The aqueous alteration of CM chondrites, a review

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The aqueous alteration of CM chondrites, a review

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Abstract

The CM chondrites are samples of primitive water-rich asteroids formed during the early solar system. They record significant interaction between liquid water and silicate rock, resulting in a mineralogy dominated by hydrated secondary phases. Their similarity to the near-Earth asteroids Bennu and Ryugu – targets of current sample return space missions – makes the analysis of CM chondrites essential to the interpretation of these enigmatic bodies. Here, we review the aqueous alteration history of the CM chondrite group.

Initially, amorphous silicate, metal and sulphides within the matrix were converted into Fe-cronstedtite and tochilinite. Later, the serpentinization of refractory coarse-grained inclusions led to the addition of Mg to the fluid phase. This is reflected in the cation composition of secondary phases which evolved from Fe-rich to Mg-rich. Although most CM meteorites are classified as CM2 chondrites and retain some unaltered anhydrous silicates, a few completely altered CM1s exist ([Meteoritical Bulletin, 2021]).

The extent of aqueous alteration can be quantified through various techniques, all of which trace the progression of secondary mineralization. Early attempts employed petrographic criteria to assign subtypes – most notably the Browning and Rubin scales have been widely adopted. Alternatively, bulk techniques evaluate alteration either by measuring the ratio of phyllosilicate to anhydrous silicate (this can be with X-ray diffraction [XRD] or infrared spectroscopy [IR]) or by measuring the combined H abundance/\(^{18}D\) compositions. The degree of aqueous alteration appears to correlate with petrofabric strength (most likely arising due to shock deformation). This indicates that aqueous alteration may have been driven primarily by impact rather than by radiogenic heating. Alteration extent and bulk O-isotope compositions show a complex relationship. Among CM2 chondrites higher initial water contents correspond to more advanced alteration. However, the CM1s have lighter-than-expected bulk compositions. Although further analyses are needed these findings could suggest either differences in alteration conditions or initial isotopic compositions – the latter scenario implies that the CM1 chondrites formed on a separate asteroid from the CM2 chondrites.

Secondary phases (primarily calcite) act as proxies for the conditions of aqueous alteration and demonstrate that alteration was prograde, with an early period at low temperatures (<70 °C), while later alteration operated at higher temperatures of 100–250 °C. Estimates for the initial water-to-rock ratios (W/R) vary between 0.2–0.7. They are based either on isotopic mass balance or mineral stoichiometry calculations – variability reflects uncertainties in the primordial water and protolith compositions and whether alteration was open or closed system.

Some CM chondrites (<36%) experienced a later episode of post-hydration thermal metamorphism, enduring peak temperatures <900 °C and resulting in a dehydrated mineralogy and depleted volatile element abundances. Heating was likely short-duration and caused by impact events. The presence of CM chondrite material embedded in other meteorites, their prominence among the micrometeorite flux and the link between CMs and rubble-pile C-type near-Earth asteroids (e.g. Bennu)
and Ryugu) implies that the CM parent body was disrupted, leaving second-generation CM asteroids to supply material to Earth.

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Keywords: CM chondrites; Aqueous alteration; Bennu; Ryugu; C-type asteroids

1. INTRODUCTION

The Mighei-like (CM) chondrites (Figs. 1 and 2) are the most abundant group of hydrated meteorites, representing ~25% of the carbonaceous chondrite (CC) class and approximately 0.7% of officially recognized meteorites. There are currently 650 CM meteorites, representing a combined mass of >200 kg (The Meteoritical Bulletin, 2021). Since the year 2000, more than 250 research articles have been published on the CM chondrites, exploring aspects of their petrology, alteration history, chemical composition, organic matter, isotopy, and spectroscopic signatures.

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Fig. 1. Optical images of CM chondrites in the laboratory (A) and found lying on Antarctic ice (B). Panel (A) shows a 932 g fragment of the Murchison meteorite (chip ref: BM.1970.5), held at the Natural History Museum, London (Copyright of the Trustees of the Natural History Museum). Panel (B) shows an in-situ an Antarctic find imaged immediately before recovery. This meteorite is MacKay Glacier (MCY) 14001 (42.6 g), recovered in January 2013 by the Italian Programma Nazionale di Ricerche in Antartide (PNRA).

Fig. 2. Polished sections of six CM chondrites viewed under SEM with BSE imaging. Samples are A) Cold Bokkeveld (CM2.1-2.7 [Lentfort et al. 2020]), B) Murray (CM2.4/2.5 [Rubin et al. 2007]), C) ALHA 81002 (CM2), D) Jbilet Winselwan (CM2.4-2.9 [Lentfort et al. 2020]), E) Mighei (CM2.3 [Rubin et al. 2007]) and F) ALH 88045 (CM1). The CM chondrite lithology has small chondrules (averaging ~300 μm) that occur at relatively low abundances (~20 vol%) in comparison to other carbonaceous chondrite groups. Note: the dark black circular holes seen in the Mighei section are ion-probe damage from previous analytical work. Scale bars are 3 mm.
Interest in this group reflects their importance as a key component in our inventory of primitive solar system materials. They are also a potential source of water and organics that may have been delivered to the developing Earth (e.g. Johnson and Fanale, 1973; Alexander et al., 2012; Marty, 2012; Piani et al., 2018; Trigo-Rodríguez et al., 2019; Vacher et al., 2020). Furthermore, the CM chondrites are close spectral matches to many asteroids from the C-type spectral class (e.g. Feierberg et al., 1985; Vilas and Gaffey, 1989; Burbine, 1998; Gaffey et al., 1993; Ostrowski et al., 2010; Cloutis et al., 2011; Takir and Emery, 2012; Takir et al., 2013, 2015; McAdam et al., 2015; Bates et al., 2020). The CM chondrites are also among the closest spectral analogues to the surfaces of near-Earth asteroids [162173] Ryugu (Le Corre et al., 2018; Kitazato et al., 2019) and [101955] Bennu (Clark et al., 2011; Binzel et al., 2015; Hamilton et al., 2019) – the two target bodies of current sample return missions Hayabusa-2 and OSIRIS-REx. Thus, understanding the formation and alteration history of the CM chondrite lithology is critical to the advancement of planetary and space science. New insights into their formation and alteration will help resolve the role, isotopic composition and behaviour of water in the outer solar system and potentially help answer the question: how much water was delivered to the early Earth? Here, we review the CM chondrite literature, focusing on the defining geological process that affected this lithology – aqueous alteration. In addition to exploring how alteration advanced, we examine the relationship between alteration, brecciation, bulk O-isotopic compositions, organics and infrared (IR) spectral properties. This review also evaluates the conditions of alteration, including the temperature and water-to-rock ratios (W/R) required to produce the hydrated CM chondrite meteorites we see today.

2. PROPERTIES OF THE CM CHONDRITES

2.1. Chondrules and matrix

The CM chondrites have average chondrule sizes around 300 μm (Figs. 2 and 3) (270 μm [±240 μm], Rubin and Wasson 1986; 300 μm, Friedrich et al., 2015) and low but variable chondrule abundances ~20 vol% (Weisberg et al., 2006). Chondrules overwhelmingly have porphyritic textures (>95%) with type I (Mg-rich, FeO-poor) varieties being more abundant (60–90%) than the type II (Mg-poor, FeO-rich) varieties (Jones, 2012).
Most chondrules are surrounded by fine-grained rims (FGRs) (Fig. 3). These represent volatile dust mantles that accreted onto chondrules whilst they resided in space as loose objects and are often layered with variable thickness (Metzler et al., 1992; Zolensky et al., 1993; Lauretta et al., 2000; Hua et al., 2002; Zega and Buseck, 2003; Chizmadia and Brearley, 2008). They are also compositionally and texturally distinct from the fine-grained matrix that accreted later, being proportionally Mg-enriched and Ca-poor, typically with coarsening outward textures and composed primarily of phyllosilicates that wrap around the host chondrule (Metzler et al., 1992; Zolensky et al., 1993; Hua et al., 2002; Zega and Buseck, 2003). Sparsely distributed glassy microchondrule droplets (<40 μm) are found within the FGRs of larger parent chondrules, as reported in Elephant Moraine (EET) 96029 and Murchison (Suttle et al., 2019a). Highly refractory phases (CAI [Ca, Al inclusions] and AOA [ameboid olivine aggregates]) are relatively minor components within the CM chondrites, occurring at approximately 1.2 area% (Hezel et al., 2008). The remaining material is fine-grained matrix which has low density, high porosity, and high permeability (Corrigan et al., 1997), although inferred initial permeability (after accretion) may have been significantly lower prior to the onset of parent body alteration (Bland et al., 2009). Except for Tagish Lake (Hildebrand et al., 2006) and the CI chondrites, the CM chondrites have the lowest bulk densities of any chondrite group (between 1700 and 2500 kg m⁻³, Macke et al., 2011) and relatively high porosities (between 14% and 37% with mean average values between 18% and 23%, Macke et al., 2011).

2.2. Mineralogy

This subsection outlines the main constituents of CM chondrites, ordered by their modal abundance, with the most abundant phases described first.

Shortly after accretion the CM parent body (or bodies) were affected by significant aqueous alteration (e.g. McSween, 1979; Bunch and Chang, 1980; Clayton and Mayeda, 1984; Tomoeoka and Buseck 1985; de Leuw et al., 2009; Fujiya et al., 2012; Jilly et al., 2014; Visser et al., 2020). Their petrography records extensive interaction between liquid water and silicate rock, resulting in hydrated mineralogy and high water contents, estimated at ~8.7–13.9 wt.% (based on the thermogravimetric analysis of 16 CM chondrites [Garenne et al., 2014]). Most of this indigenous water is held within phyllosilicates as structurally bound OH molecules, with the remainder held within Fe-(oxy)-hydroxide minerals (primarily ferrihydrite and goethite, Garenne et al., 2014). Phyllosilicates are the most abundant minerals in the CM lithology, varying between approximately 55–90 vol% (Howard et al., 2009, 2011a, 2015; King et al., 2017).

The next most abundant minerals are anhydrous Fe-Mg silicates (olivine [(Fe,Mg)₂SiO₄] and pyroxene [XY(Si,
Al$_2$O$_6$, where the X site is typically occupied by Mg, Fe$^{(II)}$, Ca or Na and the Y site occupied by Mg, Fe$^{(III)}$, Al or Cr$^3+$. They vary in abundance between 5.9 and 33.8 vol% (Howard et al., 2009, 2011a, 2015) and often have refractory Mg-rich compositions. Anhydrous silicates are the dominant components within chondrules, CAIs and AOAs but are also found as isolated grains within the matrix where they may represent chondrule fragments or dust grains accreted directly from the protosolar disk (McSween and Richardson, 1977; van Boekel et al., 2004; Scott and Krot, 2005; Vaccaro, 2017; Jacquet et al., 2020). As in other primitive carbonaceous chondrites, these anhydrous Mg-rich silicates are characterized by solar-like 16O-rich isotopic signatures and trace element compositions inherited from the solar nebula – their petrography therefore acts as a record of early condensation, chondrule formation and accretionary processes (Krot et al., 2004; Kunihiro et al., 2005; Chaumard et al., 2018; Kimura et al., 2020).

Minor phases (<5 vol%) in CM chondrites include carbonates (principally calcite [CaCO$_3$] but also aragonite [CaCO$_3$], dolomite [CaMg(CO$_3$)$_2$] and breunnerite [(Mg, Fe$_{0.5-1}$)CO$_3$] [Riciputi et al., 1994; Lee et al., 2014; Lindgren et al., et al., 2017]), magnetite (Fe$_3$O$_4$) (Howard et al., 2015; King et al., 2017), Fe sulphides (tochilinite [Fe$_2+$5-$6$(Mg,Fe$_{2+}$)$_5$S$_6$(OH)$_{10}$], pyrrhotite [Fe$_{1.3}$S] (where $x = 0$–0.2) and pentlandite [(Fe,Ni)$_8$S$_{18}$] (Zolensky, 1984; Tomeoka and Buseck, 1985; Bullock et al., 2010; Harries and Langenhorst, 2013) and Fe/Ni-metal, predominantly as kamacite (~Fe$_{90}$Ni$_{10}$) (Rubin et al., 2007; Palmer and Lauretta, 2011). The matrix in CM chondrites also contains abundant organic matter (<4 wt.%, Schmitt-Kopplin et al., 2010; Alexander et al., 2017; Vinogradoff et al., 2017), relative to other chondrite groups. Much of this (>75%) occurs as high molecular weight insoluble organic matter (IOM), with average atomic stoichiometries of C$_{100}$H$_{60}$O$_{18}$S$_{3-7}$ (Alexander et al., 2007, 2017; Vinogradoff et al., 2017). The remaining organic matter occurs as short chain soluble molecules exhibiting a diversity of functional groups, including alcohols, carboxylic acids, ketones, amines, amino acids, polyaromatic hydrocarbons, and sulfonic acids (Pizzarello et al., 2006; Orthous-Daunay et al., 2013).

