

^{53}Mn – ^{53}Cr systematics of carbonates in CM chondrites: Implications for the timing and duration of aqueous alteration

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Abstract

CM chondrites contain carbonates and other secondary minerals such as phyllosilicates, sulfides, sulfates, oxides and hydroxides that are believed to have formed by aqueous alteration reactions on their parent asteroid. We report *in situ* Mn–Cr isotope measurements in the highly aqueously altered CM2.1 chondrites QUE 93005 and ALH 83100 using secondary ion mass spectrometry (Cameca ims-1270 ion microprobe). The ^{53}Cr excesses are correlated with the $^{53}\text{Mn}/^{55}\text{Mn}$ ratio and result from the *in situ* decay of ^{53}Mn , a short-lived radioisotope with a half-life of 3.7 Ma. If we assume that carbonate grains in samples QUE 93005 and ALH 83100 are cogenetic, then the excesses define initial $^{53}\text{Mn}/^{55}\text{Mn}$ ratios ($^{53}\text{Mn}/^{55}\text{Mn}_0$) of $(4.1 \pm 1.2) \times 10^{-6}$ and $(5.1 \pm 1.7) \times 10^{-6}$, respectively. These values are comparable to those in carbonates from other CM chondrites as reported in the literature. Initial $^{53}\text{Mn}/^{55}\text{Mn}$ ratios for calculated model isochrones for individual carbonate grains range from $(3.8 \pm 1.4) \times 10^{-6}$ to $(4.8 \pm 2.1) \times 10^{-6}$ for QUE 93005 and from $(3.1 \pm 1.6) \times 10^{-6}$ to $(1.3 \pm 0.5) \times 10^{-5}$ for ALH 83100. A possible interpretation for the ranges in $^{53}\text{Mn}/^{55}\text{Mn}_0$ could be that alteration in individual CM chondrites was episodic and occurred over an extended period of time. However, isochrones based on the entire set of carbonate grains in each of the CM chondrites imply that the degree of aqueous alteration is roughly correlated with the age of carbonate formation in CM chondrites of different subtypes and that alteration on the CM parent asteroid started contemporaneously with or shortly after CAI formation and lasted at least 4 Ma.

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1. INTRODUCTION

CM chondrites consist mainly of chondrules, Ca–Al-rich inclusions (CAIs) and matrix material. Aqueous alteration in CM chondrites produced secondary phases such as carbonates, phyllosilicates, sulfides, sulfates, oxides, and hydroxides (e.g., Zolensky and McSween, 1988; Brearley and Jones, 1998). Little is known about the timescale and location of these alteration processes. Models range from

progressive alteration within an asteroidal environment (McSween, 1987; Zolensky and McSween, 1988; Rubin et al., 2007) to the possibility that significant alteration occurred in small precursor planetesimals prior to the formation of the CM asteroid (Bischoff, 1998). These models may be testable by determining absolute ages for carbonate formation in CM chondrites.

The generally accepted view is that aqueous alteration of CM chondrites was asteroidal (e.g., McSween, 1979; Bunch and Chang, 1980; Grimm and McSween, 1989; Tomeoka et al., 1989; Brearley and Geiger, 1991). Veining in CM chondrites, bulk compositional homogeneity, and the ubiquity of chondrule alteration are seen as evidence for asteroidal alteration of CM chondrites. However, Bischoff (1998) suggested that both parent body and pre-accretion-

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ary alteration occurred in CM chondrites. Based on the relationship between fine-grained rims and the coarse objects they surround (CAIs, chondrules and chondrule fragments) as well as the mineral assemblages present in the rims themselves, Metzler et al. (1992) and Bischoff (1998) concluded that CM chondrites experienced pre-accretionary alteration. This conclusion was challenged by Trigo-Rodriguez et al. (2006) who suggested that fine-grained rims in CM chondrites were produced from porous nebular materials on the CM parent asteroid by impact compaction, followed by aqueous alteration. If CM chondrites experienced pre-accretionary alteration, it was likely overprinted by subsequent aqueous alteration on the CM parent asteroid.

There is increasing evidence for a wide range of CM aqueous alteration (e.g., Browning et al., 1996; Zolensky et al., 1997; Hanowski and Brearley, 2000; Rubin et al., 2007). In 2007, Rubin et al. proposed a new alteration sequence for CM chondrites that correlates with their major mineralogical and textural characteristics. These include hydration of matrix material, alteration of primary igneous glass in chondrules, production of large PCP clumps (“poorly characterized phases” corresponding to tochilinite–cronstedtite intergrowths), oxidation of metallic Fe–Ni, alteration of chondrule phenocrysts, changes in PCP composition, and development of carbonates. Rubin et al. (2007) assigned petrologic subtypes ranging from 2.6 for the least-altered samples to 2.0 for the most highly altered CM chondrites. Based on the presence of abundant chondrule pseudomorphs in completely aqueously altered CM chondrites and their absence in CI chondrites, Rubin et al. (2007) reclassified CM1 chondrites as CM2.0. Alteration products such as carbonates can potentially provide a record of the timing of aqueous alteration.

There are only a few isotope systems that allow determination of the timing of aqueous alteration processes in carbonaceous chondrites. One method is based on the long-lived Rb–Sr system (Macedougall et al., 1984); an alternate approach is to use short-lived radionuclides such as ^{53}Mn and ^{129}I (e.g., Hohenberg et al., 2000; Pravdivtseva et al., 2003) with half-lives of 3.7 and 15.7 Myr, respectively. Several ^{53}Mn – ^{53}Cr studies (^{53}Mn decays to ^{53}Cr) have been carried out analyzing carbonates in CM and CI chondrites showing that initial $^{53}\text{Mn}/^{55}\text{Mn}$ ratios in carbonates range from $(9.4 \pm 3.6) \times 10^{-6}$ to $(0.58 \pm 0.06) \times 10^{-6}$ (e.g., Endress et al., 1996; Hutcheon et al., 1999; Brearley and Hutcheon, 2000, 2002; Brearley et al., 2001; de Leuw et al., 2007, 2009; Hoppe et al., 2007, 2008; Petitat et al., 2009a,b; Tyra et al., 2009). Here, we report Mn–Cr isotope measurements of carbonates in the CM chondrites QUE 93005 and ALH 83100 to determine whether alteration times can be resolved and, if so, whether the duration and timing of alteration correlate with the degree of aqueous alteration.

2. SAMPLES AND ANALYTICAL TECHNIQUES

We studied the mineralogical and petrographic characteristics of carbonates in seven CM chondrites of different petrographic subtypes (e.g., CM2.4 Y-791198, CM2.4 LAP

04796, CM2.2 Cold Bokkeveld, CM2.2 Nogoya, CM2.1 QUE 93005, CM2.1 ALH 83100, and CM2.0 MET 01070) and determined their compositions with the UCLA JEOL JXA-8200 electron microprobe. Detailed descriptions of these carbonates are in de Leuw et al. (2008). Carbonates in CM chondrites are relatively abundant (~ 1.4 – 2.8 vol.%) and randomly distributed in the thin sections. Two distinct types of carbonate are found in CM chondrites: calcite/aragonite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$). Calcite/aragonite is the dominant phase in CM chondrites; dolomite is much less abundant. Of the seven studied CM chondrites, all contain calcite/aragonite, but only Cold Bokkeveld, Nogoya, QUE 93005 and ALH 83100 contain dolomite (Johnson and Prinz, 1991; Johnson and Prinz, 1993; Zolensky et al., 1997; de Leuw et al., 2008). The only carbonates with high Mn/Cr ratios (>1000) suitable for Mn–Cr isotope studies using SIMS were dolomites in QUE 93005 and ALH 83100.

