

OXYGEN ISOTOPE FRACTIONATION AMONG SECONDARY CALCITE AND MAGNETITE IN CR CHONDRITES. C. E. Jilly, G. R. Huss, and K. Nagashima, Hawai'i Institute of Geophysics and Planetology, University of Hawai'i at Mānoa, 1680 East-West Road, POST 602, Honolulu, HI 96822. cjilly@hawaii.edu.

Introduction: CR chondrites are particularly well-suited for the study of aqueous alteration, as they range in petrologic type from type 3 (anhydrous) to type 1 (completely altered). In this study, we address the oxygen isotopic composition of secondary minerals in two CR chondrites: Renazzo (CR2), a witnessed fall, and GRO 95577 (CR1), an Antarctic find.

On an oxygen three-isotope plot, bulk samples and constituents of CR chondrites exhibit a range of oxygen isotopic compositions, plotting along a mixing line of slope ~ 0.7 between the TFL and CCAM line [e.g., 1,2,3]). As a broad generalization, this mixing line reflects progressive alteration of a ^{16}O -rich anhydrous reservoir by a more $^{17,18}\text{O}$ -rich H_2O reservoir [1,3,4]. However, fine scale inconsistencies reflect the extreme heterogeneity of components in CR chondrites [5]. Therefore *in situ* analyses of mineral phases are crucial to understanding mineral contributions to the CR trend.

We measured *in situ* oxygen isotopic compositions of secondary minerals to understand the nature of the aqueous reservoir and the fluid chemistry evolution during aqueous alteration. Targets for oxygen isotopic measurements are magnetite and calcite grains (Fig. 1) from sections Renazzo N1127, and GRO 95577-69.

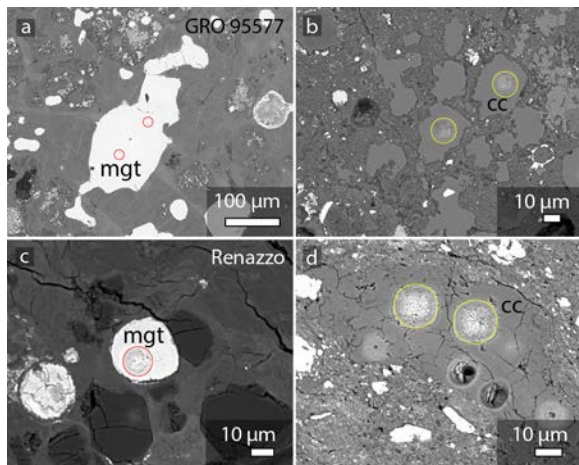


Fig. 1. BSE images of characteristic grains in GRO 95577-69 (a, b) and Renazzo N1127 (c, d). Red circles indicate magnetite SIMS pits, yellow indicate calcite SIMS pits.

Analytical Procedure: Oxygen isotopes were measured on the University of Hawai'i Cameca ims 1280 ion microprobe. Measurements used a ~ 600 pA Cs^+ primary beam focused to ~ 10 μm , and a 7×7 μm^2 raster. The sample was presputtered for 90s using a 600 pA beam and 10×10 μm^2 raster. The mass resolving power was set to ~ 5000 for ^{17}O , and ~ 2000 for ^{16}O and ^{18}O . Secondary O^- ions were counted in multicol-

lection mode using faraday cups for $^{16}\text{O}^-$ and $^{18}\text{O}^-$ and an electron multiplier for $^{17}\text{O}^-$. Each run consisted of 30 cycles of ~ 16 seconds each. After each run, $^{16}\text{OH}^-$ peaks were measured. $^{17}\text{O}^-$ was corrected for the tail of $^{16}\text{OH}^-$ using a tail/peak ratio of 20 ppm, with a typical contribution of $\sim 0.6\%$. Data were corrected for IMF using terrestrial calcite and magnetite standards.

