CARBON ISOTOPIC RATIOS OF CARBONATE IN CM CHONDRITES AND THE TAGISH LAKE METEORITE.

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Introduction: Carbonate minerals are ubiquitous in CM chondrites and formed by aqueous alteration in the 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 reasons for the variability in $\delta^{13}C$ values and the origin of the carbon in carbonates remain poorly understood.

The Tagish Lake meteorite is an ungrouped carbonaceous chondrite that is believed to be derived from a D-type asteroid [4]. The C isotopic ratios of carbonates in Tagish Lake were measured for whole-rock samples [5], but as yet there are no measurements on individual grains. Therefore, the variation in C isotopic ratios has not been investigated for the Tagish Lake carbonates.

Here we report C isotopic ratios of individual calcite ($CaCO_3$) grains in the LaPaz Icefield (LAP) 031166 CM chondrite (CM 2.1), and of both calcite and dolomite ($CaMg(CO_3)_2$) grains in the Tagish Lake meteorite. We discuss the origin of the carbon in carbonates and explore a possible link between ice in CMs and Tagish Lake and cometary ice.

Experimental: Carbon-isotope analysis on the calcite grains in LAP 031166, whose O isotopic ratios were previously reported by Lindgren et al. [6], was performed with the NanoSIMS 50 at the Atmosphere and Ocean Research Institute, The University of Tokyo. Negative secondary ions of ^{12}C, ^{13}C, ^{18}O, $^{12}C^{14}N$, and ^{28}Si, produced by rastering a Cs^+ primary ion beam (20-30 pA, ~1 μm in diameter) over 6 x 6 μm^2 sized areas, were detected simultaneously with five electron multipliers.

Carbon-isotope analyses on calcite and dolomite grains in Tagish Lake were performed with the NanoSIMS 50 at the Max Planck Institute for Chemistry, Mainz. Compared with CM carbonates, carbonate grains in Tagish Like are small (typically <10 μm). Thus, we measured C isotopic ratios by recording ion images of $^{12}C^-$, $^{13}C^-$, $^{18}O^-$, $^{12}C^{14}N^-$, and $^{28}Si^-$ (3 x 3 μm^2) produced with a Cs^+ primary ion beam (~10 pA, ~a few 100's nm in diameter).

Results and Discussion: The $\delta^{13}C_{PDB}$ and $\delta^{18}O_{SMOW}$ values of the calcite grains in LAP 031166

are plotted in Fig. 1, together with literature data of Ca-carbonate in CM chondrites [2,3,7]. Figure 2 shows the $\delta^{13}C$ values of the calcite and dolomite grains in Tagish Lake. Also shown in Fig. 2 are data obtained by acid dissolution of whole-rock samples [5].
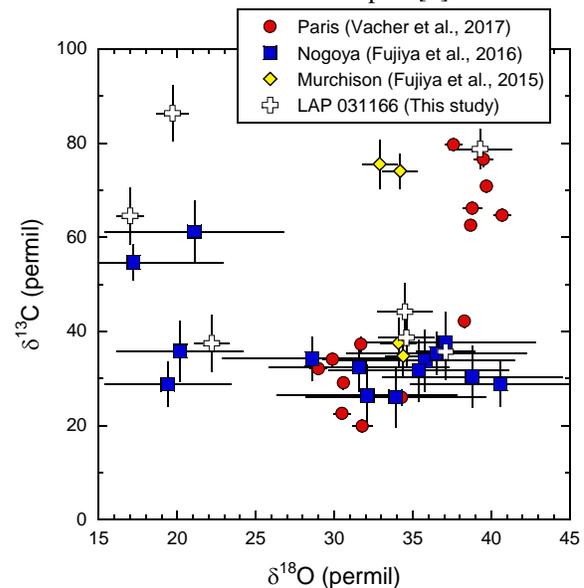

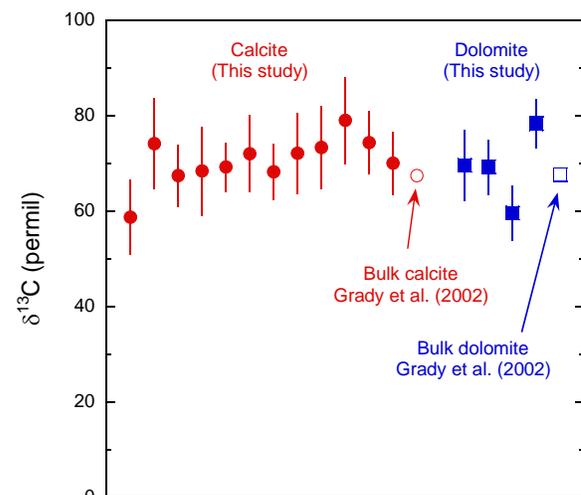**Fig. 1:** $\delta^{13}C$ and $\delta^{18}O$ values of Ca-carbonate grains in CM chondrites.

Fig. 2: $\delta^{13}C$ values of carbonate grains in Tagish Lake.

