

Mn-Cr DATING OF SECONDARY CARBONATES 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 96815. cjilly@hawaii.edu.

Introduction: The Mn-Cr system is a robust radiochronometer for dating the formation of early solar system materials. Relative ages are calculated from the beta decay of ^{53}Mn into stable daughter nuclide ^{53}Cr , with a half-life of 3.7 Myr. The system yields dates consistent with Pb-Pb [1], lending credence to its accuracy. The half-life is sufficiently long to resolve ages for the duration of aqueous alteration, thought to range from 1-15 Myr after CAI formation [2]. Carbonates are suitable targets for this system, as they fractionate Mn and Cr during formation from aqueous fluids.

The initial $^{53}\text{Mn}/^{55}\text{Mn}$ ratio in the early solar system represents a uniform isotopic abundance when Mn and Cr first fractionated in the nebula, ~4568.1 Ma [3]. However, the $(^{53}\text{Mn}/^{55}\text{Mn})_{\text{SS}}$ ratio at the time of CAI formation is poorly constrained. Current estimates for $(^{53}\text{Mn}/^{55}\text{Mn})_{\text{SS}}$ range from $(6.3 \pm 0.7) \times 10^{-6}$ to $(9.1 \pm 1.7) \times 10^{-6}$ [4, 5].

CR Carbonates. Carbonates in CR2 chondrites mostly occur as fine-grained masses, often intergrown with phyllosilicates [6]. However, in Renazzo section N1127, we found several carbonate veins, some extending up to 100 μm in length. Such veins occur in the matrix and along chondrule rims, and are composed of pure calcite with a coarser texture than other carbonate material in the matrix (fig. 1). As Renazzo is a witnessed fall, the veins are unlikely caused by terrestrial weathering. The more heavily altered CR1 chondrite, GRO 95577, contains abundant calcite grains averaging ~30 μm in diameter, all occurring in within the matrix (fig. 1).

Experimental Procedure: Two carbonates were measured in Renazzo N1127, and five grains were measured in GRO 95577-69. Manganese-chromium analyses were conducted on the University of Hawai'i's Cameca ims 1280 ion microprobe. Measurements used a ~100 pA $^{16}\text{O}^+$ primary beam, focused to ~5 μm . Three chromium isotopes ^{50}Cr (plus contributions from isobars ^{50}V and ^{50}Ti), ^{52}Cr , and ^{53}Cr were measured in multicollection mode on electron multipliers (45 seconds) followed by a peak jump to ^{55}Mn (2 seconds). The mass resolving power for ^{53}Cr and ^{55}Mn was ~6200 and for ^{50}Cr and ^{52}Cr was ~4800. A typical measurement consisted of 100 cycles. Before each measurement, the sample was presputtered for 600s using a ~300 pA beam and 5 μm raster.

Data Reduction: Data were corrected for detector background and deadtime. Instrumental mass fractionation was corrected by comparison with the $^{53}\text{Cr}/^{52}\text{Cr}$

ratio measure on the standard. Isotope ratios were calculated using total counts to minimize ratio bias (7).

Mn/Cr Relative Sensitivity Factors. Historically, CI and CM carbonate measurements have been standardized to San Carlos olivine. However, recent work [8,9], suggests that the Mn/Cr RSF [$(^{53}\text{Mn}/^{52}\text{Cr}^+)_{\text{SIMS}} / (^{53}\text{Mn}/^{52}\text{Cr})_{\text{TRUE}}$] for calcite differs significantly from that for olivine, calling into question the accuracy of previously reported Mn-Cr ages. Suitable carbonate standards are difficult to obtain, so as a temporary measure, we have continued to use San Carlos olivine as a standard, but have adjusted our sensitivity factor based on the results of [8]. This revised sensitivity factor increases the Mn/Cr ratios for our samples by ~39% relative to ratios determined from San Carlos olivine. A 15% systematic uncertainty was applied to the resulting Mn/Cr ratios.

Results and Discussion: The carbonate veins in Renazzo contain resolvable excesses in ^{53}Cr due to the decay of ^{53}Mn . On a plot of $^{53}\text{Cr}/^{52}\text{Cr}$ vs $^{55}\text{Mn}/^{52}\text{Cr}$, the measurements form an isochron with a slope of $(3.4 \pm 2.0) \times 10^{-6}$, representing the initial ratio [$(^{53}\text{Mn}/^{55}\text{Mn})_0$] at the time the carbonate vein formed (fig. 2). GRO 95577 carbonates also show excesses of ^{53}Cr , with an isochron slope of $(^{53}\text{Mn}/^{55}\text{Mn})_0 = (7.3 \pm 2.5) \times 10^{-7}$ (fig. 3). MSWD values for Renazzo and GRO 95577 (0.74 and 0.69 respectively) suggest that the scatter in the data can be explained by statistical uncertainty. The isochron validity depends on the assumption that all grains from a section were formed during a single alteration event, which is reasonable given the small scales and general homogeneity in carbonate texture.

To calculate the absolute ages of carbonate formation, we use the LEW 86010 angrite Pb-Pb age as a time anchor. The absolute LEW 86010 Pb-Pb age is given as 4557.5 ± 0.3 Ma [11], which corresponds to a $^{53}\text{Mn}/^{55}\text{Mn}$ ratio of $\sim 1.35 \times 10^{-6}$ at the time of closure [5]. Based on this anchor, $(^{53}\text{Mn}/^{55}\text{Mn})_{\text{SS}}$ was 8.31×10^{-6} at 4567.2 Ma (Pb-Pb age of CAIs [12]), and the Mn-Cr ages of Renazzo and GRO carbonates are 4562.4 (+2.5/-4.8) Ma and 4554.2 (+1.6/-2.2) Ma, respectively. This means that the aqueous alteration that produced the carbonate veins in Renazzo occurred within 2-10 Myr after CAI formation. GRO, on the other hand, shows alteration as late as 11-15 Myr after CAI formation.

