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Modal mineralogy of CI and CI-like chondrites by X-ray diffraction

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Abstract

The CI chondrites are some of the most hydrated meteorites available to study, making them ideal samples with which to investigate aqueous processes in the early Solar System. Here, we have used position-sensitive-detector X-ray diffraction (PSD-XRD) to quantify the abundance of minerals in bulk samples of the CI chondrite falls Alais, Orgueil and Ivuna, and the Antarctic CI-like chondrites Y-82162 and Y-980115. We find that Alais, Orgueil and Ivuna are dominated by a mixed serpentine/saponite phyllosilicate (81–84 vol%), plus minor magnetite (6–10%), sulphides (4–7%) and carbonates (<3%). This reflects an extended period of aqueous alteration and the near-complete transformation of anhydrous phases into a secondary mineral assemblage. The similarity in total abundance of phyllosilicate suggests that the CI chondrites all experienced the same degree of aqueous alteration on the parent body.

In contrast, Y-82162 contains a highly disordered serpentine/saponite phyllosilicate (68 vol%), sulphide (19%), olivine (11%) and magnetite (2%). This mineralogy is distinct from that of the CI chondrites, attesting to both a different starting mineralogy and alteration history. The structure and relatively low abundance of the phyllosilicate, and the high abundance of olivine, are consistent with previous observations that Y-82162 represents CI-like material that following aqueous alteration suffered thermal metamorphism at temperatures >500 °C. Similarly, Y-980115 contains disordered serpentine/saponite (71 vol%), sulphide (19%), olivine (8%) and magnetite (2%), confirming that it too is a thermally metamorphosed CI-like chondrite. We suggest that the CI-like chondrites are derived from a different parent body than the CI chondrites, which underwent short-lived thermal metamorphism due to impacts and/or solar radiation.

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1. INTRODUCTION

The CI chondrites have bulk elemental compositions nearly identical to the solar photosphere, and as such are considered the most chemically primitive samples in the meteorite collection (Anders and Grevesse, 1989; Lodders, 2003; Barrat et al., 2012). However, they are

phyllosilicate-rich, contain very few anhydrous clasts, chondrules or calcium-aluminium-rich inclusions (CAIs), and are some of the most hydrated meteorites we have available to study (e.g. Brearley, 2006). In addition, the CI chondrites have also been interpreted as regolith breccias (Endress and Bischoff, 1996; Bischoff et al., 2006). As a potential source of Earth's volatiles (Alexander et al., 2012), understanding the effects of secondary processing on the mineralogy of the CI chondrites has significant implications for constraining the nature and transport of water in the early Solar System.

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There are five recognised CI chondrites, Alais (total mass ~6 kg), Orgueil (~14 kg), Tonk (7.7 g), Ivuna (~0.7 kg) and Revelstoke (1 g). They were all recovered shortly after being seen to fall to Earth within the last ~200 years but only three of them, Alais, Orgueil and Ivuna, are sufficiently large enough for rigorous study. The mineralogy of the CI chondrites is consistent with an extended period(s) of aqueous alteration that resulted in the near-complete transformation of anhydrous precursor silicates to a secondary mineral assemblage (DuFresne and Anders, 1962; Tomeoka and Buseck, 1988; Zolensky et al., 1993; Endress and Bischoff, 1996). The mineralogical and geochemical characteristics of the CI chondrites have been used to infer that aqueous alteration took place on a parent body with high water/rock ratios at temperatures of ~150 °C (Zolensky et al., 1989; Clayton and Mayeda, 1999) and potentially lasted for up to ~15 million years (Endress et al., 1996; Hoppe et al., 2007; Fujiya et al., 2013).

Over the last ~30 years a further five meteorites with CI characteristics, Y-82162 (41.7 g), Y-86029 (11.8 g), Y-86737 (2.8 g), Y-980115 (772 g) and Y-980134 (12.2 g), have been found in the Yamoto mountains of Antarctica. Descriptions of these samples remain limited in the literature, and only Y-82162 and Y-86029 have been the subject of any detailed investigations (Tomeoka et al., 1989; Akai, 1990; Yamamoto and Nakamura, 1990; Bischoff and Metzler, 1991; Ikeda, 1991, 1992; Scorzelli et al., 1994; Tonui et al., 2003, 2014). Although they share many of the same properties as the CI chondrites, Y-82162 and Y-86029 contain less H₂O and have bulk O isotopic compositions shifted to higher values ($\delta^{17}\text{O} \sim 12$, $\delta^{18}\text{O} \sim 22$). These features have been interpreted as a significant loss of water from the phyllosilicates driven by thermal metamorphism (Mayeda et al., 1987; Tomeoka et al., 1989; Ikeda, 1992; Tonui et al., 2003, 2014). Subsequently, Y-82162 and Y-86029 have been classified as CI-like chondrites that experienced both extensive aqueous alteration and at least one post-hydration heating event (Ikeda, 1992; Tonui et al., 2003, 2014; Nakamura, 2005).

Unravelling the complex alteration history of the CI and CI-like chondrites through detailed mineralogical studies is extremely challenging because of their sub-micron grain sizes and heterogeneous textures. Many phases have been identified using optical and electron microscopy (e.g. Tomeoka and Buseck, 1988; Zolensky et al., 1993), however the limitations in spatial resolution and volumes sampled by these techniques means that the bulk mineralogy of the CI and CI-like chondrites remains poorly known. Modal mineralogy is a fundamental property of a rock that can be used to accurately derive its provenance, constrain the effects of secondary processing and interpret isotopic data (e.g. Howard et al., 2009, 2010, 2011, 2015; Alexander et al., 2012, 2013). Determining the bulk modal mineralogy of the CI and CI-like chondrites is therefore an important step towards establishing the composition of the initial starting materials, the nature and extent of the subsequent aqueous and thermal alteration, and the evolution of the interacting fluids on the parent bodies.

The modal mineralogy of the Orgueil meteorite was first determined with position-sensitive-detector X-ray

diffraction (PSD-XRD) by Bland et al. (2004). PSD-XRD can directly detect all crystalline phases and additionally observe the presence of non-crystalline phases, in heterogeneous samples. As such it has also previously been used to obtain modal data for CM (Howard et al., 2009, 2011), CV (Howard et al., 2010) and CR chondrites (Howard et al., 2015). In this study we have used PSD-XRD to quantify the abundances of minerals in bulk samples of the CI chondrites Alais, Orgueil and Ivuna, and the CI-like chondrites Y-82162 and Y-980115. Our aim was to use modal mineralogy to determine the extent of aqueous and thermal alteration experienced by CI and CI-like chondrites, and assess the relationship between these groups of meteorites.

