Manganese–chromium isotope systematics of carbonaceous chondrites

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Abstract

In this article we present the results of Cr isotope investigations of different types of carbonaceous chondrites and of the pallasite Eagle Station. The $^{53}Cr/^{52}Cr$ ratios in the bulk samples of carbonaceous chondrites are correlated with $^{55}Mn/^{52}Cr$ ratios. The slope of the correlation line yields a $^{53}Mn/^{55}Mn$ ratio of $(8.5 \pm 1.5) \times 10^{-6}$ at the time of Mn/Cr fractionation. Mapping this ratio onto an absolute time scale yields a time for this event of $4568.1 + 0.8/-1.1$ Ma ago. This time is very similar to the formation age of Efremovka CAIs of 4567.2 ± 0.6 Ma [Y. Amelin, A. N. Krot, I. D. Hutcheon, A. A. Ulyanov, Lead isotopic ages of chondrules and calcium-aluminum-rich inclusions, Science 297 (2002) 1678–1683], to a time of the chondrule formation of 4568 ± 1 Ma ago [L.E. Nyquist, D. Lindstrom, D. Mittlefehldt, C.-Y. Shih, H. Wiesmann, S. Wentworth, R. Martinez, Manganese-chromium formation intervals for chondrules from the Bishunpur and Chainpur meteorites, Meteorit. Planet. Sci. 36 (2001) 911–938], which, most likely, constrains early global high-temperature Mn/Cr fractionation in a nebular setting.

The bulk samples of carbonaceous chondrites exhibit clear ^{54}Cr excesses ($^{54}Cr*$) that are correlated with the ^{53}Cr excesses ($^{53}Cr*$) and also with Mn/Cr ratios. One possible explanation of this correlation is that $^{54}Cr*$ is also radiogenic, like $^{53}Cr*$, and was formed by the decay of the short-lived parent radionuclide ^{54}Mn. The very short half-life of ^{54}Mn of 312 days would require that both short-lived radionuclides ^{53}Mn and ^{54}Mn were generated locally in spallation reactions during the early period of an active sun. The alternative and possibly more plausible explanation is the heterogeneous addition of presolar material. The presolar component, enriched in ^{54}Cr, is mostly contained in the matrix of carbonaceous chondrites. The relative amount of matrix decreases in the sequence CI>CM>CO,CV. A large proportion of Mn is associated with the matrix while Cr preferentially resides in the chondrules. Thus, the Mn/Cr ratio also follows the sequence CI>CM>CO>CV and is correlated with ^{54}Cr.

The acid-resistant residues of carbonaceous chondrites are characterized by relatively large excesses of ^{54}Cr and moderate deficits of ^{53}Cr. The magnitude of these excesses and deficits decreases in the sequence CI, CM, CV and may imply that Cr in the CM, and CV residues is increasingly more equilibrated with Cr from the rest of the meteorites. The $^{53}Cr/^{52}Cr$ and $^{54}Cr/^{52}Cr$ ratios in the residues are anti-correlated indicating that there are at least two Cr components of possibly presolar origin. All residues have large excesses of the most neutron-rich Ti isotope, $^{50}Ti*$. The pattern of $^{50}Ti*$ does not exactly follow that observed for $^{54}Cr*$ but it is generally similar.

The Cr isotope systematic of the pallasite Eagle Station indicates that the precursor of this meteorite was a CV-type material. The $^{53}Mn–^{53}Cr$ system indicates that the Cr isotopes equilibrated in this meteorite 4557.5 ± 0.6 Ma ago.

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1. Introduction

The former presence in the solar system of various short-lived radionuclides indicates that these species were formed in stars and subsequently were rapidly transported to and injected into the growing solar system. The importance of short-lived radionuclides is that they can serve as chronometers and isotope tracers for various processes in the early solar system. However, some of these radionuclides could also be formed within the solar system due to spallation reactions with energetic particles during an early period of an active sun, which would limit their usability as chronometers.

One of these short-lived radionuclides, ^{53}Mn, with a half-life of 3.7 ± 0.4 Ma [1], is suitable for high-resolution chronological studies for the first ~ 20 Ma of solar system history [2]. The former presence of ^{53}Mn is indicated by the deviations of the relative abundances of the daughter nuclide, ^{53}Cr, compared to the terrestrial normal value. Mn and Cr are abundant elements in solar system materials and the ^{53}Mn–^{53}Cr system, thus, is potentially useful for dating a wide variety of early formed objects.

During more than a decade we have studied the ^{53}Mn–^{53}Cr isotope system in a large variety of meteorites and meteorite types [2–5]. Over the last few years, we have extended this work to the investigation of carbonaceous chondrites. Here we present the results of these studies in various types of this important group of meteorites.

Carbonaceous chondrites are commonly considered as some of the most primitive matter known. The chemical composition of the least altered type CI carbonaceous chondrites matches the chemistry of the sun more closely than any other class of meteorites. Carbonaceous chondrites are known as carriers of various isotopic anomalies. For example, the matrix of carbonaceous chondrites and calcium–aluminum-rich inclusions (CAI) exhibit an excess of ^{16}O, [e.g., 6]; anomalies in Ca, Ti, and Cr are widespread in carbonaceous chondrites and are most pronounced in the neutron-rich isotopes ^{48}Ca, ^{50}Ti, and ^{54}Cr indicating an e-process in a neutron-rich environment; FUN CAI from carbonaceous chondrites reveal deficits or excesses of materials from the sources of the s-, r-, and p-processes of heavier elements beyond the Fe peak [e.g., 7]. These are just a few examples of the diverse isotope anomalies found in these primitive chondrites. Here, we will focus mostly on the ^{53}Mn–^{53}Cr isotope system and the Cr isotopic composition in these meteorites.

The former presence of live ^{53}Mn in the solar system was first confirmed by Birck and Allègre [8] in Allende (a CV-type carbonaceous chondrite) refractory inclusions. A particular feature of the Allende CAIs that was demonstrated in this work and subsequently in [9,10], is that these non-FUN CAIs are characterized by small deficits or excesses of ^{53}Cr and relatively large excesses of ^{54}Cr. A similar result was recently obtained for a number of the Allende CAIs [11] and for the E38 inclusion from another CV-type chondrite–Efremovka [12]. The FUN CAIs reveal much larger variations of both ^{53}Cr and ^{54}Cr isotopes [9]. The anomalous abundances of ^{53}Cr and ^{54}Cr are not limited to CAI from the CV-type carbonaceous chondrites, however. It was shown [13] that Cr-rich spinels from Murchison (a CM-type carbonaceous chondrite) exhibit excesses of ^{53}Cr and ^{54}Cr similar to those observed in the FUN inclusion EK 1–4-1 [9]. A clear evidence for the presence of a presolar Cr component with anomalous Cr isotopic composition in CAI implies a complex superposition of an in situ ^{53}Mn decay product with a ^{53}Cr component of presolar origin, and therefore, the chronological implications of reported ^{53}Mn/^{55}Mn ratios in CAI are not clear [2].

A presolar and non-homogenized Cr component was also found during differential dissolution procedures of various types of carbonaceous chondrites, including leaches from Alais (CI), Felix (CO), Ivuna (CI), Karoonda (CO), Murchison (CM), Murray (CM), and Orgueil (CI) [14–16]. In some cases (Murchison, Murray, Orgueil; [14]), an anti-correlation between ^{53}Cr and ^{54}Cr excesses can also be observed. The interpretation of all these findings is complex and requires more data and further evaluation.