Renazzo carbonates have a similar $(^{53}\text{Mn}/^{55}\text{Mn})_0$ to CM carbonates $\sim 3 \times 10^{-6}$ [9]. If the RSF correction is carried out for previously published data, then Renazzo carbonates plot slightly older, but within error,

of carbonates from CI Orgueil and CI1 clasts of the Kaidun breccia ($2.8\text{--}3.0 \times 10^{-6}$) [13,14]. Newer CI measurements may range from $(3.24\text{--}4.03) \times 10^{-6}$ [15]. Secondary fayalite from MAC 88107, an ungrouped CO/CM chondrite, gives an initial ratio of $(2.45 \pm 0.33) \times 10^{-6}$ [16]. This value uses an RSF for Fe-rich olivine. Applying the same RSF corrections to previous measurements of CV fayalite increases initial ratios from 2.32×10^{-6} [17] to 3.6×10^{-6} and from 2.07×10^{-6} [18] to 3.2×10^{-6} . New measurements by [16] have a lower CV initial ratio of 2.8×10^{-6} . This places fayalite formation on CV and CO parent bodies roughly contemporaneous with carbonate production in Renazzo. However, GRO 95577 carbonates are far younger than CI, CM, CV and CO secondary phases.

The distinct ages for the Renazzo and GRO 95577 suggest that aqueous alteration on the CR parent body did not all occur in one instance, but instead was prolonged and occurred in stages. If the two meteorites come from the same CR parent body, then the GRO 95577 sample likely originated from a warmer, wetter portion of the asteroid that sustained aqueous alteration for a longer period of time. This may also explain the origin of the vein structure for the Renazzo carbonates, which could have formed during early rapid fluid advection in a drier region rather than slow diffusion through saturated matrix material.

Conclusions: We have used the Mn-Cr system to date secondary carbonates in CR chondrites. We found clear evidence for live ^{53}Mn at the time of carbonate formation for both Renazzo and GRO 95577. Absolute ages indicate that Renazzo carbonates are older than GRO carbonates, suggesting different generations of aqueous alteration on the CR parent body. Initial ratios suggest that Renazzo was aqueously altered roughly contemporaneously CM, CI, CO and CV chondrites, whereas GRO 95577 experienced later alteration.

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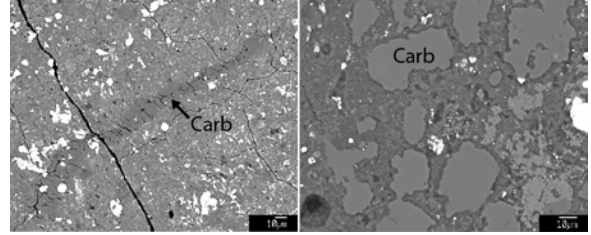


Figure 1. Carbonate vein in Renazzo n1127 (left) and multiple calcite crystals in GRO 95577-69 (right). Scale bars both 10 µm.

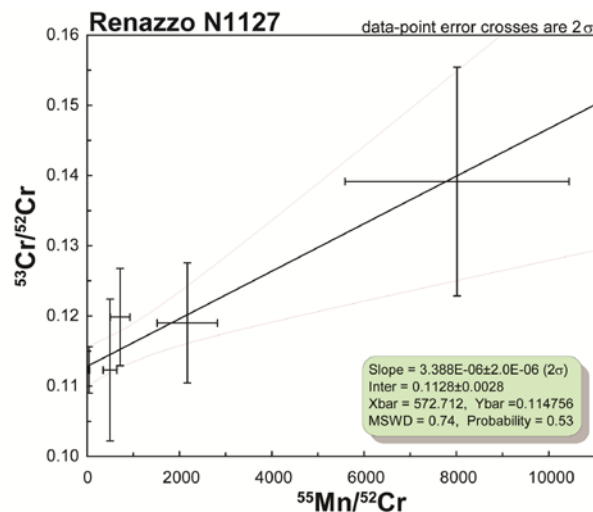


Figure 2. Mn-Cr isochron for Renazzo carbonates. Slope corresponds to initial ratio of $\sim(3.4 \pm 2.0) \times 10^{-6}$.

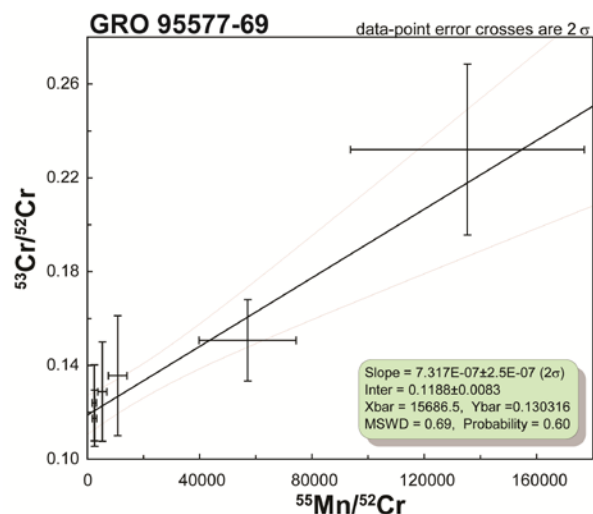


Figure 3. Mn-Cr isochron for GRO 95577-69 carbonates. Slope corresponds to initial ratio of $\sim(7.3 \pm 2.5) \times 10^{-7}$.