# *Chapter 2*

# TEMPERATURES OF AQUEOUS ALTERATION ON CARBONACEOUS CHONDRITE PARENT BODIES

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## ABSTRACT

Application of stepped phosphoric acid digestion and carbonate clumped isotope thermometry to carbonates in carbonaceous chondrites — GRO 95577 (CR1), Orgueil (CI) and Tagish Lake (ungrouped C2) — indicates that aqueous alterations on carbonaceous chondrite parent bodies occurred from -31 to 65˚C from fluids with $\delta^{18}O_{VSMOW}$ values of -29.7‰ to 11.8‰ and $\delta^{17}O_{VSMOW}$ of -14.9‰ to 7.6‰. The estimated carbonate formation temperatures decrease in the order: calcite > dolomite > breunnerite. Based on independent constraints on the ages of these carbonates and models of the evolution of the oxygen isotope compositions of parent body waters, this trend indicates that the parent bodies were cooling as the aqueous alteration proceeded. We estimate that aqueous alteration on the carbonaceous chondrite parent bodies started within 1-2 million years after the accretion of those parent bodies, and that the alteration temperatures decreased from 34˚C to 18˚C in the first ~4 million years and further to -20˚C after a total of ~6.5 million years. Our results provide the first direct measurements of the low-temperature cooling histories of C1 and C2 carbonaceous chondrite parent bodies.

## 1. INTRODUCTION

Aqueous alteration of primitive meteorites is among the earliest and most widespread geological processes in the solar system, occurring within the first tens of million of years of solar system history (Brearley, 2006). A better understanding of these processes, including precise reconstructions of alteration temperatures, would help us constrain the early conditions of the solar system and test models of thermal and chemical evolution of planetesimals.

Previous estimates of the alteration temperatures on the carbonaceous chondrite parent bodies, mostly based on the maximum thermal stabilities of matrix phases and oxygen isotope fractionations between the constituent phases in the matrix, range from <20˚C to <300˚C (Keil 2000 and references therein). As discussed before (Guo and Eiler, 2007), these two approaches either yield only upper temperature limits or require the assumption that phases in the matrix achieved mutual oxygen isotope equilibrium. In a recent study, we apply carbonate clumped isotope thermometry (Ghosh et al., 2006; Schauble et al., 2006) to carbonates in CM chondrties, showing that the aqueous alteration temperatures on the CM chondrite parent body (or bodies) ranged between 20 and 71˚C (Guo and Eiler, 2007). Carbonate clumped isotope thermometry is based on a thermodynamic homogeneous equilibrium within the carbonate lattice that orders $^{13}$C and $^{18}$O into the same carbonate ion. This thermometer is independent of the isotopic compositions of any coexisting phases and makes no assumptions regarding equilibration of carbonates with other phases. Therefore, our approach circumvents some assumption made by previous studies and provides precise (±10˚C) constraints on the temperature of aqueous alteration of the carbonaceous chondrite parent bodies.

In this study, we extended our previous work on CM chondrites by further applying carbonate clumped isotope thermometry to carbonates in other types of carbonaceous chondrites, including the CR1 chondrite, GRO 95577, the CI chondrite, Orgueil; and the ungrouped C2 chondrite, Tagish Lake. These samples contain two or more generations of distinct carbonate phases, which previous studies have established grew at different times and possibly under different conditions and from waters of different isotopic compositions. We used techniques of stepped acid digestion to separately determine the clumped isotope formation temperatures of these diverse carbonates, thereby constraining multiple points on the temperature-time path followed by each of these rocks.

## 2. SAMPLES AND METHOD

### 2.1 Samples

We analyzed carbonates from 4 splits of 3 different carbonaceous chondrites: GRO 95577 (CR1, 2 splits), Orgueil (CI, 1 split) and Tagish Lake (ungrouped C2, 1 split). Each sample split (weighing between 26 and 96 mg) was prepared from a separate fragment of a whole rock meteorite sample and ground individually into unsieved particles (grain size of ≤500 μm) with an agate mortar and pestle (Table 2-1).

Each of the three analyzed meteorites is a representative and well-studied member of their respective groups. All experienced extensive aqueous alterations as evidenced by the occurrence of abundant secondary minerals (such as phyllosilicates, carbonates, and magnetite) in their matrix, though Tagish Lake (petrologic type 2) is less altered than GRO 95577 and Orgueil (both petrologic type 1) (Weisberg and Prinz, 2000; Zolensky et al., 2002; Weisberg et al., 2006). Carbonate minerals are abundant in all three of these carbonaceous chondrites (average modal abundances of 5 vol% and 6.4 vol% in Orgueil and GRO95577 respectively, and 7-8 wt% in Tagish Lake), occurring mostly in the form of veins and isolated grains or fragments in the matrix (Endress and Bischoff, 1996; Leshin et al., 2001; Zolensky et al., 2002; Perronnet et al., 2007). However, carbonate mineralogies are significantly different among these three samples: carbonates in GRO

**Table 2-1** Isotopic analyses of carbonates in carbonaceous chondrites.

| Sample | | GRO 95577 (split 2006) | GRO 95577 (split 2007) | Orgueil[ϕ] | | | Tagish Lake | | | Estimated External Precision (1σ) |
|---|---|---|---|---|---|---|---|---|---|---|
| Petrology Type | | CR1 | CR1 | CI | | | Ungrouped C2 | | | |
| Weight (mg) | | 24.9 | 30.2 | 96.18 | | | 79.05 | | | |
| Date of Analysis | | 8/11/06 | 4/5/07 | 12/14/06-1/1/06 | | | 1/25/07-2/11/07 | | | |
| Carbonate Mineralogy | | Calcite | Calcite | Dolomite[ξ] | | Breunnerite | Calcite | Dolomite | Breunnerite | |
| $CO_2$ yield | (μmol) | 5.7 | 18.7 | 8.4 | | 4.6 | 3.9 | 28.1 | 10.2 | |
| | (μmol/g) | 229.1 | 618.9 | 87.8 | | 48.4 | 49.1 | 355.2 | 129.2 | |
| $\Delta^{17}O^*$(‰) | | -0.93 | -0.93 | 0.50 | | 0.55 | 1.49 | 1.85 | 2.07 | 0.1 |
| $\delta^{13}C_{Carbonate}$(‰) VPDB | | 69.91 | 70.79 | 67.28 | 67.77 | 40.42 | 69.05 | 73.37 | 70.72 | 0.14 |
| $\delta^{18}O_{Carbonate}$(‰) VSMOW | | 19.62 | 17.82 | 28.99 | 28.91 | 21.08 | 33.42 | 34.56 | 36.70 | 0.21 |
| $\Delta_{47}$(‰) | | 0.726 | 0.571 | 0.709 | 0.650 | 0.887 | 0.497 | 0.586 | 0.960 | 0.041 |
| Temperature (˚C) | | 8 | 43 | 12 | 24 | -20 | 65 | 39 | -31 | ~10 |
| $\delta^{18}O_{water}$(‰) VSMOW | | -12.3 | -7.1 | -5.3 | -2.7 | -29.7 | 11.8 | 5.8 | -18.6 | ~2 |
| $\delta^{17}O_{water}$(‰) VSMOW | | -7.3 | -4.6 | -2.2 | -0.9 | -14.9 | 7.6 | 4.8 | -7.6 | ~1 |

[ϕ] No $CO_2$ was yielded during our stepped extraction of calcite from Orgueil, consistent with the rare occurrence of calcite in Orgueil (Brearley and Jones 1998).

* $\Delta^{17}O$ values are averages recalculated from Leshin et al. (2001) and Clayton and Mayeda (1999) with $\lambda$=0.5164, and are used in $^{17}O$ corrections of this study (see texts for details).

[ξ] The two splits of $CO_2$ for Orgueil dolomite were derived from a single extraction. The extracted $CO_2$ were divided into two splits after exposure to dry $Ag_3PO_4$, and these two splits were then analyzed at different time on the mass spectrometer.

95577 are almost exclusively calcite [$CaCO_3$] (Perronnet et al., 2007); carbonates in Orgueil and Tagish Lake vary in compositions from calcite to dolomite [$CaMg(CO_3)_2$] (or siderite [$FeCO_3$]) and to breunnerite [$Mg(Fe,Mn)(CO_3)_2$], with their abundances decreasing in the order of dolomite > breunnerite > calcite (very rare) in Orgueil (Brearley and Jones, 1998; Brown et al., 2000; Zolensky et al., 2002).

## 2.2 Phosphoric acid digestion

Depending on their respective carbonate mineralogy, each ground meteorite sample was either reacted with anhydrous phosphoric acid at 25˚C for 18-24 hours (for GRO 95577) or subjected to a stepped phosphoric acid digestion procedure (for Orgueil and Tagish Lake) to separately measure the isotopic compositions of their constituent carbonate mineral phases — calcite, dolomite and brunnerite. Stepped phosphoric acid digestion is an experimental technique, widely applied in studies of terrestrial carbonate samples, to separately extract and determine the isotopic compositions of two or more carbonate constituents in mixtures that are too finely intermixed to physically separate. It is based on the fact that different carbonate minerals react with anhydrous phosphoric acid at different rates at any given temperature, decreasing in the order of calcite, dolomite and breunnerite/magnesite (Al-Aasm et al., 1990). These techniques have also been previously applied to meteoritic carbonates (Grady et al., 1988; Leshin et al., 2001; Benedix et al., 2003). In this study, we employed a 3-step stepped phosphoric acid digestion and extraction method, designed to release $CO_2$ from calcite, dolomite and breunnerite/magnesite during steps 1, 2 and 3 respectively:  Step 1) the ground sample was first reacted with anhydrous phosphoric acid at 50˚C, and the $CO_2$ released during the first 3 minutes was collected and assumed to represent the calcite contained in the sample; Step 2) the sample was left reacting further at 50˚C, and the $CO_2$ released between 3 minutes and 24 hours was collected and assumed to represent the dolomite contained in the sample; and Step 3) the reaction vessel was then transferred to a oil bath with a set temperature of 80˚C for 2-3 days. The $CO_2$ released during the third step was collected and assumed to represent the breunnerite/magnesite contained in the sample. The temperatures of phosphoric acid digestions at each step were controlled within ±2˚C of the desired temperatures.

The stepped phosphoric acid digestion and extraction method described above was established by experiments on synthetic mixtures of calcite and dolomite and of dolomite and magnesite (magnesite here is assumed to simulate brunnertie in the carbonaceous chondrites; both siderite and magnesite, the two composition-end-members of breunnerite, react with phosphoric acid orders of magnitude much more slowly than dolomite at given temperature, with magnesite being the slowest; Al-Aasm et al., 1990). In both cases we prepared physical mixtures having carbon equivalent molar ratios of ~1:1 between the two constituent phases (Table 2-2). The isotopic compositions of carbonate end members (calcite and dolomite) used in the test were also determined separately by complete reaction of pure end members to compare with those derived from the stepped phosphoric acid digestion. Calcite used in the synthetic mixture was purchased from Sigma-Aldrich Co. as powder; dolomite and magnesite were obtained from the mineral collection of the Division of Geological and Planetary Sciences at Caltech and then ground into powders. The phase identity of each mineral was verified using X-ray diffraction. The results of these methodological tests are presented in section 3.1.

