

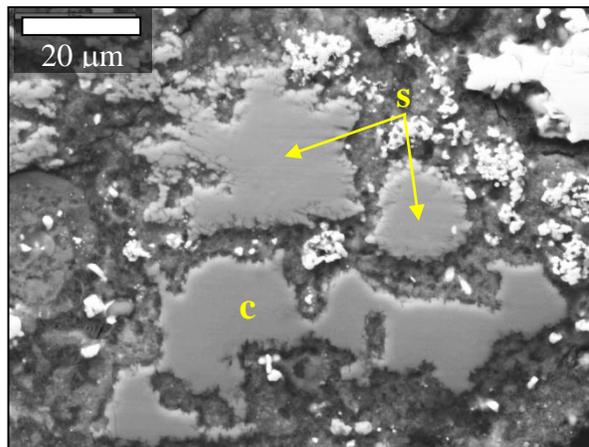
**OXYGEN ISOTOPIC COMPOSITION OF SECONDARY CARBONATES IN CR1 CHONDRITE GRO 95577.** M. A. Tyra<sup>1</sup>, A. J. Brearley<sup>1</sup>, and Y. Guan<sup>2</sup>, <sup>1</sup>Dept. of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, USA (matyra@unm.edu), <sup>2</sup>Geological & Planetary Sciences, MC 170-25, Caltech, Pasadena, CA 91125.

**Introduction:** Along with the CI and CM chondrites, the CR chondrites exhibit the most extensive evidence of aqueous alteration among the carbonaceous chondrite groups. The CRs are of particular importance, because they are the only group which shows a full range of petrologic types from type 3.0 [1] to type 1. Consequently, they provide an opportunity to study the complete evolution of aqueous alteration from incipient alteration to full hydration of protolith material.

The highly-altered CR1 chondrite, GRO 95577, contains a unique carbonate assemblage consisting of Mn-rich siderite, calcite and minor dolomite. The Mn/Cr systematics of siderite in GRO 95577 measured by NanoSIMS indicate that these grains may be much younger than any secondary carbonate mineral measured in carbonaceous chondrites to date [2]. Essentially none of the siderites show measurable <sup>53</sup>Cr excesses indicating that they formed at least 24Myr after CAI formation. This unique result raises the possibility that these siderite grains are not extraterrestrial in origin, but may have formed by weathering in the Antarctic. Several studies demonstrate that carbonates can precipitate during residence of the meteorites on the Antarctic ice [e.g. 3, 4]. In order to resolve this ambiguity, we have measured the oxygen isotopic composition of carbonates in GRO 95577 by ion microprobe. Our study demonstrates that the carbonates are unambiguously extraterrestrial in origin. Furthermore, the data represent the first oxygen isotopic compositions of individual secondary minerals in CR chondrites and provide a basis for understanding the oxygen isotopic evolution of CR chondrites during alteration from type 3 to type 1s. The data also allow a comparison of models for the oxygen isotopic evolution of CR, CM, and CI chondrites [5, 6].

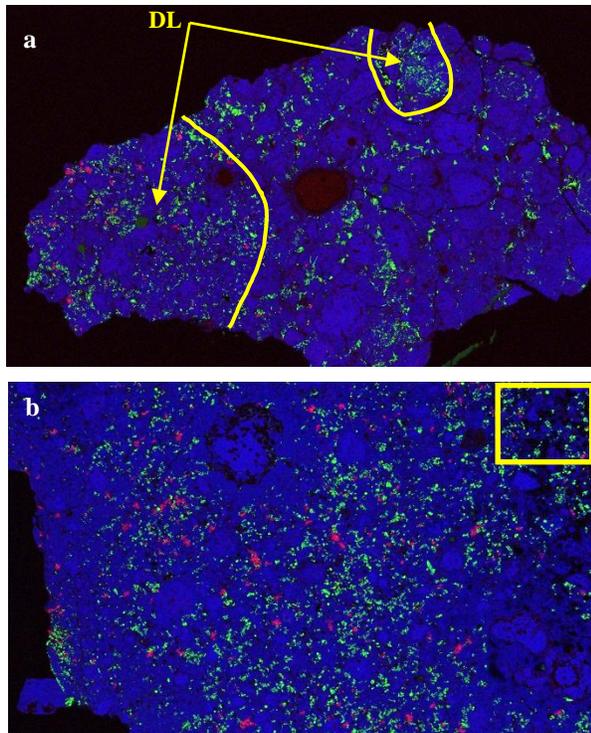
Within GRO 95577, practically all original minerals, including coarse-grained silicates in chondrules, have been pseudomorphically replaced by secondary minerals—notably hydrous phases such as serpentine and smectite [7]. Previous SIMS oxygen isotopic measurements of Ca-carbonates in CM1 and CM2 have shown that isotopic heterogeneity is present on a grain-to-grain scale that provides important constraints on the isotopic evolution of the altering fluid [8, 9, 10]. The calcite and newly-discovered siderite in GRO 95577 may also show similar isotopic heterogeneity that can be used to place constraints on the formational history of these grains.

