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LETTER

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Characterising the CI and CI-like carbonaceous chondrites using thermogravimetric analysis and infrared spectroscopy

Ashley J. King^{1*}, Jake R. Solomon², Paul F. Schofield¹ and Sara S. Russell¹

Abstract

The CI and CI-like chondrites provide a record of aqueous alteration in the early solar system. However, the CI-like chondrites differ in having also experienced a late stage period of thermal metamorphism. In order to constrain the nature and extent of the aqueous and thermal alteration, we have investigated the bulk mineralogy and abundance of H₂O in the CI and CI-like chondrites using thermogravimetric analysis and infrared spectroscopy. The CI chondrites Ivuna and Orgueil show significant mass loss (28.5–31.8 wt.%) upon heating to 1000 °C due to dehydration and dehydroxylation of abundant phyllosilicates and Fe-(oxy)hydroxides and the decomposition of Fe-sulphides, carbonates and organics. Infrared spectra for Ivuna and Orgueil have a prominent 3- μ m feature due to bound –OH/H₂O in phyllosilicates and Fe-(oxy)hydroxides and only a minor 11- μ m feature from anhydrous silicates. These characteristics are consistent with previous studies indicating that the CI chondrites underwent near-complete aqueous alteration. Similarities in the total abundance of H₂O and 3 μ m/11 μ m ratio suggest that there is no difference in the relative degree of hydration experienced by Ivuna and Orgueil. In contrast, the CI-like chondrites Y-82162 and Y-980115 show lower mass loss (13.8–18.8 wt.%) and contain >50 % less H₂O than the CI chondrites. The 3- μ m feature is almost absent from spectra of Y-82162 and Y-980115 but the 11- μ m feature is intense. The CI-like chondrites experienced thermal metamorphism at temperatures >500 °C that initially caused dehydration and dehydroxylation of phyllosilicates before partial recrystallization back into anhydrous silicates. The surfaces of many C-type asteroids were probably heated through impact metamorphism and/or solar radiation, so thermally altered carbonaceous chondrites are likely good analogues for samples that will be returned by the Hayabusa-2 and OSIRIS-REx missions.

Keywords: Meteorites, Asteroids, Aqueous alteration, Dehydration, Hayabusa-2, OSIRIS-REx

Introduction

The CI chondrites consist of abundant fine-grained (<1 μ m) phyllosilicates (serpentine interlayered with saponite) and minor amounts of Fe-oxide, sulphides and carbonates (Tomeoka and Buseck 1988; Zolensky et al. 1993; Endress and Bischoff 1996; King et al. 2015). They are interpreted as the end products of near-complete aqueous alteration of precursor anhydrous silicate components (e.g. Tomeoka and Buseck 1988; Zolensky et al.

1993). The aqueous alteration likely occurred on a parent body at temperatures of ~150 °C within the first ~15 Ma of the solar system (Endress et al. 1996; Hoppe et al. 2007; Fujiya et al. 2013). Extra-terrestrial H₂O (>10 wt.%) and organic species are plentiful in the CI chondrites leading to suggestions that they played a vital role in the delivery of volatiles and organic compounds to the early Earth (Alexander et al. 2012).

Five meteorites recovered from Antarctica within the last ~30 years are similar to the CI chondrites in terms of their mineralogy, petrography and composition. Of these, Y-82162, Y-86029 and Y-980115 have been identified as thermally altered CI-like chondrites (Tomeoka

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et al. 1989; Ikeda 1991; Nakamura 2005; Tonui et al. 2003, 2014; King et al. 2015). Evidence for thermal metamorphism comes from the dehydration of phyllosilicates and recrystallization back into fine-grained olivine (Nakamura 2005; Tonui et al. 2014), bulk O isotopic compositions shifted to higher values ($\delta^{17}\text{O} \sim 12$, $\delta^{18}\text{O} \sim 22$) than the CIs (Clayton and Mayeda 1999), and the destruction and modification of organics (Burton et al. 2014). Trace element chemistry and X-ray diffraction (XRD) patterns have been used to estimate that the temperature of the thermal metamorphism exceeded 500 °C (Nakamura 2005; Tonui et al. 2003, 2014; King et al. 2015).

The reflectance spectra of CI and thermally altered CI-like chondrites closely resemble the surfaces of some low-albedo C-type asteroids (Hiroi et al. 1993, 1996; Osawa et al. 2005), although Vernazza et al. (2015) recently argued against this link. In the next decade, two C-type asteroids, Ryugu and Bennu, will be visited by the Hayabusa-2 and OSIRIS-REx spacecraft, respectively. A major aim for both missions is to collect and return to Earth samples from the surface of these primitive bodies. However, there is evidence that the surfaces of C-type asteroids may be heterogeneous, with a mixture of hydrated and dehydrated minerals (Hiroi et al. 1993; Rivkin et al. 2003; Vilas 2008; Michel and Delbo 2010). It has therefore become important to characterise the properties of carbonaceous chondrites that experienced both aqueous alteration and thermal metamorphism. In particular, it is still not clear what the temperature, duration and source of the thermal metamorphism was.

In a previous study, we determined the modal mineralogy of bulk CI and CI-like chondrite powders using XRD (King et al. 2015). Here, we have taken aliquots of the same powders and characterised them using thermogravimetric analysis (TGA) and infrared (IR) spectroscopy. Recent work by Beck et al. (2010, 2014a) and Garenne et al. (2014) demonstrated that combined TGA and IR datasets can be used to examine the bulk mineralogy and quantify the abundance of H_2O in carbonaceous chondrites, providing useful insights into the nature and extent of aqueous and thermal alteration. Our results show that at the bulk scale, CI chondrites experienced essentially the same degree of aqueous alteration, in agreement with the findings of King et al. (2015). We estimate that the CI-like chondrites were heated to >500 °C and make a tentative analogy between the CI/CI-like chondrites and the surfaces of Ryugu, Bennu and other C-type asteroids.

Experimental

King et al. (2015) studied fusion crust free interior chips (50–200 mg) of the CI chondrites Alais, Ivuna and Orgueil and the CI-like chondrites Y-82162 and Y-980115. For the XRD measurements, the chips were powdered to a grain

size of <35 μm using an agate mortar and pestle. To monitor heterogeneity, two separate chips of Ivuna (referred to in King et al. (2015) and here as Ivu-1, Ivu-2) and three chips of Orgueil (Org-1, Org-2, Org-3) were analysed. Due to the limited amount of sample available, only single chips of Alais, Y-82162 and Y-980115 were analysed. Following the XRD measurements, the powdered samples were stored in glass vials within a desiccator.

In this work, we have obtained TGA data and IR spectra from several of the Ivuna, Orgueil, Y-82162 and Y-980115 powders studied by King et al. (2015). Using the same samples enables us to correlate datasets collected using different analytical techniques. For TGA, single aliquots of Ivu-1, Ivu-2, Org-2, Org-3 and Y-980115 were analysed. In addition, we took two separate aliquots (here called Y-82a and Y-82b) from the Y-82162 powder. For the IR measurements, we used aliquots of Ivu-1, Org-3, Y-82162 and Y-980115.

