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Manganese-chromium isotope systematics of enstatite meteorites

A. Shukolyukov^{1,*} and G.W. Lugmair^{1,2}

¹Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA 92093-0212, USA ²Max-Planck-Institute for Chemistry, Cosmochemistry, PO 3060, 55020 Mainz, Germany

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Abstract—We present results of a study of the ⁵³Mn-⁵³Cr isotope systematics in the enstatite chondrites and achondrites (aubrites). The goal of this study was to explore the capabilities of this isotope system to obtain chronological information on these important classes of meteorites and to investigate the original distribution in the inner solar system of the short-lived radionuclide ⁵³Mn. Our earlier work (Lugmair and Shukolyukov, 1998; Shukolyukov and Lugmair, 2000a) has shown that the asteroid belt bodies are characterized by essentially the same initial ⁵³Mn abundance. However, we have found the presence of a gradient in the abundance of the radiogenic ⁵³Cr between the earth-moon system, Mars, and the asteroid Vesta. If this gradient is considered as a function of the heliocentric distance a linear radial dependence is indicated. This can be explained either by an early, volatility controlled Mn/Cr fractionation in the nebula or by an original radially heterogeneous distribution of ⁵³Mn. The enstatite chondrites are suggested to form in the inner zones of the solar nebula, much closer to the Sun than the ordinary chondrites. Therefore, their investigation may be an important test on the hypothesis on a radial heterogeneity in the initial ⁵³Mn.

We have studied the bulk samples of the EH4-chondrites Indarch and Abee and the EL6-chondrite Khairpur. Although these meteorites have essentially the same Mn/Cr ratio as the ordinary chondrites, the relative abundance of the radiogenic ⁵³Cr is three times smaller than in the ordinary chondrites. Because these meteorites are primitive (undifferentiated) and no Mn/Cr fractionation had occurred within their parent bodies, this difference is a strong argument in favor of an initially heterogeneous distribution of ⁵³Mn in the early inner solar system. This finding is also consistent with formation of the enstatite chondrites in the inner zones of the solar nebula. Using the characteristic ⁵³Cr excess of the enstatite chondrites and the observed gradient, their place of origin falls at about 1.4 AU or somewhat closer to the Sun (i.e. >1.0–1.4 AU).

We also present chronological results for the enstatite chondrites and achondrites. The 'absolute' ⁵³Mn-⁵³Cr ages of the EH4-chondrites are old: ~4565 Ma. The EL6-chondrite Khairpur is ~4.5 Ma younger, which is in good agreement with the ¹²⁹I-¹²⁹Xe data from the literature. The age of the aubrite Peña Blanca Spring appears to be similar to those of the enstatite chondrites while that of the aubrite Bishopville is at least ~10 Ma younger, which is also in agreement with the ¹²⁹I-¹²⁹Xe data. The results from bulk samples of aubrites indicate that the last Mn/Cr fractionation in their parent body occurred ~ 4563 Ma ago and imply an evolution of the Mn-Cr isotope system in an environment with an higher than chondritic Mn/Cr ratio for several millions of years. *Copyright* © 2004 Elsevier Ltd

1. INTRODUCTION

For more than a decade the ⁵³Mn-⁵³Cr isotope system has been extensively studied in various solar system objects. It was clearly shown that the extinct radionuclide 53 Mn (we use T_{1/2} = 3.7 Ma; Honda and Imamura, 1971) is well suited for high-resolution chronological investigations of the early stages of the solar system history (first 15-20 Ma) (e.g., Nyquist et al., 1994; Lugmair and Shukolyukov, 1998; Endress et al., 1996; Nyquist et al., 2003). This isotope system also serves as a tracer for various processes in the early solar system and may provide constraints for models of nucleosynthesis. Mn and Cr are abundant elements in solar-system materials so that a wide variety of ancient objects can be dated using the ⁵³Mn-⁵³Cr isotope system. The results of our investigations of HED meteorites (howardites, eucrites, diogenites), angrites, chondrites, Martian meteorites (SNCs), a lunar anorthosite, pallasites and a primitive achondrite are summarized in Lugmair and Shukolyukov (1998).