**Table 2-2** Tests and establishment of stepped extraction procedures on synthetic mixtures of calcite and dolomite, and of dolomite and magnesite (carbon equivalent molar ratio ~1:1 for both).

| | Carbonate Endmembers | | | Stepped Phosphoric Acid Digestion | | | | Estimated External Precision (1σ) |
|---|---|---|---|---|---|---|---|---|
| Sample | Calcite | Dolomite | | Calcite + Dolomite ~1:1 Mixture | | Dolomite + Magnesite ~1:1 Mixture | | |
| | | Split 1 | Split 2 | Step I (Calcite) | Step II (Dolomite) | Step I (Dolomite) | Step II (Magnesite) | |
| Digestion Temperature (˚C) | 50 | 50 | 50 | 50 | 50 | 50 | 80 | |
| Digestion Time | 24hr | 24hr | 24hr | 3min | 24hr | 24hr | 56hr | |
| $\delta^{13}C_{Carbonate}$(‰) VPDB | -42.37 | -0.20 | -0.16 | -41.54 | -2.38 | -0.10 | 1.60 | 0.001 |
| $\delta^{18}O_{Carbonate}$(‰) VSMOW | 10.00 | 18.86 | 18.87 | 10.11 | 18.36 | 18.74 | 14.59 | 0.002 |
| $\Delta_{47}$(‰) | 0.395 | 0.470 | 0.495 | 0.400 | 0.481 | 0.462 | 0.319 | 0.01 |
| Components Estimated [&] | N/A | N/A | N/A | 98% Calcite<br>+<br>2% Dolomite | 95% Calcite<br>+<br>5% Dolomite | 96% Calcite<br>+<br>4% Dolomite | N/A | |

[&] The actual compositions of the stepped-extraction products estimated from their carbon isotope compositions (see section 3.1 for details).

The total yield of $CO_2$ from each meteorite sample split varied from 136.1 μmol/g to 618.9 μmol/g, increasing in the order of Orgueil > GRO 95577 (split 2006) > Tagish Lake > GRO 95577 (split 2007) (Table 1). The difference in $CO_2$ yields between the two splits of GRO 95577 samples (229.1 μmol/g vs. 618.9 μmol/g) reflects the heterogeneous distribution of carbonates inside the sample. All of these $CO_2$ yields are higher than those observed from phosphoric acid digestion of CM chondrites (39.3-127.6μmol/g; Guo and Eiler 2007), and generally agree with the estimations of carbonate abundances from petrographic observations of the samples we've studied (Endress and Bischoff, 1996; Brearley and Jones, 1998; Zolensky et al., 2002; Perronnet et al., 2007) and a previous phosphoric acid digestion study (Leshin et al., 2001). The yields of $CO_2$ from different steps of our stepped extractions (of Orgueil and Tagish Lake) are also consistent with dolomite being the most abundant carbonate phase in both Orgueil and Tagish Lake, followed by breunnerite and then calcite. Note, no $CO_2$ was evolved during the calcite extraction step for Orgueil, consistent with the rare occurrence of calcite in the Orgueil matrix (Brearley and Jones, 1998).

### 2.3 Purification of sample $CO_2$ and mass spectrometric analysis

$CO_2$ derived from phosphoric acid digestion of carbonaceous chondrites is rich in sulfur and organic contaminants and requires careful purification before isotopic analyses (Clayton and Mayeda, 1984; Grady et al., 1988; Benedix et al., 2003; Guo and Eiler, 2007). Following the procedures outlined in Guo and Eiler (2007), we exposed the $CO_2$ produced by acid digestion of chondritic samples to dry $Ag_3PO_4$, passed it through a series of glass traps cooled with an ethanol slush (–78˚C) and a pentane slush (–130˚C) and through a Supelco Q-Plot GC column held at –20°C. $CO_2$ released from GRO 95577, Orgueil and Tagish Lake were generally poor in contaminants (0.6-2.9% for all sample extractions, except the 80°C extraction for breunnerite in Tagish Lake—30.2%), based on the sample sizes before and after dry $Ag_3PO_4$ treatment. This contrasts with the consistently high (19-62%) abundances of sulfur and other contaminants in the $CO_2$ derived from phosphoric acid digestion of CM chondrites (Guo and Eiler, 2007).

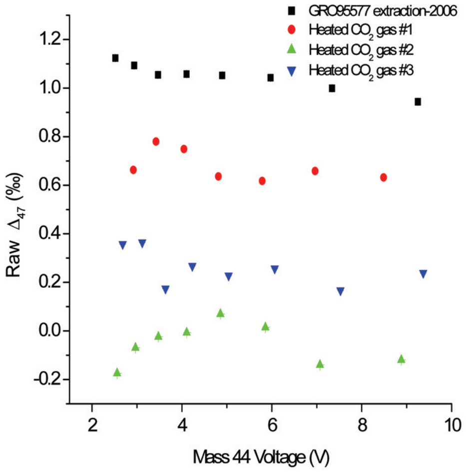
The purified $CO_2$ was then analyzed in micro-volume dual inlet mode on a Finnigan-MAT 253 gas source isotope ratio mass spectrometer, at signal intensities of 2.2-9.5V for mass 44. Note that the $CO_2$ yields from different sample extractions and extraction steps ranged from 3.9μmol to 28.1μmol. To ensure that all sample $CO_2$ was processed and analyzed under similar conditions (e.g., similar gas sizes and mass 44 voltages), we divided the extracted $CO_2$ on the vacuum line for extractions yielding $CO_2$ gases more than 6 μmol, and used only a portion of the extracted $CO_2$ (3.8μmol to 5.7μmol) in the sample purification and mass spectrometric analyses. The rest of the extracted sample $CO_2$ was sealed in pre-evacuated Pyrex tubes for future analyses. One exception is for $CO_2$ derived from dolomite extraction of Orgueil, which we divided into two splits after exposure to dry $Ag_3PO_4$. Both of these two splits of $CO_2$ were then further purified and analyzed on the mass spectrometer (Table 1). A more detailed description on the sample purification and mass spectrometric analysis can be found in our recent study of carbonates in CM chondrites (Guo and Eiler, 2007).

The isotopic compositions of the purified sample $CO_2$ ($\delta^{13}C$, $\delta^{18}O$ and $\Delta_{47}$) obtained from the mass spectrometric analyses were corrected for their $\Delta^{17}O$ values (Guo and Eiler, 2007). We assume average carbonate $\Delta^{17}O$ of Orgueil and Tagish Lake (recalculated from Leshin et al. 2001) and average matrix $\Delta^{17}O$ of CR chondrites (recalculated from Clayton and Mayeda 1999) in our corrections for samples from the respective carbonaceous chondrites (Table 1). 1‰ decrease in $\Delta^{17}O$, if unrecognized or unaccounted for, would lead to a systematic error of ~0.034‰ in sample $\Delta_{47}$ (Eiler and Schauble, 2004).

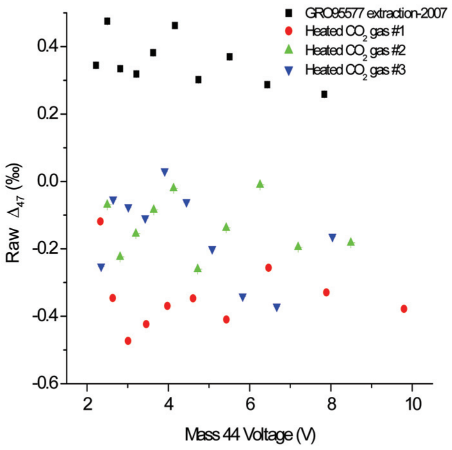
The oxygen isotope fractionation factors (α values) associated with phosphoric acid digestion were assumed to be 1.01025, 1.00930, 1.01038 and 1.00976 (Beukes et al., 1990; Das Sharma et al., 2002) for, respectively, $CO_2$ derived from 25°C calcite extraction, 50°C calcite extraction, 50°C dolomite extraction and 80°C breunnerite extraction. All reported oxygen isotope compositions of carbonates have been corrected for these analytical fractionations.

Values of $\delta^{13}C$ and $\delta^{18}O$ were standardized by comparison with $CO_2$ generated by phosphoric acid digestion of NBS-19 and are reported vs. VPDB and VSMOW, respectively. The external precision of our isotope analyses are estimated to be 0.14‰, 0.21‰, 0.04‰ (1σ) for $\delta^{13}C$, $\delta^{18}O$ and $\Delta_{47}$, respectively, based on measurements of carbonate standards with the same experimental procedures (Guo and Eiler, 2007). Note that these errors are larger than typical of carbonate clumped isotope analyses and reflect the smaller sizes and greater contamination of the samples examined in this study.

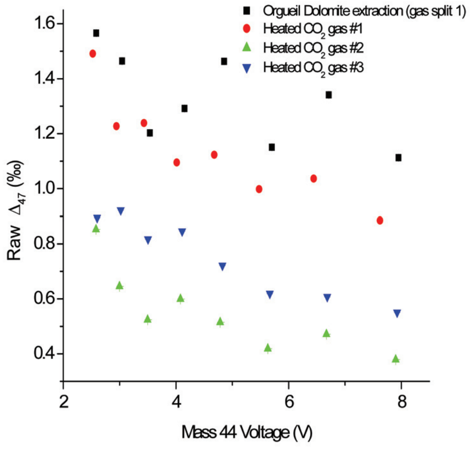
During the mass spectrometric analyses, we observed negative correlations between the raw $\Delta_{47}$ value of sample $CO_2$ (relative to the reference $CO_2$ gas) and the mass 44 voltages at which the raw $\Delta_{47}$ was obtained (Fig. 1). Similar correlations were also observed in the mass spectrometric analyses of heated $CO_2$ gases that accompany the analyses of sample $CO_2$ (all made within 1-2 days of the analyses of sample $CO_2$ for


GRO95577 extraction-2006
Heated $CO_2$ gas #1
Heated $CO_2$ gas #2
Heated $CO_2$ gas #3
Raw $\Delta_{47}$ (‰)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
2
4
6
8
10
Mass 44 Voltage (V)

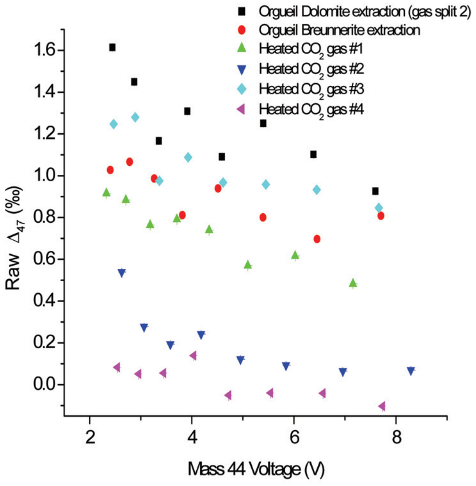
(a)


