alteration cannot be excluded as being responsible for these signatures. From this dataset, no firm conclusion can be drawn concerning the possible hydration of CV chondrites with the exception that the abundance of hydrated alteration products is quite low.

### 5.3. Thermal metamorphism and dehydration: unusual CMs

Aqueous alteration and thermal metamorphism are not mutually exclusive. The so-called heated CM and CI chondrites have been identified (Akai, 1992; Hiroi et al., 1996; Nakamura, 2005; Nakato et al., 2008; Tonui et al., 2002; Wang and Lipschutz, 1998). This sub-group shows clear textural and mineralogical evidence of aqueous alteration; yet they most likely experienced a thermal event, leading to the dehydration of phyllosilicates. Residual fingerprints of aqueous alteration are preserved, for example, the abundance of oxidized iron-bearing phases ( $\text{Fe}^{3+}/\text{Fe}_{\text{total}} > 0.5$ ; Beck et al., 2012).

The IR transmission spectra obtained of the "unusual CMs" reveal a range from a CM-like spectrum to signatures dominated by anhydrous silicates (pyroxene and olivine) (Fig. 5). Together with this variation of silicate features, a progressive dehydration is observed (Fig. 5). In the case of PCA 02010, the spectrum mimics those of CV chondrites where the signature of olivine is predominant. Because its phyllosilicates were dehydrated and re-crystallized to olivine, this object should likely be classified as a heated CM. In the case of PCA 91008, olivine and enstatite signatures are present in its IR spectrum, while its oxygen isotopes composition matches the CM field (Choe et al., 2010). Following Choe et al. (2010), its classification as heated CM chondrites is also recommended.

The observation of the dehydration of phyllosilicates and their re-crystallization to anhydrous silicates is consistent with a thermal metamorphism event. The experimental determination of the serpentine phase diagram is difficult due to the sluggish kinetics at the appropriate temperatures. However, valuable information can be gained from studies of terrestrial serpentines. In a subduction zone context, according to Schwartz et al. (2013), olivine begins to appear as a decomposition product of serpentine at temperature in excess of 460 °C. The analogy with the CCs is certainly limited by the difference in metamorphic pressure (probably only a few bars in the case of CCs). Indeed, low pressure appears to decrease the stability field of serpentine, and heating experiments on Murchison (Akai, 1992) tend to show an onset of dehydration at about 300 °C (week long experiments). In the case of the various phyllosilicate studied by Che et al. (2011) and Che and Glotch (2012), spectral changes begin to be observed when samples are heated above 300 °C.

It is important to note that with increasing temperature, the equilibrium transition path from serpentine to olivine involves intermediate stages (see for instance Evans, 2004), with first a region where antigorite and lizardite coexists, followed by a pure antigorite region and then dehydration and olivine formation. Heated CMs with such mineralogies are absent from our dataset and have not been described in the literature. Nakamura (2005) studied a series of heated CMs and CIs from Antarctica and showed that dehydration of phyllosilicates to olivine occurs through an intermediate stage where only amorphous silicates are present. Our observations of the IR transmission spectra of WIS 91600 (classified as heating staged II) suggests that no intermediate serpentine phase (antigorite or lizardite) is present, but rather a poorly crystalline phyllosilicate. A possible explanation for the difference between experiments and observations of CCs might be related to the  $P$ - $T$  path, i.e. the duration of the heating process. In addition, cation chemistry might also play a role since  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  are difficult to accommodate in the olivine structure.

Short duration thermal metamorphism through hypervelocity impacts also have the potential to dehydrate the phyllosilicates. Such a phenomenon has been observed in impact experiments conducted on serpentine minerals (Akai and Kanno, 1986), and a similar behavior has been observed during shock experiments on Murchison (Tomeoka et al., 1999; Tyburczy et al., 1986; Beck et al., 2011). However, the detailed effects on the mineralogy remain to be determined. The timing of heating is not fully constrained and three heat sources were proposed by Nakamura et al. (2005): (i) radioactive decay, (ii) impact metamorphism, and (iii) radiative solar heating. Raman spectroscopy of the organic matter tends to eliminate (i), but cannot discriminate between (ii) and (iii) (Quirico et al., submitted for publication). Some evidences for a short duration heating are present in the form of an exciton in Carbon XANES spectroscopy (Cody et al., 2008) observed for heated CM and reproduced by flash heating experiments. This would tend to support impact metamorphism as a heat source.

#### 5.4. CR chondrite: any amorphous signature?

CR chondrites typically show a high abundance of presolar grains (Huss, 2004) and heavy enrichment in bulk D/H ratio (Alexander et al., 2012; Bonal et al., 2013), leading to their consideration as possibly the most primitive CC group.