Isotopic analyses were carried out by large-radius magnetic-sector secondary ion mass spectrometry (SIMS) using the Cameca ims-1270 ion microprobe at UCLA (backscattered electron images of measured carbonate grains are presented in electronic annex EA-1). Chromium-isotope measurements were initially performed using monocollection electron multiplier (EM axial ETP electron multiplier) with magnetic field peak-switching (sample QUE 93005). After these initial experiments, we subsequently developed a combined peak-switching and multicollection analysis mode (using Hamamatsu electron multiplier (EM) and a Faraday cup (FC)) in order to reduce the total analysis time, thus reducing the risk of sputtering into the matrix below the carbonate grains (sample ALH 83100).

In monocollection mode, a $^{16}\text{O}^-$ primary beam at ~ 0.6 nA to ~ 1.2 nA with a total impact energy of 22.5 keV was used to generate positive secondary ions by focusing them into a spot of ~ 10 μm in diameter by using a 50- μm primary beam aperture in Köhler illumination. Secondary ions were accelerated by a 10 kV extraction potential and sampled with a 50 eV energy window. The mass resolving power was ~ 4800 ($m/\Delta m$), large enough to resolve potential interferences at masses 52, 53 and 55 such as $^{24}\text{Mg}^{28}\text{Si}^+$, $^{25}\text{Mg}^{28}\text{Si}^+$, $^{26}\text{Mg}^{27}\text{Al}^+$, and $^{28}\text{Si}^{27}\text{Al}^+$. Under these conditions, $^{50}\text{Ti}^+$ and $^{50}\text{V}^+$ are irresolvable isobaric interferences at mass/charge $^{50}\text{Cr}^+$. The $^{50}\text{Cr}/^{52}\text{Cr}$ ratios were therefore corrected for the ^{50}Ti and ^{50}V contributions based on measured $^{49}\text{Ti}/^{52}\text{Cr}$ and $^{51}\text{V}/^{52}\text{Cr}$, respectively. Hydrides such as $^{52}\text{CrH}^+$ and $^{54}\text{CrH}^+ / ^{54}\text{FeH}^+$ are also irresolvable from ^{53}Cr and ^{55}Mn at $m/\Delta m = 4800$. Hutcheon et al. (1998) showed that the contributions of these hydrides were $<1\%$, and consequently, could be neglected. Secondary ion intensities were further corrected for background (measured on mass 53.3) and dead time (25 ns). Individual analyses consisted of 120 cycles, each cycle representing one pass through the masses 48.7, ^{49}Ti , ^{50}Cr , ^{51}V , ^{52}Cr , ^{53}Cr , 53.3 and ^{55}Mn .

In multicollection mode, higher primary beam currents (~ 9 – 10 nA) were used in critical focusing mode which allowed a higher beam density to be delivered into a 10- μm -diameter spot. The mass resolving power ($m/\Delta m$) was ~ 6000 , large enough to resolve all potential interferences

(except for isobars and hydrides). For multicollection analyses, the detector configuration was chosen so that the following masses were analyzed during a single magnet cycle with five magnetic field switches: (1) background at mass/charge = 48.5 (L2; EM), (2) ^{50}Cr (H1; EM), (3) ^{51}V (H2; EM), (4) ^{49}Ti (L2; EM), ^{52}Cr (H1; EM), ^{53}Cr (H2; EM), background at mass/charge = 54.9 (H²; FC) and (5) ^{55}Mn (H2; EM).

Isotope ratios for San Carlos olivine were corrected for mass-dependent fractionation using an exponential law after normalizing to $^{50}\text{Cr}/^{52}\text{Cr} = 0.051859$. Mass fractionation in carbonates was corrected externally, i.e., $^{53}\text{Cr}/^{52}\text{Cr}$ ratios in QUE 93005 and ALH 83100 carbonates were normalized relative to the average value of the $^{53}\text{Cr}/^{52}\text{Cr}$ ratios measured in San Carlos olivine. Deviations in $^{53}\text{Cr}/^{52}\text{Cr}$ ratios are reported as $\delta^{53}\text{Cr}$ (‰) relative to the terrestrial ratio of 0.113459 (Papanastassiou, 1986). We used San Carlos olivine as a reference material to test for accuracy and precision of the corrections. $^{55}\text{Mn}/^{52}\text{Cr}$ ratios were calculated from $^{55}\text{Mn}^+ / ^{52}\text{Cr}^+$ using the sensitivity factor determined from San Carlos olivine ($^{55}\text{Mn}/^{52}\text{Cr} = 10.93$; Hoppe et al., 2007). We are aware that using olivine for the calibration of $^{55}\text{Mn}/^{52}\text{Cr}$ is problematic as the relative sensitivity factors differ between carbonates and olivine; thus, all ages reported here may be systematically biased (Sugiura et al., 2009). Nevertheless, the relative timing for carbonate formation is not affected because all data shown in Figs. 4 and 5 were determined using instrumental fractionation factors determined on the San Carlos olivine standard. *In situ* secondary ion mass spectrometric analysis of carbonates requires samples with high Mn/Cr ratios, preferably >1000. Although many CM carbonates have such high ratios, analyses were frequently compromised by sub-micrometer Cr-rich inclusions present in carbonates or from beam overlap of the primary ion beam onto the matrix. Alignment of the primary beam to locate regions free of extraneous Cr, and blocking ions from the periphery of the crater were aided by ion imaging and narrowing the dimensions of the field aperture in the secondary beam path.

3. MINERALOGY AND PETROGRAPHY OF CARBONATES IN QUE 93005 AND ALH 83100

As described by de Leuw et al. (2008), we analyzed more than 60 carbonate grains in QUE 93005 by electron microprobe. The bulk carbonate abundance in this meteorite is about 2.3 vol.%. Throughout this paper we refer to the CaCO_3 phase as calcite even though we do not have X-ray data confirming this identification. Calcite occurs as irregularly shaped aggregates ranging between 50 and 100 μm ; dolomite occurs as single crystals in the matrix. Representative calcite and dolomite grains are shown in Fig. 1a and b. Dolomite grains in QUE 93005 range from 10 to 30 μm and are smaller than co-existing calcite. Both calcite and dolomite are randomly distributed within the thin section and no petrographic correlation between these two phases was observed. A prominent feature of dolomite in QUE 93005 is that each single dolomite crystal is surrounded by a thin, feathery pentlandite rim (Fig. 1b). In contrast, most calcite aggregates contain patches of blocky

pentlandite, pyrrhotite and “intermediate sulfides” containing moderate amounts of Ni (Chokai et al., 2004) (Fig. 1a). All analyzed carbonates in QUE 93005 contain significant amounts of MgO, MnO and FeO. Dolomites have much higher MnO and FeO contents than co-existing calcites (up to 5.0 and 8.0 wt.% versus 1.1 and 0.91 wt.%, respectively).

ALH 83100 has a slightly higher carbonate content than QUE 93005; the total carbonate content in ALH 83100 is about 2.8 vol.%. Carbonates range between 20 and 100 μm in size; about 60 carbonate grains were analyzed by electron microprobe. Carbonates are found mainly within the matrix (Fig. 1c and d). In rare cases carbonates were found in the cores of replaced chondrules. Compared to dolomites in QUE 93005, none of the dolomites in ALH 83100 is surrounded by a thin, feathery pentlandite rim. Dolomites in ALH 83100 have higher MnO and FeO contents than calcite (up to 3.8 and 5.4 wt.% versus 0.48 and 0.88 wt.%, respectively). In both ALH 83100 and QUE 93005, the Cr contents in the secondary carbonates are below the detection limit of the electron probe (<0.04 wt.%).

Brearley and Hutcheon (2000, 2002) and Brearley et al. (2001) reported zoning in carbonates from other CM chondrites studied using cathodoluminescence (CL). We observed no compositional zoning in carbonates studied by SEM and EPMA (no CL has been used, however).

A unique feature of dolomites in CM chondrites is that they deviate from the typical 1:1 Ca–Mg stoichiometry, all having Ca/Mg ratios >1, making them different from dolomites in the more-altered CI carbonaceous chondrites. Our study focuses on large carbonate grains with high Mn/Cr ratios (>1000) that were free of inclusions and any visible cracks. To minimize the statistical uncertainty, we used a beam spot $\geq 10 \mu\text{m}$ in diameter and thus required a minimum crystal size of $\sim 15 \mu\text{m}$. It is important to have crystals with high Mn and very low Cr contents; this combination can yield a high abundance of radiogenic ^{53}Cr relative to non-radiogenic ^{53}Cr .