GRO95577 extraction-2007
Heated $CO_2$ gas #1
Heated $CO_2$ gas #2
Heated $CO_2$ gas #3
Raw $\Delta_{47}$ (‰)
0.4
0.2
0.0
-0.2
-0.4
-0.6
2
4
6
8
10
Mass 44 Voltage (V)

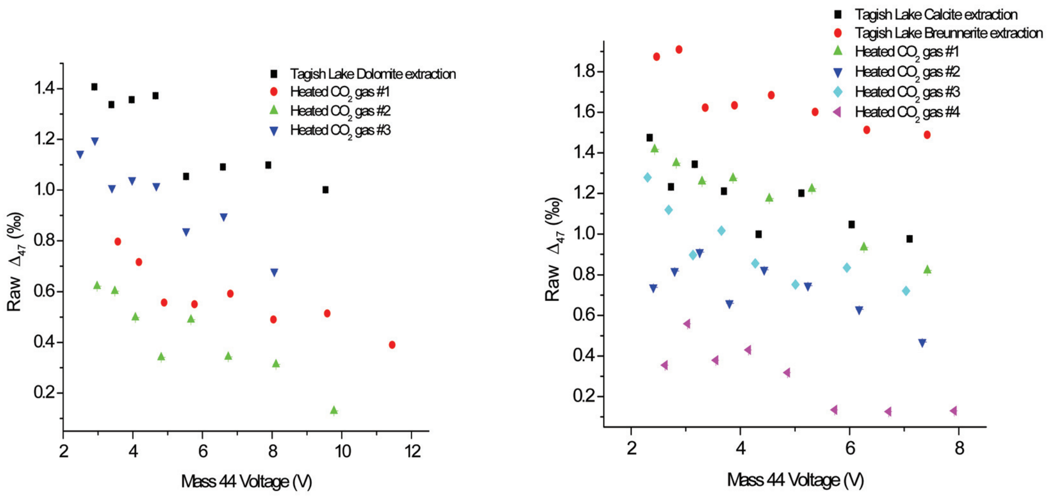
(b)


Orgueil Dolomite extraction (gas split 1)
Heated $CO_2$ gas #1
Heated $CO_2$ gas #2
Heated $CO_2$ gas #3
Raw $\Delta_{47}$ (‰)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
2
4
6
8
Mass 44 Voltage (V)

(c)


Orgueil Dolomite extraction (gas split 2)
Orgueil Breunnerite extraction
Heated $CO_2$ gas #1
Heated $CO_2$ gas #2
Heated $CO_2$ gas #3
Heated $CO_2$ gas #4
Raw $\Delta_{47}$ (‰)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
2
4
6
8
Mass 44 Voltage (V)

(d)



(e) (f)

**Figure 2-1** Negative correlations between raw $\Delta_{47}$ of analyte $CO_2$ (both meteoritic sample $CO_2$ and their accompanying heated $CO_2$ gases) and their mass 44 voltages during the mass spectrometric analyses: (a) GRO 95577 split 2006 extraction; (b) GRO 95577 split 2007 extraction; (c) Orgueil dolomite extraction (gas split 1); (d) Orgueil dolomite extraction (gas split 2); (e) Tagish Lake calcite and breunnerite extractions; (f) Tagish Lake breunnerite extraction. These negative correlations were suspected to be related to a drift in the linearity of the mass spectrometer, and were corrected through a voltage correction procedure before deriving the sample $\Delta_{47}$ (section 2.3). Each data point in the figures represents one acquisition (consisting of 10 cycles of sample-standarad comparisons) of the mass spectrometric analyses.

which that heated gas was used as a standard). These heated $CO_2$ gases are used to standardize measurements of the $\Delta_{47}$ value of sample $CO_2$; they were prepared by heating $CO_2$ gas of bulk isotopic compositions similar to sample $CO_2$ at 1000˚C to achieve stochastic distribution of all isotopes among all isotopologues (i.e., $\Delta_{47}$=0‰) (see Eiler and Schauble 2004 and Ghosh et al. 2006 for more details). These correlations were not observed in our previous study of carbonates in CM chondrites (Guo and Eiler, 2007), and we suspect they reflect an instrument non-linearity (the appearance of this artifact coincides with related phenomena, like a dependence of measured $\Delta_{47}$ values on the difference in $\delta^{47}$ between sample and standard). To correct for these effects, we normalized the raw $\Delta_{47}$ of analyte $CO_2$ to a heated gas standard run at the same sample voltage. The normalization was achieved by first least-squares fitting the observed 'raw $\Delta_{47}$'~'voltage' correlations with linear functions, and then deriving the normalized $\Delta_{47}$ (at 5V) based on the obtained linear functions. We chose 5V as the normalization voltage in our correction because the statistical errors from the least-squares fitting of the "raw $\Delta_{47}$"~"voltage" correlations near their minimum at this voltage (i.e., because 5V lies in the middle of the voltage range of our analyses, 2.2-9.5V). We evaluated the effects of this voltage correction on the accuracy and precision of our results in section 3.2.

It is also noted that even after our most stringent purification procedures, all samples of $CO_2$ extracted from the chondrite samples contained detectable levels of contaminants, as monitored by the intensity of the mass-48 ion beam during mass spectrometric analysis. Values of $\Delta_{48}$ for sample gases, defined as $\Delta_{48} = \left(\frac{R^{48}_{\text{measured}}}{R^{48}_{\text{stochastic}}} - 1\right) \times 1000$, varied up to 4000‰. Past studies of the clumped isotope composition of $CO_2$ have shown that isobaric interferences at masses 48 and/or 49 can be correlated with isobaric interferences at mass 47, and therefore provide a basis for recognizing samples that are too contaminated for accurate analysis (Eiler and Schauble, 2004). However, we did not observe any consistent correlations between $\Delta_{47}$ and $\Delta_{48}$ among different samples of $CO_2$ extracted from carbonaceous chondrites (Fig. 2-2). This suggests that the particular contaminants that are present in these samples are not associated with a significant isobaric interference at masses 44 through 47 and thus do not affect our determination of sample $\Delta_{47}$. While this conclusion seems supported from our results to-date (figure 2), future measurements of this kind should explore additional methods of sample purification to remove the remaining trace contaminants.

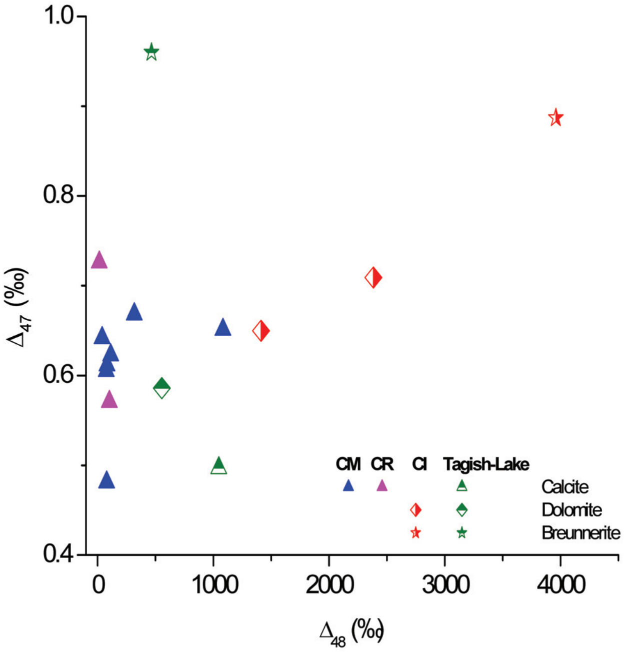


**Figure 2-2** Absence of correlations between $\Delta_{47}$ and $\Delta_{48}$ of meteoritic sample $CO_2$. $\Delta_{48}$ here is an index for the amount of contaminants remaining in the sample $CO_2$ after extensive purification. The absence of correlation indicates negligible influences of the remaining contaminants on the sample $\Delta_{47}$ (see texts for details). Also shown are the $\Delta_{47}$ and $\Delta_{48}$ of $CO_2$ derived from phosphoric acid digestion of carbonates in CM chondrites (Guo and Eiler 2007).

## 2.4 Estimation of carbonate formation temperatures

Determinations of $\Delta_{47}$ values of $CO_2$ derived from phosphoric acid digestion of carbonaceous chondrites enable us to use carbonate clumped isotope thermometry (Ghosh et al., 2006) to estimate the formation temperatures of the carbonate minerals contained within them, and thus the temperatures of at least one stage of the aqueous alteration of their respective parent bodies (Guo and Eiler, 2007). This approach requires that we know the temperature calibration of the clumped isotope thermometer for each carbonate mineral. This calibration is constrained by experiments and measurements of natural and synthetic materials only for biogenic and inorganic calcite and biogenic aragonite between temperatures of 0 and 50˚C (Ghosh et al., 2006; Came et al., 2007; Ghosh et al., 2007). In a recent theoretical study, Guo et al. (2008) predict the temperature dependence of the clumped isotope thermometer for a variety of carbonate minerals (calcite, aragonite, dolomite, magnesite and witherite), by combining previously published theoretical estimations of the $^{13}C$-$^{18}O$ and $^{18}O$-$^{17}O$ clumping effects (representing the two most abundant isotopologues responsible for $\Delta_{47}$ anomaly, $^{13}C^{18}O^{16}O^{16}O^{2-}$ and $^{12}C^{18}O^{17}O^{16}O^{2-}$) in the carbonate minerals (Schauble et al., 2006) with the estimated fractionations of multiply-substituted isotopologues associated with phosphoric acid digestion of each of these carbonate minerals. The theoretically predicted calibration for calcite exhibits weaker temperature dependence than the experimentally determined calibration, but intersects the experimental calibration line at ~30˚C and approximates the trend of experimental data (there is a less than 0.03‰ difference between the two over the temperature range of 10-50˚C; Fig. 2-3). This level of disagreement is to be expected when considering the approximations one must make in a purely theoretical treatment, and suggests that the model of Guo et al. (2008) provides a good first-order reference frame for the behavior of isotopic clumping in $CO_2$ extracted from carbonates by phosphoric acid digestion. Guo et al. (2008) predict that the calibration lines for the calcite, dolomite and magnesite clumped isotope thermometers (i.e., the relationships between $\Delta_{47}$ of $CO_2$ extracted from these minerals and their growth

