



The abundance and stability of “water” in type 1 and 2 carbonaceous chondrites (CI, CM and CR)

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Abstract

Carbonaceous chondrites record processes of aqueous alteration in the presence of hydrated and hydroxylated minerals, which could have provided a source of water in the inner solar system (Alexander et al., 2012, 2013). In this study, thermogravimetric analysis (TGA) was performed on 26 CM chondrites, which cover a range of degree of aqueous alteration from 2.0, such as Meteorite Hills (MET) 01070, to 2.6, such as Queen Alexandra Range (QUE) 97990, in order to quantify their water content. In addition, by measuring the release of volatile elements as a function of temperature, we obtained information on the mineralogy of water-bearing phases and provide indicators of aqueous alteration based on water released by phyllosilicates. These analyses are combined with infrared spectroscopy (IR) made on meteorite pellets heated up to 300 °C. The infrared features (–OH band at 3- μ m and SiO₄ around 10- μ m) revealed a correlation with TGA. The two techniques are in agreement with the scheme of aqueous alteration proposed by Rubin et al. (2007) and Alexander et al. (2013) based on phyllosilicate abundance.

The low temperature (200–400 °C) mass loss observed in TGA is attributed to Fe-oxy-hydroxydes (ferrihydrite, goethite). However, the proportion of these minerals formed by terrestrial alteration remains unknown. TGA also revealed two anomalous CM chondrites, Pecora Escarpment (PCA) 02012 and PCA 02010. Their TGA curves are significantly different from those of “regular” CMs with little mass loss, which can be related to the dehydration history of these meteorites in response to a heating event (Raman measurements also point toward a thermal event, Quirico et al., 2013). In the case of more mildly heated chondrites, such as with Wisconsin Range (WIS) 91600, the TGA curve presents similar mass loss to the other CMs.

Seven bulk measurements of CR chondrites and 3 measurements of matrix-enriched parts of CR meteorites were also studied by TGA, and confirm the low hydration level of chondrules and a significant alteration of the matrix. The water content of the matrix of the CM 2.6 QUE 97990 was estimated and compared to TGA of the matrix enriched portion of the CR2 EET 92159 and that of Orgueil.

Results suggest a similar aqueous alteration degree between Orgueil and the matrix of CMs (around 25 wt.%) and a lower alteration of the CR2 matrix (11 wt.% of H₂O).

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1. INTRODUCTION

The earliest record of liquid water activity in the Solar System is founded in carbonaceous chondrites (de Leuw et al., 2009; Fujiya et al., 2012, 2013). In these rocks, low temperature mineral assemblages are commonly encountered, including anhydrous phases (carbonates, sulphides, iron-oxides and salts) as well as hydrated and hydroxylated minerals (phyllosilicates and hydroxides) (Brearley and Jones, 1998). These minerals were produced by interaction of metals and anhydrous silicates with a H₂O-rich fluid, and the subsequent precipitation of secondary phases. These phases can preserve some of the original fluid in their crystal structure in the form of water molecules or –OH groups. Through this process, carbonaceous chondrites were enriched in hydrogen, and could therefore have contributed an important source of water on Earth (e.g. Morbidelli et al., 2000; Dauphas, 2000; Albarède, 2009; Trigo-Rodríguez and Martin-Toress, 2012).

However, not all meteorite groups experienced aqueous alteration, with the most hydrated samples belonging to the CI (type 1), CM and CR (type 2) carbonaceous chondrite groups (respectively around 20 wt.%, 9 wt.% and a smaller amount in the case of CR) (e.g. Zolensky and McSween, 1988; Brearley and Jones, 1998; Brearley, 2006; Rubin et al., 2007; Howard et al., 2009; Trigo-Rodríguez and Blum, 2009). Many carbonaceous chondrites are regolith breccias (Endress and Bischoff, 1996; Bischoff et al., 2006) indicating impact fragmentation.

The location and timing of the aqueous alteration process has remained controversial. In the literature the first hypothesis was that hydrated minerals were formed by condensation of gases cooling in the solar nebula (Lewis, 1972; Grossman and Larimer, 1974; Barshay and Lewis, 1976; Toppani et al., 2005). Another hypothesis, based on kinetic models, proposes a possible alteration at low temperature in the solar nebula (Prinn and Fegley, 1989). The most accepted model of aqueous alteration nowadays is a process occurring on the asteroidal parent body, from the melting of accreted H₂O ice (McSween, 1979; Bunch and Chang, 1980; Tomeoka and Buseck, 1985; Zolensky and McSween, 1988; Zolensky et al., 1993; Browning et al., 1996, 2000; Hanowski and Brearley, 2001; Trigo-Rodríguez et al., 2006). According to Mn–Cr dating of carbonates, this process occurred 4–5 million years after the formation of calcium aluminum inclusions (CAIs) (de Leuw et al., 2009; Fujiya et al., 2012, 2013).

Our objective here is to characterize the variability of the water content within carbonaceous chondrites and to understand the geological processes responsible for it (progressive hydration, thermal event). We also aim to understand the stability of water within the various chondrites studied by measuring their thermal stability. To do this, we use thermogravimetric analysis (TGA) to determine the water content (adsorbed water, pore water, structural water and hydroxyl groups –OH) in a series of carbonaceous chondrites (CI, CM, CR). The number of hydroxyl groups present within the phyllosilicates is used as a tracer of the intensity of aqueous alteration (Howard et al., 2009). A relationship between the TGA data and infrared

spectroscopy (IR) is drawn to validate the method. In addition, in order to further understand hydration of the CR chondrite matrix, TGA was performed on matrix-enriched portions, leading to a better insight into the alteration of this meteorite group.

2. METHODOLOGY, SAMPLES AND ANALYTICAL PROCEDURES

2.1. Methodology

Two different methods were used to study the alteration of chondrites: TGA and IR spectroscopy. TGA was used to quantify the amount of hydrogen in the samples by measuring the mass loss upon heating. The first derivative (DTG) of the TGA curve enables us to determine the maximum peak temperature of each mass loss and gives an indication of the host mineral of volatile elements. Previous studies (Guggenheim and Van Gross, 2001; Che et al., 2011; Lafay et al., 2012) as well as our own measurements (Appendix B.1) on phyllosilicate standards show that dehydroxylation occurs between 400 and 770 °C.

IR spectroscopy was performed on CM chondrites heated to 300 °C in order to remove terrestrial water as well as H₂O from (oxy)hydroxides. The relative intensity of silicate bands was used as an indicator of aqueous alteration, in particular, those of olivine SiO₄ modes (11.2 and 19.5 μm) with regards to serpentine SiO₄ modes (around 10 and 22 μm).

2.2. Samples studied

CI, CM and CR chondrites have distinct petrographical properties. The typical matrix volume proportion is 100% for CI, 70% for CM chondrites, compared to 30–50% for CR chondrites, and the chondrule volume proportion is 20–30% and 50–60%, respectively for CM and CR (Brearley and Jones, 1998). Another difference between these chondrite groups is the abundance of opaque phases, with CR chondrites containing more Fe–Ni metal than CM and CI chondrites (Weisberg and Huber, 2007). For the CM chondrites, the bulk mineralogy is dominated by serpentine, a hydrous magnesium–iron phyllosilicate (Howard et al., 2009, 2011) formed by the hydration of anhydrous Fe–Mg silicates (Bunch and Chang, 1980; Zolensky and McSween, 1988; Tomeoka et al., 1989; Browning et al., 1996; Rubin et al., 2007). These phyllosilicates can contain a significant quantity of water, up to 9–10 wt.%, in hydroxyl groups bonded on minerals (Barber, 1981; Tomeoka and Buseck, 1985).

The CI Orgueil, 26 CM chondrites and 7 CRs were studied (see Table 1 for the full sample list). Herein, we present the TGA data for a selected set of 8 CM chondrites (that were found to be representative of the CM diversity) and the 7 CR chondrites in order to ease the reading of the paper. All data obtained on the other meteorites are shown in the Supplementary online material (Appendix A.1, A.2 and A.3). The CMs were selected to cover the subtype range from 2.0 to 2.6 (Rubin et al., 2007). The CR chondrites studied are all classified as CR2 except for Grosvenor

Table 1

Summary of chondrites studied with their type, weathering grade, petrological grade, and weight loss as a function of temperature by TGA. Samples designed as heated CM chondrites were recognized as so by [Alexander et al. \(2012\)](#) and [Quirico et al. \(2013\)](#).

	Type /subtype	Fall/ <i>find</i>	Weathering grade	Petrologic grade	Mass loss 0–200 °C (wt.%)	Mass loss 200–400 °C (wt.%)	Mass loss 400–770 °C (wt.%)	Mass loss 770–900 °C (wt.%)	Total mass loss (wt.%)
CI									
*Orgueil	CI	Fall	–	1	7.4	5.2	12.2	2.7	27.5
CR									
GRO 03116	CR	Find	B/C	2	3	1.2	x	x	x
GRA 06100	CR	Find	B	2	1.7	x	x	x	x
GRO 95777	CR	Find	B or B/C	1	5.9	3	9.3	0.9	19.1
RBT 04133	CR	Find	B/C	2	2.7	1.5	x	x	x
EET 92159	CR	Find	B/C	2	2.7	1.5	x	x	x
QUE 99177	CR	Find	BE	2	2.8	1.5	0.3	x	x
MET 00426	CR	Find	B	2	2.4	1.1	0.3	x	x
EET 92159 ME	CR	Find	B/C	2	3.7	2.9	4.1	0.5	11.2
QUE 99177 ME	CR	Find	BE	2	3.8	3.6	2.7	0.3	10.4
MET 00426 ME	CR	Find	B	2	3.1	2.2	1.2	x	x
CM									
ALH 83100	CM	Find	Be	1/2	2.3	1	12.9	0.7	16.9
ALH 84029	CM	Find	Ae	2	2.2	1	12.3	0	15.5
ALH84044	CM	Find	Ae	2	2.5	1.2	11.7	0.3	15.7
DOM 08003	CM	Find	B	2	5.4	3.3	11.6	1.1	16
LAP 02333	C2/CM	Find	A/Be	2	3.6	3	6.3	1.3	14.2
LAP 02336	CM	Find	B	2	5	3.6	5.3	2	15.9
LAP 03718	CM	Find	BE	2	3.3	3.6	6.2	1.6	14.7
LEW 85311	C2/CM	Find	Be	2	3.6	4.1	5.8	1.7	15.2
LEW 85312	C2/CM	Find	B	2	3.7	2.7	5.5	0	11.9
LEW 87022	CM	Find	B	2	3.3	4.3	8.1	0.4	16.1
LEW 90500	C2/CM	Find	B	2	2.1	2.3	8.1	1.4	13.9
LON 94101	C2/CM	Find	Be	2	2.3	3.5	7.1	0	12.9
MCY 05230	CM	Find	B	2	2.6	3.7	7.3	1.9	15.5
MET 01070	CM	Find	Be	1/2,0	2	1.4	9.7	1.2	14.3
QUE 97990	CM	Find	Be	2/2,6	4	2.6	6.1	2.3	15
Murchison	CM	Fall	W1-2	2/2,5	2.7	3.5	7.3	1.9	15.4
Heated CM?									
DOM 03183	CM	Find	B	2	2.8	0.7	8.9	0.2	12.6
MAC 88100	CM	Find	Be	2	4	1.3	10.5	0	15.8
Heated CM									
ALH 84033	CM	Find	Ae	2	4.8	2.9	4	0.8	12.5
EET 87522	CM	Find	Be	2	4.4	0.9	4.6	0.6	10.5
EET 96029	C2/CM	Find	A/B	2	5.1	3.7	4.5	0.7	14
MIL 07700	CM	Find	A	2	6.3	0.7	4.8	0	11.8
PCA 02010	CM	Find	B	2	1.9	1.1	x	x	x
PCA 02012	CM	Find	B	2	3.1	1.7	x	0.7	x
WIS 91600	C2/CM	Find	A/Be	2	5	0.5	7.4	2	14.9
Ungrouped C2									
EET83355	C2	Find	A/B	2	3.8	0.9	2.7	0.3	7.7

