

## Composition of ice in asteroids constrained from carbonate minerals in carbonaceous chondrites

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Carbonate minerals in carbonaceous chondrites formed by aqueous alteration in the parent bodies. Previous studies have shown that C isotopic ratios of carbonates in CM chondrites are highly variable among individual grains even in a single meteorite. The reasons for the variability in  $\delta^{13}\text{C}$  values and the origin of the carbon in carbonates remain poorly understood. Here we report C isotopic ratios of individual calcite ( $\text{CaCO}_3$ ) grains in the LaPaz Icefield (LAP) 031166 CM chondrite (CM 2.1), and of both calcite and dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) grains in the Tagish Lake meteorite, measured with Secondary Ion Mass Spectrometry (SIMS). We discuss the origin of the carbon in carbonates and explore a possible link between ice in CMs and Tagish Lake and cometary ice.

An apparent contrast between carbonates in LAP 031166 as well as other CMs analyzed previously and Tagish Lake can be seen: the  $\delta^{13}\text{C}$  values of CM carbonates are highly variable, ranging from  $\sim 20$  to  $80\text{‰}$ , whereas all Tagish Lake carbonates have high  $\delta^{13}\text{C}$  values of  $\sim 70\text{‰}$ . To explain these observations, we propose here mixing of at least two C reservoirs with different  $\delta^{13}\text{C}$  values. The candidates of C reservoirs include  $\text{CO}_2$  and CO accreted as ice, and organic matter.  $\text{CO}_2$  is the major C-bearing species in cometary ice. If C from organic matter contributed to the carbonate C, organic matter must have been oxidized to  $\text{CO}_2$  which requires strong oxidants such as peroxide. The upper limit on the amounts of  $\text{CO}_2$  produced by oxidation of organic matter with peroxide is estimated to be  $\sim 0.1$  wt%, which is far smaller than the carbonate C abundance of Tagish Lake ( $\sim 1.3$  wt%). Thus, the C reservoir with a high  $\delta^{13}\text{C}$  value is almost certainly  $\text{CO}_2$  accreted as ice. On the other hand, the C reservoir(s) with a low  $\delta^{13}\text{C}$  value is poorly constrained: both organic matter and CO are possible. The  $\delta^{13}\text{C}$  values of IOM in CMs and Tagish Lake are from  $-17$  to  $-19\text{‰}$  and from  $-13$  to  $-15\text{‰}$ , respectively. The  $\delta^{13}\text{C}$  value of trapped CO in Murchison is approximately  $-32\text{‰}$ .

Here we assume that the  $\delta^{13}\text{C}$  value of  $\text{CO}_2$  ice is  $80\text{‰}$ . Also, we assume that other C reservoirs (i.e., organic matter or CO) with low  $\delta^{13}\text{C}$  values from  $-10$  to  $-30\text{‰}$  contributed to the carbonate C. The fact that Tagish Lake carbonates have homogenous and high  $\delta^{13}\text{C}$  values indicates larger contribution from  $\text{CO}_2$  ice to the Tagish Lake carbonates than the CM carbonates. The abundance of the carbonate C in Tagish Lake is  $\sim 1.3$  wt% and the  $\delta^{13}\text{C}$  value of the Tagish Lake carbonates is  $\sim 70\text{‰}$ . Thus, from mass balance calculation,  $\text{CO}_2$  ice accounts for 89-91% of the carbonate C in Tagish Lake. Likewise, the average abundance of the carbonate C in CMs is  $\sim 0.17$  wt% and the average  $\delta^{13}\text{C}$  value of CM carbonates is  $\sim 45\text{‰}$ . For the case of CMs,  $\text{CO}_2$  ice accounts for 61-68% of the carbonate C. Based on the values above and water contents in CMs and Tagish Lake, we can calculate  $\text{CO}_2/\text{H}_2\text{O}$  mole ratios of ice accreted to the CM and Tagish Lake parent bodies to be  $\sim 0.018$  and  $\sim 0.28$ , respectively. The  $\text{CO}_2/\text{H}_2\text{O}$  mole ratios of CM and Tagish Lake ice are compared with those of cometary ice. The  $\text{CO}_2/\text{H}_2\text{O}$  ratio of the CM ice is smaller than in any comet observed while the Tagish Lake ice has a  $\text{CO}_2/\text{H}_2\text{O}$  ratio within the range of comets. These observations may suggest a genetic link between D-type asteroids from which Tagish Lake is likely derived, and comets. On the other hand, C-type asteroids from which CM chondrites is likely derived, may have accreted closer to the Sun (and therefore, at higher temperature) than D-type

asteroids and comets where CO<sub>2</sub> ice partially sublimated.

Keywords: carbonaceous chondrite, carbonate mineral, carbon isotopic ratio