4. ISOTOPIC COMPOSITIONS OF QUE 93005 AND ALH 83100

We determined Mn–Cr systematics of 11 carbonate grains from CM2.1 QUE 93005 and 12 carbonate grains from CM2.1 ALH 83100 (Table 1 and 2). We obtained replicate analyses on eight carbonates from QUE 93005 and three carbonate grains from ALH 83100, for a total of 35 measurements (20 for QUE 93005 and 15 for ALH 83100). Variations in the Mn/Cr ratios between two spots of an individual crystal reflect the heterogeneity in the Cr content of the carbonates (Table 2). Eight measurements in QUE 93005 showed excesses in ^{53}Cr with the highest excess of $\sim 1100\text{‰}$ and a Mn/Cr ratio of $\sim 34,500$. Six measurements in ALH 83100 showed excesses, with the highest $\delta^{53}\text{Cr}$ value of $\sim 170\text{‰}$ and a Mn/Cr ratio of ~ 3300 . The remaining measurements show no resolvable excesses of ^{53}Cr . The ^{53}Cr excesses in both samples are linearly correlated with the $^{53}\text{Mn}/^{55}\text{Mn}$ ratio, indicating the *in situ* decay of ^{53}Mn at the time of carbonate formation, demonstrating that ^{53}Mn was still extant at the time the carbonates formed. Assuming

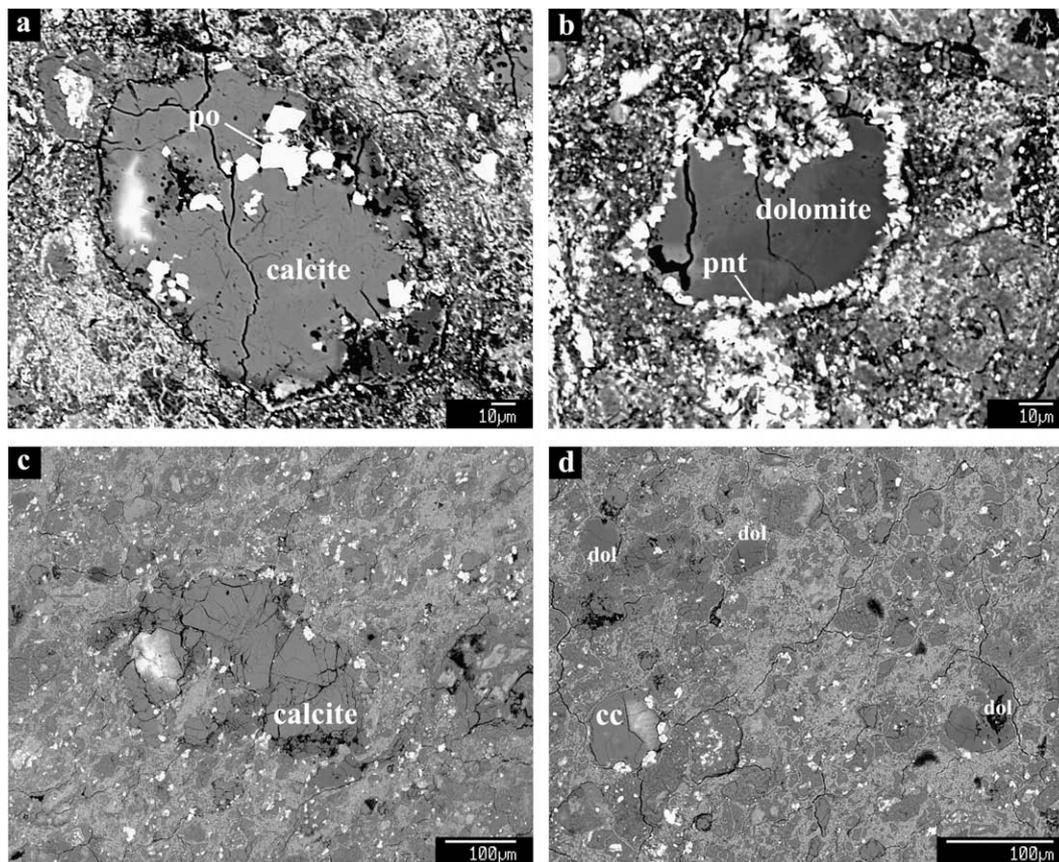


Fig. 1. Backscattered electron images of representative calcite (CC) and dolomite (dol) grains in samples QUE 93005 and ALH 83100. (a) Calcite grains in QUE 93005 are associated with blocky pyrrhotite (po). (b) Single dolomite grains in QUE 93005 are surrounded by a feathery pentlandite rim. Calcite (c) grains in ALH 83100 are similar to the ones in QUE 93005; dolomite grains (d) are not surrounded by a pentlandite rim such as occurs in QUE 93005.

Table 1

Electron microprobe analyses (in mol%) of measured calcites (cc) and dolomites (dol) in the CM2.1 chondrites QUE 93005 and ALH 83100.

| QUE 93005 | dol-1 | dol-2 | dol-3 | dol-4 | dol-5 | dol-6 | dol-7 | dol-8 | dol-9 | cc-1 | cc-2 | |
|-------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|--------|--------|
| CaCO ₃ | 54.4 | 50.3 | 49.8 | 51.3 | 50.1 | 53.8 | 50.9 | 54.2 | 54.8 | 83.9 | 97.4 | |
| SrCO ₃ | b.d. | b.d. | 0.05 | b.d. | 0.05 | 0.07 | b.d. | b.d. | b.d. | 0.07 | b.d. | |
| MgCO ₃ | 36.7 | 37.3 | 32.8 | 33.1 | 40.8 | 38.0 | 31.7 | 33.6 | 34.3 | 9.1 | 0.57 | |
| MnCO ₃ | 3.7 | 3.7 | 6.6 | 6.6 | 3.6 | 3.6 | 6.9 | 4.8 | 4.9 | 1.6 | 1.1 | |
| FeCO ₃ | 5.1 | 8.6 | 10.7 | 9.0 | 5.5 | 4.6 | 10.5 | 7.4 | 5.9 | 5.3 | 0.88 | |
| ALH 83100 | dol-1 | dol-2 | dol-3 | dol-4 | dol-5 | dol-6 | dol-7 | dol-8 | dol-9 | dol-10 | dol-11 | dol-12 |
| CaCO ₃ | 52.4 | 51.5 | 48.5 | 50.2 | 51.5 | 52.7 | 51.8 | 51.3 | 51.2 | 53.2 | 52.0 | 48.8 |
| SrCO ₃ | 0.05 | 0.05 | 0.06 | b.d. | b.d. | b.d. |
| MgCO ₃ | 40.3 | 40.1 | 39.2 | 39.6 | 39.4 | 39.7 | 41.4 | 42.9 | 41.2 | 39.4 | 40.3 | 41.3 |
| MnCO ₃ | 2.9 | 2.8 | 4.9 | 3.4 | 3.5 | 3.1 | 2.6 | 1.7 | 2.7 | 3.1 | 2.9 | 2.8 |
| FeCO ₃ | 4.3 | 5.5 | 7.4 | 6.8 | 5.6 | 4.6 | 4.2 | 4.2 | 4.8 | 4.4 | 4.7 | 7.0 |

b.d., below detection limit of 0.04 wt.%

that the carbonates in each sample formed simultaneously, the slopes of the correlation lines, determined by a weighted least-squares fit, correspond to initial $^{53}\text{Mn}/^{55}\text{Mn}$ ratios of $(4.1 \pm 1.2) \times 10^{-6}$ (2σ error) for QUE 93005 (Fig. 2) and $(5.1 \pm 1.7) \times 10^{-6}$ (2σ error) for ALH 83100 (Fig. 3). These values are in agreement with a previous study of carbonates from ALH 84034 by Brearley and Hutcheon (2000). Solid

correlation lines in Figs. 2 and 3 assume that the measured carbonate grains in samples QUE 93005 and ALH 83100 are cogenetic. However, several authors (e.g., Hoppe et al., 2007, 2008; Petitat et al., 2009a,b) have shown that internal isochrones of individual carbonate grains have a spread in their initial $^{53}\text{Mn}/^{55}\text{Mn}$ ratios, ranging from $(0.58 \pm 0.06) \times 10^{-6}$ to $(2.21 \pm 0.16) \times 10^{-6}$ (Petitat et al.,