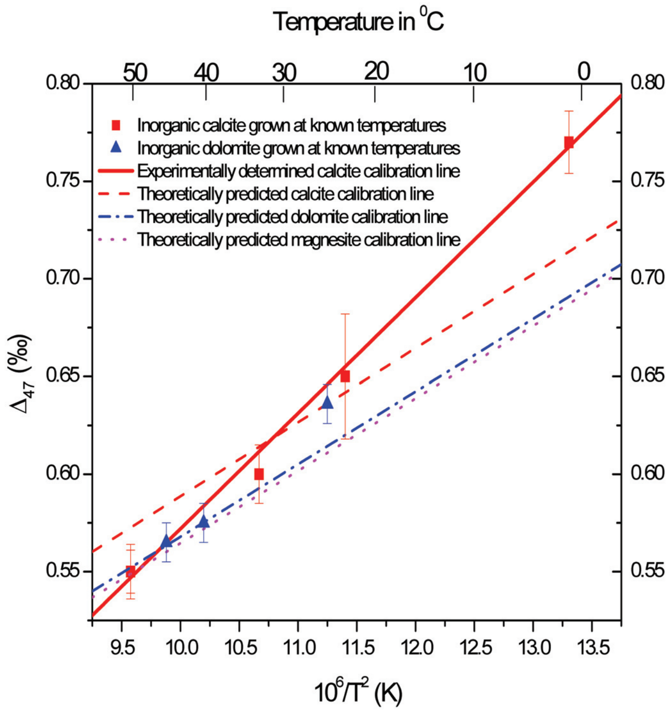


**Figure 2-3** Comparison between the experimentally determined $\Delta_{47}$-T calibration line for calcite (Ghosh et al., 2006) and the theoretically predicted $\Delta_{47}$-T calibration lines for calcite, dolomite and magnesite (Guo et al., 2008). Also shown for comparison are the preliminary dolomite $\Delta_{47}$-T calibration data from samples grown and synthesized at known temperatures (triangles; Eiler et al. 2008 and J. Ferry, personal communications).

temperatures) should be similar to each other, with differences less than 0.025‰ among the three at any given temperature. This variation is significant compared to the most precise measurements of $\Delta_{47}$ values of $CO_2$ from carbonates (e.g., Came et al., 2007), but is smaller than the estimated external precision of our measurements of carbonates in carbonaceous chondrites (0.04‰). This predicted similarity among different carbonate minerals is supported by the preliminary data from a recent attempt to experimentally determine the $\Delta_{47}$-T calibration line for dolomite (Eiler et al. 2008 and J. Ferry personal communication). The $\Delta_{47}$ derived from inorganic dolomite grown at known temperatures

(45˚C, 40˚C and 25˚C) is almost indistinguishable from the experimentally determined calcite calibration line (Fig. 2-3). Based on these theoretical models and empirical evidence, we therefore adopt the experimentally determined $\Delta_{47}$-T calcite calibration line, $\Delta_{47} = \frac{0.0592 \times 10^6}{T^2}$-0.02 (T in Kelvin, Ghosh et al. 2006), to estimate the formation temperatures for all the carbonate minerals (calcite, dolomite and breunnerite) in the carbonaceous chondrites. Nevertheless, we recognize that future refinements of calibrations for these materials could lead to modest (~5-10˚C) changes in the inferred temperatures of dolomite and magnesite growth.

According to the above $\Delta_{47}$-T calibration line, the analytical precision from our $\Delta_{47}$ analyses (0.04‰, 1σ; section 2.3) translates to about ±10˚C (1σ) precision in our estimated carbonate formation temperatures. This is significantly worse than the external precision and calibration accuracy for large, pure samples of calcite and aragonite, but is sufficient for improving our understanding of the thermal histories of charbonaceous chondrites.

## 3. RESULTS AND DISCUSSION

### 3.1 Test of the stepped phosphoric acid digestion procedure

Tests of our method of stepped phosphoric acid digestion were conducted on synthetic mixtures of known proportions of calcite and dolomite and of dolomite and magnesite (Table 2-2). The results of these analyses show that this method successfully reproduced the isotopic compositions (including $\delta^{13}C$, $\delta^{18}O$ and $\Delta_{47}$ values) of the end members, as independently constrained through analyses of pure aliquots of them. In particular, the differences in $\Delta_{47}$ between the calcite and dolomite portions extracted from stepped digestion and their corresponding pure end members are less than 0.02‰ (Table 2-2).

We further evaluate the effectiveness of our stepped extraction method in separating different carbonate end members by calculating the contributions of undesired end members in the stepped-extraction products. For example, the fraction of dolomite that reacted with phosphoric acid during our intended stepped-extraction of calcite from a mixture of calcite and dolomite, $f_{\mathrm{StepCal\text{-}Dol}}$, can be computed as:

$$f_{\mathrm{StepCal\text{-}Dol}}=\frac{\delta^{13}C_{\mathrm{StepCal}}-\delta^{13}C_{\mathrm{Cal}}}{\delta^{13}C_{\mathrm{Dol}}-\delta^{13}C_{\mathrm{Cal}}}=\frac{(-41.54)-(-42.37)}{(-0.18)-(-42.37)}=0.02 \quad ,$$

where $\delta^{13}C_{\mathrm{StepCal}}$, $\delta^{13}C_{\mathrm{Cal}}$ and $\delta^{13}C_{\mathrm{Dol}}$ are the carbon isotopic compositions of the nominal calcite portion of our stepped-extraction, of the pure calcite end member, and of the pure dolomite end member, respectively. Similarly, we can estimate the fraction of calcite that remained in the sample after the ‘calcite’ step and reacted during our intended stepped-extraction of dolomite in a calcite-dolomite mixture mixture ($f_{\mathrm{StepDol1\text{-}Cal}}$), or the fraction of magnesite reacted during our intended stepped-extraction of dolomite from a mixture of dolomite and magnesite mixture, $f_{\mathrm{StepDol2\text{-}Mag}}$:

$$f_{\mathrm{StepDol1\text{-}Cal}}=\frac{\delta^{13}C_{\mathrm{StepDol1}}-\delta^{13}C_{\mathrm{Dol}}}{\delta^{13}C_{\mathrm{Cal}}-\delta^{13}C_{\mathrm{Dol}}}=\frac{(-2.38)-(-0.18)}{(-42.37)-(-0.18)}=0.05$$

$$f_{\mathrm{StepDol2\text{-}Mag}}=\frac{\delta^{13}C_{\mathrm{StepDol2}}-\delta^{13}C_{\mathrm{Dol}}}{\delta^{13}C_{\mathrm{Mag}}-\delta^{13}C_{\mathrm{Dol}}}=\frac{(-0.10)-(-0.18)}{(1.60)-(-0.18)}=0.04 \quad ,$$

where $\delta^{13}C_{\mathrm{StepDol1}}$ and $\delta^{13}C_{\mathrm{StepDol2}}$ are the carbon isotopic compositions of the nominal dolomite portion from our stepped-extraction of a mixture of calcite and dolomite, and of the nominal dolomite portion from our stepped-extraction of a mixture of dolomite and magnesite, respectively. $\delta^{13}C_{Mag}$ is the carbon isotopic compositions of the pure magnesite end member; this is assumed to be the same as the carbon isotopic composition of nomimal magnesite portion from our stepped-extraction of the mixture of dolomite and magnesite since we didn't determine the isotopic composition of the pure magnesite end member directly due to limited available amounts of magnesite powders. This is an obvious weakness in our tests of the stepped extraction methodology, and should be addressed by repeating the stepped extraction procedure on synthetic mixtures that include well characterized magnesite. Nevertheless, the results of these experiments on synthetic mixtures of carbonates are consistent with the conclusion that our stepped-extraction method is ≥95% efficient at isolating each target carbonate phase.

Finally, one more constraint on the effectiveness of our stepped-extraction method comes from the yields of $CO_2$ at each extraction step. For example, the first step of our stepped-extraction of the calcite-dolomite mixture yielded 1.08 times the amount of $CO_2$ as the second step. This difference is very nearly equal to the ratio of the amounts of calcite and dolomite present within the mixture (7.06 mg of calcite vs. 6.94 mg of dolomite, corresponding to a carbon equivalent molar ratio of 1.07).

### 3.2 Temperature of carbonate growth in the carbonaceous chondrites

The apparent temperatures of carbonate formation (±10˚C, 1σ) implied by our measurements of carbonaceous chondrites are: 8 to 43˚C for calcite in GRO 95577; 18˚C for dolomite and –20˚C for breunnerite in Orgueil; 65˚C for calcite, 39˚C for dolomite and –31˚C for breunnerite in Tagish Lake (Table 2-1). Our estimated formation temperatures for breunnerite in Orgueil and calcite and breunnerite in Tagish Lake are beyond the temperature range of experimental calibration of the carbonate clumped isotope thermometer (0-50˚C; Gosh et al., 2006). However, theoretical calculations (as those employed in Schauble et al. 2006) indicate the temperature dependences of $\Delta_{47}$ in carbonate systems remain almost the same over the temperature range of our interest, -30 to 70˚C; therefore, we estimate that extrapolation of the experimentally determined predicted relationship between $^{13}C$-$^{18}O$ clumping effects in carbonate minerals and temperature from the constrained range of 0-50˚C to the wider range of -30˚C and 70˚C leads to less than 0.02‰ errors in $\Delta_{47}$ (E. Schauble, personal communications). Therefore our extrapolation of experimentally determined $\Delta_{47}$-T calibration line does not introduce a significant additional error in our temperature estimates.

Our estimated alteration temperatures, though consistent with previous estimations of alteration temperatures on the parent bodies of CR chondrite (<150˚C, Zolensky et al. 1993), CI chondrite (<50˚C, Leshin et al. 1997; 50-150˚C, Zolensky et al. 1993; 150˚C, Clayton and Mayeda 1984, 1999) and Tagish Lake (50-100˚C, Leshin et al., 2001), lie mostly at the low temperature ends of previous estimations. We suspect this reflects the inaccuracy of some of the assumptions made in previous studies,. For example, Clayton and Mayeda (1984) extrapolated their aqueous alteration model for CM chondrites to CI chondrites, assuming the anhydrous minerals (olivines and pyroxenes, precursor to aqueous alteration) in CI chondrites have the same oxygen isotope compositions as those in CM chondrite, and suggested that CI chondrite parent bodies have experienced aqueous alterations of higher temperatures than CM chondrite parent bodies (150˚C vs. <20˚C; Clayton and Mayeda 1984, 1999). However, later ion microprobe analyses of oxygen isotopes in single olivine and pyroxene grains separated from CI chondrites

(Orgueil and Ivuna) demonstrated the above assumption was invalid; the anhydrous minerals in CI chondrites are instead more $^{16}$O-depleted than those in CM chondirtes (Murchison) (Leshin et al., 1997). With the newly determined oxygen isotope compositions of anhydrous minerals in CI chondrites, Leshin et al. (1997) revised the Clayton and Mayeda (1984)'s aqueous alteration model, and estimated the alteration temperature on CI chondrite parent bodies to be less than 50˚C. This revised estimation on alteration temperatures for CI chondrites agrees well with our estimated formation temperatures for dolomite in Orgueil (18±10˚C, 1σ).