TGA

Between 10 and 15 mg of Ivu-1, Ivu-2, Org-2, Org-3, Y-82162 (Y-82a and Y-82b) and Y-980115 were analysed using a TA Instruments SDT Q600 TGA at the Natural History Museum, London, UK. Each sample was loaded into an alumina crucible and analysed under an N_2 flow of 100 ml min^{-1} . Mass loss from the samples was recorded as they were heated from 25 to 1000 °C at a rate of 10 °C min^{-1} . For comparison, we also analysed standards of minerals (grain size <35 μm) known to be present in significant quantities within the CI and CI-like chondrites. These included serpentines (antigorite, lizardite, chrysotile and cronstedtite), smectites (saponite, nontronite, montmorillonite), Fe-(oxy)-hydroxides (synthetic ferrihydrite, goethite, limonite) and carbonates (calcite, dolomite).

The mass resolution of the TGA is 0.1 μg , meaning that a 10 % mass loss from a 10-mg sample results in an error of only 0.01 %, and this is lower for a 15-mg sample. Instead, the main source of uncertainty comes from the sample weighing, which was done to a precision of 0.01 mg. This gives an error of ~ 0.1 % for samples between 10 and 15 mg. The combined maximum error on the measured mass loss fraction is therefore ~ 0.1 %.

IR spectroscopy

Transmission mid-IR spectra were obtained from ~ 3 mg of Ivu-1, Org-3, Y-82162 and Y-980115 mixed with ~ 300 mg of KBr and compressed to form 13-mm-diameter pellets. We also prepared pellets of several standard minerals (grain size <35 μm) including serpentines (antigorite, cronstedtite), smectites (saponite, montmorillonite) and San Carlos olivine, which were analysed during the same analytical session.

Measurements of the meteorite and standard mineral pellets were made under a low vacuum using a benchtop Bruker Vertex 80V FTIR interferometer at beamline B22 of Diamond Light Source, Didcot, UK. The spot size of the beam was $\sim 15 \mu\text{m}$, and spectra were collected in the $5000\text{--}400 \text{ cm}^{-1}$ ($2\text{--}25 \mu\text{m}$) range with a resolution of 2 cm^{-1} . The pellets were initially analysed having been stored at room temperature. However, to minimise the effects of adsorbed water (e.g. Beck et al. 2010, 2014a), we repeated the measurements after drying them at $300 \text{ }^\circ\text{C}$ for 2 h.

Results

TGA—standard minerals

Figure 1 shows the DTG ($\text{wt.\%/}^\circ\text{C}$) curves for the phyllosilicate, Fe-(oxy)hydroxide and carbonate standard minerals. The DTG curve shows how the weight of the sample changes during heating. The peak

position as a function of temperature is often characteristic of mineral groups and/or individual phases. For the smectites, we observe significant mass loss at $<200 \text{ }^\circ\text{C}$. This is due to the dehydration of interlayer H_2O , which is absent from the serpentines. However, phyllosilicates are also prone to adsorbing H_2O from the atmosphere. As we have no way of quantifying the effects of this adsorption, we do not focus on this region of the DTG curves. Instead, we concentrate on higher temperatures, with Fig. 1a showing that both the smectites and serpentines lose mass between 300 and $800 \text{ }^\circ\text{C}$ due to dehydration and dehydroxylation. This temperature range is in excellent agreement with previous investigations of phyllosilicate dehydration and dehydroxylation (Guggenheim and Koster van Groos 2001; Che et al. 2011; Garenne et al. 2014).

The Fe-(oxy)hydroxides ferrihydrite and limonite both dehydrate at $<200 \text{ }^\circ\text{C}$ before the loss of bound $-\text{OH}$ at

