

## Type 1 aqueous alteration in CM carbonaceous chondrites: Implications for the evolution of water-rich asteroids

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(Received 13 May 2016; revision accepted 27 February 2017)

**Abstract**—The CM carbonaceous chondrite meteorites experienced aqueous alteration in the early solar system. They range from mildly altered type 2 to almost completely hydrated type 1 chondrites, and offer a record of geochemical conditions on water-rich asteroids. We show that CM1 chondrites contain abundant (84–91 vol%) phyllosilicate, plus olivine (4–8 vol%), magnetite (2–3 vol%), Fe-sulfide (<5 vol%), and calcite (<2 vol%). The CM1/2 chondrites contain phyllosilicate (71–88 vol%), olivine (4–20 vol%), enstatite (2–6 vol%), magnetite (2–3 vol%), Fe-sulfides (1–2 vol%), and calcite (~1 vol%). As aqueous alteration progressed, the abundance of Mg-serpentine and magnetite in the CM chondrites increased. In contrast, calcite abundances in the CM1/2 and CM1 chondrites are often depleted relative to the CM2s. The modal data support the model, whereby metal and Fe-rich matrix were the first components to be altered on the CM parent body(ies), before further hydration attacked the coarser Mg-rich silicates found in chondrules and fragments. Based on the absence of tochilinite, we suggest that CM1 chondrites experienced increased alteration due to elevated temperatures (>120 °C), although higher water/rock ratios may also have played a role. The modal data provide constraints for interpreting the composition of asteroids and the mineralogy of samples returned from these bodies. We predict that “CM1-like” asteroids, as has been proposed for Bennu—target for the OSIRIS-REx mission—will have a high abundance of Mg-rich phyllosilicates and Fe-oxides, but be depleted in calcite.

### INTRODUCTION

The CM carbonaceous chondrites are the most abundant meteorite group to have experienced significant hydration by extraterrestrial water (McSween 1979; Tomeoka and Buseck 1985; Zolensky et al. 1997; Brearley 2006). They consist of aqueously altered high-temperature silicate clasts, chondrules, and calcium-aluminum-rich inclusions (CAIs) set within a fine-grained (<1 μm) matrix of phyllosilicates, oxides, sulfides, and carbonates. The aqueous alteration is generally understood to have taken place when accreted ices melted on asteroid parent bodies. Mn-Cr ages of the carbonate grains suggest that the alteration lasted for ~10 Myr (Endress et al. 1996; De Leuw et al. 2009; Fujiya et al. 2012). Remote sensing studies suggest that the CM chondrites originate from the dark C-type asteroids (specifically the Ch- and Cgh-types) that

dominate the main asteroid belt (e.g., Cloutis et al. 2011; DeMeo and Carry 2015). The CM chondrites therefore offer a detailed record of geological processes and events that were widespread in the early solar system, and can help constrain the role of hydrous primitive bodies in forming planetary systems.

The CM chondrites have been the subject of numerous studies over the last ~50 yr (McSween 1979; Tomeoka and Buseck 1985; Browning et al. 1996; Zolensky et al. 1997; Hanowski and Brearley 2001; Rubin et al. 2007; Howard et al. 2009, 2011a). Most (>95%) are classified as type 2 meteorites having suffered only partial alteration of the original anhydrous mineralogy. Their mineralogical, textural, and isotopic characteristics indicate that the aqueous alteration occurred under high water/rock ratios of 0.3–0.6 and at temperatures <100 °C (DuFresne and Anders 1962; Clayton and Mayeda 1984, 1999; Zolensky et al.

1989; Baker et al. 2002; Guo and Eiler 2007). However, the CM chondrites are complex, heterogeneous rocks that experienced pervasive alteration to varying degrees; they span a petrologic range, from mildly altered type 2 meteorites such as Paris (Hewins et al. 2013; Rubin 2015) to almost completely hydrated type 1 meteorites (Zolensky et al. 1997; Rubin et al. 2007).

The CM1 chondrites represent some of the most hydrated extraterrestrial materials available for study. The original mineral assemblage of these rocks has been transformed into secondary phases and they are dominated by phyllosilicates, with pseudomorphic chondrules and almost no anhydrous clasts remaining (Zolensky et al. 1997; Rubin et al. 2007). Amino acid abundances in CM1 chondrites are depleted relative to the CM2s (Botta et al. 2007; Glavin et al. 2011). The O isotopic compositions of the CM1 chondrites are similar to the least altered CM2 chondrites, implying that CM1 hydration may have occurred under similar water/rock ratios to the CM2 chondrites, but either at elevated temperatures ( $>100$  °C) or for a longer period of time within localized regions of the parent body(ies) (Clayton and Mayeda 1984, 1999; Zolensky et al. 1997). The mineralogy and composition of CM1 chondrites provide important insights regarding the geochemical conditions of the aqueous reactions, and the distribution and evolution of fluids and temperatures on primitive asteroids.

The CM1 chondrites are also of interest as they bear some resemblance to the surface of the largest C-type asteroid Ceres, which is currently being studied by the Dawn mission (e.g., De Sanctis et al. 2015), and have tentatively been linked to the near-Earth low albedo B-type asteroid Bennu (Clark et al. 2011). In the next decade, the OSIRIS-REx mission will visit and study Bennu, and aims to return to Earth up to ~2 kg of material from its surface (Lauretta et al. 2015). In addition, samples from the near-Earth Cg-type asteroid Ryugu will be returned by the Hayabusa-2 mission in 2020 (Tachibana et al. 2014). It has therefore become increasingly important to characterize the CM1 chondrites in order to help the selection of sampling sites and provide context for both spectral data and the returned asteroid materials.

Position-sensitive detector X-ray diffraction (PSD-XRD) has previously been used to determine the modal mineralogy of  $>20$  CM2 chondrites, but only two CM1 chondrites and one CM1/2 (intermediate between type 1 and 2 aqueous alteration) (Howard et al. 2009, 2011a, 2015). Modal mineral abundances can be used to understand the nature and extent of hydration and support isotopic (e.g., Alexander et al. 2012) and spectral analyses (e.g., Beck et al. 2014a; McAdam et al. 2015). Here, we have used PSD-XRD to determine the

bulk modal mineralogy of a further six CM1 and five CM1/2 chondrites. Our aim was to investigate variations in the degree of aqueous alteration in the CM1 chondrites, and examine the relationship between the CM1s and other heavily altered carbonaceous chondrites.

## EXPERIMENTAL

### Samples

There are currently 24 CM1 and 22 CM1/2 carbonaceous chondrites listed in the *Meteoritical Bulletin*. With the exception of three CM1s and three CM1/2s that are desert finds, they were all recovered from Antarctica by either the Antarctic Search for Meteorites (ANSMET, USA) or the National Institute for Polar Research (NIPR, Japan).

Howard et al. (2011a) reported bulk modal mineralogy of the CM1 chondrites Meteorite Hills (MET) 01070 and Scott Glacier (SCO) 06043, and the CM1/2 Allan Hills (ALH) 83001. In this work, we have analyzed fusion crust-free, interior chips of six CM1 chondrites: Grosvenor Mountains (GRO) 95645, LaPaz Icefield (LAP) 02277, Miller Range (MIL) 05137, MIL 07689, Northwest Africa (NWA) 4765, and Moapa Valley; and five CM1/2 chondrites: LAP 031166, LAP 031214, MIL 090288, MacKay Glacier (MCY) 05231, and NWA 8534.

Of these meteorites, only LAP 02277, Moapa Valley, and LAP 031166 are described in any detail within the literature. LAP 02277 consists of phyllosilicates, with 2.4 vol% sulfide, plus rare anhydrous silicate and Fe,Ni-metal ( $\leq 0.02$  vol%) grains (Rubin et al. 2007). In LAP 02277, chondrules replaced by phyllosilicates, oxides, and sulfides are elliptical and display a foliation (Rubin et al. 2007). Moapa Valley has elliptical chondrule pseudomorphs of phyllosilicate and possibly tochilinite. Sulfides are present, but magnetite and calcite are rare in the matrix, and there are open fractures filled with chalcedony (Irving et al. 2009). LAP 031166 retains some anhydrous silicate grains in chondrule pseudomorphs that are otherwise comprised of phyllosilicates and calcite (Lee et al. 2014). The chondrules are elliptical and show a strong foliation, with abundant fractures that are often filled with gypsum (Lee et al. 2014; Lindgren et al. 2015).

For the PSD-XRD analyses, ~50 mg chips of the CM1 and CM1/2 chondrites were powdered using an agate mortar and pestle to a grain size of  $<35$   $\mu\text{m}$  to minimize potential grain size artifacts (Batchelder and Cressey 1998; Cressey and Batchelder 1998; Bland et al. 2004). Chips of this size are sufficiently large to be representative of the bulk meteorite (Howard et al.

2009, 2011a, 2015; King et al. 2015a). After powdering, the samples were immediately packed into an aluminum sample well using the sharp edge of a spatula to create a high degree of randomness and reduce the effects of preferred crystal alignments (Batchelder and Cressey 1998).