2. SAMPLE DESCRIPTION

2.1. CI chondrites

We have studied fusion crust free, interior chips of the CI chondrites Alais, Orgueil and Ivuna. For Alais a single ~200 mg chip was analysed; for Orgueil a ~200 mg chip (Org-1), plus two additional ~50 mg chips (Org-2 and Org-3) were analysed, and for Ivuna two separate ~50 mg chips (Ivu-1 and Ivu-2).

The main component of CI chondrites is a dark, fine grained (<<1 μm) matrix comprised mostly of serpentine interlayered with saponite (Tomeoka and Buseck, 1988; Tomeoka, 1990; Brearley, 1992; Zolensky et al., 1993). Framboidal magnetite occurs within the matrix and may have formed through precipitation from a gel-like phase (e.g. Kerridge et al., 1979a). Other phases present include carbonates (e.g. dolomite, calcite and breunnerite) (Fredriksson and Kerridge, 1988; Johnson and Prinz, 1993; Endress and Bischoff, 1996), sulphides (e.g. pyrrhotite, pentlandite and cubanite) (Kerridge et al., 1979b; Bullock et al., 2005), and terrestrially formed sulphates (e.g. gypsum) (Gounelle and Zolensky, 2001).

There is evidence that the CI chondrites experienced subtle differences in their alteration history. Any diversity may be related to the initial accreted abundances of matrix, chondrules, CAIs, metal and ice, or the local water/rock ratios and geochemical conditions. Phyllosilicate compositions in Alais, Orgueil and Ivuna are similar and fall between the serpentine and smectite (saponite) end members (Tomeoka and Buseck, 1988; Tomeoka, 1990; Brearley, 1992; Zolensky et al., 1993). However, there are variations in the size and texture of the phyllosilicates. While most phyllosilicates in the CI chondrites are fine grained and poorly crystalline, in Alais and Ivuna well crystallised phyllosilicates often occur as coarse (10s μm in size) fragments and clusters that are not commonly found in Orgueil (Tomeoka and Buseck, 1988; Tomeoka, 1990; Brearley, 1992). It has been proposed that the fine phyllosilicates were produced through increased alteration of the coarser phyllosilicate materials, implying that Orgueil is the most aqueously altered CI chondrite (Tomeoka and Buseck, 1988).

In Alais and Orgueil ferrihydrite is observed intergrown with serpentine and saponite suggesting that it formed from increasing alteration of the phyllosilicates (Tomeoka and

Buseck, 1988; Tomeoka, 1990; Brearley, 1992; Zolensky et al., 1993). Ferrihydrite is absent from Ivuna indicating that it may have avoided this alteration event, with the caveat that to date no studies have proved the extra-terrestrial origin of ferrihydrite in the CI chondrites. On the other hand, Bullock et al. (2005) argued that smaller and more “corroded” pyrrhotite grains, plus the scarcity of pentlandite in Orgueil and Ivuna, was the result of them undergoing more alteration than Alais. A similar conclusion was reached by both Hyman and Rowe (1983) and Endress and Bischoff (1996), who reported higher abundances of magnetite and carbonate in Orgueil and Ivuna relative to Alais, respectively.

2.2. CI-like chondrites

We analysed single, interior, ~50 mg chips of Y-82162 and Y-980115. The CI-like chondrites are dominated by a mixture of serpentine and saponite with a similar chemical composition to that found in the CI chondrites (Tomeoka et al., 1989; Ikeda, 1992; Zolensky et al., 1993; Tonui et al., 2003). Other phases identified in the CI-like chondrites include magnetite, sulphides and carbonates. Fine grained olivine is abundant in the matrix of Y-82162, and textural and structural data indicates that it was produced through partial dehydration and dehydroxylation of the phyllosilicates (Tomeoka et al., 1989; Akai, 1990; Bischoff and Metzler, 1991; Ikeda, 1991, 1992; Tonui et al., 2003, 2014). However, the conditions, timing and duration of the metamorphism remain poorly constrained, as does the extent of the preceding aqueous alteration.

Recent studies have suggested that Y-980115 is also a thermally metamorphosed CI-like chondrite. Fujiya et al. (2013) mention that Y-980115 is paired with Y-82162 but this link is not confirmed elsewhere in the literature. Islam et al. (2012) reported that H is depleted in Y-980115 relative to the CI chondrites, and Harries and Langenhorst (2011) suggested that in Y-980115 a 4C-pyrrhotite precursor phase was probably converted to troilite (plus pentlandite) by thermal metamorphism. The hypothesis that Y-980115 is a thermally metamorphosed CI-like chondrite is further supported by the study of Burton et al. (2014), who found that Y-980115 is depleted in amino acids relative to Orgueil and Ivuna.

3. EXPERIMENTAL

3.1. PSD-XRD

Each meteorite sample was powdered using an agate mortar and pestle to a grain size of <35 μm to avoid potential grain size artefacts during the analyses (Cressey and Batchelder, 1998; Batchelder and Cressey, 1998; Bland et al., 2004). The powders were then immediately packed into aluminium sample wells using the sharp edge of a spatula to create a high degree of randomness in grain orientation, minimising the effect of preferred crystal-alignments (Batchelder and Cressey, 1998). XRD patterns were obtained using an INEL X-ray diffractometer with a curved 120° PSD in a static geometry relative to the X-ray beam

and sample (Cressey and Schofield, 1996). A Ge 111 crystal monochromator was used to select Cu $K\alpha_1$ radiation. The beam was at an incident angle of 4.2° to the flat top of the sample, and the sample was rotated throughout the analyses. The size of the beam was restricted using post monochromator slits to 0.24 \times 2.00 mm for the smaller (~50 mg) samples and 0.24 \times 5.00 mm for the larger (~200 mg) ones.

The powdered meteorites were analysed for 16 h (except for Alais which was analysed for 6 h) in order to achieve good signal-to-noise ratios. After identifying the peaks in the meteorite diffraction patterns, we then analysed pure standards of each mineral present. As the geometry of the diffractometer is fixed and all angles (0–120°, 2θ) are measured simultaneously, the analytical conditions remained identical between measurements of the meteorites and mineral standards. The standards were packed into the aluminium wells using the same procedure as for the meteorites and then analysed for 30 min. Differences in the incident beam flux throughout an experimental run were monitored by analysing a non-crystalline Fe-(oxy)hydroxide standard and a polished Fe-metal block at the start of each day. The diffractometer is very stable over periods of months to years (e.g. Schofield et al., 2002), and variations in the beam flux were <1% during this study.