Finally, the matrix contains submicron presolar grains (Davidson et al., 2014; Floss and Haenecour, 2016; Leitner et al., 2020). These are particles formed in the outflows of cooling low-mass red giant or asymptotic giant branch stars (AGB). They predominantly occur as Fe-rich silicates but also include graphite, SiC, diamond and refractory oxides, all with distinctive extreme isotopic excursions (Floss and Haenecour, 2016; Leitner et al., 2020). In CM

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**Fig. 5.** Bulk O-isotope compositions of CM chondrites and the inferred isotopic compositions of their two initial reservoirs. Bulk CM chondrite compositions can be understood as a product of mixing between a 16O-rich (isotopically light) anhydrous CM protolith and 16O-poor (isotopically heavy) water-ice. The exact position of the initial CM water is poorly constrained, several estimates are shown as blue circles and taken from: A and B – Clayton and Mayeda (1999), C – Clayton and Mayeda (1984), D – Young et al. (1999), E – Verdier-Paoletti et al. (2017) and F – Fujiya (2018). Collectively these estimates form a trendline – parallel to that of the CM mixing line that is referred to as the CM water (CMW) line (here plotted as a solid blue line). Bulk chondrite compositions are taken from Clayton and Mayeda (1999) and Ivanova et al. (2010), while the anhydrous CM protolith values are taken from Clayton and Mayeda (1999), Piralla et al. (2020) and Kimura et al. (2020). The position of the initial CM water composition has significant implications for the alteration history of the CM lithology. The bulk compositions of CM chondrites can be directly measured, while the composition of the anhydrous protolith is relatively well-constrained from in-situ measurements on the most 16O-rich phases (refractory Mg-rich chondrule and CAI silicates) or from the bulk composition of the potential CM3: A 12169 (Kimura et al., 2020). However, the position of the initial CM water (once known) will allow accurate estimation of the initial W/R ratios present at the onset of aqueous alteration. Assuming the initial CM water composition was a single point and not a range, the resulting span in bulk compositions of CM meteorites implies that W/R ratios on the CM parent body were variable. Also shown are the Young and Russell line (Y&R, Young and Russell, 1998), the primary chondrules mineral line (PCM, Ushikubo et al. 2012) and the terrestrial fractionation line (TFL, Lodders and Fegley, 1998).
chondrites much of the accretionary presolar grain content has been destroyed by later parent body geological processing. Thus, presolar grains occur at relatively low abundances (<100 ppm) when compared to the less-processed CC groups, such as the CO and CR chondrites (Davidson et al., 2014; Floss and Haenecour, 2016).

2.3. Bulk chemistry

The CM chondrites are part of the CC group which show a wider range of redox states than the OC or EC meteorites (Rubin et al., 1988). They have elemental abundances similar to those of the Sun’s photosphere and to the CI chondrites. However, the CM chondrites also have a distinctive bulk chemical composition (Kallemeyn and Wasson, 1981; Braukmüller et al., 2018; Friedrich et al., 2018). They are characterised by refractory lithophile elements enriched by a factor of 1.2 above CI abundances, and volatile elements homogeneously depleted by a factor of 0.63 below CI values (Bland et al., 2005; Braukmüller et al., 2018). In addition, among the CM chondrites (and other CC groups) the relative abundance of elements held in chondrules and matrix appear complementary, meaning that their bulk chemical (and isotopic) compositions sum to produce a CI chondritic signature despite differences in the composition and relative abundance of chondrules and matrix in different CC groups. If correct, the existence of chemical complementarity would reflect a pre-accretionary chemical process and require that (for each chondrite class) both chondrules and matrix formed sequentially from a single, solar-like reservoir (Bland et al., 2005, 2009; Palme et al., 2015; Friend et al., 2018; Hezel et al., 2018). However, several studies have argued that complementarity is unsupported by isotopic data (Piralla et al., 2020), while others have argued for alternative hypotheses to explain a complementarity signature (e.g. Jacquet et al., 2012; van Kooten et al., 2019).

2.4. Bulk oxygen isotope composition

The bulk O-isotopic composition of the CM chondrites (relative to the Vienna Standard Mean Ocean Water [VSMOW] reference [Lodders and Fegley, 1998]) varies between $\delta^{17}$O: $-5.98\%$ to $+4.06\%$, $\delta^{18}$O: $-2.07\%$ to $+11.91\%$, and $\Delta^{17}$O: $-4.90\%$ to $-2.00\%$ with mean average values of $\delta^{17}$O: $0.43\%$, $\delta^{18}$O: $6.55\%$, and $\Delta^{17}$O: $-2.97\%$ (Fig. 5 and Clayton and Mayeda, 1999; Lee et al., 2019a; Kimura et al., 2020). Bulk and matrix separates from CM falls and nominally unweathered CM finds plot along a single trendline in $\delta^{17}$O vs. $\delta^{18}$O isotope space with a slope of $-0.7$ and a $\delta^{18}$O intercept of $-4.23\%$, occasionally referred to as the CM mixing line (Rowe et al., 1994; Clayton and Mayeda, 1999; Ireland et al., 2020). Likewise, the bulk compositions of the CO chondrites and the recently proposed CY chondrites (King et al., 2019a; Suttle et al., 2020a) also plot along this same trendline but at lighter and heavier compositions, respectively (Fig. 5 and Clayton and Mayeda, 1999). In addition, an increasing number of C2-ungrouped (hereafter C2-ung) meteorites (including Acfer 094, North West Africa [NWA] 5958 and Adelaide) also plot along this trendline infilling the isotopic gap between the CO and CM chondrite groups (Choe et al., 2010). This linear relationship represents mixing between two primitive reservoirs, an inner $^{16}$O-rich solar-like silicate reservoir upon which additions from an outer $^{16}$O-poor component were added (Rowe et al., 1994; Clayton and Mayeda, 1999; Sakamoto et al., 2007; Marrocchi et al., 2018; Ireland et al., 2020). While the $^{16}$O-rich refractory component preserved in chondrule and CAI silicates was most likely formed by photodissociation reactions and shelf-shielding of carbon monoxide in the primordial molecular cloud (Fig. 16 in Ireland et al., 2020), the $^{16}$O-poor component reflects the cold primitive composition of the molecular cloud unaffected by stellar activity and accreted into the chondritic bodies as volatile water-ice (Sakamoto et al., 2007; Marrocchi et al., 2018; Ireland et al., 2020). This ice would later melt and interact with silicates in aqueous alteration reactions.

2.5. Bulk hydrogen isotopic composition

 Indigenous hydrogen in CCs is present primarily in two reservoirs – H within organic matter and H held in hydrated minerals (predominantly phyllosilicates as $\text{-OH}$ bonds) (Kolodny et al., 1980; Robert and Epstein, 1982; Mullie and Reisse, 1987; Alexander et al., 2010, 2012; Piani et al., 2012, 2015, 2018; Patzek et al., 2020). However, once meteorites land on the Earth’s surface they are further affected by the addition of H, added as adsorbed terrestrial water and newly formed weathering phases (Alexander et al., 2010, 2012; Vacher et al., 2020). Early studies measured bulk H abundance and isotopic composition without pre-treatment to remove terrestrial H and/or before the recognition of different H reservoirs (Boato, 1954; Kerridge, 1985; Pearson et al., 2001). However, later studies refined analysis techniques, using modest heating (generally <200 °C) under vacuum to degas terrestrial water (e.g. Vacher et al., 2020). Organic phases can be extracted and measured directly by acid leaching (e.g. Pizzarello et al., 1991; Alexander et al., 2010), while water held in phyllosilicates can be released by heating above the temperature at which phyllosilicates dehydrate (Kolodny et al., 1980; Robert and Epstein, 1982; Halbout et al., 1986). Furthermore, recent advances in analytical protocol have facilitated the in-situ micron-scale measurement of $\delta$D composition on individual organic or hydrated components within a meteorite’s matrix (Piani et al., 2012). Collectively these studies have demonstrated that the primordial water in primitive CCs is characterised by D-poor compositions, while organic matter tends to have D-rich compositions (Robert and Epstein, 1982; Alexander et al., 2010, 2013; Piani et al., 2012, 2015, 2018). In CM chondrites primordial water $\delta$D values (given relative to VSMOW [Lodders and Fegley, 1998]) are estimated at $\delta$D $\approx -427\%$ by Alexander et al. (2012) and at $\delta$D: $-350\%$ $\pm 40\%$ by Piani et al. (2018). However, Piani et al. (2018) also suggested that a second D-rich water source (with compositions $\delta$D $\approx -69\%$ $\pm 163\%$) may have been present in the CM chondrites, the signal of which
has been identified in the least-altered regions of the CM chondrite Paris (Piani et al., 2018). Conversely, the H-isotope composition of the organic matter in CM chondrites have high δD values (>600‰, Robert and Epstein, 1982; Pizzarello et al., 1991; Alexander et al., 2007, 2010), with an inferred pristine isotopic composition of around δD: +3500‰ (Alexander et al., 2012). During aqueous alteration organics and water reservoirs may have interacted by progressive isotopic equilibration, resulting in intermediate δD compositions for later-formed organics and hydrated minerals (Alexander et al., 2007, 2010, 2015, 2017; Piani et al., 2015).

3. THE SUBCLASSIFICATION OF CM CHONDRITES

The CM chondrites experienced variable amounts of aqueous alteration (McSween, 1979; Kerridge and Bunch, 1979; Kojima et al., 1984; Browning et al., 1996; Zolensky et al., 1997; Rubin et al., 2007; Howard et al., 2015). Most members are subclassified as petrologic type 2 (in the scheme of Van Schmus and Wood, 1967) and termed CM2. They contain between 54–84 vol% phyllosilicate (Howard et al., 2009, 2011a, 2015). The CM2 chondrites are the most abundant grouping, representing approximately 85% of the CM population (The Meteoritical Bulletin, 2021). They contain partially replaced chondrules (Fig. 3) and altered refractory inclusions (Fig. 6). Despite a single designation, the degree of aqueous alteration represented within the CM2 classification varies widely (Browning et al., 1996; Zolensky et al., 1997; Hanowski and Brearley, 2001; Rubin et al., 2007; Howard et al., 2015). Mildly altered meteorites such as CM Paris contain ~45 vol% anhydrous silicates, retain some unaltered glass within chondrule cores and primitive amorphous silicate within their fine-grained matrix (Marrocchi et al., 2014; Hewins et al., 2014; Rubin, 2015). Conversely, some intensively altered CM2 chondrites (e.g. QUE 93005) have minimal surviving mafic silicates (<15%), minimal unoxidized metal and much of their matrix is composed of large phyllosilicate clumps (Velbel et al., 2015; Rubin et al., 2007). Because the replacement of chondrules occurs at differing rates, CM2 chondrites may contain some completely replaced chondrules (pseudomorphs) as described in Nogoya (Bunch and Chang, 1980; Velbel et al., 2012).

In the extreme case, some CM chondrites suffered complete alteration and are classified as type 1 meteorites (termed CM1s [Grady et al., 1987; Zolensky et al., 1996, 1997; King et al., 2017], or CM2.0 in the Rubin scale – Rubin et al., 2007). They have the highest phyllosilicate abundances (84–91 vol%), minimal olivine (4–8 vol%) and minor quantities of accessory magnetite, Fe-sulphides and carbonates (King et al., 2017). All their chondrules have been completely replaced by phyllosilicates, oxides and sulphides, resulting in residual pseudomorphic outlines (Fig. 2F) (Grady et al., 1987; Zolensky et al., 1996, 1997). The CM1s bear a close resemblance to the CI chondrites but have distinctly CM-like chemical compositions, a CM mineralogy and retain faint outlines of their accretionary texture, which are otherwise absent in the CI chondrites. Approximately 4.2% of the CM population are classified as CM1 chondrites (The Meteoritical Bulletin, 2021). Their relatively low abundances could be a sampling bias, arising due to rapid disintegration whilst in space, during atmospheric entry or due to terrestrial weathering. To date all known CM1 chondrites are finds that have suffered at least modest weathering (King et al., 2017). However, the recently recovered CM Mukundpura (Ray and Shukla, 2018) may either be the first CM1 fall or contain CM1 clasts, held within a CM2 lithology (Rudraswami et al., 2019; Potin et al., 2020).

In between the CM1 and CM2 chondrites the transitional designation: CM1/2 used to classify, approximately

Fig. 6. Ca-, Al-rich inclusions (CAIs) in CM chondrites. Panels are ordered (A to F) by their approximate degree of alteration from minimally altered (A) to intensely altered (F). Like chondrules, CAIs are often mantled by FGRs. They are typically irregular shaped and small (<100 μm) and occur at low abundances. Aqueous alteration results in their progressive dissolution and replacement.
5% of the CM population (The Meteoritical Bulletin, 2021). They have phyllosilicate contents between 71 and 88 vol% and anhydrous silicate contents between 6 and 26 vol% (King et al., 2017). The remaining 5% of CM meteorites are simply classified as “CM” in the Meteoritical Bulletin (The Meteoritical Bulletin, 2021) and require further examination.

4. WHERE DID AQUEOUS ALTERATION OCCUR?

Most studies conclude that aqueous alteration occurred predominantly on the CM parent body(ies), facilitated by the melting of water–ice grains present in the accretionary assemblage (e.g. McSween, 1979; Kerridge and Bunch, 1979; Bunch and Chang, 1980; Tomeoka and Buseck, 1985; Grimm and McSween, 1989). There is abundant evidence for parent body-hosted alteration, this includes the presence of centimetre-scale alteration fronts seen in thin section (e.g. Fig. 6 in Jacquet et al., 2016) that record the passage of fluid through the parent body, mineralized veins which cut through both matrix and chondrules (Lee et al., 2012; Lindgren et al., 2017), large phyllosilicate clusters (>60 μm, Rubin et al., 2007) and the redistribution of soluble elements from refractory inclusions into the matrix (Bunch and Chang, 1980; Lee et al., 2019b; Suttle et al., 2019a). Alternative evidence can be found from paleomagnetic studies investigating the thermal remanent magnetism preserved in CM chondrites (Cournede et al., 2015). They have identified a stable post-accretion component and interpreted this as evidence of an active dynamo system generating a magnetic field on a differentiated parent body. Critically, this stable component is recorded in secondary magnetite and pyrrhotite minerals formed during aqueous alteration. This relationship therefore requires that aqueous alteration occurred after accretion on the parent asteroid (Cournede et al., 2015).

Despite these observations some studies have argued that pre-accretionary aqueous alteration played at least a limited role (Metzler et al., 1992; Bischoff, 1998; Ciesla et al., 2003; Ciesla and Lauretta, 2005). Metzler et al. (1992) suggested that the hydrated FGRs surrounding chondrules (examples of which are shown in Fig. 3) were most likely aqueously altered in a nebula setting. They argue that the presence of unequilibrated assemblages with phyllosilicates in direct contact with unoxidized metal, fragments of chondrule glass and unaltered olivine/pyroxene requires that aqueous alteration did not occur in-situ (otherwise these highly susceptible phases would also have been altered). Instead, the various component minerals must have formed earlier and then accreted onto the margins of loose chondrules in the nebula. Because aqueous alteration reactions between nebula gas and crystalized phases are prohibitively slow (Metzler et al., 1992), alteration environments would require higher pressures and temperatures, perhaps originating during shock waves (Ciesla et al., 2003; Ciesla and Lauretta, 2005).