The former presence of ⁵³Mn in these meteorites is indicated in the form of variations in the relative abundance of the radiogenic daughter isotope, ⁵³Cr. In most cases these variations are due to Mn/Cr fractionation processes, which occurred during or before meteorite or parent body formation at a time when ⁵³Mn was still extant (e.g., Lugmair and Shukolyukov, 1998; Nyquist et al., 2001). We have determined the relative and 'absolute' ⁵³Mn-⁵³Cr ages in a number of meteorites of different classes. To obtain 'absolute' ages the relative ⁵³Mn-⁵³Cr ages were mapped onto an absolute time scale by anchoring to the precise Pb-Pb age of the angrites LEW86010 and Angra dos Reis (Lugmair and Galer, 1992). We have previously shown that the ⁵³Mn-⁵³Cr chronometer is reasonably robust and, in many cases, is not sensitive to late secondary events (Lugmair and Shukolyukov, 1998). When available, the results obtained with other isotope chronometers are generally consistent with the ⁵³Mn-⁵³Cr results. Based on the studies of ⁵³Mn-⁵³Cr isotope system (combined with the results obtained with other short- and long-lived isotope chronometers) in various meteorites we estimated the formation time of the first high temperature condensates (Ca-Al rich inclusions-CAI) in the solar system, inferred constraints on the duration of plan-

^{*} Author to whom correspondence should be addressed (ashukolyukov@ucsd.edu).

etesimal accretion, established the time of planetary melting, mantle and core formation for Vesta, and constrained the timing of igneous processes and thermal metamorphism within planetesimals (Lugmair and Shukolyukov, 1998; Lugmair and Shukolyukov, 2001).

The other important issue is a possible heterogeneity in the original ⁵³Mn distribution. It is well known that the solar nebula was isotopically homogeneous to a large degree. This is a result of prolonged and thorough mixing of various nucleosynthetic components of different origin already at the molecular cloud stage. The exceptions, such as CAI or presolar grains from primitive meteorites with isotopic anomalies (e.g., Papanastassiou, 1986; Zinner, 1997) are rare and probably do not play a significant role on a large planetary scale. In some cases, however, we find small differences in the isotopic compositions even on a planetary scale. For example, it was recently shown (Podosek et al., 1999; Shukolyukov and Lugmair, 2001) that even bulk samples of carbonaceous meteorites reveal small excesses of ⁵⁴Cr (as compared to other meteorite classes, Earth, Mars and Moon).

In contrast to the ancient, essentially well mixed solar nebula material, short-lived radionuclides were injected into and/or formed within the solar nebula just before or during solar system formation (e.g., Cameron and Truran, 1977; Shu et al., 1996). It is relevant to note that certain stable nuclei were also generated. This is particularly important for the ⁵³Mn-⁵³Cr isotope system because sources producing 53Mn will also produce Cr isotopes in non-solar ratios (Nichols et al., 1999). It is not known if all these newly formed nuclides were distributed homogeneously within the solar system during a relatively short time of a few million years. A simple chronological use of these radionuclides in various solar system objects is appropriate only if they were originally homogeneously distributed in the materials from which these objects were subsequently formed. Thus, the problem of their homogeneous or heterogeneous distribution in the early solar system is of prime importance.

Our recent studies of the 53Mn-53Cr isotope system in various meteorites (Lugmair and Shukolvukov, 1998; Shukolvukov and Lugmair, 2000a) have indicated that the relative abundance of radiogenic ⁵³Cr is consistent with an essentially homogeneous original distribution of ⁵³Mn within the asteroid belt. The ⁵³Mn-⁵³Cr chronometer therefore can be directly used for dating samples which originated in this region. On the other hand, we have found that all studied meteorite classes indicate a clear excess of ⁵³Cr as compared to the Earth and a lunar sample also exhibits a terrestrial ⁵³Cr/⁵²Cr ratio. The ⁵³Cr/⁵²Cr ratios in Martian meteorites are intermediate between those in the Earth-Moon system and asteroid belt bodies. If the variations in the ⁵³Cr/⁵²Cr ratios are considered as a function of heliocentric distance, a radial dependence of the relative abundances of radiogenic ⁵³Cr is indicated: i.e., the relative ⁵³Cr excess increases approximately linearly with distance from the sun (Lugmair and Shukolyukov, 1998). This linear gradient is based on experimental data only assuming normal 50 Cr/52 Cr and experimentally determined ⁵⁴Cr/⁵²Cr ratios, which are normal within error. It can be explained either by an early volatility controlled Mn/Cr fractionation within the nebula (e.g., Cassen and Woolum, 1997) or by an original radial heterogeneous distribution of ⁵³Mn. Unfortunately, model calculations of the Mn/Cr ratios in the bulk terrestrial planets are not sufficiently precise to ascertain the validity of a volatility driven scenario and until now we did not have strong arguments in favor of the ⁵³Mn heterogeneity hypothesis. Both scenarios are discussed in detail in Lugmair and Shukolyukov, 1998 and further in Shukolyukov and Lugmair (2000a) and will not be repeated here.

