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Fluid evolution in CM carbonaceous chondrites tracked through the oxygen isotopic compositions of carbonates

P. Lindgren a, M.R. Lee a,⇑, N.A. Starkey b, I.A. Franchi b

a School of Geographical and Earth Sciences, Gregory Building, Lilybank Gardens, Glasgow G12 8QQ, United Kingdom
b Planetary and Space Sciences, The Open University, Milton Keynes MK7 6AA, United Kingdom

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Abstract

The oxygen isotopic compositions of calcite grains in four CM carbonaceous chondrites have been determined by Nano-SIMS, and results reveal that aqueous solutions evolved in a similar manner between parent body regions with different intensities of aqueous alteration. Two types of calcite were identified in Murchison, Mighei, Cold Bokkeveld and LaPaz Icefield 031166 by differences in their petrographic properties and oxygen isotope values. Type 1 calcite occurs as small equant grains that formed by filling of pore spaces in meteorite matrices during the earliest stages of alteration. On average, the type 1 grains have a $\delta^{18}O$ of ~32–36‰ (VSMOW), and $\Delta^{17}O$ of between ~2‰ and ~1‰. Most grains of type 2 calcite precipitated after type 1. They contain micropores and inclusions, and have replaced ferromagnesian silicate minerals. Type 2 calcite has an average $\delta^{18}O$ of ~21–24‰ (VSMOW) and a $\Delta^{17}O$ of between ~1‰ and ~3‰. Such consistent isotopic differences between the two calcite types show that they formed in discrete episodes and from solutions whose $\delta^{18}O$ and $\delta^{17}O$ values had changed by reaction with parent body silicates, as predicted by the closed-system model for aqueous alteration. Temperatures are likely to have increased over the timespan of calcite precipitation, possibly owing to exothermic serpentinisation. The most highly altered CM chondrites commonly contain dolomite in addition to calcite. Dolomite grains in two previously studied CM chondrites have a narrow range in $\delta^{18}O$ (~25–29‰ VSMOW), with $\Delta^{17}O$ ~1‰ to ~3‰. These grains are likely to have precipitated between types 1 and 2 calcite, and in response to a transient heating event and/or a brief increase in fluid magnesium/calcium ratios. In spite of this evidence for localised excursions in temperature and/or solution chemistry, the carbonate oxygen isotope record shows that fluid evolution was comparable between many parent body regions. The CM carbonaceous chondrites studied here therefore sample either several parent bodies with a very similar initial composition and evolution or, more probably, a single C-type asteroid.

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Keywords: CM carbonaceous chondrites; Calcite; Oxygen isotopes; Aqueous alteration

1. INTRODUCTION

C-type asteroids are rich in water, hydroxyls and organics (Clark et al., 2010), and so are of particular importance for understanding the transfer throughout the Solar System of volatiles and other compounds of biological importance. In recognition of their significance, these bodies are the targets of forthcoming missions, including OSIRIS-Rex, which will return samples of (101955) Bennu (Emery et al., 2014; Lauretta et al., 2015). Pieces of one or more C-type asteroids are also available for study in the form of Mighei-like (CM) carbonaceous chondrite meteorites (e.g., Burbine et al., 2002; Kasuga et al., 2013). The principal carriers of hydroxyls in these rocks are phyllosilicates, which have formed by the aqueous alteration of primary silicates, metals, sulphides and amorphous materials (e.g., McSween, 1979a,b; Bunch

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and Chang, 1980; Tomeoka and Buseck, 1985). The liquid water that mediated alteration originated from melting of ices in the parent body interior (DuFresne and Anders, 1962), but the nature of these fluids and their spatial and temporal dynamics are poorly understood. Currently unanswered questions include: was alteration a single event, or did it take place in multiple pulses? was the water static, or did it flow? were temperatures stable, or did they change over the timespan of aqueous alteration? did all parent body regions evolve in the same manner, or did alteration trajectories locally differ? These questions have been addressed in models of parent body evolution, some of which postulate a closed system (e.g., Clayton and Mayeda, 1984, 1999; Bland et al., 2009; Velbel et al., 2012) whereas others invoke single-pass or convective fluid flow (e.g., Young et al., 1999; Young, 2001; Palguta et al., 2010).