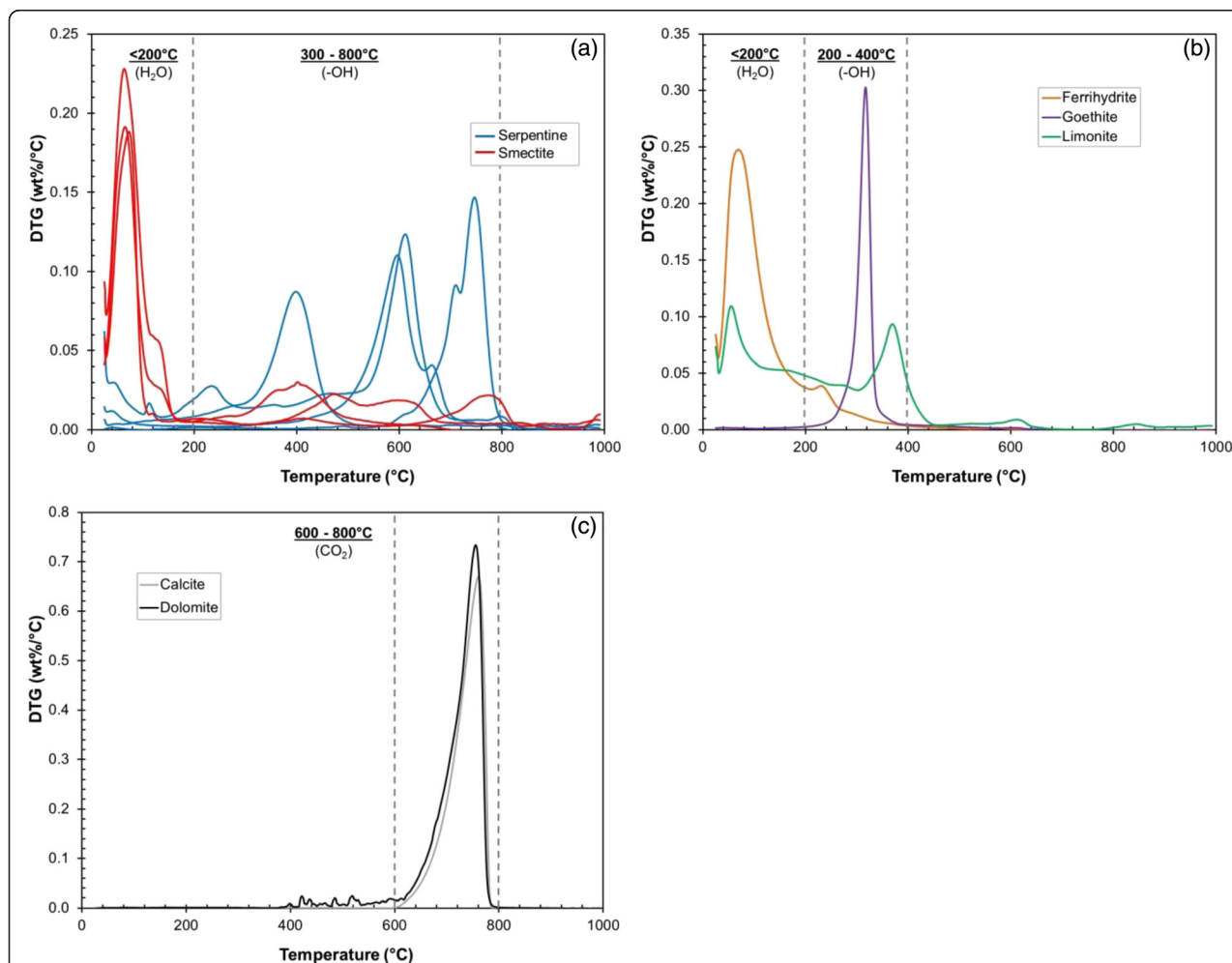


Fig. 1 DTG curves ($\text{wt.\%/}^\circ\text{C}$) for phyllosilicate (a), Fe-(oxy)hydroxide (b) and carbonate (c) standard minerals. At $<200 \text{ }^\circ\text{C}$, the phyllosilicates and Fe-(oxy)hydroxides suffer significant mass loss due to dehydration of both structural and adsorbed terrestrial H_2O . Further mass loss due to dehydration and dehydroxylation occurs between 300 and $800 \text{ }^\circ\text{C}$ for phyllosilicates and 200 and $400 \text{ }^\circ\text{C}$ for Fe-(oxy)hydroxides. Carbonates decompose and produce CO_2 between 600 and $800 \text{ }^\circ\text{C}$

200–400 °C (Fig. 1b). Goethite, containing only –OH groups, shows a sharp mass loss at ~300 °C. Carbonates do not contain H₂O and instead decompose and produce CO₂. Figure 1c shows that the decomposition and associated mass loss for our calcite and dolomite standards occurs at temperatures of 600–800 °C, consistent with other studies (Rodriguez-Navarro et al. 2009; Nozaki et al. 2006). However, it should be noted that the exact temperature for carbonate decomposition during TGA is strongly influenced by the grain size of the sample, and there are reports of calcite decomposition at 750–900 °C (e.g. Garenne et al. 2014).

TGA—CI and CI-like chondrites

The mass loss and DTG curves for Ivuna (Ivu-1), Orgueil (Org-3), Y-82162 (Y-82a) and Y-980115 are shown in Fig. 2. Curves for different aliquots of the same meteorites (e.g. Ivu-2, Org-2 and Y-82b) were nearly

identical and are summarised in Table 1. The average total mass loss (25–1000 °C) is 28.7 wt.% for the Ivuna samples and 30.3 wt.% for Orgueil. The average total mass loss for Y-82162 is 14.1 wt.%, and the total mass loss for the single Y-980115 sample is 18.8 wt.%. From our standard mineral data, we are able to divide the DTG curves for the CI and CI-like chondrites into different temperature regions, some of which overlap, related to the minerals present. However, due to possible differences in the composition of our standard minerals and those in the meteorites, we do not attempt to perform any definitive phase identification.

The CI chondrites contain >80 vol.% phyllosilicate (serpentine/saponite), plus minor amounts of carbonate (mainly dolomite) and ferrihydrite (Tomeoka and Buseck 1988; Zolensky et al. 1993; Endress and Bischoff 1996; King et al. 2015). A combination of mass loss from these phases is clearly what we observe in the DTG curves for

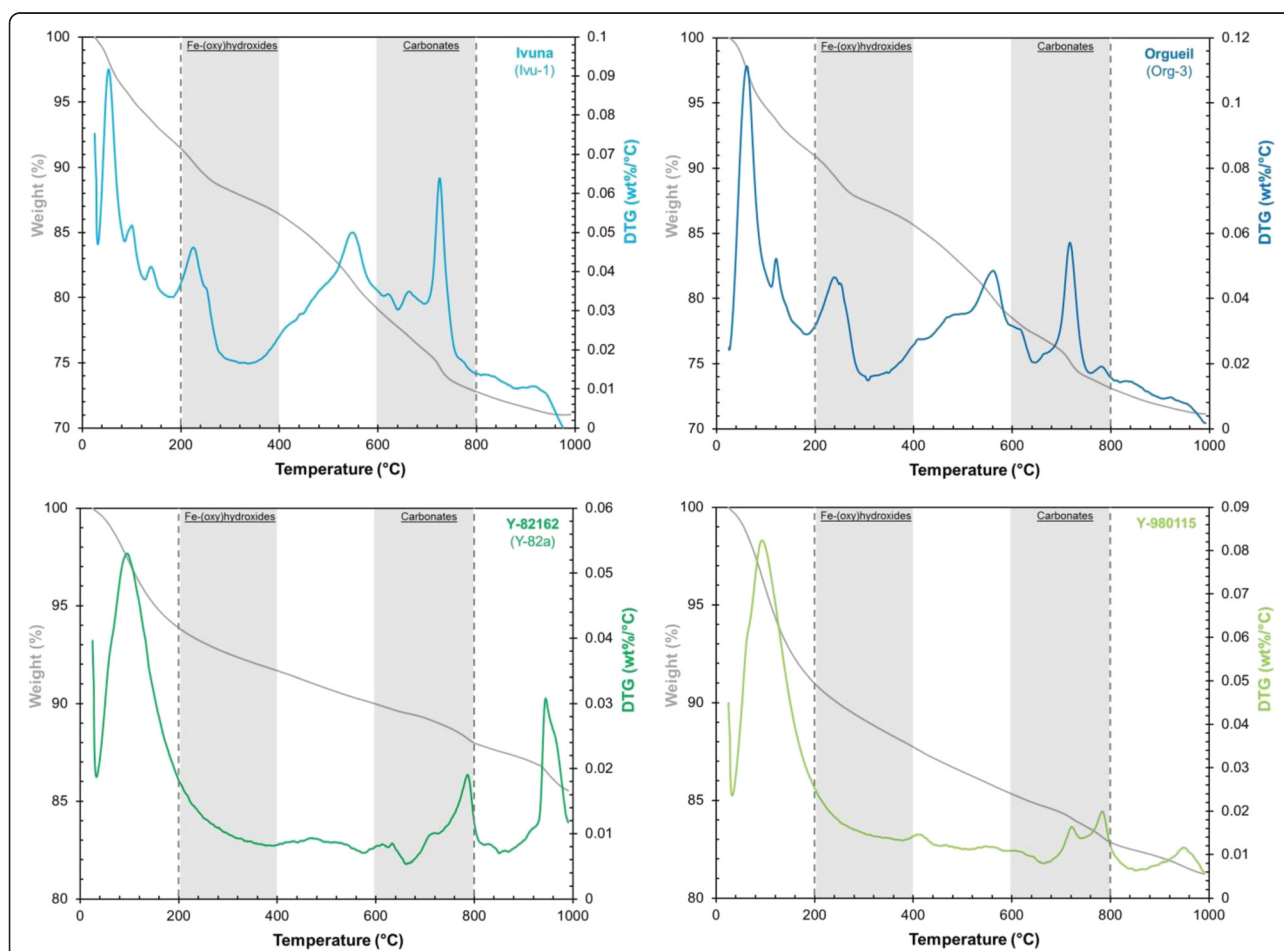


Fig. 2 Mass loss and DTG curves for CI chondrites Ivuna and Orgueil, and CI-like Y-82162 and Y-980115. Ivuna and Orgueil show significant mass loss between 200 and 800 °C due to the dehydration and dehydroxylation of abundant phyllosilicates formed during aqueous alteration. However, small amounts of Fe-(oxy)hydroxides (200–400 °C) and carbonates (600–800 °C) are present in the CI chondrites and also contribute to the mass loss in this temperature region. In contrast, Y-82162 and Y-980115 show little mass loss until 700–800 °C. This is due to these meteorites having experienced a thermal metamorphic event(s) that dehydrated the phyllosilicates

Table 1 Mass loss (wt.%) as a function of temperature for the CI and CI-like chondrites.