The ^{53}Mn–^{53}Cr isotope system was also used for constraining the time of aqueous activity on primitive carbonaceous chondrite parent bodies. For example, the study of carbonates in the carbonaceous chondrite polymict breccia Kaidun [17], which we will come back to later, suggests a time span of no more than 1 Ma between the formation of Kaidun carbonates and CAIs– a rather unexpected result–while the Mn–Cr isotope systematic in carbonates from two CI chondrites [18] indicates a time difference of ~ 8 Ma.

The first analysis of the Cr isotopic composition in a bulk sample of Allende [8] has indicated that the ^{54}Cr/^{52}Cr ratio is elevated. In contrast, in a later study [19], no ^{54}Cr excess in bulk Allende was detected. However, these authors observed small excesses of ^{54}Cr in bulk samples of the CI chondrite Orgueil and the CM chondrite Murchison. An excess of ^{54}Cr was confirmed for the bulk samples of Allende, Orgueil and in two CM

chondrites [15], while the $^{54}Cr/^{52}Cr$ ratio in the bulk sample of the CI chondrite Ivuna was indistinguishable from the terrestrial normal. These contradictions were due to relatively large uncertainties in measurements of the Cr isotopic compositions at that time. However, overall analysis of the data suggests that an excess of ^{54}Cr in bulk samples of carbonaceous chondrites is indeed present. Subsequently, with refined analytical procedures and mass spectrometers of newer generations, it was established that bulk samples of all types of carbonaceous chondrites exhibit clear and characteristic excesses of ^{54}Cr [this work, 20].

2. Experimental techniques

The procedures for sample preparation, dissolution, and chemical separation of Cr using cation exchange chromatography were similar to those described in [2]. The isotopic analyses of Cr were carried out on the thermal ionization mass spectrometers VG-54E single-collector and Micromass Sector 54 multi-collector in single-collector mode. The concentration measurements were made by ICP-OES. As usual, the isotopic variations of ^{53}Cr are measured as the deviation of the $^{53}Cr/^{52}Cr$ ratio from the normal terrestrial $^{53}Cr/^{52}Cr$ ratio and these variations are expressed in ε-units (1 ε is 1 part in 10^4). The Cr isotopes were normalized to ^{52}Cr and corrected for mass fractionation according to an exponential law with the use of $^{50}Cr/^{52}Cr=0.051859$ [26] as internal standard, where the $^{50}Cr/^{52}Cr$ ratio was assumed to be the same as in the terrestrial standard. Using this value, instrumental fractionation during a measurement ranged typically from -7 to -2‰/a.m.u.

In our method of data reduction, we usually use a second-order mass fractionation correction that is based on the $^{54}Cr/^{52}Cr$ ratio. The application of the second-order fractionation correction was discussed in [2]. We observe the presence of a residual mass fractionation effect after the application of a strict exponential law. After normal exponential correction, we found a strong linearly correlated variation ($R \sim 0.99$; slope 2.15) of these residual effects on $^{53}Cr/^{52}Cr$ versus $^{54}Cr/^{52}Cr$ for the laboratory standards. These residual effects are independent of instrumental fractionation, are determined by the actual location of sample evaporation on the filament (relative to the ion-source optics), semi-quantitatively depend on the horizontal position of the filament relative to the ion-source extraction slit, and most likely are due to a residual magnetic field within the source. When determining $^{53}Cr/^{52}Cr$ ratios for samples, these mass discrimination effects were corrected by utilizing the parameters (slope and intercept)

obtained from the $^{53}Cr/^{52}Cr$ vs $^{54}Cr/^{52}Cr$ correlation line from several hundred Cr standard measurements. This procedure provides a considerable improvement of the precision and, thus, the resolution of the $^{53}Cr/^{52}Cr$ ratios between different sample types. This way, a typical uncertainty ($2\sigma_{mean}$) in the average $^{53}Cr/^{52}Cr$ ratio from ~ 20 to 25 runs (300 ratios for each run) is 4–6 ppm. The applicability of this technique to samples with non-terrestrial $^{54}Cr/^{52}Cr$ will be discussed below.

3. Results and discussion

3.1. Bulk samples of carbonaceous chondrites

We have measured the Cr isotopic composition and the Mn and Cr concentrations in large bulk samples of carbonaceous chondrites of different types: Orgueil (CI), Ivuna (CI), Murray (CM), Kainsaz (CO), Allende (CV), and in the Bencubbin-like (CB) meteorite Hammadah Al Hambra 237 (HH237). Several extended abstracts, containing many of the results, were published previously [21–25].

Implicit in the application of the second-order fractionation correction is the assumption of no excess or deficit in ^{54}Cr. However, this is not the case for the carbonaceous chondrites. It was shown earlier that even bulk samples of carbonaceous chondrites have resolvable excesses of ^{54}Cr (see Introduction), and therefore, the second-order fractionation correction cannot be applied to these samples if true values for $^{53}Cr/^{52}Cr$ are desired. Thus, to attain a reasonable precision, we had to conduct a large number of repeat measurements for each sample. The results of the analyses of the bulk samples of carbonaceous chondrites are presented in Table 1.

The measured Mn and Cr concentrations and the Mn/Cr ratios agree well (within 2–5%) with data from the literature [e.g., 27]. This indicates that the analyzed samples are representative for the total rock materials of these meteorites.

The bulk samples of all carbonaceous chondrites reveal variable deviations in both ^{53}Cr ($^{53}Cr*$) and ^{54}Cr ($^{54}Cr*$) from the terrestrial standard values (Table 1). For comparison, the same sample of Ivuna has been analyzed at the Max-Planck-Institute for Chemistry in Mainz with a similar Micromass Sector 54 mass spectrometer. The data from two labs indicate good agreement. In contrast to the other carbonaceous chondrites, HH237 is characterized by a deficit of ^{53}Cr ($-0.15\pm0.09\,\epsilon$) at a low $^{55}Mn/^{52}Cr$ ratio of 0.082, while its $^{54}Cr*$ is similar to that of Allende.

It was shown earlier [8-10] that most Allende CAIs exhibit ^{54}Cr excesses of $\sim 7\,\epsilon$. A rough estimate,

Table 1
Manganese and chromium concentrations, Mn/Cr ratios, $^{53}Cr/^{52}Cr$ and $^{54}Cr/^{52}Cr$ ratios in the bulk samples of carbonaceous chondrites

Sample	Weight (g)	Mn (ppm)	Cr (ppm)	$^{55}Mn/^{52}Cr$ (±5%)	Number of runs	ε(53)	ε(54)
Orgueil CI	0.992	1820	2529	0.812	110	0.39±0.10	1.51±0.20
Ivuna CI	0.225	1989	2720	0.824	71	0.41±0.11	1.59±0.24
					51 [a]	0.42±0.11 [a]	1.47±0.20 [a]
Murray CM	0.101 [b]	1803	3186	0.639	93	0.27±0.09	1.13±0.21
Kainsaz CO	1.03	1670	3520	0.536	91	0.20±0.10	1.02±0.24
Allende CV	2.38	1364	3545	0.434	70	0.10±0.09	0.85±0.17
HH237 CB	0.679	181	2492	0.082	148	−0.15±0.09	0.87±0.19

The presented uncertainties are $2\sigma_{mean}$.
[a] Measured at Max-Planck-Institute in Mainz.
[b] Aliquot from a powdered 5 g total rock sample.

however, indicates that the anomalous Cr in CAIs cannot be the only cause for the elevated $^{54}Cr/^{52}Cr$ ratio in bulk Allende (and in the other carbonaceous chondrites with a smaller number of CAIs). An average Cr concentration in Allende CAIs is ∼400 ppm [8,28], the Cr concentration in bulk Allende is 3545 ppm (Table 1), and the abundance of CAIs in Allende is 9.3 vol.% [29]. Thus, Cr from CAIs can be responsible for only ∼10% of the observed ^{54}Cr excess (+0.85 ε). Another component(s) with an elevated abundance of ^{54}Cr has to exist. This, of course, is even more valid for the more primitive carbonaceous chondrites with a progressively lower abundance of CAI material yet higher $^{54}Cr*$.