### PSD-XRD

Modal mineral abundances were obtained using an INEL X-ray diffractometer with a curved  $120^\circ$  PSD in a static geometry relative to the X-ray beam and sample (Cressey and Schofield 1996). For full details of the experimental procedure used for analyzing hydrated carbonaceous chondrites, we refer the reader to Bland et al. (2004), Howard et al. (2009, 2011a), and King et al. (2015a). Briefly,  $\text{Cu K}\alpha_1$  radiation was selected using a Ge 111 crystal monochromator. The size of the beam was restricted using postmonochromator slits to  $0.24 \times 2.00$  mm at the flat top of the rotating sample. XRD patterns were collected from powdered meteorite samples for 16 h to achieve good signal-to-noise ratios. Mineral standards for phases identified in the meteorite XRD patterns, and whose presence has previously been reported from scanning (SEM) and transmission (TEM) electron microscope studies (McSween 1979; Tomeoka and Buseck 1985; Browning et al. 1996; Zolensky et al. 1997; Lauretta et al. 2000), were analyzed for 30 min. Differences in the incident beam flux were monitored by measuring a polished Fe-metal block throughout the experimental run and varied by  $<1\%$  during this study.

A profile-stripping method developed in our laboratory was used to determine the final modal mineralogy of the meteorites (Cressey and Schofield 1996; Batchelder and Cressey 1998; Cressey and Batchelder 1998; Schofield et al. 2002). Schofield et al. (2002) demonstrated the excellent agreement between the profile-stripping method and Rietveld refinements, and it has successfully been applied to a range of extraterrestrial rocks (Bland et al. 2004; Menzies et al. 2005; Howard et al. 2009, 2010, 2011a; Dunn et al. 2010; King et al. 2015a). The XRD pattern of a mineral standard was scaled to the same measurement time as the meteorite sample (e.g.,  $\times 32$  for a 16 h measurement). Following this, the intensity of the mineral standard pattern was reduced by a factor until it matched its intensity in the diffraction pattern of the meteorite. The standard pattern was then subtracted to leave a “residual” meteorite pattern before the process was repeated for each mineral identified in the meteorite. This continued until there were zero counts in the residual pattern and the sum of the fit factors was one. The fit factors for the mineral standards were then corrected for relative differences in X-ray

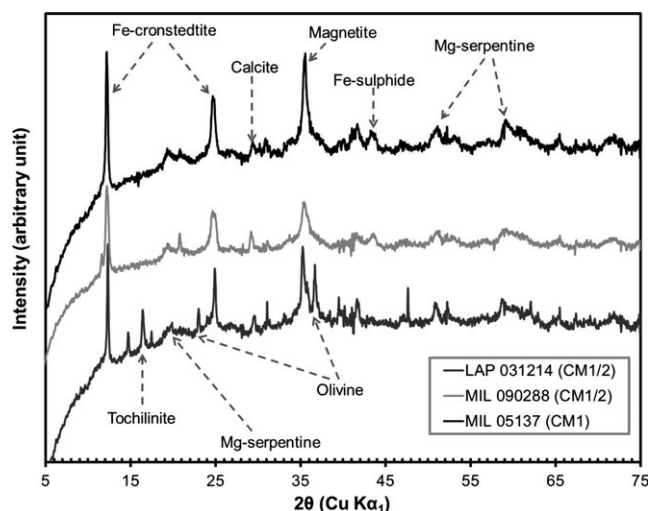


Fig. 1. Representative PSD-XRD patterns for CM1 and CM1/2 carbonaceous chondrites. Note that LAP 031214 (CM1/2) and MIL 090288 (CM1/2) are offset on the Y-axis.

absorption to give their final volume fractions in the meteorites (e.g., see table 2 in Howard et al. 2009).

Modal mineral abundances were determined for phases present at typically  $>1$  vol% and we conservatively estimate the uncertainties for the experiment as a whole at  $<5$  vol%. Howard et al. (2009, 2011a) estimated uncertainties for CM modal mineral abundances by varying the mineral standard factor until the fit was noticeably worse. This resulted in uncertainties of 2–4% for crystalline phases, and 3–5% for fine-grained, poorly crystalline phyllosilicates. In our recent work on CI chondrites, uncertainties in the modal abundances were identified as being  $<1.2\%$  from linear least-squares fitting procedures (King et al. 2015a).

## RESULTS

### XRD patterns

Figure 1 shows representative XRD patterns for the CM1 and CM1/2 chondrites. The main crystalline phases identified (not all phases in every meteorite) include gypsum, olivine, enstatite, magnetite, and Fe-sulfides (pyrrhotite and pentlandite). Calcite is the only carbonate recognized, although dolomite is known to be present in the most altered CM chondrites (Zolensky et al. 1997; De Leuw et al. 2009; Lee et al. 2014; Tyra et al. 2016). The main diffraction peak of dolomite ( $\sim 31^\circ$ ,  $2\theta$   $\text{Cu K}\alpha_1$ ) is close to a major peak for enstatite, and if the abundance of dolomite in the sample is low, these peaks can be difficult to resolve. However, enstatite is not a significant component of the CM1

chondrites, and we have previously identified dolomite at ~3 vol% in the highly altered CI chondrites (King et al. 2015a). This suggests that dolomite abundances in the CM1 chondrites are <3 vol%, in agreement with the study of Lee et al. (2014), where the highest dolomite abundance for a CM chondrite was 2.3 vol%.

We observe diffraction peaks at ~12° and ~25°, and much broader features at ~19° and ~61°. Howard et al. (2009, 2011a) interpreted these peaks as arising from relatively crystalline Fe-rich serpentine and fine-grained, poorly crystalline Mg-Fe serpentine, respectively. This is consistent with TEM observations of phyllosilicates in CM chondrites (Tomeoka and Buseck 1985; Lauretta et al. 2000). Howard et al. (2009, 2011a) did not attempt to distinguish between the different serpentine polytypes, rather referring to them as “Fe-cronstedtite” and “Mg-serpentine.” For consistency, we adopt the same nomenclature in this work; however, we remind the reader, first, that cronstedtite is by definition an Fe serpentine, and, second, that phyllosilicates in CM chondrites are compositionally diverse and we are not implying that these are endmembers.

Figure 2 confirms the agreement between our mineral standards and phases within the CM1 and CM1/2 chondrites, and demonstrates the profile-stripping method employed to determine modal mineralogy from the XRD patterns. As described in the Experimental section, each mineral standard pattern was reduced in intensity by a factor (value in parentheses in Fig. 2) to match the meteorite diffraction pattern before being subtracted out. This was repeated for all phases until there were zero counts left in the pattern and the sum of the fit factors was one, indicating that all major and minor phases were accounted for. Amorphous and highly disordered materials present in the meteorites can be identified from residual patterns that do not reduce to zero after removal of the crystalline phases (e.g., Howard et al. 2015; King et al. 2015a), but were not observed in this study.

### Modal Mineralogy for CM1s

The modal mineralogy of the CM1 and CM1/2 chondrites is summarized in Table 1. The CM1 chondrites contain abundant (84–91 vol%) phyllosilicate (Fe-cronstedtite + Mg-serpentine) with minor amounts of magnetite (2–3 vol%), Fe-sulfide (<5 vol%), and calcite (<2 vol%). Olivine abundances are 4–8 vol%, but significant enstatite (2 vol%) was only detected in NWA 4765.

Gypsum is present in both MIL 05137 and MIL 07689 at ~2 vol%, while tochilinite, which in CM chondrites is commonly intergrown with the phyllosilicates (Tomeoka and Buseck 1985; Rubin et al.

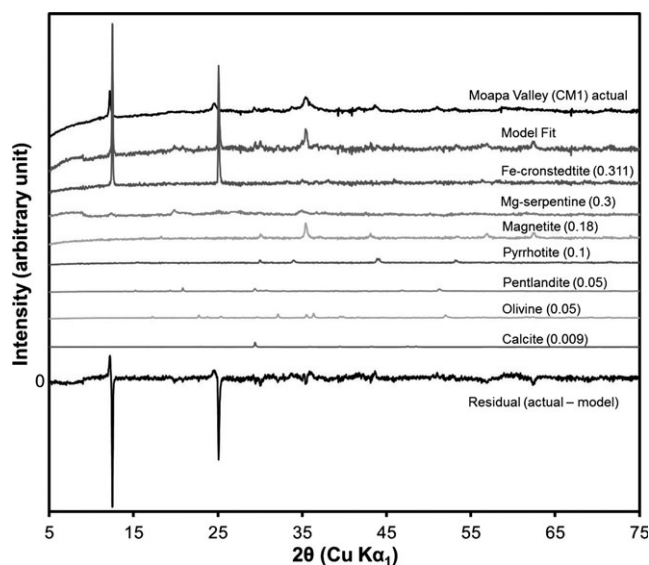


Fig. 2. PSD-XRD pattern for Moapa Valley (CM1) shown alongside a model pattern. The model pattern is constructed by summing together the mineral standard patterns in their relative proportions (value in parentheses) as determined during the profile-stripping routine. Subtracting the model from the meteorite pattern results in a residual of zero counts, indicating that all major and minor phases are accounted for. Peaks for Fe-cronstedtite are affected by crystallinity differences between the standards and meteorites, and are also prone to preferred crystallographic alignments. This can lead to large negative peaks in the final residual and as such they are not used in the profile-stripping.

2007), was identified from a peak at ~16° in the XRD pattern of GRO 95645. We are unable to determine the abundance of tochilinite as we do not have a pure standard available for the profile-stripping. However, as the peak is very small and the final residual for GRO 95645 still reaches zero counts, we account for the tochilinite through the subtraction of the Fe-cronstedtite and/or Mg-serpentine standards and confirm that its abundance in GRO 95645 is probably <1 vol%.

