RADIOGENIC $^{53}$Cr* IN ORGUEIL CARBONATES: CHRONOLOGY OF AQUEOUS ACTIVITY ON THE CI PARENT BODY; Ian D. Hutchence and Douglas L. Phinney, Isotope Sciences Division, Lawrence Livermore National Laboratory, Livermore, CA, 94551.

The petrographic and mineralogical features characteristic of CI carbonaceous chondrites, including carbonate- and sulfate-filled veins [1], magnetite morphologies [2] and the ubiquitous presence of carbonates [3] provide strong evidence for the action of aqueous fluids (water) on the CI parent planetesimal. Although commonly described as "early", the time scale of aqueous alteration is not well constrained. Dolomitic (Ca-Mg) carbonates in Orgueil are characterized by very low $^{87}$Sr/$^{86}$Sr ratios, consistent with the lowest values reported for Allende, and must have been deposited within ~50 Ma of Allende refractory inclusions [4, 5], while $^{53}$Cr* excesses in some, but not all, carbonates in two CI chondrites [6, 7] suggest an even earlier onset of aqueous activity. We present here a new study of the Mn-Cr isotope system in Mn-rich carbonates (brunnerite) in Orgueil, providing unambiguous evidence of large excesses of radiogenic $^{53}$Cr* from the in situ decay of short-lived $^{53}$Mn ($t_{1/2}$ ~ 3.7 Ma). The inferred initial abundance of $^{53}$Mn, $^{53}$Mn/$^{55}$Mn ~ 2 x 10^-6, implies early formation of these Orgueil carbonates, within ~16 Ma of Allende Ca-, Al-rich inclusions [8].

The carbonates analyzed in this study occur in Orgueil as isolated grains, as described by Fredriksson and Kerridge [9], have generally irregular morphologies (although the carbonate highest in Cr$_2$O$_3$ is nearly euhedral) and range in size from ~150 to 400 µm. While the major element compositions fall within the range typical of Orgueil breunnerites [9], four of the five carbonates analyzed here are chemically heterogeneous, exhibiting large variations in Mg, Cr, Mn and Fe contents on spatial scales from < 1 to ~20 µm. The variation in MnO and Cr$_2$O$_3$ is particularly striking, as the Mn/Cr ratio varies by up to a factor of ~100 within two carbonates. Chromium isotope compositions of the Orgueil carbonates and terrestrial standards were measured with the LLNL IMS-3f ion microprobe at a mass resolving power of ~3000. Molecular interferences are fully resolved but $^{50}$Ti is an unresolved isobaric interference with $^{50}$Cr and $^{50}$Cr/$^{52}$Cr ratios were corrected for the $^{50}$Ti contribution based on $^{49}$Ti/$^{52}$Cr. The Cr isotope ratios were corrected for mass-dependent fractionation by normalizing to $^{50}$Cr/$^{52}$Cr = 0.051859 using an exponential law; deviations in $^{53}$Cr/$^{52}$Cr are reported as $\delta^{53}$Cr (‰) relative to 0.113386. $^{55}$Mn/$^{52}$Cr ratios were calculated from $^{55}$Mn*/$^{52}$Cr* using a sensitivity factor determined with synthetic silicate and phosphate standards.