Results: Oxygen-isotope analyses were performed on 3 calcite grains (4 analyses), and 3 magnetite grains (3 analyses) in Renazzo N1127. Although carbonate and magnetite grains are abundant in Renazzo, most were too small (< 5 μm) for *in situ* SIMS measurement. Large grains are ubiquitous in GRO 95577-69, where we measured 25 calcite grains (25 analyses) and 8 magnetite grains (11 analyses). Data are plotted in Fig. 2. Calcites from GRO and Renazzo plot in distinct regions. The GRO analyses are tightly clustered, and the Renazzo calcites form an array near the terrestrial fractionation line (TFL). Magnetites from GRO and Renazzo plot in overlapping arrays around the TFL. The $\Delta^{17}\text{O}$ values for both calcite and magnetite show a small spread (Fig. 3), ranging from about -1.5 – 1.5 ‰.

Discussion: GRO 95577 (CR1) is a breccia [5] containing abundant dark lithic inclusions. Section GRO 95577-69 consists of one main lithology and a small inclusion of a second lithology (~ 1 mm). The main lithology is petrographically similar to the dark lithology reported in [6]. However, unlike [6], which reported calcite appearing solely in the matrix, large (> 60 μm) calcite grains were found as pseudomorphs for the mesostasis in a GRO 95577 chondrule. Calcite oxygen-isotope measurements were taken from both matrix and chondrule grains in the main lithology. The oxygen compositions are uniform.

Despite the apparent similarity between thin section GRO 95577-69 and the section reported in [6], the oxygen isotope results are dissimilar. [6] found that the CR1 calcites spanned an array near the TFL from $\delta^{18}\text{O} \sim 25$ – 35 ‰, and attributed the spread to changes in T or oxygen composition of the water during precipitation. Our results instead suggest that calcite was formed under relatively constant physico-chemical conditions (e.g., [3]). The difference in these two studies could reflect the heterogeneity of CR chondrites [5], as the measurements in [6] were taken from three lithologies across two thin sections, while our measurements came from one lithology.

The 3 Renazzo calcite grains measured here were located in distinct clasts, and reflect a similar trend to the CR calcite in [6], and to calcite in CM chondrites

[e.g., 8,9]. The array can be attributed to changing fluid chemistry, such as variation in temperature, water/rock ratio, and evolving oxygen composition [1,3,6]. However, the interpretation of fluid evolution depends on the model referenced. [10] gave compelling evidence that alteration in chondritic parent bodies was an isochemical, closed-system process. In a closed-system model, decreasing $\delta^{17}\text{O}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ in aqueously formed minerals may indicate progressive alteration and fluid evolution on the parent body [1,9]. However, pre-terrestrial calcite veins such as those observed in Renazzo [11] may suggest fluid flow was present. In an open-system model dominated by fluid flow [e.g., 12], progressive alteration would instead lead to greater values of $\delta^{17}\text{O}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$. The relative degree of alteration of each clast must be better defined to determine which model fits this system.

All magnetites were from altered Fe, Ni metal nodules in chondrule interiors. The Renazzo grains were from 3 separate clasts; the GRO 95577 magnetites were from both the main and minor lithologies, with each lithology outlining the same array of $\delta^{18}\text{O} \sim -17$ to -10‰ . That the GRO magnetites show a range of compositions while the calcites do not may indicate that the minerals formed at different times or different stages of the alteration process. Compared to other chondrite groups (UOC, CV, CI, CM, CK) our magnetite plots on a unique trend with distinctly low $\delta^{18}\text{O}$ values [13,14,15,16]. Low $\delta^{18}\text{O}$ may be explained by magnetite-water fractionation at low temperatures, although fractionation factors for temperatures below $<300^\circ\text{C}$ are still poorly constrained (e.g., [17]).

Terrestrial weathering is of great concern, particularly regarding iron oxides. Renazzo, a fall, likely escaped such weathering. However, GRO 95577 is an Antarctic find of weathering grade B. Antarctic glacial ice has extremely negative values of $\delta^{18}\text{O} \sim -35$ to -50‰ [18,19], therefore small amounts of weathered oxides may alter oxygen compositions toward the TFL and to negative $\delta^{18}\text{O}$ values. However, as a fall, Renazzo magnetite surely was not altered by glacial water, and displays an overlapping trend with GRO 95577 magnetite of low $\delta^{18}\text{O}$, supporting a pre-terrestrial origin for the minerals. The calcite measured from GRO does not exhibit a large depletion of $\delta^{18}\text{O}$, suggesting that it was not formed by alteration from glacial meltwater [19,7] Furthermore, resolvable Mn-Cr ages of carbonate grains in Renazzo and GRO95577 suggest that they were formed during aqueous processes between ~ 2 – 13 Myr after CAI formation [11].