Phase quantification was achieved using a profile-stripping method developed in our laboratory and fully described by Cressey and Schofield (1996), Batchelder and Cressey (1998), Cressey and Batchelder (1998) and Schofield et al. (2002). The veracity of this method was demonstrated in a blind test phase quantification round robin of crystalline mixtures organised by the International Union of Crystallography (Madsen, 1999; Madsen et al., 2001). Furthermore, results from this technique have been shown to be in excellent agreement with those from Rietveld methods (Schofield et al., 2002). The diffracted intensity from a specific phase will be reduced in direct proportion to the volume fraction of that phase within a mixture. This is true for all features across the diffraction pattern, including both diffuse features derived from poorly crystalline phases and disordered materials, and sharp scattering features from well crystalline components. Consequently, this method is not restricted to the quantitative assessment of mixtures of well crystalline phases, but is equally applicable to samples containing poorly or non-crystalline components. As such, this technique has been successfully used to study a range of complex terrestrial (Batchelder and Cressey, 1998; Rodgers and Cressey, 2001; Schofield et al., 2002) and extra-terrestrial (Bland et al., 2004; Menzies et al., 2005; Howard et al., 2009, 2010, 2011, 2015; Dunn et al., 2010) rocks containing mixtures of crystalline and poorly crystalline phases.

A detailed description of the profile-stripping process is provided elsewhere (Cressey and Schofield, 1996; Schofield et al., 2002; Howard et al., 2009), so the method will only be briefly outlined here. The diffraction pattern of a mineral standard was initially scaled to the same measurement time as the meteorite sample (e.g. $\times 32$ for a 16 h measurement). Next the standard pattern was reduced in intensity by a factor until it matched its intensity in the diffraction pattern of

the sample, at which point it was subtracted to leave a residual meteorite pattern. The process was repeated for each mineral standard until there were zero counts in the residual pattern and the sum of the fit factors was one. This indicated that all the major and minor phases present within the meteorite were accounted for. The fit factors for the mineral standards were then corrected for relative differences in X-ray absorption to give their final volume fractions in the meteorite (e.g. see Howard et al., 2009).

Modal abundances were determined for each phase present in the CI chondrites at ~ 1 vol% and above. Trace phases, crystalline or otherwise, with proportions $< \sim 1$ vol% were not observed in this study. Uncertainties in the modal abundances were estimated by varying the value of a mineral standard factor until the fit “by-eye” was obviously much poorer. The uncertainty of the fit, expressed as a percentage of the mineral standard factor, was then used to calculate the uncertainty in modal abundance. This resulted in uncertainties of 2–4% for crystalline anhydrous phases and 3–5% for fine grained, poorly crystalline phyllosilicates. These uncertainties are similar to those reported in other studies of carbonaceous chondrites using PSD-XRD (Howard et al., 2009, 2011). As an additional check we also used a linear least-squares routine to fit the standard patterns to the meteorite patterns (Schofield et al., 2002). The process confirmed our mineral standard factors, and the uncertainty of the fits by this method yielded typical absolute uncertainties in the modal abundances of $< 1.2\%$. However, considering potential uncertainties across the whole experiment, rather than the fitting procedure alone, we prefer to remain conservative in our estimate of the uncertainties.

4. RESULTS

4.1. PSD-XRD patterns

Fig. 1 shows XRD patterns for the CI chondrites Alais, Orgueil and Ivuna. The crystalline phases identified are

magnetite, dolomite, sulphides (mainly pyrrhotite) and olivine. Relatively broad diffraction peaks at $\sim 19^\circ$, $\sim 34^\circ$ and $\sim 60^\circ$ (2θ Cu $K\alpha_1$) are attributed to fine grained, poorly crystalline phyllosilicates, which in CI chondrites largely consist of intimately mixed saponite and Fe-bearing, Mg-rich serpentine (Tomeoka and Buseck, 1988; Zolensky et al., 1993). Due to the intergrown nature of the serpentine and saponite we do not attempt to deconvolute the two phases and instead report only the total phyllosilicate abundance. To remove this “phase” during the profile-stripping routine we used a poorly crystalline, mixed serpentine/saponite standard from our laboratory, whose diffraction pattern shows a high degree of affinity with the phyllosilicate in the CI chondrites. The mass absorption coefficient of this standard was determined using the CI chondrite phyllosilicate composition reported by Tomeoka and Buseck (1988).

Fig. 2 confirms the good match between our mineral standards and phases in the CI chondrites. It demonstrates how mineral standard patterns can be summed in their relative proportions as identified during profile-stripping, and used to construct a model pattern that is in excellent agreement with the sample pattern. After subtracting the phyllosilicate and crystalline phases, the residual patterns for Alais and Orgueil did not reduce to zero indicating the presence of a non-crystalline material. Although we cannot rule out amorphous silicate-related phases, we found that the shape and remaining counts of the residual pattern was an excellent match with the diffraction pattern of a synthetic ferrihydrite standard. This phase has previously been observed in both Alais and Orgueil (Tomeoka and Buseck, 1988; Zolensky et al., 1993). In contrast, for Ivuna subtraction of the crystalline phases and phyllosilicate reduced the residual to zero indicating that within the detection limits of this study (~ 1 vol%) there was no ferrihydrite.

Fig. 3 shows XRD patterns for the CI-like chondrites Y-82162 and Y-980115. The main diffraction peaks are attributed to olivine (Fe_{80}), sulphide (troilite) and

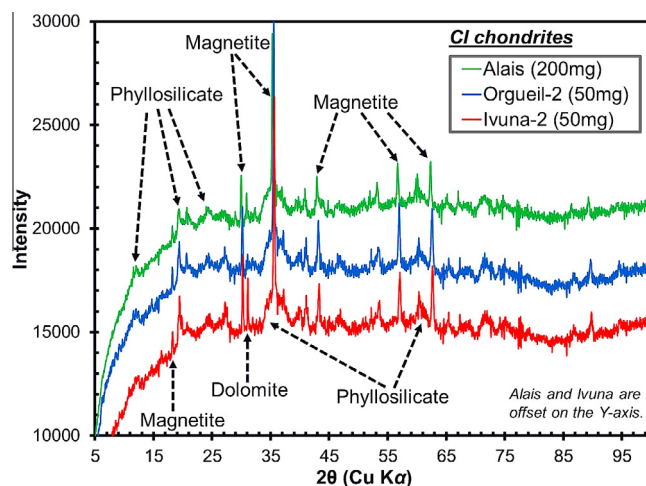


Fig. 1. PSD-XRD patterns for the CI chondrites Alais (green), Orgueil (blue) and Ivuna (red), showing the main identified phases. Alais and Ivuna are offset on the Y-axis for clarity.

