

OXYGEN AND CARBON ISOTOPIC RATIOS OF CARBONATES IN THE NOGOYA CM CHONDRITE.

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Introduction: CM chondrites exhibit evidence for aqueous alteration to variable degrees [1,2]. Physico-chemical conditions (e.g., temperature, water to rock ratio, and open/closed system) under which aqueous alteration occurred have been the subject of debate. Carbonate is a secondary mineral of aqueous alteration and recorded O and C isotopic compositions of water and dissolved inorganic C species (e.g., CO_3^{2-}) from which it formed [e.g., 3,4]. The O and C isotopic compositions of water and dissolved C changed with increasing alteration, and their evolution depends on water/rock ratios and whether aqueous alteration occurred in an open or closed system [5-8]. The O and C isotopic ratios of carbonates were also determined by formation temperatures [9]. Thus, carbonates potentially provide information about the alteration environment in the CM chondrite parent body. Although the O and C isotopic compositions of carbonates are highly variable even in a single meteorite [e.g., 10], much is unknown about how the O and C isotopic compositions changed and what predominantly controlled them.

In this study, we conducted in-situ O- and C-isotope measurements on calcite grains in the Nogoya CM 2.2-2.3 chondrite. Detailed petrological and mineralogical observations along with O-isotope measurements in previous studies have suggested that carbonates in CM chondrites did not form in a single event but formed intermittently [11,12]. Isotope measurement of carbonates in multiple “generations” could shed light on the evolution of O and C isotopic compositions during aqueous alteration.

Experimental: We prepared a polished thin section of the Nogoya CM chondrite and coated it with Au. We observed the thin section with an SEM-EDS and searched for Ca-carbonate grains large enough for subsequent isotope measurements. Oxygen- and C-isotope measurements were performed with the NanoSIMS 50 at AORI, UTokyo. $^{16,17,18}\text{O}^-$ ions (in O-isotope measurement), or $^{12,13}\text{C}^-$, $^{18}\text{O}^-$, $^{12}\text{C}^{14}\text{N}^-$, and $^{28}\text{Si}^-$ ions (in C-isotope measurement) produced by a 20-30 pA Cs^+ ion beam were detected with a FC and two EMs, or with four EMs, respectively. In C-isotope measurement, $^{12,13}\text{C}^-$ ions were detected with the same EM in a combined peak-jumping/multi-detection mode. $^{18}\text{O}^-$, $^{12}\text{C}^{14}\text{N}^-$, and $^{28}\text{Si}^-$ ions were monitored in the C-isotope measurement to check the presence of possible contamination such as organic matter or silicate. Typical errors on $\delta^{17,18}\text{O}$ and $\delta^{13}\text{C}$ values were 5.3 ‰ and 6.4 ‰

(2σ), respectively. Oxygen and C isotopic ratios were normalized by using terrestrial calcite with known O and C isotopic ratios measured by a conventional method.

Results and discussion: We found many Ca-carbonate grains by the SEM observation. Although we do not have any data to distinguish the polymorphism of the Ca-carbonate (i.e., calcite or aragonite), we hereafter describe the Ca-carbonate as calcite because aragonite is less common in more-heavily altered CM chondrites [13].

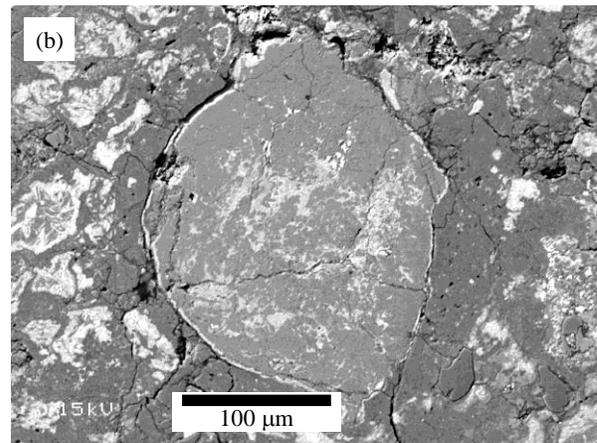
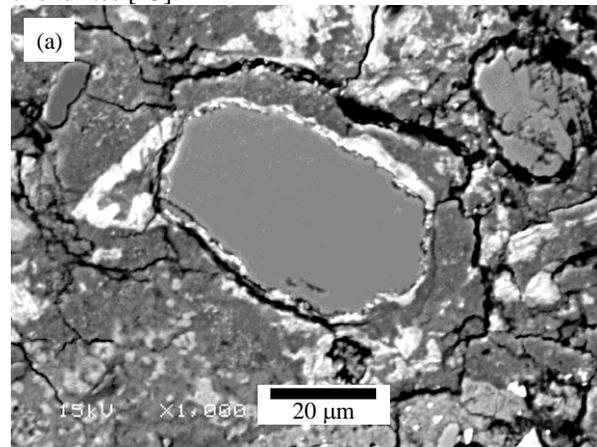


Fig. 1: Backscattered electron images of calcite grains found in the Nogoya thin section. (a) type 1 grain, (b) type 2 grain.