Conclusions: We successfully measured *in situ* oxygen isotopes for secondary calcite and magnetite in two CR chondrites. The spread in the data suggests fluid evolution occurred between different clasts.

However, oxygen isotopes in calcite from one clast of GRO 95577 suggest that the grains formed under tightly constrained conditions. This data supports the notion that aqueous alteration on the CR parent body was complex, with different clasts representing large-scale variations in alteration conditions. We intend to extend this study to constraining alteration temperature using water-calcite and water-magnetite fractionations.

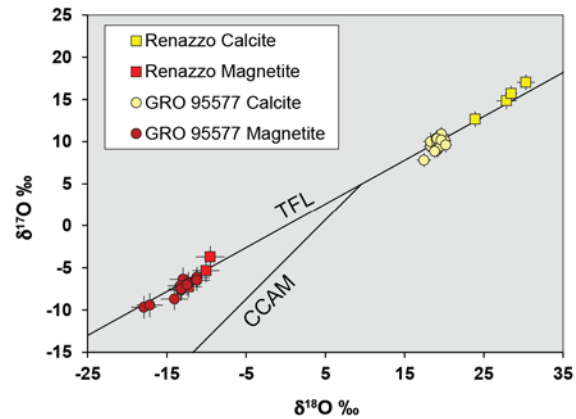


Fig. 2. Oxygen isotopic compositions of calcite and magnetite in GRO 95577 and Renazzo, Error bars are 2σ .

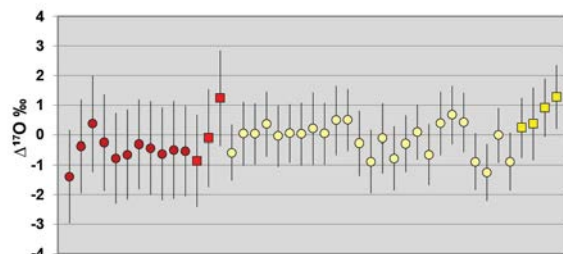


Fig. 3. $\Delta^{17}\text{O}$ values for calcite and magnetite in Renazzo and GRO 95577. Color scheme is same as in Fig. 1, errors are 2σ . Data points arranged by mineral, not in measurement order.

References: [1] Clayton R. N. and Mayeda T. K. (1999) *GCA* 63, 2089-2104. [2] Choi B.-G. et al. (2009) *MetSoc.* 72, #5339. [3] Schrader D. L. et al. (2011) *GCA*, 75, 308-325. [4] Weisberg M. K., et al. (1995) *Proc. NIPR Symp. Antarct. Meteorit.*, 8, 11-32. [5] Weisberg M. K. et al. (1993) *GCA* 57, 1567-1586. [6] Tyra M. A. et al. (2011) *LPSC XLII*, #1639. [7] Weisberg M. K. and Huber H. (2007) *MAPS* 42, 1495-1503. [8] Clayton R. N. and Mayeda T. K. (1984) *EPSL* 67, 151-161. [9] Benedix G. K. et al. (2003) *GCA* 67, 1577-1588. [10] Bland et al. (2009) *EPSL* 287, 559-568. [11] Jilly C. E. et al. (2013) *LPSC XLIV*, # 2474. [12] Young et al. (1999) *Science* 286, 1331-1335. [13] Choi B.-G. et al. (1998) *Nature*, 392, 577-579. [14] Choi B.-G. et al. (2001) *MAPS* 35, 1239-1248. [15] Rowe et al. (1994) *GCA* 58, 5341-5347. [16] Davidson et al. (2013) *LPSC XLIV*, #2522. [17] Chacko T. et al. (2001) in *Rev. Min. Geochem* 43, 1-81. [18] Gooding J. L. (1986) in *Inter. Work. Antarct. Met. 1*, 48-54. [19] Faure G. et al. (1988) *Nature*, 332, 352-354.

Acknowledgements: This research is supported by NASA through NAI cooperative agreement NNA04CC08A (K. Meech, PI) and NASA grant NNX11AG78G (G.R. Huss, PI). Special thanks to the Meteorite Working Group and the Vienna Museum of Natural History for sample allocation.