A characteristic of the matrices of the least altered CR chondrites is the presence of abundant amorphous silicates (Abreu and Brearley, 2010; Floss and Stadermann, 2009), that are likely Solar System products (vs presolar) and some of which might be hydrated (Abreu and Brearley, 2010; Alexander et al., 2012, 2013; Keller and Messenger, 2012; Guillou et al., 2014). The infrared spectra measured on CR2 chondrites show strong crystallinity

in the cases of RBT 04133 and GRA 06100 in which olivine dominates the spectra. From the IR perspective, these two samples are clearly anomalous with regard to the CR group. The oxygen isotope of RBT 04133 suggests affinities with CR chondrites (Davidson et al., 2009), while evidence of short duration thermal metamorphism has been found in GRA 06100 (Abreu and Staneek, 2009; Alexander et al., 2012, 2013; Briani et al., 2013).

In the case of the three other CR2 studied, the 10- $\mu\text{m}$  features show a mixture of multiple crystalline silicates phases. Because matrix is abundant in CR chondrite (30–50%), the presence of amorphous silicates might be hidden by absorption from crystalline materials (i.e., chondrules olivine and pyroxenes).

Amorphous silicates have been identified in the interstellar medium, where well crystalline silicates are amorphized by high-energy heavy ions (Kemper et al., 2004). Amorphous silicates can be found in chondrule mesostasis glass (and therefore are Solar System products) but also as a matrix component in UOCs (Alexander et al., 1989), COs (Nittler et al., 2013), CM (Chizmadia and Brearley, 2008; Leroux et al., 2013) and CR (Abreu and Brearley, 2010; Floss and Stadermann, 2009), but their presolar nature is debated. Still, the preservation of matrix amorphous silicates can be seen as an indicator of little parent body processing. Our observations suggest that they are a minor component of CR chondrites, as previously also observed with IR by Bonal et al. (2013). A more precise estimate of the maximum abundance of amorphous material would require a more extensive analysis of the dataset (full inversion of the spectra) and would suffer from the ambiguity between matrix amorphous phases and chondrule mesostasis.

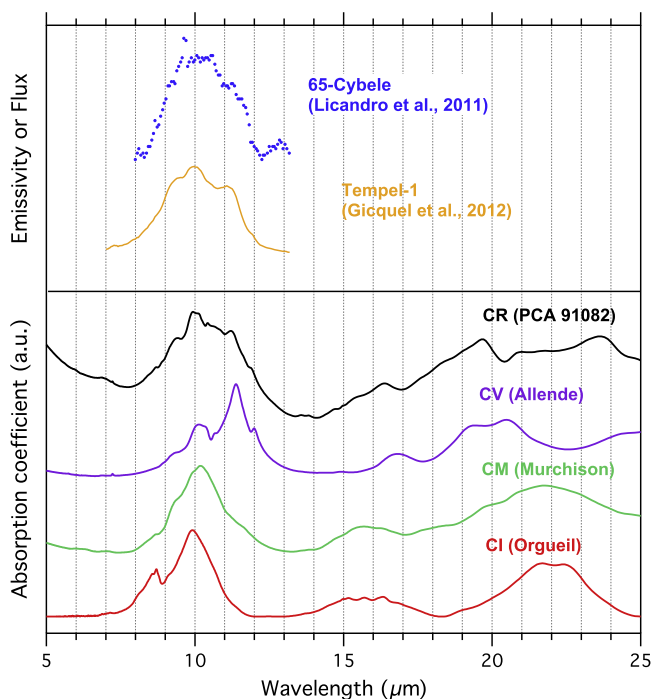
#### 5.5. A tentative comparison with small bodies and beyond

A chemical and mineralogical continuum might exist between asteroids and comets (Gounelle, 2011). However, these two types of astronomical objects are typically observed with distinct observational methods. Asteroid mineralogies are often inferred from their visible and near-infrared (VNIR) reflectance spectra (where, chiefly, Fe and –OH related absorptions features are observed), while information about cometary mineralogy often comes from measurements of the dust tail by its thermal emission in the 7–13  $\mu\text{m}$  region.

In the case of asteroids, the presence of hydration has been inferred, indirectly (since not probing directly –OH) from  $\text{Fe}^{3+}$  related absorption (Vilas et al., 1994; Vilas, 1994; Fornasier et al., 1999), as well as more directly by observation of –OH (Jones et al., 1990; Rivkin et al., 2002; Takir and Emery, 2012) and  $\text{H}_2\text{O}$  related features in the 3- $\mu\text{m}$  region (Campins et al., 2010; Rivkin and Emery, 2010; Takir and Emery, 2012; although a –OH attribution is possible, Beck et al., 2011).

Cometary dust mineralogy has been inferred mostly from observations of the 10- $\mu\text{m}$  silicate feature (Gehrz and Ney, 1992; Hanner et al., 1994; Crovisier et al., 1997; Harker et al., 2005), which provides information on the  $\text{SiO}_4$  tetrahedron network, and therefore can only give indirect constraints on the presence of hydration. Although comets can have properties that suggest formation at very low temperature conditions, the mineralogy of cometary dust contains phases that likely formed under very high temperature within the Solar Nebula. Such a result was initially suggested by observations of Halley and Hale-Bopp (Hanner et al., 1994; Crovisier et al., 1997; Wooden et al., 1999), and then confirmed by the Stardust sample return mission (Brownlee et al., 2006; Zolensky et al., 2006) as well as observations during the Deep Impact experiment (Harker et al., 2005).