Overall, our estimated alteration temperatures for GRO 95577, Orgueil and Tagish Lake, are within or below those estimated for CM chondrites (20 to 71˚C, also based on carbonate clumped isotope thermometry; Guo and Eiler 2007). The similarity of alteration temperatures among different groups of carbonaceous chondrites precludes alteration temperature variations as the principle cause of differences in their extents of alteration, and suggests instead other factors such as water/rock ratio and/or duration of aqueous alteration exerting greater control. This suggestion is consistent with results from recent aqueous alteration model on carbonaceous chodrite parent bodies (Young, 2001; J. Palguta, 2007), where regions with high flux of fluid flow on the carbonaceous parent bodies demonstrate most intense alterations.

One surprising finding from this study is the sub-zero formation temperatures (-20˚C and -31˚C respectively, ±10˚C, 1σ) we estimated for breunnerite in Orgueil and Tagish Lake. This is in contrast with the common belief that all carbonates in carbonaceous chondrites precipitated from liquid water at temperatures above 0˚C, and suggests the existence of low temperature brines on the parent bodies of the carbonaceous chondrites.

The eutectic temperatures for the NaCl-$H_2O$, NaCl-KCl-$H_2O$, NaCl-$MgCl_2$-$H_2O$ and NaCl-$CaCl_2$-$H_2O$ systems are -21.2˚C, -22.9˚C, -35˚C, and -52˚C, respectively (Spencer et al. 1990) or ammonia–water mixtures (eutectic temperatures of -97˚C; Gaspatrik 2003). Thus, our data suggest that the pore fluids present during the very last stages of aqueous alteration of the carbonaceous chondrites were rich in salt and/or ammonia. Note that, although increases of pressures (e.g., through impact) could also permit the existence of pure liquid water at these low temperatures (as low as -22˚C at pressure of 209.9MPa; IAPWS 1993), the sustained presence of water in the liquid form as required by the formation of breunnerite make this a less likely possibility.

Formation of brine-like fluid on carbonaceous chondrite parent bodies has previously been proposed, based on the very high Na/Ca ratios (and possibly high absolute concentrations of Na) inferred for the carbonate-forming fluid (Riciputi et al., 1994). Recent discoveries of fluid inclusions bearing halite [NaCl] and sylvite [KCl] in Monahans 1998 and Zag regolith breccias (two metamorphosed H5 chondrites; Zolensky et al. 1999, Rubin et al. 2002) provides more direct evidence for the presence of brines on chondrite parent bodies. These halides are found in highly metamorphosed meteorites, but are thought to have formed on other bodies at low temperature (<100˚C and <70˚C respectively) and became incorporated into these H5 chondrite parent bodies as part of petrographically distinct clasts, e.g., the CI clast in Zag (Zolensky et al., 1999; Bridges et al., 2004; Zolensky et al., 2008). Furthermore, Zolenky et al. (1999) demonstrated that the fluid inclusions in Monahans 1998 have eutectic temperatures of ~ -40˚C, indicating they may contain divalent cations such as $Fe^{2+}$, $Ca^{2+}$, $Mg^{2+}$, in addition to $Na^+$ and $K^+$. This is consistent with our above proposal that the parent fluid from which the last generations carbonates in carbonaceous chondrite precipitated was a brine. Detailed examination of CI clasts in Zag (the potential sources of halite) did reveal the presence of aggregates of Ca-Mn-Mg-Na carbonates inside the clast, along with other secondary minerals such as magnetite, pyrrhotite and phyllosilicates (Zolensky et al., 2003). Future studies should aim to characterize the isotopic and trace element compositions of these carbonates and test them further against our hypothesis of that breuunerite in these meteorites formed from low temperature brines.

The fact that breunnerite in the carbonaceous chondrites formed at temperatures as low as -31˚C doesn't necessarily imply the aqueous alteration of silicate minerals on the carbonaceous chondrite parent bodies was active at these temperatures. It is also possible (and perhaps more likely) that breunnerites precipitated from brines after the silicate-alteration reaction had already ceased (due to the slow kinetics under such low temperatures).

As discussion in section 2.3, the sample $\Delta_{47}$ used in the above temperature estimations were derived after a voltage correction, to account for the observed negative correlations between the raw $\Delta_{47}$ of sample $CO_2$ and the mass 44 voltages at which the raw $\Delta_{47}$ was obtained during our mass spectrometric analyses. Here, we evaluate the effects of the voltage correction on our results by recalculating the carbonate formation temperatures, 1) without any voltage correction (i.e., using the average raw $\Delta_{47}$ of analyte $CO_2$ in the standardization of the $\Delta_{47}$ of sample $CO_2$); 2) with voltage correction at the mass 44 voltage of 7V (Table 2-3). For all the meteorite samples we analyzed, the above two approaches yielded carbonate formation temperatures only 2-26˚C different from our

**Table 2-3** Effects of voltage correction on the estimations of carbonate formation temperatures and of the oxygen isotope compositions of alteration fluid.

| Sample | | GRO 95577 (split 2006) | GRO 95577 (split 2007) | Orgueil | | | Tagish Lake | | |
|---|---|---|---|---|---|---|---|---|---|
| Petrology Type | | CR1 | CR1 | CI | | | Ungrouped C2 | | |
| Carbonate Mineralogy | | Calcite | Calcite | Dolomite | | Breunnerite | Calcite | Dolomite | Breunnerite |
| Voltage Correction at 5V | $\Delta_{47}$(‰) | 0.726 | 0.571 | 0.709 | 0.650 | 0.887 | 0.497 | 0.586 | 0.960 |
| | Temperature (˚C) | 8 | 43 | 12 | 24 | -20 | 65 | 39 | -31 |
| | $\delta^{18}O_{water}$(‰) VSMOW | -12.3 | -7.1 | -5.3 | -2.7 | -29.7 | 11.8 | 5.8 | -18.6 |
| | $\delta^{17}O_{water}$(‰) VSMOW | -7.3 | -4.6 | -2.2 | -0.9 | -14.9 | 7.6 | 4.8 | -7.6 |
| No Voltage Correction | $\Delta_{47}$(‰) | 0.739 | 0.583 | 0.699 | 0.662 | 0.899 | 0.589 | 0.648 | 1.036 |
| | Temperature (˚C) | 6 | 40 | 14 | 21 | -19 | 39 | 25 | -36 |
| | $\delta^{18}O_{water}$(‰) VSMOW | -12.9 | -7.7 | -4.8 | -3.2 | -29.5 | 7.3 | 2.9 | -20.2 |
| | $\delta^{17}O_{water}$(‰) VSMOW | -7.6 | -4.9 | -2.0 | -1.2 | -14.8 | 5.2 | 3.4 | -8.4 |
| Voltage Correction at 7V | $\Delta_{47}$(‰) | 0.720 | 0.555 | 0.737 | 0.583 | 0.876 | 0.492 | 0.584 | 0.982 |
| | Temperature (˚C) | 10 | 48 | 6 | 40 | -18 | 67 | 40 | -34 |
| | $\delta^{18}O_{water}$(‰) VSMOW | -12.1 | -6.3 | -6.6 | 0.4 | -29.1 | 12.1 | 5.8 | -19.6 |
| | $\delta^{17}O_{water}$(‰) VSMOW | -7.2 | -4.2 | -2.9 | 0.7 | -14.6 | 7.7 | 4.9 | -8.1 |

preferred approach (i.e., voltage normalization at 5V). The difference is the biggest for calcite in Tagish Lake: its formation temperature estimated without any voltage correction is 26˚C lower than what estimated from our preferred approach (39˚C v.s. 65˚C). For all the other samples, the differences in estimated formation temperatures from different approaches are less than 16˚C without any systematic trends. These differences in temperature estimations are within or close to the external errors typical of our analyses (±10˚C, 1σ).

### 3.3 Isotopic compositions of the alteration fluid

$\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VSMOW}$ values of carbonates in the carbonaceous chondrites we examined vary from 40.42‰ to 73.37‰ and 17.82‰ to 36.70‰ respectively (Table 2-1), and fall within or close to the values from previous isotopic studies of carbonates in Orgueil and Tagish Lake (phosphoric acid digestion, Grady et al., 1998 and Leshin et al., 2001; ion microprobe, Zito et al., 1998, Engrand et al., 2001a and Engrand et al., 2001b). Our results are consistent with previous ion microprobe observations by Zito et al. (1998), which revealed that isotopic compositions (both $\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VSMOW}$) of carbonates in Orgueil decrease in the order of dolomite and breunnerite (67.52‰ vs. 40.42‰ in $\delta^{13}C_{VPDB}$, and 28.95‰ vs. 21.08‰ in $\delta^{18}O_{VSMOW}$). This study constitutes the first isotopic study of carbonates in GRO 95577, showing $\delta^{13}C_{VPDB}$ of 69.91‰ and 70.91‰ and $\delta^{18}O_{VSMOW}$ of 17.82‰ and 19.62‰, respectively for the two GRO 95577 splits we analyzed. Note that $\delta^{13}C_{VPDB}$ values of most carbonates studied here cluster around 70‰ (ranging from 67.52‰ to 73.37‰), except for the breunnerite in Orgueil which has a significantly lower $\delta^{13}C_{VPDB}$ of 40.42‰.

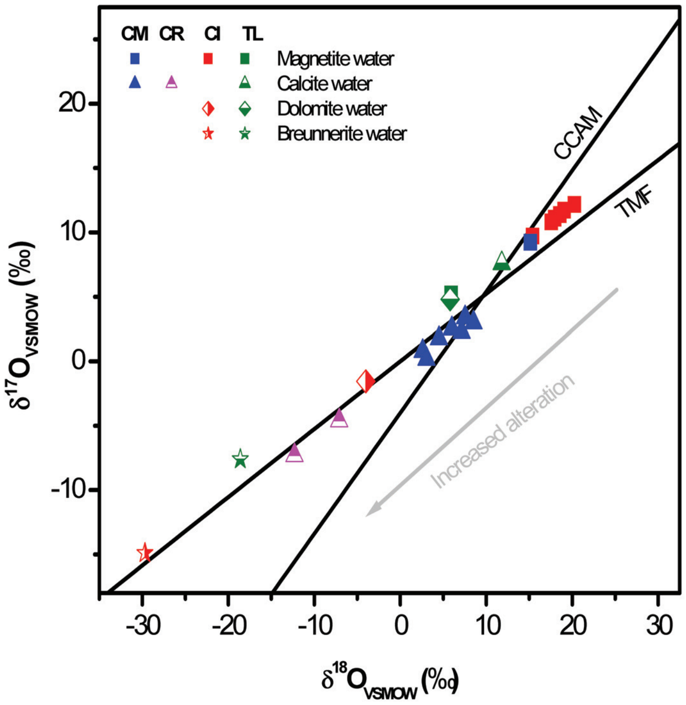


**Figure 2-4** Oxygen isotope compositions (all values reported vs. VSMOW) of water in equilibrium with carbonaceous chondrite carbonates at their known growth temperatures (Guo and Eiler 2007 and this study). Also shown for comparison are the oxygen isotope compositions of the water in equilibrium with magnetites in CM and CI chondrites and in Tagish Lake (TL) (squares, estimated from $\delta^{18}O_{VSMOW}$ of magnetites reported in Rowe et al. 1994 and Engrand et al. 2001b, with an equilibrium fractionation factor of -13‰ between magnetite and water). The terrestrial mass fractionation line ('TMF') and carbonaceous chondrite anhydrous mineral line ('CCAM') are shown for reference.