3.1.1. Chronological considerations

It is well known that the Mn/Cr ratios in bulk carbonaceous chondrites decrease in the sequence CI–CM–CO–CV. For example, the measured $^{55}Mn/^{52}Cr$ ratios are 0.82 (Ivuna CI), 0.81 (Orgueil CI), 0.64 (Murray CM), 0.54 (Kainsaz CO), and 0.43 (Allende CV) (Table 1). This may be due to nebular fractionation caused by volatility-controlled Mn loss from hot regions [e.g., 30,31]. It may also be due to different proportions of matrix rich in Mn. An alternative hypothesis could be that the fractionation was post-accretional: heating by ^{26}Al and ^{60}Fe at the planetesimal stage may have been important. Whichever scenario is true, if we assume that the initial Cr isotopic composition and the ^{53}Mn abundance were the same in the zone where the precursor material for these objects formed then the $^{53}Cr/^{52}Cr$ ratios in bulk carbonaceous chondrites should constrain the $^{53}Mn/^{55}Mn$ ratio at the time when their Mn/Cr ratios were established.

In Fig. 1, we plotted the measured $^{53}Cr/^{52}Cr$ ratios versus the respective $^{55}Mn/^{52}Cr$ ratios for the bulk samples of carbonaceous chondrites and the CB chondrite HH237. The data points form a well-defined correlation line. The data point for a bulk sample of

Tagish Lake [32] falls within uncertainty on this line. If this line is considered as an isochron, its slope corresponds to a $^{53}Mn/^{55}Mn$ ratio of $(8.5\pm1.5)\times10^{-6}$ at the time of Mn/Cr fractionation. This is the highest $^{53}Mn/^{55}Mn$ ratio that we have ever obtained. The initial $^{53}Cr/^{52}Cr$ ratio at that time is −0.21±0.09 ε. This result is consistent with an earlier less precise estimate of $\leq 2\times10^{-5}$ [19]. To determine the time of the Mn/Cr fractionation, we use, as we have done in the past [2], the angrite LEW 86010 as an absolute time marker. The absolute Pb–Pb age of LEW 86010 is 4557.8±0.5 Ma [33] and the $^{53}Mn/^{55}Mn$ ratio at the time of isotope closure in this meteorite is $(1.25\pm0.07)\times10^{-6}$ [2]. Thus, assuming a homogeneous initial distribution of the ^{53}Mn abundance within the asteroid belt region, the Mn/Cr fractionation within the carbonaceous chondrite precursors occurred 4568.1+0.8/−1.1 Ma ago. This time is very similar to recent data on the CAI formation age from the CV chondrite Efremovka. It was shown [34] that the weighted average of two U–Pb dates for the
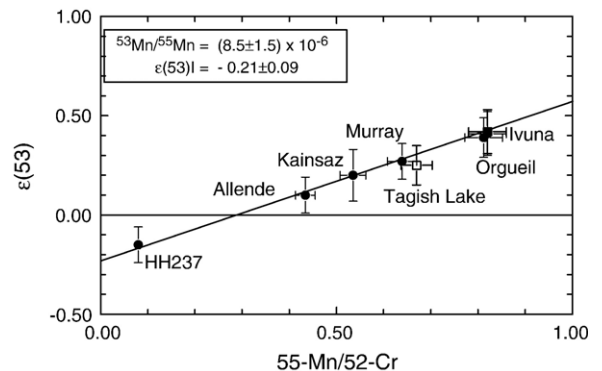

Fig. 1. Correlation of $^{53}Cr/^{52}Cr$ ratios (expressed in ε units as relative deviations from the terrestrial standard in parts in 10,000) and $^{55}Mn/^{52}Cr$ ratios in bulk carbonaceous chondrites. The slope of the best fit line corresponds to the $^{53}Mn/^{55}Mn$ ratio at the time when the Mn–Cr isotope systems became closed in these bulk samples.

CAI E49 and CAI E60 from this meteorite gives the best estimate for the timing of CAI formation at 4567.2 ± 0.6 Ma ago. A more recent revised value for CAI E60 is 4567.1 ± 0.16 Ma [35]. An earlier, less precise dating of Allende CAIs (4566 ± 2 Ma) [36] is consistent with this value. Thus, the time of 4568 Ma ago could constrain either an early global high-temperature Mn/Cr fractionation in a nebular setting, assembly of the carbonaceous chondrite parent bodies including incorporation of various proportions of matrix within a short period of time, or high-temperature processing at the planetesimal stage occurring essentially contemporaneous with CAI formation, which we consider less likely.

The Pb–Pb ages of various objects are usually consistent with the absolute Mn–Cr ages obtained using LEW 86010 as a time marker. For example, an absolute Mn–Cr age of the H-chondrite Forest Vale of 4560.9 ± 0.8 Ma [37] agrees well with a Pb–Pb age of 4560.8 ± 0.7 Ma [38]. The LL-chondrite St. Severin also shows agreement between the Mn–Cr and Pb–Pb ages: 4554.6 ± 1.4 Ma and 4553.6 ± 0.7 Ma, respectively [38,39]. Recent studies of the D'Orbigny angrite now also indicate consistent Mn–Cr and Pb–Pb ages: 4562.9 ± 0.7 Ma and 4563.9 ± 0.6 Ma, respectively [40,41]. In some cases, though, the ages may seem discordant. For example, the H-chondrite Ste. Marguerite has a Mn–Cr age of 4564.9 ± 0.7 Ma [37] but a phosphate Pb–Pb age of 4562.7 ± 0.6 Ma [38]. However, this age difference most likely reflects the difference in closure times between the U–Pb system in the phosphates of Ste. Marguerite and the Mn–Cr system in the bulk meteorite, since the whole rock Pb–Pb age of 4566.7 ± 1.6 Ma [38] agrees reasonably well with the Mn–Cr age. Thus, the general concordance of the ages implies that the initial ^{53}Mn abundances in various objects in the asteroid belt were essentially similar.

The obtained time for the Mn/Cr fractionation in carbonaceous chondrite materials is in fact the same within error as that given in [42] for the timing of the Chainpur and Bishunpur chondrule formation (or the Mn/Cr fractionation in chondrule precursors): 4568 ± 1 Ma. Apparently, this time may indicate a period of intense thermal processing of inner solar system material [43]. (The age for chondrule formation of 4568 Ma was calculated using a ^{53}Mn/^{55}Mn ratio for LEW 86010 of $\sim 1.40 \times 10^{-6}$ [44] while using a value of $\sim 1.25 \times 10^{-6}$ [2] yields a slightly older age of 4569 Ma.) Thus, formation of CAIs, the establishment of the Mn/Cr ratio in carbonaceous chondrite precursors, and formation of chondrules (or the Mn/Cr fractionation in their precursors) appears to have occurred essentially at the same time.

On the other hand, the investigations of ^{26}Mg excesses in Al-rich chondrules [45], Mg-rich chondrules [46], and ferromagnesian chondrules [47] have shown that the inferred ^{26}Al/^{27}Al ratios at the time of their formation (or last isotopic equilibration) were >3–7×10^{-6}. Using a canonical ^{26}Al/^{27}Al ratio for CAIs of 5×10^{-5}, the time span between CAI formation and formation of these chondrules was on the order of ~ 2 Ma or somewhat less. However, the younger "age" may most likely reflect the time of chondrule crystallization or re-equilibration, while the ^{53}Mn/^{55}Mn value for chondrules [42] may mark the time of Mn/Cr fractionation in the chondrule precursor material that occurred some time earlier than chondrule crystallization.