### Modal Mineralogy for CM1/2s

Phyllosilicate abundances in LAP 031166, MIL 090288, and NWA 8534 are 84–88 vol%, while LAP 031214 and MCY 05231 contain only 72 and 74 vol%, respectively (Table 1). All of the CM1/2 chondrites contain olivine and enstatite, with total anhydrous silicate abundances of 7–24 vol%, plus calcite (~1 vol%), magnetite (2–3 vol%), and Fe-sulfides (1–2 vol%). Gypsum is only detected in LAP 031166 (3 vol%), LAP 031214 (<1 vol%), and MIL 090288 (3 vol%).

In addition to having noticeably less phyllosilicate, for LAP 031214 and MCY 05231, we identify a strong peak from tochilinite in the XRD patterns (Fig. 1).

Table 1. Modal mineralogy of CM1 and CM1/2 carbonaceous chondrites. Approximately 50 mg of sample was analyzed by PSD-XRD. For the CM chondrites, the mass absorption coefficient for the phyllosilicates was calculated from the compositions given by Tomeoka and Buseck (1985) and Browning et al. (1996). To accommodate potential uncertainties across the entire experiment, and in keeping with similar studies (Howard et al. 2009, 2011a), we conservatively estimate the uncertainties as 2–4% for crystalline anhydrous phases and 3–5% for fine-grained, poorly crystalline phyllosilicates. However, we note that fitting of the standard patterns using a linear least-squares routine yields uncertainties in modal abundances of typically <1% (King et al. 2015a). The phyllosilicate fraction (PSF = total phyllosilicate abundance/(total anhydrous silicate + total phyllosilicate abundance)] is used to assign each sample a petrologic type in the Howard et al. (2015) classification scheme.

Sample (split no.)	Olivine (vol%)	Enstatite (vol%)	Magnetite (vol%)	Sulfide (vol%)	Calcite (vol%)	Gypsum (vol%)	Fe-cronstedtite (vol%)	Mg-serpentine (vol%)	Total Phyllosilicate (vol%)	PSF Classification	
LAP 031214 (11)	CM1/2	18.2	5.9	2.3	1.1	1.0	0.3	30.8	40.4	71.2	1.5
MCY 05231 (9)	CM1/2	19.6	3.4	1.6	1.3	1.0		36.9	36.2	73.1	1.5
MIL 090288 (5)	CM1/2	3.8	3.0	2.3	2.3	0.9	3.3	18.2	66.2	84.4	1.2
LAP 031166 (17,5)	CM1/2	5.0	1.5	2.0	1.4	0.9	2.4	21.5	65.3	86.8	1.2
NWA 8534	CM1/2	5.1	1.5	2.9	1.7	0.7		20.0	68.1	88.1	1.2
GRO 95645 (11)	CM1	8.0		3.2	3.3	1.2		31.9	52.4	84.3	1.2
NWA 4765	CM1	3.6	2.3	3.3	2.4	0.9		15.9	71.6	87.5	1.2
LAP 02277 (33)	CM1	5.3		1.9	2.2	1.7		20.6	68.3	88.9	1.2
Moapa Valley	CM1	4.1		3.1	4.4	0.9		20.4	67.1	87.5	1.1
MIL 05137 (6)	CM1	3.6		2.7	2.0	0.9	1.7	17.9	71.2	89.1	1.1
MIL 07689 (6)	CM1	3.8		3.1	0.1	0.4	1.7	20.6	70.3	90.9	1.1

Again, we are unable to determine the amount of tochilinite without a pure standard, but its peak in LAP 031214 and MCY 05231 is more intense than in GRO 95645, suggesting a higher abundance and/or crystallinity. Howard et al. (2009, 2011a) observed a tochilinite peak in XRD patterns of all CM2 chondrites, and McSween (1987) calculated tochilinite abundances of 6–7 vol% in the matrix. However, McSween (1987) noted that such high abundances were likely overestimates due to the presence of magnetite and sulfides, and Zolensky et al. (1993) subsequently reported <2 vol% in CM2 chondrites. Similar to GRO 95645, the final residuals for LAP 031214 and MCY 05231 have zero counts without subtracting a tochilinite standard. This is because we effectively removed the tochilinite component along with the phyllosilicates in the profile-stripping and suggests that its abundance in LAP 031214 and MCY 05231 is no more than a few percent.

## DISCUSSION

### Degree of Aqueous Alteration

The CM chondrites span a petrologic range, from mildly altered type 2 meteorites to almost completely hydrated type 1 samples. A major objective in the study of CM chondrites has been the definition of an accurate alteration sequence, which is a crucial step toward understanding the composition of the precursor materials, the nature and source of the altering fluids, and the geochemical conditions of hydration. Furthermore, a high-resolution petrologic classification scheme can provide a useful basis for interpreting other data sets, such as isotopic compositions (e.g., Alexander et al. 2012) and spectral properties (e.g., Beck et al. 2014a; McAdam et al. 2015).

Traditionally, progressive alteration sequences for the CM chondrites have been devised from multiple petrographic and geochemical characteristics. McSween (1979, 1987) proposed an alteration sequence for a limited number of CM chondrites based on a decrease in the Fe/Si ratio of the matrix as its abundance increased in the meteorites. Browning et al. (1996) reported that the average matrix phyllosilicate composition becomes increasingly Mg-rich with alteration, and using the alteration model of Tomeoka et al. (1989), combined this with petrographic observations, such as the abundance of isolated anhydrous clasts and fraction of chondrule alteration, to define the CM Mineralogic Alteration Index (MAI). However, the MAI has been shown to have a strong positive correlation with the year a meteorite fell and thus may have been disturbed by the effects of

terrestrial weathering (Bland et al. 2006; Velbel and Palmer 2011).

Rubin et al. (2007) redefined high-resolution petrologic subtypes for CM chondrites using several criteria, including the abundance of “silicates and oxides,” “metal in chondrules/matrix,” and “sulfide,” and the composition of the carbonates present. On the original Rubin et al. (2007) scheme, the CM chondrites were classified from 2.6, reflecting low-to-moderate aqueous alteration, to completely altered type 2.0 meteorites (i.e., CM1 chondrites). The scale was recently extended with the discovery of the Paris meteorite, which is classified as a 2.7–2.9 (Hewins et al. 2013; Rubin 2015).

Rather than using petrographic and geochemical indicators, which can be challenging to analyze due to the fine grain sizes and heterogeneous textures of most CM chondrites, Howard et al. (2009, 2011a) inferred the degree of aqueous alteration from total phyllosilicate abundances measured in bulk samples using PSD-XRD. They suggested that progressive aqueous alteration of the CM chondrites transformed the original anhydrous silicates into phyllosilicates. Assuming that the initial mineralogy was the same, the abundance of phyllosilicate relative to silicates is, therefore, a useful indicator of the degree of hydration. Phyllosilicate abundances in the CM chondrites were found to range from ~70 vol% in the least altered samples to >85 vol% in the highly altered meteorites. From this, Howard et al. (2009, 2011a) proposed an alteration sequence in good agreement with the Rubin et al. (2007) scale, and subsequently found to correlate with hydrogen abundances (Alexander et al. 2013) and infrared (IR) spectral features (Beck et al. 2014a) of the same CM chondrites.

Howard et al. (2015) presented the phyllosilicate fraction (PSF = total phyllosilicate abundance/[total anhydrous silicate + total phyllosilicate abundance]) as a new method for classifying all hydrated carbonaceous chondrites. In this scheme, the PSF is converted to a petrologic type from 3.0 (unaltered) to 1.0 (complete hydration). Subtypes within this are defined by 5 vol% increments in phyllosilicate abundance; a type 3.0 chondrite has a PSF of <0.05, a type 2.0 of 0.5, and type 1.0 of >0.95. Using this method, Howard et al. (2015) classified 24 CM chondrites as types 1.6 to 1.2.

We follow the approach outlined by Howard et al. (2009, 2011a, 2015) and use the total abundance of phyllosilicate as a proxy for the relative degree of aqueous alteration in the CM1 and CM1/2 chondrites. Figure 3 shows the total abundance of phyllosilicate against the abundance of anhydrous silicate for all 35 CM chondrites analyzed by PSD-XRD to date. LAP 02277, MIL 05137, MIL 07689, NWA 4765, and

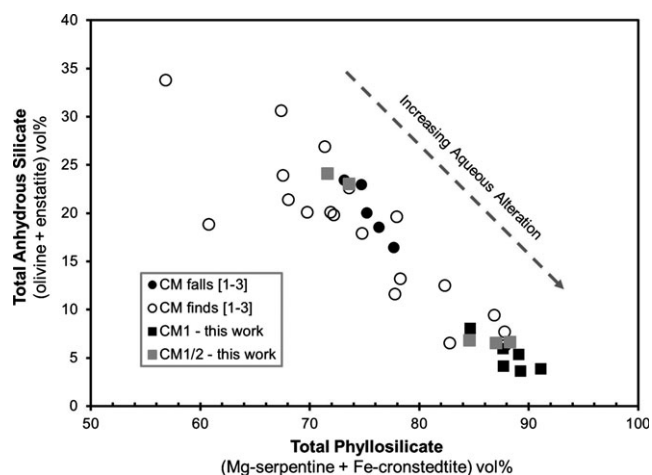


Fig. 3. Total abundance of phyllosilicate (Mg-serpentine + Fe-cronstedtite) and anhydrous silicate (olivine + enstatite) in 35 CM chondrites analyzed by PSD-XRD. In this work, we report abundances for six CM1 and five CM1/2 chondrite finds. The remaining CM data are taken from [1] Howard et al. (2009), [2] Howard et al. (2011a), and [3] Howard et al. (2015).

