

CONSISTENTLY HIGH $\delta^{13}\text{C}$ CARBONATES IN CR CHONDRITES: IMPLICATION FOR ACCRETED ICE IN A COLD AND DISTANT REGION FROM THE SUN. T. Ushikubo¹, A. Yamaguchi², M. K. Weisberg^{3,4}, M. Kimura², and D. S. Ebel^{4,5}, ¹Kochi Institute, JAMSTEC, 200 Monobe-otsu, Nankoku, Kochi 783-8502, Japan (ushikubot@jamstec.go.jp), ²National Institute of Polar Research, 10-3 Midoricho, Tachikawa, Tokyo 190-8518, Japan, ³Kingsborough College, CUNY, Brooklyn, NY 11235, USA, ⁴American Museum of Natural History, New York, NY 10024, USA, ⁵Columbia University, New York, NY 10024, USA.

Introduction: Carbonate is one of the major secondary products in type 1 and type 2 chondrites. Since they precipitated from fluid during early hydrothermal activity in chondrite parent bodies at ca. 4563 Ma [1, 2], carbonate's chemistry and isotopic signatures are useful to understand the source of volatiles and the evolution of fluids in chondrite parent bodies [3]. Recently, consistently high carbon isotope ratios ($\delta^{13}\text{C}_{\text{VPDB}} \sim +70\%$) were recognized in carbonates from the Tagish Lake meteorite. The accretion of CO_2 ice was proposed as the source of this heavy carbon [4]. Interestingly, Tagish Lake contains FeO-rich chondrules with $\Delta^{17}\text{O} \geq 0\%$ [5, 6], which are absent in CV and CM chondrites but are characteristic of cometary chondrule-like objects [7, 8]. These are consistent with the idea that the Tagish Lake parent body accreted further from the Sun than the parent bodies of CV and CM chondrites.

CR chondrites also contain FeO-rich chondrules with $\Delta^{17}\text{O} \geq 0\%$ [9, 10]. Furthermore, carbonate with high $\delta^{13}\text{C}_{\text{VPDB}}$ (hereafter $\delta^{13}\text{C}$) values are recognized in some CR chondrites [3]. CR chondrite parent bodies might have accreted in a cold and distant region from the Sun like the Tagish Lake parent body. We performed in-situ O and C isotopic measurements of carbonates in CR chondrites by SIMS to clarify this potential relationship. Here, we report those findings.

Samples and Methods: A Renazzo thin section (AMNH 588-t2-ps3A) and two epoxy mounts of Antarctic meteorites (Y-790112 & Y-8449, allocated by NIPR) were prepared for this study. The Renazzo thin section was lightly ground to remove previous C coating. Petrologic observation of the final polished surfaces was performed with the Hitachi SU1510 SEM equipped with an EDS system using a thin Au coating (<10 nm in thickness) at Kochi Institute.

Oxygen and C isotope ratios of Ca-rich carbonates were measured with the CAMECA IMS 1280-HR at the Kochi Institute. An Au coating (~30 nm in thickness) was applied to the samples' surfaces. For O isotope analyses, a focused Cs^+ primary beam (20 kV, ~20 pA, ~2×3 μm in size) was used, and secondary ions (10 kV) were detected with a Faraday cup (FC) for $^{16}\text{O}^-$ and two electron multipliers (EM) for $^{17}\text{O}^-$ and $^{18}\text{O}^-$. The intensity of the $^{16}\text{OH}^-$ signal was checked after each measurement. A typical $^{16}\text{O}^-$ count rate was

~ 1.8×10^7 cps. For C isotope analyses, a focused Cs^+ primary beam (20 kV, ~100 pA, ~5 μm in diameter) was used, and secondary ions (10 kV) were detected with a FC ($^{12}\text{C}^-$) and two EMs ($^{13}\text{C}^-$, $^{13}\text{CH}^-$). A typical $^{12}\text{C}^-$ count rate was ~ 9×10^5 cps. Other analytical conditions were the same as those in [11]. Data of unknown samples were normalized to those of bracketing analyses of the UWC-3 calcite standard ($\delta^{13}\text{C}_{\text{VPDB}} = -0.91 \pm 0.08\%$, $\delta^{18}\text{O}_{\text{VSMOW}} = 12.49 \pm 0.06\%$ [12]). Typical reproducibility (2 SD) was $\pm 0.7\%$ for $\delta^{18}\text{O}$, $\pm 0.9\%$ for $\Delta^{17}\text{O}$, and $\pm 1.9\%$ for $\delta^{13}\text{C}$.