We estimated $\delta^{18}O_{VSMOW}$ values of the fluids from which these carbonates grew by combining the carbonate formation temperatures established by clumped isotope thermometry with the temperature-dependent carbonate-water oxygen isotope fractionations established by previous studies— either experimental (for calcite, Kim and O'Neil 1997; and dolomite, Vasconcelos et al. 2005) or theoretical (for magnesite, Rosenbaum 1997 and Schauble et al. 2006). These data and experiments constrain the water from which carbonates grew to have $\delta^{18}O_{SMOW}$ values of: -12.3‰ to -7.1‰ for calcite in GRO 95577; -4.0‰ for dolomite and -29.7‰ for breunnerite in Orgueil; and 11.8‰ for calcite, 5.8‰ for dolomite and -18.6‰ for breunnerite in Tagish Lake (±2‰, 1σ; Table 2-1, Fig. 2-4). Assuming that the carbonates we analyzed have $\Delta^{17}O$ values equal to the averages previously determined by Leshin et al. (2001) and Clayton and Mayeda (1999), our results indicate that the $\delta^{17}O$ values of waters from which carbonates grew varied between –14.9‰ and 7.6‰.

Again, our estimated formation temperatures for breunnerite in Orgueil and Tagish Lake (-20˚C and -31˚C, respectively) is beyond the temperature range of theoretically estimated magnesite-water oxygen isotope fractionation relationship (valid ≥0˚C; Rosenbaum 1997 and Schauble et al., 2006), forcing us to extrapolate that trend to arrive at an estimated $\delta^{18}O$ value for water. This extrapolation is justified by the general invariance of temperature-dependence of oxygen isotope fractionations over this temperature range. In addition, our suggestion that breunnerite precipitated from low temperature brines containing divalent cations such as $Ca^{2+}$ and $Mg^{2+}$ (section 3.2), raises the possibility of an oxygen isotope 'salt effect' (Horita, 2005) during carbonate precipitation (that is, a dependence of the carbonate-water oxygen isotope fractionation on the salinity of the solution). Consideration of these isotope salt effects would tend to increase our estimated oxygen isotope compositions of alteration fluids (Horita, 2005). The exact magnitude of the effect depends on the cation compositions of the brine (especially concentrations of $Ca^{2+}$ and $Mg^{2+}$), and could be as much as several per mil (Horita, 2005). For example, for brines with the same cation composition as the eutectic point of NaCl-$MgCl_2$-$H_2O$ system (1.10mol NaCl and 2.48mol $MgCl_2$ per kg $H_2O$; Spencer et al., 1990), an oxygen isotope salt effect of -2.7‰ is expected at 25˚C (Horita, 2005).

The matrices of carbonaceous chondrites are also rich in a variety of secondary phases (i.e., aqueous alteration products) other than carbonates, such as magnetite and phyllosilicates (Brearley and Jones, 1998). The oxygen isotope compositions of these phases must also reflect the conditions of aqueous alterations and the $\delta^{18}O$ values of alteration fluid, though they may have grown at temperatures different from those of carbonate precipitation, and these phases are less likely than carbonates to fully equilibrate with co-existing fluid. Nevertheless, we can examine the plausibility of the fluid $\delta^{18}O$ values we established through carbonate clumped isotope measurements by estimating the oxygen isotope compositions of alteration fluids from which magnetite formed. We adopt previously measured oxygen isotope compositions of magnetites in CI and CM chondrites (Rowe et al., 1994) and in Tagish Lake (Engrand et al., 2001b), and assume an oxygen isotope fractionation of -13‰ between magnetite and water (Rowe et al., 1994). We didn't include in our discussion the oxygen isotope compositions of meteorite matrix water (extracted through stepped pyrolysis of bulk meteorite samples), due to the large uncertainties associated with the nature of the extracted water and thus with the quantitative interpretations of their isotopic compositions (Baker et al., 2002).

Over all, these estimated $\delta^{18}O$ and $\delta^{17}O$ for the alteration fluids within each carbonaceous chondrite group are all significantly lower than those estimated for their respective primary water (Clayton and Mayeda, 1999), and decrease in the order of magnetite > calcite > dolomite > breunnerite in CI and CM chondrites and in the order of calcite > dolomite ~magnetite > breunnerite in Tagish Lake (Fig. 4). The differences in isotopic composition between the model reactant water and that water from which secondary mineral phases grew are consistent with the expectation that water evolves toward lower $\delta^{18}O$, $\delta^{17}O$, and $\Delta^{17}O$ as a result of reaction with host rock (Clayton and Mayeda, 1999; Guo and Eiler, 2007).

### 3.4 Implications for the chemical and thermal evolution of the carbonaceous chondrite parent bodies

In this section, we develop a general interpretation of our results in the context of a quantitative model for the aqueous alteration of carbonaceous chondrites that was previously developed for CM chondrites (Guo and Eiler, 2007). This model approximates aqueous alteration of the carbonaceous chondrite parent bodies as a serpentinization reaction (Clayton and Mayeda, 1999; Eiler and Kitchen, 2004; Guo and Eiler, 2007):

$$\mathrm{Mg_2SiO_4 + MgSiO_3 + 2H_2O \rightarrow Mg_3Si_2O_5(OH)_4} \qquad \text{(I)}$$

The oxygen isotopic composition of the alteration fluid is influenced by the progress of this reaction, evolving toward lower $\delta^{18}O$ and $\delta^{17}O$ as the reaction proceeds. The isotopic evolution of alteration fluid can be evaluated through the relations (Clayton and Mayeda, 1999; Guo and Eiler, 2007):

$$\delta^{18}O_{w,f} = \frac{\delta^{18}O_{w,i} + (\delta^{18}O_{r,i} - \frac{9}{7}\Delta^{18}O_{s\text{-}w})\,p}{1+p} \qquad (1)$$

$$\delta^{17}O_{w,f} = \frac{\delta^{17}O_{w,i} + (\delta^{17}O_{r,i} - \frac{9}{7}\Delta^{17}O_{s\text{-}w})\,p}{1+p} \qquad (2)$$

$$\Delta^{17}O_{w,f} = \left( \frac{1+\delta^{17}O_{w,f}/1000}{(1+\delta^{18}O_{w,f}/1000)^{0.5164}} - 1 \right) \times 1000 \qquad (3)$$

where $\delta^{18}O_{w,f}$, $\delta^{17}O_{w,f}$ and $\Delta^{17}O_{w,f}$ denote the oxygen isotopic composition of the aqueous fluid; $\delta^{18}O_{w,i}$ , $\delta^{17}O_{w,i}$ and $\delta^{18}O_{r,i}$ , $\delta^{17}O_{r,i}$ denote the initial (i.e., before the aqueous alteration) oxygen isotopic compositions of the aqueous fluid and the anhydrous reactant minerals; $\Delta^{18}O_{s\text{-}w}$ and $\Delta^{17}O_{s\text{-}w}$ are the oxygen isotope fractionations between serpentine and water at the temperatures of alteration (Wenner and Taylor, 1971); 'p' is the reaction progress parameter (Clayton and Mayeda, 1999; Guo and Eiler, 2007), denoting the ratio of moles of oxygen in the reacted rock to moles of oxygen in initial water. 'p' ranges from 0 to 3.5; a value of 0 corresponds to the absence of alteration reaction, and a value of 3.5 corresponds to the maximum extent of alteration (i.e., all water has been consumed in the alteration reaction I).

The initial oxygen isotope compositions of the anhydrous minerals in the evolution models (i.e., $\delta^{18}O_{r,i}$ and $\delta^{17}O_{r,i}$) were taken as the averages determined from previous studies (CM chondrite, Clayton and Mayeda 1999; CR chondrite, Clayton and Mayeda 1999; CI chondrite, Leshin 1997). The initial oxygen isotope compositions of the alteration fluid (i.e., $\delta^{18}O_{w,i}$, $\delta^{17}O_{w,i}$), for CM, CI and CR chondrites were adopted from the values estimated in Clayton and Mayeda (1999) following a two-stage exchange model (Clayton and Mayeda, 1984). Note that, there are no available estimations of the initial oxygen isotope compositions of the alteration fluid for Tagish Lake. Our attempts to derive the value ourselves, following the same aqueous alteration model as in Clayton and Mayeda (1984, 1999) and using the experimentally determined isotopic compositions of different phases in Tagish Lake (anhydrous minerals, Leshin et al., 2001, Engrand et al., 2001a; matrix, Engrand et al., 2001a; carbonate formation water, this study), yielded a water/rock ratio that exceeds the limit of Clayton and Mayeda (1984) model (4.64 v.s. limit of 3.76). We suspect two factors might have contributed to this complication: (1) the experimental uncertainties associated with the oxygen isotope compositions of anhydrous minerals and matrix in Tagish Lake, both of which were determined with ion microprobe with 1~2‰ uncertainties in $\delta^{17}O$ and $\delta^{18}O$; and, (2) the complex lithologies present in Tagish Lake — the dominant carbonate poor lithology vs. the less abundant carbonate-rich lithology (Zolensky et al., 2002). It is not certain whether these two lithologies are genetically related to each other (Zolensky et al., 2002) and whether they went through aqueous alterations from the same water reservoirs (Baker et al., 2002). Therefore, an accurate modeling of the alteration reaction on Tagish Lake parent body should make sure the isotopic compositions of the anhydrous minerals, of matrix and carbonate formation water employed in the model come all from the same lithology. This however seems impossible at this moment due to absence of such complete dataset for Tagish Lake. We therefore focus on the discussion of forward models for CM CR and CI chondrite parent bodies in this study.

The temperatures of aqueous alteration on the carbonaceous chondrite parent bodies changed over the course of alterations, as evidenced by the variations of carbonate formation temperatures within the same chondrite sample (section 3.2). Ideally, we should quantitatively incorporate these temperature changes into our model (e.g., as functions of reaction progress). However, given the absence of any independent quantitative constraints on the co-variations of alteration temperature and reaction progress, such a treatment is out of the range of this study. Instead, in our current model we assume the alteration temperature to be the average of our estimated carbonate formation temperatures for each chondrite (or chondrite group), and remain constant throughout the aqueous alteration. For the purpose of comparison, we also ran our models at different alteration temperatures, covering the full range of carbonate formation temperatures observed in each chondrite group (dotted lines in Fig. 2-5). Fortunately, the general evolution trends of oxygen isotope composition of the alteration fluid are not sensitive to alteration temperatures (Fig. 2-5), and thus our model results are not systematically biased by the above simplification. We summarize all the parameters employed in our model in Table 2-4.