In this work we extend our investigations of ⁵³Mn-⁵³Cr systematics to enstatite chondrites and achondrites. The study of these unique classes of meteorites may help to distinguish between the two scenarios mentioned above. We also present results on the ⁵³Mn-⁵³Cr isotope system in aubrites (enstatite achondrites) in an attempt to investigate a potential genetic relationship with the enstatite chondrites and to constrain the timing of processes on their parent bodies.

2. ENSTATITE CHONDRITES

Enstatite chondrites have a unique bulk and mineralogical composition. The main silicate is enstatite. These meteorites are rich in metallic nickel-iron, whose content is highly variable, and contain various sulfides such as troilite, oldhamite, alabandite, niningerite, and daubreelite (see, for example, Keil, 1968; Sears et al., 1982 and Kallemeyn and Wasson, 1986). The enstatite chondrites are among the most reduced natural assemblages. The extremely low degree of oxidation is the primary evidence that enstatite chondrites formed nearer to the Sun than other groups of chondrites (e.g., Baedecker and Wasson, 1975). The enstatite chondrites comprise two groups: high-Fe (EH) and low-Fe (EL) (Sears et al., 1982). These groups are usually assigned to different parent bodies (PBs) (e.g., Kallemeyn and Wasson, 1986; Kong et al., 1997). In the oxygen three-isotope diagram the E-chondrites occupy a region well removed from the other chondrite classes and lie on the terrestrial fractionation line (Clayton et al., 1976), as expected for materials that formed in the hot innermost region of the nebula (Kallemeyn and Wasson, 1986). In various models of formation of the inner planets E-chondrite type material is deemed to be a significant constituent (e.g., Wänke and Dreibus, 1988).

In the present context, the importance of E-chondrites is that their ⁵³Mn-⁵³Cr systematics could potentially verify the presence of a radial gradient in the original ⁵³Mn distribution since, according to literature data, their Mn/Cr ratios are similar to those in ordinary chondrites. If this gradient did exist in the early solar nebula and if E-chondrites did form in the inner zones of the solar nebula then the relative abundance of radiogenic ⁵³Cr in bulk samples of E-chondrites should be lower than in ordinary chondrites and the other "asteroid belt" bodies. Moreover, we may be able to determine a probable place of their origin. Recent analyses of E-chondrites by Wadhwa et al. (1997) do not allow to find an answer to these questions because any possible differences in the relative ⁵³Cr abundances for the bulk meteorites cannot be resolved by ion probe. The earlier pioneering study of the E-chondrite Indarch using TIMS (Birck and Allègre, 1988) is inconclusive for this purpose because the precision of the Cr isotopic measurements was not sufficient at that time. In addition, a bulk sample has not been studied and there is an apparent contradiction between the high initial ⁵³Cr/⁵²Cr ratio obtained from the sulfide data

Table 1. Manganese and chromium concentrations, Mn/Cr ratios, and ⁵³Cr excesses in enstatite chondrites.

Sample	Weight (g)	Mn (ppm)	Cr (ppm)	⁵⁵ Mn/ ⁵² Cr (±5%)	Number of runs	ε(53)
			Inda	rch		
TR 1	1.00	2078	3211	0.731	87	0.17 ± 0.03
TR 2 ^a	0.761	2135 ^b	3010 ^b	0.801 ^b		0.16 ± 0.07^{b}
Leach 1		819	82.5	11.2	17	2.54 ± 0.07
Leach 2		620	72.4	9.67	19	2.41 ± 0.04
Leach 3		431	2143	0.227	21	0.02 ± 0.04
Residue		265	712	0.420	15	0.07 ± 0.05
			Abo	ee		
TR	1.49	1326	3341	0.448	19	0.08 ± 0.05
Clast 1 ^a	0.163	5067 ^b	3195 ^b	1.79 ^b		0.46 ± 0.07^{b}
Leach		1393	569	2.76	15	0.70 ± 0.04
Residue		3674	2626	1.58	13	0.41 ± 0.04
			Khair	rpur		
TR 1	1.07	2207	4060	0.614	14	0.14 ± 0.04
TR 2 ^a	0.306	2323 ^b	3392 ^b	0.773 ^b	_	0.16 ± 0.07^{b}
Leach 1		1101	32	38.8	16	4.30 ± 0.06
Leach 2		980	637	1.74	20	0.23 ± 0.07
Leach 3		209	2712	0.087	15	0.09 ± 0.04
Residue		33	11.8	3.16	4	0.42 ± 0.13

Mn and Cr concentrations in the leaches and residues are calculated using the initial sample weight. TR—total rock. The normalizing 50 Cr/ 52 Cr ratio is 0.051859 (Shields et al, 1966). The standard values for 53 Cr/ 52 Cr and 54 Cr/ 52 Cr are 0.1134507 and 0.0282085, respectively. The uncertainties in ϵ (53) are $2\sigma_{mean}$. The uncertainty in the value of 53 Cr/ 52 Cr measured for terrestrial standards is not included. *Indarch:* Leach 1–0.5 N acetic acid, Leach 2–9 N acetic acid, Leach 3–8 N HNO₃.