Sample		25–200 °C	200–400 °C	300–800 °C	800–1000 °C	Total mass loss (25–1000 °C)	H ₂ O (200–800 °C)	H (wt.%)
Ivuna	Ivu-1	8.5	5.1	15.4	1.8	29.0	18.7	2.1
	Ivu-2	7.9	5.1	15.4	1.9	28.5	18.7	2.1
	Average	8.2	5.1	15.4	1.8	28.7	18.7	2.1
Orgueil	Org-2	10.8	5.6	15.3	2.2	31.8	18.7	2.1
	Org-3	9.1	5.3	14.4	2.0	28.9	17.8	2.0
	Average	10.0	5.5	14.8	2.1	30.3	18.3	2.0
Y-82162	Y-82 (a)	6.1	2.2	4.6	2.4	14.5	5.9	0.7
	Y-82 (b)	6.0	2.2	5.0	1.5	13.8	6.3	0.7
	Average	6.1	2.2	4.8	2.0	14.1	6.1	0.7
Y-980115		9.0	3.2	6.3	1.6	18.8	8.1	0.9

Most mass loss occurs between 25 and 800 °C, and the DTG curves are divided into different temperature regions related to dehydration of terrestrial adsorbed H₂O (25–200 °C) and the dehydration and dehydroxylation of Fe-(oxy)hydroxides (200–400 °C) and phyllosilicates (300–800 °C). We determine the abundance of H₂O in the CI and CI-like chondrites by assuming that all the mass loss between 200 and 800 °C is H₂O (see “H₂O abundances in CI chondrites” section)

Ivuna and Orgueil. At temperatures <200 °C, there is dehydration of both interlayer H₂O from phyllosilicates and Fe-(oxy)hydroxides, plus adsorbed terrestrial H₂O that we cannot easily quantify. We therefore discount this region of the curve, other than to note that the peak at 100–150 °C is probably dehydration of the terrestrial sulphates known to contaminate the CI chondrites (Gounelle and Zolensky 2001). Ivuna and Orgueil show a mass loss event at 200–300 °C, comparable to the dehydroxylation temperature of ferrihydrite. The other Fe-(oxy)hydroxides tend to lose –OH at slightly higher temperatures (see Fig. 1b). The most significant mass loss for Ivuna and Orgueil occurs between 300 and 800 °C. This is consistent with the dehydration and dehydroxylation of the abundant serpentine and smectite phases, and the decomposition of carbonates at 600–800 °C. Above 800 °C, Ivuna and Orgueil show relatively little mass loss (~2 wt.%).

The CI-like chondrites show a broad mass loss from 0 to 200 °C that is distinct from the CI chondrites and probably reflects terrestrial contamination. The broadness of the mass loss represents the range and disordered nature of the H₂O/–OH bonding environments. We speculate that this might partly be because the CI-like chondrites are finds that spent an unknown period of time on the Antarctic ice sheet, whereas Ivuna and Orgueil were recovered shortly after their fall.

In contrast to the CI chondrites, Y-82162 and Y-980115 experienced a period of thermal metamorphism that resulted in lower amounts of a dehydrated phyllosilicate and abundant anhydrous olivine (Tomeoka et al. 1989; King et al. 2015). The effects of the thermal metamorphism are apparent in the DTG curves, with Y-82162 and Y-980115 showing very little mass loss from 200 to 700 °C before small events at 700–800 °C. The temperature at which this small mass loss takes place is consistent with peaks in the

Ivuna and Orgueil DTG curves suggesting, at least qualitatively, that the mineralogy is similar. Low mass loss has previously been reported in a number of thermally altered CM chondrites studied with TGA by Garenne et al. (2014), and also in several stones of the Sutter’s Mill meteorite (Beck et al. 2014b; Pizzarello and Garvie 2014).

The CI-like chondrites also both show a mass loss at 950–1000 °C, which is significantly larger for Y-82162 than Y-980115. Troilite is much more abundant in these CI-like chondrites (~20 vol.%) than in CI chondrites (King et al. 2015) and has been observed breaking down into Fe-metal around this temperature (Tonui et al. 2014). Alternatively, this could result from high temperature decomposition of a carbonate phase (e.g. Garenne et al. 2014), although these are low in abundance.

Quantifying H₂O

TGA is a useful tool for quantifying the abundance of H₂O in carbonaceous chondrites. We have estimated the abundance of H₂O in the CI and CI-like samples by assuming that all of the mass loss between 200 and 800 °C is due to dehydration and dehydroxylation of phyllosilicates and Fe-(oxy)hydroxides (Table 1). Using this method, we determine an average H₂O abundance of 18.7 and 18.3 wt.% for the Ivuna and Orgueil samples, respectively. For Y-82162, the average H₂O abundance is only 6.1 wt.%, and for Y-980115, it is 8.1 wt.%. However, these values likely overestimate the abundance of H₂O in the CI and CI-like meteorites as other phases, such as carbonates, Fe-sulphides and organics, although present in low abundances, will also cause some mass loss as they decompose in this temperature range (see “H₂O abundances in CI chondrites” section).

IR spectroscopy

Figure 3 shows the mid-IR spectra (5–25 μm) from Ivuna (Ivu-1), Orgueil (Org-3), Y-82162 and Y-980115.