ALH, Allan Hills; DOM, Dominion Range; EET, Elephant Moraine; GRA, Graves Nunataks; GRO, Grosvenor Mountains; LAP, LaPaz Ice Field; LEW, Lewis Cliff; LON, Lonewolf Nunataks; MAC, MacAlpine Hills; MCY, MacKay Glacier; MET, Meteorite Hills; MIL, Miller Range; PCA, Pecora Escarpment; QUE, Queen Alexandra Range; RBT, Roberts Massif; WIS, Wisconsin Range.

x: no quantification of mass loss available due to an overlap of mass gain.

ME: matrix-enhanced.

* [Appendix A.3, \(E\)](#).

Mountains (GRO) 95577, which is a CR1. Two kinds of samples were characterized by TGA: (1) bulk meteorite fragments; (2) matrix-enhanced fractions that were prepared for 3 CRs (EET 92159, QUE 99177, MET 00426). These CRs have been chosen for their primitive mineralogy

([Abreu and Brearley, 2010](#)). Samples were crushed in a mortar into small grains (<100 µm), and the matrix was extracted manually under a binocular microscope by micro-manipulation grain by grain in order to obtain a total mass of 10–15 mg.

2.3. Tga

TGA was performed with a TGA/SDTA 851^c Mettler Toledo. A fragment of the bulk meteorite was ground manually (around 50 mg) in a mortar. 10 mg of this powder was extracted for TGA analysis and put inside a 150 μ l alumina crucible, with a pierced cover, under a 50 mL/min inert N₂ atmosphere. The sample was heated from 25 °C to 1200 °C with a heating rate of 10 °C/min. The TGA mass resolution is 1 μ g, which corresponds to an absolute error of 0.1% for a mass loss fraction of 10%. The sample was weighed with a precision of 0.01 mg, which is equivalent to 0.1% error on a sample of 10 mg. Hence, the global absolute error on the mass loss fraction is 0.2%. The error on the temperature measurement is around 0.25 °C.

2.4. Decomposition of the TGA curves

TGA curves were used to quantify the hydrogen budget of meteorites and were decomposed over different temperature ranges (Fig. 1). The first part of the mass loss curve, from 25 to 200 °C, corresponds to the release of molecular water. There are different types of molecular water which could coexist, as shown by the DTG curves with two peaks between 25 and 200 °C, which are likely to be due to the release of adsorbed H₂O molecules for the first peak and mesopore water for the second. The second part of mass loss between 200 and 400 °C was attributed, at first-order, to the release of H₂O from (oxy)-hydroxide minerals, which is the temperature range we found for the decomposition of ferrihydrite and goethite (Appendix B.1). The third part, from 400 to 770 °C, was assigned to the release of hydroxyl groups (–OH) from phyllosilicates and the last part, between 770 and 900 °C, was attributed to CO₂ released from calcium carbonates (Appendix B.1), with possible

contributions from sulfates. The DTG curve can be used as an indicator of the mineralogy by identification of peak position as a function of temperature. The Appendix B.1 presents the DTG curves of different standards (chrysotile, cronstedtite, greenalite, goethite, ferrihydrite, clay and calcite), with peaks indicating the release temperature of the volatile element associated to each mineral. The Appendix B.2 is an example of the decomposition of Orgueil to identify the volatile elements and mineral host based on DTG curves. It is possible to identify specific minerals and differentiate phyllosilicates minerals. Due to the absence of standards with the exact same chemistry as carbonaceous chondrites phyllosilicates, in our study we did not use the DTG curves to identify precisely the mineral host, but we rather use temperature ranges. The Appendix B.3 presents DTG curves of iron sulfides (pyrite, pyrrhotite, troilite and a mixing of pentlandite and pyrrhotite). The main decomposition occurs between 400 and 650 °C and could overlap with phyllosilicate dehydroxylation.

2.5. Reproducibility test for TGA

A series of 6 experiments on the same meteorite, LAP 02336 (CM2), was performed to determine the deviation of the values due to the heterogeneity of the meteorite. The results are given in Table 2 and Fig. 2. The total mass loss in the range 200–900 °C varies from 12.4 to 9.7 wt.% (standard deviation: $\sigma = 0.93$ wt.%, $n = 6$). The abundance of (oxy)hydroxides is very similar in the 6 experiments with values comprised between 3.1 and 3.7 wt.% ($\sigma = 0.23$ wt.%, $n = 6$). The variation in the phyllosilicate temperature range (400–770 °C) is greater with values between 4.0 and 6.4 wt.% ($\sigma = 0.95$ wt.%, $n = 6$), while those of carbonates (770–900 °C) range from 1.1 to 2.8 wt.% ($\sigma = 0.54$ wt.%, $n = 6$). As explained previously, the mass loss fraction error

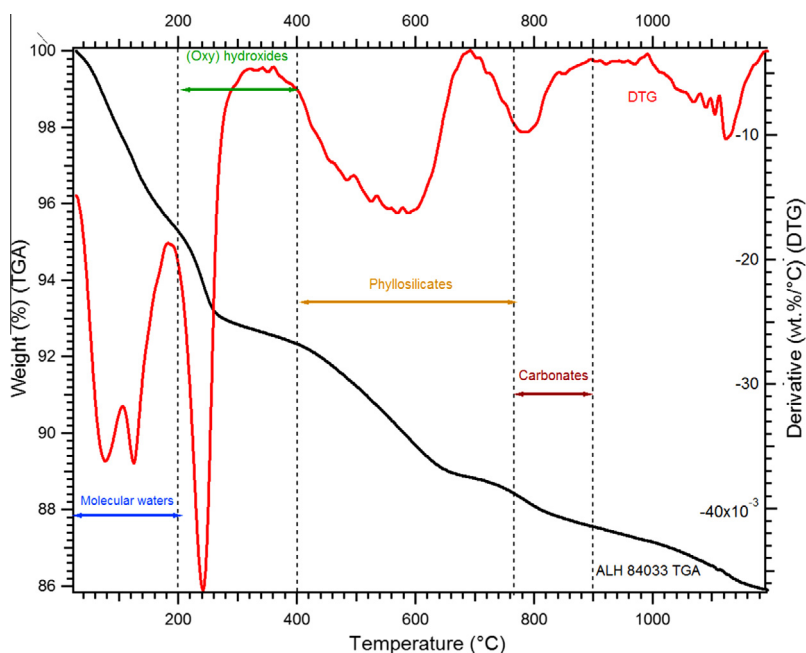


Fig. 1. TGA and DTG curves on ALH 84033. Decomposition in different types of mineralogy as a function of temperature.

Table 2

Weight loss of LAP 02336 (CM2) as a function of temperature by TGA repeated 6 times to study the variability.

	Weight loss between 0 and 200 °C	Weight loss between 200 and 400 °C	Weight loss between 400 and 770 °C	Weight loss between 770 and 900 °C	Total weight loss	Weight loss between 200 and 900 °C
LAP 02336 (1)	3.9	3.1	4.0	2.8	13.8	9.9
LAP 02336 (2)	5.0	3.6	5.3	2.0	15.9	10.9
LAP 02336 (3)	4.5	3.1	4.0	2.6	14.2	9.7
LAP 02336 (4)	4.3	3.4	5.9	1.1	14.7	10.4
LAP 02336 (5)	4.8	3.7	6.4	2.3	17.2	12.4
LAP 02336 (6)	4.0	3.4	6.0	2.1	15.5	11.5
Average	4.4	3.4	5.3	2.2	15.2	10.8
Standard deviation	0.39	0.23	0.95	0.54	1.1	0.93

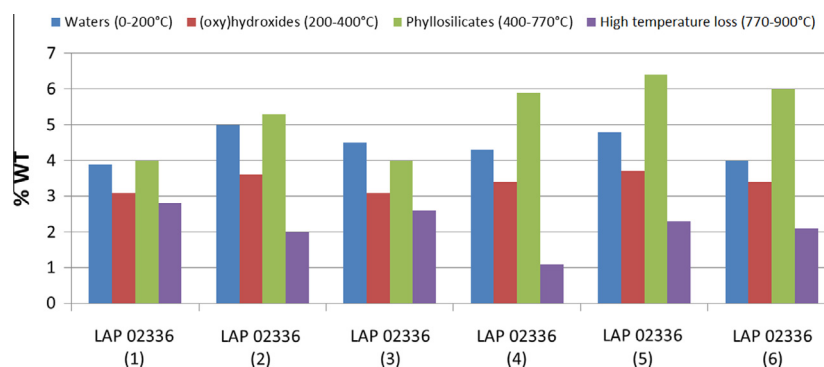


Fig. 2. Histogram of six TGA measurements on LAP 02336. Each measurement was decomposed in four parts as a function of temperature and shows the mass loss (wt.%) of the sample.

in our experimental conditions is typically 0.2%, and, therefore, this dispersion clearly shows the heterogeneity of the meteorite on a small scale.

Most carbonaceous chondrites and particularly CM chondrites are breccias, where materials with different thermal or aqueous alteration histories can be mixed (Trigo-Rodríguez et al., 2006; Herd et al., 2011; Jenniskens et al., 2012). This involves a mixing of diverse alteration or metamorphic history. The reproducibility test also reveals that the most significant relative variation occurs for the high-T mass loss (carbonates) where a nugget effect might occur (strong local spatial heterogeneity). For this reason, the mass loss in this temperature range will not be discussed in this manuscript.