Nonetheless, there seems to be a dilemma when taking into account the Mn–Cr data on Kaidun obtained by ion microprobe [17]. It was shown that carbonates in the Kaidun carbonaceous chondrite formed at the same time with an initial ^{53}Mn/^{55}Mn ratio of $\sim 9.4 \times 10^{-6}$, indicating a time of ~ 4569 Ma ago. Since carbonate formation (by aqueous activity) in a meteorite parent body must obviously post-date formation of the first solids one is led to the conclusion that 4568–4569 Ma can only be a lower limit for the solar system age, as has been suggested earlier [43]. If true, then a Pb–Pb age of 4567.2 ± 0.6 Ma [34] would not mark the time of actual CAI formation but would reflect a later re-equilibration. Consequently, the Mn/Cr fractionation in the formation region of carbonaceous chondrites could have occurred some time after the formation of CAIs. Obviously, at present, there are insufficient data to distinguish between these scenarios.

Whichever scenario is correct, it is important to note that the results obtained here, together with data from the literature, again demonstrate how fast processes of accretion, heating, differentiation, and core formation occurred in the early solar system. The Mn–Cr isotope systematic in eucrites and diogenites indicates that mantle differentiation preceded by core formation in a 500-km howardite–eucrite–diogenite parent body occurred at ~ 4565 Ma ago [2,48]—only about 3 Ma after an extensive nebular Mn/Cr fractionation and apparent formation of the first solar system condensates.

3.1.2. Excess of ^{54}Cr in the bulk samples of carbonaceous chondrites

A characteristic feature of carbonaceous chondrites is that, in contrast to other meteorite classes, their bulk samples exhibit clear ^{54}Cr excesses. Moreover, except for HH237, these excesses are correlated with the ^{53}Cr excesses (Fig. 2). Obviously, since ^{53}Cr* is correlated with Mn/Cr (Fig. 1), then ^{54}Cr* must also be correlated
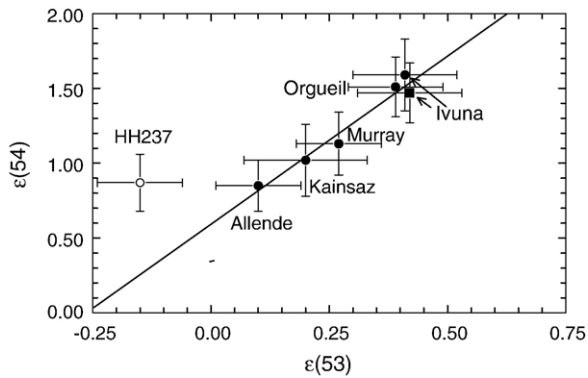
Fig. 2. Correlation of $^{53}Cr/^{52}Cr$ and $^{54}Cr/^{52}Cr$ isotope anomalies in bulk carbonaceous chondrites. Since, with the exception of HH237, these anomalies correlate the $^{54}Cr/^{52}Cr$ isotope anomalies are also correlated with $^{55}Mn/^{52}Cr$ (see Fig. 1).

with Mn/Cr ratios. (Note that the $^{53,54}Cr/^{52}Cr$ excesses are also correlated with Fe/Cr and moderately volatile elements/Cr and anti-correlated with refractory Ca/Cr and Al/Cr.) The most primitive meteorites Ivuna and Orgueil exhibit the largest $^{53}Cr^*$ and $^{54}Cr^*$ of $\sim 0.4\varepsilon$ and $\sim 1.5\varepsilon$, respectively, while the most heavily heated Allende shows the smallest excesses of $\sim 0.10\varepsilon$ and $\sim 0.85\varepsilon$. HH237 does not follow this trend as its $^{54}Cr^*$ is the same as that in Allende (Fig. 2). How can one explain these correlations?

For example, we can assume that $^{54}Cr^*$ is also radiogenic, like $^{53}Cr^*$, and was formed by the decay of the short-lived parent radionuclide ^{54}Mn. But the half-life of ^{54}Mn of 312 days is much too short for this nuclide to have been transported alive from a stellar source. We then would be forced to conclude that both short-lived radionuclides ^{53}Mn and ^{54}Mn were generated locally in spallation reactions on Fe, Mn, Ni, etc. during the very early period of an active Sun. But this would also require that the spallogenically produced $^{53,54}Mn$ was rapidly mixed with *normal* Mn and was homogeneously merged with the material in the region where the carbonaceous meteorites were formed. Further, if one considers the $^{53}Cr/^{52}Cr–^{55}Mn/^{52}Cr$ correlation as an isochron, then one may also do so for the $^{54}Cr/^{52}Cr–^{55}Mn/^{52}Cr$ system. This correlation yields a slope of $(4.9\pm1.5)\times10^{-6}$ with an $\varepsilon(54)$ $I=0.09\pm0.36$. This slope then could be taken to indicate a $^{54}Mn/^{55}Mn$ ratio of $\sim 4.9\times10^{-6}$ at the time of Mn/Cr fractionation. Since the production ratio of $^{53}Mn/^{54}Mn$ from the before-mentioned target elements is unlikely to be very much different from unity, this would suggest a time span on the order of a year between production, fractionation, and freeze out —an admittedly mind-boggling concept.

There is, of course, an alternative scenario, which may not be less far-fetched. This would invoke production of $^{53,54}Mn$ and mixing with *normal* Mn in the nebula that is followed immediately by Mn/Cr fractionation. After an arbitrary period of time, during which the fractionated zones must have remained largely undisturbed, the formation of solid bodies has occurred. Then, however, the anomalies we see in the meteorites today are due to fossil (or perhaps partly fossil in the case of $^{53}Cr^*$) decay products and, consequently, the correlations derived from the data have no time meaning with regard to the meteorites. They, however, would still indicate the time of Mn/Cr fractionation. In this context, the fact that HH237 has the same $^{54}Cr^*$ as Allende but has much lower and Mn/Cr correlated $^{53}Cr^*$ could be explained in the following way. After ^{54}Mn had fully decayed, the HH237 material condensed out of material in the CV forming region and experienced yet another depletion of Mn relative to Cr. The time interval after total decay of ^{54}Mn and HH237 formation must have been short relative to the ^{53}Mn half-life since the $^{53}Cr^*–^{55}Mn/^{52}Cr$ correlation is still maintained.

In this context, it may be interesting to note another puzzling observation of ^{63}Cu excesses recently found in carbonaceous chondrites [49]. One of the suggested explanations is that the excess ^{63}Cu is a daughter product of short-lived ^{63}Ni ($T_{1/2}=100$ years), which formed by irradiation during the T-Tauri phase of the sun. These ^{63}Cu excesses are coupled with ^{16}O excesses that may also be generated within the solar system [50,51]. Interestingly, we have also noted earlier [21] a rather unexpected relation between $^{54}Cr^*$ and ^{16}O excesses. All studied samples that plot on the oxygen isotope diagram along or close to the CAI line have $^{54}Cr^*$: CAIs [e.g., 9,10], carbonaceous chondrites, the Eagle Station pallasite (most likely formed from CV3 type-material, see below), HH237 and QUE94411 [21]. It is not clear what all these correlations actually mean or what the reason for their existence are. All attempts at their explanation would be highly speculative at present and will not be made here.