Moapa Valley contain the highest abundances of phyllosilicate (88–91 vol%) and lowest abundances of silicate (4–6 vol%), consistent with their classification as CM1 chondrites. The phyllosilicate abundance of the CM1 GRO 95645 is lower (85 vol%), and in better agreement with the CM1/2 chondrites LAP 031166, MIL 090288, and NWA 8534 (85–88 vol% phyllosilicate, 7 vol% silicate). The presence of tochilinite, which is usually consumed during early stages of aqueous alteration (Tomeoka et al. 1989; Howard et al. 2009, 2011a), also suggests that GRO 95645 is less altered than the other CM1s, and we note that it was originally classified as a C2 meteorite (Grossman 1998). Applying the PSF scheme of Howard et al. (2015), we resolve that MIL 05137, MIL 07689, and Moapa Valley are the most altered CM chondrites with petrologic type 1.1 (which from equation 2 in Howard et al. [2015] translates as type 2.0 on the Rubin et al. [2007] scale), while LAP 02277, LAP 031166, MIL 090288, GRO 95645, NWA 4765, and NWA 8534 are all petrologic type 1.2.

Two of the CM1/2s, LAP 031214 and MCY 05231, contain significantly less phyllosilicate (72–74 vol%) and more silicate (23–24 vol%) than the other meteorites analyzed in this study. Figure 3 shows that these abundances are more consistent with the mildly altered CM2 chondrites. In the PSF scheme, LAP 031214 and MCY 05231 are classified as type 1.5s (type 2.4 on the Rubin et al. [2007] scale), similar to CM2 chondrites such as Murchison and Murray (Howard et al. 2015). It is unknown whether LAP 031214 and MCY 05231 are

breccias or contain clasts of varying degrees of alteration. Nevertheless, we suggest that LAP 031214 and MCY 05231 should be reclassified as CM2 chondrites; a conclusion that is further supported by the presence of tochilinite in both of these meteorites.

### Abundances of Minor Phases

The samples analyzed in this study are all finds, with eight originating from Antarctica and three from hot deserts. The residence time of meteorites in Antarctica is considerably longer, on the order of  $10^5$  yr compared to 15,000–20,000 yr in hot deserts (Bland et al. 2006). During this time, the primary mineralogy of a meteorite is susceptible to contamination from terrestrial weathering. This can include the alteration of phyllosilicates, oxidation of sulfides into oxides and sulfates, and both the destruction and formation of carbonates and organics (Bland et al. 2006).

Terrestrial alteration likely has a negligible effect on the total abundance of the major phyllosilicate component in the CM1 and CM1/2 meteorites (Howard et al. 2015), but could influence the abundances of the minor phases such as magnetite and Fe-sulfide. A terrestrial carbonate component has been reported in the CM chondrites (Tyra et al. 2007); however, ages of ~4.5 Gyr from Mn-Cr dating, stable isotope compositions, and textural relationships suggest that most carbonates in CM chondrites are preterrestrial in origin (e.g., Lee et al. 2012, 2013, 2014; Tyra et al. 2012, 2016).

All of the samples analyzed have low weathering grades (typically grade A or B), and we worked with fresh interior chips not previously directly exposed to the atmosphere. Gypsum was detected in five of the Antarctic samples, but we saw no evidence for Fe-(oxy) hydroxides, the presence of which can be identified from residual XRD patterns (see King et al. 2015a). Figure 4 shows how abundances of magnetite, Fe-sulfides, and calcite vary in 35 CM chondrites that represent both falls and finds from different terrestrial environments. We note that calcite abundances in the CM falls, and also most of the finds are <2 vol%, whereas a small number of Antarctic meteorites contain higher abundances >2 vol%. For magnetite and Fe-sulfide, there are no correlations clearly related to the terrestrial history of the meteorites and we argue that the trends described in the following section are the result of parent body aqueous alteration and not terrestrial weathering.

### Magnetite

Figure 4a shows that the abundance of magnetite steadily increases from <1 vol% in the least altered

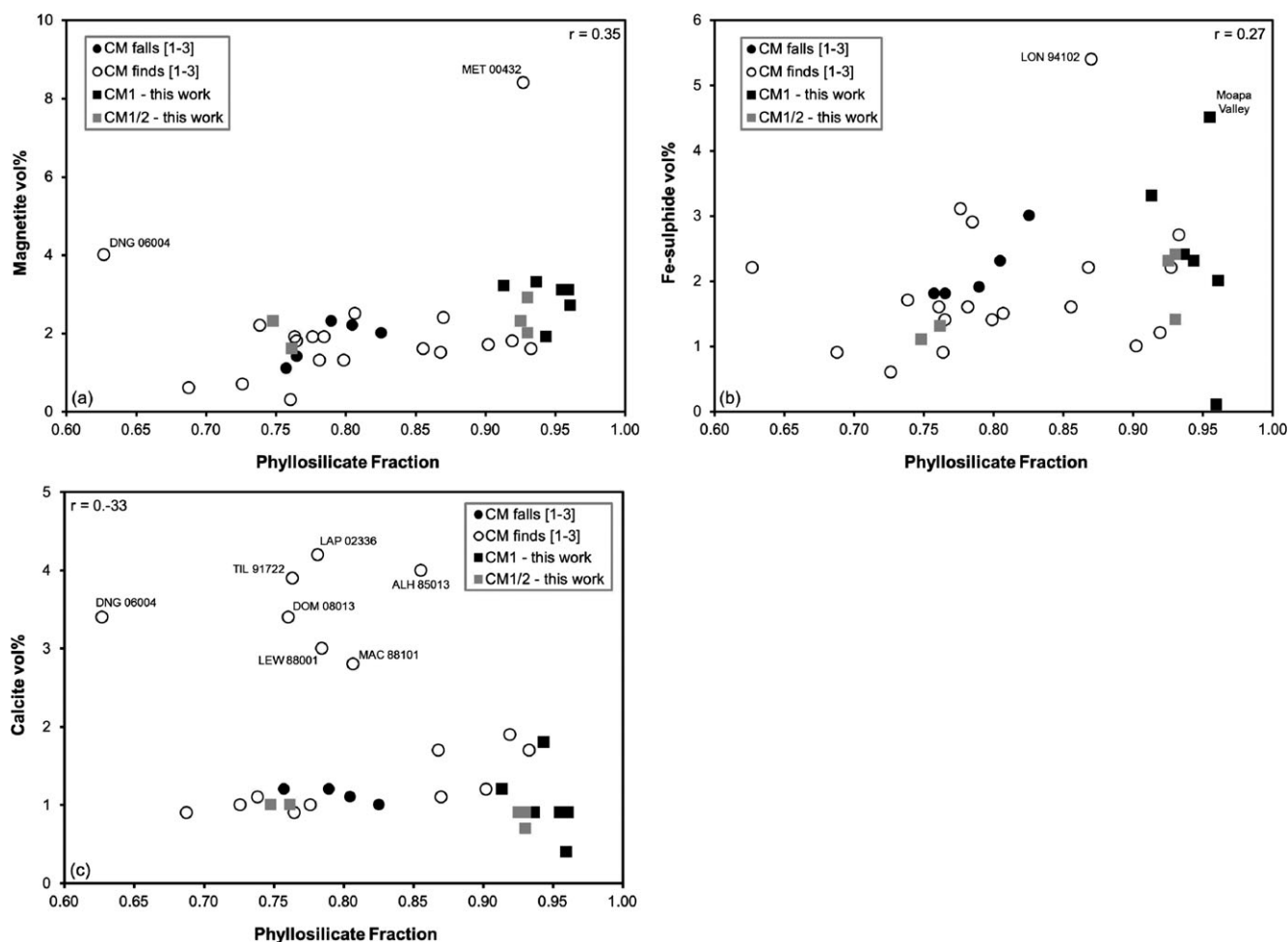


Fig. 4. Variations in the abundance of (a) magnetite, (b) Fe-sulfide, and (c) calcite with increasing aqueous alteration in the CM chondrites. The degree of alteration is determined from the phyllosilicate fraction (total phyllosilicate abundance/[total anhydrous silicate + total phyllosilicate abundance], see text for details). Data for 21 CM2, 1 CM1/2, and 2 CM1 chondrites (falls and finds) are taken from [1] Howard et al. (2009), [2] Howard et al. (2011a), and [3] Howard et al. (2015).

CMs to ~3 vol% in the CM1s. A couple of CM2 chondrites, DNG 06004 and MET 00432, have high magnetite abundances (>4 vol%) that are more comparable to the ungrouped C2 meteorites Essebi, Bells, and WIS 91600 (Howard et al. 2015), and the CI chondrites (King et al. 2015a).

