

## ISOTOPIC RECORDING OF CONTRIBUTION OF OUTER DISK WATER ICES IN CM CHONDRITES

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**Introduction:** Anhydrous silicates of CM carbonaceous chondrites were accreted with sub-millimeter water ice grains, leading to episodes of low temperature hydrothermal alteration that have strongly modified their petrography. The origin of this water ice is controversial, but two principle sources are generally considered: (i) a local origin and (ii) an outer disk origin [1]. However, the respective proportions of local and outer disk water ices accreted into chondrites are still a matter of debate. The recent discovery of the least altered CM Paris [2] offers a unique opportunity to quantitatively estimate the contributions of the (i) D-poor and  $^{16}\text{O}$ -rich local and (ii) D-rich and  $^{17,18}\text{O}$ -rich outer Solar System water ices. In this study, we report the bulk D/H ratio of the Paris chondrite and the O-isotopic analysis Ca-carbonates to quantitatively estimate the proportion of outer ices in the inner Solar System during the accretion of CM chondrites.

**Methodology:** Ca-carbonates were observed in two sections of the Paris chondrite 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<sup>+</sup> primary Gaussian beam of 5nA (spot of  $\approx 15 \mu\text{m}$ ) was measured in multi-collection mode (three Faraday cups). The determination of  $[\text{H}_2\text{O}^+]$  and D/H of Paris were performed on-line using an elemental analyzer connected to a VG Isoprime Isotope Ratio Mass Spectrometer (IRMS) according to the procedure developed by [3].

**Results:** The O-isotopic compositions of Paris Ca-carbonates vary widely, from 24.2‰ to 40.8‰ in  $\delta^{18}\text{O}$  and 11.6‰ to 23.8‰ in  $\delta^{17}\text{O}$  and reveal the existence of two distinct populations of carbonates. Combined with the literature data from other CM chondrites, the O-isotopic compositions of CM carbonates define two statistically different trends: (i) the ISS-trend ( $\Delta^{17}\text{O} < 0$ , slope of 0.65) and (ii) the ISM-trend ( $\Delta^{17}\text{O} > 0$ , slope > 1). The three aliquots of Paris show reproducible water content ( $[\text{H}_2\text{O}^+] = 4.8 \text{ wt\%}$ ) and hydrogen isotopic composition (D/H =  $175 \times 10^{-6}$ ).

**Discussion:** The main ISS-trend defines a continuous trend that result from the isotopic equilibration between  $^{17,18}\text{O}$ -rich fluids and  $^{16}\text{O}$ -rich anhydrous minerals [4]. The fluid from which the ISS-carbonates precipitated had near terrestrial  $\Delta^{17}\text{O}$  values, demonstrating that most water ices accreted by CM chondrites had a dominantly local origin from the inner solar system (i.e.,  $\Delta^{17}\text{O} \approx 0$ ) [5]. On the contrary, the significant  $^{17,18}\text{O}$  enrichment of ISM carbonates implies the presence of outer water ices with  $\Delta^{17}\text{O} \gg 0$  within CM chondrites [6]. The contribution of outer water ices can be quantitatively calculated from isotopic mass balance calculations. The O-isotopic compositions of the local fluids from which carbonates precipitated can be estimated at different temperatures (10-150 °C). Hence, for each temperature, we calculated the O-isotopic composition of the fluid ( $\delta^{17,18}\text{O}_{\text{fluid}}$ ) resulting from mixing of local water ( $\delta^{17,18}\text{O}_{\text{w-ISS}}$ ) with varying proportion of  $^{17,18}\text{O}$ -rich outer water ice ( $\delta^{17,18}\text{O}_{\text{w-ISM}}$ ) [7, 8] from this equation:  $\delta^{17,18}\text{O}_{\text{fluid}} = f \times \delta^{17,18}\text{O}_{\text{w-ISS}} + (1 - f) \times \delta^{17,18}\text{O}_{\text{w-ISM}}$ . The results demonstrate that ISM-carbonates precipitated from fluids that accommodated 8-35% of  $^{17,18}\text{O}$ -rich outer water ices. This estimation is confirmed by the bulk D/H ratio of Paris that shows significant D enrichment (i.e., D/H =  $175 \times 10^{-6}$ ) relative to the mean (D/H) of CM chondrites ( $139 \times 10^{-6}$ ). Given the recent (D/H) estimation of: (i) the local CM water [4] and (ii) the cometary ice of the Comet 67P [9], the D enrichment observed in Paris can be explained by a contribution of 21% of outer water ice, supporting our mass balance calculation based on the O-isotopes. This interpretation is also supported by the distinct C/H vs. D/H correlation reported for the Paris' matrix compared to the other CM chondrites [10]. The detection of outer water ice in Paris could be linked to its low H<sub>2</sub>O content relative to other CMs (i.e., 4.8 wt.% vs.  $\approx 9 \text{ wt\%}$ ; [11]), which would preclude the dilution of  $^{17,18}\text{O}$ - and D-rich water ices by local water during the alteration processes. The occurrence of outer water ices in CM chondrites requires inward radial transport in the protoplanetary disk, suggesting that this transport took place early in the history of the Solar protoplanetary disk.

**References:** [1] Lunine J. I. (2006) *Meteorites & the Early Solar System II*, 309. [2] Hewins R. H. et al. 2014. *Geochimica & Cosmochimica Acta* 124:190-222. [3] Lupker M. (2012) *Geochimica & Cosmochimica Acta* 84:410-432. [4] Verdier-Paoletti M. J (2017) *Earth and Planetary Science Letters* 458:273-281. [5] Alexander C. M. O. et al. (2012) *Science* 337:721-723. [6] Vacher L. G. et al. (2016) *The Astrophysical Journal Letters* 827:L1. [7] Sakamoto N. et al. (2007) *Science* 317:231-233. [8] Nittler L. R. (2015) *LPSL XLVI*, Abstract #2097. [9] Altweig K. et al. (2015) *Science* 337:1261952. [10] Piani L. (2017) *LPSL XLVIII*, Abstract #1203. [11] Rubin A. E. (2007) *Geochimica & Cosmochimica Acta* 71:2361-2382.