Table 2

Cr-isotopic composition of QUE 93005 and ALH 83100 carbonates. Note that most carbonates were analyzed in duplicate.

| Sample | $\delta^{53}\text{Cr} \pm 1 \text{ s.e.}$ | $^{55}\text{Mn}/^{52}\text{Cr} \pm 1 \text{ s.e.}$ |
|-------------------------------|---|--|
| <i>QUE 93005</i> ^a | | |
| dol-1 | 6.2 ± 12.6 | 4.9 ± 0.3 |
| dol-2 | 13.3 ± 6.7 | 157 ± 1 |
| dol-2 | −5.9 ± 10.3 | 301 ± 9 |
| dol-3 | 10.6 ± 5.0 | 217 ± 4 |
| dol-3 | 33.6 ± 10.2 | 725 ± 57 |
| dol-4 | 278 ± 30 | 6454 ± 633 |
| dol-4 | 111 ± 23 | 1692 ± 137 |
| dol-5 | −1.4 ± 2.1 | 29.1 ± 0.2 |
| dol-5 | 39.2 ± 14.4 | 1081 ± 16 |
| dol-6 | 7.1 ± 1.5 | 1.9 ± 0.01 |
| dol-6 | 5.3 ± 1.7 | 7.2 ± 0.01 |
| dol-6 | 7.2 ± 5.8 | 249 ± 10 |
| dol-7 | 16.8 ± 6.0 | 471 ± 4 |
| dol-7 | 1110 ± 47 | 34,494 ± 2003 |
| dol-8 | −1.6 ± 0.6 | 0.8 ± 0.01 |
| dol-9 | −4.2 ± 2.6 | 25.1 ± 0.4 |
| dol-9 | 1.0 ± 2.7 | 71.1 ± 0.7 |
| cc-1 | 0.8 ± 2.3 | 13.3 ± 0.1 |
| cc-1 | −4.6 ± 2.4 | 17.2 ± 0.1 |
| cc-2 | 22.9 ± 12.6 | 274 ± 14 |
| <i>ALH 83100</i> ^b | | |
| dol-1 | −3.7 ± 0.6 | 14.8 ± 0.1 |
| dol-1 | 155 ± 24 | 1262 ± 132 |
| dol-2 | −4.1 ± 1.2 | 36.3 ± 1.6 |
| dol-3 | −2.5 ± 0.9 | 24.5 ± 0.8 |
| dol-4 | 14.0 ± 6.6 | 556 ± 38 |
| dol-5 | −2.1 ± 1.7 | 34.4 ± 0.4 |
| dol-6 | 0.0 ± 5.9 | 299 ± 13 |
| dol-6 | 104 ± 17 | 1708 ± 170 |
| dol-7 | −2.0 ± 1.6 | 28.4 ± 0.2 |
| dol-8 | −0.6 ± 1.3 | 30.1 ± 1.4 |
| dol-9 | 23.0 ± 10.5 | 782 ± 42 |
| dol-10 | 34.9 ± 16.7 | 1713 ± 44 |
| dol-11 | 61.6 ± 19.5 | 1430 ± 68 |
| dol-12 | 170 ± 29 | 3332 ± 262 |
| dol-12 | 20.7 ± 9.7 | 425 ± 39 |

Replicate analyses (labeled with the same number) of an individual grain display variations in the Mn/Cr ratio. 1 s.e. = 1 standard error.

^a Measured in monocollection mode.

^b Measured in multicollection mode.

2009a,b) and 2.1×10^{-6} to 3.4×10^{-6} (Hoppe et al., 2007) for Orgueil breunnerites and from $(3.20 \pm 0.30) \times 10^{-6}$ to $(6.26 \pm 0.80) \times 10^{-6}$ (Petitat et al., 2009a,b) and 3.7×10^{-6} to 4.7×10^{-6} (Hoppe et al., 2007) for Orgueil dolomites. If we assume that dol-7 and dol-4 (see Table 2) in QUE 93005 represent carbonates that formed during different alteration episodes and if we calculate new isochrones excluding either dol-7 or dol-4 from the calculations, we get initial $^{55}\text{Mn}/^{55}\text{Mn}$ ratios of $(4.8 \pm 2.1) \times 10^{-6}$ and $(3.8 \pm 1.4) \times 10^{-6}$, respectively (new isochrones are represented by dashed and dotted lines in Fig. 2). If we do similar calculations for ALH 83100, we obtain initial $^{55}\text{Mn}/^{55}\text{Mn}$ ratios ranging from $(3.1 \pm 1.6) \times 10^{-6}$ to $(1.3 \pm 0.5) \times 10^{-5}$ (represented by dashed and dotted lines in Fig. 3). However, the relatively high $^{55}\text{Mn}/^{55}\text{Mn}$ initial ratio of $(1.3 \pm 0.5) \times 10^{-5}$ is con-

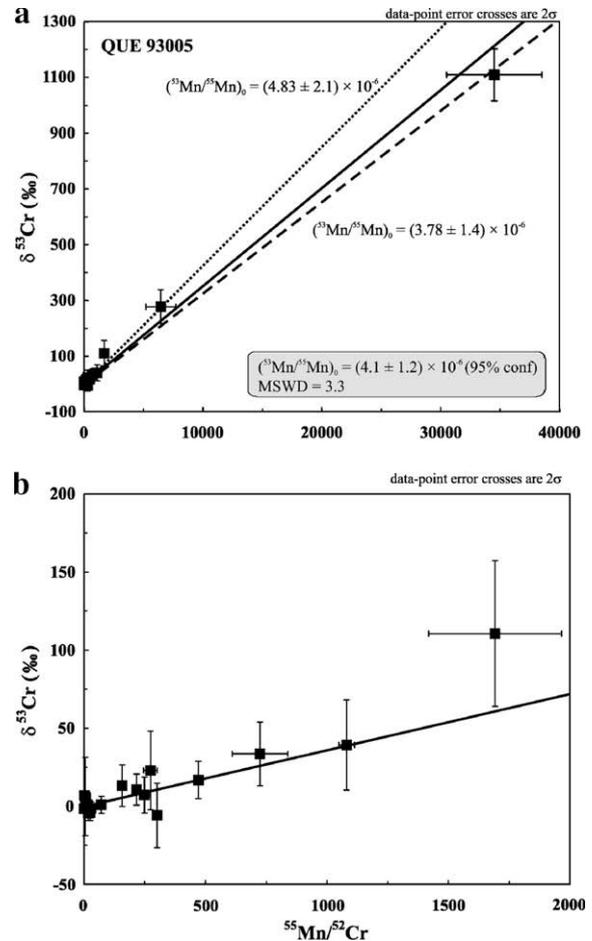


Fig. 2. (a) ^{53}Mn – ^{53}Cr evolution diagram for eleven carbonate grains in the CM2.1 chondrite QUE 93005. (b) An expanded-scale view of a part of the plot near the origin. The data are plotted as $\delta^{53}\text{Cr}$, the per mil deviation from the $^{53}\text{Cr}/^{52}\text{Cr}$ ratio measured in the San Carlos olivine standard. The slope of the line fitted to all data yields the initial $^{55}\text{Mn}/^{55}\text{Mn}$ ratio (solid line). Dotted and dashed correlation lines are calculated assuming that each excess represents a distinct alteration event; these calculations probably show that alteration was episodic and occurred over an extended period of time. (MSWD = mean square weighted deviation).

trolled by one outlier (dol-1) which can either be real (and therefore represents a distinct alteration event that occurred much earlier) or an analytical artifact. If the calculated isochrones that are based on single data points that show excesses in ^{53}Cr were included, a possible interpretation would be that alteration in CM chondrites was episodic and occurred over an extended period of time.