The Cr isotopic compositions of five Orgueil carbonates were determined in this study. One carbonate is relatively Cr-rich with $^{55}$Mn/$^{52}$Cr of 30-40 and $\delta^{53}$Cr values of ~0, consistent with normal Cr. The remaining grains are Cr-poor with $^{55}$Mn/$^{52}$Cr ratios between ~700 and 100,000 and contain clearly resolved $^{53}$Cr excesses with enhancements in the $^{53}$Cr/$^{52}$Cr ratio of up to nearly a factor of 2.5 ($\delta^{53}$Cr = 1455 ‰). The magnitudes of the $^{53}$Cr excesses are linearly correlated with the respective $^{55}$Mn/$^{52}$Cr ratios (Fig. 1), indicative of the in situ decay of $^{53}$Mn and demonstrating that short-lived $^{53}$Mn was still extant at the time of carbonate formation on the CI parent body. The slope of the correlation line on a $^{53}$Mn-$^{53}$Cr evolution diagram (Fig. 1), determined by a weighted least squares fit to all the carbonate data, corresponds to ($^{53}$Mn/$^{55}$Mn)$_0$ = (1.97±0.18) x 10^-6. The slope is controlled by the data from grain #11, 5 analyses of which yielded $^{55}$Mn/$^{52}$Cr ratios between ~700 and 102,000 with corresponding $\delta^{53}$Cr values between ~20 and 1450 ‰. Data from carbonates #1 and 8 also lie within two standard deviations of this line but data from grains #5 and 10 lie distinctly above the line and define a second correlation line with slope corresponding to ($^{53}$Mn/$^{55}$Mn)$_0$ = (3.4±0.4) x 10^-6. This difference in slope has several possible interpretations. Petrographic evidence suggests several stages of alteration and carbonate deposition [1] and the difference in $^{53}$Cr*/$^{55}$Mn may have chronological significance, corresponding to an interval of ~ 3 Ma between episodes of aqueous activity. This scenario is similar to the variation in the times of formation of dolomites and breunnerites suggested from Sr
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isotope studies [5]. Alternatively, isotopic disequilibrium among metamorphic minerals subjected to several alteration events is not unexpected and the variation in $^{53}\text{Cr}^\ast/^{55}\text{Mn}$ may reflect either the growth of carbonates from isotopically disparate fluids or partial Cr isotopic reequilibration, similar to that observed for the Al-Mg system in CAI.

The observations of radiogenic $^{53}\text{Cr}^\ast$ in the Orgueil carbonates enable us to evaluate the time scale of aqueous activity on the CI parent body using the $^{53}\text{Mn}-^{53}\text{Cr}$ chronometer. If we assume the $^{53}\text{Mn}/^{55}\text{Mn}$ ratio of $4.4 \times 10^{-5}$, inferred from studies of Allende CAI [8], indicates the initial solar system abundance of $^{53}\text{Mn}$, and that differences in $^{53}\text{Cr}^\ast/^{55}\text{Mn}$ reflect decay of $^{53}\text{Mn}$ prior to incorporation into the host, these Orgueil carbonates were deposited ~16 Ma after crystallization of Allende CAI. Relative to bulk Orgueil ($^{53}\text{Mn}/^{55}\text{Mn} = 2 \times 10^{-5}$) [10], the time difference is ~12 Ma. This Mn-Cr chronology is in good agreement with the 50 Ma upper limit set by Sr isotope studies of Orgueil dolomites [5] and with the evidence of $^{53}\text{Cr}^\ast$ in one Ivuna carbonate [7] but is inconsistent with the conclusion that aqueous alteration leading to carbonate formation occurred > 20 Ma after (anhdyrous) parent body metamorphism [10]. The rapid time scale suggests aqueous activity on the CI parent body commenced either shortly after planetary accretion or, perhaps, occurred contemporaneously. The $^{53}\text{Cr}^\ast/^{55}\text{Mn}$ ratio in the Orgueil carbonates is similar to that found in three groups of differentiated meteorites, the angrites ($^{53}\text{Cr}^\ast/^{55}\text{Mn} \sim 1.4 \times 10^{-6}$) [11, 12], the pallasites ($^{53}\text{Cr}^\ast/^{55}\text{Mn} \sim 2.3 \times 10^{-6}$) [8] and the IIIAB irons ($^{53}\text{Cr}^\ast/^{55}\text{Mn} \sim 2.8 \times 10^{-6}$) [13], suggesting aqueous alteration on the CI parent body and cooling of the interiors of differentiated planetesimals below the respective closure temperatures for Cr diffusion in olivine and Fe-phosphate were contemporaneous events.


Figure 1: $^{53}\text{Mn} - ^{53}\text{Cr}$ evolution diagram for Orgueil Fe-Mg carbonates. Different symbols represent different grains. Line is least squares fit to all data. Uncertainties are $\pm 2\sigma$. 

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