The acquisition of transmission IR spectra of CCs provides analog measurements for IR emission by fine-grained materials (i.e., asteroid surfaces and cometary dust tails). Fig. 10 displays a comparison of typical spectra from the CC groups together with



**Fig. 10.** Comparison of selected carbonaceous chondrites transmission IR spectra to emission spectra of Tempel 1 dust (Gicquel et al., 2012) and 65-Cybele (Licandro et al., 2011). PCA = Pecora Escarpment.

dust emission spectra of Comet Tempel-1 (Gicquel et al., 2012). This exercise reveals that among the four CC groups, only one shows a possible match with Tempel 1 dust, i.e. the CR chondrites. This CC group was also shown to be the most resembling to anhydrous interplanetary dust particles and CHON particles from Comet Halley, based on the composition of their organic. All three other groups can be excluded as constituting the bulk of Tempel 1 dust. Although the similarity of the CR chondrite PCA 91082 spectra and that of Comet Tempel 1 might be striking, this certainly does not prove a genetic link between CR and comets, but mineralogical similarities are suggested from the IR spectra.

Finally, several mid-IR emission spectra of asteroids reveal vibrational features (Emery et al., 2006; Vernazza et al., 2010; Licandro et al., 2011), that are indicative of the presence of fine-grained material at their surface (Vernazza et al., 2012). This is the case of several members of the Themis family (Licandro et al., 2012), among which two members are Main-Belt-Comets (Hsieh and Jewitt, 2006; Jewitt, 2012). The presence of ice and organics at the surface of 24 Themis has also been proposed (Campins et al., 2010; Rivkin and Emery, 2010; Jewitt and Guilbert-Lepoutre, 2012), which is adding more evidence for a possible link between 24 Themis and comets. Similar reflectance spectra were also measured for another outer belt asteroid, 65 Cybele (Licandro et al., 2011). In Fig. 10, the emission spectrum of 65 Cybele is compared to the transmission spectra of CI, CV, CM and CR chondrites. Unlike the observation for Tempel 1, there is no evident match between a given meteorite and the spectrum of 65 Cybele. The most similar spectrum, in terms of maximum of absorption and overall shape, is the one of the CR chondrites PCA 91082, which would confirm that hydrated silicates are not dominant at the surface of Cybele (Licandro et al., 2011).

## 6. Conclusions

This work demonstrates the potential for the classification of CCs based on IR spectroscopy. This method, which is inexpensive

in term of the amount of time and material required, is able to unraveling the mineralogical diversity of these meteorites. In this study, the diversity observed can be understood in the light of parent body processes. The following conclusions can be drawn:

- It is essential to characterize meteorites with respect to mineral standards to understand their spectroscopic properties and relations to small extraterrestrial bodies. As an example, highly-crystalline terrestrial serpentine minerals do not reproduce the IR spectra of CM chondrites, although serpentines have been reported to be the dominant component. This is related to the poor crystallinity, and to the presence of nanometer multiple phase intergrowths, as well as cation substitutions.
- From IR spectra, it is possible to determine the relative extent of aqueous alteration by using water-related absorption at 3- $\mu\text{m}$ , as well as the shape of the 10  $\mu\text{m}$   $\text{SiO}_4$  stretching band. For CMs, the variations in the IR spectra can be explained by the progressive replacement of mafic silicates by phyllosilicates leading to the progressive disappearance of the 11.2  $\mu\text{m}$  olivine feature. This evolution is in agreement with measurements of bulk phyllosilicate contents (Howard et al., 2009) and petrographical observations. (Rubin et al., 2007).
- As reported in many studies, the phyllosilicates present in CCs are not identical to each other. The IR spectra of CM chondrites and the CR1 GRO 95577 are interpreted to be  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  substituted serpentines. The phyllosilicates present in CI are distinct and resemble saponite as described before (Tomeoka and Buseck, 1988). Saponite is also likely present in the Niger C2 chondrites.
- Anomalous and heated CI and CM chondrites were also studied. They reveal the presence of a dehydration trend, where all phyllosilicates were dehydrated and re-crystallized to olivine in the most extreme cases (PCA 02010, PCA 91008).
- The five spectra obtained from CV chondrites are remarkably similar. They all show the dominance of olivine. Subtle variations in the position of the  $\text{SiO}_4$  modes reveals that the Fe content in the olivine increases from almost pure forsterite ( $\text{Fo}_{98}$ ) to more fayalitic olivine ( $\text{Fo}_{70-90}$ ) in the order Kaba–Grosnaja–Vigarano–Mokoai–Allende. This evolution is likely due to a metamorphic re-equilibration of chondrule olivines with matrix phases.
- A comparison with emission spectra of dust tails from the Tempel 1 comet shows that only one group of CCs matches the observed feature around 10- $\mu\text{m}$ , the CR group. A genetic link between CR2 and comets is not proven, but mineralogical similarities are suggested from the IR spectra.

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