Oxygen and carbon isotope compositions of Ryugu's carbonates: Constraints on the conditions of aqueous alteration

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The Hayabusa2 spacecraft collected CI-chondrite-like materials from the near-Earth asteroid 162173 Ryugu [1]. Ryugu materials are mainly composed of secondary minerals that formed by aqueous alteration, e.g., phyllosilicates, carbonates, sulfides, and oxides. In this study, we performed *in-situ* O and C isotope measurements of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) in Ryugu samples A0058 and C0002 as well as the Ivuna meteorite to investigate the conditions of the aqueous alteration. We used secondary ion mass spectrometry (SIMS; CAMECA ims-1280HR) at Hokkaido University with a suite of dolomite-ankerite standards [2] and a calcite standard "UWC3" [3].

The $\delta^{18}O$ values of the calcites (24‰ to 46‰) in C0002 and Ivuna show a larger variation than those of the dolomites in C0002, A0058, and Ivuna (26‰ to 31‰) (Fig. 1). The average $\Delta^{17}O$ value of the C0002 and Ivuna calcites is 1.37 ± 0.40‰ (2SE). The $\Delta^{17}O$ values of the C0002, A0058, and Ivuna dolomites are systematically lower than those of the calcites, and the average $\Delta^{17}O$ value of the dolomites (0.26 ± 0.23‰, 2SE) is closer to the whole-rock values of two Ryugu samples [4] (0.30‰ and 0.58‰). Like the $\delta^{18}O$ values, the dolomites in A0058, C0002, and Ivuna have a relatively narrow range of $\delta^{13}C$ values from 67‰ to 75‰ (Fig. 2). On the other hand, the $\delta^{13}C$ values of the calcites in C0002 and Ivuna are highly heterogeneous, ranging from 65‰ to 108‰, and they are commonly higher than those of the Ryugu and Ivuna dolomites.

If, when the carbonates precipitated they were in O and C isotope equilibrium with the aqueous fluid, their O and C isotope compositions would have been determined by the mass dependent equilibrium isotopic fractionation, which depends on temperature, between carbonates and water for O, and that between carbonates and dissolved CO_3^{2-} (and other dissolved C-bearing chemical species) for C [5]. Thus, the O and C isotope compositions of carbonates would reflect those of water and CO_3^{2-} as well as their formation temperatures. The $\delta^{18}O$ variation of ~22‰ observed in the Ryugu calcites (Fig. 1) corresponds to formation temperatures that varied from 0 °C to 150 °C. However, the lack of a correlation between $\delta^{18}O$ and $\delta^{13}C$ values implies that variable formation temperatures alone cannot explain the observed $\delta^{18}O$ and $\delta^{13}C$ variations (Fig. 2). Rather it seems likely that both the $\delta^{18}O$ value of water and the $\delta^{13}C$ value of CO_3^{2-} varied temporally. Because the $\Delta^{17}O$ values of the fluids likely decreased as water-rock interaction progressed [6], the calcites with systematically higher $\Delta^{17}O$ values should have formed from less "evolved" fluids and likely crystallized earlier than the dolomites (Fig. 1).

It seems likely that the temporal variation in the $\delta^{13}C$ values of the C reservoirs and in their chemical speciation occurred due to a change of O fugacity (fO_2). Oxygen fugacity varied along with the production of H_2 via the oxidation of Fe in metal and silicates by H_2O and the subsequent escape of H_2 from the system. To see how the $\delta^{13}C$ values of carbonates will change with varying fO_2, we consider a rather simple model, where gaseous CO_2 and CO and carbonates (and dissolved CO_2, HCO_3^-, and CO_3^{2-}) are in C isotopic equilibrium and the CO_2/CO ratio increases with increasing fO_2. At first, the CO_2/CO ratio may have been characterized by that of the accreted ices, which may be around unity or higher as observed in cometary ices [7]. We assume that the $\delta^{13}C$ value of the bulk gas (CO_2+CO), $\delta^{13}C_{bulk}$, is constant regardless of the CO_2/CO ratio. Because the C isotopic fractionation factor between CO_2 and CO is positive at any temperature, e.g., 93‰ at 0 °C [8], both the $\delta^{13}C$ values of CO_2 and CO will decrease monotonically with increasing fO_2 to keep $\delta^{13}C_{bulk}$ constant, and the $\delta^{13}C$ values of carbonates will also decrease (Fig. 2). In this context, the dolomites with lower $\delta^{13}C$ values likely formed at higher fO_2 and/or temperature than the calcites. This, combined with the O isotope signatures of the carbonates, implies that the calcites formed during prograde alteration over wide ranges of fO_2 and temperature, whereas the dolomites formed later from peak temperature to retrograde cooling when the aqueous fluids and silicates approached O isotope equilibrium [9].