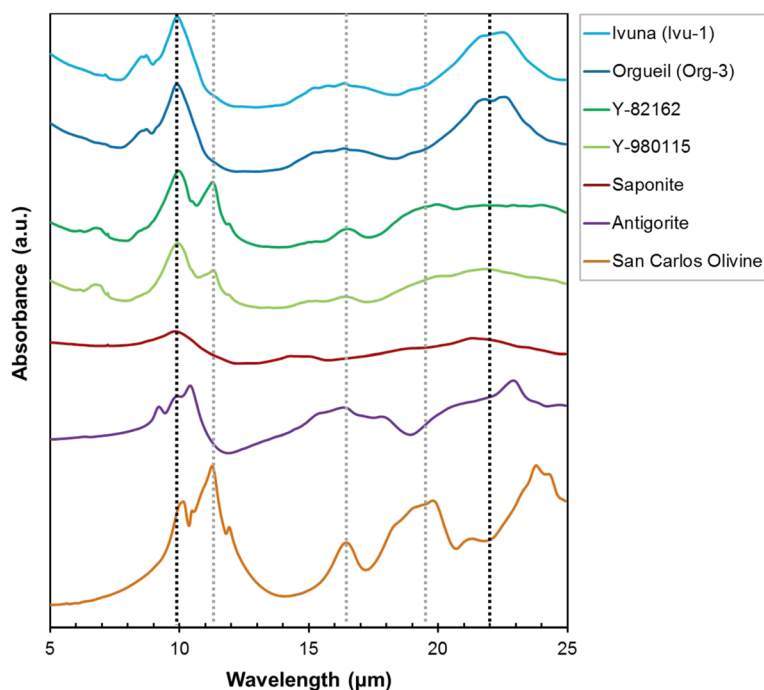


Fig. 3 Mid-IR spectra for CI chondrites Ivuna and Orgueil, and CI-like Y-82162 and Y-980115. Also shown are spectra from saponite, antigorite and olivine standard minerals. Ivuna and Orgueil spectra have a peak at $\sim 9.9 \mu\text{m}$ and a doublet at $\sim 23 \mu\text{m}$ from the Si–O stretching and bending modes (*dashed black lines*). Y-82162 and Y-980115 spectra have a broad peak at $\sim 9.9 \mu\text{m}$ and intense peaks at ~ 11.2 , ~ 16.5 and $\sim 19.5 \mu\text{m}$ that are consistent with olivine (*dashed grey lines*)

Included on Fig. 3 are spectra for the saponite, antigorite and olivine standards. The main features in the spectra for Ivuna and Orgueil are a peak at $\sim 9.9 \mu\text{m}$ and a doublet at $\sim 23 \mu\text{m}$ from the Si–O stretching and bending modes, which we attribute to the abundant phyllosilicates present in these meteorites. The position of the 10- μm feature best matches the saponite standard, in agreement with the findings of Beck et al. (2014a). Our data are also similar to the reflectance mid-IR spectra of McAdam et al. (2015), who suggested that Orgueil is dominated by a Mg-rich trioctahedral phyllosilicate. In addition, Ivuna and Orgueil have a peak at $\sim 8.5 \mu\text{m}$ from terrestrial sulphates (Gounelle and Zolensky 2001).

For Y-82162 and Y-980115, we again observe a broad peak at $\sim 9.9 \mu\text{m}$, the position of which is similar to saponite. However, the doublet at $\sim 23 \mu\text{m}$ is less prominent, and we see intense peaks at $\sim 11.2 \mu\text{m}$, $\sim 16.5 \mu\text{m}$ and $\sim 19.5 \mu\text{m}$ that are consistent with the presence of olivine.

We observe differences in the 3- μm region for the Ivuna and Orgueil samples analysed at room temperature and again after heating to $300 \text{ }^\circ\text{C}$. At room temperature, there is a broad feature from 2.7 to $3.5 \mu\text{m}$, with a sharp peak seen at $\sim 2.71 \mu\text{m}$. This broad feature has been reported before and is attributed to a combination of terrestrial adsorbed water, interlayer H_2O in smectites, and hydrous components associated with Fe-

(oxy)hydroxides within the CI chondrites (Sato et al. 1997; Osawa et al. 2005; Beck et al. 2010; Takir et al. 2013). Heating the samples to $300 \text{ }^\circ\text{C}$ removes not only the terrestrial contamination but also, as demonstrated by the TGA results, the extra-terrestrial interlayer H_2O . In the $300 \text{ }^\circ\text{C}$ spectra, we therefore only detect the $\sim 2.71 \mu\text{m}$ peak, which comes from the –OH stretching mode and is assigned to the hydroxyl ions structurally bound within the phyllosilicates and Fe-(oxy)hydroxides.

Figure 4 shows the 3- μm regions of the CI and CI-like spectra obtained after heating. Ivuna and Orgueil display the sharp peak at $\sim 2.71 \mu\text{m}$ due to bound –OH ions, whereas it is almost absent from Y-82162 and Y-980115. A noticeable reduction in the intensity of the 3- μm feature is a common characteristic of thermally altered carbonaceous chondrites (Sato et al. 1997; Osawa et al. 2005; Beck et al. 2014a).

Discussion

H_2O abundances in CI chondrites

We estimate the abundance of H_2O in the CI chondrites by assuming that mass loss between 200 and $800 \text{ }^\circ\text{C}$ is entirely due to dehydration and dehydroxylation of phyllosilicates and Fe-(oxy)hydroxides. For Ivuna and Orgueil, this gives H_2O abundances of 18.7 and 18.3 wt.%, respectively. Using a similar approach Garenne et al. (2014) determined a H_2O content for

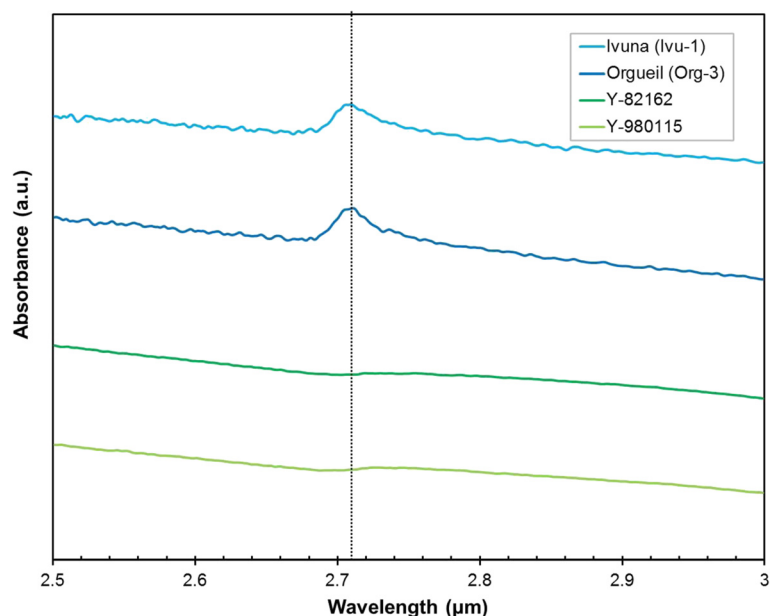


Fig. 4 3- μm region for CI chondrites Ivuna and Orgueil, and CI-like Y-82162 and Y-980115. Ivuna and Orgueil display a sharp peak at $\sim 2.71 \mu\text{m}$ due to bound $-\text{OH}$ ions in the phyllosilicates. This feature is almost absent from the Y-82162 and Y-980115 spectra as the phyllosilicates were dehydrated by a thermal metamorphic event(s)

Orgueil of 17.4 wt.%. Their abundance is slightly lower than ours as they only take into account mass loss from 200 to 770 °C and suggest that everything above this temperature is carbonate decomposition. The average mass loss of our Orgueil samples between 200 and 770 °C is 17.7 wt.% and within error of the Garenne et al. (2014) study. However, based on our phyllosilicate mineral standards (Fig. 1a), we believe that extending the temperature range to 800 °C is necessary, at least for the CI chondrites, as saponite is a significant component of these meteorites that undergoes dehydroxylation at 700–800 °C.