5. THE PROGRESSION OF AQUEOUS ALTERATION

5.1. What was the hypothetical unaltered CM3 chondrite like?

The matrices in some of the least-altered CM chondrites contain extremely fine-grained amorphous silicates (Barber, 1981; Chizmadia and Brearley, 2008; Hewins et al., 2014; Marrocchi et al., 2014; Rubin, 2015; van Kooten et al., 2018; Lee et al., 2019a; Kimura et al., 2020; Vollmer et al., 2020). They are similar to the highly primitive glass with embedded metal and sulphide (GEMS) grains found in cometary dust (Bradley, 1994; Noguchi et al., 2017) and are therefore referred to as GEMS-like (Leroux et al., 2015). Both GEMS and the GEMS-like phases found in chondrites are oxygen-rich moderately volatile amorphous materials dominated by Mg, Fe, Si and S. They may have formed by condensation directly from the proto-solar nebula or were modified from more primitive condensates by prolonged solar radiation (Keller and Messenger, 2011, 2013). GEMS and GEMS-like phases most likely represent...
the “building blocks” of chondritic matrix, as evidenced by their ubiquity among primitive materials, including cometary dust (Noguchi et al., 2017), micrometeorites (Suttle et al., 2020b), CM chondrites, CR chondrites (Le Guillou et al., 2015) and ordinary chondrites (Dobrică and Brearley, 2020).

In addition to the GEMS-like material the CM3 matrix (Fig. 7) would have also contained crystalline phases, notably an abundance of submicron forsterite and enstatite crystals, as well as metal grains and pyrrhotite – similar to the assemblages reported from other primitive chondrite groups and C-ung meteorites (Greshake, 1997; Scott and Krot, 2005; Vaccaro, 2017; Noguchi et al., 2017; Singerling and Brearley, 2018; van Kooten et al., 2018; Davidson et al., 2019). The abundance of metal within the CM3 matrix likely exceeded >2 vol%, (Rubin et al., 2007; Rubin, 2012, 2015). Bland et al. (2007) reported the occurrence of micron-scale CAIs, LiCr-

oxide and high abundances of presolar grains in the highly primitive meteorite Acfer 094 (C2-ung) – the CM3 matrix is expected to have been similar. Furthermore, the matrix of the CM3 chondrite would also have contained a significant fraction of water–ice, which, whilst frozen would have remained largely inert (Suttle et al., 2020c) – preventing aqueous alteration reactions. Recent analysis of Acfer 094 identified a region of ultra-high porosity interpreted as evidence of previously ice-filled pores (Matsumoto et al., 2019) – the relative abundance of water initially accreted by the CM3 lithology is discussed further in Section 8.3.

In CM chondrites chondrules (<510 µm, Rubin and Wasson, 1986), CAIs (<100 µm, Hezel et al., 2008) and AOAs are relatively small in comparison to other chondrite groups. They have refractory Mg-rich chemical compositions and light 16O-rich isotopic compositions (e.g. Chaumard et al., 2018). The unaltered CM3 would contain glass and feldspar within their chondrules – phases which are rarely found in CM2 chondrites. Owing to the effects of aqueous alteration CAIs in CM chondrites (Fig. 6) rarely survive unaltered. They often contain partially altered spinel, pyroxene, olivine and hibonite intermixed with secondary minerals such as Fe-rich phyllosilicates, calcite (Armstrong et al., 1982; Greenwood et al., 1994; Rubin, 2007, 2015) and in one instance sodalite (Lee et al., 2019b). The rarity, or in many cases absence of mellite in CAIs is frequently attributed to destruction by aqueous alteration (Greenwood et al., 1994; Rubin, 2007, 2015; Lee et al., 2019b), however, the lack of mellite may instead reflect a primary feature inherited from the solar nebula (MacPherson and Davis 1994; Simon et al., 2006; Marrocchi et al., 2014).

Recently Kimura et al. (2020) analysed three Antarctic CM chondrites (Asuka (A) 12085, A 12169 and A 12236) and suggested that they represent the least-altered members of the CM class yet identified. In particular, they argued that A 12169 should be considered a CM3. This meteorite does indeed retain many of the properties expected from an unaltered chondrite. It retains abundant primary glass and feldspar within the chondrule mesostasis, while chondrule phenocrysts lack evidence of alteration. Similarly, the matrix lacks hydrated minerals and contains only micron-sized Ca-carbonate grains. However, although phyllosilicate is apparently absent from the matrix, some of the chondrule glass has been altered to phyllosilicates (in 36% of chondrules) – attesting to at least minor interaction with liquid water. Even if the A 12169 is not an unaltered CM3, its discovery and minimally altered state provide crucial insights into the primary accretionary characteristics of the CM chondrite lithology. The A 12169 CM has average chondrule diameters of 260 µm, chondrule abundances of 38.6 vol%, refractory inclusion abundances of 4.8 vol% and matrix abundance at 53.4 vol% with minor phases metal (2.3 vol%) and sulphides (1.4 vol%) at higher abundances than those reported from Paris.

5.2. Qualitative description of aqueous alteration

The earliest stages of alteration in the CM lithology may have been similar to the CO and CV chondrites. Evidence for an initial short-duration episode of alkali-halogen metamorphism was recently reported within a CAI in the CM2 chondrite Meteorite Hills (MET) 01075. The presence of the feldspathoid sodalite implies alteration of a melilitic or anorthite precursor by small quantities of Na-rich, CI-bearing fluids at high-temperatures (>100 °C) and relatively low W/R ratios (Lee et al., 2019b).

The progression of aqueous alteration in the CM chondrites is well documented (Fig. 7). Initially, the GEMS-like amorphous silicates were converted into phyllosilicates and sulphides. Alteration occurs rapidly in the presence of alkali-line water (Nakamura-Messenger et al., 2011) through leaching (of Mg and S) and oxidation (of Fe), generating a nanophase assemblage of phyllosilicate and hydrated sulphide (McSween, 1987; Le Guillou et al., 2015; Noguchi et al., 2017; Vacher et al., 2019a). Concurrent with the alteration of GEMS, kamacite grains altered to form either Fe-sulphides (tchilitinite), cronstedtite or magnetite depending on the microchemical environment and the local activity of Si, S and Fe (Palmer and Laurota, 2011). These reactions produced an extremely fine-grained intermixed assemblage composed of phyllosilicate and sulphide that ultimately replaced much of the primary matrix. The resulting texture is characteristic of mildly aqueously altered CM chondrites (Fig. 8). This mineral assemblage was initially referred to in the literature as PCPs (poorly characterized phase [Fuchs et al., 1973; McSween, 1979, 1987; Kerridge and Bunch, 1979; Bunch and Chang, 1980; Zolensky, 1984; Tomeoka and Buseck, 1985]), but is now more commonly referred to as tochilitine-cronstedtite intergrowths (TCIs, Zolensky et al., 1993; Rubin et al., 2007; Pignatelli et al., 2017; Vacher et al., 2019a). As aqueous alteration advanced, TCIs were progressively replaced by phyllosilicates with larger grain sizes and high degrees of crystallinity. This resulted in the development of large relatively homogenous phyllosilicate clumps (20–60 µm, Rubin et al., 2007). Simultaneously, submicron tochilitinite grains were dissolved and reprecipitated as larger euhedral pyrrhotite grains, resulting in a lowering of FeO/SiO2 and S/SiO2 ratios within the phyllosilicate clumps (McSween, 1979, 1987; Rubin et al., 2007).
Intermediate aqueous alteration is characterized by the replacement of anhydrous silicates (Fig. 7). Typically, substitution reactions resulted in the direct replacement of olivine and pyroxene crystals by phyllosilicates, forming pseudomorphic crystals. To facilitate isovolumetric replacement required the import/export of dissolve species to/from the site of alteration and thus open system behaviour (at least on a localized 10–100 s of micron length scale). The conversion of olivine to serpentine under these conditions is best explained by a 5:2 stoichiometric ratio (Velbel 2014). Iron-rich (ferroan) olivines are more susceptible to alteration than Mg-rich compositions (Wogelius and Walther, 1992; Zolensky et al., 1993; Hanowski and Brearley, 2001) and were therefore preferentially replaced early in the alteration sequence. Fe-rich anhydrous silicates experienced centripetal replacement, characterized by alteration from the margin inwards (Velbel 1993; Velbel et al., 2015). In contrast, Mg-rich olivine and pyroxene grains experienced meshwork replacement (Wicks and Whittaker, 1977; Velbel et al., 2012, 2015), characterized by the exploitation of existing microstructural weaknesses, forming narrow veinlets that penetrate crystal cores along fractures, dislocation defects and cleavage planes, whilst infilling pore space (Lee and Lindgren, 2015). As a result of differences in exposed surface area, mineral composition and grain size, chondrules alter at different rates (Hanowski and Brearley, 2001). This can create apparent localized differences in the degree of alteration which instead reflect isochemical composition-dependent alteration rates. As olivine is dissolved, the activity of Mg in the alteration fluid rose, leading to the precipitation of increasingly Mg-rich serpentine. This demonstrates that the composition of secondary phases were controlled by the composition of the alteration fluid and not by the composition of the host phase being replaced (Velbel et al., 2012, 2015). Consequently, alteration advanced by Fe/Mg-serpentine replacing Fe-cronstedtite as the main secondary phase. Simultaneously, already formed Fe-cronstedtite experienced substitution reactions, and evolved towards more Mg-rich compositions (Howard et al., 2009; Velbel and Palmer, 2011; Elmaleh et al., 2015).

Carbonates precipitated from the fluid phase during both the early and intermediate stages of aqueous alteration. Calcite is the most abundant carbonate (Fig. 9) (0.9–4.2 vol%, Howard et al., 2015) although other, more complex species including aragonite, dolomite and brucine also formed (e.g. Lee et al., 2014) – because these phases are generally absent from XRD data, it can be inferred that they typically occur at abundances <0.5 vol%. Although carbonates represent a minor phase in the CM lithology, they are an important source of information on the alteration environment and the timescales of alteration, they are covered in detail in Sections 8 and 11.

The CM1 chondrites represent the most advanced stages of aqueous alteration on the CM lithology (Fig. 7). They experienced complete replacement of their primary accretionary assemblage by secondary minerals resulting in a homogenized texture with only pseudomorphic chondrule and CAI outlines remaining. They are dominated by relatively coarse-grained Fe/Mg-serpentines (Grady et al., 1997; Zolensky et al., 1996, 1997), distinct from the finer-grained and approximately equal proportions of serpentine and saponite found in CI chondrites (which are also classified as type 1 materials [Van Schmus and Wood, 1967]). In comparison to CM2s, the CM1s also have higher magnetite abundances (2–3 vol%), low carbonate contents (<2 vol% calcite) and lack tochilinite – potentially indicating alteration temperatures above T > 120°C (King et al., 2017).
5.3. Quantitative characterisation

The degree of aqueous alteration recorded in an individual meteorite may be evaluated in several ways. Initially studies focused on a small number of meteorites and attempted to define a relative sequence of alteration (McSween, 1979; Bunch and Chang 1980; Tomeoka and Buseck 1985; Burgess et al., 1991; Zolensky et al., 1993). These studies used geochemical and textural criteria that could be acquired under scanning electron microscope (SEM), evaluating the abundance and/or composition (often as elemental ratios [e.g. Fe/Si]) of the matrix. Proxies for the degree of alteration were inferred from the progressive increase in Mg content of phyllosilicate as alteration advanced (McSween, 1979, 1987; Tomeoka and Buseck, 1985; Zolensky et al., 1993; Browning et al., 1996), the ratio of oxidized to reduced phases (Burgess et al., 1991), or comparison of bulk composition to CI values (Bunch and Chang, 1980). However, quantifying the degree of aqueous alteration and summarizing this as a single number provides a more useful assessment of alteration extent than relative scales based on only a small number of meteorites. This is because new samples can be rapidly evaluated and compared against the existing population of studied samples.

5.3.1. The Browning and Rubin Scales

Browning et al. (1996) proposed three parameters to quantify the degree of aqueous alteration in CM chondrites: (1) the mineralogic alteration index (MAI) which reflects the progress of Fe/Mg-serpentine replacing Fe-cronstedtite within the CM matrix, (2) the volume percent of isolated matrix silicates and (3) the volume percent of chondrule alteration. By using metrics that consider both the replacement of matrix and coarse-grained inclusions the Browning scale attempted to produce a representative assessment of alteration extent. The most notable and controversial characteristic of the Browning scale is the MAI. This is calculated by averaging several wide beam electron microprobe analyses (EMPA) collected from the matrix. The resulting chemical compositions are used to infer phyllosilicate composition, assuming that the volume analysed is composed primarily of serpentine group phyllosilicates with idealized stoichiometries. After correcting for the abundance of Fe\(^{3+}\) expected in S-bearing minerals, the MAI is calculated as: $$\text{MAI} = 2 - \left( \frac{\text{Fe}^{3+}/(2 - \text{Si})}{N} \right)$$ This index (which ranges from 0 [cronstedtite] to 2 [Mg-serpentine]) attempts to calculate the amount of Fe\(^{3+}\) held in phyllosilicates. Although several studies have found the MAI to be a useful metric for tracing aqueous alteration extent (e.g. Benedix et al., 2003; Airieau et al., 2005; Brearley, 2006; Takir et al., 2013) other studies have questioned its validity (e.g. Bland et al., 2006; Rubin et al., 2007; Velbel and Palmer, 2011). Velbel and Palmer (2011) argued that the MAI metric is fundamentally flawed since it relies on inaccurate phyllosilicate stoichiometries. In addition, it fails to consider how other cations (such as Al) alter the behaviour of Fe partitioning into different lattice sites within the phyllosilicate structure. Furthermore, the MAI appears susceptible to modification by terrestrial weathering and potentially also to curatorial storage (Bland et al., 2006).