Fresh insights into parent body aqueous alteration may come from carbonates, which host 0.03–0.60 wt.% of the 1.2–3.1 wt.% carbon in CM meteorites (Alexander et al., 2013, 2015). These minerals comprise aragonite, calcite, dolomite and breunnerite (Barber, 1981; Johnson and Prinz, 1993; Lee, 1993; Lee and Ellen, 2008; de Leuw et al., 2010; Lee et al., 2014). $^{53}$Mn-$^{53}$Cr dating has shown that calcite and dolomite precipitated within five million years of Solar System formation (Fujiiya et al., 2012). The carbon and oxygen isotopic compositions of these carbonate minerals can be used to explore the provenance of aqueous solutions and the nature of their interaction with the parent body. Previous studies have shown that individual CM chondrites contain populations of carbonate minerals whose oxygen isotopic compositions provide good evidence for multiple episodes of precipitation from aqueous fluids of different oxygen isotopic compositions and/or temperatures (e.g., Benedix et al., 2003; Guo and Eiler, 2007; Tyra et al., 2012, 2016; Lee et al., 2013; Fujiya et al., 2015).

Here we have determined the oxygen isotopic compositions of calcite grains in four CM carbonaceous chondrites in order to investigate how aqueous alteration environments evolved within and between different parent body regions. As the selected meteorites have been altered to contrasting extents, their aqueous systems are likely to have varied in one or more of: (i) temperature; (ii) longevity; (iii) water/rock ratio. If, for example, results indicate that carbonates in the different meteorites formed at contrasting temperatures, then the implications could be that the CM chondrites have sampled different parts of an aqueous system containing water moving along a thermal gradient. Conversely, strong similarities in fluid evolution between meteorites may be more indicative of a static aqueous system within parent body regions that were originally chemically and isotopically homogeneous. Either way, results of this work will provide new insights into the nature of one of the earliest Solar System processes.

2. MATERIALS AND METHODS

2.1. Petrographic characterisation of carbonates

This study has used the CM carbonaceous chondrites Murchison, Mighei, Cold Bokkeveld and LaPaz Icefield (LAP) 031166. These meteorites differ in their degree of aqueous alteration, as expressed using three classification schemes (Table 1). Hereafter we refer to the extent of aqueous alteration of the CM chondrites using the petrologic subtype notation of Rubin et al. (2007).

One carbon coated thin section or polished block of each of the meteorites was studied (Table 1). Calcite grains were located and characterised by backscattered electron (BSE) and secondary electron (SE) imaging using two field-emission scanning electron microscopes (SEM), both operated at high vacuum and 20 kV/≈2 nA: a FEI Quanta 200F and a Zeiss Sigma. Chemical analyses and elemental maps were acquired by energy-dispersive X-ray spectrometry (EDS) using an Oxford AZtec microanalysis system attached to the Zeiss SEM. The abundances of calcite grains were determined by point counting on the Quanta SEM, whereby the sample was manually systematically traversed (using the frame-by-frame stage movement function), and the material in the centre of the field of view at each step was identified by imaging and EDS. The point counting was undertaken at ×2000 magnification and a step-size of 150 μm, with 3000 points typically being counted for each meteorite.

2.2. NanoSIMS oxygen isotope analyses of carbonates

Owing to the small size of the calcite grains they were analysed for their oxygen isotope composition using a Nano Secondary Ion Mass Spectrometry (SIMS) 50L at the Open University (OU), U.K. (Figs. S1–S4). The analyses were performed by rastering the focussed primary beam over a small area and integrating the total ion signal. A Cs$^+$ ion beam with a current of ~30 pA was used for the analyses (~60 pA for pre-sputter). Secondary ions were measured in multi-collection mode, with $^{16}$O measured on a Faraday cup, and $^{17}$O, $^{18}$O, $^{28}$Mg$^{16}$O, $^{40}$Ca$^{16}$O and $^{56}$Fe$^{16}$O measured on electron multipliers. The major cation oxides allowed real time monitoring of the mineral compositions. The mass resolving power was set to >10,000 ( Cameca, NanoSIMS definition, based on the measured peak width it is the slope between 10% and 90% of the peak), which was sufficient to resolve the interference of $^{18}$OH on the $^{17}$O peak. Charge compensation was applied using the electron gun. Areas for analysis were 5 × 5 μm or 3 × 3 μm, with a larger area for pre-sputter (7 × 7 μm) in order to implant Cs ions evenly and reach sputter equilibrium across the area to be analysed. Analysis times, including pre-sputter, were typically ~8 min with total counts of $^{16}$O in a single analysis being 6 × 10$^9$. Isotope ratios were normalised to Vienna Standard Mean Ocean Water (VSMOW) using analyses of a calcite standard that bracketed the sample analyses in order to generate δ$^{17}$O and δ$^{18}$O values, and also to provide corrections for instrumental mass fractionation. The errors quoted combine internal errors for each analysis with the standard deviation of the mean of the associated standards.