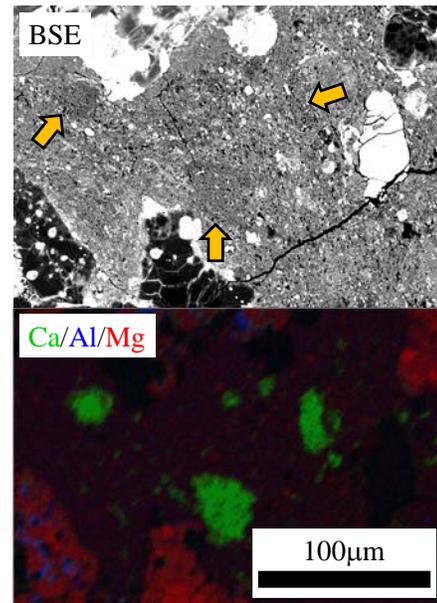


Figure 1. An example of Ca-rich carbonates in Y-8449 (BSE and EDS composite images). Carbonate grains are commonly porous and fine-grained. In this area, three carbonate grains (yellow arrows) were selected for isotope measurements.

Results and Discussion:

Fine-grained texture of Ca-rich carbonates in the CR chondrites. Carbonate grains were found in the matrix or along the rim of chondrules (Fig.1). They were near-pure Ca-carbonate (>90% CaCO_3), but a few Mg-rich dolomitic grains were also found during our preliminary survey. Carbonate grains are commonly porous and fine-grained. They sometimes include tiny magnetite and silicate grains.

Oxygen and C isotopic signatures of Ca-rich carbonates in CR chondrites. Oxygen isotope ratios of CR Ca-rich carbonate are distributed along the trend line of slope ~ 0.64 (Fig. 2) which was defined by a previous CR carbonate study [13]. As discussed in [13], the O isotope trend line parallel to the CM calcite trend line indicates that the oxygen isotopic composition of the fluid source (accreted ice) of CR chondrites was distinct from that of the fluid source of CM chondrites.

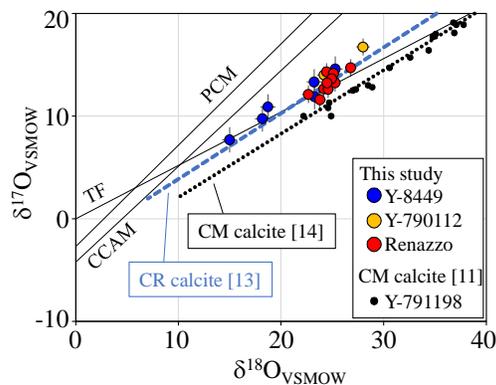


Figure 2. Oxygen isotope ratios of Ca-rich carbonates of the studied CR chondrites (errors: 2SD). Those of calcites of Y-791198 (CM) [11], which were obtained with the same analytical procedure at Kochi Institute, are also shown for comparison. CR and CM carbonates exhibit distinct trend lines which are consistent with the previously reported trend lines for CR [13] and CM [14] calcites. Reference lines (TF/CCAM/PCM) are also shown.

Carbon isotope measurements of carbonates were difficult because of their porous textures. Because of the high C ion yield of organic matter (OM) (typically $\gg 20\times$ that of carbonate), a small amount of contamination strongly affects the measured C isotopic composition of carbonates. Figure 3 shows all obtained data. We applied a strict rule and accept carbonate data within $\pm 10\%$ relative to the averaged ion yield of the calcite standard (UWC-3) because (i) $\pm 10\%$ variation was observed for standard analyses, (ii) high intensity ($> 2\times$ rel. to UWC-3) and low $\delta^{13}\text{C}$ value data were obtained when the primary beam hit irregular surface, indicating contamination of OM or permeated epoxy, (iii) carbonate-free matrix data suggest contaminants have low a $\delta^{13}\text{C}$ value. We found that Ca-rich carbonates consistently have high $\delta^{13}\text{C}$ values ($\geq 50\%$, Fig. 3). Although some carbonates with high $\delta^{13}\text{C}$ values were found in CM chondrites, many CM carbonates have $\delta^{13}\text{C}$ values of 20 to 40‰ [15]. Consistently high $\delta^{13}\text{C}$ values of the CR carbonates show similar characteristic to Tagish Lake carbonates [4].