Later, Rubin et al. (2007) proposed a new quantitative alteration scale. This varies between a hypothetical unaltered CM3.0 and a completely replaced CM2.0 (equivalent to the CM1 designation). Like the Browning scale, the Rubin scale is based on multiple criteria, including...
FeNi-metal abundance, percentage of unaltered mafic silicates, the chemical composition [FeO/SiO2] of phyllosilicate clumps and the dominant species of carbonate and sulphide. However, unlike the Browning scale, the Rubin scale relies on directly measured/observed criteria rather than attempting to infer phyllosilicate compositions (as the MAI does). Rubin et al. (2007)’s initial analysis assigned meteorites spanning the range CM2.0-CM2.6. However, definition of a less-altered samples with petrologic subtypes from CM2.7–3.0 have since been proposed by several studies (e.g. Marrocchi et al., 2014; Hewins et al., 2014; Rubin 2015; Lee et al., 2016; 2019a; Kimura et al., 2020; Lentfort et al., 2020). Since its introduction, the Rubin scale has been widely adopted by numerous studies looking to classify CM meteorites (or their constituent clasts).

The advantage of the Rubin and Browning schemes lie in their ability to estimate the degree of alteration quickly using a set of simple petrographic criteria on accessible and widely available microanalysis instruments (primarily SEM). However, most CM chondrites are breccias, representing amalgamations of several related but distinct lithologies (Metzler et al., 1992; Bischoff et al., 2006; Nakamura, 2006; Lindgren et al., 2013; Lentfort et al., 2020), with clasts exhibiting different degrees of aqueous alteration – as demonstrated by Boriskino (Vacher et al., 2018; Verdier-Paletti et al., 2017), Lonewolf Nunatak 94,101 (Lindgren et al., 2013), Sutter’s Mill (Zolensky et al., 2014), Mukundpura (Potin et al., 2020), Paris (Hewins et al., 2014; Rubin, 2015) and many others. This means that researchers analysing different thin sections of the same meteorite can arrive at different estimates for the extent of aqueous alteration (as summarized in Table 7 of Cloutis et al., 2011). The presence of polymict breccias with multiple CM lithologies exhibiting different alteration extents therefore complicates subclassification. To address this problem, an individual meteorite can be more accurately characterized by assigning a petrologic range rather than a single number – the phyllosilicate fraction (PSF) – calculated as: total phyllosilicate/total anhydrous silicate + total phyllosilicate, and used to assign a petrologic subtype between 3.0 (no alteration) and 1.0 (fully altered) (Howard et al., 2015). In addition to being a relatively quick technique, after analysis the powdered sample can be used for other bulk analysis techniques. Furthermore, this method can be applied to any carbonaceous chondrite, not just CM chondrites but also the CRs (Howard et al., 2015), COs (Alexander et al., 2018), CIIs (King et al., 2015a), CYs (Suttle et al., 2020a), and C-ung chondrites (Howard et al., 2015), allowing the degree of aqueous alteration to be compared across meteorite groups.

(2) Light element analysis: An alternative approach uses bulk H, C and N abundances as well as their isotopic compositions to evaluate alteration extent (Fig. 10 and Browning et al., 1996; Alexander et al., 2012, 2013). In CM chondrites with no evidence of weathering nor metamorphic heating bulk δD values vary between ~250‰ and +100‰, H abundances vary between 0.9 and 1.5 wt. %, C/H ratios vary between 0.9 and 2.7 and δ15N between ~10‰ and +50‰ (Alexander et al., 2013). In general, more advanced aqueous alteration is characterized by lower δD values, higher H abundances, lower C/H ratios and lighter δ15N values. These trends trace the progressive destruction of organics, the incorporation of H into phyllosilicates and the isotopic exchange between water depleted in δD and 13C-rich isotopically heavy organics (Alexander et al., 2012, 2013).

A statistically robust positive correlation (p-value: 0.000289) exists between (1) PSF and (2) bulk H abundances as shown in Fig. 10. Although this trend has a high degree of confidence, the relationship is weak (R2 = 0.46, Pearson = +0.65) suggesting that phyllosilicates are only one of the main reservoirs for H in CM chondrites. Hydrogen is also present in organic matter (Mullie and Reisse, 1987; Alexander et al., 2007, 2017; Vinogradoff et al., 2017). Furthermore, Vacher et al. (2020) showed that carbonaceous chondrite bulk H abundances are often heavily affected by the addition of terrestrial H (typically representing ~10–30% of their H budget). This is added to meteorites as adsorbed water and as weathering phases. These terrestrial additions complicate the use H abundances as a metric for characterizing the extent of aqueous alteration. To overcome such problems Vacher et al. (2020) argue that samples should be de-gassed prior to H analysis by heating to ~120 °C for 48 hours. This ensures that any absorbed water is released, and weathering phases thermally decompose. However, such heating may also affect any indigenous tochilinite (Hanna et al., 2020) whose thermal breakdown temperature occurs around ~120 °C (Fuchs et al., 1973; Zolensky, 1984; Zolensky et al., 1997).

(3) IR spectroscopy: A third technique often used to quantify the alteration extent of CM chondrites is IR spectroscopy. There are multiple spectral features across IR spectrum including weak absorptions at short wavelengths associated with Fe- and Mg-bearing phyllosilicates (0.7 µm, 0.9 µm, 1.1 µm and 2.3 µm [e.g. Cloutis et al., 2011; Beck et al., 2018], a highly informative absorption

1 Relative to the δD composition of the CM lithology’s accretionary assemblage
band located at ~3 μm related to M—OH bonds (Feierberg et al., 1985; Miyamoto and Zolensky, 1994; Sato et al., 1997; Beck et al., 2010, 2018; Takir and Emery, 2012; Takir et al., 2013, 2015) and several features at mid-IR wavelengths produced by silicate Si—O bonds (e.g. Beck et al., 2014, 2018; McAdam et al., 2015; Bates et al., 2020; Hanna et al., 2020). Many of these features correlate closely with alteration extent as inferred by petrographic or mineralogical metrics indicating that IR is a reliable method for quantifying alteration. Each of the main IR techniques are discussed in detail in Section 10.

6. IMPACT BRECCIATION AND ITS RELATIONSHIP TO ALTERATION

Radiogenic heating, arising due to the decay of short-lived isotopes such as 26Al was the most likely source of heat energy driving parent body geological processes in most chondrites, including the CM chondrites (e.g. Grimm and McSween, 1989; Miyamoto, 1991; Keil, 2000; McSween et al., 2002; Krot et al., 2006; Bland and Travis, 2017; Visser et al., 2020). However, impact events are also commonly suggested as a source of heat energy for alteration reactions (Rubin, 2012; Vernazza et al., 2016; Quirico et al., 2018; Amsellem et al., 2020). The CM chondrites display a subtle correlation between their degree of aqueous alteration and their petrofabric strength (Rubin, 2012; Hanna et al., 2015; Lindgren et al., 2015; Vacher et al., 2018). Although most CM chondrites are classified with an S1 shock stage – defined as unshocked (with peak pressures <5 GPa, Scott et al., 1992; Lindgren et al., 2015), abundant evidence of brittle deformation arising due to impact compaction has been observed. This includes oblate flattened chondrules (Scott et al., 1992; Nakamura, 2006; Hanna et al., 2015), fracture melt veins and extensive brecciation (Kerridge and Bunch, 1979; Bischoff et al., 2006; Nakamura, 2006; Zolensky et al., 2014; Verdier-Paoletti et al., 2019; Lentfort et al., 2020). Vacher et al. (2018) compared lithologies in Boriskino against experimentally shocked CMs chondrite material, showing that some parts of the CM lithology may have experienced peak shock pressures between 10 and 30 GPa – such high-energy impact events are expected to impart significant heating into the target body (Tomeoka et al., 1999; Davison et al., 2010) and could have resulted in catastrophic disruption. The CM chondrites also preserve evidence of ductile deformation, present as a weak but pervasive foliation generated by phyllosilicates wrapping around chondrules (Fujimura et al., 1983; Rubin 2012; Lindgren et al., 2015).

Shock deformation would have facilitated aqueous alteration both through heating and by the generation of new fracture networks, thereby increasing porosity and permeability while improving fluid flow through the parent body. Rubin (2012) suggested that efficient shock wave attenuation within the porous CM lithology may have effectively shielded olivine grains from high shock pressures and thus made the CM chondrites appear less shocked, when evaluated using the criteria of Scott et al. (1992), which relies primarily on shock features preserved in olivine grains. Numerical modelling supports this suggestion, demonstrating that even at low impact velocities (~1.5 km/s) a chondritic body allows rigid chondrules (and matrix olivines) to survive unheated while the matrix experiences transient and extreme flash heating (at >700 °C...
and > 10 GPa, Bland et al., 2014). Conversely, experimental impact studies at hypervelocity (<2 kms⁻¹) into a small quantity of CM chondrite target rock demonstrate that phyllosilicates can survive impact even at high peak pressures, up to ~ 32 GPa (Akai and Sekine 1994) and instead responds to high peak pressures by catastrophic disruption forming an overabundance of fine-grained debris and thereby releasing dust into interplanetary space (Tomoeoka et al., 1999), some of which falls to earth as micrometeorites with clear CM affinities (Taylor et al., 2012; Suttle et al., 2017, 2019b).

Alternatively, Lindgren et al. (2015) argued that although the CM chondrites contain abundant evidence of impact processing, their low (S1) shock states (based on the classification criteria of Scott et al. (1992)) suggest that the CM parent body was affected by repeated low-intensity impact events, rather than a single large event. This would allow impact deformation features to develop while not subjecting olivine grains to high shock pressures. Calcite grains in CM chondrites appear to support this hypothesis – they demonstrate clear evidence of episodic growth (Lee et al., 2012, 2014; Tyra et al., 2016; Vacher et al., 2018). Vacher et al. (2018) argued that the two main generations of calcite (referred to as T1 and T2 [detailed in Section 8.1]) appear to have formed before and after compaction respectively, thus implying that initial alteration was likely facilitated by radiogenic heating while later alteration episodes could have been driven by the residual heat imparted from an impact.

7. RELATIONSHIP BETWEEN O-ISOTOPES AND ALTERATION

7.1. Bulk O-isotope compositions

The relationship between the extent of aqueous alteration and a CM chondrites’ bulk O-isotopic composition is unresolved (Fig. 11). Early studies analysed relatively small numbers of meteorites and suggested a positive correlation between degree of alteration and progressively heavier isotope compositions (Fig. 3 in Browning et al., 1996; Fig. 8 in Rubin et al., 2007). Intuitively, we may expect such a correlation if alteration operated as a closed system. This is because the degree of aqueous alteration in the CM lithology appears to be proportional to the amount of accreted water–ice (as shown in Fig. 11). Furthermore, because the primordial water–ice accreted by CCs had 16O-poor heavy isotope compositions (Clayton and Mayeda, 1999; Chaumard et al., 2018; Ireland et al., 2020), the amount of accreted water–ice should be directly proportional to the resulting bulk O-isotope composition (Schrader et al., 2011). Thus, the two variables (bulk O-isotope values and degree of aqueous alteration) are united by their co-dependence on the amount of initial water–ice.

However, studies analysing a larger population of CM chondrites have questioned this relationship (Fig. 7 in Alexander et al., 2013; Fig. 9 in Beck et al., 2014). Although higher phyllosilicate contents appear to show a weak correlation with progressively heavier O-isotope compositions.

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**Fig. 11.** Relationship between bulk O-isotope composition (given as Δ¹⁷O [%ε]) and extent of aqueous alteration (phyllosilicate fraction). Data from 17 meteorites are displayed, including 10 CM2s, 4 CM1s and 3 thermally metamorphosed CMs. Phyllosilicate abundance data were derived from Howard et al. (2015), King et al. (2017) and Lee et al. (2019b), while bulk O-isotope data are from Clayton and Mayeda (1999), King et al. (2017) and the Meteoritical Bulletin (2021). When only the CM2 chondrites are evaluated this produces a trelline with an R² value 0.63–63% of the data’s variance is explainable by the trelline. A positive Pearson coefficient of +0.79, demonstrates a strong correlation between these variables, while a p-value <0.005 reflects a high statistical confidence in the trend’s existence. Interestingly however, CM1 chondrites (shown in green) appear to plot off this trend, instead plotting at lighter-than-expected values given their high phyllosilicate contents. Although all CM1 chondrites are affected by terrestrial weathering that may have compromised their compositions. No unweathered CM1 falls are known, however, CM1 clasts within either Boriskino (Verdier-Paoletti et al., 2019) Mukundpura (Potin et al., 2020) could potentially resolve this issue. The isotopically light compositions of CM1 chondrites could suggest that alteration extent and bulk O-isotope composition are not closely correlated in the most intensely altered CM materials. This could indicate the CM1s originate from a different parent body to the CM2 chondrites.
among the CM2 chondrites (Fig. 11), an opposite response of progressively lighter compositions defines the more altered CM1s (Fig. 11). A similar trend is present among hydrated CR chondrites; bulk O-isotope composition and degree of alteration show a weak correlation (Schrader et al., 2011), but several examples can be found of meteorites which break this association, notably the intensely altered CR1 chondrite GRO95577 which is isotopically lighter than other less-altered CRs, including Al Rais (Schrader et al., 2011).