Abee: Leach-9 N acetic acid.

Khairpur: Leach 1-9 N acetic acid, Leach 2-1.8 N HCl, Leach 3-8 N HNO₃.

^a-used for the leaching experiment.

^b -calculated from mass balance of leach fractions.

and the close to terrestrial ${}^{53}\text{Cr}/{}^{52}\text{Cr}$ ratio for the silicate fraction.

In this section we present the experimental results obtained for three E-chondrites. These data were in part presented earlier in abstract form (Shukolyukov and Lugmair, 1998a; 1999).

2.1. Indarch

We started our investigation of the enstatite chondrites with the EH4 chondrite Indarch (IND). To obtain phases with different Mn/Cr ratios we have utilized a differential dissolution procedure similar to that described by Birck and Allègre (1988). Different sulfides were dissolved in acids with different acidities. A 0.76 g bulk sample was ground in a boron carbide mortar to a grain-size smaller than 125 μ m. Before the acid treatment the sample was thoroughly washed in acetone under ultrasonication. The sulfides, containing Mn and Cr in different proportions, were dissolved in acids with increasing acidity: 0.5 N acetic acid (Leach 1), 9 N acetic acid (Leach 2), and 8 N HNO₃ (Leach 3). After each step the sample was washed repeatedly with distilled water and the washes and the leach were combined. The silicate residue was dissolved in an HF/ HNO₃ mixture. We have also studied a total rock sample (TR) of IND. To ensure good representation of bulk chemistry for the whole rock a large (1.0 g) sample was analyzed. We have measured the isotopic composition of Cr, and Mn and Cr concentrations in these samples. The chemical separation of Cr and the mass spectrometric procedure were similar to those

described in Lugmair and Shukolyukov, 1998. The isotopic analyses of Cr were made with a VG-54E thermal ionization single-collector mass spectrometer and the concentration measurements were done with ICP-OES. The results are presented in Table 1 and Figure 1.



Fig. 1. 53 Mn- 53 Cr isotope systematics in the EH4 chondrite Indarch. TR—total rock. Leach 1–0.5 N acetic acid, Leach 2–9 N acetic acid, Leach 3–8 N HNO₃. The 53 Cr/ 52 Cr ratio in TR Indarch is clearly lower than that in the bulk ordinary chondrites (open symbol) while the Mn/Cr ratios are the same.

The isotopic variations of ⁵³Cr are measured as the deviation of the ⁵³Cr/⁵²Cr ratio from the normal terrestrial ⁵³Cr/⁵²Cr ratio. These variations are expressed in ε -units (1 ε is 1 part in 10^4). In our previous work we used uncertainties in the isotope ratios that are based on the 1σ distribution of the individual run results and were used to reflect external 'intermediate' term reproducibility. These uncertainties are more conservative than normally used $2\sigma_{\text{mean}}$ uncertainties (see Lugmair and Shukolyukov, 1998 for details). We note, however, that the measured differences in $\varepsilon(53)$ between meteorite phases with equilibrated Cr isotopes are considerably smaller than the presented uncertainties (see Lugmair and Shukolyukov, 1998, Fig. 6-8, Fig. 10-12). In addition, during recent years we measured a dozen of terrestrial rocks and geological standards and found that the total spread in $\varepsilon(53)$ is only ± 4 ppm while the uncertainties based on the 1σ distribution are 6–11 ppm. The results for the terrestrial rocks are presented in Shukolyukov and Lugmair (1998b) and Kyte et al. (2003). Thus, the uncertainties based on the 1σ distribution appear to be too conservative and, therefore, we decided to select the customary approach and use the normal $2\sigma_{\mathrm{mean}}$ uncertainties. The comparison of data for the laboratory standard and the terrestrial rock (processed through chemistry) indicates that there is no difference between samples and standards data due to potential differences in work function of the filament or a matrix effect as a result of variation in chemistry.