We recently showed (de Leuw et al., 2008) that calcite formation occurred in the least-altered CM chondrites and that with progressive aqueous alteration, formation of more complex carbonates (e.g., dolomite) occurred. Because initial $^{55}\text{Mn}/^{55}\text{Mn}$ ratios are the highest in carbonates from the least-altered samples (e.g., CM2.4) and thus yield the oldest ages, we exclude the model that carbonate formation in CM chondrites of lower petrographic subtype (e.g., CM2.1) formed earlier and re-equilibrated continuously. We therefore favor the working model that aqueous

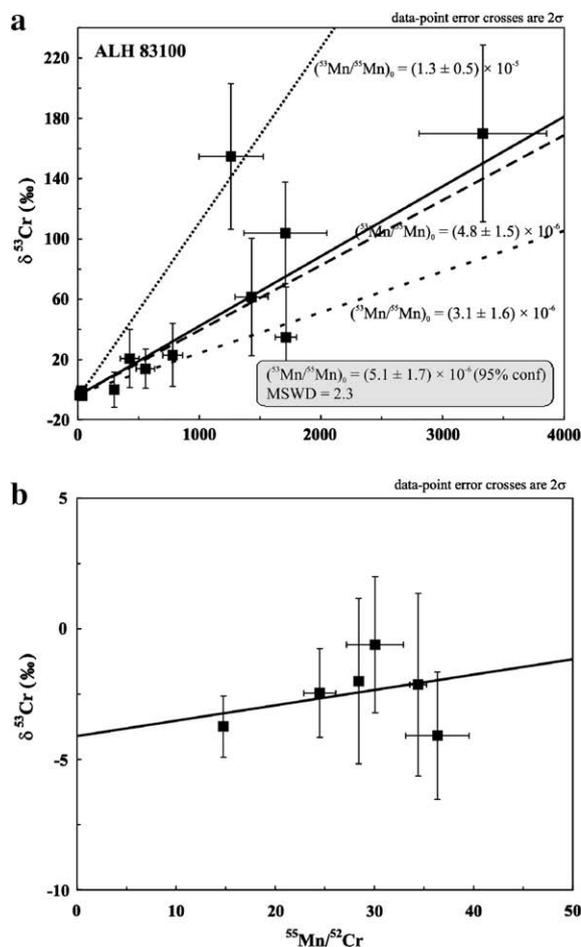


Fig. 3. (a) ^{53}Mn – ^{53}Cr evolution diagram for twelve carbonate grains in the CM2.1 chondrite ALH 83100. (b) Expanded-scale view of a part of the diagram near the origin. Deviation from the terrestrial standard are plotted as δ values (‰ deviations). Excesses of ^{53}Cr are observed and indicate the presence of live ^{53}Mn at the time of carbonate formation. The best-fit slope through all data points gives the initial $^{53}\text{Mn}/^{55}\text{Mn}$ ratio (solid line); dashed and dotted correlation lines are calculated based on individual data points that show excesses in ^{53}Cr .

alteration started contemporaneously throughout the CM parent body and that CM chondrites of lower petrographic subtype experienced alteration over a longer period of time than CM chondrites of higher petrographic subtype. One would expect to find a spread of Mn–Cr ages in an individual chondrite of lower petrographic subtype, but due to analytical limitations we were only able to measure dolomite grains in CM chondrites; these grains alone have Mn/Cr ratios high enough to make them suitable for isotopic measurements. [If they could be measured, co-existing calcite grains would probably yield older ages as they are expected to have formed before dolomite.] Because carbonates in the analyzed samples were relatively small compared to the beam size of the ion probe, we were not able to produce real internal isochrones of single dolomite grains. Even though Brearley and Hutcheon (2000, 2002) showed that carbonate grains were zoned and thus the cores of

these grains should have older ages than the surrounding concentric zones, measurement with a wide ion beam will yield average grain ages. Therefore, in our discussion below, we use isochrones that are based on the entire set of carbonate grains in each of the CM chondrites. Because we measured the final carbonate products that formed during aqueous alteration, the slope of the “bulk” correlation line can be used to infer the average time of carbonate formation in CM chondrites.

5. DISCUSSION

Several schemes have been proposed to rank the degree of alteration in CM chondrites. In this paper we follow the alteration sequence proposed by Rubin et al. (2007). To constrain the duration of aqueous alteration, we need to assess the age difference between carbonates in highly altered and minimally altered CM members. CM chondrite carbonates measured in this study are from the highly altered rocks QUE 93005 (CM2.1) and ALH 83100 (CM2.1). To calculate the duration of alteration, we required a value for a less-altered CM chondrite; results for the moderately altered CM2.4 chondrite Y-791198 were obtained by Brearley and Hutcheon (2002) using the LLNL ims 3f ion microprobe. Three of their six calcites show resolvable ^{53}Cr excesses; their SIMS measurements range up to $\sim 600\%$ for $\delta^{53}\text{Cr}$. The slope of the correlation line on a ^{53}Mn – ^{53}Cr evolution diagram corresponds to an initial $^{53}\text{Mn}/^{55}\text{Mn}$ ratio of $(8.7 \pm 1.5) \times 10^{-6}$.

The standard equation for short-lived radionuclides (where $\lambda = 1.87 \times 10^{-7} \text{ yr}^{-1}$), $\Delta\tau_{1-2} = \frac{1}{\lambda} \ln \left[\frac{(^{53}\text{Mn}/^{55}\text{Mn})_2}{(^{53}\text{Mn}/^{55}\text{Mn})_1} \right]$ yields a calculated time difference of carbonate formation between CM2.1 QUE 93005 and CM2.4 Y-791198 of $4.02^{+1.56}_{-2.22}$ Ma (uncertainties are 2σ); the age difference between ALH 83100 and Y-791198 is $2.85^{+1.70}_{-2.51}$ Ma. The formal time difference between carbonate formation in CM2.1 QUE 93005 and CM2.1 ALH 83100 is $1.17^{+1.96}_{-0.80}$ Ma, similar to the analytical error. We therefore assume that carbonates in these two chondrites formed at about the same time. Tyra et al. (2009) recently studied the CM2.1 chondrite ALH 84034 (which is paired with ALH 83100) and determined an initial $^{53}\text{Mn}/^{55}\text{Mn}$ ratio of $(4.27 \pm 0.5) \times 10^{-6}$, a result consistent with our studies.

When comparing carbonate data from different groups of carbonaceous chondrites, the timeframe for aqueous alteration becomes larger. Endress et al. (1996) studied dolomites from the CI chondrites Orgueil and Ivuna and obtained an initial $^{53}\text{Mn}/^{55}\text{Mn}$ ratio of $(1.99 \pm 0.16) \times 10^{-6}$. Their result is similar to, but lower than, the results obtained by Brearley and Hutcheon (2000), Brearley et al. (2001) and de Leuw et al. (this study) for CM carbonates, but is consistent with results on other CI carbonates (Hoppe et al., 2004; Petit et al., 2009a,b). Measurements of carbonates in three lithologies (CR, CM and one unusual carbonaceous chondrite lithology) of the Kaidun polymict breccia yield the highest initial $^{53}\text{Mn}/^{55}\text{Mn}$ ratio of $(9.4 \pm 1.6) \times 10^{-6}$ (Hutcheon et al., 1999), nearly a factor of five higher than the $^{53}\text{Mn}/^{55}\text{Mn}$ value of carbonates in

CI chondrites. However, [Petitat et al. \(2009a,b\)](#) reported new Mn–Cr isotope measurements of carbonates in Kaidun which do not reproduce the data by [Hutcheon et al. \(1999\)](#). The calculated alteration timeframe between Kaidun (using the [Hutcheon et al., 1999](#) value) and the highly altered CI chondrites Orgueil and Ivuna is $8.29^{+0.92}_{-1.11}$ Ma. This interval represents the minimum period over which aqueous activity occurred on carbonaceous-chondrite parent bodies.