The lack of a clear correlation implies that additional factors were important in controlling alteration extent. It is possible that the anhydrous protolith of the CM1s may have had a different starting composition to that of the CM2 protolith, perhaps as a result of different relative abundances of their anhydrous components (chondrules, CAIs and matrix [Zanda et al., 2006]). If true, this would imply that two CM groups represent material from different parent bodies. Alternatively, variables other than the initial water and initial protolith compositions may have affected the degree of alteration. One possibility is temperature. Higher temperatures (potentially reflecting deeper regions within a large parent body) may have promoted more advanced alteration irrespective of O-isotope composition (King et al., 2017; Vacher et al., 2019b). However, alteration temperatures inferred from carbonate isotopic calculations (Fig. 12 and discussed further in Section 8.1) do not support this suggestion (Verdier-Paolletti et al., 2017; Telus et al., 2019). Instead, alteration may have operated as an open system (Young et al., 1999; Elmaleh et al., 2015; Alexander et al., 2015; Bland and Travis, 2017; Friedrich et al., 2018) allowing fluids and gases to flow away from the site of alteration and either escape into interplanetary space or move to other areas within a heterogenous parent body (e.g. as in the giant convecting mudball model – Bland and Travis, 2017). Under open system behaviour, the escape of reaction products (e.g. CH₄ and H₂, Guo and Eiler, 2007; Alexander et al., 2015) would force reaction equilibria to generate more products, thereby promoting more advanced alteration (Le Guillou et al., 2015) and facilitating a decoupling of O-isotope compositions from the degree of alteration. However, if the chondrule-matrix complementarity hypothesis is correct then open system alteration (allowing the escape of isotopically light ¹⁸O-rich fluids or gases from the parent body) would be ruled out (Bland et al., 2005; Palme et al., 2015; Friend et al., 2018; Hezel et al., 2018). Preservation of a complementarity signature in meteorites found at the Earth’s surface would require none of their original chemical or isotopic components to have escaped from the body, including during parent body alteration.

A former relationship between bulk O-isotopes and the degree of aqueous alteration may have existed but was subsequently erased. Most CM chondrites are finds (>97%) and therefore terrestrial weathering may have compromised their O-isotypic compositions. Data from the CM1 chondrites (summarized in Table 2 of King et al. (2017)) reveals evidence of partial equilibration with Antarctic waters, which has shifted their compositions towards lighter values (Fig. 11), making their pre-atmospheric compositions difficult to resolve (as explained in Greenwood and Franchi (2004) and Alexander et al. (2018)). Previously, Airieau et al. (2005 [Fig. 3]) noted a strong correlation between the fall age of CM meteorites and their O-isotope composition, implying that residence on Earth may have progressively altered the bulk isotopic compositions of CM material, shifting these to lower δ¹⁸O values, even while the samples were in curation. However, when a larger number of CM falls are considered (Fig. 13) this trend is not observed, demonstrating that it was instead an artefact of small sample statistics. Thus, time at the Earth’s surface alone does not appear to affect CM O-isotope composition, although time spent exposed to terrestrial weathering does affect isotopic compositions. The analysis of CM falls therefore provides the only opportunity to measure the fresh, unweathered O-isotope compositions. In recent years, several new CM falls have been characterised isotopically (e.g. Sutter’s Mill [Jenniskens et al., 2012], Maribo [Haack et al., 2012], Aguas Zarcas and Kolang [The Meteoritical Bulletin, 2021] [shown in Fig. 13]) or are currently under investigation (e.g. Mukundpura). However, none of these are classified as CM1 chondrites, preventing analysis of the relationship between bulk O-isotopes and the most extreme alteration extents (without the effects of terrestrial weathering overprints). A possible solution lies in the analysis of CM1 clasts held within fresh CM falls. Both the Mukundpura and Boriskino falls appear to contain fragments of CM1 material (Verdier-Paolletti et al., 2019; Potin et al., 2020) although there are currently no published O-isotope analyses from these clasts. In the absence of data, the question of whether weathering efficiently erases evidence of a former relationship remains unresolved.

Finally, a parent body mechanism may have erased the relationship between bulk O-isotopes and the degree of aqueous alteration. The most likely explanation would be thermal metamorphism. Experimentally heated CMs show a preferential loss of light ¹⁸O-rich oxygen, released from phyllosilicates during dehydration reactions, which results in a passive enrichment in heavier ¹⁶O-poor bulk compositions (Clayton and Mayeda, 1999; Ivanova et al., 2010, 2013; Lindgren et al., 2020). However, previous work comparing ~20 unheated and thermally metamorphosed CMs demonstrates that no clear relationship between O-isotopes and heating extent (Fig. 4 in Nakamura, 2005). This is most likely because the highly variable pre-metamorphic O-isotope compositions of CM chondrites and their differing degrees of thermal processing combine to generate a diverse array of O-isotope compositions. Thus, the relationship between bulk O-isotopes and aqueous alteration extent remains unclear.

7.2. The O-isotopic composition of secondary phases

Although the relationship between bulk O-isotope compositions and the degree of aqueous alteration remains unclear, at a finer scale the O-isotopic composition of secondary phases closely traces how aqueous alteration advanced—providing insights into the chronology of mineralization, the conditions of alteration and the evolution
of the parent body’s O-isotope system (Yurimoto et al., 2008).

Oxygen in secondary phases originates from two sources: oxygen recycled from accretionary phases, which have $^{16}$O-rich compositions (Yurimoto et al., 2008; Chaumard et al., 2018; Ireland et al., 2020) and oxygen derived from the alteration fluid, which started with large $^{17,18}$O enrichments. Estimates for the exact isotopic composition of the primordial CM water at the onset of aqueous alteration vary significantly (Fig. 5). Most other studies give values between $\delta^{17}$O = 9.2‰ and $\delta^{18}$O = 15.9‰ (Clayton and Mayeda, 1999) and $\delta^{17}$O = 35‰, $\delta^{18}$O = 55‰ (Fujiyama 2018). Secondary phases that formed early (e.g. tochilinite, T1 calcites and Fe-cronstedtite) record the heaviest O-isotopic compositions (Rowe et al., 1994; Benedix et al., 2003; Vacher et al., 2019a). However, as alteration advanced the composition of the fluid phase was progressively enriched in light $^{16}$O arising due to the dissolution alteration.
of $^{16}$O-rich accretionary phases (Rowe et al., 1994; Benedix et al., 2003; Yurimoto et al., 2008). Airieau et al. (2005) demonstrated how the $^{17}$O composition of sulfates (primarily gypsum) in CMs becomes progressively lighter as the degree of alteration increases. Similar trends are observed for magnetite (Telus et al., 2019), phyllosilicates (Halbout et al., 1986; Baker et al., 2002) and carbonates (Tyra et al., 2012; Verdier-Paoletti et al., 2017; Vacher et al., 2019b; Telus et al., 2019). Taken together estimates for the inferred O-isotope composition of water in CM chondrites (both estimates of the primordial starting composition and later evolved compositions) form a single trendline (Fig. 5). This line is referred to as the CM water (CMW) line (Verdier-Paoletti et al., 2017) and reflects how the O-isotope composition of water on the CM parent body progressively evolved as a result of equilibration with $^{16}$O-rich anhydrous solids. The CMW line plots parallel to the CM mixing line but with a distinct intercept ($\alpha_{0} = 2.12$, Verdier-Paoletti et al., 2017). The distance between the CMW line and the CM mixing line is a function of temperature during alteration and can therefore be used as a proxy to investigate the conditions on the parent body (Verdier-Paoletti et al., 2017; Vacher et al., 2019b). This is discussed in the following Section 8.1 with a focus on carbonates.

8. CONDITIONS OF AQUEOUS ALTERATION

8.1. Carbonates and their use as proxies for alteration

In CM chondrites several carbonate species are present, the most abundant is calcite, with minor phases including dolomite, aragonite and breunnerite (Riciputi et al., 1994; Lee et al., 2012, 2014). Calcite precipitated from the fluid phase, initially infilling void space, forming vugs and acting as a cement. Later generation calcite grew upon existing secondary phases or replaced primary anhydrous silicates, occasionally leading to the generation of chondrule pseudomorphs composed of calcite (Fig. 12 in Lee et al., 2014). Early alteration produced Fe-bearing calcite while later alteration favoured the precipitation of Mg-bearing calcite (Lee et al., 2014). The minor element cation compositions of calcite therefore mirror the evolution trend observed in phyllosilicates, further demonstrating that secondary phase compositions are directly related to the composition of the alteration fluid, both in terms of their chemistry (Velbel et al., 2012, 2015) and isotopic composition (Lindgren et al., 2017).

Calcite mineralisation was complex, with episodic growth periods interrupted by dissolution. Two main populations of calcite are recognized (Riciputi et al., 1994; Lee et al., 2013; Tyra et al., 2012, 2016; Lindgren et al., 2017; Vacher et al., 2017, 2019b). The first generation of calcites (T1) formed before the main growth windows for phyllosilicate and sulphides. These early calcites may have coprecipitated with other complex carbonates (e.g. breunnerite) facilitated by the presence of increasingly Mg-rich solutions (Lee et al., 2012). Meanwhile the later generation of calcites (T2) formed after phyllosilicates and sulphides (Lindgren et al., 2017). The second generation T2 calcites also replaced primary ferromagnesian silicates as well as infilling fractures to form veins (Lee et al., 2013).

Assuming that terrestrial alteration overprints can be ruled out (Tyra et al., 2007) carbonate in CM chondrites can be considered as “snapshots” of the C- and O-isotope systems at their time of formation. By analysing multiple grains, we can therefore explore how conditions evolved...
during aqueous alteration and track which isotopic reservoirs acted as sources of C and O for carbonates. In CM chondrites carbonates have highly variable $^{13}C$-rich compositions (relative to the Vienna Pee Dee Belemnite [VPDB] reference [Lodders and Fegley, 1998]). These generally range from $\delta^{13}C$: $+5\%e$ to $\delta^{13}C$: $+80\%e$ (Grady et al., 1988; Guo and Eiler, 2007; Alexander et al., 2015; Tyra et al., 2016; Vacher et al., 2017; Telus et al., 2019; Fujiya et al., 2020). Two main reservoirs could have acted as a source of $C$ for carbonates: soluble organic matter (Fujiiya et al., 2015, 2020; Tyra et al., 2016; Vacher et al., 2017) and C-rich ices (Alexander et al., 2015; Telus et al., 2019). As the CM lithology warmed volatile ices would have evaporated, generating C-bearing gases (either CO or CO$_2$). The oxidation of metal and organics would have further added small quantities of C-bearing gases (Alexander et al., 2015), while the alteration of anhydrous silicates released H$_2$ gas that could have reacted with CO/CO$_2$ to form CH$_4$ (Guo and Eiler, 2007; Alexander et al., 2015; Telus et al., 2019). In carbonate grains where both $\delta^{13}C$ and $\delta^{18}O$ measurements have been collected, a positive correlation is often reported. This may indicate that C-bearing gases were the dominant source of C for carbonates (Guo and Eiler, 2007; Alexander et al., 2015; Telus et al., 2019). Under such a scenario the largest $^{13}C$ enrichments could be explained if open system behaviour allowed isotopically light $^{13}C$ to preferentially escape the parent body (Guo and Eiler, 2007; Alexander et al., 2015). In contrast, Vacher et al. (2017) and Fujiya et al. (2020) argued that no systematic relationship between $\delta^{13}C$-$\delta^{18}O$ in carbonates exists with either positive or negative trends possible. Instead, they suggest that soluble organic water was more likely the dominant source of C owing to its high abundance in the CM matrix and similar isotopic composition ($\delta^{15}C$: $<+60\%e$). In their model, the heaviest carbonate compositions ($\delta^{13}C$: $<-80\%e$) could result from fractionation effects during oxidation and/or heating of organic matter (Vacher et al., 2017).

In contrast to C-isotopes, our understanding and interpretation of O-isotope compositions in carbonates is better resolved. Calcite O-isotope compositions are heavier than both bulk compositions and matrix separates. Typically, calcites range within $\delta^{17}O$: $-5\%e$ to $\delta^{18}O$: $15\%e$–$40\%e$ (Verdier-Paoletti et al., 2017). Second generation T2 calcites (Fig. 9D) are always isotopically lighter than the early-formed T1 calcites (Fig. 9A–C) (Tyra et al., 2012; Lindgren et al., 2017; Vacher et al., 2019b), consistent with the well-established trend of $^{16}O$-enrichment in secondary phases as aqueous alteration proceeded (Section 7.2). Collectively, both calcite generations define a single mass-independent trendline in $\delta^{18}O$/$\delta^{16}O$ isotope space (with slope values between 0.53 and 0.71), suggesting that their compositions solely reflect isotope exchange between $^{16}O$-rich silicates and $^{16}O$-poor fluids (Clayton and Mayeda, 1984, 1999; Benedix et al., 2003; Verdier-Paoletti et al., 2017). However, Vacher et al. (2019b) later argued that the two calcite generations should be considered separately. They showed that T2 calcites cluster around a single value while T1 calcites define a clear mass-dependent trend [slope $= 0.52$] that is indistinguishable from the terrestrial fractionation line (TFL).

The O-isotopic composition of calcites are dependent upon both the composition of the alteration fluid and the ambient temperature at their time of formation (Watkins et al., 2013). As a result, precipitation temperatures for both T1 and T2 calcites can be estimated providing insights into the conditions of alteration and how these changed over time (Fig. 12). Calcite temperature estimates require measured grain compositions, an inferred value for the fluid composition (at the time of formation) and an understanding of O-isotope fractionation behaviour between the fluid and calcite (Watkins et al., 2013). The greatest uncertainty in these estimates therefore lies in the values selected for the O-isotopic composition of the fluid phase. This is difficult because, currently, initial fluid compositions are poorly-constrained (Fig. 5 and Verdier-Paoletti et al., 2017; Fujiya 2018) and because the fluid phase evolved as aqueous alteration advanced (Yurimoto et al., 2008; Vacher et al., 2019b). Furthermore, direct measurements of fluid composition cannot be obtained by measuring other non-carbonate secondary phases because all minerals were affected to some degree by isotopic fractionation effects (Yurimoto et al., 2008).