The Mn/Cr ratios in the acetic acid Leaches 1 and 2 are considerably larger than those in the 8 N HNO₃ Leach 3. This probably indicates that Leaches 1 and 2 contain a large portion of Mn from more readily soluble alabandite (MnS) while Leach 3 is enriched in Cr from less soluble daubreelite (Cr_2FeS_4). The ⁵³Cr excesses are well correlated with the respective ⁵⁵Mn/⁵²Cr ratios (Fig. 1). If the best fit line through the data points is taken as an isochron its slope yields a 53 Mn/ 55 Mn ratio of (2.8 ± 0.1) \times 10⁻⁶ and the initial ⁵³Cr/⁵²Cr ratio of $-0.03 \pm 0.03 \epsilon$ at the time of isotopic closure. In contrast, a clear correlation between the ⁵³Cr/⁵²Cr and ⁵⁵Mn/⁵²Cr ratios was not observed in the earlier IND investigation by ion probe (Wadhwa et al., 1997) since the data points for individual sulfide grains do not fall on a single line. This is most likely due to some diffusive redistribution of Mn and Cr after partial or complete decay of ⁵³Mn (Wadhwa et al., 1997). Another possibility is a partial Mn loss from high Mn/Cr phases suggesting an array with much steeper slope at much lower Mn/Cr ratios, although sphalerite data points scatter widely.

The most remarkable and important feature is that the ⁵³Cr excess for TR1 (0.17 \pm 0.03 ε) clearly deviates from that of the ordinary chondrites (0.48 \pm 0.03 ε) while its ⁵⁵Mn/⁵²Cr ratio is chondritic (~0.73). A less precise ⁵³Cr/⁵²Cr ratio of ~0.16 ε calculated from mass balance based on the leach and residue data is consistent with this value. The IND isochron passes clearly below the chondritic data point (Fig. 1). It has to be noted that the ⁵⁵Mn/⁵²Cr ratios in large bulk samples of ordinary chondrites show only a modest variation. Indeed, this ratio is 0.77 in the L-chondrite Finney, 0.77 in the H-chondrite Plainview, and 0.76 in the H-chondrite Dimmit (Lugmair and Shukolyukov, 1998). These data agree well with the results for the H-chondrites Ste. Marguerite (~0.79) and Richardton (~0.72) (Polnau and Lugmair, 2001). Moreover, the ⁵⁵Mn/⁵²Cr ratios calculated from the average chondrite compositions

(Wasson and Kallemeyn, 1988) for H-, L-, and LL-chondrites are 0.72, 0.75, and 0.79, respectively. Thus, we assign to ordinary chondrites an average value of 0.76 and call it "chondritic."

All Cr isotopes were normalized to ⁵²Cr and corrected for mass fractionation according to an exponential law with the use of ${}^{50}Cr/{}^{52}Cr = 0.051859$ (Shields et al., 1966) as internal standard. Instrumental fractionation for normal sample loads ranged typically from -7 to -1.8 permil per amu using this value. In our method of data reduction we use a second order mass fractionation correction based on the ⁵⁴Cr/⁵²Cr ratio. The application of the second order fractionation correction was discussed in Lugmair and Shukolyukov, 1998. We only note here that we observed the presence of a residual mass fractionation effect from the application of a strict exponential law. After normal exponential correction we found a strongly linearly correlated variation (R \sim 0.99; slope 2.15) of these residual effects on ⁵³Cr/⁵²Cr versus ⁵⁴Cr/⁵²Cr for the laboratory standards. We found later that these effects mostly depend on the actual location of sample evaporation on the filament (relative to the ion-source optics) and semiquantitatively depend on the horizontal position of the filament relative to the extraction slit. These effects are different in magnitude for different ion-sources. When determining ⁵³Cr/⁵²Cr ratios for samples, these mass discrimination effects were corrected by utilizing the parameters (slope and intercept) obtained from the ${}^{53}Cr/$ ⁵²Cr vs. ⁵⁴Cr/⁵²Cr correlation line from several hundred Cr standard measurements. These residual effects were independent of instrumental fractionation. The application of the second order fractionation correction assumes no excess or deficit of ⁵⁴Cr, which is the case for most of the meteorite classes studied (at least within an uncertainty of ~ 0.1 to $\sim 0.3 \epsilon$), including ordinary chondrites, angrites, HEDs, main-group pallasites, mesosiderite clasts, primitive achondrites, brachinites, Martian meteorites, and Moon (Lugmair and Shukolyukov, 1998). A potential excess of ⁵⁴Cr would translate into an apparent deficit of ⁵³Cr. To ensure that the observed difference between ordinary chondrites and IND is not an artifact due to an anomalous ⁵⁴Cr/⁵²Cr ratio in IND and the second order fractionation correction applied to the ⁵³Cr/⁵²Cr ratios, we have conducted 87 repeat measurements of the TR Cr isotopic composition.

