Thermal Evolution of Hydrated Asteroids Inferred from Oxygen Isotopes

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Received 2019 July 25; revised 2019 August 14; accepted 2019 August 15; published 2019 September 6

Abstract

Chondrites are fragments of unmelted asteroids that formed due to gravitational instabilities in turbulent regions of the Solar protoplanetary disk. Hydrated chondrites are common among meteorites, indicating that a substantial fraction of the rocky bodies that formed early in the solar system accreted water ice grains that subsequently melted due to heat released by the radioactive decay of 26Al. However, the thermal histories of asteroids are still largely unknown; increased knowledge would provide fundamental information on their timing of accretion and their physical characteristics. Here we show that hydrated meteorites (CM chondrites) contain previously uncharacterized calcium carbonates with peculiar oxygen isotopic compositions ($\Delta^{17}O \approx -2.5\%$), which artificially produce the mass-independent trend previously reported for carbonates. Based on these isotopic data, we propose a new model to quantitatively estimate the precipitation temperatures of secondary phases (carbonates and serpentine). It reveals that chondritic secondary phases recorded a gradual increase in temperature during the extent of aqueous alteration, from $-10^\circ$C to a maximum of $250^\circ$C. We also show that the thermal path of C-type asteroids is independent of the initial oxygen isotopic composition of the primordial water ice grains that they accreted. Our estimated temperatures for hydrated asteroids remain lower than those experienced by other carbonaceous chondrites, providing strong constraints for modeling the formation conditions and size distribution of water-rich asteroids, especially in anticipation of the return of samples of water-rich asteroids to Earth by the OSIRIS-REx and Hayabusa2 missions.

Key words: meteorites, meteors, meteoroids – minor planets, asteroids: general – protoplanetary disks

1. Introduction

Dark C-type asteroids dominate the main-belt asteroid population and are genetically related to hydrous primitive CI and CM carbonaceous chondrites (Vilas & Gaffey 1989; Hiroi et al. 1996; Vilas 1994; Burbine et al. 2002; Lauretta et al. 2019). CM chondrites are the most common water-rich meteorites, and CM-like matter represent an important fraction of exogenic clasts reported in other groups of meteorites, implying that CM parent bodies are widespread in the asteroid belt (Briani et al. 2012). CM chondrites are complex aggregates of high-temperature components formed in the disk and low-temperature secondary minerals formed during subsequent parent-body fluid circulations. The latter provide key constraints on the origin of water accreted by asteroids (Vacher et al. 2016; Piani et al. 2018) as well as their accretion and evolution histories (Young et al. 2003; Fujiya et al. 2015; Vacher et al. 2017; Verdier-Paoletti et al. 2017). CM chondrites are therefore important samples because they show varying degrees of alteration that can be easily estimated by their chemical alteration index (Rubin et al. 2007; Marrocchi et al. 2014; Vacher et al. 2018). Among secondary minerals, carbonates are of primary importance as they represent direct proxies of the asteroidal fluids from which they formed and can, in theory, be used to decipher their thermal evolution (Clayton & Mayeda 1984). However, determining carbonate precipitation temperatures requires knowledge of the O isotopic compositions of their parental fluids, which itself requires knowledge of the carbonate precipitation temperatures, leading to a seemingly circular problem.

The temperature of CM carbonate precipitation remains largely underconstrained and proposed values cover a large range of temperatures. More generally, the sequence of formation of the different secondary phases (carbonates, serpentine) is poorly understood. Based on “clumped-isotopes” and oxygen isotopic analyses, it has been proposed that CM carbonates could have precipitated at both low and medium temperatures, in the range of 0°C–75°C (Clayton & Mayeda 1984; Benédix et al. 2003; Guo & Eiler 2007) and 50°C–350°C (Alexander et al. 2015; Verdier-Paoletti et al. 2017). However, these two different methodologies do not take into account the petrographic relationship between carbonates and serpentine (Fuchs et al. 1973; Zolensky et al. 1997; Brearley 2006; Rubin et al. 2007; Lee et al. 2013, 2014; Vacher et al. 2018), which can constrain the evolution of the fluid over time. In addition, different types of carbonates are present in CM chondrites (Lee et al. 2013, 2014; Vacher et al. 2017) but no specific attention has been paid on their respective oxygen isotopic compositions. The objectives of this Letter are thus to determine the oxygen isotopic composition of petrographically characterized carbonates in order to quantify the thermal evolution of hydrated asteroids. To do so, we surveyed a suite of different CM chondrites characterized by varying degrees of alteration: CM2.6/2.7 Maribo (van Kooten et al. 2018), CM2.5 Murchison (Rubin et al. 2007), CM2.4/2.7 Jbelti Winselwan (King et al. 2018), and CM2.0 Mukundpura (Rudraswami et al. 2018). Based on oxygen isotopic compositions of carbonates, we propose a new isotopic alteration model that reconciles petrographic observations and formation temperatures of CM carbonates.