Calcite analyses used an in-house calcite standard with a composition of δ$^{18}$O 15.47 ± 0.07‰ (1σ) VSMOW that was determined from six replicate analyses on a ThermosGasbench II connected to a Delta Advantage mass spectromet-
For these measurements powdered aliquots were reacted with anhydrous H$_3$PO$_4$ at 72 ± 1°C for 1 h. The CO$_2$ generated was then flushed from the head-space of the reaction vessel, dried through Nafion traps before being passed through a Poraplot Q fused silica capillary column to separate other possible contaminants prior to analyses on the mass spectrometer. For the standards, δ$^{17}$O was assumed to lie on the terrestrial fractionation line (TFL; defined as δ$^{17}$O = 0.52 × δ$^{18}$O). Ten analyses of the calcite standard gave a reproducibility of ±1.2–1.4‰ (2σ) for δ$^{18}$O, and ±1.2–2.1‰ (2σ) for Λ$^{18}$O. The sample and standard were positioned in separate blocks mounted on the same sample holder. Using identical analytical procedures to those presented here, Starkey and Franchi (2013) found no statistically significant variation in oxygen isotope ratios when measuring polished samples of San Carlos olivine mounted in different positions across the NanoSIMS holder (up to 40 mm distance apart). NanoSIMS results are expressed as δ$^{17}$O, δ$^{18}$O and Λ$^{18}$O (i.e. δ$^{17}$O=0.52 × δ$^{18}$O), where Λ$^{17}$O is a measure of departure from the TFL.

3. RESULTS

3.1. Calcite abundance and petrographic characteristics

Calcite in the four CM chondrites ranges in abundance from 1.23 to 1.87 vol.% (Table 2). Two petrographically distinct types of grains can be recognised in each meteorite, and are referred to as types 1 and 2 (after Tyra et al., 2012) (Fig. 1). Type 1 grains occur in the fine-grained matrix (Fig. 1a and b). They are typically equant and monocrystalline, can have euhedral terminations, and are rimmed by serpentine and/or tochilinite. Type 2 grains may be present in the matrix but are more commonly hosted in chondrules or chondrule pseudomorphs (Fig. 1c and d). These grains are usually larger than type 1 (some grains can be several hundreds of micrometres in size; Lee et al., 2014), lack a characteristic shape, are typically polycrystalline, contain micropores and inclusions, and lack serpentine/tochilinite rims (Fig. 1c–f). Type 1 calcite is more abundant than type 2 in each meteorite (Table 2).

3.2. Oxygen isotopic composition of calcite

Calcite grains in each of the four studied meteorites can differ significantly in their oxygen isotopic compositions. The NanoSIMS results are here described with reference to the two petrographic types of calcite (Table 2, Figs. 2 and 3, Figs. S1–S4). The five grains of type 1 calcite in Murchison are distinct in their δ$^{18}$O values from the three type 2 grains (~34–39‰ vs 26–18‰, respectively). One of the type 1 analyses plots below the TFL, as do all of the type 2 datapoints. Previous NanoSIMS studies of Murchison calcite have recorded high δ$^{18}$O values that are consistent with mainly analysing type 1 grains: 27–37‰ (Brearley et al., 1999), 34–38‰ (Bonal et al., 2010), 30–39‰ (Horstmann et al., 2014), 33–34‰ (Fujiiya et al., 2015). Mighei type 1 grains have a wide range in δ$^{18}$O (~16–40‰), and all but one is within error of the TFL. The sole type 2 grain analysed has a δ$^{18}$O value in the middle of the type 1 group and plots on the TFL. Nine type 1 grains were analysed in Cold Bokkeveld, and have a δ$^{18}$O of 30–39‰. The four type 2 grains have a broader compositional range (δ$^{18}$O 12–37‰). Five Cold Bokkeveld grains plot below the TFL (three type 1, two type 2) whereas the other eight are within error of the line. The LAP 031166 data form two clusters. The five type 1 grains have a δ$^{18}$O of ~35–39‰. Three of the four type 2 grains are much lighter (δ$^{18}$O 17–22‰) whereas the other plots within the type 1 cluster. Two of the type 1 grains are above the TFL and one of the type 2 grains is below the TFL. Tyra