Magnetite initially formed in CM chondrites through the oxidation of Fe,Ni-metal (Rubin et al. 2007). Howard et al. (2009, 2011a, 2015) reported metal in only the least hydrated CMs indicating that it was consumed during the earliest stages of aqueous alteration. Similarly, we do not detect metal in any of the CM1 and CM1/2 chondrites, although small metallic grains with magnetite rims have been observed in some CM1s (Zolensky et al. 1997; Rubin et al. 2007). As alteration proceeded and the abundance of metal declined, oxidation of free Fe released via reactions between the fluids and Fe-

cronstedtite probably became the dominant source of magnetite (Howard et al. 2015). Zolensky et al. (1997) suggested that during the last stages of aqueous alteration, magnetite abundances in CM1 chondrites were further enhanced by oxidation and replacement of sulfides, although we do not observe a systematic decrease in the abundance of Fe-sulfide in the most altered samples.

#### Fe-Sulfide

Figure 4b shows a weak correlation between the abundance of sulfides and degree of aqueous alteration recorded in the CM chondrites. One of the first products of hydration was large clumps of tochilinite–cronstedtite intergrowths (TCI), formerly referred to in the literature as “poorly characterized phases” (PCP) (Fuchs et al. 1973). Rubin et al. (2007) showed that with alteration the number of TCI clumps declines, and



suggested that as this happens, sulfur from the tochilinite is expelled to form increasingly abundant Fe-sulfides.

Rubin et al. (2007) perceived a possible gap between the abundances of Fe-sulfides in the most altered CM2 chondrites, such as QUE 93005 (1.2 vol%), and the CM1s LAP 02277 (2.4 vol%) and MET 01070 (2.8 vol%). This hiatus is not observed in the abundance and chemistry of other phases within the CM chondrites and cannot be unambiguously identified from Fig. 4b. Rubin et al. (2007) examined a limited number of CM1 meteorites using optical and electron microscopy. Our Fe-sulfide abundance for LAP 02277 (2.3 vol%) is in excellent agreement with the Rubin et al. (2007) study, although Howard et al. (2011a) found less Fe-sulfide in MET 01070 (1.2 vol%) and more in QUE 93005 (2.2 vol%). King et al. (2015b) reported an even higher abundance of Fe-sulfide (3.2 vol%) in a separate chip of QUE 93005.

The three meteorites we infer to be the most altered CM1s (from their PSF) contain very different abundances of sulfide. MIL 05137 has an Fe-sulfide abundance of 2.0 vol%, similar to other highly altered CM chondrites, whereas Moapa Valley contains 4.5 vol%, and MIL 07689 has a very low abundance of 0.1 vol%. Low abundances could reflect the dissolution of Fe-sulfide or its replacement by magnetite during the late stages of hydration. In this scenario, we would predict that MIL 07689 might have a higher magnetite abundance, but as Fig. 4a and Table 1 show, despite large differences in Fe-sulfide abundance, all three meteorites contain the same amount of magnetite. Alternatively, the breakdown of Fe-sulfide during terrestrial weathering could provide S for the formation of sulfate phases (Gounelle and Zolensky 2001). However, the abundance of gypsum measured in 10 CM chondrites, including MIL 05137 (1.7 vol%) and MIL 07689 (1.7 vol%), is not inversely correlated with the abundance of Fe-sulfide (Fig. 5).

The large scatter in the Fe-sulfide abundances in Fig. 4b could reflect impact brecciation and the redistribution of Fe-sulfide on the CM parent body. However, we see no reason why this process would have preferentially affected the Fe-sulfide over other minor phases, such as magnetite, where we do see a clear trend with the degree of alteration. We suggest that Fe-sulfide abundances are instead sensitive to local differences in the accreted mineralogy, water/rock ratio, temperature, or duration of alteration. For example, Velbel et al. (2015) showed how excess Fe leached from chondrules during late-stage aqueous alteration could be incorporated into sulfide rims surrounding the resulting pseudomorph. They identified Fe-sulfide rims in QUE 93005, but not around comparable pseudomorphs in the

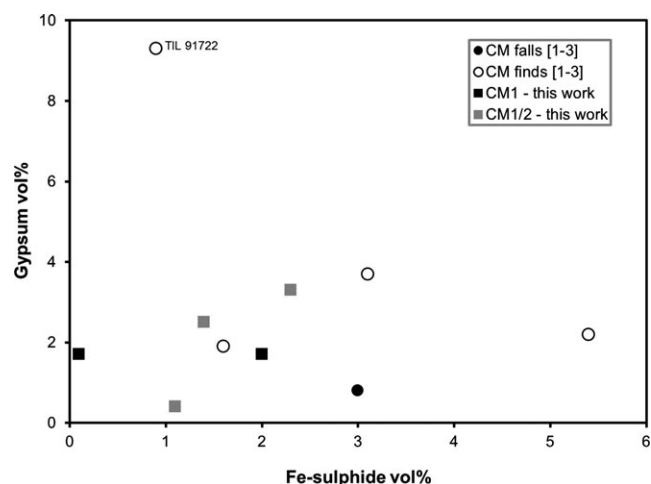


Fig. 5. Abundance of Fe-sulfide and gypsum in 10 CM chondrites analyzed by PSD-XRD in this work, [1] Howard et al. (2009), [2] Howard et al. (2011a), and [3] Howard et al. (2015).

CM chondrites ALH 81002 and Nogoya, suggesting that there were discrete geochemical environments where the availability and/or mobility of S differed.

### Calcite

Lee et al. (2014) proposed a carbonate precipitation sequence that provides a framework for understanding calcite abundances in the CM chondrites. In their model, aragonite formed first in the CM2 chondrites due to high Mg/Ca ratios, whereas higher initial temperatures enabled the formation of dolomite in the CM1s during the earliest stages of hydration. Calcite precipitated shortly after in both CM2 and CM1 chondrites, cementing pore spaces generated during melting of small ice grains. As alteration progressed, each of these carbonate phases was subsequently replaced by phyllosilicates and sulfides (tochilinite in the CM2s and Fe-sulfide in the CM1s). Finally, a late-stage second generation of calcite formed during replacement of remaining anhydrous silicates and in the CM1s continued dedolomitization, with Lee et al. (2014) suggesting this was possibly triggered by impacts and affected multiple regions (i.e., both CM2- and CM1-forming) on the parent body at the same time.

Previous studies using CO<sub>2</sub> concentrations (Grady et al. 1988; Benedix et al. 2003; Guo and Eiler 2007; Alexander et al. 2015) and X-ray mapping of thin sections (De Leuw et al. 2009; Lee et al. 2014) have always indicated that calcite abundances in CM2 chondrites are not related to the degree of aqueous alteration. Figure 4c shows that calcite abundances in the CM2 chondrites are highly variable and range from 0.9–4.2 vol%. There is no clear correlation with the degree of alteration. This supports the model of Lee

et al. (2014), whereby after cementation, there was little change in the overall calcite abundance. If, as proposed by Lee et al. (2014), late-stage calcite formation did occur, it would have required dissolution of the original carbonates, so the net effect on the total calcite abundance was probably negligible. Higher calcite abundances (>2 vol%) in some CM2 chondrites could represent differences in the local accreted mineralogy, such as the number of CAIs and concentration of organic species; variable melting of HCN, CO<sub>2</sub>, and CO ices; the effects of brecciation (Endress and Bischoff 1996; Morlok et al. 2006); or terrestrial alteration.

Figure 4c and Table 1 show that, with the exception of LAP 02277 and GRO 95645, there is a general trend of CM1 and CM1/2 chondrites being depleted in calcite relative to abundances in the CM2 chondrites. This characteristic was first noted by Zolensky et al. (1997), although several CM1s have since been reported as having calcite abundances comparable to the CM2s (e.g., Rubin et al. 2007; De Leuw et al. 2009; Howard et al. 2011a; Lee et al. 2014). Assuming a homogeneous starting mineralogy, the Lee et al. (2014) model predicts that calcite abundances would decline during replacement by phyllosilicates and Fe-sulfide. This process must have been more severe for the CM1s, consistent with them having experienced an increased degree of aqueous alteration. Possible reasons for more extensive hydration include a longer period of alteration, higher temperatures, or higher water/rock ratios, and are discussed in detail in the following sections.

### Mineralogical Changes with Aqueous Alteration of CM Chondrites

Accretion of the CM parent body(ies) brought together a mixture of anhydrous fine-grained and/or amorphous anhydrous silicates, coarser silicate grains and fragments, chondrules, CAIs, organics, and H<sub>2</sub>O-ice particles. Astronomical observations and models indicate that hydrated silicates and carbonates may also have been present in the proto-planetary disk (Malfait et al. 1999; Kemper et al. 2002; Ciesla et al. 2003), although most are expected to have formed on asteroids. The starting mineralogy and texture of the CM chondrites are often considered to be something akin to that of the primitive CO chondrites (McSween 1977) or the ungrouped carbonaceous chondrite Acfer 094 (Greshake 1997). Following accretion, radiogenic heating and perhaps heat generated by impacts melted the H<sub>2</sub>O-ice particles and initiated the transformation of the original components into secondary mineral assemblages (Brearley 2006). Aqueous alteration on the CM parent body(ies) was probably episodic and lasted

several millions of years (Rubin 2012; Tyra et al. 2012, 2016; Lee et al. 2013). In order to constrain the relationship between different CM chondrites and to quantify the varying degrees of aqueous alteration they record, several groups have proposed models describing how the mineralogy changes with increasing hydration (McSween 1979; Tomeoka and Buseck 1985; Browning et al. 1996; Hanowski and Brearley 2001; Rubin et al. 2007; Howard et al. 2015). In general, the models are broadly consistent with one another, and for a summary, the reader is referred to table 1 in Velbel et al. (2015). In the following paragraphs, we describe how the bulk modal mineralogy of CM chondrites changes with alteration and discuss where the CM1s fit into the current models.

