MANGANESE-CHROMIUM SYSTEMATICS OF CALCITE IN THE CM CHONDRITES QUE 93005 AND MET 01070 DETERMINED USING A NEW MATRIX-MATCHED STANDARD. Patrick H. Donohue[1]*, Gary R. Huss[1], and Kazuhide Nagashima[1]; [1]Hawai'i Institute of Geophysics and Planetology, University of Hawai'i at Mānoa, Honolulu, Hawai'i 96822, USA (*phd2@hawaii.edu)

Introduction: All CM chondrites have experienced some degree of aqueous alteration, the products of which include carbonates [1–3]. However, many questions remain about the timing of alteration, including whether the parent body experienced a single continuous or multiple pulses of alteration, potentially recorded by multiple stages of carbonate precipitation. Much of this alteration appears to have occurred early in solar system history, within the period when ^{53}Mn was present [4–7]. ^{53}Mn is a short-lived radionuclide, decaying to ^{53}Cr with a half-life of 3.7 million years. The Mn-Cr isotopic system is a useful recorder for dating early solar system processes [5,8–10]. Meteoritic carbonates typically contain minor Mn but very little Cr, and so have high Mn/Cr ratios making them good candidates for dating. Picking apart these timescales at fine intervals requires revisiting carbonate formation using appropriate sample context, as well as new analytical standards.

Mn-Cr analysis of meteoritic carbonates requires high spatial resolution, moderate mass resolving power, and low detection limits. SIMS instruments meets these needs, but introduce a new problem in that there is a difference in the relative ionization efficiency of Mn and Cr. This can be accounted for by using a standard of known composition, but historically there were no good carbonate standards bearing Mn and Cr. This recently changed when Sugiura et al. [11] produced synthetic Mn- and Cr-bearing calcite grains. They must be used carefully due to zonation and microcrystallinity, but it is clear that these are better than previously used standards such as San Carlos olivine. Many previous studies using non-matrix-matched standards need to be revisited using matrix-matched materials. To this end, we have been developing synthetic carbonate standards. Our new Mn- and Cr-bearing synthetic calcite standard described in [12] was used here to correct the relative ionization yields of Mn and Cr.

In this study, we have obtained a new set of Mn-Cr measurements from calcite in the Queen Alexandria Range (QUE) 93005 and Meteorite Hills (MET) 01070 CM chondrites. Both are of low petrologic type (2.1 and 2.0, respectively). Additional analyses of carbonates in other CM chondrites of petrologic types 2.1 to 2.5 will be presented at the meeting.

Samples: QUE 93005 (thin section QUE 93005,9 investigated here) is a highly aqueously altered CM2.1 chondrite. The carbonate petrography of this sample has been studied in detail [1,2], including investigation of the Mn-Cr system [5,13–15]. QUE 93005 contains abundant carbonates, including calcite/aragonite (2.1 modal %), dolomite (1.8%), and rare breunnerite [14], also found in the section we studied.

MET 01070 (thin section MET 01070,40 investigated here) is among the most aqueously altered of the CM group (2.0). The carbonate petrography and Mn-Cr system has also been previously investigated [1,6,14]. MET 01070 contains abundant Ca-carbonates (1.5 modal %) and rare dolomite (absent in some thin sections) [1,6]. No dolomite was found in our section.

Isotopic Analysis: Mn and Cr isotopic compositions of calcite were measured in both meteorites. The carbonate Mn-Cr systematics have been previously investigated, providing a comparison with our data acquired using a new standard. Our measurements were made using a University of Hawai'i Cameca ims 1280 ion microprobe. Secondary ions were created using spot analysis with a ~100 pA primary beam focused to ~5×6 µm diameter. We measured for up to 125 cycles in combined multicollection and peak-jumping mode in the order: $^{52}Cr^+$ with $^{53}Cr^+$ (45 s), $^{55}Mn^+$ (2 s), and $^{40}Ca^{16}O^+$ (1.2 s). The $^{40}Ca^{16}O^+$ mass was monitored to assess beam stability. Repeat measurements of a new calcite standard yielded an average relative sensitivity factor (RSF) of 0.61 ± 0.08 (n = 11). Because many meteoritic analyses did not run for the full 125 cycles, the RSF was recalculated to the appropriate number of cycles for these analyses because the RSF changes as a function of analysis time (e.g., due to pit depth, charge build up).

We analyzed two Ca-carbonate grains in QUE 93005,9, and nine in MET 01070,40, and obtained multiple measurements on some grains (Fig. 1). Both samples show correlations of excess ^{53}Cr with higher $^{55}Mn/^{52}Cr$ ratios, supporting the *in situ* decay of ^{53}Mn. The initial $^{53}Mn/^{55}Mn$ ratios, $(^{53}Mn/^{55}Mn)_0$, were calculated from the slopes of the internal isochrons (a model isochron in the case of QUE 93005). The $(^{53}Mn/^{55}Mn)_0$ were $(5.0 \pm 0.6) \times 10^{-6}$ for QUE 93005, and $(3.8 \pm 0.4) \times 10^{-6}$ for MET 01070. Assuming a homogenous ^{53}Mn distribution in the early solar system, the initial ratios for the meteorites can be used to calculate absolute ages. We anchor to the D'Orbigny angrite using its calculated $(^{53}Mn/^{55}Mn)_0$ ratio of $(3.8 \pm 0.4) \times 10^{-6}$ [16] and U-isotope-corrected Pb-Pb age of 4563.37 ± 0.25 [17,18]. The absolute age of carbonate formation in QUE 93005 is $4565.7^{+1.4}_{-1.1}$ Myr, and for MET 01070 the carbonate absolute age is $4564.2^{+1.5}_{-1.2}$ Myr. Relative to the CAI formation age of 4567.3 ± 0.16 [Pb-Pb; 17], the ages correspond to calcite formation at $1.6^{+1.4}_{-1.1}$ Myr after CAIs for QUE 93005 and $3.1^{+1.5}_{-1.2}$ Myr for MET 01070.