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Sample number (type)</th>
<th>Recovery</th>
<th>Aqueous alteration indices</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Petrologic$^1$</td>
</tr>
<tr>
<td>Murchison</td>
<td>BM1988.M23, P19260 (PB)$^1$</td>
<td>Fall, 1969, Australia</td>
<td>CM2.5</td>
</tr>
<tr>
<td>Mighei</td>
<td>P725310 (PTS)$^1$</td>
<td>Fall, 1889, Ukraine</td>
<td>CM2.3</td>
</tr>
<tr>
<td>Cold Bokkeveld</td>
<td>BM 1727, P1925610 (PB)$^1$</td>
<td>Fall, 1838, South Africa</td>
<td>CM2.2</td>
</tr>
<tr>
<td>LAP 031166</td>
<td>15 (PTS)$^2$</td>
<td>Find, 2003, Antarctica</td>
<td>CM2.1</td>
</tr>
</tbody>
</table>

PB = Polished resin block.
PTS = Polished thin section.
na denotes not analysed.
$^1$ Loaned by the Natural History Museum London.
$^2$ Loaned by the NASA Johnson Space Center Antarctic meteorite collection.
$^3$ The petrologic subtype scheme (Rubin et al., 2007).
$^4$ Classification based on the normalised fraction of phyllosilicate (Howard et al., 2015).
$^5$ Classification based on bulk water/OH content (Alexander et al., 2013).
et al. (2007, 2012) found that types 1 and 2 calcite in the EET 96006-paired meteorites were chemically indistinguishable, thus showing that the trace element composition of pore fluids had not changed in parallel with their oxygen isotopic composition (or temperature).

4. DISCUSSION

Calcite grains differ in their oxygen isotopic compositions within and between each of the four studied CM chondrites, thus showing that these meteorites contain a temporally and/or spatially resolved record of parent body evolution. In order to maximise the new insights that can be gained from the isotope data, they are discussed below in the framework of the petrographic properties and contexts of the calcite grains, and synthesised with results from previous grain-scale and bulk isotopic studies. These results will then enable testing of models for the evolution of aqueous solutions in C-type asteroids within the first five million years of Solar System history.

Fig. 1. Images of type 1 (T1) and type 2 (T2) calcite grains that were analysed by NanoSIMS, with the datapoints identified (all analysed grains are shown in Figs. S1–S4). (a) BSE image of a type 1 grain in Mighei (Mig_cct1_7). The serpentine/touchilinite grain rim is white, and labelled ST. (b) BSE image of a type 1 grain in Cold Bokkeveld (CB_cct1_14). (c) Type 2 calcite in Mighei, which has partially replaced a chondrule. The image is made from a false-coloured X-ray map that has been overlain on a SE image. The X-ray map has been made by blending colours from four element maps: Mg (red), Si (turquoise), S (yellow) and Ca (blue). This blending renders the chondrule silicates (Ch) dark green and brown, sulphides yellow, and calcite blue. (d) BSE image of the boxed area in (c) showing the location of point Mig_cct2_1. (e) BSE image of type 2 calcite in LAP 031166. (f) BSE image of the boxed area in (e) showing location of point LAP_cct2_1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
4.1. Formation of types 1 and 2 calcite

The petrographic characteristics of types 1 and 2 calcite grains, and the petrologic subtypes of meteorites within which they occur, can help to constrain when these carbonates formed during aqueous alteration. This information can then be used to ‘pin’ the oxygen isotope data obtained by NanoSIMS to specific periods in parent body evolution.

Given that most grains of type 1 calcite have been partially replaced by serpentine and/or tochilinite, whereas none of the type 2 grains have been so affected, type 1 calcite is interpreted to have formed first. The euhedral shapes of some of the type 1 grains and their lack of inclusions suggest that they have filled pore spaces in the matrix, possibly after ice grains (as discussed by Lee et al., 2014). The presence of type 1 calcite in Murchison shows that it had
formed by the time that aqueous alteration had reached the CM2.5 stage. As calcite with similar petrographic characteristics also occurs in Elephant Moraine (EET) 96029 and Paris, which are the least aqueously altered CM chondrites yet described (both CM2.7) (Hewins et al., 2014; Marrocchi et al., 2014; Lee et al., 2016), type 1 calcite must have been one of the first products of parent body aqueous alteration. The calcium required to produce calcite at this early stage is most likely to have been sourced from the dissolution of chondrule mesostasis, plagioclase and melilite. These components are so susceptible to aqueous alteration that they are very scarce even in EET 96029 and Paris (Marrocchi et al., 2014; Rubin, 2015; Lee et al., 2016). Thus, a significant proportion of the type 1 calcite grains in each of the four meteorites is interpreted to have formed by the time that they had been aqueously altered to a level equivalent to CM2.7 2.5. The occurrence of type 1 calcite in LAP 031166 (CM2.1) shows that these early-formed carbonate grains were preserved during subsequent aqueous processing. The serpentine and tochilinite that replaced type 1 calcite is likely to have formed from ions derived from components that were less susceptible to dissolution, including olivine, Fe-sulphide and Fe, Ni metal.