Among the initial reactions to occur during hydration of the CM chondrites were the oxidation of metal to magnetite and alteration of glassy mesostasis in chondrules (Hanowski and Brearley 2001; Maeda et al. 2009; Hewins et al. 2013; Lee et al. 2016). The first process to affect the bulk mineralogy was the hydration of the fine-grained and/or amorphous materials in the matrix and rims surrounding larger fragments, chondrules, and CAIs (Chizmadia and Brearley 2008; Le Guillou and Brearley 2014; Le Guillou et al. 2015; Leroux et al. 2015). The matrix and rim material was more susceptible to alteration due to its large surface area-to-volume ratio. The high Fe contents of the matrix and rims resulted in solutions that were very Fe-rich, and therefore the subsequent formation of Fe-cronstedtite (McSween 1979; Zolensky et al. 1993). In the least altered CM chondrites, Fe-cronstedtite is the main phyllosilicate (Howard et al. 2009, 2011a, 2015). The first generation of carbonates precipitated in the early stages of hydration, while the alteration of sulfides liberated S and promoted the formation of TCIs (e.g., Tomeoka and Buseck 1985).

As hydration progressed, increasingly Mg-rich olivines and pyroxenes became altered (Fig. 6), leading to more Mg-rich solutions. The formation of Fe-cronstedtite was inhibited and Mg-serpentine began to dominate the phyllosilicate component. Figure 7 shows that as aqueous alteration continues both the total abundance of phyllosilicate and the relative fraction of the phyllosilicate that is Mg-serpentine increases. The breakdown of tochilinite released S, Fe, and Mg into solution, and phyllosilicate and Fe-sulfide started to replace the first generation of carbonates.

After all other materials were hydrated, the last phases to be altered were the coarse Mg-rich olivines and pyroxenes in chondrules and isolated fragments (Hanowski and Brearley 2001; Velbel et al. 2012, 2015). In some highly altered CM2s, coarse anhydrous silicates are partially hydrated, with the liberated Fe combining

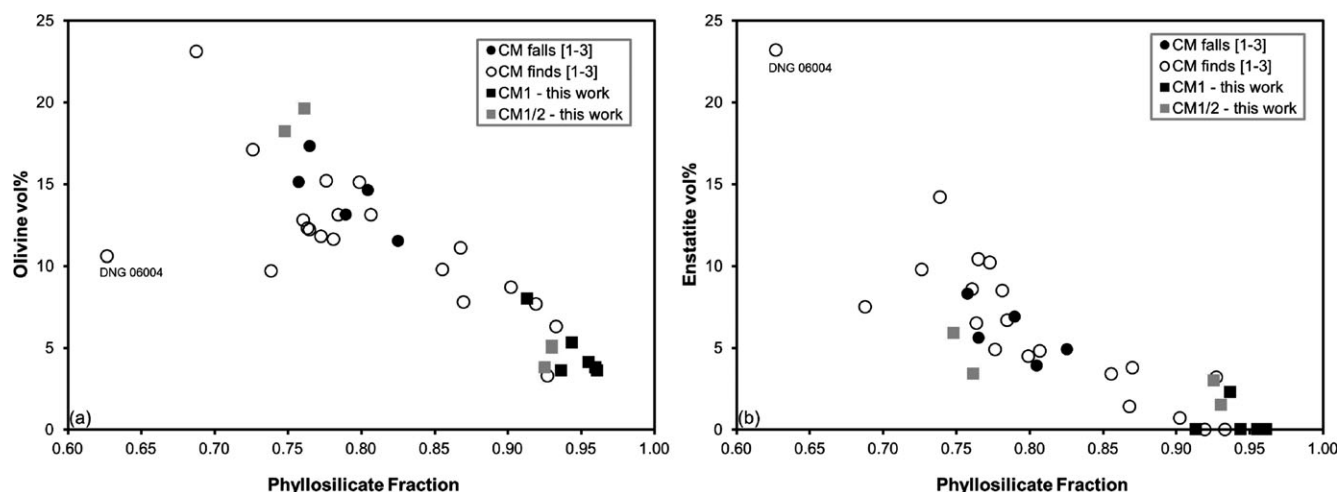


Fig. 6. Variations in the abundance of (a) olivine and (b) enstatite with increasing aqueous alteration in the CM chondrites. The degree of alteration is determined from the phyllosilicate fraction (total phyllosilicate abundance/[total anhydrous silicate + total phyllosilicate abundance], see text for details). Data for 21 CM2, 1 CM1/2, and 2 CM1 chondrites (falls and finds) are taken from [1] Howard et al. (2009), [2] Howard et al. (2011a), and [3] Howard et al. (2015).

with S to form Fe-sulfides at the margins of pseudomorphs (Velbel et al. 2015). Type 1 aqueous alteration was reached when any remaining coarse Mg-rich olivine and pyroxene were hydrated, leaving CM chondrites consisting of abundant phyllosilicate (84–91 vol%), magnetite, and Fe-sulfide. Mg-serpentine continued to dominate, although Velbel et al. (2012, 2015) argued that at this stage the composition of the phyllosilicate was partly independent of the anhydrous silicate being altered. We find that the CM1 chondrites typically contain <20 vol% Fe-cronstedtite, compared to ~35 vol% in the CM2s (Table 1), reflecting the formation of Mg-rich serpentine (plus magnetite) as Mg from anhydrous silicates exchanged with Fe in the cronstedtite (Howard et al. 2015). During the final stages of aqueous alteration, a second generation of carbonate formed in multiple regions on the CM parent body(ies), but this had little effect on the overall carbonate abundance (Lee et al. 2014).

### Conditions for Aqueous Alteration of CM1 Chondrites

The relatively uniform bulk element compositions of the CM chondrites suggest that fluid migration during aqueous alteration was very low (McSween 1979; Rubin et al. 2007; Bland et al. 2009). On the other hand, models describing convection on hydrous parent bodies can reproduce some of the mineralogical and isotopic properties of CM chondrites (Young et al. 1999; Travis and Schubert 2005; Palguta et al. 2010). In either case, partial pseudomorphs of coarse silicates imply that the alteration ceased, because the supply of fluid was completely consumed (Velbel et al. 2012, 2015). The

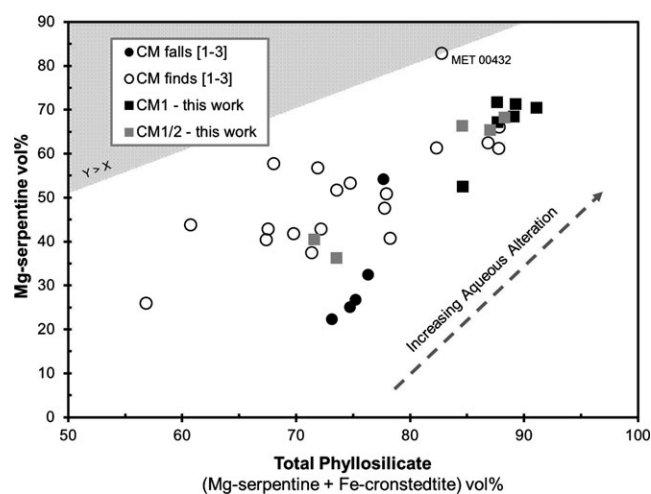


Fig. 7. Total abundance of phyllosilicate (Mg-serpentine + Fe-cronstedtite) versus the abundance of Mg-serpentine in CM chondrites. Data for 21 CM2, 1 CM1/2, and 2 CM1 chondrites are taken from [1] Howard et al. (2009), [2] Howard et al. (2011a), and [3] Howard et al. (2015). As aqueous alteration continues, both the total abundance of phyllosilicate and the fraction of the phyllosilicate that is Mg-serpentine increase.

increased degree of hydration witnessed in the CM1 chondrites could, therefore, reflect a longer duration of alteration, higher temperatures, or higher water/rock ratios (McSween 1979; Clayton and Mayeda 1984, 1999; Tomeoka and Buseck 1985; Zolensky et al. 1989, 1997; Browning et al. 1996; Hanowski and Brearley 2001; Rubin et al. 2007). Below we describe the current evidence for and against each of these conditions being the cause of the more extensive aqueous alteration.

The Mn-Cr ages of carbonates suggest that the onset and end of aqueous alteration in both CM2 and CM1 chondrites occurred at approximately the same time. The first generation of carbonates in CM2 and CM1 chondrites started precipitating at  $\sim 4563$  Ma (Fujiya et al. 2012), and Lee et al. (2014) argued that the final period of calcite formation occurred in both the CM2- and CM1-forming regions simultaneously toward the end of alteration. Some additional minor aqueous alteration of the CM1s may have taken place to remove any remaining anhydrous silicates, but was not extensive enough to replace the second-generation calcite (Lee et al. 2014). The duration of aqueous alteration of CM1 and CM2 chondrites was probably similar, although new Mn-Cr ages for carbonates in the CM1 chondrites would help to better constrain this parameter.