Despite these uncertainties, the reconstructed alteration temperatures for calcites from independent studies generally show good agreement (Fig. 12). First generation T1 calcites formed at low temperatures (20–70 °C, Guo and Eiler, 2007; 10–100 °C, Vacher et al., 2019b) while second generation T2 calcites formed at higher temperatures (110–245 °C, Vacher et al., 2019b). Other studies which did not discriminate between calcite generations have temperature estimates that reflect the full range of conditions (59–167 °C, Verdier-Paoletti et al., 2017; <150 °C, Fujiya, 2018; –36–214 °C, Verdier-Paoletti et al., 2019). The perspective from calcite formation temperatures thus indicates that alteration operated along a prograde thermal path (increasing temperatures with time), concurrent with a decreasing W/R ratio (as water was progressively consumed in hydration reactions [Rosenberg et al., 2001]). Finally, the analysis of dolomite O-isotopes in three CM1s suggest alteration temperatures were between 65–185 °C (Telus et al., 2019). Similarly, Verdier-Paoletti et al. (2017, 2019) found no discernible difference in carbonate formation temperatures between the CM2 and CM1 chondrites. Thus, both studies support the idea that temperature was not responsible for differences in alteration extent between these two groups.

8.2. Conditions inferred from petrology, modelling, and experiments

Aqueous alteration operated under neutral to alkaline conditions (pH $\sim 7–12$, Zolensky, 1984; Zolensky et al., 1989; Rosenberg et al., 2001; Guo and Eiler, 2007; Chizmadia and Brearley, 2008; Palmer and Lauretta, 2011; Vacher et al., 2019a). Alkaline fluids promote the dissolution of anhydrous silicates as hydrolysis reactions break M$^{2+}$–O bonds, liberating SiO$_4$ tetrahedra into solution (Oelkers et al., 2018). Because dissolution rates are highly dependent on pH, water activity, temperature and exposed mineral surface area, increasingly alkaline (higher pH) systems with high water activities, higher temperatures and
large areas of exposed olivine/pyroxene promote serpen-
tinization reactions (Lamadrid et al., 2017; Oelkers et al.,
2018). At the nanoscale, a biphasic layered structure develops
on the silicate surface during dissolution. This is character-
ised by two amorphous regions, an inner Fe-rich
hydrated and oxidized region and an outer Mg-bearing
and water-rich zone (Le Guillou et al., 2015).

The early stages of aqueous alteration in CM chondrites
were dominated by the generation of intergrown TCIs. They
appear to have developed from multiple precursors in-
cluding FeNi metal grains, anhydrous silicates
(Pignatelli et al., 2017) and amorphous silicates
(Hewins et al., 2014; Leroux et al., 2015). Based on the experimental
reproduction of TCI-like assemblages Vacher et al. (2019a)
suggested that TCIs form first by the precipitation of
tochilinite from S-bearing, Fe-rich fluids under reducing
conditions. This was followed by a later episode of Fe-
cronstedtite precipitation from S-poor and more oxidising
fluids. However, the simultaneous precipitation of both
phases could have occurred at temperatures between 80
and 120 °C, with mildly alkaline fluids (pH = 7–8) and
reducing conditions (log $O_2$ = −65 to −60). Pignatelli
et al. (2016) similarly concluded that different or alternating
environmental regimes were likely required to produce
TCIs. They suggested that early alteration therefore operated
dermataneously as a series of localized microenvironments
evolving independently with time.

The growth of cronstedtite requires high Fe activities
(Fe/Si > 2.25) to stabilize the 1:1 layered structure of cron-
stedtite. At lower Fe activities 2:1 layered phyllosilicates
(such as talc, vermiculite, and montmorillonite) form
(Vacher et al., 2019a). Palmer and Lauretta (2011) showed
that the alteration of kamacite releases up to 81% of its ini-
tial Fe content into solution during alteration. The destruc-
tion of kamacite therefore acts as an essential Fe donor for
the formation of Fe-cronstedtite. However, as Fe activity
decreased and increasing quantities of anhydrous (Mg-
rich) silicates were dissolved the fluid composition evolved,
 favouring the formation of Fe/Mg-serpentines. The input
of Al and Mg into the fluid phase led to the partial dissolu-
tion and replacement of cronstedtite, by leaching of Fe$^{2+}$
and the formation of new serpentine minerals (Elmaleh
et al., 2015).

The advanced stages of alteration in CM chondrites are
-dominated by the serpentinization of chondrules and CAIs.
These reactions, along with the earlier oxidation of metal
produce H$_2$ gas. Open system behaviour would allow the
escape of H$_2$ gas and prevent the system achieving equilib-
rium, thereby promoting more advanced alteration whilst simultane-
ously sustaining oxidising conditions (Guo and Eiler, 2007).
Alternatively, H$_2$ gas may have been consumed in second-
ary reactions, for example reacting with inorganic carbon
species to form methane (Guo and Eiler, 2007; Elmaleh et al.,
2015). However, the presence of unfracti-
nated soluble element abundances in carbonaceous chon-
drites (including the CMs) instead argues for a closed
system alteration model with limited flow of fluids (Bland
et al., 2009) or a convecting mudball model in which soluble
elements are not fractionated because the system is thoro-
guously mixed (Bland and Travis, 2017). These two mutually
exclusive scenarios may be reconcilable if, during aqueous
alteration the parent body exhibited a form of partial open
system behaviour in which small molecules with very high
diffusivities (such as H$_2$ gas) acted under open system condi-
tions, while larger molecules (including H$_2$O and CH$_4$)
were prevented from escaping. Whether aqueous alteration
in the CM chondrites was either an open or closed system
or allowed large scale fluid flow or limited escape of gases
remains unanswered. Resolving this question will signifi-
cantly aid our understanding of the aqueous alteration
dynamics and provide constraints on other alteration vari-
able, including the initial W/R ratio.

8.3. Reconstructing water-to-rock ratios (W/R)

Water-to-rock ratios can be estimated by mass balance
calculations using either bulk O-isotope compositions
(Fig. 5 in Clayton and Mayeda, 1999; Brearley, 2006;
Fig. 2a in Fujiya 2018) or elemental (either H or O) stoi-
chiometry (Howard et al., 2015). Stoichiometric approaches
are useful for constraining the minimum initial water
needed to reproduce the hydrated mineralogy in a given meteorite. Howard et al. (2015) calculated values of 17
wt.% H$_2$O for an average CM1 bulk composition. This is
consistent with previous estimates by Kallemeyn and
Wasson (1981) and translates to a W/R of ~0.2. However,
aqueous alteration may have operated with water in excess
of the stoichiometric value. Under open system behaviour
H$_2$ produced in oxidation reactions can escape. As a result,
stoichiometric calculations cannot provide reliable upper estimates for the W/R ratio. Alternatively, O-isotopic mass
balance calculations act as an independent approach, but
again suffer relatively large uncertainties originating due
to a poorly-constrained composition of the primordial
CM water (Fig. 5). Most estimates of the initial W/R ratios
for the CM lithology fall between 0.2 and 0.7 (Fig. 14).
Values likely span a range reflecting variable conditions
across the parent body due, for example to the heteroge-
neous accretion of ices and variable porosity and permeabil-
ity limiting water access to some regions (Bland et al., 2009;
Rubin, 2012). A range of W/R ratios appear to be reflected in
the different degrees of alteration extent preserved in dif-
f erent CM meteorites (Rubin et al., 2007).

In a relative sense the CM lithology accreted more
water than the nominally anhydrous CO and CV chon-
drites (W/R: 0.01–0.1 and 0.1–0.2 respectively
[Marrrochi et al., 2018]) and potentially similar quantities
to the CR chondrites (Marrocchi et al., 2018) and CY
chondrites (King et al., 2019a, 2019b). The CI chondrites
most likely accreted the highest W/R ratios of any group,
as demonstrated by their high surviving water contents
(18–21 wt.% inferred from TGA over the temperature
range 200–900 °C [Garenne et al., 2014; King et al.,
2015b]), heavy bulk O-isotope compositions (Clayton
and Mayeda, 1999) and completely hydrated and oxidized
mineral assemblages (King et al., 2015a, 2015b). Water-to-
rock ratio estimates for the CI chondrites are poorly
resolved and estimated at >0.6 (Zolensky et al., 1989;
Clayton and Mayeda, 1999; Brearley, 2006; Zolotov,
2012; Pravdivtseva et al., 2018).
9. ORGANIC MATTER AND AQUEOUS ALTERATION

Hydrated CCs contain an abundant and diverse complement of organic matter (Schmitt-Kopplin et al., 2010), much of this is in the form of IOM (Alexander et al., 2017; Vinogradoff et al., 2017). Recently Vollmer et al. (2020) reported in-situ analyses on localised regions of highly primitive organic matter in the CM chondrite Mabo. This organic matter contained high abundances of C=O double bonds and isotopically light nitrogen (d15N: /C24/C0 200‰ [relative to terrestrial values]), characteristics suggesting these grains were inherited from the interstellar medium and survived later parent body alteration.

Some studies have concluded that the degree of aqueous alteration shows no clear relationship with the organic matter, as investigated using Raman spectroscopic analysis (e.g. Fig. 7 in Busemann et al., 2007; Quirico et al., 2014). In contrast, Vinogradoff et al. (2017) analysed two CM2 meteorites (Paris and Murchison) whose component clasts (on average) represent different alteration extents. They demonstrated that hydrothermal alteration results in aromatization and oxidation of the IOM whilst also decreasing nitrogen and free radical abundances. Likewise, Chan et al. (2017) analysed the association of organics and carbonates in five CM chondrites. They demonstrated that the two generations of calcite have distinctly different organic matter abundances. First generation calcites lack embedded organic matter, suggesting formation from highly oxidising fluids. Meanwhile second generation calcites contain abundant organic matter and therefore precipitated from fluids rich in soluble organic matter. Furthermore, the organic matter present in second-generation calcites experienced high temperatures (thermal maturation). This chronology requires that some fraction of the organic matter now observed in CM meteorites was created during aqueous alteration and potentially indicates that at higher temperatures, CO2 gas liberated from the thermal decomposition of first-generation calcites may have reacted to form new organic phases (Chan et al., 2017). Comparing CM2 and CM1 chondrites Botta et al. (2007) noted that amino acid contents in the CM1s are always lower than the less-altered CM2 chondrites. This may further support the suggestion that CM1 chondrites experienced more oxidizing conditions and potentially higher temperatures than the CM2 chondrites.

10. CHARACTERIZING AQUEOUS ALTERATION USING IR SPECTROSCOPY

Infrared spectroscopy is a powerful tool for investigating aqueous alteration (Fig. 15). Spectroscopic analysis can detect changes in mineralogy, mineral cation composition and the degree of hydration. Furthermore, spectroscopic analysis is unique among our inventory of analytical techniques, because data collected from meteorite samples can be compared against equivalent data collected by telescope or spacecraft from asteroid surfaces. Thus, spectroscopic information gained from meteorites directly informs our analysis of remote sensing data, helping to resolve the grain size, composition and parent body affinities of asteroids (e.g. Johnson and Fanale, 1973; Vilas and Gaffey, 1989; Burbine, 1998; Ostrowski et al., 2010; Takir et al., 2015; McAdam et al., 2015; Vernazza et al., 2016; Le Corre et al., 2018; McSween et al., 2018; Cloutis et al., 2018; Kitazato et al., 2019; Hamilton et al., 2019; Bates et al., 2020; Hanna et al., 2020).

10.1. The visible and near-IR region

At short wavelengths (0.7–2.5 μm [Fig. 15A]) the visible and near-IR (VNIR) reflectance spectra of CM chondrites appear as smooth profiles with weak absorption bands. They are characterized by moderately blue-sloped (decreasing reflectance with increasing wavelength) or moderately red-sloped (increasing reflectance with increasing wavelength) profiles (e.g. Vernazza et al., 2016). Spectral slope is influenced by many factors including sample temperature, texture (rock vs. powder), grain size, the abundance of opaque minerals (e.g. metal and magnetite), the abun-
A) Visible and near-IR reflectance spectra

- Fe$^{2+}$/Fe$^{3+}$ charge transfer
- Fe$^{3+}$ crystal field transitions
- Mg-OH
- 3 μm region: M-OH

B) Mid-IR transmission spectra

- Absorption max.
- Si-O stretching feature: ‘Olivine shoulder’
- Si-O bending feature: ‘Olivine shoulder’

C) Mid-IR reflectance spectra (particle size <35 μm)

- Christiansen feature
- Transparency feature
dance of organic phases, viewing geometry and overprints by terrestrial weathering. Early studies working with powdered samples noted how grain size controlled spectral slope with finer grains producing more red-sloped spectra (Johnson and Fanale, 1973; Burbine, 1998). However, Cloutis et al. (2011) instead concluded that darker spectra and those with a higher abundance of matrix tended to have bluer slopes. Later McAdam et al. (2015) observed that spectral slope (calculated between 0.6 μm and 2.4 μm) is weakly correlated with phyllosilicate abundance, with lower phyllosilicate abundances producing red-sloped spectra. However, they cautioned that spectral slope is not directly correlated with mineralogy and should therefore not be used to infer composition. More recently Bates et al. (2020) illustrated that spectral slope (calculated between 0.65 μm and 1.05 μm) appears to decrease as phyllosilicate and magnetite abundances increase, leading to general rule that more altered CM chondrites tend to have bluer spectral slopes. In addition, some CMs have shallow absorption bands (with depths <12% [Cloutis et al., 2011]) located at 0.7 μm, 0.9 μm, 1.1 μm and 2.3 μm that are associated with Fe-bearing and Mg-bearing phyllosilicates (Vilas and Gaffey, 1989; Cloutis et al., 2011; McAdam et al., 2015; Beck et al., 2018) and whose band depths correlate with phyllosilicate abundance (Cloutis et al., 2011; Beck et al., 2018). The work of Potin et al. (2019) compared the spectral response of meteorite chips and powdered meteorites. They demonstrated that powdered samples (which approximate asteroid regolith) produce darker spectra but also preserve stronger absorption features. By contrast, meteorite chips, whose spectra are more relevant to the analysis of rubble-pile asteroids such as Bennu and Ryugu (objects which lack a fine-grained regolith covering) instead have brighter spectra but with weaker absorption features. Both features, slope and absorption bands can therefore be useful in resolving mineralogy and alteration extent.