2. Material and Methods

2.1. Scanning Electron Microscope (SEM) Imaging

Calcite grains were located in carbon-coated (i) polished sections of Murchison, Mukundpura, and Jbelti Winselwan (samples provided by the Muséum National d’Histoire Naturelle in Paris) and (ii) thin section of Maribo (section
provided by the Natural History Museum of Denmark in Copenhagen) using a SEM JEOL JSM-6510 equipped with an energy dispersive X-ray detector (Bruker-AXS XFlash, silicon drift detector) at Centre de Recherches Pétrographiques et Géochimiques (CRPG; Nancy, France). Back-scattered electron (BSE) imaging were performed with a 3 nA electron beam current operated at 15 kV.

2.2. Oxygen Isotope Analyses of Calcite

Calcite oxygen isotopic compositions were analyzed using a CAMECA IMS 1270 E7 at CRPG laboratory. A Cs+ primary ion beam (~15 x 10 μm spot area) with a current of ~5 nA was used in order to collect 16O, 17O and 18O secondary ions in multi-collection mode using three Faraday cups (L2, FC2, and H1). Charge compensation was applied using a normal-incidence electron gun. Mass resolving power (MRP = M/ΔM) was adjusted to ~7000 to resolve interference from 16OH on the 17O peak and achieve maximum flatness on the top of the 16O and 18O peaks (entrance and exit slits of FC2 were adjusted to ~70 μm and ~170 μm, respectively). 16O and 18O secondary ions were collected on L2 and H1, respectively (slit 1, MRP ≈ 2500). Pre-sputter on a large area (~20 x 20 μm) was applied before each measurement during 60 s in order to remove the carbon coating at the surface of the calcite grains. Acquisition time was set to ~5 s and measurements were repeated over 30 cycles to achieve counting statistics (~0.2‰ (1σ) for δ18O and ~0.3‰ for δ17O. Isotope ratios (13/16O and 18/16O) are presented in per mil (‰) relative to standard mean ocean water (SMOW):

$$\delta^x_{\text{SMOW}}(‰) = \left( \frac{O^{16}_{\text{sample}} + O^{18}_{\text{sample}}}{O^{16}_{\text{SMOW}} + O^{18}_{\text{SMOW}}} - 1 \right) \times 1000 \quad (1)$$

where x represents 17O or 18O and SMOW the ratios of the SMOW standard. We measured two in-house terrestrial standards to define the Terrestrial Fractionation Line (TFL): (i) quartz (SiO2) from Brazil (δ18O = 9.6‰, δ16O = 2 x 106 cps and δ18O = 4.2 x 106 cps) and (ii) calcite (CaCO3) from Mexico (δ18O = 23.6‰, δ16O = 2 x 109 cps and δ18O = 4.2 x 106 cps; 0.3 wt% of MgO). The instrumental mass fractionation (IMF) for calcite matrix was determined from our in-house Mexican calcite standard at the beginning and end of each analytical session. IMF values for each sample analysis were then calculated by accounting for the linear deviation over the time of the IMF values. Typical measurement errors (2σ), accounting for errors on each measurement and the external reproducibility of the standard, were estimated to be ~0.5‰ for δ18O, ~0.6‰ for δ17O, and ~0.7‰ for Δ17O (i.e., Δ17O = δ17O - 0.52 x δ18O), where Δ17O represents the departure from the TFL.

3. Results

In the four CM chondrites surveyed in this work (Table 1), calcite grains surrounded by Fe–S-rich serpentine/tochalilinite (hereafter T1 calcite; Figure 1a) and serpentinite-free polycrystalline calcite grains containing Fe–Ni sulfide inclusions (hereafter T2 calcite; Figure 1b) have only been observed in two sections (Jbilet Winselwan and Mukundpura). The O isotopic compositions of T1 calcite grains measured herein vary widely, with δ18O values ranging from 23.1 to 44.3‰, δ17O from 11.1 to 23.4‰ and Δ17O from −2.8 to +1.8‰ (Figures 1c and 5, Table 2), whereas T2 calcite grains have homogeneous compositions with δ18O values ranging from 12.6 to 18.4‰, δ17O from 4.2 to 8.1‰ and Δ17O from −4 to −0.8‰ (Figures 1c and 5, Table 3).