The expected mass loss from H_2O between 200 and 800 °C can be calculated from the bulk modal mineralogy of the CI chondrites. Ivuna and Orgueil contain ~ 80 wt.% serpentine interlayered with saponite in roughly equal proportions and < 5 wt.% ferrihydrite (Bland et al. 2004; King et al. 2015). Stoichiometry and our TGA measurements indicate that from 200 to 800 °C, dehydroxylation causes a mass loss of ~ 12 wt.% for antigorite and ~ 4 wt.% for saponite and ferrihydrite. Serpentine and saponite in CI chondrites are unlikely to be end-member compositions. Nevertheless, the standards indicate that in this temperature region, the combined mass loss due to H_2O released from the phyllosilicates and ferrihydrite should be ~ 6.5 wt.%, which is considerably less than estimated abundances from the TGA measurements.

Garenne et al. (2014) compared TGA-derived H abundances to those measured using mass spectrometry by Alexander et al. (2013). Although they found a correlation

between the datasets (see Fig. 9 in Garenne et al. 2014), the TGA H abundances were generally 10–15 % higher. The discrepancy is the result of assuming that all mass loss from the meteorites between 200 and 800 °C (or 770 °C) is H_2O . Garenne et al. (2014) proposed that additional mass loss in this temperature region could be coming from the release of SO_2 as Fe-sulphides decompose. We argue that this can only partly explain the difference because, whilst pyrrhotite and pentlandite do breakdown between 400 and 600 °C (e.g. Burgess et al. 1991), they occur in relatively low abundances (< 10 wt.%, Bland et al. 2004; King et al. 2015) within CI chondrites. Furthermore, Fe-sulphide decomposition and SO_2 production would require external oxygen, the source of which in the experiment is unclear (Court and Sephton 2014).

Dolomite is the main carbonate in CI chondrites and decomposes at 600–800 °C (Fig. 1c). The dolomite abundance in the Ivuna samples (Ivu-1 and Ivu-2) is ~ 2 wt.% (King et al. 2015). Dolomite occurs in the Orgueil powders (Org-2 and Org-3) at < 1 wt.%, although its abundance could be as high as ~ 5 wt.% (Endress and Bischoff 1996). If we assume an upper limit of 5 wt.% dolomite, its thermal decomposition would cause a mass loss of 1.2 wt.%. Subtracting this from our average mass loss between 200 and 800 °C for Ivuna and Orgueil gives values of 17.5 and 17.1 wt.%, values that still overestimate the H_2O abundance. An additional source of mass loss in this temperature region could be the release of H_2O , CO_2 and SO_2 from the insoluble organic matter (IOM) present at ~ 2 wt.% in CI chondrites (Alexander

et al. 2007). The IOM is refractory but has a complex and heterogeneous composition that probably causes it to decompose over a broad temperature range rather than as a single mass loss event (Court and Sephton 2014).

In a study to estimate the contribution of volatiles to the Earth from micrometeorites, Court and Sephton (2014) used stepped pyrolysis IR spectroscopy to quantify yields of H₂O, CO₂ and SO₂ from Orgueil during heating to 1000 °C. For the temperature range 250–800 °C, they reported yields of 4.1 wt.% CO₂ and 3.8 wt.% SO₂. If we use these CO₂ and SO₂ contributions to correct our measured mass loss between 200 and 800 °C, the estimated H₂O abundance becomes 10.4 wt.% for Orgueil and 10.8 wt.% for Ivuna. Applying the correction therefore leads to H contents ~20 % lower than those of Alexander et al. (2012). We explain this as the Alexander et al. (2012) measurements including H₂O released from saponite and ferrihydrite at low temperatures (<200 °C) and from refractory organics at high temperatures (>800 °C).

Degree of aqueous alteration

There has been a move towards resolving differences in the relative extent of aqueous alteration in carbonaceous chondrites using bulk H contents (Alexander et al. 2013), total phyllosilicate abundances (Howard et al. 2009, 2011, 2015) and IR spectral features (Beck et al. 2010, 2014a; McAdam et al. 2015). In general, good agreement is found between alteration scales determined using these methods. Different approaches have been developed because more traditional classification techniques, such as optical and electron microscopy, are hampered by the fine grain size of highly altered meteorites and can produce conflicting results. Most studies looking at the

composition and textures of phyllosilicates (Tomeoka and Buseck 1988), sulphides (Bullock et al. 2005) and carbonates (Endress and Bischoff 1996) indicate that Orgueil is the most altered member of the CI chondrite group. Differences in hydration between the CI chondrites are likely related to multiple episodes of alteration and/or variations in the local conditions on the parent body (Endress and Bischoff 1996).

Here, we assess the relative degree of hydration for the CI chondrites by combining H₂O and phyllosilicate abundances with mid-IR spectra. In order to semi-quantify the degree of alteration from the IR spectra, we subtract a continuum and then ratio the integrated 3 μm (2.68–2.80 μm, –OH) and 11 μm (10.75–11.75 μm, anhydrous silicate) band intensities. As all data were collected from the same bulk CI and CI-like powders, we minimise potential problems related to sample heterogeneity that may have affected other studies.

Aqueous alteration of CI chondrites transformed anhydrous silicates into phyllosilicates (Tomeoka and Buseck 1988; Zolensky et al. 1993). Assuming a similar starting mineralogy, increased hydration is therefore expected to result in a meteorite containing more H₂O and phyllosilicates and an increased 3 μm/11 μm ratio. Figure 5 shows the 3 μm/11 μm ratio versus the H₂O content determined from TGA in this study, and phyllosilicate abundances of King et al. (2015), for the CI chondrite powders Ivuna (Ivu-1) and Orgueil (Org-3), and the CI-like powders Y-82162 and Y-980115. We remind the reader that H₂O contents from the TGA are higher than those measured by other techniques (see “H₂O abundances in CI chondrites” section); however, as we are looking at relative differences in our data, we can

