OXYGEN ISOTOPES IN SECONDARY MINERALS IN CR CHONDRITES: COMPARING COMPONENTS OF DIFFERENT PETROLOGIC TYPE. C. E. Jilly-Rehak, G. R. Huss, and K. Nagashima. University of Hawai'i at Mānoa, 1680 East-West Road, POST 602, Honolulu, HI 96822, USA. cjilly@hawaii.edu.

Introduction: *In situ* O-isotope analyses of secondary mineral phases are crucial to understanding the aqueous alteration process. On a three-O-isotope plot, bulk samples and constituents of CR chondrites plot along a slope ~0.7 mixing line, thought to represent the progressive alteration of a ^{16}O-rich anhydrous reservoir by a more ^{17,18}O-rich H_2O reservoir [1-3]. While this mixing line serves as a broad generalization for progressive alteration, there are fine scale inconsistencies [3]. To clarify this issue, we measured O isotopes of secondary minerals from CR chondrites of varying petrologic type, and from different components including matrices, chondrules, and dark inclusions. Furthermore, empirically derived fractionation factors for secondary minerals [e.g., 4,5] can be used to determine the fluid temperature, shedding light on the complex alteration conditions on the CR parent body.

Methods: Using the University of Hawai'i Cameca IMS 1280 ion microprobe, we measured O isotopic compositions of calcite, dolomite, and magnetite grains in four CR chondrites: MIL 090292,12 (CR 2.0), Al Rais USNM 6997 (CR 2.3), Renazzo N1126 (CR 2.4), EET 92159,20 (CR 2.8) [6]. A 25 pA Cs^+ primary beam gave a 2-3 μm spot size. We measured $^{16}O^-$, $^{17}O^-$, and $^{18}O^-$ on a faraday cup and two electron multipliers, respectively. The MRP for $^{17}O^-$ was 5800, sufficient to resolve interferences from $^{16}OH^-$. Grains were pre-sputtered for 180s, and each run consisted of 30 cycles of 45s each, with a total run time of ~25min. After each run, $^{16}OH^-$ peaks were measured. The $^{17}O^-$ signals were corrected for the tail of $^{16}OH^-$ using a tail/peak ratio of 20 ppm, with a typical contribution of ~0.6‰. Thin sections MIL 090292,12 and Renazzo N1126 were subsequently polished with 0.05μm alumina powder for electron backscatter diffraction (EBSD) analysis.

Results: The O composition of calcites range from $\delta^{18}O \approx 9 - 35$‰ (Fig. 1), consistent with previous measurements in other CR samples [7,8]. All calcite grains measured here come from the matrix in the host lithology. Calcites in Al Rais are the isotopically heaviest yet measured in CRs. Calcite in CRs of higher petrologic type show greater variation in $\Delta^{17}O$, and a wider spread in $\delta^{18}O$ as compared to lower petrologic types. Dolomite was found only in dark inclusions in EET 92159 and Renazzo, with average $\delta^{18}O$ compositions of about 26‰ and 24‰, respectively.

The O compositions of magnetites range from $\delta^{18}O \approx -17$‰ $-$ 5‰. Magnetite in EET 92159 clusters around $\delta^{18}O = -3$‰. Matrix framboids, spherules, and magnetite nodules from chondrules in Al Rais, EET

92159, and Renazzo N1126 fall on the same trend as previous CR measurements (Fig. 1). Five magnetite analyses in Renazzo N1126 were from a dark inclusion, with O isotopes slightly below the CR trend at $\Delta^{17}O \approx -1.9$‰. MIL 090292 magnetite grains all came from altered metal nodules in chondrules, and plot at $\Delta^{17}O \approx -3.5$‰, ranging from $\delta^{18}O = -7$ to -4‰. Dolomite was found only in dark inclusions in EET 92159 and Renazzo, with average $\delta^{18}O$ compositions of about 26‰ and 24‰, respectively. EBSD analyses showed no bands for magnetite grains in Renazzo N1126 or MIL 090292, although bands for silicates were visible.

