MONITORING THE THERMAL EVOLUTION OF THE CM PARENT BODY-(IES) WITH IN SITU OXYGEN ISOTOPE ANALYSES.

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Introduction: CM carbonaceous chondrites have recorded episodes of aqueous alteration on their parent bodies, but their alteration conditions remain largely under-constrained. Oxygen isotope compositions (i.e., $\delta^{17,18}O$) of secondary phases, such as serpentine and carbonates, are powerful tools to decipher the temperature and the evolution of the altering fluid [1]. There is no consensus on the formation temperatures of CM carbonates. Based on 'clumped-isotopes' and O-isotopic analyses, it has been proposed that CM carbonates could have precipitated at both low and medium temperatures, in the range of 0-75°C [1,2] and 50-300°C [3]. However, these two different methodologies do not take account the petrographic relationship between carbonates and serpentine, which can constrain the evolution of the fluid over time. Here we report *in situ* O-isotopic analyses of Ca-carbonates and propose a new isotopic alteration model that reconciles petrographic observations and formation temperatures of CM carbonates.

Methodology: We performed *in situ* isotopic analyses of calcite grains in polished sections of the CM2 Murchison and Mukundpura. Detailed observations of calcite were made using a scanning electron microscope (SEM) JEOL JSM-6510 equipped with an Energy Dispersive X-ray (EDX) Genesis detector. O-isotopic compositions were measured using a CAMECA ims 1280 HR2 ion microprobe at CRPG (Nancy, France). A Cs^+ primary beam of 5nA (spot size $\approx$ 15 μm) was used to measure ^{16}O, ^{17}O, and ^{18}O in multi-collection mode (three Faraday cups: L'2 for ^{16}O ($10^{10}\Omega$), FC2 for ^{17}O ($10^{11}\Omega$) and H1 for ^{18}O ($10^{11}\Omega$)).

Results: Only calcite grains surrounded by serpentine (hereafter T1 calcite, [4, 5]) were found in the two polished sections of Murchison (**Fig. 1a**). O-isotopic measurements show that Murchison's T1 calcites have $\delta^{18}O$ values between 25.5 and 41.5‰, $\delta^{17}O$ values between 14.5 and 23.5‰ and $\Delta^{17}O$ values between -1.1 and 1.8‰ (relative to SMOW, n = 24). In contrary, two types of carbonates were found in the polished section of Mukundpura: (i) T1 calcite grains and (ii) polycrystalline grains of calcite containing Fe-Ni sulfide inclusions (hereafter T2 calcite, [5, 6]) (**Fig. 1b**). O-isotopic analyses on Mukundpura's Ca-carbonates reveal that (i) T1 calcites have $\delta^{18}O$ values between 27.4 and 38.2‰, $\delta^{17}O$ values between 13.3 and 18.5‰ and $\Delta^{17}O$ values between -1.4 and -0.2‰ (n = 8), whereas (ii) T2 calcites have $\delta^{18}O$ values between 12.4 and 18.6‰, $\delta^{17}O$ values between 4.2 and 7.3‰ and $\Delta^{17}O$ values between -4 and -0.9‰ (n = 13).
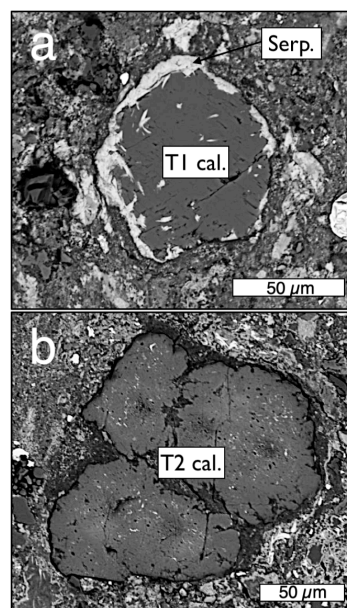

Fig. 1 (a) BSE image of a T1 calcite surrounded by Fe-Mg-rich serpentine in the CM Murchison. (b) BSE image of a polycrystalline aggregates of T2 calcite in the CM Mukundpura.

Discussion: The O-isotopic compositions of T1 calcites in Murchison and Mukundpura define two similar trends falling near to the Terrestrial Fractionation Line (hereafter TFL) with slopes close to 0.52, within errors: (i) $\delta^{17}O$ = 0.51 ($\pm$ 0.04) x $\delta^{18}O$ – 0.95 ($\pm$ 1.24) for Murchison and (ii) $\delta^{17}O$ = 0.49 ($\pm$ 0.06) x $\delta^{18}O$ – 0.44 ($\pm$ 2.16) for Mukundpura (**Fig. 2**). The slope of 0.52 defined by T1 calcite cannot result from the isotopic exchange between a ^{16}O-poor fluid and ^{16}O-rich anhydrous silicates, which should follow a mass-independent O-isotopic fractionation [6]. Instead, it implies that T1 calcite precipitated along a temperature gradient from fluids with similar isotopic compositions (**Fig. 2**). In contrast, T2 calcites show homogeneous O-isotopic compositions, indicating precipitation from a fluid that did not experienced significant $\Delta^{17}O$ variations. From petrographic observations, it has been proposed that T2 calcite corresponds to a later episode of alteration, from an evolved fluid enriched in ^{16}O caused by its isotopic equilibration with ^{16}O-rich anhydrous minerals [4, 5]. This interpretation is also consistent with the negative $\Delta^{17}O$ values shown by T2 calcite compared to T1 calcite. Thus, it appears difficult to apply a linear regression model between T1 and T2 Ca-carbonates (which provides a slope ≈ 0.6-0.65

[3, 6, 7, 8], **Fig. 2**), especially if serpentine formed between the precipitation events of T1 and T2 calcite.