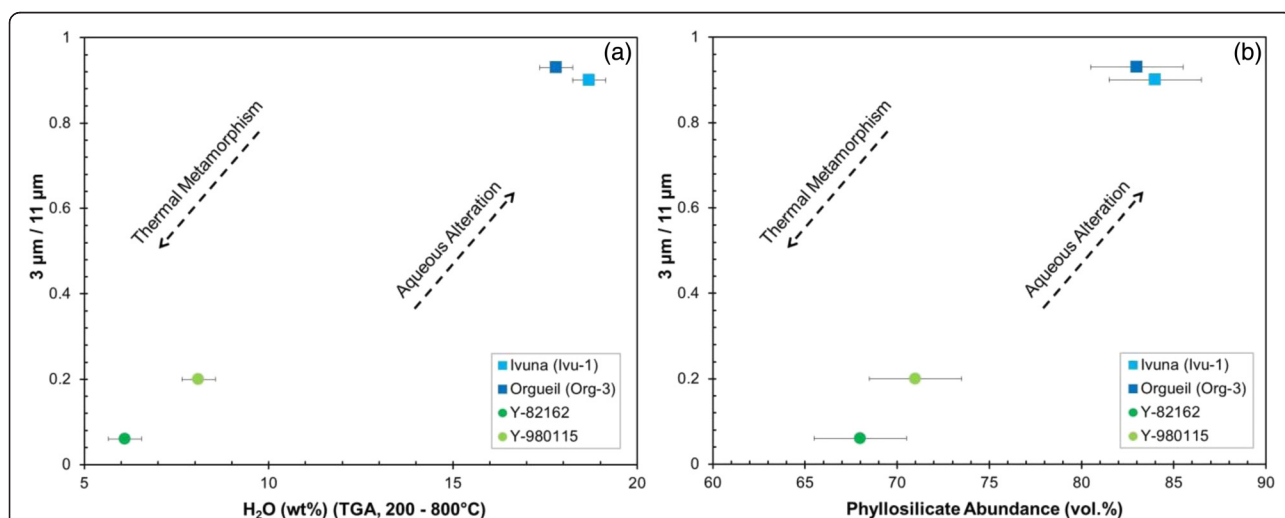


Fig. 5 3 μm/11 μm versus H₂O (wt. %) determined from TGA (a) and phyllosilicate abundances (vol. %) (b) from King et al. (2015). The similarity in H₂O abundance, 3 μm/11 μm ratio and phyllosilicate abundance suggests that Ivuna and Orgueil experienced equal degrees of aqueous alteration. Relative to Y-82162, Y-980115 contains a higher abundance of H₂O and phyllosilicate and has an increased 3 μm/11 μm ratio, suggesting that it experienced less dehydration

use them here to estimate the degree of hydration. The H₂O content and 3 μm/11 μm ratio for Ivuna and Orgueil are the same within the analytical uncertainty indicating that these CI chondrites experienced equal degrees of aqueous alteration. This is consistent with the almost identical total phyllosilicate abundances that we previously determined for these powders (Fig. 5b, King et al. 2015), and also the similar bulk H contents reported by Alexander et al. (2012). The CI chondrite Alais, which was not studied here, contains the same abundance of phyllosilicate as Ivuna and Orgueil, suggesting that it too suffered the same degree of hydration (King et al. 2015).

The genetic relationship between the CI and CI-like chondrites suggests that they probably underwent a similar degree of aqueous alteration. Broad reflections in XRD patterns indicate that the olivine within the CI-like meteorites is fine-grained and poorly crystalline (e.g. King et al. 2015), consistent with it being a secondary phase that recrystallized from the phyllosilicate during thermal metamorphism (Tonui et al. 2003, 2014; Nakamura 2005). This implies that essentially all of the original silicates were hydrated, as is observed in the CI chondrites (e.g. Tomeoka and Buseck 1988; King et al. 2015). Quantifying the degree of hydration in the CI-like chondrites, as we do for the CIs, is difficult because the characteristics of aqueous alteration have been overprinted by the metamorphism. This is apparent in the significantly lower abundances of H₂O and phyllosilicate, and reduced 3 μm/11 μm ratios, in Y-82162 and Y-980115 compared to Ivuna and Orgueil.

Thermal metamorphism of CI-like chondrites

We infer a possible difference in the nature of the thermal metamorphism that affected Y-82162 and Y-980115. Figure 5 shows that Y-980115 contains more H₂O and has an increased 3 μm/11 μm ratio relative to Y-82162. We interpret this as Y-980115 having experienced less dehydration than Y-82162. The modal mineralogy supports this conclusion; Y-980115 contains a higher abundance of partially dehydrated phyllosilicate and less recrystallized olivine (King et al. 2015). We argue that Y-980115 was either heated to a lower metamorphic temperature than Y-82162, and/or the duration of thermal metamorphism was shorter. This finding is consistent with the classification, based on the crystallinity of secondary silicate and sulphide phases, of Y-980115 as a stage II meteorite heated to 250–500 °C (Nakamura et al. 2015) and Y-82162 as a stage II/III meteorite heated to ~500 °C (Nakamura 2005). However, from the similarity of their XRD patterns, we proposed that both Y-980115 and Y-82162 are stage III meteorites heated to 500–750 °C (King et al. 2015).

The DTG curves also offer a possible method for estimating the metamorphic temperatures experienced by the CI-like chondrites. In Fig. 2, we observe almost continuous mass loss up to 800 °C for Ivuna and Orgueil. The CI-like chondrites Y-82162 and Y-980115 on the other hand show no major mass loss events (except a small peak at ~400 °C) until ~700 °C, suggesting that the phyllosilicates had already been dehydrated to this temperature prior to analysis. The CI-like meteorites then suffer a mass loss event at just above 700 °C, which is larger for Y-980115, but still significantly lower than that seen at the same temperature in Ivuna and Orgueil. From 750–800 °C, Y-82162 and Y-980115 display a very similar mass loss that is also consistent with the CI chondrites. The DTG curves therefore suggest that the metamorphic temperatures for Y-82162 and Y-980115 were on the order of 700–800 °C, with heating of Y-980115 perhaps towards the lower end of that range.

We are confident in stating that Y-82162 and Y-980115 were heated to >500 °C, in agreement with the temperatures required to transform serpentine back into olivine (e.g. Brindley and Hayami 1963). Comparison of the CI-like chondrites with mineral textures in artificially heated Murchison CM chondrite suggests that the metamorphism of Y-82162 and Y-980115 occurred over hours to several years (Nakato et al. 2008). Short-lived metamorphism is further supported by the response of organics in naturally heated carbonaceous chondrites (Yabuta et al. 2010; Orthous-Daunay et al. 2013). The decay of ²⁶Al in the early solar system could have generated temperatures >500 °C in a large water-rich body but only on a timescale of >10⁶ years (Miyamoto 1991). A more likely source of metamorphism is shock heating from impacts (e.g. Nakato et al. 2008). The exact duration of impact heating depends on variables such as the size, composition and velocity of the both the impactor and target material, although for meteorites the timescale is predicted to be short (Beck et al. 2005). We would expect impact heating to create regions on a parent body with very different thermal histories, which may explain the variations in metamorphic temperature we find for Y-82162 and Y-980115. Evidence for heterogeneous heating is also observed in the Sutter's Mill CM chondrite (e.g. Beck et al. 2014b) but is otherwise scarce in thermally altered carbonaceous meteorites. From our data alone, we cannot exclude solar radiation as the cause of the metamorphism, with Chaumard et al. (2012) demonstrating that small bodies passing within <0.1 A.U. of the Sun are heated to >500 °C in days to years.