We observe good agreement between most of experimentally estimated isotopic compositions of alteration fluids (including those estimated based on magnetite $\delta^{18}O$, carbonate $\delta^{18}O$ and growth temperature) and those predicted by the forward models (Fig. 2-5): the experimentally estimated oxygen isotopic compositions of alteration fluids lie on or very close to the predicted trend of evolving water oxygen isotope composition. However, our estimated oxygen isotopic compositions of alteration fluids for calcite formation in one split of GRO9557 (split 2006) and breunnerite formation in Orgueil fall beyond the total range of $\delta^{18}O$ expected from the forward model of aqueous alteration (i.e., requiring $p>3.5$). This implies that the aqueous alteration had reached the maximum extent on the parent bodies of GRO 95577 and Orgueil, consistent with previous petrographic studies on these two meteorites and their classification as petrographic type 1 carbonaceous chondrites (Brearley and Jones, 1998; Weisberg and Prinz, 2000). At the same time, this observation also suggests processes other than alteration reactions affected the oxygen isotopic compositions of the alteration fluids. Given that the

**Table 2-4** Forward evolution models for the oxygen isotope compositions of the alteration fluid on CM, CR and CI carbonaceous chondrite parent bodies.

| | | CM chondrite | | CR chondrite | | CI chondrite | | |
|---|---|---|---|---|---|---|---|---|
| Initial Water[&] | $\delta^{18}O_{water}$(‰) | 28.1 | | 28.1 | | 23.4 | | |
| | $\delta^{18}O_{water}$(‰) | 17.7 | | 17.7 | | 13.9 | | |
| | $\Delta^{17}O_{water}$(‰) | 3.2 | | 3.2 | | 1.9 | | |
| Mean Anhydrous Solids[&] | $\delta^{18}O_{water}$(‰) | -4.2 | | -1 | | 4.8 | | |
| | $\delta^{18}O_{water}$(‰) | -7.4 | | -2.8 | | 1.8 | | |
| | $\Delta^{17}O_{water}$(‰) | -5.2 | | -2.3 | | -0.7 | | |
| Alteration Temperature[ϕ] (˚C) | | 28 | | 25 | | 5 | | |
| Serpentine/water fractionation[&] | $\Delta^{18}O_{s-w}$ (‰) | 12.5 | | 12.8 | | 15.5 | | |
| | $\Delta^{17}O_{s-w}$ ‰) | 6.4 | | 6.6 | | 8.0 | | |
| Alteration fluid[ξ] | | Essebi Magnetite | CM Calcite (average) | GRO 95577 Calcite Split 2006 | GRO 95577 Calcite Split 2007 | CI Magnetite (average) | Orgueil Dolomite | Orgueil Breunnerite |
| Reaction progress[ξ] (p) | | 0.4 | 0.96 | N/A | 3.4 | 0.2 | 2.5 | N/A |

[&] The oxygen isotope compsitions of the initial water and anhydrous solids are drived from previous studies of carbonaceous chondrites (Clayton and Mayeda 1999, Leshin et al.1997, Engrand et al. 2001a, Leshin et al. 2001 and this study; see text and Appendix for details); The oxygen isotope fractionations between serpentine and water at the selected alteration temperatures are derived from (Wenner and Taylor 1971).

[ϕ] Alteration temperatures are assumed to be the average formation temperaures of carbonate minerals in carbonaceous chondrites (Guo and Eiler 2007, and this study)

[ξ] The progress of alteation reactions at the formation of different secondary phases in the carbonaceous chondrite matrix, estimated from experimentally determined oxygen isotope compositions of the corresponding alteration fluilds. ‘N/A’ denotes cases where the experimentally determined oxygen isotope compositions of the alteration fluid fall out of the predictions from our forward evolution models (see text for details).

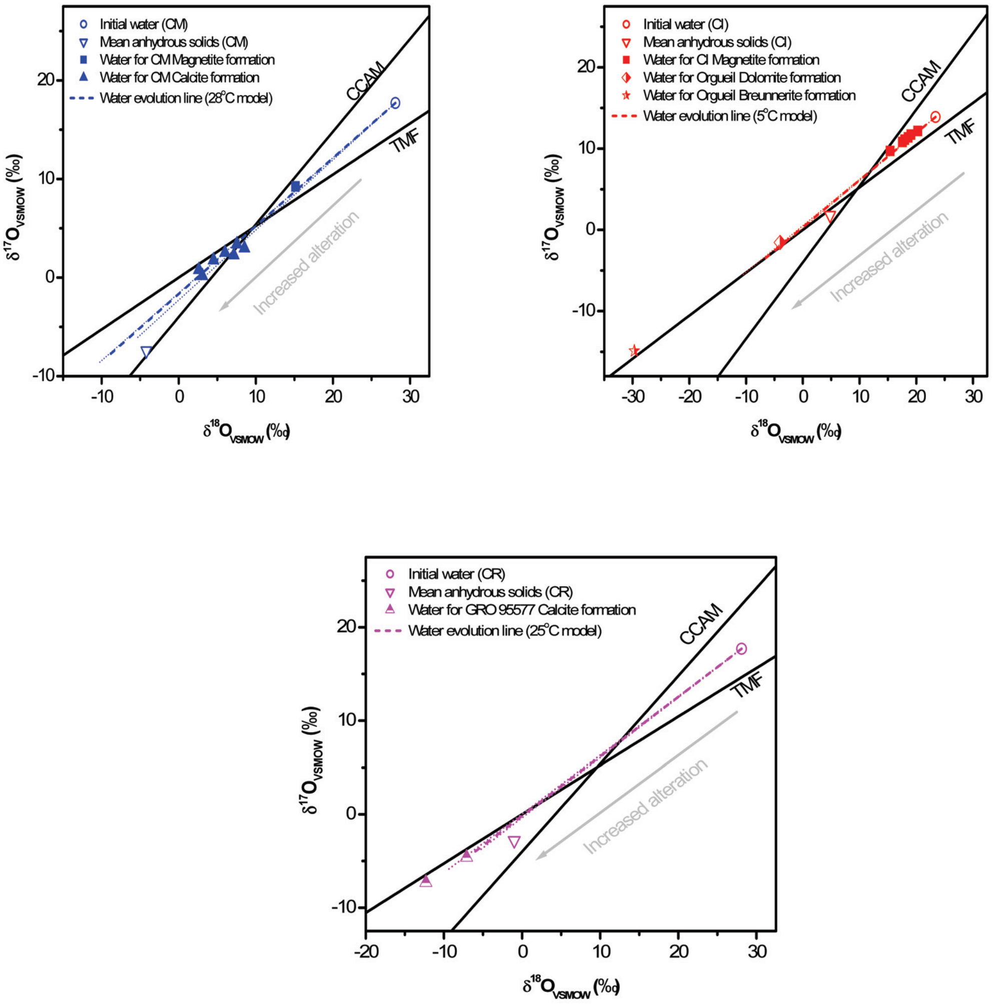


**Figure 2-5** Comparison between the experimentally estimated oxygen isotope compositions of alteration water with those calculated by the forward model of aqueous alteration: (a) CM chondrite; (b) CI chondrite; (c) CR chondrite. The temperatures of water-rock reaction are assumed to be the average formation temperatures of carbonate minerals in carbonaceous chondrites. The open squares and inverted triangles shows the location of estimated initial water and typical anhydrous solids for each group of carbonaceous chondrites (Table 2-4). Dotted lines represent the model results with temperatures of water-rock reactions set at the lowest (upper dotted line) and highest (lower dotted line) formation temperatures observed for carbonates in each chondrite group. Model results with different alteration temperatures (dashed lines and dotted lines) closely resemble each other, suggesting the general evolution trend of oxygen isotope compositions of the alteration fluid is not very sensitive to the alteration temperatures. The terrestrial mass fractionation line ('TMF') and carbonaceous chondrite anhydrous mineral line ('CCAM') are shown for reference.

estimated formation temperatures for calcite in GRO 95577 (split 2006) and breunnerite in Orgueil (6±10˚C and -20±10˚C, 1σ, respectively) are either very close to or below the freezing point of water, we propose partial freezing of the alteration fluids during late stages of aqueous alteration lead to further depletion in their $\delta^{18}O$. For example, with Rayleigh distillation isotope fractionation during ice formation (i.e., gradual freezing with isotopic equilibrium maintained between the newly formed ice and residual water at all times), depletions as much as 7.1‰ in the $\delta^{18}O$ of the residual water can be expected when 90% of water freezes into water ice (O'Neil, 1968). The freezing induced reduction in the $\delta^{18}O$ value of alteration fluids is also consistent with the observation that the relatively large changes in $\delta^{18}O$ at the end of the alteration process (i.e., at low T and $\delta^{18}O$ of water) were accompanied by smaller changes in fluid $\Delta^{17}O$ than those expected to result from reactions with host rock, e.g., 0.05‰ and 0.22‰ variations in $\Delta^{17}O$ vs. 26‰ and 24.4‰ variations in $\delta^{18}O$ between dolomite and breunnerite in Orgueil and Tagish Lake respectively (Leshin et al. 2001 and this study).

In the context of the aqueous alteration model we presented above (i.e., higher extents of alteration correspond to lower $\delta^{18}O$ values of the fluid), our results imply that magnetite and carbonates formed in the order of magnetite > calcite > dolomite > breunnerite during aqueous alteration of carbonaceous chondrites parent bodies. This is consistent with previous studies of $\Delta^{17}O$ for magnetite and carbonates in carbonaceous chondrites (magnetites have higher $\Delta^{17}O$ than carbonates inside CM and CI chondrites; Rowe et al., 1994 and Engrand et al. 2001b), and with the formation sequences determined for magnetite and different types of carbonates in CM chondrites (carbonate Mn/Cr chronometry, Brearley and Hutcheon 2000, Brearley et al. 2001) and CI chondrites (magnetite Xe-I chronometry, Pravdivtseva et al. 2003; carbonate cation chemistry, Endress and Bischoff 1996; carbonate Mn/Cr chronometry, Hoppe et al. 2007; carbonate Rb/Sr chronometry, Macdougall 2000). In addition, based on Xe-I chronometry halites in Monahans 1998 and Zag regolith breccias were estimated to formed at ~4559Ma (i.e., 8.2 Myrs after formation of CAIs in CV chondrites; Busfield et al. 2004). These halite formation ages are significantly older than most secondary mineral phases in carbonaceous chondrite (Fig. 2-7), consistent with our proposition that they formed at late stages of aqueous alteration from aqueous brines.

