

OXYGEN ISOTOPES OF CARBONATE AND MAGNETITE RECORD FLUID EVOLUTION ON THE RYUGU ASTEROID K.A. McCain¹, N. Matsuda¹, M.-C. Liu¹, K.D. McKeegan¹, A. Yamaguchi^{2,14}, M. Kimura², N. Tomioka³, M. Ito³, M. Uesugi⁴, N. Imae^{2,14}, N. Shirai⁵, T. Ohigashi⁶, R. C. Greenwood⁷, K. Uesugi⁴, A. Nakato⁸, K. Yogata⁸, H. Yuzawa⁶, Y. Kodama[†], A. Tsuchiyama⁹, M. Yasutake⁴, R. Findlay⁷, I. A. Franchi⁷, J. A. Malley⁷, K. Hirahara¹⁰, A. Takeuchi⁴, S. Sekimoto¹¹, I. Sakurai¹², I. Okada¹², Y. Karouji¹³, T. Yada⁸, M. Abe⁸, T. Usui⁸, S. Watanabe¹², and Y. Tsuda^{8,14}, ¹Dept. of Earth, Planetary, and Space Sciences, University of California, Los Angeles, CA 90095, USA (kamccain@ucla.edu, nozomi32@ucla.edu), ¹UCLA, ²NIPR, ³JAMSTEC Kochi, ⁴JASRI/SPRING-8, ⁵Tokyo Met. Univ., ⁶UVSOR/IMS, ⁷Open Univ., ⁸JAXA/ISAS, ⁹Ritsumeikan Univ., ¹⁰Osaka Univ., ¹¹Kyoto Univ., ¹²Nagoya Univ., ¹³JAXA/JSEC, ¹⁴SOKENDAI, [†]Now at Toyo Corp.

Introduction: The Hayabusa2 mission returned approximately 5.4 g of material from the C-type asteroid Ryugu. This material is highly aqueously altered and resembles the CI chondrites [1]. Because aqueous alteration products record information about the fluid from which they form, oxygen isotopic compositions of the alteration mineralogy of Ryugu can be used to constrain the isotopic composition and temperature of the water when the minerals formed.

We received dry-polished sections of particles A0037 and C0009 as part of the Phase2 curation Kochi team. The A0037 and C0009 particles were acquired from the 1st and 2nd touchdown sites respectively, and contain aqueous alteration products including carbonate (Ca-carbonate, dolomite, breunnerite), magnetite, and phyllosilicates [2,3]. To constrain the sequence of aqueous alteration of Ryugu components, we performed oxygen isotopic analyses of carbonate and magnetite in both particles.

Samples and Methods: We studied two polished sections prepared from the Ryugu A0037 and C0009 particles after an SR-XCT experiment [3]. The petrologic study of these sections were presented in [3,4]. In-situ oxygen isotope analyses of carbonate (dolomite and Ca-carbonate) and magnetite were performed using the UCLA CAMECA ims-1290 ion microprobe. In addition to the Ryugu samples, we also measured dolomite and magnetite in the Alais CI chondrite to serve as a comparison.

SIMS methods. We measured the oxygen isotopic compositions of carbonate and magnetite under three different conditions (3O-I, 3O-II, and 3O-III) based on the grain size. In session 3O-I, a primary Cs⁺ beam of ~3 nA was focused to a ~15 μm spot. Secondary ¹⁶O⁻, ¹⁷O⁻, and ¹⁸O⁻ ions were collected simultaneously using three Faraday cups to achieve the highest possible precision. In the second session (3O-II), we used a ~700 pA focused Cs⁺ beam with a diameter of ~10 μm and simultaneously detected the secondary ions using two Faraday cups and an electron multiplier (EM). In the third session (3O-III), we used a ~60 pA primary beam focused to a diameter ~3 μm and collected signals with a FC and two EM in multicollection mode.

We evaluated the contribution of ¹⁶OH⁻ to the ¹⁷O⁻ signal after each analysis and corrected for it. Before each dolomite analysis session, a suite of 4 dolomite standards of various Fe compositions were measured to quantify the matrix effects as a function of Fe content [5].

Results and Discussion: Oxygen isotopic compositions of carbonate and magnetite in A0037 and C0009 are shown in Figure 1. The bulk oxygen isotopes of Ryugu samples [6] and in-situ O isotope compositions of dolomite and magnetite from Alais (CI) are also plotted as a reference. Two backscattered electron (BSE) images of dolomite, magnetite, and Ca-carbonate are shown in Figure 2.

O isotopic composition of dolomite. The oxygen isotopic compositions of Ryugu dolomite in particle A0037 plot near the TF line with mean $\Delta^{17}\text{O}$ values of ~ +0.5 ‰, but several dolomite grains have $\Delta^{17}\text{O}$ resolved from 0‰, suggesting there may be variations in $\Delta^{17}\text{O}$ up to ~ +1.5 ‰. The oxygen isotopic composition of dolomite is consistent with CI-chondrite dolomite (Figure 1). The mean $\Delta^{17}\text{O}$ composition of dolomite cannot be resolved from the mean $\Delta^{17}\text{O}$ of bulk Ryugu particles [6], though Ryugu dolomite is enriched in $\delta^{18}\text{O}$ compared to the bulk. We suggest that mass-dependent variations observed in bulk O isotopic analyses of Ryugu material may be partially explained by variation in dolomite abundance in the bulk aliquots.