4. Discussion

Together, T1 and T2 calcite grains define a mass-independent trend with δ17O = (0.61 ± 0.03) x δ18O−(3.3 ± 1.1) (Figures 1c−(d)) that is similar, within errors, to those commonly reported in different CM chondrites (Vacher et al. 2018). As a first approximation, this trend suggests that the O isotopic compositions of CM carbonates is essentially controlled by variable degrees of isotopic exchanges between 16O-rich anhydrous silicates and a 17,18O-rich fluid (Figure 1d; Verdier-Paletti et al. 2017; Marrocchi et al. 2018). However, the O isotopic compositions of T1 calcites alone define a distinct trend with δ17O = (0.53 ± 0.06) x δ18O−(1.2 ± 2.2) that is indistinguishable, within errors, from the TFL (i.e., Δ17O = −0.4 ± 1.0; Figure 1e). Conversely, T2 calcites exhibit clustered δ17O−δ18O values (Figures 1c and 5, Table 3) with Δ17O = −2.6 ± 1.0, which artifically produce the aforementioned mass-independent trend when taken together with T1 calcites (Figure 1d). This demonstrates that petrographic
observations of carbonates are essential for understanding the O isotopic evolution of asteroidal fluids and the constraints that they bear.

Based on mass-balance calculations, tentative attempts at estimating the O isotopic composition of primordial water accreted by CM chondrites have led to widely ranging and contrasted results due to assumptions on the O isotopic composition of the anhydrous protolith and asteroidal thermal evolution ($\delta^{18}O_{\text{fluid}} = 16\text{--}55\%e$, $\delta^{18}O_{\text{fluid}} = 9\text{--}35\%e$ and $\Delta^{17}O_{\text{fluid}} = 0.9\text{--}6.6\%e$; Clayton & Mayeda 1999; Verdiere-Paolletti et al. 2017; Fujiya 2018). However, these values correspond to the initial water composition and do not represent the oxygen isotopic compositions of fluids from which carbonates precipitated, which had Earth-like compositions with $\Delta^{17}O \approx 0\%e$ (Figure 1(c); Vacher et al. 2016; Verdiere-Paolletti et al. 2017). Quantitative estimates of the O isotopic compositions of the parental fluids of carbonates have been obtained by CO$_2$ clumped-isotope thermometry (Δ$^{47}$; Guo & Eiler 2007), which corresponds to anomalous enrichments of mass 47 (i.e., $^{13}C^{18}O^{16}O$) in CO$_2$ derived from H$_2$PO$_4$ digestion of carbonates (Ghosh et al. 2006). Based on measurements performed on the CM chondrites Murchison and Murray, dominated by T1 calcites, Guo & Eiler (2007) estimated that the O isotopic compositions of their alteration fluids ranged from $\delta^{18}O = 2\%e$ and $\Delta^{17}O = -0.6\%e$ (hereafter $W_{\text{min}}$; Figure 2(a)) to $\delta^{18}O = 6.8\%e$ and $\Delta^{17}O = -0.5\%e$ (hereafter $W_{\text{max}}$; Figure 2(a)). Because these fluids experienced oxygen isotopic exchanges with the anhydrous CM chondrite protolith ($\delta^{18}O = -3.8\%e$, $\delta^{13}O = -6.5\%e$; Figure 6), they define two trends that delimit the possible O isotopic compositions of CM alteration fluids (blue shaded area in Figure 2(a)). Considering these extreme trends, the precipitation temperatures of each T1 calcite grain can be calculated according to the isotopic fractionation factor α (Watkins et al. 2013), which corresponds to the distance between the minimum and maximum trends and the O isotopic compositions of carbonates in the three oxygen isotope diagram. This estimation leads to respective minimum ($T_{\text{min}}$) and maximum ($T_{\text{max}}$) precipitation temperatures of $-9 \pm 11^\circ$C and $5 \pm 14^\circ$C for Maribo, $19 \pm 22^\circ$C and $50 \pm 34^\circ$C for Murchison, $15 \pm 21^\circ$C and $33 \pm 29^\circ$C for Jbilet Winselwan, and $12 \pm 17^\circ$C and $34 \pm 22^\circ$C for Mukundpura (1σ; Table 1 and Figure 3(a)). On average, this gives minimum and maximum precipitation temperatures for all T1 calcites of $7 \pm 22^\circ$C and $29 \pm 32^\circ$C, respectively (1σ).