10.2. The three-micron region

At longer wavelengths, the three-micron region (~1.8–4.0 μm [Fig. 15A]) provides information on a range of molecular vibrations. Primarily this region is used to analyze M=OH bonds present in hydrated phyllosilicates (Feierberg et al., 1985; Miyamoto and Zolensky, 1994; Sato et al., 1997; Beck et al., 2010, 2014; Takir and Emery, 2012; Takir et al., 2013, 2015; Lindgren et al., 2020) but also provides information on C=H bonds in organics (Kebukawa et al., 2011; Orthous-Daunay et al., 2013), C=O bonds in carbonates (Takir et al., 2013), S=H bonds in organosulfur compounds (Nava et al., 2020) and N=H bonds in ammoniated phases (Bishop et al., 2002; McSween et al., 2018). Unfortunately, the three-micron region is complicated to interpret for several reasons. Absorption by water molecules in Earth’s atmosphere significantly limits the potential of ground-based telescopes to observe this spectral feature on asteroids (Feierberg et al., 1985; Gaffey et al., 1993; Takir et al., 2015). Conversely, lab-based analyses of powdered meteorite samples are readily affected by adsorbed terrestrial water. This modifies the shape of the three-micron region and therefore requires heat-treatment to remove. Samples must then be analysed without further exposure to air, requiring measurements to be collected in a vacuum, which has the additional advantage of more accurately mimicking the environment of an airless body (Beck et al., 2010, 2014; Takir et al., 2013, 2019; Bates et al., 2020). The resulting spectra typically have shallower features with better-defined (sharper) absorption bands and therefore produce closer matches to asteroid spectra (in comparison to samples that were not heated or those that were collected under ambient temperature and pressure) (Takir et al., 2019; Bates et al., 2020; Beck et al., 2020). Recently however, Hanna et al. (2020) demonstrated that polished sections are less affected by adsorbed terrestrial water. They argued that the conventional heat-treatment protocol may also alter the native water complement through the modification of highly heat-sensitive phases (notably by the thermal decomposition of tochilinite).

Hydrated CCs generally have an asymmetric profile over the three-micron region, with a steep shoulder on the short wavelength side and a shallow sloping shoulder on the long wavelength side. Both band centre and band depth correlate with the total phyllosilicate content and with phyllosilicate cation composition, allowing changes in the Fe/Mg ratio to be observed (Fig. 15A). Sharper and deeper bands located at shorter wavelengths correspond to more advanced alteration resulting from higher phyllosilicate contents and more Mg-rich compositions (Beck et al., 2010; Takir et al., 2013, 2019; Bates et al., 2020; Hanna et al., 2020). Recently Beck et al. (2020) demonstrated that band depth at 2.75 μm and 2.80 μm corresponds to water
content at a ~ 4 wt.% uncertainty level (Beck et al., 2020). Band area has also been found to be a useful metric as it correlates with both magnetite and Fe-rich phyllosilicate abundance (Bates et al., 2020). Analysis of the three-micron spectral region on asteroids could therefore potentially be used to infer approximate surface composition and water contents.

10.3. The mid-IR region

At mid-IR (MIR) wavelengths (5–25 μm [Fig. 15B and C]) Si–O vibrational features originating from silicates are detectable. Consequently, phyllosilicates dominate the spectra of CM chondrites over these wavelengths. However, this region also produces complex features associated with mineral optical properties, volume scattering and surface scattering effects. Here we discuss transmission and reflectance spectra separately as they reveal distinctly different features.

Transmission spectra of CM chondrites (Fig. 15B) produce a single relatively narrow smooth feature located at ~10 μm – corresponding to the presence of serpentine minerals (Sandford, 1984; Beck et al., 2014). Some spectra also have smaller olivine bands located at 11.2 μm (with additional bands at 16.5 μm and 19.5 μm) (Sandford, 1984; Beck et al., 2014). The intensity of the three micron hydration feature (Section 10.2) and the strength of the 11.2 μm olivine feature are anticorrelated, reflecting the progressive loss of anhydrous silicates and an increasing phyllosilicate content as aqueous alteration advanced (Beck et al., 2014).

In reflectance (Fig. 15C), the spectral signature and resulting shape of phyllosilicate vibrational features are strongly affected by grain size. Spectra collected from polished sections more accurately reflect the spectra obtained from coarse-grained and rocky surfaces (Hanna et al., 2020). They show the Christiansen feature, a reflectance minimum located between 8 and 11 μm, originating due to the refractive index of a sample approaching the refracting index of the surrounding medium. This feature moves relative to the Si–O bending minimum (located at ~10 μm). As phyllosilicate content increases, the Christiansen feature shifts to longer wavelengths (moving from approximately 8.5 μm to 9.0 μm), while simultaneously the Si–O bending minimum migrates to shorter wavelengths (approximately 10.6–10.3 μm). Thus, the separation between these two features decreases as alteration extent increases (Hanna et al., 2020). Because the correlation between these variables is robust this relationship could be applied to the future analysis of new CM chondrites or even used to infer the alteration extent of distant C-type asteroid surfaces (Hanna et al., 2020).

Spectra obtained from fine-grained meteorite powders (<75 μm) simulate the spectral behaviour of astroids covered by fine-grained regolith (Mustard and Hays 1997; McAdam et al., 2015; Landsman et al., 2018; Bates et al., 2020). The vibrational region at longer wavelengths than the Christiansen feature does not show the same Si–O bending features that are observed in spectra from polished sections. This is because fine-grained powders are optically thin over the 11–13 μm region, leading to volume scattering effects (e.g. Salisbury, 1993). This results in reflectance maxima termed the transparency feature, the position of which correlates with sample mineralogy. Both McAdam et al. (2015) and Bates et al. (2020) observed that the transparency feature shifted to shorter wavelengths as aqueous alteration extent increased. Additionally, in the most altered CM1/2s and CM1s, Bates et al. (2020) demonstrated that the Christiansen feature is also sensitive to the Mg content of phyllosilicates, shifting to shorter wavelengths as Mg concentration rises.

When comparing meteorite spectra to remote asteroid spectra in the MIR, an additional complication is the dominance of emitted spectral flux. In contrast to reflected light (typically measured in the laboratory and discussed above), the spectra of remote airless bodies are dominated by thermal emission with only a small contribution from reflectance (e.g. Harris 1998; Harris et al., 1998). An emissivity spectrum can be approximated from a reflectance spectrum using Kirchhoff’s law (E = 1 – R). Although this simplification is often-used (e.g. as in Lindgren et al. (2020)), it is only accurate for Lambertian surfaces (those that reflect light diffusely), and when collecting directional hemispherical reflectance. As emissivity and reflectance are heavily affected by viewing angle, directional components typically prevent quantitative analysis. Kirchhoff’s law therefore provides only a qualitative description of emissivity in the case bidirectional or biconical reflectance, which are the most common spectral datasets currently collected (Christensen and Harrison, 1993; Salisbury et al., 1994). As a result, there is now increased focus on the collection of emissivity measurements for meteorites under appropriate near-surface asteroid conditions. Such data provide more accurate comparisons to remote asteroid spectra (e.g. Donaldson Hanna et al., 2012, 2019; Glotch et al., 2018; Britt et al., 2019). This requires specific environmental chambers to accurately reproduce the thermal gradients expected in the near-subsurface of a C-type asteroid.

11. TIMESCALES OF ALTERATION

During the early solar system, several short-lived radionuclide decay systems were active. The rapid decay of unstable radionuclides produced heat which served as an energy source driving alteration processes (both low temperature aqueous alteration and higher temperature thermal metasomatism) (e.g. Grimm and McSween, 1989; Miyamoto, 1991; Keil, 2000; McSween et al., 2002; Krot et al., 2006; Visser et al., 2020). In many instances the decay of a radioactive parent to a stable daughter particle resulted in the preservation at anomalously high concentrations of some elements within mineral structures. These decay systems provide a unique resource for the dating of major events in the early solar system. Formation ages can be reconstructed where primary accretionary minerals are dated, while the timescales of parent body alteration can be reconstructed by dating secondary minerals. The $^{53}$Mn–$^{53}$Cr radiochronometer has a half-life of 3.7 Ma and is therefore capable of dating events occurring within the first 20 Ma of the solar system’s formation. Secondary carbonates fractionate Mn and Cr during forma-
tion, as a result they are suitable hosts for the $^{53}$Mn-$^{53}$Cr radiochronometer. The decay of $^{53}$Mn produced an anomalous excess $^{53}$Cr in carbonate minerals. Measuring this excess provides relative ages for carbonate minerals. However, accuracy is limited by unsuitable reference standards as well as the difficulties with the precision of $^{52}$Mn/$^{52}$Cr ratio measurements (Fujiya et al., 2012, 2013; Jilly et al., 2014).

The analyses of de Leuw et al. (2009) produce alteration ages of 4567.6–4563.0 Ma – expressed in relative terms this is between 0.6 and 4.4 Ma after the formation of (CV) CAIs (dated at 4568.2 Ma ago, Bouvier and Wadhwa 2010). More recent work suggests younger formation ages and therefore the late onset of aqueous alteration in the CM parent body (Fig. 16). The data of Fujiya et al. (2012), Jilly et al. (2014) and Visser et al. (2020) show good agreement, they analysed carbonates in six CM meteorites (and a further six CM clasts [Visser et al., 2020]). Most data give alteration ages between 4566.0 and 4560.2 Ma, equivalent to 2.3–8.0 Ma after CAIs, with an average value of ~5.1 Ma (after CAIs). Visser et al. (2020) noted that the onset and duration of parent body alteration is similar across all the carbonaceous chondrite groups measured to date (COs, CMs, CYs and CIs). Furthermore, this timing matches the peak heating expected from the decay of short-lived $^{26}$Al radioisotopes (on parent bodies with sizes >30 km diameter [Doyle et al., 2015]), implying that the primary driver of aqueous alteration was radiogenic decay (and not impact events) across all the different CC groups.

### 12. AQUEOUS ALTERATION OVERPRINTED BY THERMAL METAMORPHISM

Some CM chondrites were affected by a post hydration thermal metamorphic overprint (~200 °C to >750 °C). They have a dehydrated mineralogy (Nakamura, 2005; Nozaki et al., 2006; King et al., 2019a, 2019b; Lindgren et al., 2020), low water contents (Tonui et al., 2014; Garenne et al., 2014), volatile-depleted bulk chemical compositions (Cd, Tl, Bi, In, Zn, Te and Ag [Wang and Lipschutz, 1998; Moriarty et al., 2009; Mahan et al., 2018]), low noble gas contents (Tonui et al., 2014) and graphitized organic matter (Busemann et al., 2007; Chan et al., 2017; Quirico et al., 2018; Schmidt and Hinrichs, 2020). Notable thermally metamorphosed CM chondrites include Sutter’s Mill, EET 96029, WIS 91600, Jbilet Winselwan, A-881655, Y-793495, Y-790992, PCA 91008 and many other Antarctic finds (Wang and Lipschutz, 1998; Moriarty et al., 2009; Lee et al., 2016; King et al, 2019b; Quirico et al., 2018; King et al., 2021).

Nakamura (2005) established a scale to classify thermally metamorphosed hydrated CCs, based on

![Fig. 16. The timing of alteration on different parent bodies inferred from $^{53}$Mn-$^{53}$Cr dating of secondary carbonates in hydrated chondrites (and fayalite in the CO, CV and ordinary chondrite parent bodies). Data are displayed relative to the formation age of CV CAIs, given at 4568.2Ma ago (Bouvier and Wadhwa, 2010). Data were taken from Fujiya et al., 2012, 2013; Jilly et al., 2014; Doyle et al., 2015 and Visser et al., 2020. The onset of aqueous alteration in CM chondrites occurred later than the ordinary chondrites but otherwise appears similar in both timing and duration to values obtained from other carbonaceous chondrites (CIs, CYs, COs, Tagish Lake and CM/C1 clasts).](image-url)
mineralogical changes revealed by XRD. Minimally meteorites (stage I, <250 °C) retain clear diffraction peaks originating from hydrated phyllosilicates. However, at higher peak temperatures phyllosilicates lose structurally bound OH molecules, resulting in highly disordered structures that lack well-defined diffraction peaks (stage II, 300–500 °C). Further heating results in the partial recrystallization of this highly disordered material, forming a groundmass of nanoscale olivine. These meteorites have broad, weak diffraction peaks associated with poorly recrystallized olivine (stage III, 500–750 °C). The highest peak temperatures correspond to completely anhydrous samples with a well-developed recrystallized groundmass (stage IV, >750 °C).

Using experimental heating of the CM2 chondrite ALH 83100 Lindgren et al. (2020) explored how the thermal stages defined by Nakamura (2005) correspond to changes in bulk O-isotope composition, IR spectra, accessory mineral assemblage and Raman G/D band features, thereby providing a more holistic understanding of the effects of heating on the CM lithology.