The common presence of type 2 calcite within chondrules, occasionally forming hundreds of micrometre sized pseudomorphs (Lee et al., 2014), indicates that it is a replacement product of primary ferromagnesian silicates. As type 2 calcite occurs in Murchison, it can have precipitated before aqueous alteration had progressed beyond CM2.5; formation even earlier is suggested by the presence of grains with comparable petrographic properties in EET 96029 (Lee et al., 2014, 2016). Another line of evidence
for a relatively early origin of some of the type 2 calcite is that the chondrule-hosted silicate minerals that it has replaced are progressively destroyed during aqueous alteration; they are scarce in CM2.1 meteorites and absent from CM2.0s (Rubin et al., 2007). Thus, the type 2 calcite that occurs in the most highly altered CM chondrites (i.e., LAP 031166) must have precipitated whilst they still contained significant amounts of primary ferromagnesian silicates, and so before they had reached a level of aqueous alteration equivalent to ~CM2.1. The source of Ca for type 2 calcite is difficult to determine. It could have been derived from the dissolution of pyroxene or type 1 calcite, although input of Ca from other parent body regions is possible, and would be consistent with the presence of a vein of type 2 calcite in the CM carbonaceous chondrite Lonewolf Nunataks (LON) 94101 (Lindgren et al., 2011; Lee et al., 2013).

The occurrence of types 1 and 2 calcite in mildly altered meteorites such as Murchison shows that these carbonate grains formed mainly in the early stages of parent body processing. Such a timing is consistent with the poor correlation between the abundance of calcite in the CM chondrites and their degree of aqueous alteration (Lee et al., 2014; Alexander et al., 2015). Only if calcite had precipitated throughout aqueous alteration would its abundance be expected to correlate closely to petrologic subtype.

4.2. Determinants of carbonate oxygen isotopic compositions

Having identified the approximate points at which calcite grains formed during aqueous alteration (i.e., much of the type 1 before CM2.7 2.5; type 2 between ~CM2.7 2.5 and ~CM2.1), their oxygen isotopic compositions can be interpreted in the context of parent body evolution. The following discussions assume that carbonate mineral grains preserve a ‘snapshot’ of the oxygen isotopic compositions of solutions from which they originally precipitated (i.e., they have not re-equilibrated in step with changing fluid properties: Tyra et al., 2012).

The range in oxygen isotope values obtained from carbonate grains within any one meteorite is interpreted to reflect changes over time in the oxygen isotopic compositions and/or temperatures of aqueous solutions. The relative importance of fluid composition and temperature can be assessed by asking how δ18O, δ17O and Δ17O vary between grains. For example, if a population of grains had precipitated from a fluid of invariant Δ17O and changing temperature, δ18O and δ17O values would covary to form an array with a slope of 0.52 in a three-isotope plot (i.e., mass-dependent fractionation, parallel to the TFL). Those grains that formed at a higher temperature would have a lower δ18O and δ17O. Conversely, calcite grains that had precipitated from a fluid that was initially 18O-poor but had exchanged with a component that had a negative Δ17O, by interaction with parent body silicates at a constant temperature, would form an array with a slope that is steeper than 0.52. A regression line plotted through the 42 analyses of calcite obtained in the present study (Fig. 3) has an equation of

\[ \delta^{17}O = 0.67(\pm 0.06) \times \delta^{18}O - 5.3(\pm 1.8) \]  

(2σ; MSWD = 2.1), thus demonstrating a change in the oxygen isotopic compositions of the fluids (although this finding does not discount a simultaneous change in temperature).

The equation of a line regressed through 81 analyses of calcite from the CM chondrites Banten, Cold Bokkeveld, Maribo, Murchison and Nogoya is very similar: \( \delta^{17}O = 0.65(\pm 0.03) \times \delta^{18}O - 5.4(\pm 0.9) \) (2σ; MSWD = 1.3) (Horstmann et al., 2014). Whilst there is clear evidence for a change in fluid composition, some of the data in Fig. 3 could suggest that temperatures changed when Δ17O was static. Specifically, a line of slope 0.52 could be fitted to those grains with a δ18O of less than ~35‰.