An apparent contrast between carbonates in CMs and Tagish Lake can be seen: the $\delta^{13}C$ values of CM carbonates are highly variable, ranging from ~20 to 80‰, whereas all Tagish Lake carbonates have high $\delta^{13}C$ values of ~70‰, which are consistent with whole-rock analyses [5]. The $\delta^{18}O$ values of CM carbonates range from ~15 to 40‰, and show no systematic correlation with corresponding $\delta^{13}C$ values (Fig. 1).

To explain these observations, we propose here mixing of at least two C reservoirs with different $\delta^{13}C$ values. The candidates of C reservoirs which may have contributed to the carbonate C include CO_2 and CO accreted as ice, and organic matter. CO_2 is the major C-bearing species in cometary ice [10].

If C from organic matter contributed to the carbonate C, organic matter must have been oxidized to CO_2 which requires strong oxidants such as peroxide [1,8]. The upper limit on the amounts of CO_2 produced by oxidation of organic matter with peroxide is estimated to be ~0.1 wt% [1], which is far smaller than the carbonate C abundance of Tagish Lake (~1.3 wt% [5]). Furthermore, no organic components with high $\delta^{13}C$ values of >80‰ have been identified, except for anomalous organic grains found in insoluble organic matter (IOM) from a CR chondrite [9]. Thus, the C reservoir with a high $\delta^{13}C$ value is almost certainly CO_2 accreted as ice, which likely had a $\delta^{13}C$ value of >80‰. Interestingly, the $\delta^{13}C$ value of CO_2 in the coma of comet 67P/Churyumov-Gerasimenko measured by Rosetta (64 ± 45‰ [11]) is consistent with the conclusion above. On the other hand, the C reservoir(s) with a low $\delta^{13}C$ value is poorly constrained: both organic matter and CO are possible. The $\delta^{13}C$ values of IOM in CMs and Tagish lake are from -17 to -19‰ and from -13 to -15‰, respectively [12,13]. The $\delta^{13}C$ value of trapped CO in Murchison is approximately -32‰ [14].

Here we assume that the $\delta^{13}C$ value of CO_2 ice is 80‰. Also, we assume that other C reservoirs (i.e., organic matter or CO) with low $\delta^{13}C$ values from -10 to -30‰ contributed to the carbonate C. The fact that Tagish Lake carbonates have homogenous and high $\delta^{13}C$ values indicates larger contribution from CO_2 ice to the Tagish Lake carbonates than the CM carbonates. The abundance of the carbonate C in Tagish Lake is ~1.3 wt% and the $\delta^{13}C$ value of the Tagish Lake carbonates is ~70‰ as determined for whole-rock samples [5]. Thus, from mass balance calculation, CO_2 ice accounts for 89-91% of the carbonate C in Tagish Lake. Likewise, the average abundance of the carbonate C in CMs is ~0.17 wt% and the average $\delta^{13}C$ value of CM carbonates is ~45‰ [1]. For the case of CMs, CO_2 ice accounts for 61-68% of the carbonate C.

Based on the values above and water contents estimated by subtracting H in organic matter from the bulk H contents [12,13,15], we can calculate CO_2/H_2O mole ratios of ice accreted to the CM and Tagish Lake parent bodies to be ~0.018 and ~0.28, respectively. The CO_2/H_2O mole ratios of CM and Tagish Lake ice are compared with those of cometary ice in Fig. 3 (comet data from [16]). The CO_2/H_2O ratio of the CM ice is smaller than in any comet while the Tagish Lake ice has a CO_2/H_2O ratio within the range of comets (close to the upper limit). These observations may suggest a genetic link between D-type asteroids and comets. On the other hand, the CM parent body may have accreted closer to the Sun (and therefore, at higher temperature) than D-type asteroids and comets where CO_2 ice partially sublimated.
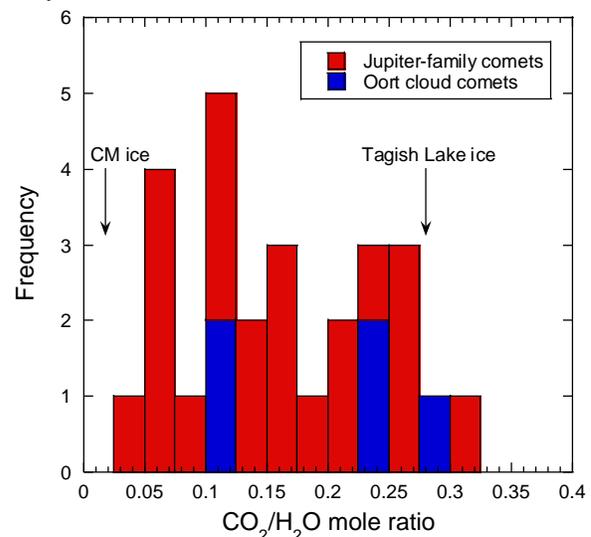

Fig. 3: Histogram of CO_2/H_2O ratios of comets and comparison with those of the CM and Tagish Lake ice.

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