Elevated temperatures would have enhanced reaction rates, leading to the increased degree of hydration observed in the CM1 chondrites. The CM2s are estimated to have formed at  $<100$  °C (DuFresne and Anders 1962; Clayton and Mayeda 1984, 1999; Zolensky et al. 1989; Baker et al. 2002; Guo and Eiler 2007), but the presence of dolomite and the absence of tochilinite, which breaks down above  $\sim 120$  °C (Zolensky et al. 1997), indicates that CM1 alteration exceeded this temperature. Investigation of a CM1 lithology mixed into the Kaidun CR2 chondrite suggests that locally the alteration of the CM1s could have reached peak temperatures as high as  $\sim 450$  °C (Zolensky et al. 1997). Alteration at higher temperatures can also explain the low abundances of soluble organics in CM1 chondrites relative to CM2 meteorites (Botta et al. 2007; Aponte et al. 2011; Glavin et al. 2011). In contrast, similarities in the H/C ratios and molecular structure of the insoluble organic matter (IOM) in both CM1 and CM2s have been interpreted as all CM chondrites experiencing aqueous alteration at very similar temperatures (Cody et al. 2008a; Alexander et al. 2014).

Water/rock ratios for aqueous alteration of CM chondrites have been estimated using a model based on variations in bulk  $\Delta^{17}\text{O}$  values (Clayton and Mayeda 1984, 1999). Zolensky et al. (1997) reported that the  $\Delta^{17}\text{O}$  values of the CM1 EET 83334 ( $-2.28$ ) and CM1/2 ALH 83100 ( $-2.50$ ) are consistent with water/rock ratios of  $\sim 0.35$ , falling toward the lower end of the range ( $0.3$ – $0.6$ ) inferred for the CM2s (Clayton and Mayeda 1984, 1999). Since that study, bulk O isotopic compositions have become available for a further four CM1 and three CM1/2 chondrites (Table 2). The  $\Delta^{17}\text{O}$  values for CM1 and CM1/2 chondrites range from  $-1.86$  to  $-2.45$  indicating that they were altered under similar water/rock ratios as the CM2 chondrites.

Table 2. Summary of bulk O isotopic compositions for CM1 and CM1/2 chondrites from the literature. For comparison, selected CM2 chondrites are also included in the table.

Meteorite		$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\Delta^{17}\text{O}$	Ref.
EET 83334	CM1	5.90	0.79	$-2.28$	[1,2]
MET 01070	CM1	5.81	0.59	$-2.44$	[3]
SCO 06043	CM1	4.36	$-0.16$	$-2.43$	[3]
Moapa Valley	CM1	6.19	0.81	$-2.45$	[4]
NWA 10853	CM1	13.54	5.29	$-1.86$	[6]
ALH 83100	CM1/2	6.38	0.82	$-2.50$	[1,2]
Y 82042	CM1/2	8.49	2.39	$-2.02$	[1]
NWA 8534	CM1/2	12.41	4.40	$-2.15$	[5]
NWA 10834	CM1/2	10.80	3.29	$-2.42$	[6]
Murchison	CM2.5	7.30	1.20	$-2.60$	[1]
Mighei	CM2.3	7.57	1.44	$-2.50$	[1]
QUE 93005	CM2.1	7.10	1.15	$-2.54$	[1]

Data are taken from [1] Clayton and Mayeda (1999), [2] Zolensky et al. (1997), [3] Howard et al. (2011b), [4] Irving et al. (2009), [5] Meteoritical Bulletin No. 103, and [6] Meteoritical Bulletin No. 105.

In the Clayton and Mayeda (1984, 1999) model, hydration of isotopically “light” (low  $\Delta^{17}\text{O}$ ) anhydrous silicates by isotopically “heavy” (high  $\Delta^{17}\text{O}$ ) water in a closed system should result in a correlation between bulk O isotopic compositions and the degree of alteration. However, several recent studies have demonstrated that no such correlation exists (Howard et al. 2011b; Alexander et al. 2013; Beck et al. 2014a), and in fact the bulk O isotopic compositions of the CM1 and CM1/2 chondrites are typically lighter than those of the CM2s (Table 2). The lack of correlation implies that aqueous alteration of CM chondrites may have occurred in an open system (e.g., Young et al. 1999), although this contradicts the relatively uniform bulk element compositions. Terrestrial contamination might be an issue; all CM1 and CM1/2 chondrites are finds, and most were recovered from Antarctica, where exposure to fluids can shift O isotopes to lighter values (Bland et al. 2000). The hot desert find Moapa Valley has similarly light O isotopic compositions, although the O isotopic composition of NWA 8534 is among the heaviest measured in CM chondrites. Further investigation is clearly required to resolve the causes of O isotope variations in CM chondrites.

In summary, it seems that CM1 and CM2 chondrites were altered for similar lengths of time and that increased hydration was driven by elevated temperatures and/or water/rock ratios, although which mechanism was dominant remains an open question. Based on the absence of tochilinite, we favor elevated temperatures and suggest that CM1 chondrites represent materials that formed either within the interior of the parent body(ies) where temperatures are expected to

have been >120 °C, or in regions closer to the surface that experienced localized heating due to convection (e.g., Palguta et al. 2010) or impact events (e.g., Lee and Nicholson 2009). Nevertheless, we cannot rule out variable water/rock ratios, which may have occurred on the CM parent body(ies) due to heterogeneous accretion of ices, fluid transport facilitated by fractures (Rubin 2012) or differential compaction (Alexander et al. 2013).

### Relationship to CII and CR1 Chondrites

The CII chondrites consist of slightly less phyllosilicate (81–84 vol%) than the CM1 chondrites (84–91 vol%) (King et al. 2015a). The nature of the CII phyllosilicates is also different, being an approximately equal mixture of fine-grained serpentine/saponite rather than the coarser serpentines found in the CM1 chondrites. Anhydrous silicates are less common in the CII chondrites (<1 vol%), possibly in part due to an absence of accreted coarse silicate grains, chondrules, and CAIs (Brearley 2006). Other notable differences include significantly higher abundances of oxides (6–10 vol%) and dolomite (~3 vol%) in the CII chondrites (King et al. 2015a). Aqueous alteration of CII chondrites is inferred to have taken place at temperatures ranging from ~50 °C (Leshin et al. 1997) to ~150 °C (Clayton and Mayeda 1999).

Instead, the mineralogy of the CM1 chondrites is more comparable to the rare CR1 chondrites, with Howard et al. (2015) reporting abundant phyllosilicate (67 vol%) plus anhydrous silicates (7 vol%), oxides (10 vol%), Fe-sulfide (9 vol%), and calcite (6 vol%) in GRO 95577. The phyllosilicates in CR1 chondrites are predominantly serpentine and have a similar composition to those in the CM chondrites (Weisberg and Huber 2007). Alteration temperatures for the CR chondrites have been estimated at <200 °C (e.g., Cody et al. 2008b).

### LAP 02277—A Thermally Metamorphosed CM1 Chondrite?

Over 20 CM chondrites that show evidence for thermal metamorphism at temperatures of 300 °C to >750 °C have been identified (Nakamura 2005; Tonui et al. 2014). The timing and source of the metamorphic event(s) are still poorly constrained. Mineral textures and organic phases suggest that the heating was short-lived, on the order of hours to several years (Nakato et al. 2008; Yabuta et al. 2010), while the recrystallization of phyllosilicates back into anhydrous silicates observed in some samples implies that the heating must have occurred after aqueous alteration (Nakamura 2005). There is currently renewed interest in

the thermally altered CM chondrites as their reflectance spectra share a number of features with the surfaces of some low albedo C-type asteroids (e.g., Hiroi et al. 1993, 1996), including Ryugu, target for the Hayabusa-2 asteroid sample return mission.

Localized temperatures >300 °C could potentially have caused thermal metamorphism of the CM1 chondrites. However, to our knowledge, no heated CM1 chondrites have been recognized, possibly because untangling the effects of both aqueous and thermal alteration is extremely challenging. One candidate is LAP 02277, which has several characteristics consistent with other thermally metamorphosed CM chondrites, although it is worth noting that the variability of the CM1s is poorly constrained. Alexander et al. (2013) reported that LAP 02277 contains only 1.1 wt% H, in contrast to the CM1s MET 01070 and SCO 06043, which each contain ~1.3 wt% H. In CM chondrites, bulk H and phyllosilicate abundances are positively correlated with the degree of aqueous alteration, while thermal metamorphism is expected to lower the H contents (Alexander et al. 2013). The low H abundance in LAP 02277 could therefore reflect less aqueous alteration and/or thermal metamorphism.

We find that LAP 02277 has an almost identical amount of phyllosilicate (~89 vol%) to the other CM1 chondrites, suggesting that it experienced the same degree of aqueous alteration but suffered thermal metamorphism. This is supported by depletions in moderately volatile elements (Moriarty et al. 2009) and very low amino acid concentrations (Botta et al. 2007). On the other hand, IR measurements show that LAP 02277 has a sharp 3 μm band from -OH bound in the phyllosilicates (Takir et al. 2013) that is distinct from the feature typically observed in thermally altered CM chondrites (Osawa et al. 2005; Garenne et al. 2016).

PSD-XRD is a useful tool for identifying thermally altered CM chondrites (e.g., King et al. 2015a, 2015b). Thermal metamorphism causes dehydration and dehydroxylation of phyllosilicates, which results in the collapse of the phyllosilicate structure and a subsequent lack of coherent diffraction when analyzed by XRD (Nakamura 2005; Tonui et al. 2014; King et al. 2015a). Figure 8 shows that the diffraction pattern for LAP 02277 is typical of nonheated CM chondrites, with distinct diffraction peaks from the Fe-cronstedtite and Mg-serpentine phyllosilicates. The pattern is inconsistent with the thermally altered CM meteorites analyzed in our laboratory (King et al. 2015b) and suggests that LAP 02277 was not heated to >300 °C, in agreement with the IR spectra presented by Takir et al. (2013).