Although the reproducibility test reveals that a variation of $\sigma = 0.95$ wt.% in the phyllosilicate range might occur for a given sample, this is below the variations observed across our sample suite. In addition, in order to have a good idea of the variability of the average aqueous alteration of a given meteorite, a second criterion is to combined IR spectroscopy with TGA.

2.6. IR spectroscopy

Small meteorite chips (around 30–50 mg) were crushed in a mortar before being mixed with KBr powder. The proportion was typically 1 mg of meteorite for 300 mg of KBr. This was mixed during 8 min at 30 Hz, and then pressed at 340 bar to obtain a compact pellet of the sample.

The typical size is 13 mm diameter with a mass of 300–320 mg. This was subsequently heated at 100 °C during 2 h and then heated at 300 °C for a further 3 h in order to release molecular water from the meteorite minerals and KBr and keep –OH groups in the phyllosilicates. These pellets were placed in a vacuum chamber to perform IR measurements. An IR microscope (BRUKER HYPERION 3000) was used to obtain spectra in transmission mode. The spectral resolution is 2 cm^{-1} and the spectra were recorded between 4000 and 400 cm^{-1} with a spot size of 3 mm diameter. 20 CMs were measured by IR from the same original meteorite fragment that was used for TGA analyses. More details about these measurements are in Bonal et al. (2013) and Beck et al. (2014).

3. RESULTS

3.1. Quantification of water in CMs by TGA

The 8 selected CMs are shown together in Fig. 3: the TGA curve (black) and DTG curve (grey) of Allan Hills (ALH) 83100 (a), ALH 84044 (b), Lewis Cliff (LEW) 85311 (c), LEW 87022 (d), Lonewolf Nunataks (LON) 94101 (e), Meteorite Hills (MET) 01070 (f), Murchison (g) and Queen Alexandra Range (QUE) 97990 (h). These meteorites have a significant total mass loss ranging from 12.9 wt.%, for the least, up to 16.9 wt.% for the most (Table 3, Fig. 4a). The mass loss curves are decomposed

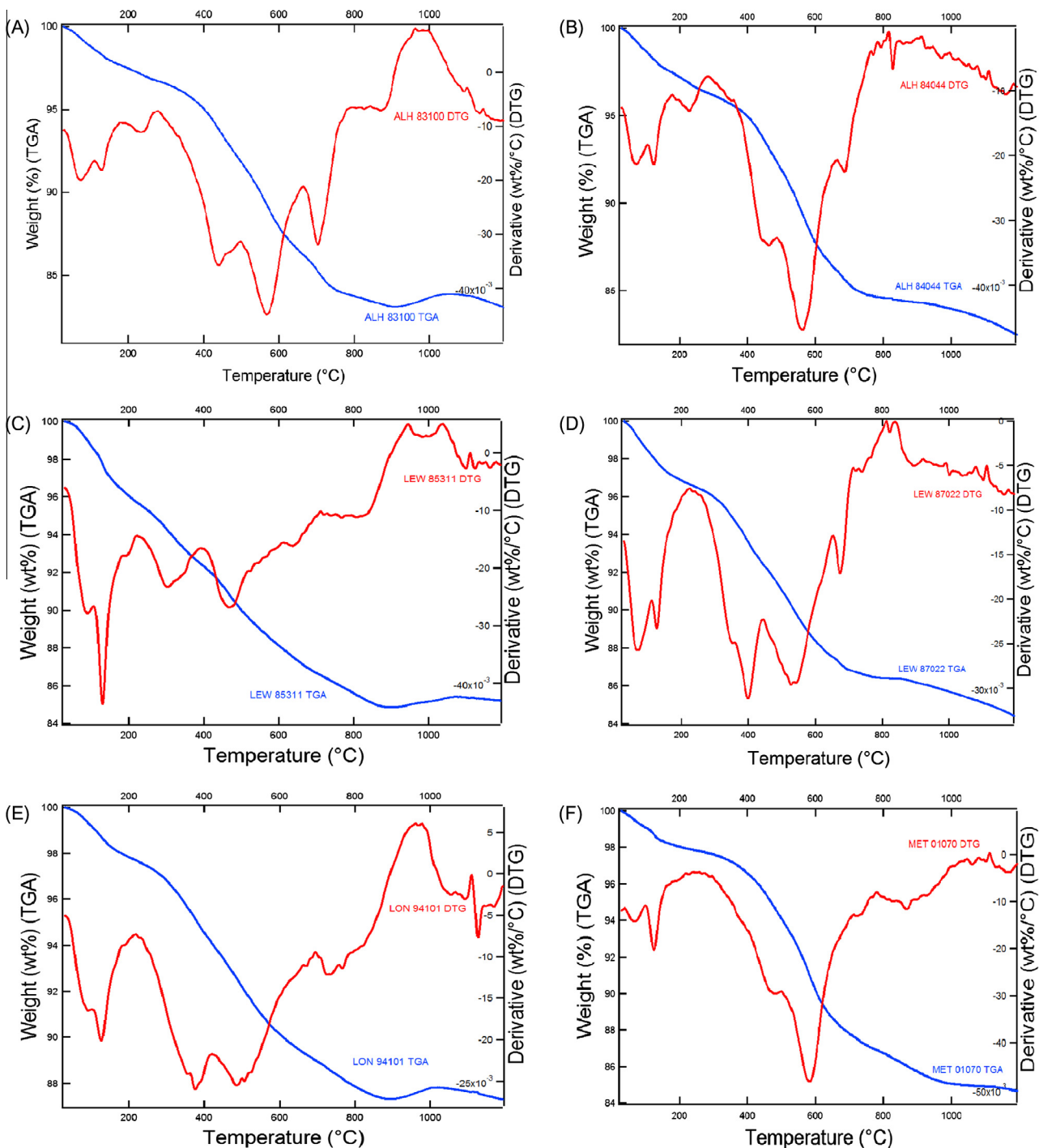


Fig. 3. TGA and DTG curves from 25 to 1200 °C for CM chondrites: (A) ALH 83100; (B) ALH 84044; (C) LEW 85311; (D) LEW 87022; (E) LON 94101; (F) MET 01070; (G) Murchison; and (H) QUE 97990.

into four temperature ranges following the pattern explained in Section 2.4. The first range between 25 and 200 °C corresponds to weakly-bonded H₂O (adsorbed and in mesopores). This part is not significant because it is likely to be sensitive to terrestrial contamination. The release of volatile elements in the second temperature range (200–400 °C) varies between 1.0 and 4.3 wt.% within our sample suite and is expected to be due to the dehydroxylation of

iron (oxy)hydroxides. It is possible that some of these mineral phases have been formed by terrestrial alteration, as will be discussed later. The part that retains most of our attention is the temperature range between 400 and 770 °C, which is assumed to correspond to the release of hydroxyl groups bound in phyllosilicates. Mass loss in this range is directly correlated to the abundance of phyllosilicates and to the degree of aqueous alteration of CM chondrites

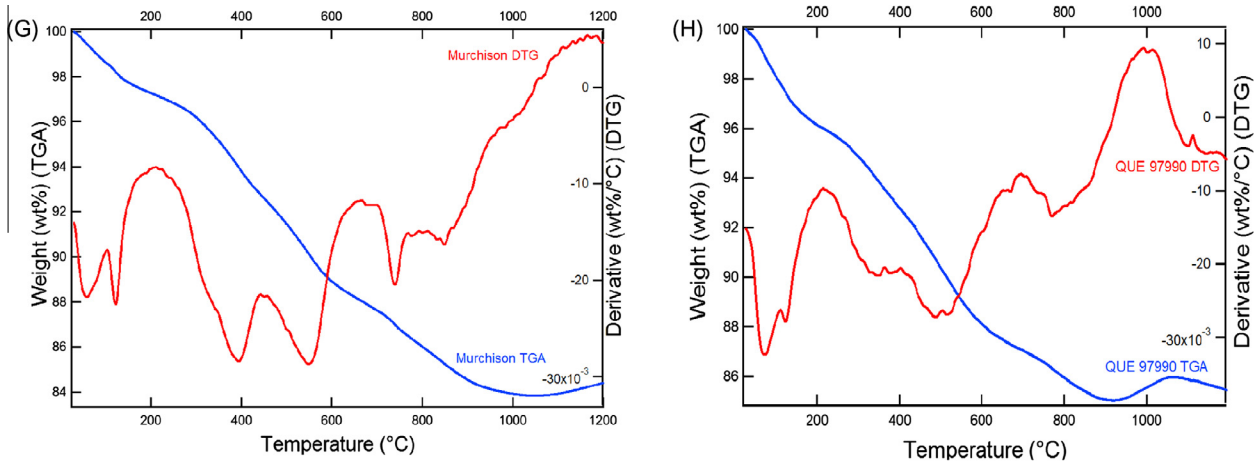


Fig 3. (continued)

Table 3
Weight loss of CMs as a function of temperature by TGA.

	Weight loss between 0 and 200 °C	Weight loss between 200 and 400 °C	Weight loss between 400 and 770 °C	Weight loss between 770 and 900 °C	Total weight loss	Weight loss between 200 and 900 °C
ALH 83100 (2.1)	2.3	1.0	12.9	0.7	16.9	14.6
ALH 84044 (2.1)	2.5	1.2	11.7	0.3	15.7	13.2
MET 01070 (2.0)	2.0	1.4	9.7	1.2	14.3	12.3
LEW 87022 (2.3)	3.3	4.3	8.1	0.4	16.1	12.8
MURCHISON (2.5)	2.7	3.5	7.3	1.9	15.4	12.7
LON 94101	2.3	3.5	7.1	0.0	12.9	10.6
QUE 97990 (2.6)	4.0	2.6	6.1	2.3	15.0	11.0
LEW 85311	3.6	4.1	5.8	1.7	15.2	11.6

(Howard et al., 2009, 2011). Table 3 highlights significant variations of mass loss in this range from 12.9 wt.% (ALH 83100) to 5.8 wt.% (LEW 85311). Mass loss between 770 and 900 °C is attributed to the release of CO₂, associated in particular with the calcium carbonates. The range of values obtained was comprised between 0 wt.% (LON 94101) and 2.3 wt.% (QUE 97990). Carbonates have not been detected in LON 94101 as shown in the study by Lindgren et al. (2011). As explained earlier, the TGA results are affected by the heterogeneity of the grains and a possible nugget effect for the less abundant phases. This effect could result from brecciation, different thermal histories or alteration process, and produces small scale spatial heterogeneity in the mineralogy. This difference in terms of quantity of secondary mineral will directly cause some errors in meteorites measurement and the quantification of mineral phases.