**Petrography:** We examined 2 petrographic thin sections—GRO 95577, 30 and GRO 95577, 52. In addition to the host CR lithology (large chondrules, ~30% matrix) [2], GRO 95577 also contains a significant component of a fine-grained “dark lithology” (DL). Calcite, siderite, and rare dolomite are present in the host and the DL [2, 7] (Figure 1). Full spectral X-ray maps of each thin section were acquired using an EDAX Apollo 40 SDD detector attached to a FEI FEG SEM (30 kV, 23 nA, ~200 μs dwell, ~30% deadtime, 1.7 μm/pixel resolution). These maps were used to determine the distribution, abundance, and chemistry of carbonates in the samples. The X-ray maps (Fig. 2) show that in both samples carbonates within DL are randomly distributed. Carbonates are restricted to the matrix between chondrules within the host. GRO 95577, 30 contains 3.2 vol. % calcite and 0.15 vol. % siderite. GRO 95577, 53 possesses 2.9 vol. % calcite and 0.17 vol. % siderite—essentially identical results.



**Figure 1.** SEM BSE image showing calcite (c) and siderite (s) in GRO 95577 DL. The shown FOV is located in Fig. 2b (yellow box).

**Isotopic Analyses:** To determine the oxygen isotopic composition of carbonates, we used the Cameca IMS 7f-GEO SIMS at Caltech (Cs<sup>+</sup> primary beam, 10 keV, ~0.1 nA, ~10 μm spot size). Secondary ions of -10 keV were collected at a mass resolving power (m/Δm) of ~5500 to separate <sup>17</sup>O<sup>-</sup> from the <sup>16</sup>O<sup>1</sup>H<sup>-</sup> interference. The <sup>16</sup>O<sup>-</sup> signal was measured with a Faraday cup (FC), and the <sup>17</sup>O<sup>-</sup> and <sup>18</sup>O<sup>-</sup> signals with an electron multiplier (EM). Sample charging was compensated with a negative electron gun (NEG) at -10 keV. Sample data were calibrated for instrumental mass fractionation (IMF) and matrix effects with suitable calcite and siderite standards.



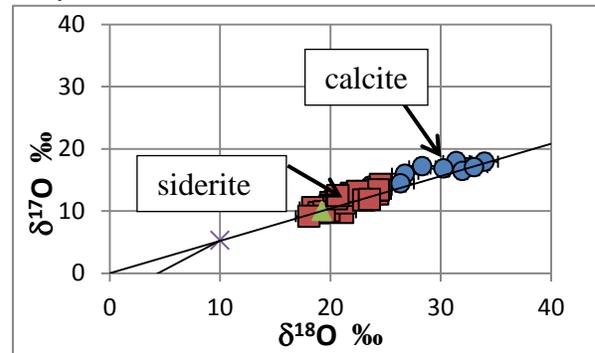
**Figure 2.** X-ray maps of GRO 95577, 30 (a) and GRO 95577, 52 (b). Red denotes siderite, green calcite, and blue silicates. DL denoted in (a) and is the entirety of (b). FOV of both maps ~1.5 cm.

Both types of carbonate (siderite and calcite) vary widely in their oxygen isotopic composition. The  $\delta^{18}\text{O}$  of calcite (10 spots in 10 grains), ranges from 24 to 35 ‰. Siderite compositions (11 spots in 8 grains), range from 18 to 27 ‰. Measured carbonate compositions in the DL and CR host lithologies are identical, within error. Although compositions overlap slightly, the majority of siderite oxygen isotopic values are distinctly lower than calcite (Fig. 3).

**Discussion:** Benedix et al. [11] tailored the 2-component model of Clayton and Mayeda [5] to explain calcite oxygen isotopic compositions in CM chondrites. In these models, asteroidal water evolved from a composition of higher  $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$ , and  $\Delta^{17}\text{O}$  values to lower values as water interacted with anhydrous silicates. Carbonates record part of the compositional evolution of the water.

The range in calcite compositions in GRO 95577 implies that either T changed significantly during precipitation or that calcite precipitated from water that varied in its oxygen isotopic composition. Isotopic variation could arise from carbonates precipitating over time from an isotopically-evolving fluid. Because water evolves to lighter oxygen isotopic values, one can say that a carbonate with lower oxygen isotopic values precipitated after a grain with higher oxygen isotopic values if the fluid was homogeneous. Isotopic heterogeneity could also originate from precipitation from

isolated fluids due to localized reactions with silicates. As calcite and siderite chemical compositions are indistinguishable in both samples and in both lithologies [2], isolation due to low permeability [e.g. 11] is unlikely, however.



**Figure 3.** Oxygen isotopic compositions of calcite and siderite.

In general, for the measured carbonates  $\delta^{18}\text{O}_{\text{cal}} > \delta^{18}\text{O}_{\text{sid}}$ . Calculated fractionation between calcite and siderite vary by 3.3‰ at 0°C and 1.8‰ at 100°C [13]. As calcite and siderite  $\delta^{18}\text{O}$  vary by up to 17‰, the isotopic differences between the two phases cannot be wholly attributed to cogenetic precipitation from the same fluid. The simplest explanation is that calcite precipitated first, siderite second, and that there was a transitional period when coprecipitation occurred.

Finally  $\delta^{18}\text{O}$  of calcite and siderite are inconsistent with formation in Antarctica. As the  $\delta^{18}\text{O}$  of Antarctic ice at meteorite stranding surfaces is ~-50‰ [14], the measured compositions of both carbonates lie outside of the range for in-situ precipitation at probable Antarctic temperatures [13]. Therefore, we conclude that the carbonate assemblages in GRO 95577 are extraterrestrial in origin. The aberrantly-young Mn-Cr ages for these secondary carbonates [2] are therefore real and extend the period of hydrothermal activity on asteroidal parent bodies to  $\geq 24\text{Myr}$  after CAI formation.

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