Isotopic model: Assuming that the O-isotopic compositions of the Murchison's water calculated by [2] from carbonate clumped-isotope thermometer (W_{min} & W_{max} in the **Fig. 2**) are robust and represent the extreme isotopic compositions of the fluid from which T1 calcite precipitated, it is then possible to determine the range of precipitation temperatures for each T1 calcite. Thus, T1 calcite precipitated from temperatures in the range of -15 to 70°C for W_{min} and -2 to 116°C for W_{max} (average values of 17 and 37°C for W_{min} and W_{max}, respectively) (**Fig. 3**). Furthermore, the temperatures of formation of serpentine and T2 calcite can also be approximated by making the assumption that (i) serpentine and T2 calcite have precipitated from the same parent fluid as T1 calcite and (ii) this fluid has isotopically exchanged with the ^{16}O-rich anhydrous minerals (changing the $\Delta^{17}O$ values of the fluid toward negative values). Thus, the isotopic variation decreases gradually as the fluid is equilibrating with the anhydrous silicates (i.e., bulk CM anhydrous, **Fig. 2**). Consequently, the temperature of formation of T2 calcite must increase with the extent of the alteration due to the decrease of the fractionation factor between calcite and water. Our temperature estimations for T2 calcites give higher temperature than previously calculated for T1 calcites, in the range of 82 to 149°C for W_{min} and 82 to 174°C for W_{max} (average values of 107 and 119°C for W_{min} and W_{max}, respectively) (**Fig. 3**). The same calculation for bulk serpentine [9] gives average temperatures of 30-46°C and 88-107°C (n = 5), according to the fractionation factor considered ([12] and [13], respectively) (**Fig. 3**).
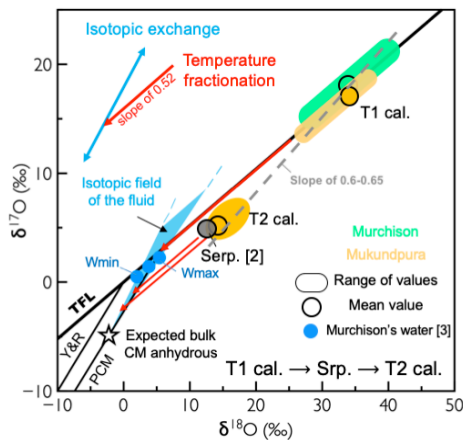
that T1 calcite precipitated at lower temperature than T2 calcite. In addition, the formation sequence of the secondary phases suggests that the alteration temperature of the CM parent body-(ies) had progressively increased with the duration of the alteration. The results of our model show that aqueous alteration of CM parent body-(ies) occurs during a prograde evolution of the temperature, where the T1 calcite are probably the first alteration mineral to form at T = 20-40°C, following by the precipitation of Fe-Mg-rich serpentine (mostly cronstedtite, [10]) and then T2 calcite at T = 110-120°C.
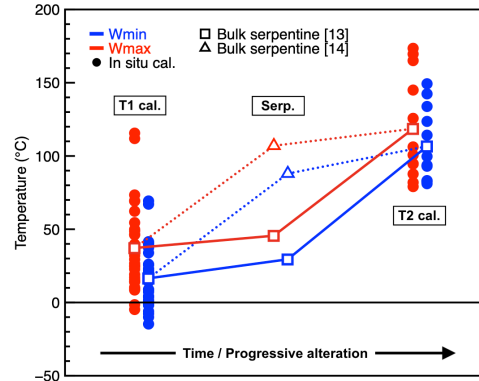

Fig. 3 Evolution of the precipitation temperature of T1 calcite, serpentine and T2 calcite as function of time (or progression of the alteration). The minimum and maximum formation temperatures were calculated using the two extreme O-isotopic composition of the Murchison's fluid (W_{min} and W_{max}, see Fig. 2). Fractionation factors from [11] and [12, 13] were used for calcite and serpentine, respectively.

Conclusions: We analyzed the *in situ* O-isotopic compositions on calcite in the CM Murchison and Mukundpura in order to track the temperature of formation of CM carbonates. Our results demonstrate that (i) CM carbonate precipitated essentially at low temperature (i.e., 20-40°C for primary and 110-120°C for secondary carbonates) and (ii) secondary minerals recorded a gradual increase of the temperature during the duration of aqueous alteration.

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Fig. 2 Three-oxygen isotope diagram showing the isotopic model of this study. The O-isotopic composition of the Bulk CM anhydrous (star) was determined by calculating the intercept between the PCM line and the trend defined by the bulk of CM chondrites [9].

Implications: Based on our isotopic model, the temperatures of formation of Ca-carbonates indicate