

Oxygen isotope analyses of magnetite in Ryugu

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Samples from the CI-like asteroid Ryugu consist mainly of minerals that were produced by aqueous alteration in its parent asteroid, such as phyllosilicates, dolomite, magnetite, and pyrrhotite [1]. A secondary ion mass spectrometer (SIMS) has been used to analyze in-situ oxygen 3-isotope ratios ($\delta^{17}\text{O}$ and $\delta^{18}\text{O}$) of these alteration minerals in order to understand the aqueous activity that Ryugu parent body had experienced. Yokoyama et al. [1] reported $\delta^{17}\text{O}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ ($= \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$) of dolomite and magnetite in the polished section A0058-C1001 of Ryugu along with those in the Ivuna CI chondrite. Nagashima et al. [2] reported $\delta^{17}\text{O}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ of dolomite, calcite, and magnetite in the Ryugu polished section C0002-C1001. In A0058-C1001, a pair of magnetite and dolomite grains were found within 100 μm of each other and with indistinguishable $\Delta^{17}\text{O}$ values of $\sim 0\text{‰}$. By applying oxygen isotope thermometry between dolomite and magnetite, [1] estimated the temperature of co-precipitation of the Ryugu dolomite and magnetite, $37 \pm 10^\circ\text{C}$. Oxygen isotope analyses from another magnetite and dolomite pair in C0002-C1001 indicate a higher equilibrium temperature of $104 \pm 22^\circ\text{C}$ [2]. However, multiple analyses of magnetite grains in Ryugu and Ivuna show a significant range of $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ [1-2], suggesting magnetite might have recorded multiple stages of aqueous activity on the Ryugu and Ivuna parent asteroid(s).

SIMS oxygen isotope analyses of magnetite are known to produce analytical artifacts due to crystal orientation that can degrade the analytical reproducibility of $\delta^{18}\text{O}$ (2–3‰ in 2SD [3]), though the effect is mass-dependent and would not affect $\Delta^{17}\text{O}$. Huberty et al. [3] used lower primary ion acceleration voltage in the Cameca IMS 1280 (changed from 10 kV to 3 kV) and improved the analytical reproducibility (0.7‰; 2SD), likely related to lower total impact energy and smaller incident angle of primary ions to sample surface. Here, we report a new set of SIMS oxygen 3-isotope analyses of magnetite in the Ryugu samples using the IMS 1280 at the University of Wisconsin-Madison under 3 kV primary acceleration voltage in order to obtain higher accuracy in $\delta^{18}\text{O}$ analyses.

We analyzed magnetite grains (typically $\leq 10 \mu\text{m}$) from two polished sections of Ryugu, A0058-C1002 and C0002-C1001. The primary Cs^+ ion beam was accelerated by +3 kV at the Cs ion source and focused to sample surface (at -10 kV) resulting in an impact energy of 13 keV. The primary beam was focused to 3 μm with 14 pA intensity and rastered over 2 μm squares, which resulted in $3 \times 4 \mu\text{m}$ SIMS pits after 10 min of analysis (Fig. 1). The $^{16}\text{O}^-$ intensity was typically 1.7×10^7 cps for magnetite. Other conditions were similar to those in [4]. The external reproducibility of $\delta^{18}\text{O}$ from 30 randomly oriented magnetite standard 5830 [3] was 1.0‰ (2SD), similar to both internal and external errors of a single grain (0.7–0.9‰). The external reproducibility of $\delta^{17}\text{O}$ and $\Delta^{17}\text{O}$ were $\sim 1.5\text{‰}$. After the analyses, SIMS pits were examined using a Hitachi S-3400 scanning electron microscope (SEM).

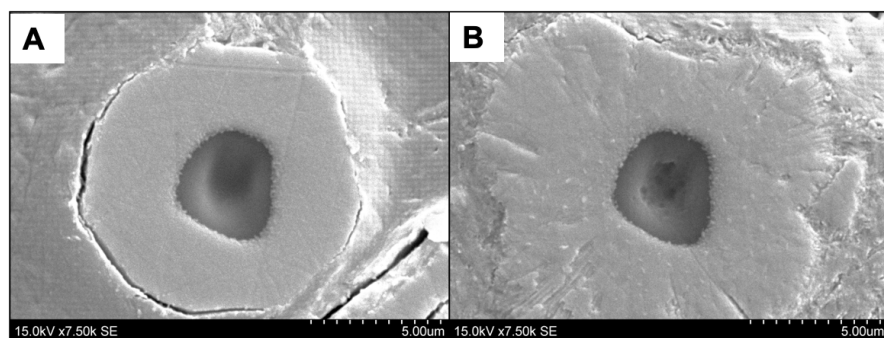


Figure 1. Two types of SIMS pit textures for magnetite grains in Ryugu after SIMS oxygen isotope analyses. Magnetite grains showing smooth SIMS pit textures (A) often show well-defined crystal faces, indicating slow growth. Magnetite grains showing porous SIMS pit textures (B) often show fibrous textures, suggesting rapid growth.