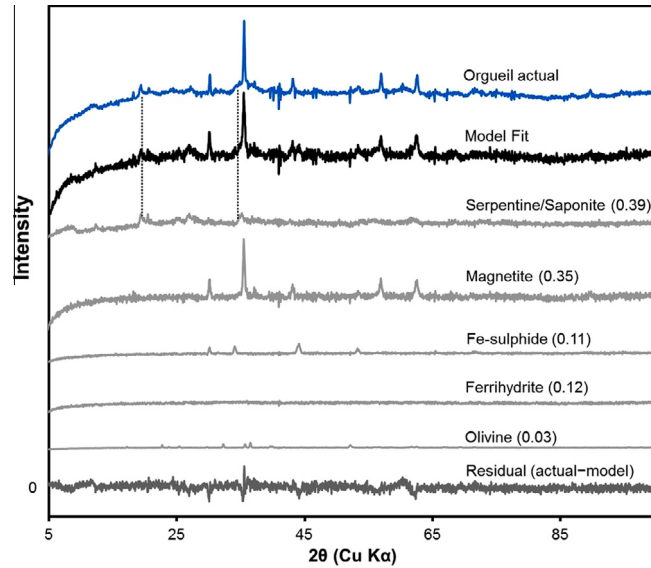


Fig. 2. PSD-XRD pattern for Orgueil shown alongside a model pattern. The model pattern is constructed by summing the mineral standard patterns (i.e. serpentine/saponite, magnetite, Fe-sulphide, ferrihydrite and olivine) in their relative proportions (value in brackets) as determined during the profile-stripping procedure. Subtracting the model pattern from the actual pattern reduces the residual to zero, confirming that all major and minor phases are accounted for, and that there is good agreement between the composition and structure of our standards and the minerals in the meteorite. The dashed vertical lines indicate the broad phyllosilicate reflections used in the profile-stripping.

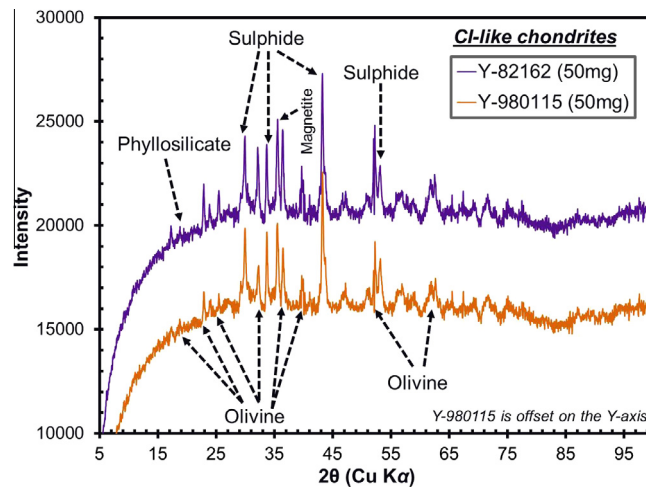


Fig. 3. PSD-XRD patterns for the CI-like chondrites Y-82162 (purple) and Y-980115 (orange), showing the main identified phases. Y-980115 is offset on the Y-axis for clarity.

magnetite. The broad peaks (at $\sim 19^\circ$, $\sim 34^\circ$ and $\sim 60^\circ$) associated with phyllosilicates in Alais, Orgueil and Ivuna are not observed in the two CI-like chondrites. Subtraction of the crystalline phases left a residual pattern, the shape of which was an excellent match to the diffuse features of the diffraction pattern of our serpentine/saponite standard (Fig. 4). Serpentine and saponite have previously been reported in Y-82162 (Tomeoka et al., 1989; Akai, 1990; Ikeda, 1991), so the lack of sharp, intense diffraction peaks from these phases in the patterns indicates that the minerals are either highly disordered, extremely fine grained, or both.

4.2. Modal mineralogy

The modal mineralogy of the Alais, Orgueil, Ivuna, Y-82162 and Y-980115 samples are provided in Table 1. The whole profile fitting statistics (as defined by Young, 1993) for the quantitative phase analysis were $R_p = 2.2\text{--}3.9\%$ for the CI chondrites and 4.4% for the CI-like chondrites, and $R_{wp} = 2.9\text{--}4.4\%$ for Orgueil and Ivuna, 10.2% for Alais (reflecting the reduced data collection time) and 5.2% for the CI-like chondrites. These values are within those generally considered to represent a good fit (e.g. Young, 1993; Izawa et al., 2010).

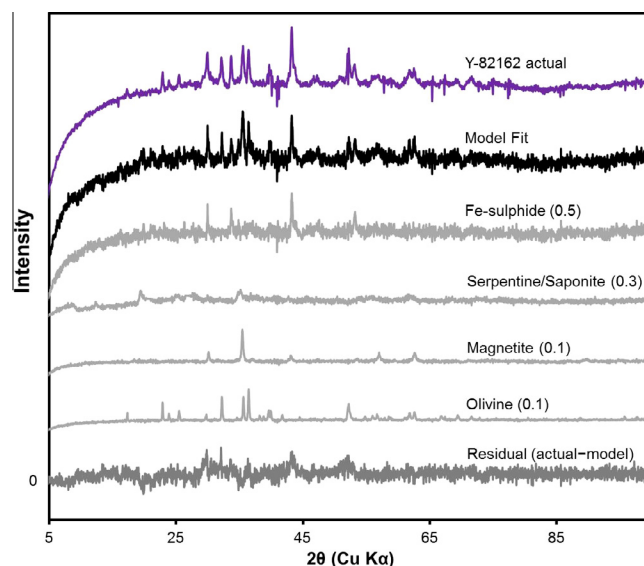


Fig. 4. PSD-XRD pattern for Y-82162 shown alongside a model pattern and the standards in their relative proportions. Unlike in the CI chondrites, we do not observe broad reflections from the phyllosilicates. Instead, after subtracting all the crystalline phases, we use the diffuse features of the serpentine/saponite in the profile-stripping.

Each of the CI chondrites contains high abundances of serpentine/saponite (81–84 vol%), plus minor magnetite (6–10%) and sulphide (4–7%). Ferrihydrate abundances in Alais and Orgueil are 2–4 vol%. Dolomite is only observed in Alais and Ivuna (2–3%), and a small amount (3%) of olivine (Fo_{80}) was detected in the Org-2 sample. From the modal mineralogy we estimate a bulk Fe content of 20.7 wt% for Alais and 22.7–23.7 wt% (average = 23.1 wt%) for Orgueil, in good agreement with the values of 22–24 wt% reported by Zolensky et al. (1993). For Ivuna, our bulk Fe content of 21.8–24.7 wt% (average = 23.3 wt%) is slightly higher than the previously reported value of 20.1 wt% (Zolensky et al., 1993).