However, an early spallation scenario alone would not resolve the complexity imposed by the observed $^{53}Cr^*–^{54}Cr^*$ correlation, particularly in light of the $\sim 4\times10^6$ difference in lifetime of the two parent nuclei. According to a study of the Cr isotopic composition in Orgueil leaches [16], $^{53}Cr^*$ and $^{54}Cr^*$ reside in different phases and appear to be decoupled on a microscopic scale. Further, we have to remember that the former presence in the solar system of the short-lived radionuclide ^{60}Fe ($T_{1/2}=1.49$ Ma) [52] suggests the injection

of material from a supernova [53] or possibly an AGB star [54]. This radionuclide cannot be generated in spallation reactions. Both supernovae and AGB stars also produce ^{53}Mn and a solar system mass balance between spallation produced and stellar derived products of this radionuclide is not known. Also, and importantly, it is not quite clear how new findings of a deficit of ^{54}Cr in some meteorite classes such as eucrites, mesosiderites, or ureilites [20,5,32] can be explained within the spallation scenario.

In order to find another, possibly more plausible explanation, we can consider the heterogeneous addition of presolar material. It was suggested [16] that ^{54}Cr* in the carbonaceous chondrites is due to the presence of a component of presolar origin with a nucleosynthetic signature as may be expected from Type Ia supernovae. Progressive chemical and physical separation of Orgueil material revealed phases with varying degrees of ^{54}Cr enrichments, up to $\sim 200\,\varepsilon$, while the ^{53}Cr variations were comparatively small [16]. A similar result has been obtained earlier [15]—a differential dissolution procedure of carbonaceous chondrites of different types–Orgueil, Murchison, Felix, Allende–yielded phases with large excesses or deficits of ^{54}Cr while ^{53}Cr excesses and deficits were minor and clearly decoupled from those in ^{54}Cr. However, as would be expected for presolar material, no associated variations in isotopes of Ca, Fe, and Zn were found. In addition, within this framework, it is difficult to explain the presence of the observed correlations in bulk samples between ^{54}Cr*, ^{53}Cr* and Mn/Cr ratios. One could speculate that the regions in the nebula where carbonaceous chondrites formed were enriched in ^{54}Cr proportionally to their Mn/Cr ratios—an admittedly ad hoc assumption.

A more likely explanation is the following. The presolar component, enriched in ^{54}Cr, is mostly contained in the matrix of carbonaceous chondrites. The relative amount of matrix is highest in the most primitive chondrites and decreases in the sequence CI>CM>CO,CV [55]. A large proportion of Mn is also associated with the volatile rich matrix while much of the Cr resides in the chondrules. As the relative amount of matrix decreases, the Mn content also decreases while the Cr concentration increases by a similar proportion. Thus, the Mn/Cr ratio follows the sequence CI>CM>CO>CV and is correlated with ^{54}Cr*. This sequence was established very early in solar system history before much of the ^{53}Mn had decayed. Later episodes of heating had obviously little effect on these correlations, with the exception of the highly processed HH237 material.

3.2. Acid-resistant residues

In order to obtain more information on the nature and the features of Cr components in carbonaceous chondrites, we measured the Cr isotopic compositions and the ^{55}Mn/^{52}Cr ratios in the acid-resistant residues from different types of carbonaceous chondrites: Ivuna (CI), Murchison (CM), Mokoia and Allende (CV). The bulk samples were treated with an HF/HNO$_3$ mixture at room temperature. This dissolution left behind tiny amounts of acid-resistant residues highly enriched in Cr, most likely a chromite–spinel phase. From mass balance, we estimate that for Ivuna and Allende, the residues comprise 10% and 11%, respectively, of the whole total rock Cr. (This estimate could not be made for Murchison and Mokoia because the original weights of the samples were not available.) The residues were further dissolved also using an HF/HNO$_3$ mixture but in a Teflon bomb at $\sim 180\,°C$. In addition, we have analyzed the easily soluble phase of Ivuna that was dissolved in the first HF/HNO$_3$ step. The ^{53}Cr/^{52}Cr, ^{54}Cr/^{52}Cr, and ^{55}Mn/^{52}Cr ratios for all these samples are given in Table 2 and are shown in Figs. 3 and 4, where the ^{50}Cr/^{52}Cr ratios in all cases were assumed to be normal.

The Ivuna residue exhibits a moderate deficit of ^{53}Cr $(-0.90\pm0.09\,\varepsilon)$ and a large ^{54}Cr* $(+13.23\pm0.20\,\varepsilon)$ (Table 2, Fig. 3). The soluble phase that contains most of the Cr has a moderate ^{53}Cr* of $+0.57\pm0.18\,\varepsilon$ and a moderate ^{54}Cr deficit of $-0.66\pm0.32\,\varepsilon$. (For comparison, spinels from Allende CAIs (Big Al, EGG2, EGG3, EGG6) [11] indicate a range of -1.59 to $-1.06\,\varepsilon$ for ^{53}Cr* and $+6.58$ to $7.71\,\varepsilon$ for ^{54}Cr*. Earlier, less precise values for spinels from Allende CAIs (G1, BR1, BR9) [59] showed similar ranges, while spinel from CAI G6 indicates ^{53}Cr*$=+0.75\,\varepsilon$ and ^{54}Cr*$=+3.4\,\varepsilon$.) Thus, an elevated ^{54}Cr/^{52}Cr in the total rock of Ivuna is most likely due to a mixture of an abundant component(s) with a moderate deficit of ^{53}Cr and a rare phase with high excess ^{54}Cr. This is consistent with the results obtained earlier [16]. It should be noted that it is unlikely

Table 2
Mn/Cr ratios, ^{53}Cr/^{52}Cr and ^{54}Cr/^{52}Cr ratios in the acid-resistant residues from carbonaceous chondrites and in the soluble phase in Ivuna

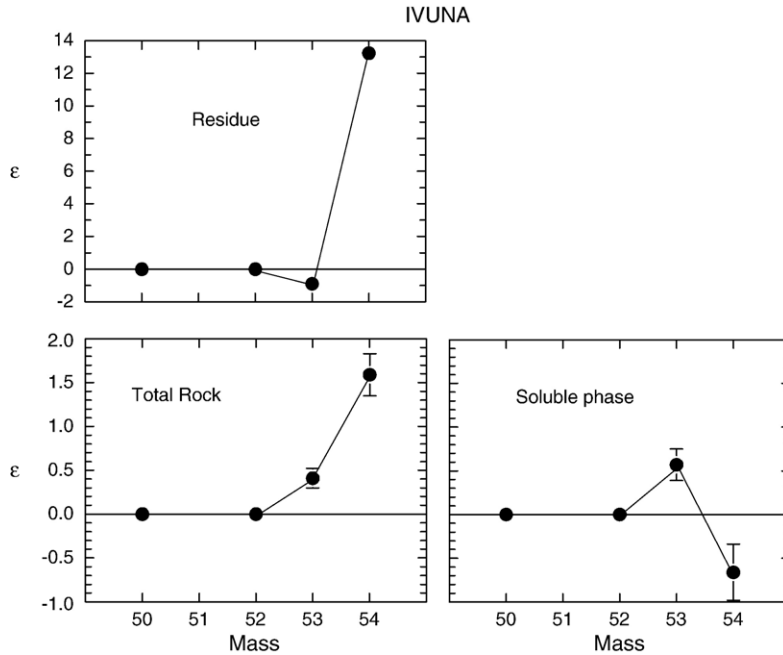| Sample	^{55}Mn/^{52}Cr ($\pm5\%$)	Number of runs	$\varepsilon(53)$	$\varepsilon(54)$
Ivuna CI	0.179	46	-0.90 ± 0.09	13.23 ± 0.20
Murchison CM	0.101	36	-0.34 ± 0.17	5.35 ± 0.29
Mokoia CV	0.026	33	-0.19 ± 0.11	3.46 ± 0.25
Alllende CV	0.078	29	0.04 ± 0.22	2.66 ± 0.39
Ivuna Soluble	0.933	35	0.57 ± 0.18	-0.66 ± 0.32

Fig. 3. Cr isotope diagrams for the acid-resistant residue, the soluble phase and the total rock samples of the CI chondrite Ivuna. The deviations from the terrestrial value for the respective masses are plotted in ε units.

that the low ^{53}Cr/^{52}Cr ratio of $-0.9\,\varepsilon$ represents a solar system initial—an unreasonably long time-scale would be implied for an early solar system age of ~4572 Ma. Instead, it is most likely that within the carbonaceous

chondrites, we can distinguish a presolar component(s) with an anomalously low abundance of ^{53}Cr.