3.2. Characterization of the hydrated mineralogy of CMs by IR

The IR spectra of the CMs are shown in Fig. 5. In this figure, the meteorites are shown in the same order as in Fig. 4a which follows the amount of mass loss between 400 and 770 °C (phyllosilicates). The spectral regions of the silicate stretching (around 10 μm) and bending modes (from 15 to 25 μm) are of special interest. They can be used

to discriminate phyllosilicates and mafic silicates. Olivine typically shows absorption peaks with maxima at 11.2 and 19.5 μm, while phyllosilicates typically show an absorption maximum for SiO₄ stretching at a lower wavelength (around 10 μm) and bands at 15.8 and 22 μm due to bending vibration of the hydroxyl group (Beck et al., 2014).

Fig. 5, from the bottom to the top, we observe a modification of the olivine band intensity at 11.2 and 19.5 μm. Conversely, a decrease of the phyllosilicate bands at 10, 15.8 and 22 μm is observed. This is directly linked to the mafic silicate/phyllosilicate ratio in the meteorites, and seems in good agreement with the TGA results. More quantitatively, a linear correlation is observed between the ratio of the integrated band of serpentine (between 20.6 and 23.2 μm) and the integrated band of olivine (between 19 and 20 μm) with the quantity of volatile element released in the temperature range 400–770 °C corresponding to the phyllosilicates (Fig. 6).

3.3. CR chondrites by TGA

TGA and DTG curves of the studied CR chondrites are given in Fig. 7. The TGA curve (black) and DTG curve (grey) of Elephant Moraine EET 92159 (a), Graves Nunataks (GRA) 06100 (b), GRO 03116 (c), Robert Massif (RBT) 04133 (d), MET 00426 (e), QUE 99177 (f) and a CR1 GRO

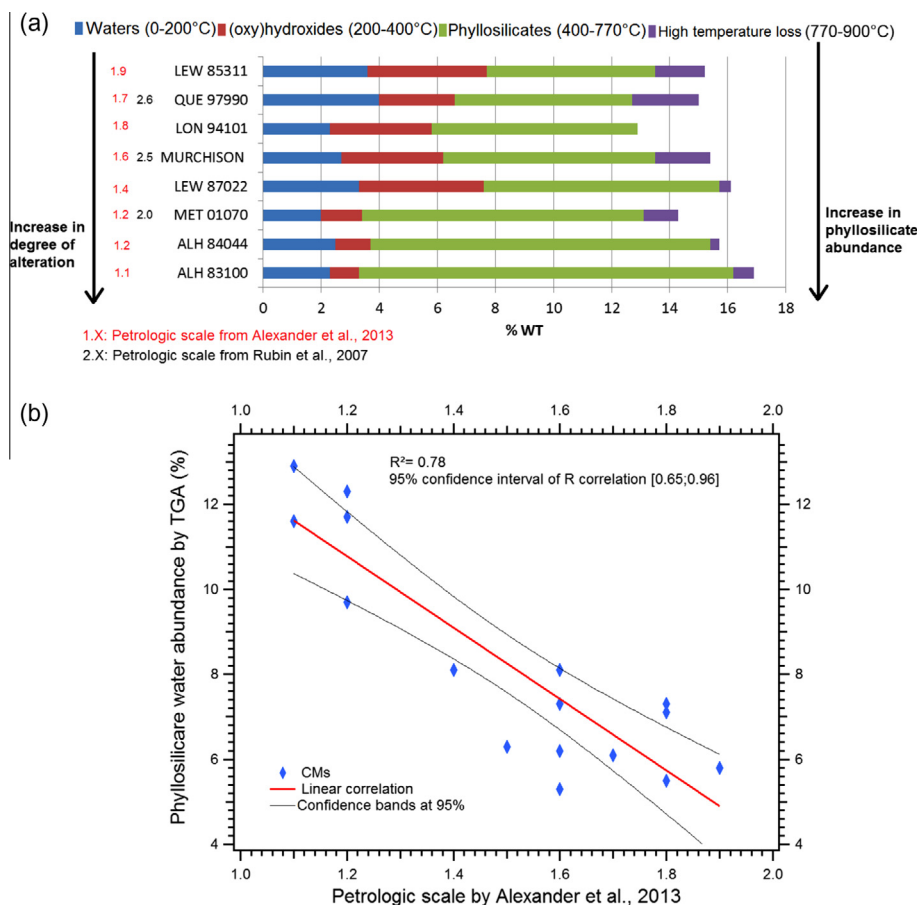


Fig. 4. (a) Horizontal stacked histogram showing the total weight loss of 8 CM meteorites during heating and divided in different temperature ranges, where each range is associated with a mineralogy and type of released water. The meteorites are organised from the one with the least weight loss between 400 and 770 °C to the most (in green). (b) Linear regression between the petrologic scale of Alexander et al. (2013) with the mass loss measured by TGA in the temperature range of 400–770 °C (phyllosilicate) for 16 unheated CM chondrites. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

95577(g) are shown. In comparison with CMs, the mass loss of CR2 is low (<5 wt.%) but not meaningful as explained below. The exception is CR1 GRO 95577 which seems to present a more extensive aqueous alteration in comparison to the other CRs studied, with a total mass loss of 19.1 wt.%. With CR2s, it is difficult to study the evolution of volatiles during the decomposition over different temperature ranges due to an increase in the mass during heating. This increase typically starts at 400–600 °C and the TGA curves result from a combined effect of mass loss due to released volatiles and mass gain. The origin of the latter will be discussed later. In fact, at the end of the experiments, some meteorites were heavier than at the start; for example, MET 00426 was around 2 wt.% heavier after the experiments. In the case of GRO 95577, the behavior is distinct and seems closer to the TG curves of CM chondrites.

As the matrix of carbonaceous chondrites is more sensitive to aqueous alteration than the chondrules (e.g. Zolensky and McSween, 1988; Tomeoka et al., 1989; Trigo-Rodríguez et al., 2006; Brearley, 2006) and considering the low water content of CRs, the matrix of CR2 chondrites was manually extracted and analyzed using TGA for the

CR2s; EET 92159, QUE 99177 and MET 00426. The TGA and DTG curves obtained are given in Fig. 8. The results show a significant difference in the total fraction of mass loss between the meteorite bulk and the matrix-enriched fraction. The total mass losses of volatile elements during heating of the matrix fractions are 11.2, 10.4 and 6.5 wt.%, respectively, while the mass losses for the bulk are 4.2, 4.6 and 3.8 wt.%, respectively. These results confirm that hydrous alteration products are mainly present in the matrix of CR chondrites. However, the chondrules are only slightly altered. Fig. 8 shows that in the case of a matrix-enriched fraction, the mass increase occurs at higher temperature than for the meteorite bulk, and the mass gain is also much lower.

4. DISCUSSION

4.1. CM chondrites, the hydration trend

The CM chondrite group shows variable degrees of aqueous alteration (e.g. McSween, 1979; Tomeoka et al., 1989; Browning et al., 1996; Rubin et al., 2007). An aqueous alteration scheme has been discussed by Rubin et al.

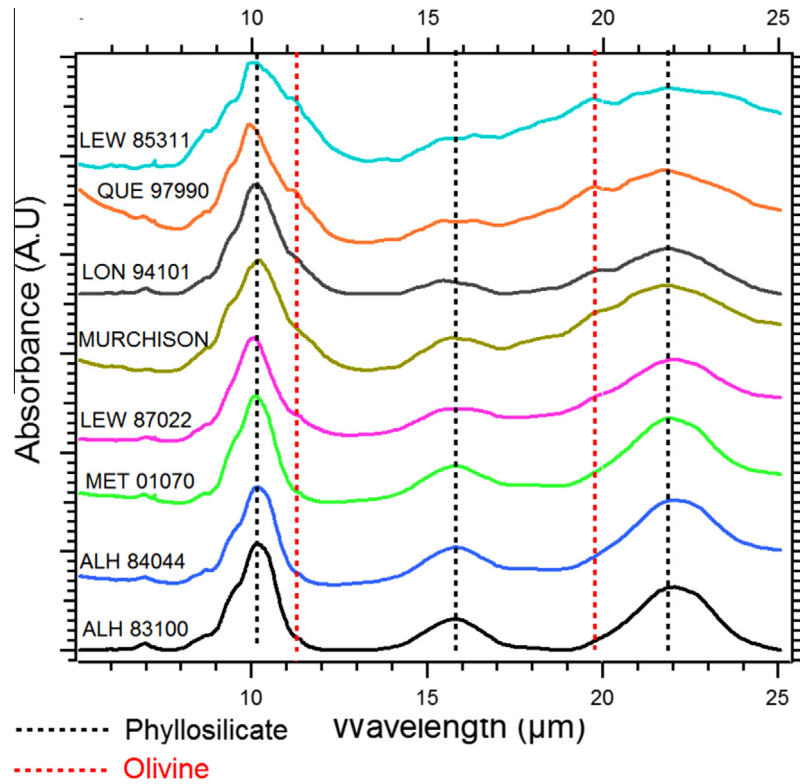


Fig. 5. IR spectra in transmission mode of the meteorites presented in the same order as in Fig. 4.

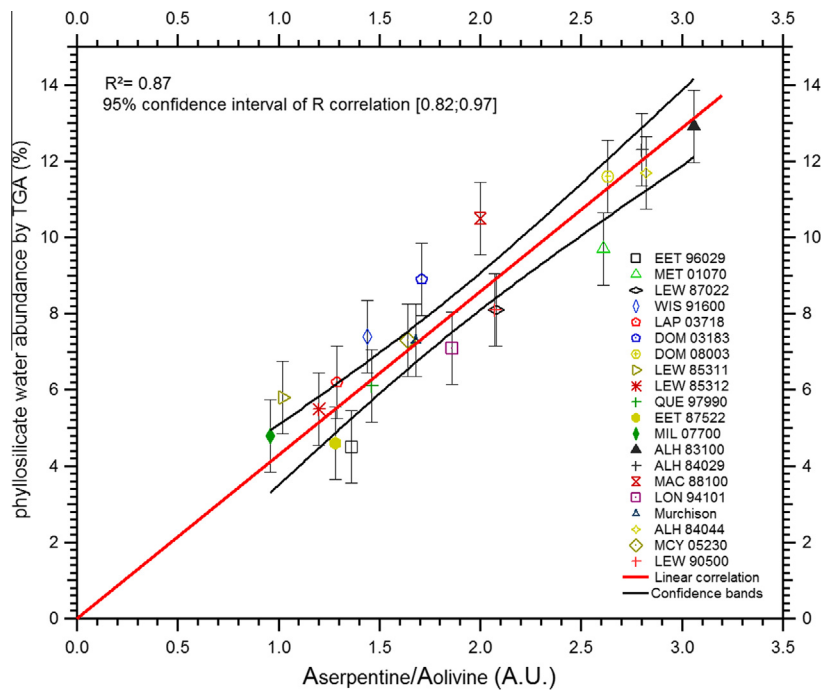


Fig. 6. Linear correlation between the surface ratio of the band of serpentinite (22 μm) and olivine (19.5 μm) with the mass loss, by TGA, in the temperature range of 400–770 °C for 20CM chondrites.