The CI-like chondrites Y-82162 and Y-980115 contain serpentine/saponite (68–71 vol%), sulphide (19%), olivine (8–11%) and magnetite (2%). For Y-82162 this gives a bulk Fe content of 27.3 wt%, higher than the 24.3 wt% estimated by Zolensky et al. (1993). We obtain a similar value of 26.9 wt% Fe for Y-980115, which as far as we are aware is the first time this has been reported for this meteorite.

5. DISCUSSION

5.1. Heterogeneity

The CI chondrites are complex rocks altered by extreme hydration and possible impact brecciation. They consist of distinct lithological units and are mineralogically and chemically heterogeneous on a fine scale (Tomeoka and Buseck, 1988; Endress and Bischoff, 1996; Morlock et al., 2006; Barrat et al., 2012). Bland et al. (2004) investigated the heterogeneity of CI chondrites by determining the modal mineralogy of a single powdered >200 mg chip and 10 smaller (<1 mg) aliquots of Orgueil. They showed that the proportions of all mineral phases except pyrrhotite varied between 5 and 20 wt% in the samples.

In order to monitor heterogeneity we analysed several different chips of Orgueil (1 × 200 mg, 2 × 50 mg) and Ivuna (2 × 50 mg), which are the most brecciated CI meteorites and could therefore display the greatest variation (Endress and Bischoff, 1996). We found that despite severe aqueous alteration and the possible effects of brecciation there was remarkably little difference in mineral abundances between the separate chips of Orgueil and Ivuna. The mineral abundances typically varied by <4 vol%, which is comparable to the expected uncertainty from the phase quantification. This suggests that our measured sample sizes are representative of the bulk modal mineralogy and perhaps implies that hydration was a relatively uniform process such that the heterogeneity observed at the mm-scale or less greatly exceeds that in the bulk rock (e.g. Morlock et al., 2006; Howard et al., 2011).

Variations in the abundances of some minor phases included the presence of olivine (3 vol%) in Org-2 but not the Org-1 or Org-3 samples. In comparison Bland et al. (2004) reported an olivine abundance of ~6 vol% in their large (>200 mg) sample. Petrographic and O isotope studies indicate that olivine grains in Orgueil are remnant primary materials (Leshin et al., 1997). They likely represent either unaltered chondrule fragments disaggregated on the CI parent body, or result from mixing of chondrule fragments from outside the parent body during brecciation. Our data hints at the first option. Within the analytical uncertainties the Orgueil samples contain the same amount of phyllosilicate; however Org-2 has the lowest abundance (82 vol%), consistent with possible incomplete aqueous alteration of this chip (see Section 5.4).

We also note that dolomite was not observed in any of our Orgueil samples, nor those analysed by Bland et al. (2004). Scanning electron microscope (SEM) analyses indicate that the abundance of dolomite in Orgueil may be as high as ~5 vol%, although there are distinct lithological units with

Table 1

Modal mineralogy of CI and CI-like chondrites determined by PSD-XRD. Where more than one sample of a meteorite was analysed the average mineral abundances are given in italics. For the CI chondrites the mass absorption coefficient for the phyllosilicates was calculated from the composition given by Tomeoka and Buseck (1988), and for the CI-like chondrites the composition given by Zolensky et al. (1993). Alais, Orgueil and Ivuna samples from the Natural History Museum, UK, and Y-82162 and Y-980115 from the National Institute of Polar Research, Japan. Values in brackets are the uncertainties determined using a linear least-squares routine to fit standard mineral patterns to the meteorite patterns. However, to accommodate potential uncertainties across the entire experiment, and in keeping with similar studies (Howard et al., 2009, 2010, 2011), we conservatively estimate the uncertainties as 2–4% for crystalline anhydrous phases and 3–5% for fine grained, poorly crystalline phyllosilicates.

Sample	Collection number	Sub-sample	Size (mg)	Phyllosilicate (vol%)	Sulphide (vol%)	Magnetite (vol%)	Olivine (F ₈₀) (vol%)	Carbonate (vol%)	Ferrihydrite (vol%)	Gypsum (vol%)
Alais			200	83 (0.6)	4 (0.4)	7 (0.2)		3 (0.2)	3 (0.2)	
Orgueil	BM.1985, M146	Org-1	200	84 (1.2)	6 (0.3)	7 (0.2)			2 (0.2)	1 (0.9)
		Org-2	50	82 (0.7)	4 (0.4)	7 (0.1)	3 (0.4)		4 (0.1)	
		Org-3	50	83 (0.4)	7 (0.3)	6 (0.1)			4 (0.2)	
		<i>Average</i>		<i>83.0</i>	<i>5.7</i>	<i>6.7</i>	<i>1.0</i>		<i>3.3</i>	<i>0.3</i>
Ivuna	BM.1991, M5	Ivu-1	50	84 (0.3)	6 (0.3)	8 (0.1)		2 (0.1)		
		Ivu-2	50	81 (0.5)	7 (0.4)	10 (0.4)		2 (0.5)		
		<i>Average</i>		<i>82.5</i>	<i>6.5</i>	<i>9.0</i>		<i>2.0</i>		
Y-82162	Sub. No. 50		200	68 (0.1)	19 (0.5)	2 (0.1)	11 (0.3)			
Y-980115	Sub. No. 93		200	71 (0.2)	19 (0.5)	2 (0.1)	8 (0.6)			

little or no dolomite (Endress and Bischoff, 1996). This is well above the detection limits of our measurements, and dolomite was easily identified in Ivuna and Alais. Orgueil is the most brecciated CI chondrite (Endress and Bischoff, 1996) and it seems that our chips sampled regions of the meteorite containing <1 vol% dolomite.

5.2. Mineralogy of Alais, Orgueil, Ivuna

The modal mineralogy of the CI chondrites Alais, Orgueil and Ivuna is consistent with petrographic observations of these meteorites (Tomeoka and Buseck, 1988; Zolensky et al., 1993; Brearley, 2006). They are also in agreement with the study of Bland et al. (2004), who reported abundances of serpentine/saponite (81.5 vol%), olivine (5.8%), magnetite (5.1%), sulphides (3.9%) and ferrihydrite (3.7%) in Orgueil. The mineral assemblage of the CI chondrites reflects an extended period of aqueous alteration that resulted in near-complete transformation of anhydrous precursor materials to abundant secondary phases (DuFresne and Anders, 1962; Tomeoka and Buseck, 1988; Zolensky et al., 1993; Endress and Bischoff, 1996). The onset of alteration probably began when ices accreted into the parent body melted and initially produced coarse (~10 μm) phyllosilicate clusters. Over a period of ~15 million years further hydration converted the coarse phyllosilicates, magnetite and sulphides into finer grained (<1 μm) phyllosilicates intergrown with ferrihydrite (e.g. Tomeoka and Buseck, 1988).