References:
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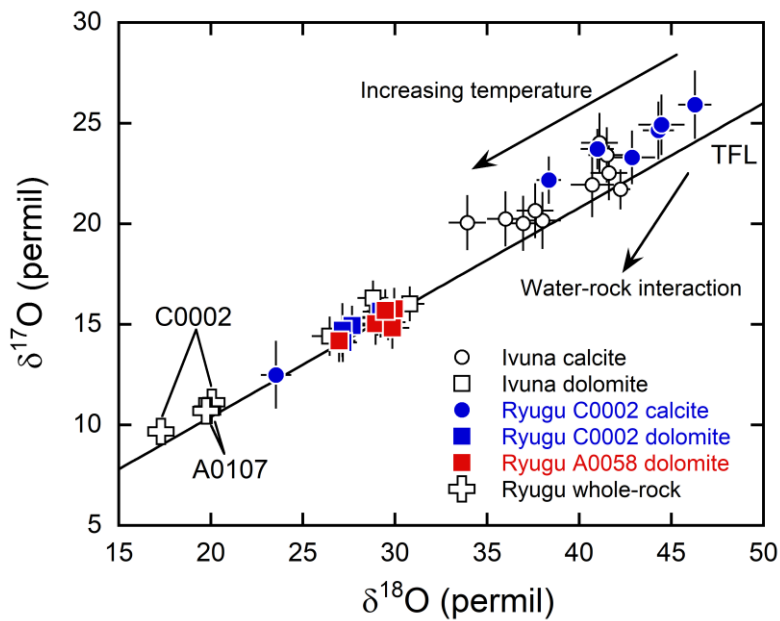
Figure 1. Oxygen isotope compositions of the calcite and dolomite grains in Ryugu and Ivuna samples.
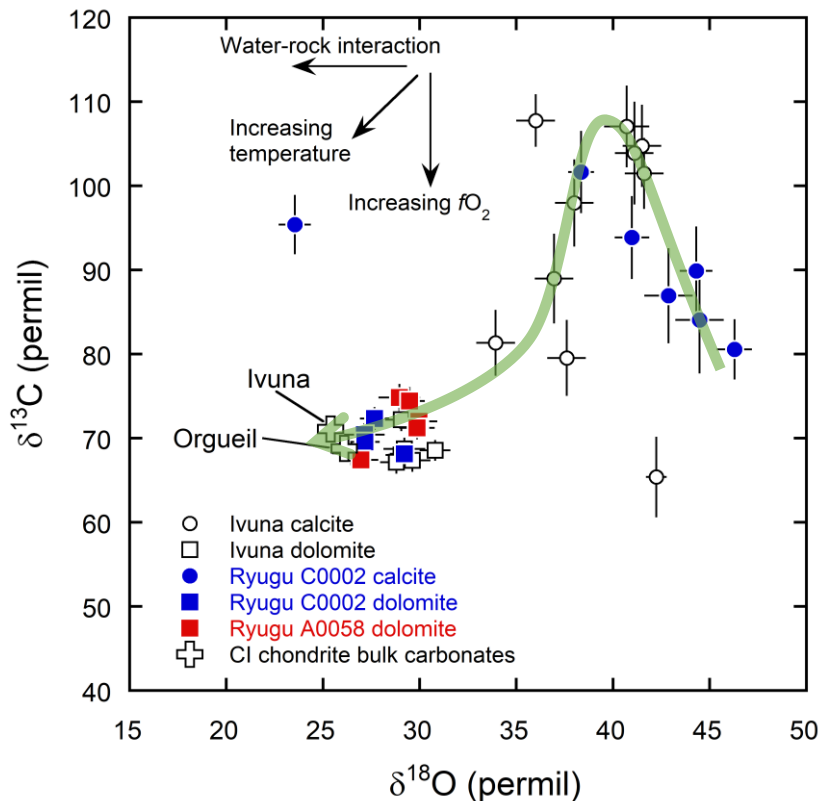

Figure 2. Comparison between C and O isotope compositions of the calcite and dolomite grains in Ryugu and Ivuna samples. A putative evolutionary trend of $\delta^{18}O$ and $\delta^{13}C$ values is shown by the green arrow.

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