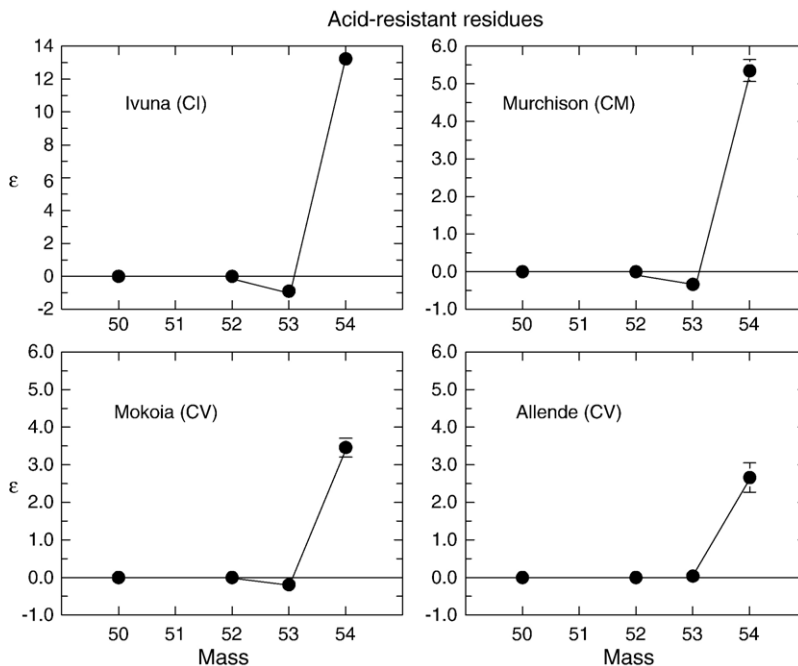The residues from Murchison and Mokoia exhibit smaller deficits in ^{53}Cr and Allende reveals slightly

Fig. 4. Cr isotope anomalies for acid-resistant residues from carbonaceous chondrites.

elevated [53]Cr (Table 2; Fig. 4). The variations of ε([53]Cr) *cannot* be due to in situ [53]Mn decay since there is no correlation observed between [53]Cr/[52]Cr and the respective [55]Mn/[52]Cr ratios (Fig 5a). Instead, ε([53]Cr) appears to decrease with increasing [55]Mn/[52]Cr ratios. The residue of the primitive Ivuna has the largest deficit of [53]Cr (~−0.9ε) and the largest [54]Cr* (~+13ε), while the more evolved CM chondrite shows a more moderate [53]Cr deficit and [54]Cr* (Table 2). The most evolved CV chondrites exhibit the highest ε([53]Cr) and the smallest [54]Cr*. This may imply that Cr in the CM and CV residues is increasingly more equilibrated with Cr from the rest of the meteorite. Moreover, the Cr isotopic composition in the acid-resistant residues is reminiscent of that found in 'normal' CAIs (i.e., moderate [53]Cr deficits and [54]Cr* of ~+7ε; [8–10]), although [54]Cr* in the Ivuna residue is almost twice as high, while it is about half that in Mokoia and Allende.

The other remarkable feature is that in contrast to the bulk samples of carbonaceous chondrites the [53]Cr/[52]Cr

Table 3
Titanium isotope anomalies in acid-resistant residues from carbonaceous chondrites

Sample	ε(47)	ε(49)	ε(50)
Ivuna CI	+0.04±0.25	+1.33±0.30	+7.17±0.35
Murchison CM	−0.34±0.25	+0.26±0.32	+5.12±0.38
Mokoia CV	+0.26±0.25	+0.43±0.31	+7.19±0.36
Alllende CV	−0.21±0.26	+0.39±0.31	+3.21±0.38

and [54]Cr/[52]Cr ratios in the residues are anti-correlated (Fig. 5b). The Allende data point does not quite fall on the correlation line, but within uncertainty, it still is consistent with the trend. The observed linearity suggests that there are at least two Cr components and these components of yet unknown and possibly presolar origin are likely to be a feature of all types of carbonaceous chondrites.

In order to test the presolar hypothesis of these components, it would be desirable to measure the isotopic composition in other elements. However, the sample solutions remaining after the Cr analyses were limited and insufficient for a thorough and systematic study. Nevertheless, we were able to perform some Ti isotopic measurements in these residual solutions to (a) search for the presence of isotopic anomalies similar to those observed in Cr and (b) if observed, to compare their magnitude and pattern with that shown above for Cr.

The results are given in Table 3, where the Ti isotopic ratios are normalized to [46]Ti, corrected for mass fractionation to our terrestrial standard value for [48]Ti/[46]Ti, and expressed in ε unit deviations (i.e., parts in 10^4) relative to the respective terrestrial isotope ratios. As can be readily seen, there is a hint of elevated [49]Ti and clear and large excesses in all residues on the most neutron-rich isotope, [50]Ti. The pattern of [50]Ti* does not exactly follow that observed for [54]Cr* in that Mokoia has about the same [50]Ti* as does Ivuna, while [50]Ti* of Murchison is lower. The excess [50]Ti in the Allende residue is the lowest with about +3ε. As has been known for many years, the average [50]Ti* in "normal" coarse-grained Allende CAI is about +9ε (see, e.g., [10]) and ranges up to +13ε or higher in some fine-grained CAI. With an approximate abundance of CAI in Allende of 10%, the [50]Ti* observed in Allende residue can be to a significant degree due to insoluble phases from CAI. However, since the abundance of CAI decreases with lower petrologic type, this cannot be the case for the other carbonaceous chondrite residues with much higher [50]Ti*. Thus, it appears that isotopically anomalous Ti is in large part associated with matrix, similar to [54]Cr*.

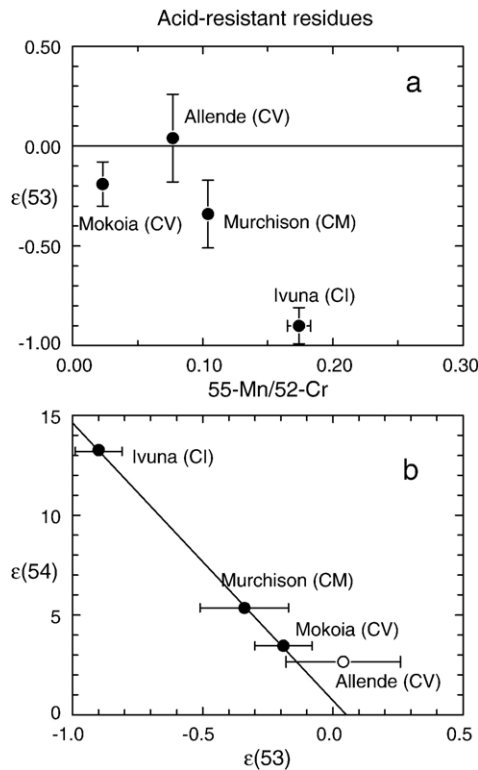Fig. 5. (a) Relative deviations of [53]Cr/[52]Cr from terrestrial Cr and the [55]Mn/[52]Cr ratios in acid-resistant residues from carbonaceous chondrites. (See text for discussion.) (b) Negative correlation of [54]Cr vs. [53]Cr anomalies in acid-resistant residues from carbonaceous chondrites.