5.3. Mineralogy of Y-82162 and Y-980115

The modal mineralogy of Y-82162 is in good agreement with previous estimates of mineral abundances using optical point counting (Tomeoka et al., 1989). The isotopic, mineralogical and petrographic characteristics of Y-82162 indicate that it is a CI-like meteorite that experienced aqueous alteration and then thermal metamorphism (Ikeda,

1992; Tonui et al., 2003, 2014; Nakamura, 2005). Dehydration and dehydroxylation of phyllosilicates causes the loss of interlayer H₂O and structural -OH, and the formation of highly disordered phases (Brindley and Hayami, 1963; Brown and Brindley, 1980). At high enough temperatures recrystallization of the phyllosilicate into fine grained anhydrous olivine takes place (Brindley and Hayami, 1963; Brown and Brindley, 1980). The XRD pattern and modal mineralogy of Y-82162 suggests that it has experienced thermal metamorphism. For example, the phyllosilicates show no strong diffraction peaks, suggesting highly disordered structures and very small domain sizes. Furthermore, the abundance of phyllosilicate in Y-82162 is low relative to the CI chondrites, and there are substantial amounts of crystalline olivine and sulphide. Trace element chemistry shows that following aqueous alteration Y-82162 suffered peak metamorphic temperatures of 600–700 °C (Paul and Lipschutz, 1990; Tonui et al., 2003, 2014), consistent with the temperatures required to convert serpentine back into olivine (Brown and Brindley, 1980).

The XRD pattern and modal mineralogy for Y-980115 is very similar to that obtained for Y-82162 in this study, and also the XRD pattern of Y-86029, another CI-like chondrite, reported by Tonui et al. (2014). This supports the hypothesis that Y-980115 belongs to this group of thermally metamorphosed CI-like meteorites. The abundances of phyllosilicate, olivine and sulphide in Y-980115 are similar to those in Y-82162 within the analytical uncertainty. However, we note that Y-980115 consists of slightly more phyllosilicate and less olivine than Y-82162. Assuming that at the start of thermal metamorphism they had the same initial bulk mineralogy, this could be due to Y-980115 either being heated to a lower metamorphic temperature or for a shorter period of time, as has been reported for other thermally altered carbonaceous chondrites (Tonui et al., 2003, 2014; Nakamura, 2005).

We are unable to determine from the XRD patterns and modal mineralogy if Y-82162 and Y-980115 are paired, or

indeed if either meteorite is paired with Y-86029. Nevertheless, we can relate our data with the four heating stages (I–IV) for thermally metamorphosed carbonaceous chondrites devised by Nakamura (2005) from XRD patterns. In their scheme Y-86029 is classified as Stage III, representing heating between 500 and 750 °C that resulted in poorly crystalline phyllosilicates and broad reflections from fine grained, low crystallinity olivine and troilite. Trace element chemistry indicates that the peak metamorphic temperature of Y-86029 was 500–600 °C (Paul and Lipschutz, 1990; Tonui et al., 2003, 2014). In comparison, Y-82162 is classified as Stage II/III, although an XRD pattern was not actually presented in the Nakamura (2005) study. Stage II heating is estimated as 250–500 °C, at which point the phyllosilicates are disordered but yet to recrystallize as olivine.

We observe well-developed olivine peaks in the XRD pattern of Y-82162 (Fig. 3) and the main sulphide peak matches well with our troilite standard. This, plus trace element chemistry (Paul and Lipschutz, 1990; Tonui et al., 2003, 2014) indicating that it was heated to higher temperatures than Y-86029, leads us to re-classify Y-82162 as a Stage III meteorite within the Nakamura (2005) scheme. The olivine and troilite peak widths and intensities in the Y-980115 pattern are very similar to those for Y-82162, demonstrating similar levels of crystallinity in these phases. We therefore classify Y-980115 as a Stage III meteorite that must have been heated to a comparable temperature (i.e. 500–750 °C) as Y-82162.

5.4. Degree of aqueous alteration

In hydrated meteorites phyllosilicates formed through aqueous alteration of precursor anhydrous silicates. For example, in the CM meteorites, chondrules, CAIs and matrix have been altered into Fe-, and Mg-rich phyllosilicates. Howard et al. (2009, 2011) reported that in the least altered CM2 chondrites modal phyllosilicate abundances are ~70 vol%, whereas the more altered CM1 samples contain >85 vol%. They argued that if the initial bulk mineralogy was the same, then the total abundance of phyllosilicate in a hydrated meteorite is an unambiguous indication of its relative degree of alteration. More recently Howard et al. (2015) proposed a new classification scheme based on the phyllosilicate fraction (total phyllosilicate/(total anhydrous silicate + total phyllosilicate)) of all hydrated meteorites. In this scheme only the total phyllosilicate abundance is needed to determine the relative degree of aqueous alteration, making it independent of chemical group, even if the physical and chemical conditions of aqueous alteration changed.

The CI chondrites were processed by multiple episodes of aqueous alteration under varying physical and chemical conditions (Endress and Bischoff, 1996). As a first approach we use the total abundance of phyllosilicate to infer the relative degree of aqueous alteration for the CI chondrites. We find that the CI chondrites contain a limited range of phyllosilicate abundances (81–84 vol%) and very little anhydrous silicate (see Table 1). The average phyllosilicate abundance for the Alais, Orgueil and Ivuna chips is

83 vol%. This indicates that unlike the CM and CR chondrites, which have clearly defined alteration sequence (Howard et al., 2009, 2011, 2015), in terms of bulk phyllosilicate abundance there is no significant difference in the extent of hydration recorded in the CI chondrites. This is consistent with their similar bulk H abundances (Alexander et al., 2012) and perhaps signals the cessation of fluid availability, truncating the process of hydration.

Previous studies relying on SEM and transmission electron microscopy (TEM) have shown that at the micron scale and below the degree and style of alteration differs between the CI samples (Tomeoka and Buseck, 1988; Endress and Bischoff, 1996; Bullock et al., 2005). In the model of Tomeoka and Buseck (1988), intense hydration initially produced relatively coarse grained phyllosilicate clusters, along with magnetite, sulphides and carbonates. Further alteration then reduced the grain size of the phyllosilicates, and caused dissolution of the magnetite and sulphides that enabled formation of ferrihydrite. Orgueil, containing fine grained phyllosilicates and ferrihydrite, plus corroded magnetite and sulphide grains, is often considered the most altered CI chondrite (Tomeoka and Buseck, 1988; Bullock et al., 2005). Meanwhile, a lack of ferrihydrite suggests that Ivuna is the least altered, although the extra-terrestrial origin of ferrihydrite is still debated.