(2007) and is based on a combination of petrographic evidence of chondrule corrosion, the presence of secondary minerals in the matrix and the measurement of the crystal

chemistry of selected alteration products. Although aqueous alteration has been identified as an isochemical process within the CM suite (McSween, 1979; Rubin

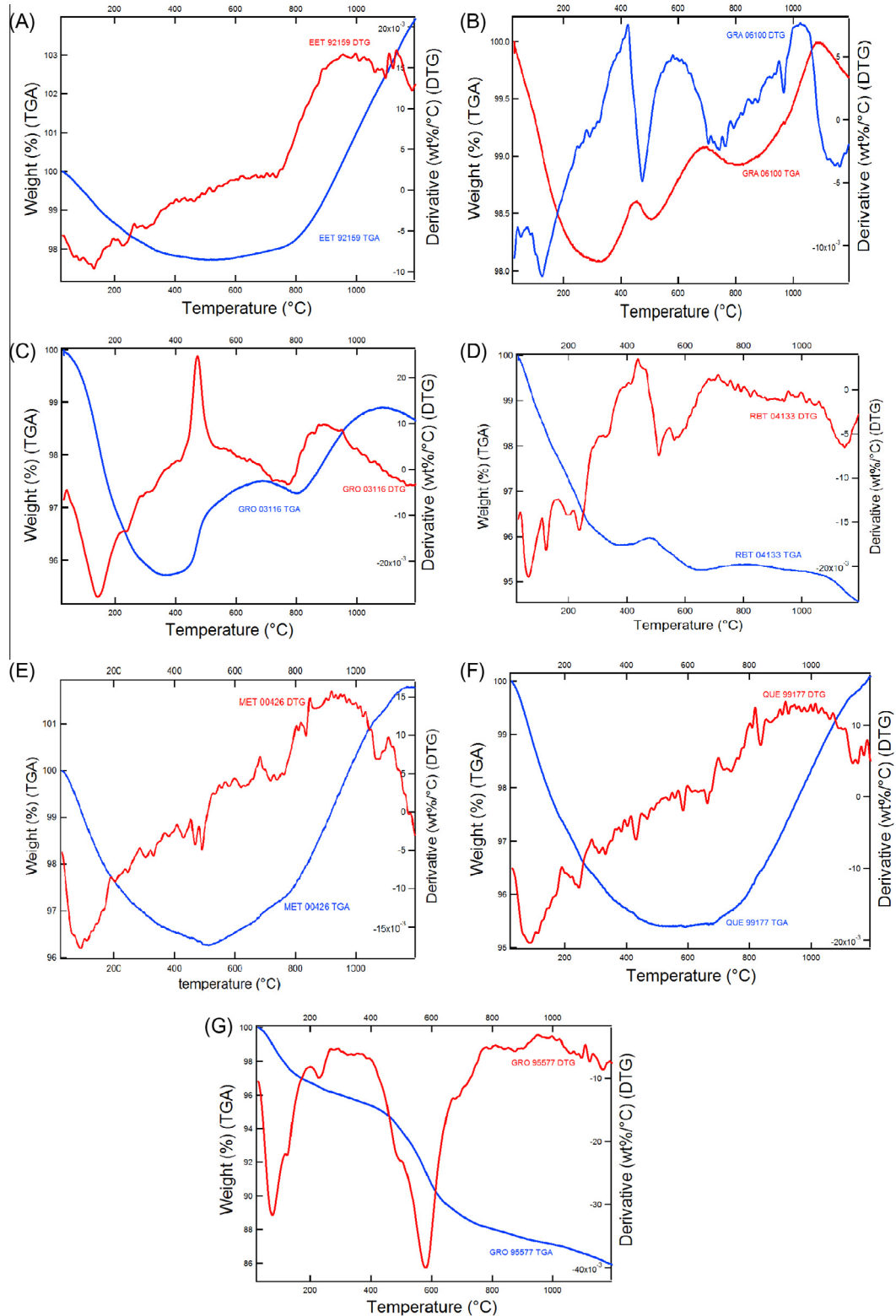


Fig. 7. TGA and DTG curves from 25 to 1200 °C for CR chondrites: (A) EET 92159; (B) GRA 06100; (C) GRO 03116; (D) RBT 04133; (E) MET 00426; (F) QUE 99177; and (G) GRO 95577.

et al., 2007), significant mineralogical differences appear between meteorites, and the construction of a scale for

aqueous alteration (absolute or relative) is fundamental to interpret cosmochemical data.

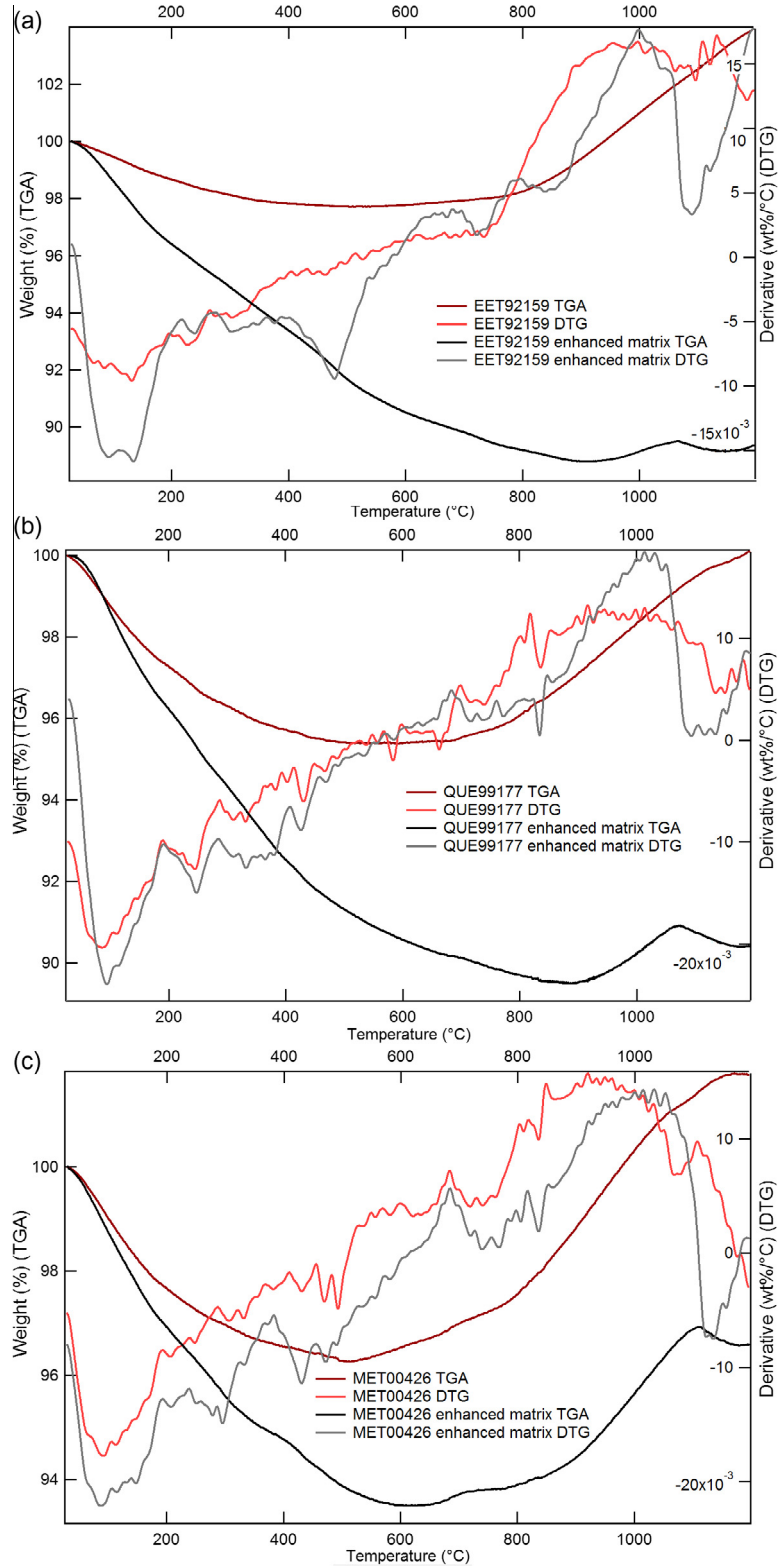


Fig. 8. TGA and DTG curves from 25 to 1200 °C. In black, the enhanced matrix part and in red the bulk part for CR chondrites: (a) EET 92159; (b) QUE 99177; and (c) MET 00426. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

As a criterion for the extent of aqueous alteration in carbonaceous chondrites, Howard et al. (2009) and Alexander et al. (2012, 2013) proposed the abundance of phyllosilicates, which correlates with the Rubin et al. (2007) classification. TGA is a simple method to characterize aqueous alteration by the amount of water contained in phyllosilicates. When chondrites are ordered according to the alteration scale defined by Rubin et al. (2007) and Alexander et al. (2013), the evolution of the phyllosilicate-contained water appears to increase with decreasing petrological types (see Fig. 4a,b and Table 1). The water abundance contained in phyllosilicate for this set of CM chondrite follows the Howard et al. (2009) classification.

Fig. 9 presents a comparison between the hydrogen budget in bulk CM2 chondrites measured by TGA and that measured by MS and elemental analyzer from Alexander et al. (2013). A reasonable correlation is found between the two methods, though TGA results still appear to be generally 10–15% higher than the Alexander et al. (2013) estimates of H abundance. All mass losses between 200 and 770 °C are considered as H₂O, but some sulfides could also be decomposed in this range. Mass losses from iron sulphides (e.g. troilite, pyrrhotite or pentlandite) that overlap with phyllosilicate dehydroxylation (see Section 4.5, Appendix B.3) could explain this difference.

The variability of phyllosilicate-contained water in our CM series (excluding the samples described as heated CM) is about a factor of 2 from LEW 85311 (5.8 wt.%) to ALH 83100 (12.9 wt.%). The volume proportion of matrix in CM is typically 60–70% (Krot et al., 2007) knowing that chondrule density is typically 1.7 times higher than matrix density, typically 3.4 g/cm³ compared to 2.0 g/cm³, respectively. Therefore, the mass proportion of matrix in CM is typically 45–55%. The factor of two difference between water content in slightly altered to greatly altered CM is therefore in rough agreement with the variation in the hydration degree of chondrules, from almost unaltered to fully transformed into phyllosilicates (Rubin et al., 2007).

