Carbon isotopic ratios of calcite grains in the LAP 031166 CM chondrite: Implications for possible link between CM and cometary ices.

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Introduction: Carbonate minerals are ubiquitous in CM chondrites, which formed by aqueous alteration in the CM chondrite parent body. Previous studies have shown that C isotopic ratios of CM carbonates are highly variable at whole-rock scales as well as among individual grains in single meteorites [e.g., 1-3]. Despite extensive studies on C isotopic ratios of CM carbonates, the reason for variability in δ13C variation and the origin of the carbonate C remain poorly understood.

Here we report C isotopic ratios of calcite (CaCO3) in the LAP 031166 CM chondrite (CM 2.1), and discuss the origin of the carbonate C and a possible link between ices in CMs and in comets. The O isotopic ratios of calcite in this meteorite were reported by Lindgren et al. [4].

Experimental: Carbon-isotope analysis was performed with the NanoSIMS 50 installed at Atmosphere and Ocean Research Institute, the University of Tokyo, on the calcite grains whose O isotopic ratios were measured previously. Negative secondary ions of 12C, 13C, 16O, 15N, and 28Si produced by rastering a Cs+ primary ion beam (20-30 pA, ~1 μm in diameter) over 6 x 6 μm2 sized areas were detected simultaneously with five electron multipliers.

Results and discussion: The δ18O and δ13C values of the calcite grains in LAP 031166 are shown in Fig. 1, together with literature data of Ca-carbonate (calcite and aragonite) in the Murchison, Nogoya, and Paris CM chondrites [3,5,6]. The δ13C and δ18O values of the CM carbonates are highly variable, ranging from ~20 to 80‰ and from ~15 to 40‰, respectively, and they do not correlate with each other.

Alexander et al. [1] have suggested that the range in δ13C can be explained by variable formation temperatures (0-130 °C) of CM carbonates which are isotopically equilibrated with gaseous C species dominated by CO (or CH4). However, this model implies that the δ13C and δ18O values of the CM carbonates would correlate, which is clearly not the case as demonstrated by this work (Fig. 1). Instead, the observed δ13C range must be produced under nearly constant temperatures.

Here we propose a modified version of the model outlined by Alexander et al. [1], where we consider mixing of CO2 and CO gases with higher and lower δ13C values, respectively. Because the equilibrium CO/CO2 ratios are <1 for δ18O higher than the iron-magnetite buffer, CO should be converted to CO2 and the CO/CO2 ratios of gas phases would have decreased with time. As the CO2/CO ratios decreased, CO2 as well as carbonates acquired lower δ13C values. Given 1000‰(calcite-CO2) of ~10-14 at 0-30 °C, where α is a C isotopic fractionation factor, the CM carbonates with the highest δ13C values of ~80‰ were equilibrated with CO2 with δ13C ~ 70‰. The δ13C value of the trapped CO in Murchison is ~30‰ [8]. The lowest δ13C values of the CM carbonates are ~20-30‰, which is common for all the CM chondrites analyzed (Fig. 1). Therefore, the gaseous C species which coexisted with the CM carbonates with the lowest δ13C values of ~20-30‰ would have been dominated by CO2, i.e., most of CO was converted to CO2. If correct, the δ13C value of the bulk gaseous C species (CO2 + CO) would be ~10‰.

Using the above numbers, mass balance calculation suggests that a CO/CO2 mole ratio of the gaseous C species which coexisted with the CM carbonates with the highest δ13C value of ~80‰ would be ~1.5, which may reflect the CO/CO2 ratio of ice accreted onto the CM parent body. The carbonate C/H2O mole ratios of most CMs range from ~0.01 to 0.1 [1]. These carbonate C/H2O ratios may set lower limits on the CO2/H2O ratio of the CM ices because of possible CO2 loss. Thus, CO2 accounts for at least 1% of the CM ices.

The inferred CO2/CO and CO2/H2O mole ratios of the CM ices are shown in Fig. 2, together with those of cometary ices [9]. Unfortunately, only upper limits on the CO2/CO ratios are obtained for most of the observed comets. Nevertheless, the CO2/CO ratios of these comets seem lower than unity, and thus, lower than those of the CM ices. Although the possible similarity between ices in CMs and in some comets cannot be ruled out, these observations suggest that ices in the two classes of bodies had a different origin, which is consistent with contrasts in the D/H ratios of water between CMs and comets [10].

**Fig. 1.** $\delta^{13}$C and $\delta^{18}$O values of Ca-carbonates in CM chondrites. Errors are $2\sigma$.

**Fig. 2.** CO/CO$_2$ and CO$_2$/H$_2$O mole ratios of the inferred CM ices and comets. Data with arrows represent upper limits. JFCs: Jupiter-family comets, OCs: Oort cloud comets. Only comets which were observed within 2.5 AU from the Sun are shown, where H$_2$O effectively sublimes from the nucleus of the comet.