SEM observations show that all SIMS spots were within magnetite grains analyzed and none of the analyses were rejected. There are two types of pit textures, smooth and porous, which often correspond to magnetite with defined crystal faces and fibrous grains, respectively (Fig. 1). Results of analyses are shown in Fig. 2. and compared to magnetite analyses reported by [1] using 20 keV impact energy. Both datasets are very similar to each other, though new data show two groups of magnetite analyses according to the range of $\delta^{18}\text{O}$ values, from -4‰ to -1‰ and from $+3\text{‰}$ to $+7\text{‰}$, which correspond to magnetite grains with smooth and porous pit textures, respectively. The $\Delta^{17}\text{O}$ values of the lower $\delta^{18}\text{O}$ group vary from 0‰ to $+2\text{‰}$, while the higher $\delta^{18}\text{O}$ group shows consistently higher $\Delta^{17}\text{O}$ values (2–3‰). Some of the smooth magnetite analyses in

A0058-C1002 are very similar to those equilibrated with dolomite in A0058-C1001 ($\delta^{18}\text{O} \sim -3\text{‰}$ and $\Delta^{17}\text{O} \sim 0\text{‰}$). Assuming that ^{16}O -poor H_2O ice accreted to the Ryugu parent asteroid, melted, and interacted with relatively ^{16}O -rich anhydrous silicates [2], these results suggest that porous (fibrous) magnetite with high $\Delta^{17}\text{O}$ values formed during an early stage of aqueous activity, while other magnetite without porosity mostly formed later stages and likely in oxygen isotope equilibrium with other minerals. However, small variations in $\Delta^{17}\text{O}$ values among magnetite with lower $\delta^{18}\text{O}$ may suggest that fluid activity in the Ryugu parent asteroid could have been localized and the oxygen isotope ratios of the fluid might have been variable.

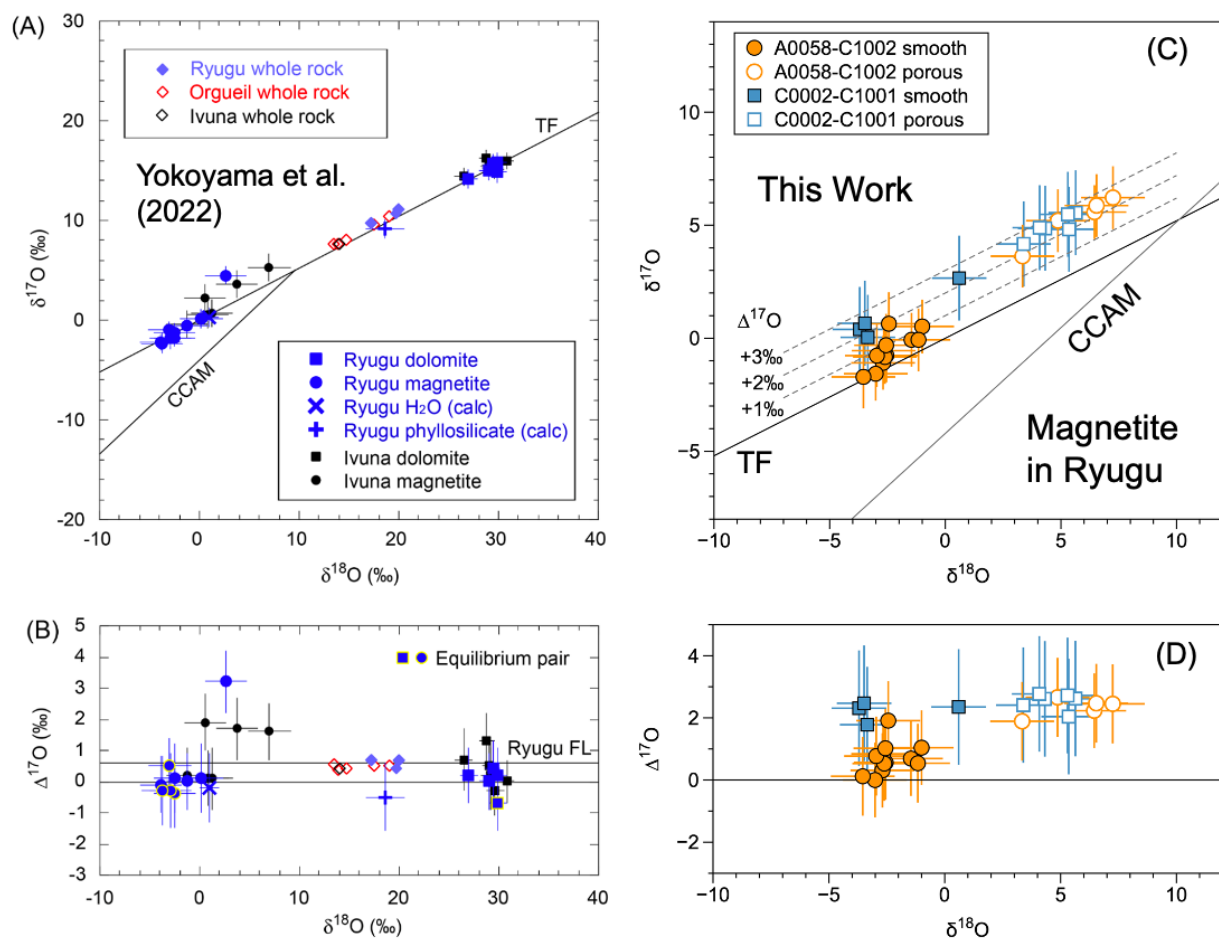


Figure 2. SIMS oxygen 3-isotope analyses of minerals in Ryugu. (A, B) Analyses of magnetite and dolomite in A0058-C1001 and Ivuna CI chondrite [1]. (C, D) Analyses of magnetite using 13 keV impact energy (This work). TF and CCAM are terrestrial mass fractionation and Carbonaceous chondrite anhydrous mineral lines [5], respectively.

References

[1] Yokoyama T. et al. *Science*, 10.1126/science.abn7850 (2022). [2] Nagashima K. et al. this volume. [3] Huberty J. M. et al. *Chemical Geology*, 276, 269–283 (2010). [4] Ushikubo T. et al. *Geochim. Cosmochim. Acta* 90, 242–264 (2012). [5] Clayton R. N. et al. *Earth Planet. Sci. Lett.* 34, 209–224 (1977).

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