The large range of $\delta^{17}O$–$\delta^{18}O$ values and constant $\Delta^{17}O$ values observed in T1 calcites (Figures 1(c)–(e), Table 2) imply that T1 calcites precipitated along a temperature gradient from alteration fluids characterized by a fixed $\Delta^{17}O$ value. On the other hand, T2 calcites (this study) and serpentine (Clayton & Mayeda 1984) formed from a more $^{16}O$-rich fluid that resulted from protracted isotopic exchange with the $^{18}O$-rich anhydrous protolith and thus evolved toward negative $\Delta^{17}O$ values (Figure 2(b)). Following the same methodology as for T1 calcites, we calculated the formation temperatures of T2 calcites to be significantly higher, with respective minimum and maximum temperatures being $109 \pm 11^\circ$C and $158 \pm 22^\circ$C for Jbilet Winselwan and $110 \pm 11^\circ$C and $139 \pm 55^\circ$C for Mukundpura (1σ; Table 1 and Figure 3(a)); respective average values are $109 \pm 29^\circ$C and $141^\circC \pm 52^\circC$ (1σ). The same calculation for bulk serpentine compositions (n = 5; Clayton & Mayeda 1999) gives minimum and maximum formation temperatures of $28 \pm 8$ to $56 \pm 13^\circ$C and $73 \pm 7$ to $98 \pm 11^\circ$C, respectively, depending on the fractionation factor considered (Zheng 1993; Früh-Green et al. 1996; 1σ; Table 1, Figure 3(a), and Figure 4).

Our petrographic and isotopic approaches reveal that T1 calcites precipitated at lower temperatures than serpentines and T2 calcites (Figure 3(a)). These results support petrographic observations suggesting that T2 calcites correspond to a later stage of alteration, as highlighted by (i) the absence of serpentine rims and (ii) the existence of an FGR, suggesting that they replaced chondrule silicates (Figure 3(b); Lee et al. 2014; Lindgren et al. 2017). This implies that fluid circulation in CM parent bodies, and thus the formation of CM secondary phases, occurred during a prograde thermal evolution (Figures 2(b) and 3(b); Vacher et al. 2019), with T1 calcites forming first at $T = -10$ to $+50^\circ$C, followed by the precipitation of (Fe,S)-rich serpentine (mostly crenstetite; Pignatelli et al. 2016, 2017) and tochilinite at $T = 30^\circC$–$100^\circC$, and finally T2 calcites at $T = 110^\circC$–$160^\circC$ (Figure 3(a), Table 1).

According to X-ray diffraction studies (Howard et al. 2011, 2009), serpentine represent the most abundant mineral in CM chondrites (75 vol% on average). Their formations (posterior to that of T1 calcites) would thus affect the isotopic
Figure 3. (a) Minimum ($T_{\text{min}}$) and maximum ($T_{\text{max}}$) precipitation temperatures of T1 calcites (circles), serpentines (brown triangles), and T2 calcites (diamonds) calculated as a function of their formation sequence/time (errors are 1σ) using previously reported fractionation factors for calcite (O’Neil et al. 1969) and serpentine (Zheng 1993; Früh-Green et al. 1996). Colors are the same as in Figure 1. (b) Schematic representation of the formation sequence of (1) T1 calcite, (2) serpentine around T1 calcite, and (3) T2 calcite, as deduced from petrographic observations and the mean $\Delta^{18}$O values of these three phases (see Figure 2(c)).