That we do not resolve a difference in alteration from the total phyllosilicate abundance in the CI chondrites reflects the coarseness of the Howard et al. (2015) classification scheme, which defines sub-types on the basis of 5% variations in phyllosilicate abundance. Tomeoka and Buseck (1988) suggested that alteration may have continued after hydration of all anhydrous silicates through late stage re-working of the phyllosilicates. This would present a challenge to applying the Howard et al. (2015) scheme to the CIs, as the end point is reached when all of the anhydrous silicate is consumed, and it is not sensitive to variations in the extent of hydration that did not change the overall abundance of phyllosilicate. However, we note that rare anhydrous silicates are present within CI chondrites (Table 1; Steele, 1990; Leshin et al., 1997; Bland et al., 2004; Frank et al., 2014) suggesting incomplete hydration, and that Howard et al. (2015) reserve type 1.0 for as yet to be found samples in which all silicate is altered.

We do find that ferrihydrite is absent from Ivuna, and that it contains more magnetite and sulphide than Alais and Orgueil, although the absolute abundances vary by less than the experimental uncertainty (<4%). Qualitatively, the modal data support the hypothesis that Ivuna avoided the late stage alteration that converted magnetite and sulphides into ferrihydrite within Alais and Orgueil. However, modal abundances for the minor phases are also likely to be extremely sensitive to the accreted mineralogy. For example, the abundances of magnetite, sulphides and carbonates are probably influenced by the starting amounts of metal, sulphur and quantity of CAIs, respectively. The initial abundances of phases prior to aqueous alteration are poorly constrained, and in seemingly unprocessed (e.g. CV3) meteorites can vary widely (e.g. Howard et al., 2010). As a result, we recommend caution before interpreting the degree of aqueous alteration in the CI chondrites from

the abundances of phases such as magnetite, sulphides, carbonates or ferrihydrite.

Evaluating the degree of aqueous alteration for the CI-like chondrites is difficult because the mineralogical changes associated with the process have been overprinted by the effects of thermal metamorphism. Coarse phyllosilicate clusters are more common within Y-82162 and Y-86029 than Alais, Orgueil or Ivuna, leading some authors to conclude that the CI-like chondrites suffered less extensive aqueous alteration (Tomeoka et al., 1989). Textural evidence indicates that most of the olivine in the CI-like chondrites is secondary, having recrystallized from the phyllosilicates during thermal metamorphism (Tomeoka et al., 1989; Akai, 1990; Bischoff and Metzler, 1991; Ikeda, 1991, 1992; Tonui et al., 2003, 2014). As hydration of accreted primary olivine (i.e. chondrules, CAIs and matrix) would have been the major source of phyllosilicate in Y-82162 and Y-980115, its very low abundance implies that the CI-like chondrites likely experienced near-complete aqueous alteration comparable to that observed in the CI meteorites. If we assume that all the olivine in the CI-like chondrites is a secondary product of thermal metamorphism, we can estimate the amount of phyllosilicate towards the end of aqueous alteration by summing the present day phyllosilicate and olivine abundances. Transformation of phyllosilicate back into olivine causes a decrease in volume of ~50% (Deer et al., 1982), which correcting for gives a value of 79 vol% for Y-82162 and Y-980115. Within the experimental uncertainty these totals are in reasonable agreement with the phyllosilicate abundances of the CI chondrites.

The abundance of sulphide in Y-82162 and Y-980115 is much higher than in the CI chondrites but the amount of magnetite is lower and there is no detectable ferrihydrite. However, again these minor phases may not be reliable indicators of aqueous alteration as their initial proportions are not known, and they were affected by thermal metamorphism. In agreement with previous studies of thermally metamorphosed carbonaceous chondrites, we find that troilite is the main sulphide mineral (Tomeoka et al., 1989; Akai, 1990; Nakamura, 2005; Tonui et al., 2014). In the heated CM meteorites troilite is generally attributed to the decomposition of tochilinite [$\text{Fe}_{5-6}(\text{Mg},\text{Fe})_5\text{S}_6(\text{OH})_{10}$] at temperatures $>250^\circ\text{C}$ (Nakamura, 2005; Tonui et al., 2014) but this phase is largely absent in the CI chondrites. Instead pyrrhotite is common (Bullock et al., 2005; Berger et al., 2011), and its conversion by thermal metamorphism is the most likely source of high troilite abundances in the CI-like meteorites (Harries and Langenhorst, 2011, 2013). Magnetite can form through thermal decomposition of tochilinite and Fe-rich phyllosilicates (Nakamura, 2005) but also starts breaking down at temperatures $>570^\circ\text{C}$ (Harries and Langenhorst, 2011, 2013).

Clearly, interpreting the mineralogy of the CI-like chondrites is challenging and relies on accurately distinguishing between the effects of both aqueous alteration and thermal metamorphism. We suggest that future studies will need to directly compare the mineralogical and chemical properties of the CI-like chondrites with artificially heated CI samples and terrestrial analogue materials.

5.5. Relationship between CI and CI-like chondrites

A genetic relationship between the CI and CI-like chondrites is inferred from their bulk O isotopic compositions. Alais, Orgueil and Ivuna have $\delta^{17}\text{O}$ values of $\sim 9\text{‰}$ and $\delta^{18}\text{O}$ of $\sim 16\text{‰}$, which have been interpreted as interaction between anhydrous silicates and fluids (Clayton and Mayeda, 1999). The O isotopic compositions of Y-82162 and Y-86029 ($\delta^{17}\text{O} \sim 12\text{‰}$, $\delta^{18}\text{O} \sim 22\text{‰}$), and we also predict Y-980115, for which to our knowledge there is no O isotope data, fall above the CI chondrite field and close to the intersection of the terrestrial and CM fractionation lines (Mayeda et al., 1987; Clayton and Mayeda, 1999; Tonui et al., 2003). They are explained as mass-dependent isotope fractionation caused by thermal metamorphism, resulting in preferential loss of isotopically light water and associated heavy isotope enrichment in the solids (e.g. Valley, 1986). The expected fractionation could be as much as 6–8‰ in $\delta^{18}\text{O}$, which if correct implies that prior to heating the O isotopic composition of the CI-like chondrites was close to the CI chondrites (Clayton and Mayeda, 1999).

