EVIDENCE FOR HIGH $\delta^{13}C$ AND $\Delta^{17}O$ FLUID IN SMALL BODIES ACCRETED IN A COLD AND DISTANT REGION FROM THE SUN.

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Introduction: Carbonate is one of the major secondary products of hydrothermal activity in chondritic parent bodies. Since it precipitated from fluid during an early stage of hydrothermal activity, the isotopic composition of carbonate is useful to understand the isotopic composition of primordial fluids [1]. Recently, consistently high $\delta^{13}C$ values (>50‰) were recognized in the Tagish Lake meteorite and CR chondrites [2,3], suggesting the isotopic compositions of fluids in parent bodies of these chondrites were different from those in CM chondrite parent bodies. In this study, we performed O and C isotope measurements of carbonate in Tagish Lake (C2-ungrouped) and Aguas Zarcas (CM2) to understand the relationship of O and C isotopic systematics of CM and CR chondrites and Tagish Lake. Although it is known that Aguas Zarcas consists of multiple lithologies, the exposed surface of Aguas Zarcas (~5mm in size) consists of a CM clast [4].

Samples and Methods: Epoxy mounts of Tagish Lake and Aguas Zarcas were prepared for this study. Standard calcite grains (UWC-3) were also mounted individually. Petrologic location of carbonates was performed with EDS on a Hitachi SU1510 SEM at the Kochi Institute, JAMSTEC. A gold coating <10 nm thick was applied to sample surfaces for SEM observation.

Oxygen and carbon isotope ratios of Ca-rich carbonates were measured with a CAMECA IMS 1280-HR at the Kochi Institute. Analytical conditions were similar to those for the previous CR carbonate measurements [2]. A gold coating of ~30 nm in thickness was applied. For O isotope analyses, a focused Cs^+ primary beam (20 kV, ~25 pA, ~1.5×2 μm in size) was used. Secondary ions (10 kV) were detected with a FC (1e12 Ω) and two EM detectors for $^{16}O^-$, $^{17}O^-$ and $^{18}O^-$, respectively. The intensity of the $^{16}OH^-$ signal was checked after each measurement. Typical spot-to-spot analytical reproducibility (2 SD) was ±0.8‰, ±1.3‰, and ±1.3‰ for $\delta^{18}O$, $\delta^{17}O$, and $\Delta^{17}O$, respectively. For C isotope analyses, a focused Cs^+ primary beam (20 kV, ~160 pA & ~3×5 μm for Tagish Lake, ~300 pA & ~6 μm for Aguas Zarcus) was used. Secondary ions (10 kV) were detected with a FC (1e12 Ω) and two EM detectors for $^{12}C^-$, $^{13}C^-$, and $^{13}CH^-$, respectively. Typical spot-to-spot reproducibility of $\delta^{13}C$ was ±2.0‰ (2 SD). After SIMS measurements, SIMS pit positions were checked by SEM, then major element compositions of carbonates were measured with a JEOL JXA8200 EPMA at the National Institute for Polar Research, Japan.

Results: All studied carbonate grains (Fig.1) which were large enough to analyze (≥10 μm) were Ca-rich (typically $(Ca_{0.99}Fe_{0.01})CO_3$). In Aguas Zarcas, we found two large grains with aggregate texture (Fig. 1c), indicating they are later-formed type-2 carbonates [5]. The $\delta^{13}C$ values of Tagish Lake carbonates are consistently high, but slightly higher than previously reported in-situ NanoSIMS data (Fig. 2a; 80 - 90‰ vs. ~70‰ [3]). In contrast, the $\delta^{13}C$ values of Aguas Zarcas carbonates are variable from +20 to 60‰ (Fig. 2a). The $\delta^{18}O$ values of carbonates in both Tagish Lake and Aguas Zarcas are similar (+32 to 37‰), however, their $\Delta^{17}O$ values are distinct (Fig. 2b; 1.6±1.3‰ vs. -1.0 ±1.5‰, 2 SD). All Aguas Zarcas carbonate data are on

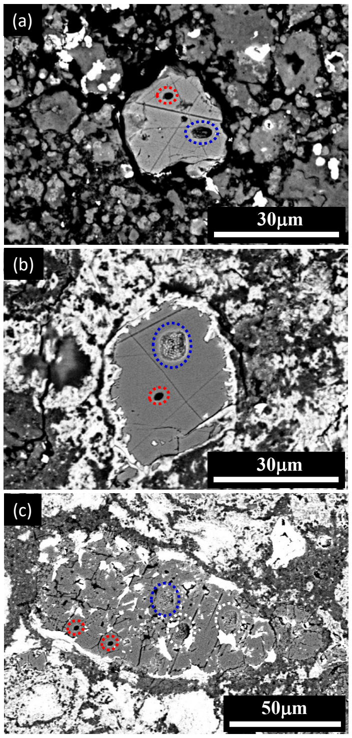

Figure 1. BSE images of typical Ca-rich carbonate grains of (a) Tagish Lake, (b) Aguas Zarcas, and (c) low $\delta^{18}O$ grain in Aguas Zarcas. Positions of SIMS O & C isotope measurements are shown by red & blue dotted circles. White circles are rejected points.

the CM calcite trend line [6]. The two type-2 carbonate grains in Aguas Zarcas (Fig. 1c) have distinct low δ^{18}O values with high δ^{13}C values. In contrast, Tagish Lake carbonate data are on the CR calcite trend line [7].