Table 1
Mean O Isotopic Compositions of Secondary Phases and Their Calculated Minimum ($T_{\text{min}}$) and Maximum ($T_{\text{max}}$) Formation Temperatures (O’Neil et al. 1969); Uncertainties are 1σ

| Meteorite     | Petrologic Subtype | Secondary Phase | Sample Number | Mean $\delta^{18}$O ($\%$) | Mean $\Delta^{18}$O ($\%$) | Mean $T_{\text{min}}$ ($^\circ$C) | Mean $T_{\text{max}}$ ($^\circ$C) |
|---------------|--------------------|-----------------|---------------|-----------------------------|-----------------------------|-----------------------------------|-----------------------------------|
| Maribo        | CM2.6/2.7 (a)      | T1 calcite      | 25            | 38.3 (±3.1)                 | −1.2 (±0.5)                 | −9 (±11)                          | 5 (±14)                           |
| Murchison     | CM2.5 (b)          | T1 calcite      | 24            | 33.7 (±4.5)                 | 0.4 (±0.8)                  | 19 (±22)                          | 50 (±34)                          |
| Jbilet Winselwan | CM2.4/2.7 (c)     | T1 calcite      | 10            | 31.4 (±4.1)                 | −1.6 (±1.2)                 | 15 (±21)                          | 33 (±29)                          |
| Mukundpura    | CM2.0 (d)          | T1 calcite      | 2             | 17.5 (±0.6)                 | −1 (±0.3)                   | 109 (±11)                         | 158 (±22)                         |
|               |                    | T2 calcite      | 8             | 33.5 (±3.8)                 | −0.7 (±0.6)                 | 12 (±17)                          | 34 (±22)                          |
|               |                    | T2 calcite      | 13            | 15.4 (±2)                   | −2.6 (±1)                   | 110 (±32)                         | 139 (±55)                         |
| Bulk CM       | ...                | Serpentine (e)  | 5             | 11.7 (±0.6)                 | −2.2 (±0.3)                 | 28 (±8) (f)                      | 56 (±13) (f)                     |
|               |                    |                 |               | 73 (±7) (g)                 |                            |                                   |                                   |

References. (a) van Kooten et al. 2018. (b) Rubin et al. 2007. (c) King et al. 2018. (d) Rudrasswami et al. 2018. (e) Clayton & Mayeda 1999. (f) Früh-Green et al. 1996. (g) Zheng 1993.

evolution of the alteration fluids, leading to a slight shift toward $^{16}$O-enriched values. As this isotopic shift is not taken into account in our model, this implies that the precipitation temperatures estimated for T2 calcites (Figure 3(a), Table 1) should be considered as maximum values. However, as the fractionation factor $\alpha$ is significantly lower for serpentine-water than for calcite-water (i.e., $1000\ln\alpha_{\text{serpentine-water}} = 6.3$ versus $1000\ln\alpha_{\text{calcite-water}} = 17.1$ at 100°C; O’Neil et al. 1969; Früh-Green et al. 1996), this approximation does not affect our main conclusions that T1 calcites precipitated at lower temperature than T2 calcites.

As the uncertainties on the O isotopic compositions of primordial water accreted by CM chondrites could also affect our conclusions, we tested our results with different initial O isotopic compositions (Figure 4). According to the currently favored self-shielding model, primordial water is hypothesized to have had a large $^{17,18}$O enrichment (i.e., $\delta^{17}$O = $\delta^{18}$O $\approx$ 180‰; Sakamoto et al. 2007) plotting on a line of slope 1 in a three oxygen isotope diagram. However, mass-balance calculations performed on the O isotopic compositions of CM chondrites at bulk and mineral scales suggest more modest enrichments in the heavy oxygen isotopes with $\delta^{17}$O = 35 ± 9‰ and $\delta^{18}$O = 55 ± 13‰ (Fujiiya 2018). Hence, we tested our results by using primordial CM water O isotopic compositions corresponding to (i) a composition intermediate between $W_{\text{min}}$ and $W_{\text{max}}$ ($W_{\text{int}}$) and (ii) the values proposed by
Figure 4. (a) $\delta^{17}$O–$\delta^{18}$O plot showing the four trends (see the text) used to calculate the influence of the initial oxygen isotopic composition of primordial water on the thermal path interpreted for water-rich asteroids. (b), (c) $\delta^{17}$O–$\delta^{18}$O plots showing the results of the model for Mukundpura and Jbilet Winselwan, respectively. In both cases, the average formation temperatures of T2 calcites are systematically higher than those estimated for T1 calcites (red dashed lines), even when accounting for variability in the $\delta^{17}$O and $\delta^{18}$O values of calcites in Jbilet Winselwan and Mukundpura (gray triangles).

