PETROGRAPHIC AND ISOTOPIC C & O SURVEY OF THE EARLIEST STAGES OF AQUEOUS ALTERATION OF CM CHONDRITES

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Introduction: CM carbonaceous chondrites are characterized by a large scale of aqueous alteration, from less altered (CM 2.7) to heavily altered (i.e., CM 2.0) [1]. A large variety of secondary phases are present in CMs, including Tochilinite-Cronstedtite Intergrowths (TCIs) and carbonates [2, 3]. TCIs are commonly observed in the matrix in close association with grains of carbonates, but the chronology of the formation of these secondary assemblages remain largely unconstrained. The recent discovery of the least altered CM 2.7 Paris [4] offers a unique opportunity to better characterize the earliest stages of fluid alteration in CM chondrites. Some Paris' Ca-carbonates have particular O-isotopic compositions that suggest the accretion of few percent of outer disk water ice grains [5]. Consequently, Paris could have kept the record of C-bearing inorganic ices from the outer part of the Solar system. However, the C-isotopic composition of the Paris' carbonates has not been determined yet while it would bring important informations on the alteration conditions and the source(s) of carbon. Here, we reported a combined petrographic and C & O isotopic study of the Paris chondrite.

Methodology: We performed petrographic observations and *in situ* isotopic analyses of Ca-carbonates in three polish sections of the Paris chondrite. Detailed observations of Ca-carbonates were made using a scanning electron microscope (SEM) JEOL JSM-6510 equipped with an Energy Dispersive X-ray (EDX) Genesis detector. Raman spectra for mineralogical identifications were obtained using a LabRAM HR spectrometer (Horiba Jobin Yvon) equipped with a 600 gr.mm^{-1} grating and an Edge filter. The confocal hole aperture and the slit aperture were 500 μm and 100 μm, respectively. C and O-isotopic compositions were measured using a CAMECA ims 1280 HR2 ion microprobe at CRPG (Nancy, France). A Cs^{+} primary Gaussian beams of 20 nA (spot of $\approx$ 20 μm) and 5nA (spot of $\approx$ 15 μm) were measured in multi-collection mode (two Faraday and three Faraday cups) for C and O-isotopes, respectively.

Results: The mineralogical characterization reveals that Ca-carbonates are essentially calcite ($\approx$ 69 %), but a significant proportion of aragonite was also identified ($\approx$ 31 %). Two populations of Ca-carbonates are found in Paris. Type 1a refers to grains that are surrounded by TCIs whereas new Type 0 refers to isolated TCI-free grains. TCI rims commonly have rectilinear shapes with planar margins that are subparallels to the central carbonate grain. Isotopic measurements show that Paris' Ca-carbonates have $\delta^{13}C$ values that range from 19 to 80 ‰ (PDB), $\delta^{18}O$ values that range from 29 to 41 %, and $\delta^{17}O$ values that range from 13 to 24 ‰ (SMOW).

Discussion: Petrographic observations suggest that the two populations of Ca-carbonates correspond to two generations of Ca-carbonate precipitation: (i) Type 1a would have precipitated at the early stage of alteration, before being partially or totally pseudomorphosed by TCIs and (ii) Type 0 Ca-carbonates could correspond to a late stage of precipitation. The range of $\delta^{13}C$ values of the Ca-carbonates is consistent with the large C-isotopic variability of soluble organic matter (SOM) (i.e., $\approx$ -15 to 60 ‰, [6]) suggesting that SOM represents the source of most of the CM carbonates. According to the $\delta^{13}C$-$\delta^{18}O$ values of Paris' Ca-carbonates, we develop an alternative model that considers that the Paris Ca-carbonates precipitated from different fluids derived from (i) variable equilibration of $^{17,18}O$-rich Primordial Water (PW) with ^{16}O-rich matrix anhydrous silicates and (ii) variable contributions of different ^{12}C- and ^{13}C-rich SOMs. Assuming that the average precipitation temperatures of CM carbonates is $\approx$ 110°C [7], the possible $\delta^{13}C$-$\delta^{18}O$ carbonate values estimated by this model can only be located in a specific area of the $\delta^{13}C$-$\delta^{18}O$ diagram delineated by (i) the extreme $\delta^{13}C$ values measured in the different SOMs and (ii) the $\delta^{18}O$ of the PW and the anhydrous CM silicates. Our model also demonstrates that—depending on the degree of alteration and the respective contribution of the SOMs—both positive and negative $\delta^{13}C$-$\delta^{18}O$ correlations can be produced during the precipitation of Ca-carbonates. However, given that carbonate precipitation can occur at variable temperatures, from fluids characterized by different degrees of equilibration and with variable ^{12}C and ^{13}C-rich SOMs, we consider it is more likely that no systematic relationship between $\delta^{13}C$ and $\delta^{18}O$ should be observed in CM chondrites, as previously reported from *in situ* analysis [8, 9].

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