The analysis of organic matter provides an alternative independent assessment of a sample’s alteration history. Insoluble organic matter is highly sensitive to heating and responds to progressively higher peak temperatures (and longer duration heating) by graphitization (e.g. Chan et al., 2019). Raman spectroscopic analysis of G and D band parameters can therefore be used as geothermometers to trace the thermal history of CCs – estimating the peak metamorphic temperature (PMT) of individual meteorites (e.g. Busemann et al., 2007; Chan et al., 2017; Visser et al., 2018; Schmidt and Hinrichs, 2020). Busemann et al. (2007) concluded that unheated CM chondrites most likely experienced PMT < 240 °C, while Visser et al. (2018) analysed CM-like clasts held within ureilites and Howardite-Eucrite-Diogenite (HED) meteorites and arrived at temperatures between 50 and 110 °C. Meanwhile, Chan et al. (2017) analysed two thermally metamorphosed samples and concluded they experienced temperatures of <310 °C (Jbilet Winselwan) and <413 °C (WIS 91600). However, strikingly different PMT estimates were reported by Schmidt and Hinrichs (2020), who suggested that both heated and unheated CM chondrites never exceeded temperatures of 330 °C. Variability in Raman temperature estimates originates due to uncertainties over the duration of heating (e.g. Chan et al., 2019; Schmidt and Hinrichs, 2020), with the response of IOM differing significantly dependent on whether heating operated over short time-scales (e.g. weeks) or long timescales (e.g. 10s of thousands of years) (Fig. 3 in Schmidt and Hinrichs, 2020). In addition, uncertainty also arises due to variability in the precursor composition of the IOM (Quirico et al., 2009) and due to natural variability within a heterogenous sample or where different clasts within a brecciated meteorite are studied. Often Raman PMT estimates produce contradictory conclusions when compared against petrographic evidence, with organic matter suggesting high peak temperatures while the sample’s mineralogy preserves hydrated phyllosilicates (as in Quirico et al., 2014). Such discrepancies could indicate an earlier episode of thermal processing that affected the organic matter prior to its inclusion into the parent body, possibly within the protosolar disk environment (Quirico et al., 2014).

Quirico et al. (2018) used a combination of Raman and IR data (2.5–20 μm) to analyse IOM in 34 CM chondrites (and a further five C2-ung chondrites). They estimated that ~36% were thermally metamorphosed, providing a conservative upper estimate on the prevalence of metamorphism among the CM chondrite population (Quirico et al., 2018). Quirico et al. (2018) defined metamorphosed samples as those with evidence of modification to their IOM although no temperature estimates were given. They identified five groups, representing unheated, weakly heated (showing only chemical alteration), moderately heated (with evidence of slight modification to IOM), strongly heated (with extensively altered IOM) and unclassified anomalous members (including the CM-like meteorites Bells and Essebi). Among their sample population two strongly heated CMs (PCA 02012 and PCA 91008) demonstrated evidence of short-duration heating – based on differences in the structure of their IOM, when compared to type 3 chondrites affected by long-duration thermal metamorphism. This finding indicates impacts were likely the cause of heating in at least some CM chondrites (Quirico et al., 2018). Close agreement between the newly defined carbon-based classification system of Quirico et al. (2018) and the mineralogical system of Nakamura (2005) implies that both proxies are reliable indicators for reconstructing the thermal histories of carbonaceous chondrites.

Recently, Amsellem et al. (2020) used the 87Rb-87Sr radiochronometer to investigate the timing of thermal metamorphism in five CM chondrites. They concluded that in all samples metamorphism occurred at least 3 Ga after the formation of the solar system. If correct, this excludes radiogenic heating as a source of energy and instead suggests impacts as the most likely. Comparing inferred metamorphism ages against the reconstructed formation ages for several C-type asteroid families the authors show possible correlations between individual meteorites and specific asteroid families (Fig. 4 in Amsellem et al., 2020). Although some dates overlap, significantly stronger evidence would be required to provide convincing links. An alternative to impact heating is solar radiant heating. This could have driven thermal metamorphism on some bodies. The OSIRIS-REx mission revealed the presence of thermally fractured rocks on Bennu, with evidence of fatigue-driven exfoliation and crack propagation (Molaro et al., 2020). Similarly, solar radiant heating has been suggested as the origin of thermal metamorphism for the CK chondrites (Chaumard et al., 2012) and as a viable energy source driving aqueous alteration reactions on comets (Nakamura-Messenger et al., 2011; Suttle et al., 2020c). In either case, the work of Amsellem et al. (2020) could be applied to the returned samples, notably for material from Ryugu which appears to be partially dehydrated – suggesting a former metamorphic event (Kitazato et al., 2019) that could be dated.

13. PARENT BODY DISRUPTION

Many CM meteorites may be samples of regolith material that once resided exposed at the surface of their parent
asteroid (Bunch et al., 1979; Bunch and Chang, 1980; Nakamura et al., 1999; Nakamura, 2006; Zolensky et al., 2014). Xenolithic fragments as observed in Murray (Bunch and Chang 1980) and Sutter’s Mill (Zolensky et al., 2014) or fragments potentially derived from the deep interior of the CM parent body (as identified in Murchison [Kerraouch et al., 2019]) combined with observations of pervasive impact-induced brecciation (e.g. Hanna et al., 2015) are strong evidence that some CM meteorites were located at the surface of their parent asteroid. Alternative evidence comes from noble gas studies. In space, exposed rocks on airless bodies are irradiated by solar wind and galactic cosmic rays. An abundance of implanted solar noble gases is therefore conclusive evidence of a regolith origin (Nakamura et al., 1999). However, not all CM chondrites have high solar noble gas contents. Nakamura (2006) analysed seven CM chondrites and concluded that only one meteorite (the thermally metamorphosed Y-793321) was likely to have been a regolith sample.

In contrast, fragments of CM chondrite and CM-like lithologies have been identified as xenolithic clasts within other extraterrestrial materials. These include the Vestan HED meteorites (Bunch et al., 1979; Gounelle et al., 2003; Rubin and Bottke, 2009; Visser et al., 2018, 2020; Patzek et al., 2020), the ordinary chondrites (Patzek et al., 2018, 2020) and among Lunar regolith samples (Wasson et al., 1975; Joy et al., 2020). Interestingly however, embedded clasts of CM material are absent among the other meteorite groups (including the CR and CI chondrites, Patzek et al., 2018). Many of these CM clasts are hydrated requiring that they survived transport without significant heating, indicating that they were transported by low-velocity impacts (Patzek et al., 2018; Joy et al., 2020). In addition to xenolithic CM clasts, CM-like material is abundant among the cosmic dust flux that reaches Earth. Numerous studies have reported micrometeorites with either direct affinities to CM chondrites (e.g. van Ginneken et al., 2012) or CM-like particles (Kurat et al., 1994; Taylor et al., 2012; Suttle et al., 2017, 2019b). This includes among the Transantarctic Mountain (TAM) micrometeorites collection whose exceptionally long accumulation ages (<2 Ma) sample the ancient dust flux reaching Earth.

Cosmic-ray exposure (CRE) age dating provides a means of evaluating how long individual meteorites spent in space, after liberation from below the surface of their parent body and before landing at the Earth’s surface (Herzog and Caffee, 2014). The CM chondrites are unusual in that they have exceptionally short cosmic ray exposure ages indicating rapid transport and recent parent body disruption. Approximately one third of CM chondrites have CRE ages <1 Ma, approximately half have CRE ages <2 Ma and all measured CMs have CRE ages <20 Ma (Morbidelli et al., 2006; Nishizumi et al., 2014; Zolensky et al., 2020). This is in stark contrast to the age profiles of other meteorite groups which extend up to >100 Ma. Short CRE ages potentially indicate a near-Earth asteroid source for some CM meteorites (Morbidelli et al., 2006; Nishizumi et al., 2014). Furthermore, the CRE age data for CM chondrites appear to show four distinct peaks (Zolensky et al., 2020), indicating multiple release events. This could represent either a single body being impacted several times or several different bodies disrupting over time. Although a tentative relationship between CRE ages and the degree of aqueous alteration has been suggested, with a general trend of younger exposure ages correlating with more aqueously altered samples (Zolensky et al., 2020) this requires further systematic investigation to confirm. If each CRE age group is found to correlate with a given alteration extent then this could be evidence of multiple CM parent bodies with distinct characteristics breaking up at different times. Alternatively, if no relationship is found then this implies the breakup of a heterogenous parent body releasing materials of differing alteration extent simultaneously.

The current Hayabusa-2 and OSIRIS-REx missions to C-type asteroids (Ryugu and Bennu respectively) have shown that these small bodies (both <1 km diameter) are rubble-pile asteroids, representing a loose gravity-bound aggregation of impact debris formed by re-accretion after a catastrophic collision of its original parent body (Walsh, 2018; Okada et al., 2020). The vast majority of small asteroids (<10 km diameter) are likely to be rubble-pile bodies, reflecting the ultimate fate of objects in the asteroid belt – collisional disintegration. (Walsh, 2018). If Ryugu and Bennu are composed of CM chondrite material (Clark et al., 2011; Binzel et al., 2015; Le Corre et al., 2018; Kitazato et al., 2019; Hamilton et al., 2019) this would in turn attest to the collisional destruction of the CM parent body and its subsequent re-accretion as a series of smaller second-generation objects. The multi-peak CRE age data could therefore reflect meteorites derived from several rubble-pile CM asteroids in near-Earth orbits.

14. SUMMARY OF ALTERATION

The accretionary CM3 lithology was altered by alkaline fluids (likely between pH 7–8 and certainly pH < 12) at relatively high W/R ratios (0.2–0.7), under oxidizing conditions and at modest but progressively higher temperatures (20–200 °C) (Fig. 17). Early alteration (Fig. 7) was dominated by the replacement of amorphous silicates and FeNi-metal. Sulphur, liberated from primary sulphides and GEMS-like silicates precipitated as tochilinite, while the dissolution of metal raised Fe activities in the alteration fluid ensuring that Fe-cronstedtite could crystallize. Early alteration was likely heterogenous characterized by a series of small microenvironments and resulted in intergrown tochilinite-cronstedtite and a first generation of calcite. By contrast, advanced alteration was more homogenous and characterized by the widespread replacement of anhydrous Mg-rich chondrule and CAI silicates with Mg-serpentines. The addition of Mg to the fluid phase corresponds to the transition from Fe-rich to Mg-rich secondary phases (a trend observed in both phyllosilicates and calcite). A small number of CM chondrites attest to complete replacement by secondary phases (CM1s). They contain only pseudomorph chondrule outlines and a mineralogy dominated by Mg-rich phyllosilicates and magnetite. Alteration also affected organics, resulting in more oxidized and aromatized compounds.
The extent of aqueous alteration as measured by the relative abundance of phyllosilicate or the degree of hydration is highly variable. More altered chondrites may have accreted proportionally more water (higher W/R ratios) and therefore show heavier bulk O-isotope compositions. However, current data from (partially weathered) CM1 chondrites show lighter-than-expected O-isotope compositions. This implies that additional factors may have also controlled the extent of alteration. This could include longer alteration timescales, higher temperatures, open system behaviour (allowing the escape of H$_2$ gas) or variability in the isotopic composition of primordial components (anhydrous protolith and CM water). To resolve this problem the community requires additional O-isotopic work on unweathered CM1 chondrites, which will accurately constrain their pre-atmospheric isotopic compositions. Unfortunately, such measurements are dependent on the discovery of new CM1 falls.

The relationship between impacts and aqueous alteration is complex. The presence of brecciated meteorites containing differently altered clasts requires that fluid interaction began before impact heating and was heterogenous on a planetesimal scale. However, the correlation between shock deformation and more advanced alteration also suggests that collisions imparted significant heat energy that drove further aqueous alteration. This could indicate multiple discrete episodes of aqueous alteration. Some CM chondrites are samples of regolith that once resided at the surface of their airless parent body.

Infrared spectroscopy (both near and mid-IR) is capable of accurately tracing the degree of aqueous alteration in laboratory samples. These studies provide critical information for the interpretation of C-type asteroid spectra and indicate that the surfaces of many asteroids were hydrated and have been subsequently dehydrated. They show close affinities to the CM lithology.

Approximately one third of CM chondrites experienced post aqueous alteration thermal metamorphism, with impacts as the likely cause of heating. Metamorphosed CMs have a dehydrated mineralogy, graphitized organic matter and depleted volatile element compositions. Metamorphism operated as an open system allowing the escape of fluids.

Finally, the CM parent body (or bodies) was/were catastrophically disrupted by impact events, as evidenced by the presence of clastic CM material present in other meteorites, the dominance of CM micrometeorites among the extraterrestrial dust flux and the presence of CM-like rubble pile asteroids (e.g. Bennu and Ryugu).

15. FUTURE OUTLOOKS

Major outstanding questions include:

1. **Did aqueous alteration operate as an open system environment?** This could be either by the escape of H$_2$/CH$_4$ gas to interplanetary space or by facilitating large-scale fluid transport within the parent body?

2. **What was the initial composition (or compositional range) of the primordial CM water?** Better constraints on the O-isotopic composition of the two initial CM components (anhydrous protolith and critically the CM water) will in turn provide a more accurate estimate of the initial W/R ratio. Constraining this value is
important for understanding the formation environment of the CM chondrites with respect to other meteorite groups, as well as resolving the source of Earth’s water.

3. **How many CM parent bodies were there?** Disparities between the CM1 and CM2 chondrites that apparently cannot be explained by longer duration alteration suggest that the CM lithology may represent more than one (closely related) early planetesimal.

4. **What was the unaltered CM3 assemblage like and how does the CM group relate to other chondritic groups?** Kimura et al. (2020) recently described the Antarctic CM A 12169 and argued that this sample should be classified as an unaltered CM3 chondrite. Whether the community adopts this suggestion remains to be seen. In either case, microanalysis studies on the least-altered CM chondrites and comparison against primitive CO and C-ung meteorites (e.g. Acfer 094) continue to provide critical reference material for reconstructing the accretionary CM lithology. Removing the effects of alteration is important because it allows us to understand the relationship between the CM chondrites and other similar carbonaceous chondrites.

5. **Can the Mn-Cr radiocronometer be used to better resolve the alteration history of CM chondrites?** We suggest that future short-lived radiocronometer work should identify and analyse a suite of T1 and T2 calcites. Such work may allow the timing and duration of the two separate calcite precipitation events in the CM lithology to be investigated (providing that age gap between the two populations is resolvable).

6. **How are CM chondrites related to C-type asteroids? And are Bennu and Ryugu second-generation CM parent bodies?** Analysis of samples returned from the two near-Earth asteroids Bennu and Ryugu will provide a rare opportunity to directly match extraterrestrial material to a known parent asteroid and further explore the geological history of the CM chondrites or a closely related asteroidal neighbour. Confirmation that at least one of these asteroids is composed of various CM lithologies would demonstrate that the original CM planetesimal was catastrophically disrupted. Furthermore, they may contain shock melt veins that allow dating of the breakup.

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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