Fujiiya (2018; $W_F$, Figure 4(a)). Isotopic exchange between these fluid compositions and the anhydrous CM protolith (Marrocchi et al. 2018) thus defines two other lines on the $\delta^{17,18}$O diagram (b and d in Figure 4(a), with lines a and c corresponding to the trends defined by $W_{\text{min}}$ and $W_{\text{max}}$, respectively) from which the precipitation temperatures of T1 and T2 calcites can be calculated according to the fractionation factor $\alpha$ (Watkins et al. 2013). The results for Jbilet Winselwan and Mukundpura (the only meteorites containing T2 calcites in this study) systematically show that T2 calcites precipitated at higher temperatures than T1 calcites (Figures 4(b)–(c)), regardless of the oxygen isotopic composition used for primordial water. Depending on the isotopic trend considered (a, b, c, or d in Figure 4(a)), the average precipitation temperatures of T1 calcites range from 10°C to 100°C, whereas T2 calcites formed between 110°C and 245°C (Figures 4(b)–(c)). We note that the absolute temperatures at which secondary phases formed is directly affected by the oxygen isotopic composition of primordial chondritic water, whose precise determination is thus fundamental to better quantifying the thermal evolution of hydrated asteroids.

Another possible source of uncertainty in estimating precipitation temperatures arises if T1 calcites experienced post-precipitation isotopic re-equilibration, especially if CM chondrites experienced peak temperatures as high as 250°C. However, this appears unlikely as T1 calcites systematically show mass-dependent oxygen isotopic variations (Figure 7), whereas isotopic exchange between initial water and anhydrous silicates during re-equilibration would have induced $\Delta^{17}$O variations (Figure 2(a)). In addition, according to the values of oxygen self-diffusion in calcite (Farver 1994; Anderson 1969), $10^4$ yr are required to isotopically re-equilibrate calcite grains of 5 $\mu$m in size at temperatures $\leq$200°C (Figure 7). Such results thus strengthen our conclusion that hydrated asteroids experienced a prograde thermal evolution with T1 calcites precipitating first, followed by serpentine and then T2 calcites.

By taking into account the petrographic type of carbonates, our hydrothermal temperature estimates for CM chondrites are higher than previously proposed (Clayton & Mayeda 1984; Benedix et al. 2003; Guo & Eiler 2007) but remain low (<250°C) compared to the peak of thermal metamorphism experienced by other groups of carbonaceous chondrites, such as CO or CV chondrites (up to 500°C–600°C; Bonal et al. 2007; Busemann et al. 2007; Cody et al. 2008; Ganino & Libourel 2017). This implies the relatively late accretion of water-rich asteroids in the protoplanetary disk, as water-poor asteroids that accreted earlier experienced significantly higher temperatures due to the radioactive decay of $^{26}$Al. Based on $\varepsilon^{54}$Cr anomalies, it has been proposed than CM chondrites accreted $\sim$3.7–5.0 Myr after the formation of CV calcium-aluminum-rich inclusions (CAIs; Fujiiya et al. 2012; Sugiuira & Fujiiya 2014; Doyle et al. 2015), after a five-fold decrease in the abundance of $^{26}$Al, whereas CO and CV chondrites accreted $\sim$2.1–2.4 and $\sim$2.4–2.6 Myr after CV CAIs, respectively (Doyle et al. 2015). Interestingly, recent spectral data provided by the Osiris-REx and Hayabusa2 asteroid sample return missions suggest that C-type asteroid Ryugu has experienced more heating than B-type asteroid Bennu (Hamilton et al. 2019; Kitazato et al. 2019). Although late shock heating could have induced such features, their different thermal history could also be the result of distinct accretion ages. The returned samples from Osiris-REx and Hayabusa2 in the near future will likely contain hydrated minerals (Kitazato et al. 2019; Lauretta et al. 2019) whose in-situ isotopic analyses could provide information on the thermal alteration processes and formation histories of asteroids Ryugu and Bennu.

5. Conclusions

In this Letter, we report the results of in-situ oxygen isotope analyses performed on alteration phases (calcium carbonates) from a suite of different hydrated meteorites (CM chondrites) to quantitatively estimate the thermal evolution of hydrated asteroids. Based on our isotopic results, we propose a new isotopic model that reconciles formation temperatures and petrographic observations of secondary minerals whose isotopic compositions recorded a gradual increase of the
temperature (up to 250°C) during a prograde evolution of the temperature, regardless the oxygen isotopic composition of the initial water. These results are fundamental because they imply that hydrated asteroids accreted relatively late in the protoplanetary disk, as their earlier accretion would have led to higher alteration temperatures due to higher concentrations of radioactive \(^{26}\)Al. Although more precise radioactive dating and numerical modeling are required, our study provides a key method to quantitatively estimate the respective thermal histories of the asteroids Bennu (Laureretta et al. 2019) and Ryugu (Sugita et al. 2019; Watanabe et al. 2019) upon the return of samples to Earth.