Implications for the fluid source. It was proposed that high $\delta^{13}\text{C}$ values of Tagish Lake carbonates can be explained by a C supply from accreted CO_2 ice [4]. If

this is the case, the similar C isotopic signatures of CR carbonates (Fig.3) also indicate accretion of isotopically similar CO_2 ice into the CR chondrite parent body. This seems consistent with the occurrence of FeO-rich (type II) chondrules with $\Delta^{17}\text{O} \geq 0\%$ in the Tagish Lake meteorite, CR chondrites, and Comet Wild2 [5-10]. The CR chondrite parent body probably accreted as far from the Sun and in region as cold as where Tagish Lake parent body accreted.

The $\Delta^{17}\text{O}$ value of a mixture of $\text{H}_2\text{O}-\text{CO}_2$ ice might have been a few ‰ higher than that of H_2O ice, which might have formed two separate FeO-rich (type II) chondrule populations: (1) $\Delta^{17}\text{O} \sim -2.5\%$ (typical in CM, CO, CV chondrites, H_2O ice as oxidant) vs. (2) $\Delta^{17}\text{O} \geq 0\%$ ($\text{H}_2\text{O}-\text{CO}_2$ ice as oxidant).

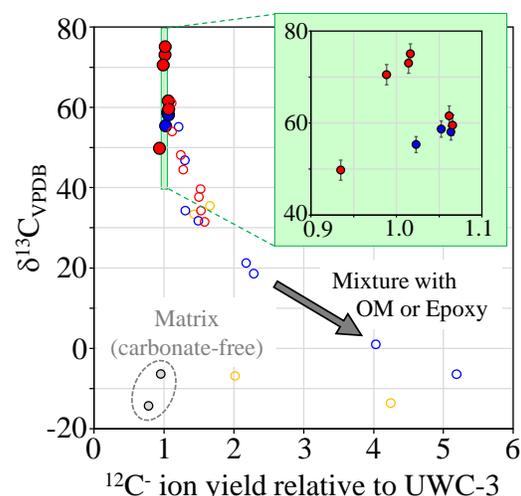


Figure 3. Carbon isotope ratios (errors: 2SD) and ^{12}C -signal intensities of carbonate grains. High intensity (> 2 of the x-axis) and low $\delta^{13}\text{C}$ value data were obtained when the primary beam hit an irregular surface, indicating contamination of organic matter or permeated epoxy. Carbonate-free matrix data also show low $\delta^{13}\text{C}$ values. Inset shows accepted CR carbonate data (within $\pm 10\%$ of ^{12}C -intensity relative to the calcite standard).

References: [1] Fujiya W. et al. (2013) *EPSL*, 362, 130-142. [2] Jilly-Rehak C. E. et al. (2017) *GCA*, 201, 224-244. [3] Alexander C. O. D. et al. (2015) *MAPS*, 50, 810-833. [4] Fujiya W. et al. (2019) *Nature Astron.*, 3, 910-915. [5] Yamanobe et al. (2018) *Polar Sci.*, 15, 29-38. [6] Ushikubo T. & Kimura M. (2021) *GCA*, 293, 328-343. [7] Nakashima D. et al. (2012) *EPSL*, 357-358, 355-365. [8] Defouilloy C. et al. (2017) *EPSL*, 465, 145-154. [9] Schrader D. L. et al. (2014) *GCA*, 132, 50-74. [10] Tenner T. J. et al. (2015) *GCA*, 148, 228-250. [11] Fujiya W. et al. (2020) *GCA*, 274, 246-260. [12] Kozdon R. et al. (2009) *Chem. Geol.*, 258, 327-337. [13] Jilly-Rehak C. E. et al. (2018) *GCA*, 222, 230-252. [14] Lindgren P. et al. (2017) *GCA*, 204, 240-251. [15] Fujiya W. et al. (2015) *GCA*, 161, 101-117.