As the matrix is fine-grained, it is more sensitive to aqueous alteration than chondrules. But several other reasons could explain why the degree of chondrule aqueous alteration more strongly varies across the CM group, as observed previously (Rubin et al., 2007; Howard et al., 2011) and confirmed with TGA results. Firstly, the duration of the process could have been different; secondly, the chemistry of the fluid might have changed; thirdly, the temperature of the fluid might have been different within the CM parent body; fourthly, the grain size of the original silicate might also have had an impact on the aqueous alteration (Lafay et al., 2012). Finally, although little fluid flow is expected due to the isochemical nature of aqueous alteration and the expected low permeability (Clayton and Mayeda, 1999; Hanowski and Brearley, 2000; Bland et al., 2009), the fluid availability and fluid/rock ratio might have differed.

Information on the timing of aqueous alteration can be gained from Mn–Cr dating (assuming ⁵³Mn was distributed homogeneously within the early solar system (Hutcheon and Phinney, 1996; Gounelle and Russell, 2005; Hoppe et al., 2007; Fujiya et al., 2013)). De Leuw et al. (2009) have

shown that: (1) carbonate precipitation occurred several million years after CAI formation; (2) a rough correlation between carbonate age and extent of aqueous alteration has been established. A study of carbonates in CI chondrites by Endreß and Bischoff (1996) shows that these minerals were probably formed at low temperature in an aqueous solution with localized compositional variation at the micrometer scale. At the same time, information on the duration of aqueous alteration can be obtained from kinetic experiments of olivine serpentinization. Unfortunately, there are only a few studies and even less data at the low temperature (0–30 °C) at which CM alteration is expected to have occurred (Guo and Eiler, 2007). Kinetic extrapolation by Velbel et al. (2012) based on Martin and Fyfe (1970) suggests that the timescale for 100 µm size olivine serpentinization at 25 °C is of the order of days to years. Recent experiments performed on Fe-bearing olivine (Malvoisin et al., 2012) showed that the reaction rate can be an order of magnitude lower than that of synthetic forsterite (Martin and Fyfe, 1970). Furthermore, these extrapolations would suggest that the duration of the process is of the order of years rather than a million years. In this case, it might suggest that the fluid availability was the limiting factor in explaining the different extents of aqueous alteration in CM chondrites.

4.2. Oxy-hydroxide, a possible marker of terrestrial weathering

In the case of meteorite finds, the residence time in cold or hot desert can have a significant impact on the mineralogy of the sample. Characterizing the level of terrestrial weathering is fundamental to understand the primitive nature of samples, and in particular, the possible oxidation of iron whose redox state controls the optical properties of meteorites (reflectance spectra, Burns (1993)) that are typically used to make the connection with asteroid observations. Terrestrial residence time can be determined by measuring ¹⁴C with terrestrial ages less than 40 k years (Jull et al., 1989) but systematic measurements in finds are absent from the literature.

It is probable that iron in fresh meteorites exists as Fe⁰ in Fe–Ni metal, Fe²⁺ in silicates and sulfides and Fe³⁺ in phyllosilicates and magnetite. High amount of ferric iron may be interpreted as the product of terrestrial alteration (Burns et al., 1995; Cloutis et al., 2011a,b) and its abundance might be used to estimate the degree of weathering (Bland et al., 1998). During terrestrial alteration, an initial rapid weathering phase is usually followed by a slow step due to a passivation mechanism by porosity reduction when metal oxidizes (Bland, 2006). However is still difficult to find a relationship between weathering grade and Fe oxyhydroxides, due to a possible pre-terrestrial alteration (Cloutis et al., 2011a,b). Goethite, limonite and ferrihydrite are iron oxy-hydroxides that are typical terrestrial weathering products (Noguchi, 1994). Ferrihydrite is found in meteorites, and was suggested as being a pre-terrestrial alteration phase (Tomeoka and Buseck, 1988). However an alternative formation mechanism, through terrestrial alteration, was proposed by Burns et al. (1995). They suggest that the

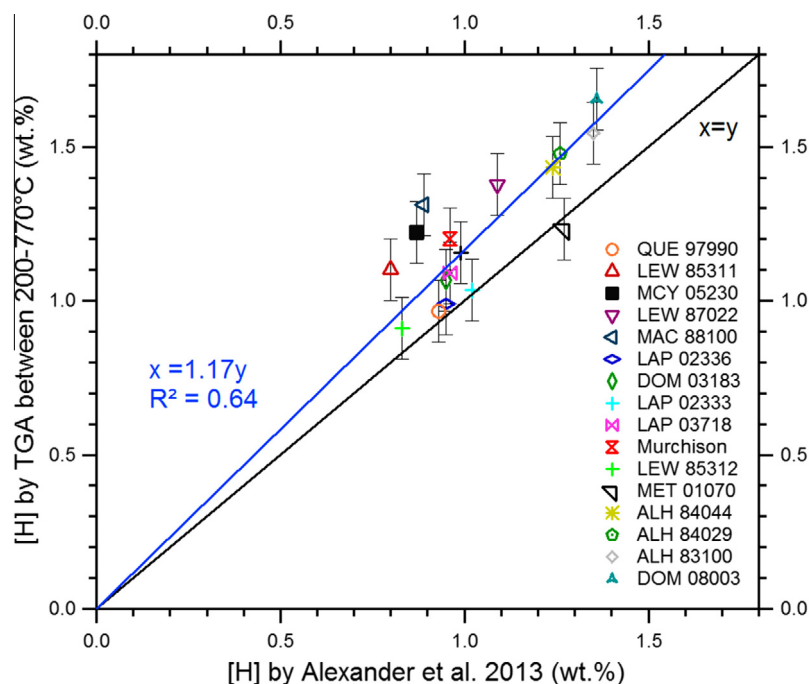


Fig. 9. CM chondrites: correlation between the hydrogen budget measured by Alexander et al. (2013) by mass spectrometer and elemental analyzer and that measured in this study.

ferrihydrate could result from oxidation of Fe^{2+} to Fe^{3+} after dissolution of magnetite, Fe-rich sulfide or Fe-rich saponite (Zolensky et al., 1993; Brearley, 1997). In our work, TGA analyses of standard phases show that the dehydroxylation of ferrihydrate occurs around 225 °C and goethite around 250 °C (Appendix B.1). The DTG curves of CM chondrites clearly show mass losses in the 200–400 °C range with a DTG peak centered at 235 °C, for instance in the case of the CM ALH 83100 (see Fig. 3). This could clearly be the result of dehydroxylation of ferrihydrate and/or goethite. The mass loss variations are between 1.0 and 4.3 wt.% in this temperature range (200–400 °C) for CM and between 1.1 and 1.5 wt.% for CR. In the case of CM, a negative relationship exists between the amount of H_2O in phyllosilicates and hydroxides (Table 3). Among the samples studied, the most hydrated (ALH 83100, ALH 84044 and MET 01070) contains the smallest amounts of hydroxides. This observation is in agreement with the scenario by Zolensky et al. (1993) where ferrihydrate is formed at the expense of Fe^{3+} -bearing phyllosilicates.

In Fig. 10(a), it appears that the meteorites studied can be divided in two groups: the first one with a high abundance of phyllosilicates (between 9 and 13 wt.%) and little (oxy)hydroxide (between 0.5 and 1.5 wt.%); and the second one with a low abundance of phyllosilicates (between 4 and 7 wt.%) and a high abundance of (oxy)hydroxides (between 2.5 and 4 wt.%). Exceptions include WIS 91600 and EET 83355, which were subjected to a thermal event as reveal by Raman spectroscopy (Quirico et al., 2013). This event could contribute to decrease the phyllosilicate abundance of these chondrites. Other samples fall outside of these

groups. Fig. 10(b) shows the weathering grade, as evaluated by the Johnson Space Center (JSC) on hand samples based on the degree of rustiness. No clear relation between weathering degree and the quantity of phyllosilicates and/or (oxy)hydroxides is observed here. The proportion of terrestrial and extraterrestrial (oxy)hydroxides is still unknown.

4.3. CM chondrites, the dehydration trend

The recognition of so-called heated CI and CM meteorites from the Japanese Antarctic meteorite collection program has shown that aqueous alteration and heating events are not exclusive processes (Akai, 1992). These meteorites have petrographical characteristics of CM or CI chondrites. However some thermal events are clearly recorded in mineralogical changes such as the transformation of phyllosilicates to anhydrous phases. Although dehydrated, fingerprints of the aqueous alteration process are preserved in these chondrites, for example the presence of a significant amount of Fe^{3+} (Beck et al., 2012). This type of chondrite might constitute a significant portion of main-belt asteroid surface material (Hiroi et al., 1993, 1996).

Our CM sample suite includes a few meteorites described as heated CM: WIS 91600, PCA 02012 and PCA 02010 (Quirico et al., 2013). WIS 91600 is described as a stage II heated carbonaceous chondrite according to the scale of Nakamura (2005). This stage is described as the beginning of mineralogical changes in the form of decomposition of serpentine to amorphous phases. The TGA curve of WIS 91600 does not reveal an unusual behavior with regard to “unheated” CM chondrites and the amount of phyllosilicates is comparable to that