Discussion: Oxygen and carbon isotopic compositions of Ca-rich carbonates in Aguas Zarcas (CM2), Tagish Lake, and CR chondrites each show distinctive characteristics (Fig. 2).

Origin of high δ^{13}C component. High δ^{13}C carbonates (here tentatively defined as δ^{13}C>40‰) are recognized in CM as well as Tagish Lake and CR chondrites, which are consistent with previous studies (up to ~80‰) [e.g., 3, 8, 9]. Except for the two type-2 carbonate grains, there is no apparent difference in major element composition and texture between the high and low δ^{13}C carbonates in Aguas Zarcas. Both carbonate types are randomly found in the studied section, suggesting redistribution of carbonate grains after crystallization in its parent body. Although δ^{18}O values of the high δ^{13}C carbonates (~-33‰) tend to be lower than those of the low δ^{13}C carbonates (~-35‰) in Aguas Zarcas, the temperature effect of equilibrium isotopic fractionation between fluid and carbonate seems unlikely to explain the C and O isotopic distributions of Ca-rich carbonates (Fig. 2a). We consider that the high δ^{13}C carbonates represent a contribution from high δ^{13}C source materials such as CO_2, CO, and highly volatile organic matter [cf. 3, 10].

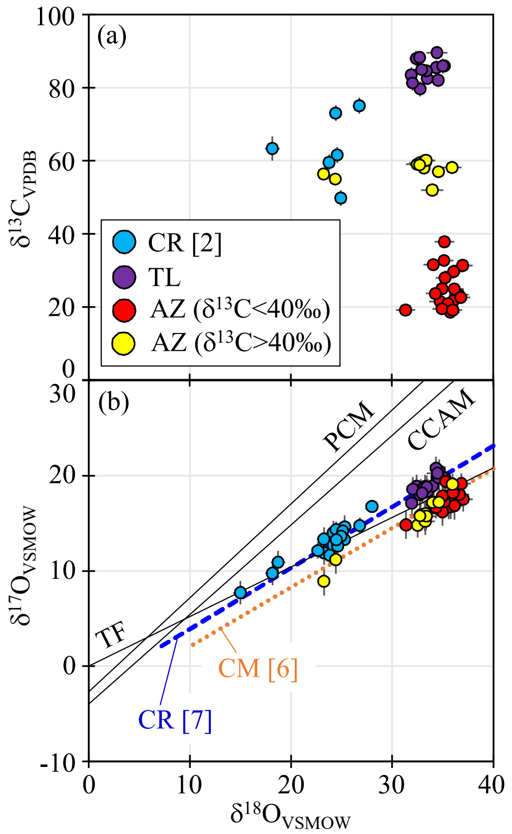

Figure 2. (a) δ^{13}C vs. δ^{18}O, and (b) oxygen 3-isotope plots of Ca-rich carbonates from Aguas Zarcas (AZ), Tagish Lake (TL). CR chondrites' Ca-rich carbonate data [2] are also shown. Calcite trend lines of CM [6] and CR [7], and three O-isotope reference lines (TF, CCAM, and PCM) are shown in (b). Errors are 2σ.

Implication for higher Δ^{17}O fluid in small bodies accreted in a cold and distant region from the Sun. Both Tagish Lake and CR carbonates lie on the same O isotope trend line [2, 7, this study]. Oxygen isotope ratios of dolomite in CI chondrites and returned samples from asteroid Ryugu are also consistent with this trend [11]. It should be noted that carbonates with elevated Δ^{17}O values are also found in some CM chondrites [9, 12]. Since the parent bodies of CR chondrites and Tagish Lake, and also asteroid Ryugu, are considered to have accreted further from the Sun than CM parent bodies [e.g., 3, 13, 14], the occurrence of carbonates with slightly higher Δ^{17}O values (by ~2‰ relative to CM carbonates) suggests accreted ice (mainly H_2O and possibly a few % of CO and CO_2 [15]) had slightly elevated Δ^{17}O values. Much higher Δ^{17}O value of ices can be expected in the outer Solar system, considering the extremely high Δ^{17}O value (~140±110‰) of H_2O vapor of comet 67P/Churyumov-Gerasimenko [10]. However, the existence of ice with slightly elevated Δ^{17}O value where the parent bodies of CR chondrites, Tagish Lake, and asteroid Ryugu, accreted is consistent with the occurrence of FeO-rich (type II) chondrules with higher Δ^{17}O values (>0‰) in CR, Tagish Lake-like meteorites, and also comet 81P/Wild 2 [e.g., 16-18].

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