Although the site of aqueous alteration on the CM parent body is widely held to be on the parent asteroid, [Bischoff \(1998\)](#) interpreted some petrographic evidence to imply pre-accretionary processes. Relative ages for the onset of aqueous alteration based on the solar-system initial value of $^{53}\text{Mn}/^{55}\text{Mn}$ may not represent the true age because the initial $^{53}\text{Mn}/^{55}\text{Mn}$ ratio is not well defined; ratios vary from $(8.5 \pm 1.5) \times 10^{-6}$ ([Shukolyukov and Lugmair, 2006](#)) to $(3.66 \pm 1.22) \times 10^{-5}$ ([Birck and Allègre, 1985](#)) and to $(4.4 \pm 1.1) \times 10^{-5}$ ([Birck and Allègre, 1988](#)). If we assume that the initial $^{53}\text{Mn}/^{55}\text{Mn}$ ratio of chondrites is represented by the lower value $(8.5 \pm 1.5) \times 10^{-6}$, inferred from the intercomparison of the Mn–Cr and Pb–Pb chronologies of CAIs and Angrites, then aqueous alteration on the CM parent body (calculated using the initial $^{53}\text{Mn}/^{55}\text{Mn}$ value of carbonates in Y-791198; [Brearley and Hutcheon, 2002](#)) started $0.12^{+0.93}_{-1.76}$ Ma after CAI formation. On the other hand, if we take the average value of $(4.4 \pm 1.1) \times 10^{-5}$ measured in Allende CAIs, aqueous alteration started much later, i.e., $8.65^{+1.42}_{-1.93}$ Ma after Allende CAIs. These results show that, depending on the choice of the initial solar-system $^{53}\text{Mn}/^{55}\text{Mn}$ ratio, aqueous alteration either began around the same time as CAI formation, consistent with pre-accretionary alteration, or alteration began a couple of million years after CAI formation, consistent with the view that aqueous alteration is solely a parent-body process.

[Lugmair and Shukolyukov \(1998\)](#) attempted to link $^{53}\text{Mn}/^{55}\text{Mn}$ ratios to absolute ages obtained from the LEW 86010 angrite, but we now show that this leads to implausible conclusions. LEW 86010 has a $^{53}\text{Mn}/^{55}\text{Mn}$ ratio of $(1.25 \pm 0.07) \times 10^{-6}$ and a U–Pb crystallization age of 4558.55 ± 0.15 Ma ([Amelin, 2008](#)). Based on the $^{53}\text{Mn}/^{55}\text{Mn}$ value of LEW 86010, the calculated formation age for Y-791198 carbonates is $4568.9^{+0.90}_{-1.08}$ Ma, slightly older than the Pb–Pb ages for CAIs from the Allende and Efremovka CV chondrites (which range from 4567.1 ± 0.1 Ma; [Amelin et al., \(2006\)](#) to 4568.5 ± 0.5 Ma; [Bouvier et al. \(2007\)](#)) (Fig. 4).

Since the commonly accepted view is that carbonate formation in CM chondrites postdates the formation of CAIs and chondrules, one is led to the conclusion that CAI ages represent only a lower limit for the age of the solar system, that the Mn–Cr system cannot be used to calculate absolute ages, or that Mn–host minerals in LEW 86010 became closed systems much later (~ 10 Ma) than did the minerals used in Pb dating. Another possible explanation is that the sensitivity factor for carbonates is different from that of San Carlos olivine ([Sugiura et al., 2009](#)) and that the true initial $^{53}\text{Mn}/^{55}\text{Mn}$ ratios for carbonates are significantly smaller; hence, the old crystallization ages may be an artifact.

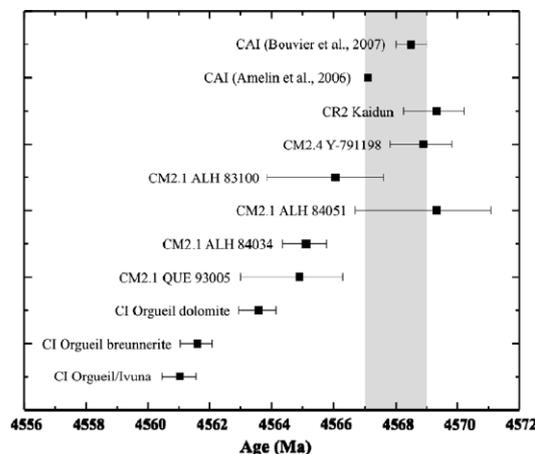


Fig. 4. If it is assumed that the Cr-isotopic composition in the nebular region where carbonaceous chondrites formed was uniform, then the initial $^{53}\text{Mn}/^{55}\text{Mn}$ ratios give relative ages. Error limits are 2σ . Carbonate ages are calculated relative to the angrite LEW 86010. Initial $^{53}\text{Mn}/^{55}\text{Mn}$ values for carbonaceous chondrites are taken from [Endress et al. \(1996\)](#), [Hutcheon et al. \(1999\)](#), [Brearley and Hutcheon \(2002\)](#), [Petitat et al. \(2009a,b\)](#) and [Tyra et al. \(2009\)](#). Absolute ages of CAIs ([Amelin et al., \(2006\)](#); [Bouvier et al., 2007](#)) are plotted for reference (gray area on the right).

The use of the initial $^{53}\text{Mn}/^{55}\text{Mn}$ value for the angrite LEW86010 still depends on the assumption that the minerals experienced closure at similar times and that $^{53}\text{Mn}/^{55}\text{Mn}$ ratios were uniform throughout the solar system. [Shukolyukov and Lugmair \(2000\)](#) showed that $^{53}\text{Mn}/^{55}\text{Mn}$ ratios appear to be heterogeneous on a solar-system wide scale, but speculated that they are probably homogeneous within limited regions such as the formation location of the carbonaceous chondrites. It seems plausible that $^{53}\text{Mn}/^{55}\text{Mn}$ was uniform in the carbonaceous-chondrite formation region and that we can therefore calculate relative ages of carbonates from different carbonaceous chondrites.

In a plot of initial $^{53}\text{Mn}/^{55}\text{Mn}$ values versus petrographic subtype, the more aqueously altered CM chondrites (QUE 93005 and ALH 83100) display lower initial $^{53}\text{Mn}/^{55}\text{Mn}$ values than the less-altered sample (Y-791198) (Fig. 5). This observation implies that the degree of aqueous alteration is correlated with the age of carbonate formation in CM chondrites. This idea is further supported by Fig. 6, which displays Mn–Cr ages of secondary carbonates in carbonaceous chondrites that are calculated relative to the carbonates in Y-791198. Fig. 6 clearly shows that carbonates in the least-altered samples are the oldest, that carbonates in the heavily aqueously altered CI chondrites are the youngest, and that aqueous alteration lasted at least 4 Ma on the CM parent body.