Because of the large number of repeat measurements these TR data can serve as a good example for a brief discussion of the effect of the second order correction. The 'first order' exponential fractionation correction is applied using a ⁵⁰Cr/ ⁵²Cr ratio of 0.051859 (Shields et al., 1966) as internal standard. If we take the raw data of TR and include uncertainties of all standards measured during the same time (also raw data) we obtain $\varepsilon(53) = +0.13 \pm 0.10$ and $\varepsilon(54) = -0.11 \pm 0.22$ $(2\sigma_{\rm mean})$. Excluding the uncertainties from the standards we obtain $\varepsilon(53) = +0.13 \pm 0.09$ and $\varepsilon(54) = -0.11 \pm 0.18$. (We normally do not include the standard uncertainties, as is customary by most authors. When the second order correction is applied, the uncertainties in the standard values are totally negligible because of the large number of standard measurements performed over the years). Since the relative deviation of $\varepsilon(54)$ is very small and consistent with the standard value (i.e., $\epsilon(54) = 0$, ${}^{54}Cr/{}^{52}Cr \equiv 0.0282085$) within error one can assume that ${}^{54}\text{Cr}/{}^{52}\text{Cr}$ is normal (to within $< 0.2 \epsilon$). If we now apply the second order correction about one half of the devia-



Fig. 2. ⁵³Mn-⁵³Cr isotope systematics in the EH4 chondrite Abee. Leach—9 N acetic acid. The Indarch isochron is shown schematically for comparison. The similar slopes of the isochrons indicate a contemporaneous formation of these two meteorites. The Abee isochron also passes well below the ordinary chondrite data point.

tion of ${}^{54}\text{Cr}/{}^{52}\text{Cr}$ (at 2 amu from the normalization isotope) is then propagated to ${}^{53}\text{Cr}/{}^{52}\text{Cr}$ (at 1 amu). In this example the correction would yield a result of $\varepsilon(53) = +0.185$ (relative to the standard value of ${}^{53}\text{Cr}/{}^{52}\text{Cr} = 0.1134507$). It has to be noted, however, that in the actual data reduction process used each single run result is corrected and the final average may be slightly different $-\varepsilon(53) = +0.17$ in this case. Of course, the resulting uncertainties will be smaller. Whatever values are used (raw or corrected) significant differences between the enstatite chondrite values and the ordinary chondrite and the terrestrial values are indicated.

2.2. Abee

To verify the result obtained for IND we have extended our study to another EH4-chondrite. Abee. We have analyzed a large (1.49 g) total rock sample (TR) and conducted a leaching experiment on a small 0.163 g clast from this meteorite. The experimental procedures for Abee and for all other studied enstatite meteorites (see below) were similar to those applied to IND. The clast was crushed and treated with 9N acetic acid. The Cr isotopic composition and Mn and Cr concentrations in TR, Clast Leach and Clast Residue are given in Table 1. Although the Mn-Cr ratio of TR is somewhat lower than chondritic, it is well-known that Abee is a chemically inhomogeneous meteorite. Abee contains clasts of up to several centimeters in dimension and some 5-mm-sized dark "inclusions" (Sears et al., 1983). Thus, this difference is most likely due to an inadequate sampling. Baedecker and Wasson (1975) give average Mn and Cr concentrations of 2.3% and 3.4% respectively, which translates into a chondritic ⁵⁵Mn/⁵²Cr ratio of 0.76. The calculated bulk clast reveals a high ⁵⁵Mn/⁵²Cr ratio of 1.79, which is probably indicative of a rather different proportion of various Mn- and Cr-bearing sulfides as compared to TR. This is also reflected in a lower Mn/Cr ratio in the Leach (9N acetic acid) than in Indarch. The data points for the Leach, TR, and Residue form a straight line (Fig. 2). If this line is



Fig. 3. 53 Mn- 53 Cr isotope systematics in the EL6 chondrite Khairpur. Leach 1—9 N acetic acid, Leach 2–1.8 N HCl, Leach 3—8 N HNO₃. The insert shows enlarged the results for the samples with small Mn/Cr ratios. The Abee and Indarch isochrons are shown schematically for comparison. The lower slope of the Khaipur isochron indicates that the Mn-Cr isotope system in this meteorite closed later than in the EHchondrites.