Discussion: *Progressive alteration on the CR parent body.* The calcite and magnetite arrays differ for each meteorite. Variations in $\delta^{18}O$ along mass-dependent fractionation lines are likely due to changes in temperature or fluid composition during alteration [9]. Arrays with variable $\Delta^{17}O$ may reflect isotopic exchange between water and a ^{16}O-enriched solid during progressive alteration. The calcites track fluid evolution as $\Delta^{17}O$ progressively decreases (in a closed system) [10-12]. The spread in the calcite data may reflect the water/rock (W/R) ratios for each petrologic type [1,3]. The extent of isotopic evolution in minerals would be less in a water-rich system than in a low W/R system [9]. Our calcite data show that high W/R (low petrologic type) samples show less evidence for fluid evolution than the low W/R samples (extent of evolution: GRO 95577 < Al Rais < Renazzo < QUE 99177).
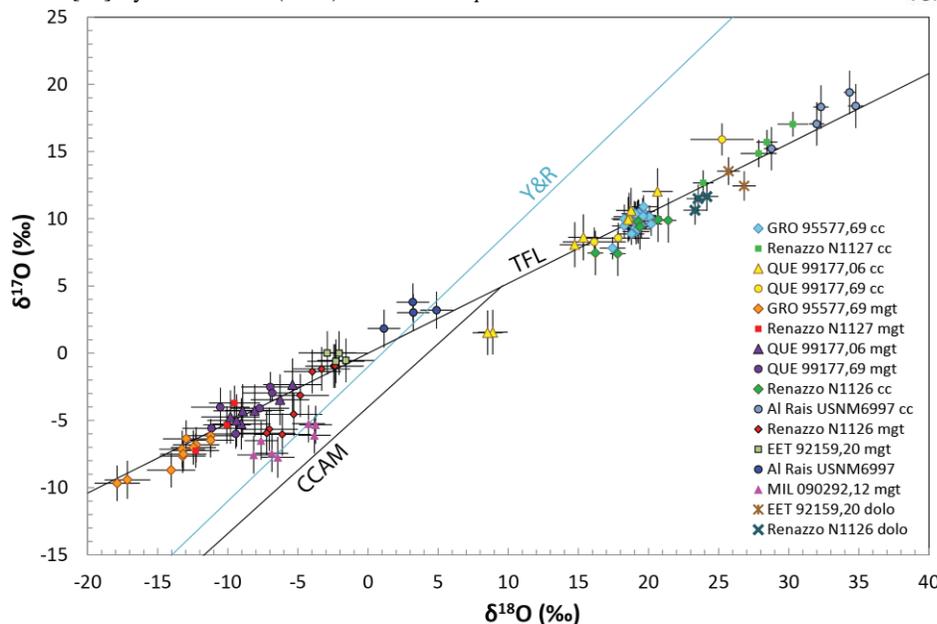
Surprisingly, the *in situ* compositions of secondary minerals do not demonstrate a correlation between composition and petrologic type. For example, the CRs of lowest petrologic type, GRO 95577 (CR 2.0) and Al Rais (CR 2.3) plot at the lightest and heaviest ends of the magnetite trend. All higher petrologic types plot between these two extremes. Such heterogeneity can explain the inconsistencies in the bulk CR trend [3].

Temperature of alteration. Though the water composition on the CR parent body is unknown [1,3], the relative ^{18}O fractionation between calcite and magnetite formed from the same fluid can yield the temperature of precipitation. An assemblage in Al Rais (Fig. 2) is a good candidate for co-precipitation. We measured both calcite and magnetite. The relative $\delta^{18}O$ fractionation is 30‰. Using the fractionation factors from [4,5], the precipitation temperature would have been ~65 ˚C (Fig. 3). This is similar to alteration temperatures for GRO 95577 [7], but would have required a fluid of a different O isotopic composition, indicating heterogeneous alteration conditions on the CR parent body.

Orientation effects in SIMS magnetite analyses. Magnetite SIMS data have been shown to vary in $\delta^{18}O$ between 3-6‰, depending on the orientation of the crystal during measurement [13,14]. As the magnetite grains measured here are randomly oriented, we would expect to see a spread in the data reflecting the various orientations. However, the lack of visible EBSD bands may indicate that the crystal structure is variable on a fine scale, and that the magnetite grains are aggregates of sub-micron crystallites. In this case, it remains unclear if the SIMS crystal orientation effect should be detectable, or if the ~6‰ spread for each meteorite represents changes in fluid chemistry.