Table 4
Manganese and chromium concentrations, Mn/Cr ratios, ^{53}Cr/^{52}Cr and ^{54}Cr/^{52}Cr ratios in the pallasite Eagle Station samples

Sample	Weight (g)	Mn (ppm)	Cr (ppm)	^{55}Mn/^{52}Cr (±5%)	Number of runs	ε(53)$_{norm}$	ε(53)$_{raw}$	ε(54)$_{raw}$
Chromite	nd	nd	nd	0.0050	114	−0.28±0.03	0.11±0.11	0.71±0.20
Olivine 1	0.165	1320	264	5.65	35	0.30±0.06	0.64±0.20	0.70±0.40
Olivine 2	0.094	1308	220	6.71	24	0.43±0.06	nd	nd

nd–not determined.

3.3. Genetic link between carbonaceous chondrites and some differentiated meteorites

Because the bulk samples of carbonaceous chondrites possess the so far unique isotopic signature of an elevated ^{54}Cr/^{52}Cr ratio and the magnitude of this relative excess in ^{54}Cr varies with petrologic type, this feature offers the possibility to test whether some 'anomalous' differentiated meteorites could be derived from carbonaceous chondrite parent material and, if so, from which type.

Eagle Station (ES) is such an example. It belongs to an anomalous group of pallasites and was shown earlier that its metal phase is enriched in refractory siderophile trace elements [56]. The oxygen isotopic composition of this meteorite falls in the range found in total-rock samples of CO3 and CV3 chondrites [57]. These findings led to the suggestion of a possible genetic connection of ES (and the other anomalous pallasites) with C3 carbonaceous chondrites [57]. The goal of our study of ES was to test to what extent the Cr isotope systematic of ES is consistent with this hypothesis. In addition, we used the ^{53}Mn–^{53}Cr isotopic information in ES to obtain chronological constraints for its formation time.

We have measured the Cr isotopic composition and the Mn/Cr ratios in ES chromite and two olivine grains. It has been shown [58] that Mn and particularly Cr in olivines from pallasites can be zoned. While the Mn content may slightly increase towards grain boundaries, the Cr content is highly depleted in the outer ~250 μm. This diffusive gain of Mn and loss of Cr by olivine must have occurred sometime after the olivine had crystallized. Thus, measured Mn/Cr ratios and radiogenic ^{53}Cr excesses may be decoupled in the outer zone. In order to minimize this problem we separated two large (165 mg and 94 mg) olivine grains and removed the outer surface layer with 6 N HCl. The relative abundances of ^{53}Cr in Olivine 1 and Olivine 2 were corrected for small spallation contributions (7 ppm and 8 ppm, respectively) as described for Omolon in [2]. The results are presented in Table 4 and are illustrated in Fig. 6.

It was noted previously from olivine and chromite samples that a ^{54}Cr excess exists in ES (∼1.2–1.6ε) [59]. However, these authors did not associate this anomaly with a potential carbonaceous chondrite precursor for the ES parent body since Cr isotopic compositions of bulk carbonaceous chondrites were not available at that time.

As discussed before ([2] and above), in order to obtain improved time resolution, we normally use the ^{54}Cr/^{52}Cr ratio for a second-order fractionation correction and, thus, it is assumed to be normal. But in ES ^{54}Cr/^{52}Cr has a significant excess. In Table 4 and in Fig. 6, we present both the corrected (with second-order fractionation correction) and the raw ratios. The application of the second-order fractionation correction provides a much better resolution for ^{53}Cr/^{52}Cr ratios. Using the corrected ratios, we found that the ^{53}Cr excesses are correlated with the respective ^{55}Mn/^{52}Cr ratios and the data points for Chr, Olv-1, and Olv-2 (open symbols) form a straight line (dashed line in Fig. 6). If this line is interpreted as an isochron, its slope yields a ^{53}Mn/^{55}Mn ratio of $(1.17±0.09)×10^{-6}$ at the time of isotopic closure. Comparing this ratio with the ^{53}Mn/^{55}Mn ratio of $(1.25±0.07)×10^{-6}$ obtained for
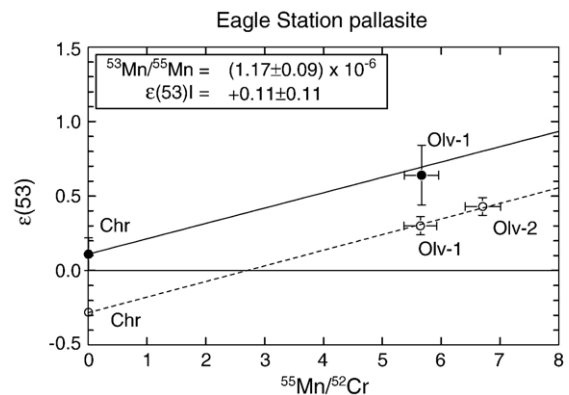

Fig. 6. Mn–Cr isochron diagram for the Eagle Station pallasite. Comparison of the raw data (filled symbols) with the second-order corrected data (open symbols), from which a precise initial ^{53}Mn/^{55}Mn ratio at the time of isotopic closure is obtained. The chromium isotopic systematic indicates that the parent body of this meteorite is derived from a CV type precursor (see text).

the angrite LEW86010 [2] and an absolute Pb–Pb age for LEW86010 of 4557.8 ± 0.5 Ma, we find that the Mn–Cr isotope system in ES has closed essentially at the same time: 4557.5 ± 0.6 Ma ago. Interestingly, this time is also indistinguishable from the time of Mn–Cr isotope closure in the main group pallasite Omolon 4558.0 ± 1.0 Ma ago [2]. However, we do not know the reason for the difference in the $^{53}Mn/^{55}Mn$ ratios for ES obtained by us $((1.17 \pm 0.09) \times 10^{-6})$ and by [59] $((2.3 \pm 0.3) \times 10^{-6})$.

With the application of the second-order fractionation correction, excesses of ^{54}Cr translate into apparent deficits of ^{53}Cr so that the data points are shifted from their true positions to lower values along the y-axis. What is important to realize, though, is that the data points are shifted *without any change of the slope* of the isochron (with the reasonable assumption that ^{54}Cr excesses are the same in Chr and Olv since pallasites are of magmatic origin that implies isotopic homogenization at the time of formation). Because the $^{53}Mn/^{55}Mn$ ratio and, therefore, the age are calculated from the slope only, this artificial shift does not influence the chronology. Thus, even for samples with anomalous ^{54}Cr, this procedure is applicable for precise calculations of the slopes of isochrons. The usefulness of the second-order fractionation correction for samples with anomalous ^{54}Cr has also been recently demonstrated for a Mn–Cr study of ureilites [5].

The data points can be returned to their correct positions using the raw ratios (i.e., as measured, only corrected for first-order instrumental mass fractionation). In order to obtain relatively precise raw $^{53}Cr/^{52}Cr$ and $^{54}Cr/^{52}Cr$ ratios, we completed a large series of repeat measurements of the Cr isotopic composition in Chromite (114 runs). Using the raw $^{53}Cr/^{52}Cr$ ratio in Chromite as a reference and the slope as calculated from the more precise "second-order" data, we obtain the true position of the ES isochron (solid line). This also provides the true initial $^{53}Cr/^{52}Cr$ ratio of $+0.11 \pm 0.11 \varepsilon$ for ES at the time of isotopic closure. The measured ^{54}Cr excess in Chromite is $0.71 \pm 0.20 \varepsilon$ (Table 4). The raw $^{53}Cr/^{52}Cr$ ratio for Olivine 1 (solid symbol, Fig. 6), with a larger uncertainty, is totally consistent with this isochron.