In terms of mineralogy, the dominant component in both the CI chondrites Alais, Orgueil and Ivuna, and the CI-like chondrites Y-82162, Y-980115 (and Y-86029), is a serpentine/saponite phyllosilicate that formed during a period of severe hydration on their parent body(ies). Phyllosilicate compositions in the CI-like chondrites are comparable with those in the CI chondrites suggesting that the composition of the primary materials and conditions of aqueous alteration were similar for each group (Tomeoka et al., 1989; Ikeda, 1992; Zolensky et al., 1993; Tonui et al., 2003). However, XRD patterns and modal mineralogy of the CI-like chondrites are distinct from those of Alais, Orgueil and Ivuna. The lower abundance ($\sim 70\text{ vol\%}$ vs. $\sim 80\text{ vol\%}$) and more disordered nature of the phyllosilicate, and the much higher abundance of olivine ($\sim 10\text{ vol\%}$), can be attributed to the CI-like chondrites having experienced thermal metamorphism at temperatures $>500^\circ\text{C}$. In contrast the CI chondrites were never heated above $\sim 150^\circ\text{C}$ (Zolensky et al., 1989; Clayton and Mayeda, 1999).

Furthermore, the much higher availability of sulphur ($\sim 20\text{ vol\%}$ sulphide vs. $\sim 5\text{ vol\%}$) implies that the pre-alteration mineralogy of the CI-like chondrites differed from that of the CI chondrites, as was first proposed by Tomeoka et al. (1989). This leads us to conclude that the CI and CI-like chondrites are derived from separate parent bodies. Spectral reflectance data has tentatively connected the CI chondrites to C-type asteroids (Osawa et al., 2005; Beck et al., 2010, 2014; Cloutis et al., 2011; Takir et al., 2013), whilst comets are also a possible source (Lodders and Osborne, 1999; Gounelle et al., 2008). We note here that modal mineralogy in combination with infrared (IR) spectroscopy is helping to strengthen links between meteorites and their parent bodies (Beck et al., 2010, 2014; McAdam et al., 2015). A significant fraction of C-type asteroids appear to have dehydrated surfaces with spectral features similar to those of the thermally metamorphosed CI-like chondrites (Hiroi et al., 1993, 1996; Osawa et al.,

2005; Cloutis et al., 2012). The timing and mechanism of the thermal metamorphism remains poorly constrained, although studies of mineral textures (Nakato et al., 2008) and organics (Yabuta et al., 2010; Orthous-Daunay et al., 2013; Quirico et al., 2014) in the heated CM chondrites indicate that the process was short-lived and probably took place on the order of hours to several years.

The CI-like chondrites were heated to 500–750 °C. Temperatures within large (>20 km) hydrous asteroids could have approached this through internal heating from the radioactive decay of ²⁶Al (Miyamoto, 1991), but the timescale for this process, 10⁶–10⁸ years, is long. Impacts almost certainly caused transient shock heating events on asteroids, which due to variations in the porosity and shock impedance of impacted materials would have created regions with very different thermal histories (e.g. Beck et al., 2005; Bland et al., 2014). However, with the exception of the Sutter's Mill CM meteorite (Jenniskens et al., 2012; Zolensky et al., 2014), thermally metamorphosed carbonaceous chondrites do not contain obvious mixtures of metamorphosed and unmetamorphosed materials. This may be because the fine grain size and lack of clasts in hydrated samples such as the CI-like chondrites make it difficult to determine if heterogeneous temperature distributions existed. An alternative source is solar radiation, with Chaumard et al. (2012) showing that meteoroids approaching within <0.1 A.U. of the Sun can be heated to >500 °C in days to years. Smaller bodies (<10 m) passing this close to the Sun would suffer global metamorphism, whilst on larger bodies a dehydrated crust might form. In this scenario the CI-like chondrites could be derived from one of the many known C-type near-Earth objects (NEOs) with low perihelia orbits such as 3200 Phaethon (Binzel et al., 2002; Morbidelli et al., 2002; Chaumard et al., 2012).

6. SUMMARY

We have used PSD-XRD to determine the modal mineralogy of the CI chondrites Alais, Orgueil and Ivuna, and the CI-like chondrites Y-82162 and Y-980115. In summary:-

- (1) Alais, Orgueil ($n = 3$) and Ivuna ($n = 2$) contain similar abundances of a serpentine/saponite phyllosilicate (81–84 vol%), magnetite (6–10%), sulphides (4–7%) and carbonates (0–3%). Despite the heterogeneous nature of these meteorites, variations in the abundances of these minerals were <4 vol% between separate chips of the same sample. The modal mineralogy of the CI chondrites is consistent with the established model whereby an extended period of aqueous alteration resulted in near-complete transformation of anhydrous precursor materials to abundant secondary phases.
- (2) Y-82162 contains highly disordered serpentine/saponite phyllosilicate (68 vol%), sulphide (19%), olivine (Fo₈₀) (11%) and magnetite (2%). The structure and low abundance of phyllosilicate, and the high abundance of olivine, supports previous studies identifying Y-82162 as a CI-like chondrite

that was altered first by aqueous alteration and then thermal metamorphism. This is apparent in the transformation of phyllosilicate back into olivine, lower H₂O contents and O isotopes shifted to heavier compositions.

- (3) The modal mineralogy of Y-980115, with disordered serpentine/saponite phyllosilicate (71 vol%), sulphide (19%), olivine (Fo₈₀) (8%) and magnetite (2%), is very similar to Y-82162, indicating that it too is a thermally metamorphosed CI-like chondrite. Along with Y-86029 (not studied here) this takes the total number of confirmed thermally altered CI-like chondrites to three. It is unclear from the XRD patterns and modal mineralogy if any of these meteorites are paired; however using the Nakamura (2005) scheme for classifying heated carbonaceous chondrites we suggest they all reached peak metamorphic temperatures of 500–750 °C (Stage III).
- (4) Based on the total abundance of phyllosilicate (83 vol%), Alais, Orgueil and Ivuna experienced the same degree of aqueous alteration. Establishing the degree of aqueous alteration in the CI-like chondrites is complicated by the overprint of thermal metamorphism. If all of the olivine recrystallized from phyllosilicate this implies that the CI-like chondrites suffered extensive aqueous alteration comparable to the CI chondrites. The initial mineralogy of the CI-like chondrites must have contained more sulphur than that of the CI chondrites suggesting that these meteorites are derived from separate parent bodies.
- (5) The timescales involved suggest that thermal metamorphism of the CI-like chondrites was caused either by impact heating or solar radiation. They may represent a parent body with a low perihelia (<0.1 AU) orbit, such as some NEOs.

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