considered as an isochron its slope yields a ⁵³Mn/⁵⁵Mn ratio at the time of isotopic closure of $(3.0 \pm 0.4) \times 10^{-6}$ with an initial ${}^{53}\text{Cr}/{}^{52}\text{Cr}$ ratio of $-0.03 \pm 0.06 \epsilon$. These values are indistinguishable within the uncertainties from those of Indarch $((2.8 \pm 0.1) \times 10^{-6} \text{ and } -0.03 \pm 0.03 \epsilon$, respectively). This indicates that the Mn-Cr isotope system closed essentially contemporaneously in these two meteorites. Note that the Abee isochron also passes below the chondritic data point (Fig. 2). At the chondritic ⁵⁵Mn/⁵²Cr ratio of 0.76 the excess of ⁵³Cr calculated from the Abee isochron is $\sim 0.17 \epsilon$, which is the same as was measured for IND TR. A raw ⁵³Cr/⁵²Cr ratio for TR Abee of $\pm 0.14 \pm 0.16 \epsilon$ is consistent with a second order corrected value of $\pm 0.08 \pm 0.05 \epsilon$. A raw ⁵⁴Cr/⁵²Cr of ± 0.07 \pm 0.35 ε is indistinguishable from the terrestrial normal value, although the uncertainty is large because of the relatively small number of measurements as compared to IND.

2.3. Khaipur

Extending our study of enstatite chondrites to the EL-class we have investigated the EL6 chondrite Khairpur (KHA). The procedures were similar to those utilized for IND. We have measured a large (1.07 g) bulk sample of KHA (TR1) and have conducted a leaching experiment on a 0.306 g fragment of KHA (TR2). We have treated TR2 with 9 N acetic acid (Leach 1), 1.8 N HCl (Leach 2), and 8 N HNO₃ (Leach 3). The silicate residue (and TR1) was dissolved in an HF/HNO3 mixture. The ⁵³Cr/⁵²Cr ratios and Mn and Cr concentrations are presented in Table 1. In contrast to the Abee clast, KHA Leach 1 (9N acetic acid) is characterized by a high ⁵⁵Mn/⁵²Cr ratio of 38.8. The ⁵⁵Mn/⁵²Cr ratio in TR1 of 0.61 is somewhat lower than chondritic and may be a sampling problem. A ⁵⁵Mn/⁵²Cr ratio in TR2 of 0.77 calculated from mass balance based on the leaches and the residue data is very much chondritic. The ⁵³Cr excesses are well correlated with the respective ⁵⁵Mn/⁵²Cr ratios (Fig. 3) and a high ⁵⁵Mn/⁵²Cr ratio in Leach 1 provides a good definition of the isochron. The 53Mn/55Mn ratio at the time of isotopic closure calculated from the slope of the KHA isochron is $(1.21 \pm 0.06) \times 10^{-6}$. This value is considerably lower than in IND and Abee, which implies that the ⁵³Mn-⁵³Cr system in KHA closed later than in EH-chondrites. Also, the initial ⁵³Cr/ 52 Cr ratio of $\pm 0.07 \pm 0.03 \varepsilon$ is higher and therefore consistent. Similar to the EH-chondrites the KHA isochron also passes below the ordinary chondrite data point (Fig. 3). At the chondritic ⁵⁵Mn/⁵²Cr ratio of 0.76 (close to the intercept of all E-chondrite isochrons) the excess of ⁵³Cr calculated from the KHA isochron is $\sim 0.15 \epsilon$. This is essentially the same value that was obtained for IND and Abee (~0.17 ϵ). A raw ⁵³Cr/ 52 Cr ratio for TR KHA of +0.13 \pm 0.14 ϵ is consistent with a corrected value of $\pm 0.14 \pm 0.04 \epsilon$. A raw ⁵⁴Cr/⁵²Cr ratio of $0.00 \pm 0.24 \epsilon$ does not show any hint of a deviation from the terrestrial normal value, although the uncertainty is also rather large. The uncertainties in raw ratios for Abee and Khairpur are typical for the measurements with a moderate number of runs.

It is appropriate to note here that, strictly speaking, the differential dissolution produces true isochrons only in the case if each leaching step provides complete dissolution of certain minerals (congruent dissolution; Y. Amelin, priv. comm.). Depending on fractionation between Mn and Cr during leaching, one can obtain for two-phase systems isochron slopes, and hence apparent ages, that are either too low or too high. If there are three or more minerals with non-zero contents of Mn and Cr in the rock, there is a higher probability of getting scatter of points due to leaching. In the case of Indarch and Khairpur with varied Mn-, Cr- bearing sulfide phases we applied four leaching steps. To retain a potentially artificial linearity, the Mn/Cr fractionation during every step should remain the same or follow a very special pattern. This appears unlikely and one could expect a scattered data point pattern, which is not the case (Fig. 1 and Fig. 3). Therefore, we consider these correlation lines as actual isochrons. For Abee we applied only two leaching steps. However, we did not leach TR but a Clast, which is very different from TR in composition (at least with respect to Mn and Cr) and most likely has different proportions of sulfide assemblages. However, the TR data point falls on the Clast isochron and, thus, it is unlikely that this isochron is an artifact. In addition, the time differences between Indarch, Abee, and Khairpur formation calculated from the slopes of the isochrons are in good agreement with the I-Xe data (see section 5.1) that would not be the case if these correlation lines were simply mixing lines.