Distinct properties of MIL 090292. MIL 090292 has been classified as a CR 2.0, based upon the phyllosilicate, sulfide, and magnetite-rich petrography [6]. Yet unlike other CRs, no Ca-carbonates have been identified. Rather, Ca resides in secondary Ca-rich silicates and phosphates. Magnetite from MIL 090292 ($\Delta^{17}O \sim -3.5$‰) plots outside of the typical range for CR chondrites ($\Delta^{17}O \sim 0$‰; Fig. 3), similar to magnetite in some CV chondrites [e.g., 15,16]. MIL 090292 magnetite must have formed under very different fluid chemistry than the other CR chondrites. The abundance of ^{16}O-enriched magnetite may explain the offset bulk composition [6] and hint at an anomalous origin.

References: [1] Clayton R. N. and Mayeda T. K. (1999) *GCA 63,* 2089–2104. [2] Choi B. G. et al. (2009) *MAPS 44 (Supplement),* A50. [3] Schrader D. L. et al. (2011) *GCA 75,* 308-325.. [4] Zheng Y.-F. (1991) *GCA 55,* 2299-2307. [5] Zheng Y.-F. (2011) *Geochem. Journal. 45,* 341-354. [6] Harju et al. (2014) *GCA 139,* 267-292. [7] Jilly C. E. et al. (2014) *LPSC XLV,* Abstract #1642. [8] Jilly C. E. et al. (2014) *Met. Soc. 77,* Abstract #5395. [9] Taylor H. P. (1977) *J. Geol. Soc. 133,* 509-558. [10] Benedix G. K. et al. (2003) *GCA 67,* 1577-1588. [11] Young E. D. et al. (1999) *Science 286,* 1331-1335. [12] Bland P. A. (2009) *EPSL 287,* 559–568. [13] Lyon I. C. et al. (1998) *Int. J. Mass Spec. Ion Proc. 172,* 115-122. [14] Huberty J. M. et al. (2010) *Chem. Geol. 276,* 269-283. [15] Choi B. G. et al. (1997) *Earth Planet. Sci. Lett. 146,* 337-349. [16] Davidson J. et al. (2014) *MAPS 49,* 1456-1474.
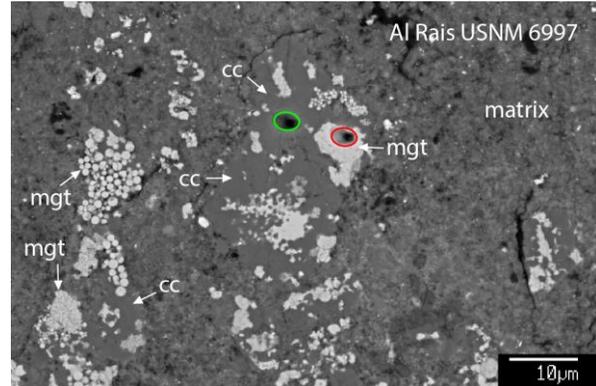

Fig. 2. BSE image of a calcite (cc) and magnetite (mgt) assemblage in Al Rais. Ion probe pits are indicated in green for cc, and red for mgt.
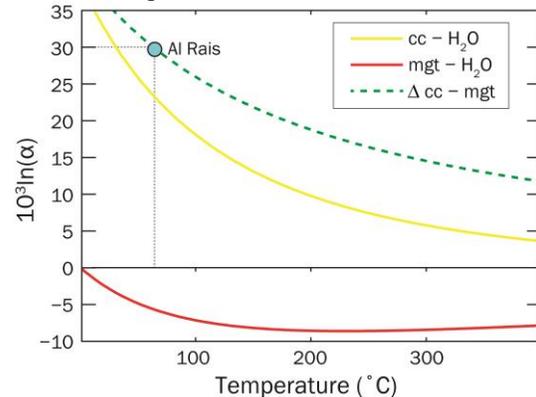

Fig. 3 (Above) Fractionation curves for calcite-water (yellow) and magnetite-water (red) [4,5]. The relative fractionation for cc and mgt is shown by the green curve. A relative fractionation of 30‰ in Al Rais corresponds to T~ 65°C.

Fig. 1 (Left). O isotopic composition of calcite (cc), magnetite (mgt), and dolomite (dolo) from CR chondrites. GRO 95577, Renazzo N1127 data from [7], QUE 99177 data from [8], all other data from this study. Error bars 2σ.