Links to Ryugu, Bennu and C-type asteroids

The surface mineralogy of asteroids is generally inferred from visible and near-IR (VNIR, 0.5–2.5 μm) reflectance

spectra. Observations in this spectral region of the Hayabusa-2 target Ryugu identify it as a C-type asteroid (Vilas 2008; Lazzaro et al. 2013; Pinilla-Alonso et al. 2013). The identification of a $\sim 0.7\text{-}\mu\text{m}$ band suggests that phyllosilicates are present, although this feature is not seen in all spectra, possibly because the surface is heterogeneous and/or dehydrated (Vilas 2008; Lazzaro et al. 2013; Pinilla-Alonso et al. 2013). Bennu, which will be visited by the OSIRIS-REx spacecraft, is classified as a B-type asteroid (Clark et al. 2011). It is almost featureless in the VNIR spectral region; however, existing spectra have slopes closely matching a Mighei (CM) matrix fraction and Ivuna artificially heated to $>700\text{ }^{\circ}\text{C}$ (Clark et al. 2011).

In this work, we present transmission mid-IR spectra of CI and CI-like chondrites. In recent years, thermal emission mid-IR spectra have been obtained for a number of low-albedo asteroids (Lim et al. 2005; Emery et al. 2006; Licandro et al. 2012), including Ryugu (Hasegawa et al. 2008; Campins et al. 2009) and Bennu (Emery et al. 2014). A direct comparison of our data and asteroids is not straightforward, in part because scattering of light can change the shape and position of absorption features between transmission and reflectance spectra (Takir et al. 2013). Mid-IR spectra of Ryugu have been interpreted as having a weak feature in the $11.4\text{--}12.5\text{-}\mu\text{m}$ region (McAdam et al. 2015). The low resolution of the asteroid spectra hampers any detailed mineralogical interpretation, but the position is comparable to the absorption bands seen from olivine, and possibly phyllosilicates, in the CI and CI-like chondrites (Fig. 3).

The situation is similar for Bennu, with Emery et al. (2014) unable to resolve any identifying features within the noise of the thermal emission mid-IR spectra. Features have been observed in this region for other low-albedo asteroids including 24 Themis, a B-type asteroid believed to have water ice on its surface (Campins et al. 2010; Rivkin and Emery 2010) and tentatively linked to CM/CI chondrites (Clark et al. 2011). It has a single feature at $\sim 12\text{ }\mu\text{m}$ that McAdam et al. (2015) proposed is consistent with reflectance spectra of the least altered CM chondrites. As Hayabusa-2 and OSIRIS-REx near Ryugu and Bennu, we anticipate that higher resolution spectra will enable improved comparisons with meteorite analogues in both the VNIR and mid-IR. Importantly, we show that hydrated and dehydrated regions on the surface of Ryugu and Bennu will be resolvable using characteristic features in the mid-IR (e.g. Fig. 3), enabling selection of the most suitable sites for sampling.

Low-albedo asteroids can also be observed in the $3\text{-}\mu\text{m}$ region, with features arising from -OH and H_2O in phyllosilicates and ices. At this wavelength, ground-based studies, and similarly laboratory measurements

of meteorites, are strongly affected by H_2O in the terrestrial atmosphere and we make no attempt to compare our CI and CI-like chondrite spectra to asteroids. However, a correlation has previously been found between the integrated intensity of the $3\text{-}\mu\text{m}$ band and H/Si ratios in carbonaceous chondrites (Miyamoto and Zolensky 1994; Sato et al. 1997). Using this relationship Rivkin et al. (2003) calculated the surface H_2O abundance for C-type asteroids from their $\sim 3\text{-}\mu\text{m}$ features. Note that the effects of observation geometry on the $3\text{-}\mu\text{m}$ band depth were not taken into account in the Rivkin et al. (2003) study. Nevertheless, out of 16 asteroids observed, 13 were reported to contain $<10\text{ wt.}\%$ H_2O , assuming a CM-like Si abundance. Low H_2O abundances are in good agreement with those in Y-82162 (6.1 wt.%) and Y-980115 (8.1 wt.%), and other thermally altered carbonaceous chondrites (Nakamura 2005), suggesting that many C-type asteroids could have dehydrated phyllosilicates at the surface.

The remaining three asteroids observed by Rivkin et al. (2003) contain $>10\text{ wt.}\%$ H_2O , with the highest abundance being $\sim 14\text{ wt.}\%$ for 106 Dione. From the TGA data, we determine that Ivuna and Orgueil contain $>18\text{ wt.}\%$ H_2O . However, as discussed above, our method likely provides an overestimate and the abundance of H_2O is much lower. Some of that H_2O also comes from ferrihydrite, which could be a product of terrestrial alteration (e.g. Zolensky et al. 1993). We suggest therefore that H_2O abundances in the CI chondrites are consistent with the most water-rich C-type asteroids reported in Rivkin et al. (2003). For these asteroids to have such high present day H_2O abundances, their surfaces must have either escaped significant thermal metamorphism or perhaps originally contained even more H_2O but are now a mixture of hydrated and dehydrated materials.

Conclusions

We have used TGA and IR spectroscopy to characterise bulk samples of CI and CI-like chondrites for which modal mineralogy was previously determined by King et al. (2015). TGA and IR spectroscopy are useful tools for quantifying hydrous and anhydrous species in these meteorites, providing new insights into the nature and extent of aqueous and thermal alteration. In summary we find the following:

- (1) The CI chondrites Ivuna and Orgueil contain the same abundance of H_2O , whilst the intensity of their 3- and $11\text{-}\mu\text{m}$ features—attributed to bound -OH in phyllosilicates and anhydrous silicates, respectively—is very similar. This is consistent with almost identical total phyllosilicate abundances and suggests that at the bulk scale, the CI chondrites experienced equal degrees of aqueous alteration.

- (2) The CI-like chondrites Y-82162 and Y-980115 contain >50 % less H₂O than the CI chondrites. The 3- μ m feature is almost absent from these meteorites, but the 11- μ m feature is intense. This is consistent with thermal metamorphism of the CI-like chondrites that caused dehydration and dehydroxylation of the phyllosilicates and subsequent recrystallization back into olivine.
- (3) Peak metamorphic temperatures experienced by the CI-like chondrites exceeded 500 °C and were possibly as high as 700–800 °C. Y-980115 contains more H₂O and has an increased 3 μ m/11 μ m ratio relative to Y-82162. It was either heated to a lower metamorphic temperature than Y-82162, or the duration of heating was shorter. The cause of the thermal metamorphism was probably impacts and/or solar radiation.
- (4) The H₂O abundances of CI chondrites are in reasonable agreement with those estimated for the surfaces of the most water-rich C-type asteroids. However, many C-type asteroids appear to contain significantly less H₂O and are more consistent with the CI-like chondrites. Thermally altered carbonaceous chondrites are likely good analogues for samples that will be returned from surfaces of C-type asteroids by the Hayabusa-2 and OSIRIS-REx missions.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

AK designed the experiments, prepared samples, collected and analysed the data and wrote the manuscript. JS collected and analysed the TGA data. PS designed the experiments, prepared samples and collected and analysed the data. SR helped discuss and interpret the data. All authors discussed the results and read and approved the final manuscript.

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