The discrepancy between the alteration history of LAP 02277 inferred from the XRD and bulk elemental and organic data may be explained by sample

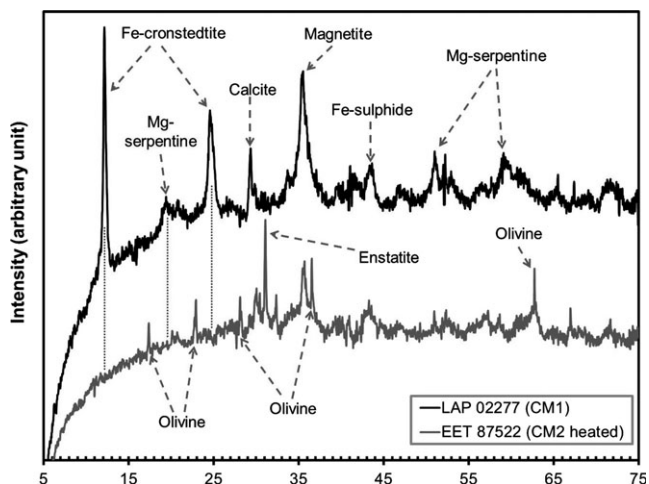


Fig. 8. PSD-XRD pattern for LAP 02277 (CM1) and thermally metamorphosed CM chondrite EET 87522 (King et al. 2015b). Thermal metamorphism causes dehydration and dehydroxylation of phyllosilicates, resulting in the collapse of the phyllosilicate structure and subsequently a lack of coherent diffraction. Diffraction peaks associated with phyllosilicates (dotted vertical lines) are not observed for EET 87522 but are clearly identified in the XRD pattern of LAP 02277 suggesting this meteorite did not experience any significant thermal metamorphism.

heterogeneity. LAP 02277 is not heavily brecciated (Rubin et al. 2007), but there is evidence that thermal metamorphism of some CM chondrites was heterogeneous at the mm-scale (Beck et al. 2014b), which might be expected if impacts fragmented and heated porous materials of varying shock impedance to create regions with distinct thermal histories.

### Implications for Asteroid Sample Return

Remote sensing observations link the CM chondrites to the primitive C-type asteroids (specifically the Ch- and Cgh-types) that dominate the population in the Main Belt (e.g., Cloutis et al. 2011; DeMeo and Carry 2015). The hydrated C-type asteroids are believed to have formed in the cold outer regions of the solar system and hold vital clues regarding the nature and distribution of water and organics. The Dawn mission is currently investigating the largest C-type asteroid Ceres, and in the next decade, the OSIRIS-REx and Hayabusa-2 spacecraft will return to Earth samples from the surfaces of the low albedo B-type asteroid Bennu and the Cg-type asteroid Ryugu, respectively.

The spectrum of Ceres does not match any known meteorite group, but has affinities with the CM chondrites (De Sanctis et al. 2015). In addition to ammoniated clays and Mg-rich carbonates, the inferred surface mineralogy includes a high abundance of Mg-

rich serpentine (De Sanctis et al. 2015), consistent with our analyses of CM1 chondrites (Fig. 7). For Bennu, Clark et al. (2011) failed to find a good match with laboratory meteorite spectra but speculated that the surface is composed of a “CM1-like” material. In reality, the surfaces of C-type asteroids are likely to have a highly diverse mineralogy, consisting of materials that suffered varying degrees of aqueous and/or thermal alteration and were mixed by impact-driven brecciation. The bulk modal mineralogy of 35 CM chondrites representing different stages of aqueous alteration can help shed light on the types of complex materials likely to be present. Importantly, trends in the abundance and chemistry of major and minor phases within the CM chondrites can provide context for the returned samples. For example, if the surface of Bennu is predominantly “CM1-like,” we predict that the returned samples will have a high abundance of Mg-rich phyllosilicates and Fe-oxides, but possibly be depleted in calcite. Similarly, if they are more “CM2-like,” Fe-rich phyllosilicates will be common, and Fe-oxides will only be a small component.

Constraining the bulk modal mineralogy is also important for accurately assessing features in the visible to mid-IR spectra of the CM chondrites. Volumetrically dominant minerals are often not spectrally dominant, with the presence of small amounts of opaque phases (e.g., magnetite, Fe-sulfides) known to strongly suppress the absorption features of phyllosilicates and have a large effect on the overall spectral shape (e.g., Cloutis et al. 2011). There have been several recent efforts to directly correlate the mineralogical changes associated with aqueous alteration with the spectral characteristics of CM chondrites and remotely infer the level of hydration on C-type asteroids (Takir et al. 2013; McAdam et al. 2015). In particular, for the CM2 chondrites, correlations between mineralogy and features such as the  $\sim 3 \mu\text{m}$  band attributed to  $-\text{OH}/\text{H}_2\text{O}$  or the  $\sim 10 \mu\text{m}$  band from Si-O bonds, have been used to understand the mineralogy and alteration history of materials on the surface of these small bodies (Takir et al. 2013; McAdam et al. 2015). Similar studies with the CM1 chondrites will further test these relationships, and as OSIRIS-REx and Hayabusa-2 approach Bennu and Ryugu, could assist in selecting the most scientifically interesting sites for sample collection.

### SUMMARY

We have used PSD-XRD to determine the bulk modal mineralogy of six CM1 and five CM1/2 chondrites. As some of the most hydrated extraterrestrial samples available for study, the

mineralogy of CM1 and CM1/2 chondrites can be used to constrain the nature and extent of aqueous reactions on primitive water-rich bodies in the early solar system. In summary, we find:

1. The CM1 chondrites LAP 02277, MIL 05137, MIL 07689, NWA 4765, and Moapa Valley contain the highest abundances of phyllosilicate (88–91 vol%) and lowest abundances of anhydrous silicate (4–6 vol%); the phyllosilicate abundance of the CM1 GRO 95645 (85 vol%) is consistent with the CM1/2 chondrites LAP 031166, MIL 090288, and NWA 8534 (85–88 vol% phyllosilicate, 7 vol% anhydrous silicate). Using the phyllosilicate fraction (PSF) scheme of Howard et al. (2015), we resolve that MIL 05137, MIL 07689, and Moapa Valley are the most altered CM chondrites with petrologic type 1.1, while LAP 02277, LAP 031166, MIL 090288, GRO 95645, NWA 4765, and NWA 8534 are all petrologic type 1.2.
2. The CM1/2s LAP 031214 and MCY 05231 contain significantly less phyllosilicate (72–74 vol%) and more silicate (23–24 vol%) than the CM1s and other CM1/2s. We suggest that they should be reclassified as CM2 chondrites.
3. The CM1 chondrites typically contain <20 vol% Fe-cronstedtite compared to ~35 vol% in the CM2s, and the relative fraction of the total phyllosilicate abundance that is Mg-serpentine is higher. This supports the model whereby Fe-cronstedtite formed during the early stages of CM alteration before increasingly Mg-rich phyllosilicates formed as coarser anhydrous Mg-rich silicates were consumed by the fluids.
4. Magnetite abundances increase with degree of alteration, from <1 vol% in the least altered CMs to ~3 vol% in the CM1s. This reflects the initial oxidation of Fe,Ni-metal, followed by oxidation of Fe released via reactions between the fluids and phyllosilicates and finally replacement of Fe-sulfide. In contrast, there is a weak correlation between the abundance of Fe-sulfide and degree of aqueous alteration recorded in the CM chondrites, which can be explained if local geochemical variations influenced the availability and/or mobility of S.
5. Many CM1 and CM1/2 chondrites are depleted in calcite relative to the CM2 chondrites. During aqueous alteration, the replacement of carbonates by phyllosilicates and Fe-sulfide must have occurred at a faster rate in the CM1s than the CM2s. Based on the absence of tochilinite, we suggest that CM1 chondrites experienced increased aqueous alteration due to elevated temperatures (>120 °C), although higher water/rock ratios may also have existed on the parent body(ies).
6. Trends in the modal mineralogy of hydrated carbonaceous chondrites will play an important role in understanding samples returned from the surface of primitive C-type asteroids. We predict that “CM1-like” asteroids, such as Bennu, will have a high abundance of Mg-rich phyllosilicates and Fe-oxides but possibly be depleted in calcite, whereas “CM2-like” samples will contain more Fe-rich phyllosilicates and only minor Fe-oxides.

*Acknowledgments*—US Antarctic meteorite samples are recovered by the Antarctic Search for Meteorites (ANSMET) program which has been funded by NSF and NASA, and characterized and curated by the Department of Mineral Sciences of the Smithsonian Institution and Astromaterials Curation Office at NASA Johnson Space Center. Hot desert meteorite samples were provided by Laurence Garvie at the Center for Meteorite Studies, Arizona State University, USA. Jens Najorka is thanked for assistance with the PSD-XRD analysis, as are Paula Lindgren, Pierre Beck, and Adrian Brearley for their thoughtful comments and suggestions that helped improve this manuscript. This work was supported by the Science and Technology Facilities Council (STFC), UK, through grant ST/J001473/1.

*Editorial Handling*—Dr. Adrian Brearley

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