The raw $^{54}Cr/^{52}Cr$ ratio in Olivine 1 is $+0.70 \pm 0.40 \varepsilon$. Because the set of measurements for this sample was not as extensive as that for Chromite, the uncertainty is larger. Nevertheless, it is totally consistent with the raw $^{54}Cr/^{52}Cr$ ratio in Chromite (Table 4). Thus, we conclude that the relative ^{54}Cr excess of $+0.71 \pm 0.20 \varepsilon$ as measured in Chromite is characteristic for the whole ES parent body. A comparison of this value with the

data for the carbonaceous chondrites (Table 1) indicates a clear similarity of the $^{54}Cr/^{52}Cr$ ratios in the ES and the Allende parent bodies. This strongly supports the idea of a genetic link between ES and CV3 type material.

An initial $^{53}Cr/^{52}Cr$ ratio of $+0.11 \pm 0.11 \varepsilon$ at the time of isotopic closure in ES is also consistent with CV3-type material as a precursor for ES. Indeed, if ES material evolved in an environment with a $^{55}Mn/^{52}Cr$ ratio of ~ 0.43 (as measured for Allende) until the Cr isotopes were finally equilibrated ~ 4558 Ma ago $(^{53}Mn/^{55}Mn = 1.17 \times 10^{-6}$ at that time), one can calculate that (regardless of the initial solar system $^{53}Mn/^{55}Mn$ ratio) the $^{53}Cr/^{52}Cr$ ratio at the time of isotopic closure in ES should be only $\sim 0.04 \varepsilon$ lower than the present-day $^{53}Cr/^{52}Cr$ ratio in bulk Allende $(+0.10 \pm 0.09 \varepsilon$, Table 1). This small difference cannot be resolved, and the similarity of both values is consistent with the formation of ES from a CV3-like precursor.

4. Summary

(1) The bulk samples of all carbonaceous chondrites exhibit variable deviations from the terrestrial standard value in both $^{53}Cr/^{52}Cr$ and $^{54}Cr/^{52}Cr$ ratios. The $^{53}Cr/^{52}Cr$ ratios are correlated with the respective $^{55}Mn/^{52}Cr$ ratios. The slope of the correlation line yields a $^{53}Mn/^{55}Mn$ ratio of $(8.5 \pm 1.5) \times 10^{-6}$ at the time of Mn/Cr fractionation with an initial $^{53}Cr/^{52}Cr$ ratio at that time of $-0.21 \pm 0.09 \varepsilon$. Using the angrite LEW 86010 as an absolute time marker yields a time for the Mn/Cr fractionation of $4568.1 + 0.8/-1.1$ Ma ago. This time is very similar to the formation age of Efremovka CAIs of 4567.2 ± 0.6 Ma [34], to a time of the Chainpur and Bishunpur chondrule formation at 4568 ± 1 Ma ago inferred from the data by [42] and, most likely, constrains early global high-temperature Mn/Cr fractionation in a nebular setting. However, a ~ 2 Ma time span between CAI formation and formation of chondrules calculated based on various $^{26}Al–^{26}Mg$ studies [e.g., 45,46] is inconsistent with this scenario as may be a very old age for carbonate formation in the Kaidun carbonaceous chondrite of ~ 4569 Ma [17].

(2) In contrast to other meteorite classes, the bulk samples of carbonaceous chondrites exhibit clear ^{54}Cr excesses that are correlated (except for HH237) with the ^{53}Cr excesses and also with Mn/Cr ratios. The most primitive meteorites Ivuna and Orgueil exhibit the largest ^{53}Cr and ^{54}Cr

excesses, while the most evolved Allende shows the smallest. We considered several scenarios to explain this correlation. One possibility is that ^{54}Cr* is also radiogenic, like ^{53}Cr*, and was formed by the decay of the short-lived parent radionuclide ^{54}Mn. The very short half-life of ^{54}Mn of 312 days, however, precludes the transport of live ^{54}Mn from a stellar source and would require that both short-lived radionuclides ^{53}Mn and ^{54}Mn were generated locally in spallation reactions during the early period of an active sun. But this scenario meets many difficulties. A more plausible and our preferred explanation is the heterogeneous addition of presolar material. The presolar component, enriched in ^{54}Cr, is mostly contained in the matrix of carbonaceous chondrites. The relative amount of matrix is highest in the most primitive chondrites and decreases in the sequence CI>CM>CO,CV [55]. A large proportion of Mn is also associated with the matrix, while Cr preferentially resides in the chondrules. Thus, the Mn/Cr ratio also follows the sequence CI>CM>CO>CV and is correlated with ^{54}Cr*. While any other scenario would put into serious question the usefulness and robustness of the ^{53}Mn–^{53}Cr system as a chronometer, our preferred 'matrix addition' scenario does not. In addition, the generally very good agreement between Mn–Cr ages and ages from other short- and long-lived chronometers indirectly also argues for this explanation.

(3) The differential dissolution of Ivuna has shown that an elevated ^{54}Cr/^{52}Cr ratio in the total rock is due to a mixture of an abundant component(s) with a moderate deficit of ^{54}Cr and a rare phase with high ^{54}Cr excess. The acid-resistant residues of carbonaceous chondrites are characterized by relatively large excesses of ^{54}Cr and moderate deficits of ^{53}Cr. The residue of the primitive Ivuna has the largest ^{54}Cr* ($\sim$ +13 ε), the more evolved CM chondrite shows successively more moderate ^{54}Cr*, and the most evolved Allende exhibits the smallest ^{54}Cr* ($\sim$ +2.7 ε). This may imply that Cr in the CM and CV residues is increasingly more equilibrated with Cr from the rest of the meteorites. In the residues, no correlation is observed between ^{53}Cr/^{52}Cr and the ^{55}Mn/^{52}Cr ratios and the variations of ^{53}Cr/^{52}Cr cannot be due to in situ ^{53}Mn decay. In contrast to the bulk samples of carbonaceous chondrites, the ^{53}Cr/^{52}Cr and ^{54}Cr/^{52}Cr ratios in the residues are anti-correlated, indicating that there are at least

two Cr components of possibly presolar origin. All residues have large excesses of the most neutron-rich Ti isotope, ^{50}Ti. Similar to ^{54}Cr*, the excess of ^{50}Ti is the largest in the Ivuna residue and the lowest in the Allende residue. The pattern of ^{50}Ti* does not exactly follow that observed for ^{54}Cr* since Mokoia has about the same ^{50}Ti* as does Ivuna, while ^{50}Ti* of Murchison is lower.

(4) Using the ^{54}Cr excesses in carbonaceous chondrites as a tracer of a genetic link between carbonaceous chondrite materials and a differentiated meteorite has shown that the ^{54}Cr excess of +0.71±0.20 ε found in the anomalous pallasite Eagle Station is similar to that measured in the bulk sample of Allende. The initial ^{53}Cr/^{52}Cr ratio of +0.11±0.11 ε at the time of isotopic closure is also consistent with an evolution in a reservoir with a Mn/Cr ratio similar to that of bulk Allende. Thus, the Cr isotope systematic indicates that the precursor of Eagle Station was indeed CV-type material as was suggested earlier based on the chemical composition and the oxygen isotopes [56,57]. The ^{53}Mn–^{53}Cr isotope systematic indicates that the Cr isotopes equilibrated in this meteorite 4557.5±0.6 Ma ago, essentially at the same time as in the main group pallasite Omolon [2].

Acknowledgments

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