The CM chondrite ALH 84051, measured by [Tyra et al. \(2009\)](#), deviates from the trend. Even though ALH 84051 is paired with ALH 83100 and ALH 84034 and is thus subtype 2.1, [Tyra et al. \(2009\)](#) measured a high $^{53}\text{Mn}/^{55}\text{Mn}$ value of $(9.4 \pm 3.6) \times 10^{-6}$. Within the large error bars on ALH 84051, the result is marginally consistent with our $^{53}\text{Mn}/^{55}\text{Mn}$ value of $(5.1 \pm 1.7) \times 10^{-6}$ for ALH 83100 carbonates. The discrepancy may result from the number of

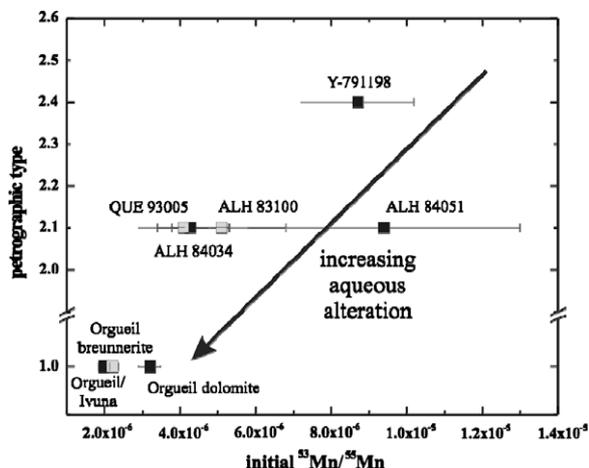


Fig. 5. Plot of initial $^{53}\text{Mn}/^{55}\text{Mn}$ versus petrographic type of carbonaceous chondrites. Initial $^{53}\text{Mn}/^{55}\text{Mn}$ values decrease with increasing aqueous alteration. Data for Y-791198, ALH 84034, ALH 84051 and Orgueil are taken from Endress et al. (1996), Brearley and Hutcheon (2002), Petit et al. (2009a,b) and Tyra et al. (2009).

carbonates measured. Our result is based on measurements of 12 dolomite grains, whereas Tyra et al. (2009) measured only three dolomite grains in ALH 84051. Additional measurements on ALH 84051 may reduce the large error and may shift the results to a lower value that is more consistent with our data. Further measurements on that sample are needed to resolve the issue.

Additional data from different CM subtypes are also needed to verify the apparent correlation between the degree of aqueous alteration and the age of carbonate forma-

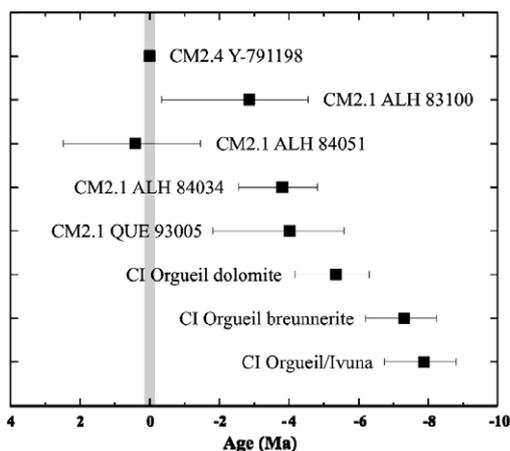


Fig. 6. Manganese–chromium ages of carbonates in CM and CI chondrites. Age differences are calculated relative to carbonates in the CM2.4 chondrite Y-791198 (represented by gray area). Error limits are 2σ . The figure shows that aqueous alteration lasted at least ~ 4 Ma on the CM parent body and at least ~ 8 Ma on carbonaceous-chondrite parent bodies. Initial $^{53}\text{Mn}/^{55}\text{Mn}$ values for some of the carbonaceous chondrites are taken from Endress et al. (1996), Hutcheon et al. (1999), Brearley and Hutcheon (2002), Petit et al. (2009a,b) and Tyra et al. (2009).

tion and to constrain the duration of aqueous alteration processes on the CM parent body. Unfortunately, our extensive searches have not uncovered suitable carbonates in CM2.2–2.6 samples.

6. SUMMARY AND CONCLUSIONS

Mineralogic and isotopic observations of CM chondrites indicate that they experienced varying degrees of aqueous alteration resulting in the formation of secondary minerals. Aqueous alteration on carbonaceous-chondrite parent bodies must have begun very early, within a couple of million years after the formation of the oldest known solar-nebula materials (refractory inclusions). This upper limit is much shorter than that of the 20- or 50-Myr interval inferred from previous studies of CI chondrites (MacDougall et al., 1984; Endress et al., 1996). We favor aqueous alteration having occurred in asteroidal settings (rather than in the solar nebula or in small planetesimals prior to the formation of chondrite parent bodies). The results imply that aqueous alteration was one of the earliest processes in the chemical evolution of the solar system. We still need a better understanding of the mechanism (internal versus external) of asteroidal heating and the distribution (homogeneous versus heterogeneous) of short-lived radionuclides in order to provide absolute dates for the onset of aqueous alteration of chondritic meteorites.

The data presented in this study were obtained using San Carlos olivine as the standard material, and therefore, the ages may include significant systematic errors. Nevertheless, the relative timing and duration of carbonate formation will not change because all of the data were determined using the same standard. The data suggest that the degree of aqueous alteration in CM chondrites is correlated with the age of carbonate formation, with the most aqueously altered CM chondrites having the lowest $^{53}\text{Mn}/^{55}\text{Mn}$ values. This is supported by the relatively low $^{53}\text{Mn}/^{55}\text{Mn}$ values of the highly aqueously altered CI chondrites. Based on our data and on previous results, we deduce that alteration on the CM parent body lasted at least 4 Ma, a timeframe that represents the minimum period of aqueous alteration. Aqueous alteration of the set of all carbonaceous-chondrite parent bodies lasted longer, at least ~ 8 Ma, based on our data combined with previous studies of carbonates in Kaidun and in CI chondrites.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2009.09.011.

