

Carbon and O isotopic ratios, trace element abundances and cathodoluminescence observation of calcite in Murchison.

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Introduction: Carbonates are ubiquitous in CM chondrites. Their O and C isotopic compositions have been extensively studied. Calcite in CM chondrites generally has high $\delta^{18}\text{O}_{\text{SMOW}}$ values up to ~40 ‰, reflecting its low temperature formation (e.g., [1]). Carbon in CM calcite is also isotopically heavy with variable $\delta^{13}\text{C}_{\text{PDB}}$ values ranging from ~20 to 80 ‰ (e.g., [2]). The reason for the $\delta^{13}\text{C}$ variation is unclear, but it can probably be attributed to diverse C sources in aqueous fluids and/or Rayleigh-type isotopic fractionation [3].

In this study, we analyzed C and O isotopic ratios, trace element abundances and cathodoluminescence (CL) intensities of calcite in Murchison to explore 1.) C sources of carbonates, and 2.) whether Rayleigh fractionation resulted in the $\delta^{13}\text{C}$ variation.

Experimental: CL images of Murchison calcite were obtained with the Mini CL by Gatan at Univ. Tokyo. $^{12}\text{C}^-$ and $^{13}\text{C}^-$, and $^{24}\text{Mg}^+$, $^{44}\text{Ca}^+$, $^{55}\text{Mn}^+$ and $^{56}\text{Fe}^+$ were analyzed on multiple spots in single calcite grains with the NanoSIMS 50 at AORI using ~30 pA Cs^+ and ~100 pA O^- primary beams, respectively. Oxygen isotopic ratios were measured with the IMS 1280-HR at CRPG-CNRS using a ~130 pA Cs^+ primary beam. Finally, $^{24}\text{Mg}^+$, $^{43}\text{Ca}^+$, $^{55}\text{Mn}^+$ and $^{57}\text{Fe}^+$ were analyzed with the NanoSIMS 50 at MPI for Chemistry using a 1 nA O^- primary beam because the previous $^{56}\text{Fe}^+$ measurement was partially unsuccessful.

Results and Discussion: We found heterogeneity of $\delta^{13}\text{C}$ values, trace element abundances and CL intensities not only among different grains in the same thin section but also in single grains. There are two distinct types of calcite with respect to $\delta^{13}\text{C}$ values, trace element abundances, and CL intensities: one with high $\delta^{13}\text{C}$ values of ~76 ‰, low trace element abundances (e.g., Mn) of several ppm and no CL signatures, while the other has low $\delta^{13}\text{C}$ values of ~32 ‰, Mn abundances of several hundred ppm and CL zoning. In contrast, O isotopic ratios are similar for both types of grains ($\delta^{18}\text{O} \sim 34$ ‰).

Based on the O isotopic ratios and the model by [3], the $\delta^{13}\text{C}$ variation expected from Rayleigh fractionation of C is much smaller than observed, excluding Rayleigh fractionation as the sole mechanism to produce the $\delta^{13}\text{C}$ variation. Alternatively, the presence of at least two C sources with different isotopic ratios is invoked. The C sources with $\delta^{13}\text{C} > 80$ ‰ would be organic components, which have been identified as locally ^{13}C -enriched grains in meteoritic insoluble organic matter [4]. Thermodynamic calculations show that calcite with lower Fe abundances formed under more reduced conditions. The fact that the two types of calcite were found in the same thin section suggests that micro-environments with diverse physicochemical conditions such as redox states were present at scales of 100's μm .

References: [1] Benedix G. K. et al. 2003. *GCA* 67:1577-1588. [2] Grady M. M. et al. 1988. *GCA* 52:2855-2866. [3] Guo W. and Eiler J. M. 2007. *GCA* 71:5565-5575. [4] Hashizume K. et al. 2011. *Nature Geosci.* 4: 165-168.