There is good evidence for correlated changes to δ18O and Δ17O when grains from several CM chondrites are considered together, but this approach may mask differences between meteorites. Therefore, analyses of calcite in the four samples used in the present study are here discussed individually. Murchison and Cold Bokkeveld both show a correlated fall in δ18O and Δ17O (Table 3, Fig. 2). With regards to Murchison, the five analyses with the highest δ18O are within error of the TFL, whereas the five analyses with a lower δ18O have negative Δ17O. Eight of the Cold Bokkeveld analyses plot in a cluster (δ18O ~35 39‰) and all but one of them is within error of the TFL. Four of the five analyses with a lower δ18O are below the TFL. The Mighei data show less of a clear trend; only one data-point is below the TFL, although it is the analysis with the lowest δ18O. The LAP 031166 grains do not show a consistent relationship between δ18O and Δ17O. Eight of the 11 analyses are within error of the TFL; the two that plot above the TFL are within the high δ18O cluster, and the one that is below the TFL is in the low δ18O cluster. Therefore, the populations of grains in individual meteorites also show that δ18O and Δ17O covary, indicating a change in the oxygen isotopic composition of the solutions, although the evidence is strongest in Murchison and Cold Bokkeveld. This result is consistent with slopes of 0.61 0.62 obtained for regression lines plotted through analyses of calcite grains in each of Sutter’s Mill, EET 96006-paired and LON 94101 (Jenniskens et al., 2012; Tyra et al., 2012; Lee et al., 2013).

4.3. Relative timescales of fluid evolution

NanoSIMS data from grains in individual CM chondrites and in multiple meteorites demonstrate a temporal change in the oxygen isotopic composition of aqueous solutions, but do not reveal the ‘direction’ of evolution. As the studied meteorites contain two generations of calcite, any consistent differences between them will reveal how the fluids evolved. Types 1 and 2 calcite differ in their average δ18O values in Murchison, Cold Bokkeveld and LAP 031166, and also in three other CM chondrites studied previously (Table 4). As the average δ18O value of type 1 calcite in all of these meteorites is heavier than type 2, solutions must have evolved towards lower values of δ18O and Δ17O in each of these six parent body regions. Although the average δ18O values of types 1 and 2 calcite are quite different in Murchison, Cold Bokkeveld and LAP 031166 (Table 4), in two of these meteorites some type 2 grains plot in the type 1 field (Fig. 2a and b). These apparent anomalies may be because: (i) the grains in question
occur in clasts that have a different fluid evolution to the rest of the meteorite; (ii) they are type 1 grains that have been misidentified as type 2; (iii) the two modes of formation of calcite, namely pore filling type 1 and replacive type 2, were not in all cases temporally distinct.

Average isotopic compositions of the two types of calcite are similar in all of the six CM chondrites included in Table 4 (i.e., type 1 $\delta^{18}O \sim 32–38\%e$; type 2 $\delta^{18}O \sim 18–24\%e$). Thus, the types 1 and 2 calcite are interpreted to have formed in two episodes, and when aqueous solutions in six parent body regions had reached approximately the same two points in their compositional evolution. Results from Mighei do not fit this pattern. The range in $\delta^{18}O$ of type 1 calcite (16–40\%e) suggests that its precipitation was more continuous in the parent body region that this meteorite has sampled.

### 4.4. Origin and significance of dolomite

Differences in average $\delta^{18}O$ values between grains of types 1 and 2 calcite show that they precipitated at two different periods during parent body evolution. In the intervening period aqueous solutions had evolved isotopically by interaction with $^{16}O$-rich parent body silicates; temperatures may also have increased. The nature of parent body environments may be explored further using the oxygen isotopic composition of dolomite in two highly aqueously altered CM chondrites: Allan Hills (ALH) 84049 (CM2.0; Tyra et al., 2016) and Sutter’s Mill (CM2.0–2.1; Jenniskens et al., 2012) (Table 5).

On the assumption that aqueous solutions in ALH 84049 and Sutter’s Mill evolved by a coupled fall in $\delta^{18}O$ and $\Delta^{17}O$ (i.e., in the same manner as revealed by calcite in the six CM chondrites listed in Table 4), the average $\delta^{18}O$ values of dolomite grains in these two meteorites (~25–29\%e; Table 5) suggest that they formed between types 1 and 2 calcite. Although types 1 and 2 calcite were not distinguished by Jenniskens et al. (2012), the compositional range of calcite in this CM chondrite is wider than that of dolomite (i.e., $\delta^{18}O$ 13.2–39.2\%e for calcite vs 23.5–26.1\%e for dolomite). Such a difference would be consistent with dolomite forming between separate generations of calcite. Note that contrasts in calcite-water and dolomite-water fractionation factors are insufficient to account for the observed differences in $\delta^{18}O$ values between two minerals (e.g., dolomite precipitated over the 80–350 °C temperature range is enriched in $^{18}O$ by 0.7–2.6\%e relative to calcite (Horita, 2014)).