The authors are grateful to Nordine Bouden and Johan Villeneuve for their assistance with the isotopic measurements. Laurette Piani is thanked for helpful scientific discussions. The Muséum National d’Histoire Naturelle (Paris) and The Natural History Museum of Denmark (Copenhagen) are also thanked for providing samples of Mukundpura and sections of Maribo chondrites. We thank Prof. Frederic Rasio for his editorial handling and the anonymous reviewer for comments that contributed to improve the quality of the manuscript. This research was funded by l’Agence Nationale de la Recherche through grant ANR-587 14-CE33-0002-01 SAPINS (PI Yves Marrocchi). This is CRPG contribution #2714.

Appendix

This Appendix shows (i) the oxygen isotopic composition of carbonates in the different chondrites selected for this study, (ii) the bulk oxygen isotopic compositions used to calculate the primordial isotopic composition of the anhydrous protolith, and (iii) the time required for the complete re-equilibration of calcites (Clayton & Mayeda 1999; Hewins et al. 2014; Ushikubo et al. 2012; Petitat et al. 2011; Fujiya et al. 2012; Doyle et al. 2015; Farver 1994).

Table 2

| #     | \(\delta^{18}\)O | \(2\sigma\) | \(\delta^{17}\)O | \(2\sigma\) | \(\Delta^{13}\)O | \(2\sigma\) |
|-------|----------------|---------|----------------|---------|----------------|---------|
| CC7   | 32.7           | 0.3     | 15.5           | 0.5     | −1.5           | 0.8     |
| CC21-1| 33.3           | 0.3     | 16.5           | 0.8     | −0.8           | 1       |
| CC21-2| 33.9           | 0.3     | 16.3           | 0.7     | −1.3           | 0.9     |
| CC22  | 33.7           | 0.3     | 17.1           | 0.5     | −0.4           | 0.8     |
| CC20  | 34.1           | 0.4     | 16.9           | 0.6     | −0.9           | 0.9     |
| CC27  | 34.9           | 0.2     | 16.5           | 0.5     | −1.7           | 0.7     |
| CC30  | 35.8           | 0.3     | 17.8           | 0.5     | −0.8           | 0.7     |
| CC10  | 37.3           | 0.6     | 18.1           | 0.6     | −1.3           | 1       |
| CC11  | 37.7           | 0.2     | 18.4           | 0.5     | −1.3           | 0.7     |
| CC4-2 | 38             | 0.3     | 18.6           | 0.5     | −1.1           | 0.8     |
| CC4-1 | 41.6           | 0.3     | 19.9           | 0.5     | −1.7           | 0.7     |
| CC5   | 38.3           | 0.3     | 18.9           | 0.6     | −1.1           | 0.8     |
| CC17  | 38.3           | 0.3     | 17.8           | 0.6     | −2.2           | 0.8     |
| CC9   | 39.3           | 0.3     | 20             | 0.5     | −0.4           | 0.8     |
| CC33  | 39.5           | 0.3     | 19.1           | 0.5     | −1.4           | 0.5     |
| CC32  | 39.5           | 0.3     | 19.6           | 0.7     | −0.9           | 0.9     |
| CC13  | 40             | 0.5     | 20.5           | 0.6     | −0.3           | 1       |
| CC3   | 40.2           | 0.3     | 20             | 0.6     | −0.9           | 0.7     |