As reported in the previous studies [11-13], two types of calcite grains with distinct mineralogical characteristics were found. Following the definition by [13], we describe these calcite grains as type 1 and 2 grains. Most type 1 grains are single crystals and have serpen-

tine/tochilinite rims (Fig. 1a). They are likely to have precipitated from pore fluids. On the other hand, type 2 grains are polycrystalline and microporous, and do not have rims. They appear to have replaced other minerals (Fig. 1b). Some type 2 grains appear to have replaced whole chondrules. Type 2 grains typically have sulfide inclusions.

Oxygen isotopic compositions are highly different between type 1 and 2 grains, but similar within each type ($\delta^{18}\text{O}_{\text{SMOW}} = 34.7\text{‰}$ (type 1) and 19.3‰ (type 2) on average) (Fig. 2). The average $\Delta^{17}\text{O}$ values are -2.5‰ (type 1) and -5.4‰ (type 2). These data are in good agreement with those reported by previous studies [11,12]. The $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values indicate that type 2 calcite formed later than type 1 calcite, because progressive alteration led to O-isotope exchange between water and anhydrous silicate with lower $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values than water. The lack of serpentine/tochilinite rims around type 2 grains also suggests that type 2 grains formed after type 1 grains were replaced by serpentine/tochilinite.

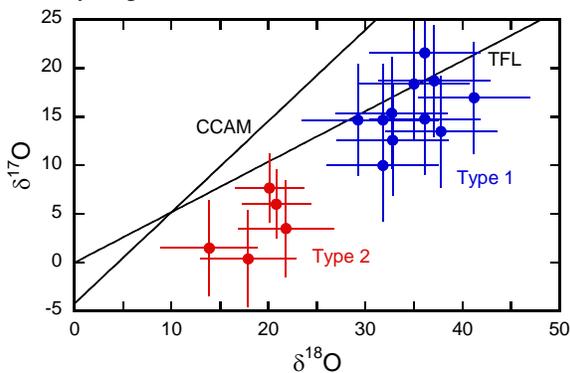


Fig. 2: Oxygen isotopic ratios of type 1 and 2 calcite grains.

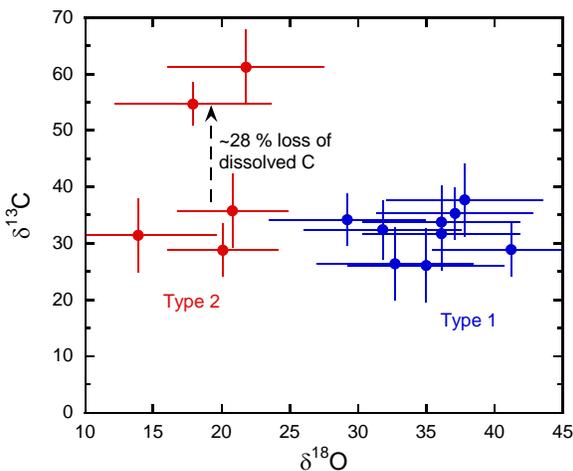


Fig. 3: $\delta^{13}\text{C}$ values against $\delta^{18}\text{O}$ values of type 1 and 2 calcite grains.

Carbon isotopic ratios of type 1 grains are similar ($\delta^{13}\text{C}_{\text{PDB}} = 31.8\text{‰}$ on average), whereas type 2 grains have variable $\delta^{13}\text{C}$ values ranging from 28.8 to 61.2‰ (Fig. 3). These observations indicate an increase in $\delta^{13}\text{C}$ values in later stages of aqueous alteration.

The O and C equilibrium isotopic fractionation factors between carbonate and water, and between carbonate and dissolved/gaseous C species, respectively, are smaller at higher temperatures. As a result, both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ would have changed to lower values with increasing temperatures assuming reasonable O and C isotopic compositions of water and dissolved/gaseous C species. Therefore, the variation in O and C isotopic compositions of calcite observed in this study cannot be explained by change in formation temperatures alone as suggested by [9].

No components with $\delta^{13}\text{C} > 40\text{‰}$ in organic matter from a less-altered CM chondrite, Murchison, has been found [14]. Therefore, the apparent $\delta^{13}\text{C}$ increase in later stages of aqueous alteration observed here is unlikely to be attributed to the addition of a ^{13}C -rich C from organic matter to aqueous fluids by oxidation.

It has been suggested that the Rayleigh-type isotopic fractionation driven by the escape of ^{13}C -poor CH_4 could have led to ^{13}C enrichments of the dissolved inorganic C [7]. The observed $\delta^{13}\text{C}$ increase of $\sim 30\text{‰}$ can be explained if $\sim 28\%$ of the dissolved C was reduced to produce CH_4 and was lost at 28°C . If true, aqueous alteration in CM chondrites would have occurred in an open system at least in later stages.

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