As dolomite occurs only in CM2.0–2.2 meteorites (de Leuw et al., 2010; Lee et al., 2014), conditions were conducive to its precipitation just in those parent body regions that were highly aqueously altered. In these regions, the evolving fluids may have briefly surpassed the threshold for dolomite precipitation, for example, owing to a high Mg/Ca ratio. Alternatively, a short-lived increase in temperature could have catalysed dolomite formation by overcoming the barrier to precipitation from the hydration of magnesioferrite. The return to calcite precipitation, to form type 2 grains, may have been due to a fall in temperature or a change in fluid chemistry, for example selective removal of magnesium by precipitation of dolomite or Mg-rich serpentine. This model of carbonate precipitation is consistent with the observation that dolomite in the CM chondrites has commonly been replaced by calcite (Lee et al., 2012, 2014), and findings of Tyra et al. (2016) that in ALH 84049 the two carbonate minerals formed in different episodes. However, the model should be tested further by determination of the oxygen isotopic compositions of grains of dolomite and types 1 and 2 calcite in the same meteorite.

### 4.5. Variations in solution compositions between parent body regions

The grain-scale data acquired from each meteorite tracks the compositional evolution of aqueous solutions within discrete millimetre-centimetre size parent body regions. However, given that only small numbers of grains were analysed in each sample, these datasets cannot be used with confidence to answer the question of whether fluids evolved...
differently between parent body regions. This problem of unrepresentative sampling by NanoSIMS can be addressed by using the oxygen isotopic compositions of carbonates in bulk samples of CM meteorites. Results from each sample will be an average of the meteorite’s grain population, and differences between meteorite samples will indicate how grain populations vary between parent body regions.

The δ18O values of carbonates in bulk samples have a wide range: ~36–20‰ (five CM chondrites analysed by Benedix et al., 2003) and ~35–15‰ (average 25‰; 45 CM chondrites analysed by Alexander et al., 2015) (Fig. 3). As the maxima and minima of these ranges are close to the compositions of types 1 and 2 calcite (i.e., ~38–32‰ and ~24–18‰, respectively; Table 4), we suggest that these two calcite types occur in many meteorites and in very different relative proportions. The latter assumption is consistent with point counting results showing that the type 1 to type 2 calcite ratio varies from 1–17, just in four CM chondrites (Table 2). The bulk meteorite data can be used to test our conclusion that δ18O and Δ17O fell between precipitation of the two types of calcite because meteorites with a low bulk carbonate δ18O should be rich in type 2 calcite that has a relatively low Δ17O. Results from the five CM chondrites studied by Benedix et al. (2003), which include three of those used in the present study (Murchison, Mighei, Cold Bokkeveld), confirm that bulk carbonate δ18O and Δ17O covary (r² = 0.62, n = 11 analyses). Indeed, regression lines for NanoSIMS data acquired in the present study and the bulk data in Benedix et al. (2003) are similar (Fig. 3). To summarise, the grain-scale data from each CM chondrite shows that aqueous solutions evolved towards a lower δ18O and Δ17O, possibly accompanied by an increase in temperature. The bulk data suggest that in some parent body regions nearly all of the calcite precipitated from cool ‘juvenile’ fluids giving a bulk carbonate δ18O of ~35‰ (i.e., type 1). In other regions, the calcite precipitated from ‘evolved’ fluids that had become isotopically lighter by interaction with the parent body, and may also have been hotter. These CM chondrites are dominated by type 2 calcite and so have a bulk carbonate δ18O of ~15‰. An ‘average’ CM chondrite will contain both calcite types and have a bulk carbonate δ18O of ~25‰.

Our interpretations of the bulk carbonate data differ to those reached by Alexander et al. (2015). They concluded that fluid compositions varied little between parent body regions (δ18O ~5‰) so that the ~35–15‰ range in bulk carbonate δ18O values largely reflects contrasts in average temperatures (~0–130 °C). Indeed, differences in the average temperature of carbonate precipitation were demonstrated by Guo and Eiler (2007). They used clumped isotope thermometry to analyse carbonates in bulk samples of Murchison, Murray and Cold Bokkeveld. Temperatures obtained from six of seven samples were indistinguishable within error (20–35 °C, ±10 °C), but calcite in one of the three samples of Cold Bokkeveld gave a temperature of 71 °C (±10 °C). Thus there is clear evidence that fluid temperatures varied during carbonate precipitation, but our grain scale data show that solution compositions also changed. Both processes can be reconciled by envisaging one or more parent bodies within which carbonates were precipitating from fluids that were increasing in temperature as they reacted with primary silicates. This temperature increase may have been linked to serpentinisation, which is an exothermic reaction.