REFERENCES

- Amelin Y. (2008) U–Pb ages of angrites. *Geochim. Cosmochim. Acta* **72**, 221–232.
- Amelin Y., Wadhwa M., and Lugmair G. (2006) Pb–Isotopic dating of meteorites using ^{202}Pb – ^{205}Pb double-spike: comparison with other high-resolution chronometers. *Lunar Planet. Sci.* **37**, #1970 (abstr.).
- Birck J.-L. and Allègre C. J. (1985) Evidence for the presence of ^{53}Mn in the early solar system. *Geophys. Res. Lett.* **12**, 745–748.
- Birck J.-L. and Allègre C. J. (1988) Manganese–chromium isotope systematics and the development of the early solar system. *Nature* **331**, 579–584.
- Bischoff A. (1998) Aqueous alteration of carbonaceous chondrites: evidence for preaccretionary alteration – a review. *Meteorit. Planet. Sci.* **33**, 1113–1122.
- Bouvier A., Blichert-Toft J., Moynier F., Vervoort J. D. and Albarede F. (2007) Pb–Pb dating constraints on the accretion and cooling history of chondrites. *Geochim. Cosmochim. Acta* **71**, 1583–1604.
- Brearely A. J. and Geiger T. (1991) Mineralogical and chemical studies bearing on the origin of accretionary rims in the Murchison CM2 carbonaceous chondrite. *Meteoritics* **26**, 323.
- Brearely A. J., and Hutcheon I. D. (2000) Carbonates in the CM1 chondrite ALH84034: mineral chemistry, zoning and Mn–Cr systematics. *Lunar Planet. Sci.* **31**, #1407 (abstr.).
- Brearely A. J. and Hutcheon I. D. (2002) Carbonates in the Y791198 CM2 chondrite: Zoning and Mn–Cr systematics (abstr.). *Meteorit. Planet. Sci.* **37**, A23.
- Brearely A. J. and Jones R. H. (1998) Chondritic meteorites. *Rev. Mineral.* **36**, 313–398.
- Brearely A. J., Hutcheon I. D., and Browning L. (2001) Compositional zoning and Mn–Cr systematics in carbonates from the Y791198 CM2 carbonaceous chondrite. *Lunar Planet. Sci.* **32**, #1458 (abstr.).
- Browning L., McSween H. and Zolensky M. (1996) Correlated alteration effects in CM carbonaceous chondrites. *Geochim. Cosmochim. Acta* **60**, 2621–2633.
- Bunch T. and Chang S. (1980) Carbonaceous chondrites – II: carbonaceous chondrite phyllosilicates and light element geochemistry as indicators of parent body processes and surface conditions. *Geochim. Cosmochim. Acta* **44**, 1543–1577.
- Chokai J., Zolensky M., Le L., Nakamura K., Mikouchi T., Monkawa A., Koizumi E., and Miyamoto M. (2004) Aqueous alteration mineralogy in CM carbonaceous chondrites. *Lunar Planet. Sci.* **35**, #1506 (abstr.).
- de Leuw S., Rubin A. E., Schmitt K., and Wasson J. T. (2007) Carbonates in the CM chondrite QUE 93005: mineral chemistry and Mn–Cr systematics (abstr.). *Meteorit. Planet. Sci.* **42**, #5038 (abstr.).
- de Leuw S., Rubin A. E., Schmitt K., and Wasson J. T. (2008) Carbonates and associated sulfide rims in CM chondrites: complex formational histories. *Lunar Planet. Sci.* **39**, #1197 (abstr.).
- de Leuw S., Rubin A. E., Schmitt K. and Wasson J. T. (2009) Mn–Cr Systematics for the CM2.1 chondrites QUE 93005 and ALH 83100: implications for the timing of aqueous alteration. *Lunar Planet. Sci.* **40**, #1794 (abstr.).
- Endress M., Zinner E. and Bischoff A. (1996) Early aqueous activity on primitive meteorite parent bodies. *Nature* **379**, 701–703.
- Grimm R. E. and McSween H. Y. (1989) Water and the thermal evolution of carbonaceous chondrite parent bodies. *Icarus* **82**, 244–280.
- Hanowski N. P. and Brearely A. J. (2000) Iron-rich aureoles in the CM carbonaceous chondrites Murray, Murchison, and Allan Hills 81005: evidence for in situ aqueous alteration. *Meteorit. Planet. Sci.* **35**, 1291–1308.
- Hohenberg C. M., Hudson B., Kennedy B. M. and Podosek F. A. (2000) Reexamination of anomalous I–Xe ages: Orgueil and Murchison magnetites and Allegan feldspar. *Geochim. Cosmochim. Acta* **64**, 4257–4262.
- Hoppe P., MacDougall D. and Lugmair G. W. (2004) High spatial resolution ion microprobe measurements refine chronology of Orgueil carbonate formation. *Lunar Planet. Sci.* **35**, #1313 (abstr.).
- Hoppe P., MacDougall D. and Lugmair G. W. (2007) High spatial resolution ion microprobe measurements refine chronology of carbonate formation in Orgueil. *Meteorit. Planet. Sci.* **42**, 1309–1320.
- Hoppe P., MacDougall D. and Lugmair G. W. (2008) Extinct manganese-53 in carbonates from the Orgueil meteorite. *New Astron. Rev.* **52**, 467–470.
- Hutcheon I. D., Krot A. N., Keil K., Phinney D. L. and Scott E. R. D. (1998) ^{53}Mn – ^{53}Cr dating of fayalite formation in the CV3 chondrite Mokoia: evidence for asteroidal alteration. *Science* **282**, 1865–1867.
- Hutcheon I. D., Weisberg M. K., Phinney D. L., Zolensky M. E., Prinz M., and Ivanov A. V. (1999) Radiogenic ^{53}Cr in Kaidun carbonates: evidence for very early aqueous activity. *Lunar Planet. Sci.* **30**, #1722 (abstr.).
- Johnson C. A., and Prinz M. (1991) Carbonate compositions in CM and CI chondrites and Mg–Fe–Mn partitioning during aqueous alteration. *Lunar Planet. Sci.* **22**, #644 (abstr.).
- Johnson C. A. and Prinz M. (1993) Carbonate compositions in CM and CI chondrites and implications for aqueous alteration. *Geochim. Cosmochim. Acta* **57**, 2843–2852.
- Lugmair G. W. and Shukolyukov A. (1998) Early solar system timescales according to ^{53}Mn – ^{53}Cr systematics. *Geochim. Cosmochim. Acta* **62**, 2863–2886.
- MacDougall J. D., Lugmair G. W. and Kerridge J. F. (1984) Early solar-system aqueous activity–Sr isotope evidence from the Orgueil CI meteorite. *Nature* **307**, 249–251.
- McSween H. Y. (1979) Alteration in CM carbonaceous chondrites inferred from modal and chemical variations in matrix. *Geochim. Cosmochim. Acta* **43**, 1761–1770.
- McSween H. Y. (1987) Aqueous alteration in carbonaceous chondrites: mass balance constraints on matrix mineralogy. *Geochim. Cosmochim. Acta* **51**, 2469–2477.
- Metzler K., Bischoff A. and Stöffler D. (1992) Accretionary dust mantles in CM chondrites: evidence for solar nebula processes. *Geochim. Cosmochim. Acta* **56**, 2873–2897.
- Papanastassiou D. A. (1986) Chromium isotopic anomalies in the Allende meteorite. *Astrophys. J.* **308**, L27–L30.
- Petit M., Gounelle M., McKeegan K. D., Mostefaoui S., Marrocchi Y., Meibom A., and Zolensky M.E. (2009) ^{53}Mn – ^{53}Cr systematics of Kaidun dolomites. *Meteorit. Planet. Sci.* **44**, #5425 (abstr.).
- Petit M., McKeegan K., Gounelle M., Mostefaoui S., Marrocchi Y., Meibom A., and Leshin L. A. (2009) Duration and sequence

- of carbonate crystallization on the Orgueil protolith: ^{53}Mn – ^{53}Cr systematics of their evolution in O and C isotopic composition. *Lunar Planet. Sci.* **40**, #1657 (abstr.).
- Pravdivtseva O. V., Hohenberg C. M., and Meshik A. M. (2003) The I-Xe age of Orgueil magnetite: New results. *Lunar Planet. Sci.* **34**, #1863 (abstr.).
- Rubin A. E., Trigo-Rodriguez J. M., Huber H. and Wasson J. T. (2007) Progressive aqueous alteration of CM carbonaceous chondrites. *Geochim. Cosmochim. Acta* **71**, 2361–2382.
- Shukolyukov A. and Lugmair G. W. (2000) On the ^{53}Mn heterogeneity in the early solar system. *Space Sci. Rev.* **92**, 225–236.
- Shukolyukov A. and Lugmair G. W. (2006) Manganese–chromium isotope systematics of carbonaceous chondrites. *Earth Planet. Sci. Lett.* **250**, 200–213.
- Sugiura N., Ichimura K., Fujiya W., Takahata N., and Sano Y. (2009) A preliminary study on $^{55}\text{Mn}/^{52}\text{Cr}$ relative sensitivity for a synthetic calcite: implications. *Meteorit. Planet. Sci.* **44**, #5316 (abstr.).
- Tomeoka K., McSween H. Y. and Buseck P. R. (1989) Mineralogical alteration of CM carbonaceous chondrites: a review. *Proc. NIPR Symp. Antarct. Meteorites* **2**, 221–234.
- Trigo-Rodriguez J. M., Rubin A. E. and Wasson J. T. (2006) Non-nebular origin of dark mantles around chondrules and inclusions in CM chondrites. *Geochim. Cosmochim. Acta* **70**, 1271–1290.
- Tyra M. A., Brearley A. J., Hutcheon I. D., Ramon E., Matzel J., and Weber P. (2009) Carbonate formation timescales vary between CM1 chondrites ALH84051 and ALH 84034. *Lunar Planet. Sci.* **40**, #2474 (abstr.).
- Zolensky M. E. and McSween H. Y. (1988) Aqueous alteration. In *Meteorites and the Early Solar System* (eds. J. F. Kerridge and M. S. Matthews). University of Arizona Press, pp. 114–143.
- Zolensky M. E., Mittlefehldt D. W., Lipschutz M. E., Wang M.-S., Clayton R. N., Mayeda T. K., Grady M. M., Pillinger C. and Barber D. (1997) CM chondrites exhibit the complete petrologic range from type 2 to 1. *Geochim. Cosmochim. Acta* **61**, 5099–5115.

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