Discussion: The Mn-Cr systematics of QUE 93005 are within uncertainty of findings from previous $(^{53}Mn/^{55}Mn)_0$ determinations of (4.1 ± 1.2) × 10^{-6} [5] and (4.37 ± 0.19) × 10^{-6} [15] for carbonates within the sample, primarily analyzing dolomite. These correspond to relative ages of 3.1 ± 1.3 Myr and 2.8 ± 0.2 Myr after CAIs, respectively. However, the prior analyses were not obtained using matrix-matched standards. We have yet to re-analyze dolomite in the sample using a matrix-matched standard. A dolomite standard for RSF corrections is in development [12] and will be used to obtain more accurate Mn-Cr systematics for this phase. Dolomite in CM chondrites typically contains a few weight percent Mn, in contrast to calcite (generally <1 wt.% Mn), and so analysis of dolomite will provide more constraints on the Mn-Cr isochron.

The petrography of carbonates in MET 01070 have been previously investigated [1,5,6,14], but this is the first result for Mn-Cr systematics. A prior study found the Mn/Cr ratios of carbonates in the sample were <1000 [5], too low for SIMS measurements, but we located several grains with high ratios ($^{55}Mn/^{52}Cr$ up to 22,000). A recent C and O isotope study of MET 01070 found a bimodal distribution of C and O isotopes, suggesting at least two populations of calcite in the sample. The Mn-Cr results presented here do not require multiple populations. However, we continue investigations of petrographic relationships to look for other potential candidates for SIMS analysis. The timing of carbonate formation of this highly altered sample is consistent with previously discussed CM chondrite carbonates.

The ages for QUE 93005 and MET 01070 calcite formation overlap within uncertainty. These CM chondrites have experienced similar degrees of aqueous alteration (being types 2.1 and 2.0, respectively). The apparent spread of ages between the two is suggestive of temporally distinct periods of alteration for the two meteorites. This may result from the meteorites originating on distinct bodies of different size. Alternatively, they may have formed at different depths or environments within the same parent body. After 2010 when the MnCr-calcite standard was synthesized by [11], several studies have used it in reassessing Mn-Cr systematics of CM chondrite carbonates. Calcite in Murchison (CM 2.5) and Yamato 791198 (CM 2.4), and dolomite in Allan Hills (ALH) 83100 (CM 2.1) and Sayama (CM 2.1) yielded consistent formation ages of $4563.4^{+0.4}_{-0.5}$ Myr [19]. Sutter's Mill (CM 2.0/2.1) dolomite Mn-Cr age of $4563.7^{+1.1}_{-1.5}$ Myr also overlaps this range [20]. Our $4565.7^{+1.4}_{-1.1}$ Myr age for QUE 93005 calcite crystallization is potentially older than these samples, and would require rapid accretion and aqueous alteration of the parent body, but the age is currently based on a model isochron. Additional analyses of calcite should further refine the QUE 93005 isochron. We have also identified dolomite within the sample that will be analyzed once we have an appropriate standard [see ref. 12]. Further refining these relationships will require careful selection and characterization of additional carbonate phases for analysis.

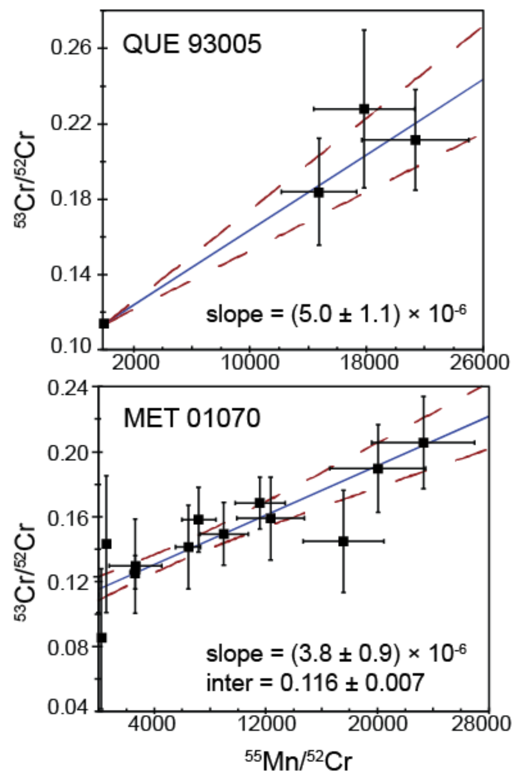

Fig. 1. $^{52}Cr/^{53}Cr$ vs. $^{55}Mn/^{52}Cr$ ratios of Ca-carbonates in QUE 93005,9 and MET 01070,40. The intercept for QUE 93005 has been forced through the intercept using average values from standard analyses. Fitted line (solid) and error envelopes (dashed) calculated using Isoplot [21].

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