The reaction progress (‘p’) corresponding to different alteration fluids range from 0.2 to 3.4, respectively for magnetite and carbonate formation in different carbonaceous chondrites (Table 2-4). In particular, the reaction progresses estimated for calcite in GRO 95577 (p=3.4) lies almost at the maximum value plausible for p in our model (p=3.5). This suggests, calcite in GRO95577 formed at the very last stages of the aqueous alteration on its parent body.

Combined with our estimated carbonate formation temperatures (Guo and Eiler 2007 and this study), these observations suggest that the carbonaceous chondrite parent bodies were cooling as aqueous alteration proceeded (Fig. 2-6). This conclusion is consistent with Guo and Eiler (2007)’s previous inference based on the variations of carbonate formation temperatures and $\delta^{18}O$ of the alteration fluid among different splits of Cold Bokkeveld. We quantify the rate of cooling on the carbonaceous chondrite parent bodies by combining our estimated carbonate formation temperatures with their formation ages determined in previous Mn-Cr chronometry studies (Brearley et al., 2001; Krot et al., 2006; Hoppe et al., 2007). All the Mn-Cr chronometric ages were (re)normalized with the angrite Lewis Cliff (LEW) 86010 as the time anchor ($^{53}$Mn/$^{55}$Mn ratio of 1.25±0.07×10$^{-6}$ and absolute Pb-Pb age of 4557.8±0.5Ma; Lugmair and Galer 1992), following conventions from previous studies (Lugmair and Shukolyukov, 1998; Krot et al., 2006; Hoppe et al., 2007). A half-life time of 3.7Myr has been assumed for

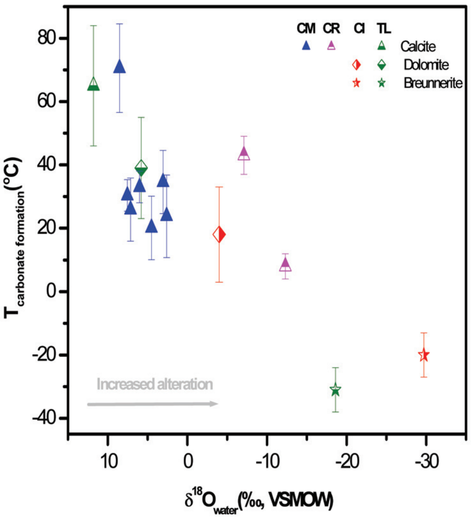


Fig. 2-6

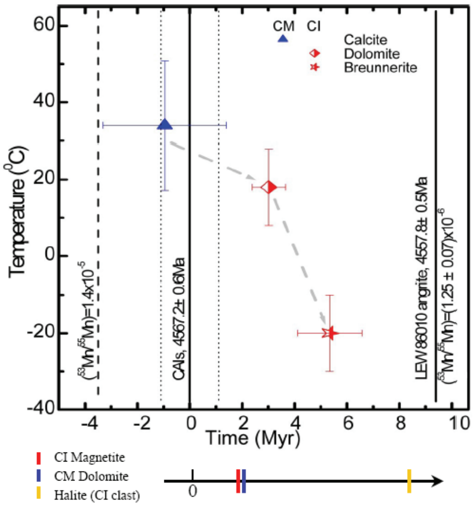


Fig. 2-7

**Figure 2-6** Negative correlation between the carbonate formation temperatures and the oxygen isotope compositions of alteration fluid from which the carbonates grew. This negative correlation indicates the carbonaceous chondrite parent bodies were cooling as the aqueous alterations proceeded. Error bars denote 1 standard error (1σ).

**Figure 2-7** Estimated thermal evolution of carbonaceous chondrite parent bodies, based on the formation temperatures of carbonates in different carbonaceous chondrite (Guo and Eiler 2007 and this study) and the corresponding formation ages of these carbonates (Brearley et al. 2001; Krot et al. 2006; Hoppe et al. 2007). The absolute ages of CAIs from CV chondrites, ages of angrite LEW 86010 and ages calculated with initial $^{53}$Mn/$^{55}$Mn ratio of 1.4×10$^{-5}$ are shown for reference (Krot et al. 2003). Also shown for comparison (at the bottom) are the formation ages of magnetite in CI chondrite, of dolomite in CM chondrite and halite in Monahans 1998 and Zag (H6 chondrite) (Brearley and Hutcheon, 2000; Pravdivtseva et al., 2003; Busfield et al., 2004). The estimated formation age for magnetite in Tagish Lake (at least 50 Myrs later than the ages of CI magnetite; Busfield et al. 2001) falls outside the range of this plot. Error bars denote 1 standard error (1σ).

$^{53}$Mn decay (McKeegan and Davis, 2003). Combination of these data (available for CM calcite, CI dolomite and CI breunnerite) implies aqueous alteration on the carbonaceous chondrite parent bodies started within 1-2 million years after formation of the CAIs in CV chondrites (4567.2±0.6Ma) (Krot et al., 2006), with the alteration temperatures decreasing from 34˚C to 18˚C in the first 4 million years and further to -20˚C after ~6.5 million years (Fig. 2-7).

Several theoretical studies have attempted to model the thermal evolution of small planetesimals similar in size to the carbonaceous chondrite parent bodies (Grimm and McSween, 1989; Cohen and Coker, 2000; Young, 2001; Travis and Schubert, 2005). Unfortunately, these studies either didn't document in detail the thermal evolutions at different depths inside the parent bodies (Grimm and McSween, 1989; Cohen and Coker, 2000), assumed a relative late accretion of the parent bodies (i.e., relatively low initial $^{26}$Al/$^{27}$Al; Grim and McSween 1989, Young 2001, Travis and Schubert, 2005), and/or focused on only a very short time span of the thermal evolution of the parent body (e.g., the first million year after parent body accretion; Young 2001). These gaps in previous modeling studies preclude a detailed comparison between our experimental results and the predictions from available thermal models (Fig 2-8). However, if we assume the first chondritic carbonate (i.e., CM calcite) formed shortly after the accretion of the carbonaceous chondrite parent body (e.g., within 1 million years) while the formation age differences between different chondritic carbonates are unchanged (in other words, shifting the formation ages of all chondritic carbonates behind by the same amount of ~4.8 Myrs), our experimentally estimated alteration temperatures agree almost perfectly with the thermal evolution of a layer 10km from the surface of a 50km radius parent bodies as modeled by Travis and Schubert (2005) (Fig. 2-9). The exact implication of this agreement needs to be investigated further in the future with more thorough and detailed thermal modeling (e.g., models with earlier accretion of carbonaceous chondrite parent bodies, and variable sizes of parent bodies).

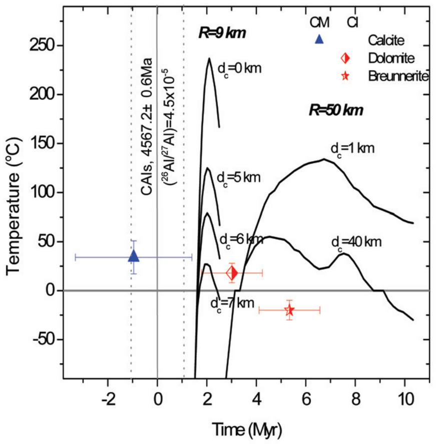


Fig. 2-8

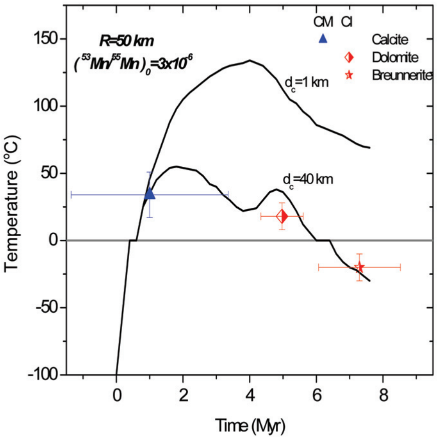


Fig. 2-9

**Figure 2-8** Comparison of our estimated thermal evolution of carbonaceous chondrite parent bodies with the predictions from available thermal models. The model predictions, for the 9km radius parent body and 50km radius parent body, are reproduced from Young et al. (2001) and Travis and Schubert (2005) respectively. Different lines represent layers with different distances (‘$d_c$’) from the center of the modeled parent bodies. The start time for each model was calibrated relative to the formation age of CAIs in CV chondrites ($^{26}Al/^{27}Al$ ratio of $4.5\times10^{-5}$ and absolute Pb-Pb age of 4567.2±0.6Ma; Amelin et al. 2002, McKeegan and Davis 2003), based on their initial $^{26}Al/^{27}Al$ ratios ($1\times10^{-5}$ and $3\times10^{-6}$ respectively) assumed in the modeled parent bodies. The decay of $^{26}Al$ has a half-life time of 0.7Myr (McKeegan and Davis, 2003). Error bars denote 1 standard error (1σ).

**Figure 2-9** Agreement of our estimated thermal evolution of carbonaceous chondrite parent bodies with the modeled thermal evolution for a layer 10km from the surface of a 50km radius parent body (Travis and Schubert 2005), when constraints on carbonate formation ages are relaxed (see text for details). The implication of this agreement needs to be investigated further by future modeling studies. Different lines represent layers with different distances (‘$d_c$’) from the center of the modeled parent bodies. Error bars denote 1 standard error (1σ).

## 4. SUMMARY

Despite their differences in the extent of aqueous alteration, we show that temperatures of aqueous alteration on different carbonaceous chondrite parent bodies were all relatively low (–31 to 71˚C; ±10˚C, 1σ) and varied significantly (as much as 96˚C; Tagish Lake) during the course of alteration. This similarity in alteration temperatures among different groups of carbonaceous chondrites implies factors other than alteration temperature (e.g., water/rock ratio or duration of aqueous alteration) as the primary causes for their differences in the extents of aqueous alteration. The sub-zero formation temperatures (-20˚C±10˚C and -31˚C±10˚C respectively, 1σ) we estimated for breunnerite in Orgueil and Tagish Lake, indicate formation of the low temperatures brines or ammonia–water mixtures during the late stages of aqueous alteration on the carbonaceous chondrite parent bodies. The formation of water ice at these sub-zero temperatures is suspected to have led to further reductions in $\delta^{18}O$ of the alteration fluid.

Different types of carbonates within the carbonaceous chondrites formed at different stages of the aqueous alteration on their parent bodies, with calcite earlier than dolomite than breunnerite. Our determination of the respective formation temperatures for different carbonates (through stepped phosphoric acid digestions) demonstrates the carbonaceous chondrite parent bodies were cooling as the aqueous alteration proceeded, and furthermore enables us to quantitatively constrain the cooling rate. To the best of our knowledge, this study provides the first quantitative experimental constraints on the thermal evolution of small planetesimals typical of petrology type 1 and 2 carbonaceous chondrite parent bodies.

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