| Table 2 (Continued) |

| #     | \(\delta^{18}\)O | \(2\sigma\) | \(\delta^{17}\)O | \(2\sigma\) | \(\Delta^{13}\)O | \(2\sigma\) |
|-------|----------------|---------|----------------|---------|----------------|---------|
| CC7   | 23.1           | 0.7     | 11.1           | 0.8     | −0.9           | 1       |
| CC-3  | 25.2           | 0.4     | 11.3           | 0.7     | −1.9           | 0.7     |
| CC-11 | 31.5           | 0.5     | 13.7           | 0.8     | −2.8           | 0.9     |
| CC-3  | 32.2           | 0.7     | 17.1           | 1.5     | 0.4            | 1.6     |
| CC-2  | 32.3           | 0.6     | 14.3           | 0.7     | −2.4           | 0.8     |
| CC-7  | 32.5           | 0.5     | 14.1           | 0.7     | −2.8           | 0.7     |
| CC-9  | 33.4           | 0.5     | 15.4           | 0.7     | −1.9           | 0.7     |
| CC-8  | 33.7           | 0.5     | 15.1           | 0.8     | −2.4           | 0.8     |
| CC-1  | 34.1           | 0.5     | 16.4           | 0.7     | −1.3           | 0.8     |
| CC-10 | 36.1           | 0.5     | 19.1           | 0.8     | 0.3            | 0.8     |
| Mean  | 33.7           | 18      | −1.6           | 0       |
| StdDev| 4.5            | 2.4     | 0.8            | 0       |
| CC-6  | 23.1           | 0.7     | 11.1           | 0.8     | −0.9           | 1       |
| CC-3  | 25.2           | 0.4     | 11.3           | 0.7     | −1.9           | 0.7     |
| CC-11 | 31.5           | 0.5     | 13.7           | 0.8     | −2.8           | 0.9     |
| CC-3  | 32.2           | 0.7     | 17.1           | 1.5     | 0.4            | 1.6     |
| CC-2  | 32.3           | 0.6     | 14.3           | 0.7     | −2.4           | 0.8     |
| CC-7  | 32.5           | 0.5     | 14.1           | 0.7     | −2.8           | 0.7     |
| CC-9  | 33.4           | 0.5     | 15.4           | 0.7     | −1.9           | 0.7     |
| CC-8  | 33.7           | 0.5     | 15.1           | 0.8     | −2.4           | 0.8     |
| CC-1  | 34.1           | 0.5     | 16.4           | 0.7     | −1.3           | 0.8     |
| CC-10 | 36.1           | 0.5     | 19.1           | 0.8     | 0.3            | 0.8     |
| Mean  | 33.7           | 18      | −1.6           | 0       |
| StdDev| 4.5            | 2.4     | 0.8            | 0       |

Note. Shaded rows denote multiple analyses of the same grain.
Figure 5. $\delta^{17}$O–$\delta^{18}$O plots showing the mass-dependent trends (black solid line) defined by T1 calcites (circles) for each CM chondrite: (a) Maribo, (b) Murchison, (c) Jbilet Winselwan, and (d) Mukundpura. Shaded areas represent the 95% confidence interval for each slope. T2 calcites (diamonds) are also shown for Jbilet Winselwan (c) and Mukundpura (d), the only chondrites studied herein containing T2 calcites. Errors are 2σ.

Figure 6. $\delta^{17}$O–$\delta^{18}$O plot showing the O isotopic composition of the anhydrous CM protolith (i.e., the theoretical anhydrous bulk CM composition: $\delta^{18}$O = −3.8‰ and $\delta^{17}$O = −6.5‰; gray star) determined from the linear correlation of the CM bulk composition (green circle; Clayton & Mayeda 1999; Hewins et al. 2014). The anhydrous CM protolith corresponds to the intercept between the bulk CM trend ($\delta^{17}$O = 0.69 × $\delta^{18}$O−3.8; $n$ = 36) and the PCM line ($\delta^{17}$O = 0.987 × $\delta^{18}$O−2.7; Ushikubo et al. 2012). CCAM = Carbonaceous chondrite anhydrous minerals line.

Figure 7. Time (Myr) required for the complete re-equilibration of early precipitated T1 calcite as a function of grain size (radius) and temperature, calculated using oxygen self-diffusion parameters for calcite (Farver 1994). The gray shaded region at 10 Myr corresponds to the duration estimated for fluid circulations in asteroidal parent bodies (Petit et al. 2011; Fujiya et al. 2012; Doyle et al. 2015).
Table 3
Oxygen Isotopic Compositions of T2 Calcite Grains in the CM Chondrites
Jbilet Winselwan and Mukundpura

| #     | \(\delta^{18}O\) 2σ | \(\delta^{17}O\) 2σ | \(\Delta^{17}O\) 2σ |
|-------|-----------------|-----------------|--------------------|
| CC15  | 17.1 0.4        | 8.1 0.9         | 0.8 0.9            |
| CC14  | 17.9 0.5        | 8.1 0.8         | 0.3 0.0            |
| Mean  | 17.5 8.1        | 8.1 1.3         | 0.3 0.3            |
| StDev | 0.6 0.6         | 0.6 0.6         | 0.3 0.3            |

Note. Shaded rows denote multiple analyses of the same grain.

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