O isotopic composition of Ca-carbonate. The Ca-carbonate found in particle C0009 ranges in composition from $\Delta^{17}\text{O}$ ~ 0 to +3 ‰ and $\delta^{18}\text{O}$ ~ +33 to +38 ‰. This variation requires that the O isotopic composition of the fluid evolved over the course of Ca-carbonate precipitation. The composition of Ryugu Ca-carbonate differs significantly from calcite separated from Orgueil, which has a constant value of $\Delta^{17}\text{O}$ ~ 0 ‰ and a lower $\delta^{18}\text{O}$ = +25.5 ‰ [9]. We suggest that this difference reflects substantial variation in aqueous alteration processes between Ryugu and the CI chondrites: The Ca-carbonate in Ryugu precipitated from water which was in the process of equilibrating with ¹⁶O-

poor anhydrous silicate, while calcite in Orgueil precipitated after this equilibration had occurred.

One Ca-carbonate grain designated “Ca 2” and shown in Figure 2b resembles T1C calcite in its petrography, which is found in the CM chondrites and considered to form during the early stages of aqueous alteration [10]. “Ca 2” has the highest value of $\Delta^{17}\text{O}$ we have measured in Ryugu carbonate to date at $\Delta^{17}\text{O} \sim +3$ ‰, and therefore serves as a record of the composition of the fluid near the onset of aqueous alteration.

O isotopic composition of magnetite. Magnetite in A0037 has $\Delta^{17}\text{O} \sim +3$ ‰ which is identical to the “Ca 2” Ca-carbonate grain and distinct from dolomite. We conclude that magnetite was among the earliest minerals to precipitate during the alteration of the Ryugu protolith, predating most carbonate formation. We suggest the following order for the sequence of aqueous alteration on Ryugu: first, magnetite and some Ca-carbonate precipitated when the water $\Delta^{17}\text{O}$ was $\sim +3$ ‰. Next, as the fluid exchanged oxygen with ^{16}O -rich anhydrous silicate [11], Ca-carbonate formation continued as $\Delta^{17}\text{O}$ fell from $\sim +1.5$ to 0.5 ‰. Finally, most dolomite formed at about $\Delta^{17}\text{O} \sim +0.5$ ‰. Magnetite inclusions found enclosed in dolomite [3] support this sequence (Figure 2a).

Formation temperature of Ca-carbonate and magnetite. The $\Delta^{17}\text{O}$ compositions of magnetite and the early-forming carbonate “Ca 2” are identical within error, suggesting that they formed from a fluid of the same oxygen isotopic composition. This provides us an opportunity to constrain the temperature of the fluid during the early stages of fluid activity on Ryugu. For an average magnetite composition of $\delta^{18}\text{O} \sim +2.0 \pm 1.1$ ‰ and the composition of “Ca 2” of $\delta^{18}\text{O} = +38.0 \pm 0.8$ ‰, we estimate the formation temperature of “Ca 2” and magnetite to be $23\text{--}47^\circ\text{C}$ [12,13].

Additional results, including measurements of $\delta^{13}\text{C}$ in carbonate, will be presented at the meeting.

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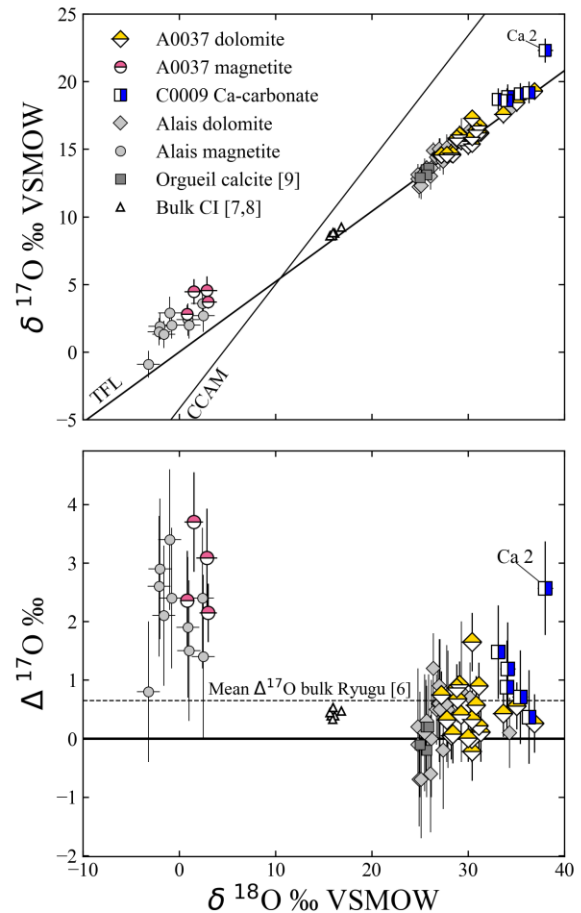


Fig. 1. Oxygen isotopic compositions of carbonate and magnetite in Ryugu particles A0037 and C0009. Bulk Ryugu [6], CI chondrite [7,8] and SIMS analyses of magnetite and carbonate [9] in CI chondrites are plotted for reference.

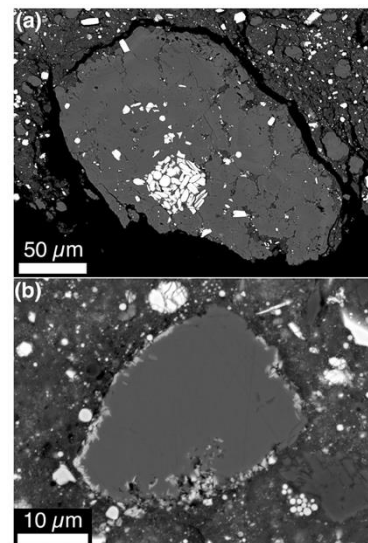


Fig. 2. BSE images of (a) dolomite with white magnetite inclusions in Ryugu particle A0037 and (b) “Ca 2” Ca-carbonate with sulfide rim in Ryugu particle C0009.