5. IMPLICATIONS FOR MODELS OF PARENT BODY EVOLUTION

The open system model for carbonaceous chondrite aqueous alteration (Young et al., 1999) predicts that carbonates formed from aqueous solutions of a constant Δ17O that had flowed along a temperature gradient would lie along a line with a slope of ~0.52 in a three-isotope plot. Results from the present study however demonstrate a coupled fall in δ18O and Δ17O for calcite grains within the CM chondrites (i.e., a slope of >0.52). This finding is consistent with the closed system model for aqueous alteration, which proposes that carbonates precipitated from water that was initially 16O-depleted and changed in composition by reaction with 16O-rich anhydrous silicates (Clayton and Mayeda, 1984, 1999). With regards to any one meteorite, the later-formed calcite grains will have a lower δ18O and Δ17O than those that precipitated first. Fluid temperatures probably also increased over the timespan of carbonate precipitation. Such heating need not require fluid flow and could equally have been produced locally in static solutions, for example as a by-product of serpentinisation. The very low permeability of CM carbonaceous chondrite meteorites supports the closed system model (Bland et al., 2009), as does the absence of evidence for fractionation of water-soluble elements (discussed by Velbel et al. (2012)). The presence of a vein of type 2 calcite in the CM chondrite LON 94101 (Lee et al., 2013), and dolomite veins in the CM chondrite Scott Glacier (SCO) 06043 (Lee et al., 2014), show that the late-stage ‘evolved’ aqueous solutions locally moved along fractures that had formed by brittle deformation of the parent body. However, given the scarcity of mineral veins in the carbonaceous chondrites in comparison to the ubiquity of type 2 calcite (Lindgren et al., 2015), it is likely that any fracture-mediated fluid flow would have been over short (~centimetre) length scales.

As the four calcite-bearing meteorites used in the present study all contain grains with a broad range of δ18O values, the pattern of fluid evolution that they define must have been widespread, and such similarities in environmental conditions are underscored by the ubiquitous presence of two petrographically and isotopically distinct types of calcite. Nonetheless, the occurrence of dolomite in the most highly altered CM chondrites (CM2.0–2.2) shows that all CM chondrite parent body regions did not all evolve in exactly the same manner.

6. CONCLUSIONS

1. The broad range in oxygen isotopic compositions of calcite grains in the CM carbonaceous chondrites Murchison, Mighei, Cold Bokkeveld and LAP 031166 indicates an extended period of carbonate precipitation under changing environmental conditions;
2. The $\delta^{18}$O and $\Delta^{17}$O values of aqueous solutions decreased over time owing to progressive reaction with parent body silicates in a closed system, and probably in parallel with an increase in temperature. Thus, the oxygen isotopic compositions of carbonate grains in any one meteorite can be used to infer their relative order of precipitation;

3. Many CM chondrites have evidence for two discrete episodes of calcite precipitation, producing types 1 and 2 calcite, with dolomite also being formed in highly altered (i.e., CM2.0–2.2) parent body regions;

4. Grains of type 1 calcite formed by the filling of pore spaces in meteorite matrices. Calcium for these grains was sourced from dissolution of very soluble components including chondrule mesostasis, plagioclase and mellilite. In any one meteorite, most type 2 calcite is interpreted to have precipitated after type 1, and by replacement of primary ferromagnesian silicate minerals;

5. Dolomite probably formed in response to a thermal pulse or a brief increase in fluid Mg/Ca. The oxygen isotopic compositions of grains in ALH 84049 and Sutter’s Mill are consistent with their precipitation between types 1 and 2 calcite, but this conclusion needs to be tested by oxygen isotopic analysis of all three grain types where they occur in the same meteorite;

6. Large differences between parent body regions in the relative proportions of types 1 and 2 calcite are reflected in the wide range of isotopic compositions of carbonates in bulk meteorite samples. In some parent body regions most calcite precipitated from juvenile fluids (type 1) whereas in others it formed mainly from evolved solutions (type 2). The reasons for differences in the relative proportions of the two calcite types remain unclear, but given that type 2 calcite typically forms after type 1, it could be linked to contrasts in the longevity of aqueous alteration;

7. The ubiquitous presence within the CM carbonaceous chondrites of two petrographically and isotopically distinct generations of calcite demonstrates such a strong similarity in parent body evolution as to suggest that they could sample a single C-type asteroid.

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**APPENDIX A. SUPPLEMENTARY DATA**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2017.01.048.


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