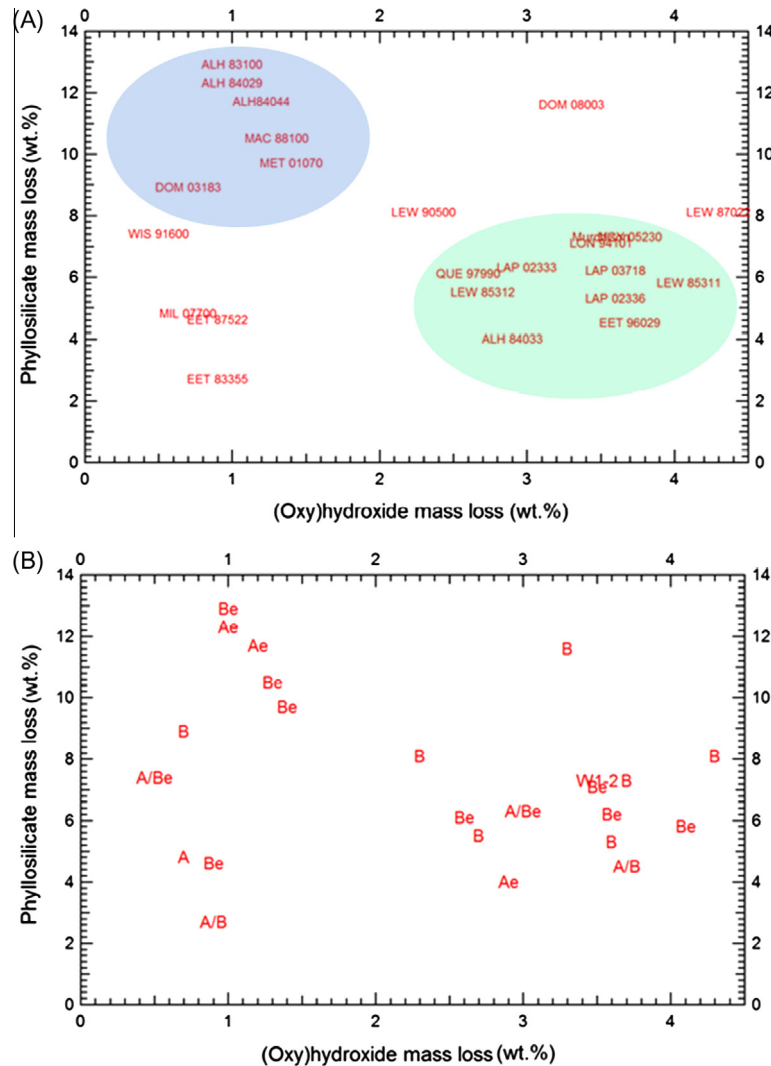


Fig. 10. CM chondrites: (A) From TGA, the relation between mass loss due to (oxy)hydroxide and mass loss due to phyllosilicates. (B) From TGA and degree of weathering, the relation between mass loss due to (oxy)hydroxide and mass loss due to phyllosilicates.

measured for CM 2.4 to 2.6 (See [Appendix, Fig. A3\(D\)](#)). From the TGA itself, it is not possible to classify this sample as a heated CM.

In the case of PCA 02010 and PCA 02012, unusual behaviors are observed when compared to other CM chondrites ([Fig. 11](#)) as both samples show very low mass losses below 400 °C and an intermediate phase of mass gain in the 400–800 °C range, rather than a continuous mass loss in their TGA curves. These measurements are consistent with IR spectra of the bulk rock powder that are dominated by olivine signatures ([Beck et al., 2014](#)), and show a lesser intensity of their 3- μm band (related to $-\text{OH}$ and H_2O). The combination of these results suggests that these samples lost almost all their water. There are three possible origins of the heat source that induced the dehydration observed in PCA 02010 and PCA 02012: first, the radioactive heating during transport; second, long duration heating by radioactive decay; and finally, short duration heating during impact. In the case of PCA 02012, [Nakato et al. \(2013\)](#) propose a very short heating event of the order of

several 10s of seconds to a 100 h up to 900 °C, based on organic maturity and Fe–Mg interdiffusion between chondrule olivine and matrix. Almost all CM chondrites are breccias ([Bischoff et al., 2006](#)) and typically have a high porosity ([Britt and Consolmagno, 2000](#)). Due to their high porosity, a shock wave going through a CM-chondrite-like material would probably dissipate significant heat through pore collapse and compaction. Porosity is a first-order parameter controlling post-shock heating. For example, the peak temperature, reached for a non-porous basaltic rock at 10 GPa shock pressure, will be of a magnitude of 100 °C ([Malavergne et al., 2001](#)). In the case of basalt with a porosity of 30%, a peak temperature of 2000 °C will be reached for a 10 GPa peak shock pressure ([Beck et al., 2007](#)). Shock experiments on Murchison have indeed shown that dehydration and partial melting can be achieved for relatively low shock pressures (20–30 GPa, [Tomeoka et al., 1999](#)). It means, in the case of CMs, a low degree of shock could have induced a significant short duration heating. If shock waves appear to be a valuable heat source

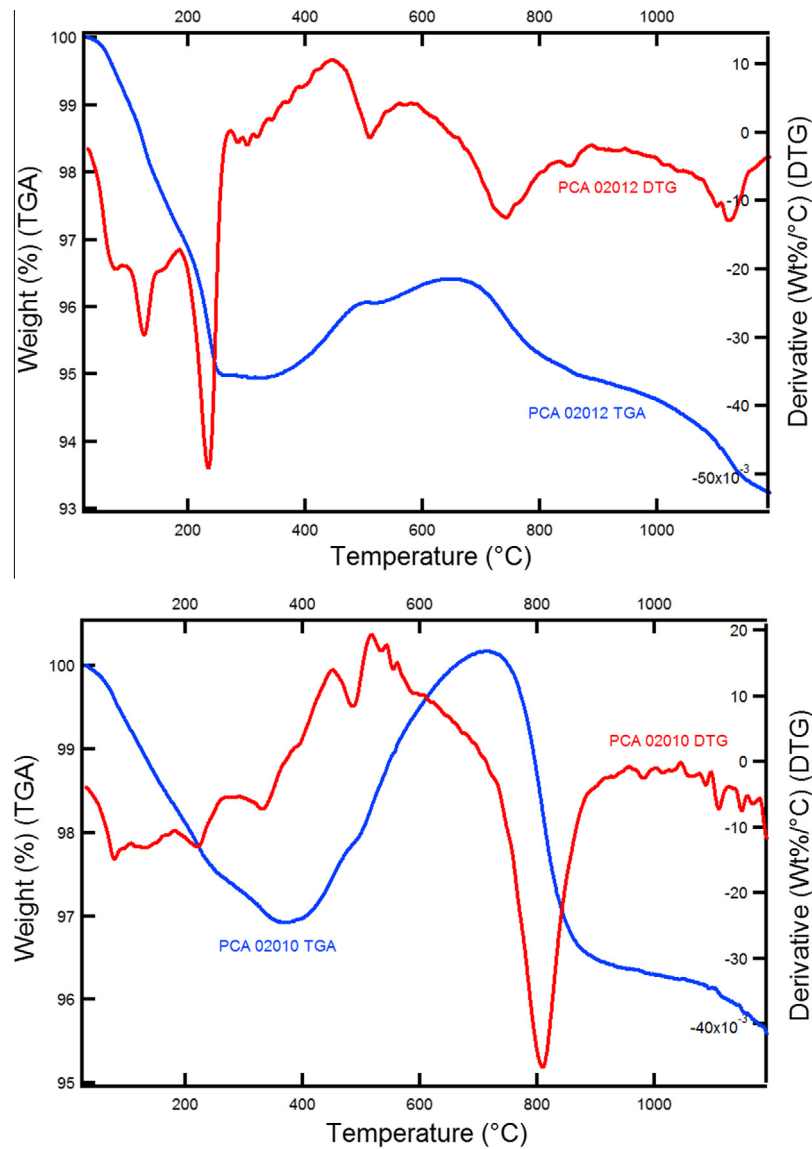


Fig. 11. TGA and DTG curves from 25 to 1200 °C for PCA 02012 and PCA 02010 (heated CMs).

to explain thermal metamorphism of type carbonaceous chondrites type 1 or 2, the radioactive heating hypothesis was until recently overlooked. From coupled dynamic and thermal simulation of meteor orbital evolution, Chaumard et al. (2012) showed that some Near Earth Objects (NEOs) might have been significantly heated (up to >1000 K) during their lifetime. These models were applied to explain the texture of the CK matrix and their relation to CV chondrites. The models might well be applied to explain the peculiar nature of heated CM chondrites, but to date there is no clear argument to favor such a mechanism with regard to shock-wave heating.

4.4. Aqueous alteration of CR chondrites

CR chondrites are petrographically distinct from CI and CM, with typically larger chondrules (Weisberg and Huber, 2007) and their unaltered chondrules have specific oxygen isotopes (Clayton and Mayeda, 1999). The “typical” CR

with usually unaltered glassy mesostasis is less altered than “typical” CM. They also contain a relatively high amount of Fe–Ni metal (around 7–9 vol.% compared to 0.1 vol.% for CM chondrite; Krot et al., 2007). This metal is generally present (up to 45 vol.% of the metal inside the chondrules and 15 vol.% at chondrule margins in chondrules) dominated by Mg-rich phases (Weisberg et al., 1993; Brearley and Jones, 1998; Krot et al., 2007; Schrader et al., 2010). Aqueous alteration has modified CR chondrite mineralogy, and variability is a consequence of fluid circulation (Trigo-Rodríguez et al., 2013). GRO 95577 has been described as CR1 (or equivalent to a CM2.0 in Rubin et al., 2007); on the other hand, MET 00426 and QUE 99177 are considered the least altered CR chondrites where matrix mineralogy shows abundant amorphous silicates, and an elevated concentration of presolar grains (Abreu and Brearley, 2007; Floss and Stadermann, 2009). However, some hydrated phase signatures were identified by IR spectroscopy in the latter samples (Bonal et al., 2013). Indeed, TGA curves

obtained from the 7 CRs studied reveal small mass losses on bulk samples (even mass gain) except for CR1 GRO 95577. This meteorite presents a very different composition and alteration with regards to the CR2 chondrites. The chondrules of GRO 95577 are completely hydrated (Weisberg and Huber, 2007) and are clearly visible on the TGA curves (see Fig. 7). In fact, the TGA and DTG curves of GRO 95577 are similar to those obtained for altered CM chondrites, with a total mass loss (200–900 °C) of around 13 wt.%. This meteorite shares petrographical characteristics with CR chondrites, in particular, Renazzo (Perronnet et al., 2007; Weisberg and Huber, 2007). However, its water content is comparable to that measured typically in CM chondrites. As the latter contain a much higher volume proportion of chondrules (60 vol.% chondrule compared to 30 vol.% in the case of CM chondrites (Krot et al., 2007)), in order to achieve such a high value of water content, a significant proportion of chondrules from GRO 95577 has to be altered.

For the other studied CRs, the mass loss from the bulk rock is below 5 wt.% and together with mass gain, this prevents analysis of water content. For this reason, a matrix-enriched portion of the meteorites was manually prepared by micro-manipulation and analyzed by TGA. For EET 92159 bulk sample, the TGA measured around 2 wt.% mass loss up to 800 °C, whereas there was around 11 wt.% mass loss up to 800 °C for the enhanced matrix sample. For QUE 99177 bulk sample, the mass loss is around 4.5 wt.% up to 700 °C and around 10 wt.% up to 700 °C for the enhanced matrix sample. For MET 00426 bulk sample, the mass loss measured is around 3.8 wt.% up to 500 °C and around 6 wt.% up to 500 °C for the enhanced matrix sample (see Fig. 8). In the three cases, a mass gain is still observed. However, the temperature necessary to produce the mass gain changes for the matrix enhanced sample. Indeed, it occurs at a higher temperature, and almost no mass gain is observed in the case of EET 92159 up to 1000 °C. This suggests that this effect of mass gain is probably related to chondrule mineralogy.

Although it is difficult to estimate how pure the matrix-enriched portion is, it still provides valuable information on the alteration history of CR chondrites. Indeed, the amount of mass loss from 200 to 770 °C from the enriched portion of QUE 99177 (8 wt.%) reveals that a mineral host for water has to be present in the matrix of this sample. IR spectroscopy previously revealed hydration features in QUE 99177 and MET 00426 (Bonal et al., 2013). Furthermore, measurement of hydration on the matrix-enriched portion by TGA is in reasonable agreement with the estimated value of 5 wt.% by Abreu and Brearley (2010). If the presence of amorphous silicates is confirmed as a major component of the bulk matrix mineralogy in CR chondrites, then these silicates have to be hydrated. Hydrated and amorphous silicates can be produced during the alteration of mafic silicates (e.g. Brearley and Jones, 2002), but as partially altered olivine was not observed, this tends to rule out this scenario. Abreu and Brearley (2010) rather favor a scenario in which pre-existing amorphous silicates are partially hydrated (a gel-like material), and

recrystallisation into phyllosilicates is precluded by a low temperature or the composition of material. After discussing in detail the possible mechanism for the formation of the amorphous silicates found in CR chondrites, Abreu and Brearley (2010) favored a solar nebula context, where disequilibrium condensation precluded the formation of highly crystalline phases. The identification of significant hydration of these amorphous silicates raises the question of the origin of the water incorporated in these phases.

4.5. A comparison of aqueous alteration of the CR, CM and CI matrices

As the chondritic matrix is extremely fine-grained, highly porous and permeable, it reacts readily with water. It will be the first component used to indicate aqueous alteration. Based on the TGA results, it is possible to compare aqueous alteration of the matrix of the various meteorite groups. Fig. 12 presents a comparison of the hydrogen mass balance in the matrix of CR, CM and CI chondrites (EET 92159, QUE 97990, and Orgueil, respectively). For the CI chondrite, as this meteorite group is almost entirely devoid of chondrule-like material, bulk meteorite measurements can therefore be seen as representative of the matrix. Orgueil is also a breccia and show some fine-scale heterogeneity (Morlok et al., 2006; Barrat et al., 2012). CM chondrite, QUE 97990 was selected for the present comparison because the chondrules are reported to be almost anhydrous and hydrations mainly occur in the matrix (Rubin et al., 2007). To obtain an estimate of matrix hydration from bulk meteorite measurement, a 70 vol.% proportion of the matrix is used as well as a chondrule/matrix density ratio of 1.7 (*i.e.* the matrix represents 55 wt.% of the CM chondrites). For CR chondrites, enhanced matrix measurement is used. In the case of EET 92159, 2.3 wt.% of volatile elements have been measured in the bulk and 11.2 wt.% in the matrix-enriched part. There is therefore a factor of 5 in the mass loss between bulk CR and the matrix. Using the hypothesis of 35 vol.% matrix (density typically around 2), 60 vol.% chondrule (density typically 3.4) and 5 vol.% metal (density typically around 8) (Krot et al., 2007), the proportion of matrix is thus around 22 wt.%. As a consequence, the factor of five differences between the TGA measurement of the matrix-enriched portion and bulk rock measurement is in good agreement with the matrix being the major host of aqueous alteration products.

Comparison between Orgueil and the present estimate for the matrix of the CM chondrite QUE 97990 reveals a first-order mass loss similarity. However, small differences are found, of about 1.1 wt.% in the case of phyllosilicate content. These differences are within the uncertainties due to matrix mass proportion estimates and possible minor contributions to mass loss from other components (*i.e.* sulfides). The modal mineralogy of Orgueil reveals that serpentines constitute around 71 wt.% of the matrix (Bland et al., 2004). Based on a typical mass loss of 13 wt.% attributed to the phyllosilicate standards (Appendix B.1) we can deduce from TGA analysis that phyllosilicates constitute around 90 wt.% of Orgueil. Orgueil is highly brecciated, with abundant clastic matrix around fragments (Endreß and Bischoff, 1993;

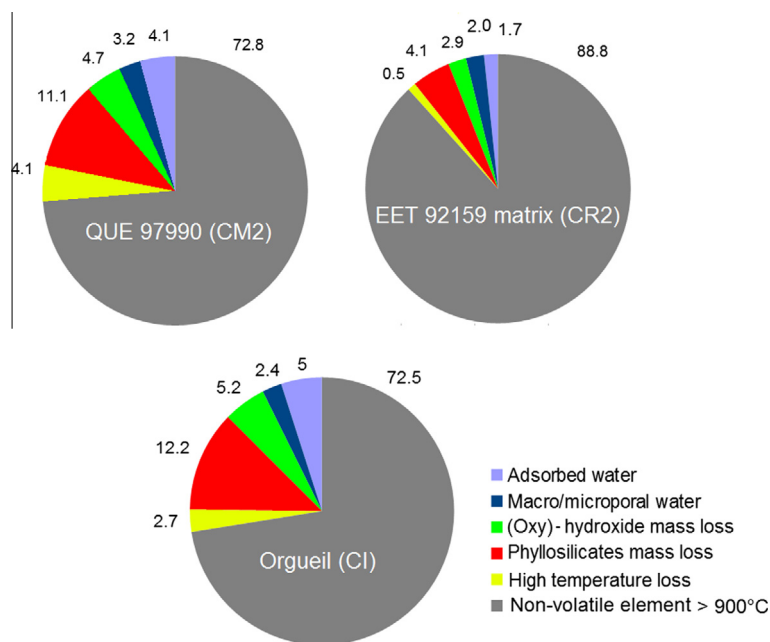


Fig. 12. Pie charts of volatile and non-volatile elements of the matrix of 3 groups of meteorites (CM, CR and CI). Values are in wt.%. The CM values were normalised and the CR values were measured by TGA.

Morlok et al., 2006). Orgueil contains some fine grain phyllosilicates with clear evidence of alteration rim around pyrrhotite as a result of the brecciation degree (Endreß and Bischoff, 1996). Endreß and Bischoff (1996) propose a link between the degree of aqueous alteration and degree of brecciation.

Concerning the CM QUE 97990 and the TGA data of Mg-rich chrysotile, it was found that phyllosilicates constitute around 85 wt.% of the matrix. The similarity in the amount of phyllosilicates of the “least” altered CM QUE 97990 and Orgueil confirms that the petrological subtype and qualification of aqueous alteration in CMs are only correlated with the alteration of chondrules, and that matrix hydration occurred early in the hydration sequence.

If CI and CM chondrites show similarity in their mass losses when comparing TGA data from their matrices, the calculation for the CR EET 92159 reveals a much lower mass loss. In fact, about 4.1 wt.% mass loss is attributed to phyllosilicates, which is much lower than 11.1 and 12.2 wt.% for QUE 97990 and Orgueil, respectively. If the mass loss between 400–770 °C is due to OH bonded in a phyllosilicate, so a typical proportion of 32 wt.% is found (using a mass loss of 13 wt.% for serpentine). Abreu and Brearley (2010) suggest that this mass loss could be due to the presence of partially-hydrated amorphous silicates in the CR matrix. The lower amount of water in the CR chondrite matrix with regards to the CI and CM matrices cannot be related to a heating event since amorphous silicates are likely to recrystallize upon moderate heating (Roskosz et al., 2011). More recently Trigo-Rodríguez et al. (2013) showed that EET 92159 contains many unequilibrated components and that this CR chondrite experienced aqueous alteration on the parent body. They propose an alteration by water of pyrrhotite and metal

grains, mobilizing Fe and S elements to produce some sulfide rich rims and magnetite. Based on these results, the petrologic subtype of CR2 EET 92159 could be between 2.6 and 3.0, and the intensity of aqueous alteration of the matrix of CM 2 QUE 97990 and CI 1 Orgueil is very similar. Therefore, strictly speaking, the petrologic type of the matrix could be the same. This petrologic type for aqueous alteration is based on the meteorite bulk. However, CI, CR and CM chondrites have different compositions and matrix/chondrule proportions and brecciation effects could produce heterogeneities in the alteration degrees of the same chondrites. Due to the efficiency of matrix alteration, the petrologic type for aqueous alteration is strongly dependent on the proportion of the chondrules. If the petrologic type represents the aqueous alteration experienced in terms of temperature, quantity of water on the parent body or time, comparing the CI, CM and CR could be difficult due to this difference in matrix/chondrule ratio.

5. CONCLUSION

In the present study, TGA and IR spectroscopy were performed on 26 CMs and 7 CRs in order to quantify the extent of aqueous alteration experienced by these groups of chondrites. Several conclusions have been drawn.

Firstly, the hydrogen quantity in carbonaceous chondrites can be inferred from TGA as different hosts: (i) weakly-bonded H₂O (loss between 25 and 200 °C), (ii) H₂O in hydroxides (200–400 °C), (iii) -OH from phyllosilicates (400–770 °C) and (iv) a high T loss (calcium carbonates and sulfates, 770–900 °C).

Secondly, the amount of -OH within phyllosilicates correlates with the -OH related IR absorptions measured in transmission mode. It also correlates with the scale of aque-

ous alteration as established by Rubin et al. (2007) and with the modal phyllosilicate abundance found by Howard et al. (2009, 2011).

Thirdly, the phyllosilicate –OH budget within “regular” CM (not described as heated) varies between 6.1 and 12.9 wt.% for QUE 97990 and ALH 83100, respectively. Simple calculation based on matrix/chondrule proportions in CM chondrites confirms that these variations are due to the progressive hydration of chondrules.

Fourthly, PCA 02010 and PCA 02012 are unusual CM chondrites characterized by a much lower estimated amount of H₂O. This can be interpreted as resulting from a dehydration event. These samples are likely heated CM chondrites, having experienced a short duration high-temperature event.

Fifthly, the abundance of dehydroxylation of an oxyhydroxide (e.g. ferrihydrite, goethite) was measured by TGA, its variation being comprised between 1 wt.% for ALH 83100 and 4.3 wt.% for LEW 85311. The origin of these phases is not yet well understood. They could come from the parent body or from terrestrial weathering processes.

Finally, CR1 and CM2 chondrites are altered to a similar extent with a total mass loss around 19 wt.%. In the case of the studied CR2, even for samples described as very pristine (i.e. MET 00426 and QUE 99177), significant hydration of the matrix was observed. This suggests that the silicates that constitute the matrices of these samples are hydrated. The origin of these phases, however, remains enigmatic but some evidences points toward a parent body hydration process.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.gca.2014.03.034>.

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