3. ENSTATITE ACHONDRITES

Enstatite achondrites, or aubrites, are brecciated enstatite pyroxenites that consist mostly of FeO-free enstatite. The aubrites appear to be close relatives to the enstatite chondrites. The aubrites and the EH and EL chondrites have essentially the same oxygen isotopic compositions (e.g., Clayton et al., 1984). Therefore it is believed that they probably formed from a reservoir of similar composition, presumably in the same region of the solar system. The aubrite PB(s) were highly reduced. All aubrites except Shallowater are fragmental or regolithic breccias and formed in an enstatite meteorite PB, probably similar to the EH- and EL-PB(s), that melted and differentiated (e.g., Keil, 1989). The aubrites are depleted in siderophile and chalcophile elements; however, the nature and timing of a possible core formation event have not been worked out (Hewins and Newson, 1988).

We have extended the investigation of 53 Mn- 53 Cr isotope systematics to the aubrites in an attempt to unravel the chronology of the aubrite PB, to ascertain if their 53 Mn- 53 Cr data are consistent with that of the E-chondrites and the observed gradient in the 53 Cr/ 52 Cr ratios. We have studied the aubrites Pena Blanca Spring (PBS), Bishopville (BISH), and Cumberland Falls (CF). To obtain phases with different Mn/Cr ratios we have utilized (for PBS and BISH) a differential dissolution procedure similar to that used for the E-chondrites: the sulfides containing Mn and Cr in different proportions were dissolved in acids with increasing acidity and the silicate residues were dissolved in an HF/HNO₃ mixture. Preliminary results were presented earlier in abstract form (Shukolyukov and Lugmair, 2000b).

3.1. Peña Blanca Spring

We have treated a 1.62 g bulk sample progressively with 9 N acetic acid (Leach 1), 0.6 N HCl (Leach 2), 2.3 N HCl (Leach 3), and 8 N HNO₃ (Leach 4). The isotopic compositions of Cr, the Mn and Cr concentrations in the leaches, in the silicate residue, and in a 0.898 g total rock sample have been measured. The results are given in Table 2.

The ⁵⁵Mn/⁵²Cr ratios vary in a wide range from as low as 0.06 for Leach 4 up to 57.9 for Leach 1, which reflects the dissolution of various sulfides with very different Mn and Cr concentrations. But in contrast to the E-chondrites, the ⁵³Cr excesses reveal only a small variation (+0.94 to +1.36 ε) and are not correlated with the respective ⁵⁵Mn/⁵²Cr ratios (Fig. 4).

The variation of the measured ⁵³Cr/⁵²Cr ratios in the leaches and the residue indicates that some ⁵³Mn was still extant at the time of PBS formation. However, the lack of a correlation between the ⁵³Cr/⁵²Cr and the respective Mn/Cr ratios suggests a disturbance of the 53Mn-53Cr isotope system during a late secondary event. This disturbance might have caused a redistribution of the radiogenic ⁵³Cr among various mineral phases during diffusive processes. Because PBS is a breccia this scenario appears to be very probable. On the other hand, if we consider all PBS sulfides as a single phase a correlation between the 53 Cr excesses and the 55 Mn/ 52 Cr ratios appears to exist (Fig. 5). The values of ⁵³Cr/⁵²Cr and ⁵⁵Mn/⁵²Cr for the "bulk sulfides" (Leaches 1-4) have been calculated from mass balance and are 1.10ϵ and 2.87, respectively. Because the range in the ⁵⁵Mn/⁵²Cr ratios is small, and at relatively high values, this does not allow precise definitions of the slope and initial ⁵³Cr/⁵²Cr ratio. Nevertheless, the existence of a correlation implies that the secondary event(s) affected only the sulfides. If this correlation is considered as an isochron, the 53 Mn/ 55 Mn ratio at the time of isotope closure is (2.4 \pm 1.0) \times 10^{-6} and the initial ${}^{53}\text{Cr}/{}^{52}\text{Cr}$ ratio is $+0.51 \pm 0.30 \epsilon$. Thus, the relative ⁵³Mn abundance in PBS is similar to that in the studied enstatite chondrites.

3.2. Bishopville

A 0.860 g bulk sample of BISH was treated with 0.6 N HCl (Leach 1) followed by 8 N HNO_3 (Leach 2). We have measured

Table 2. Manganese and chromium concentrations, Mn/Cr ratios, and ⁵³Cr excesses in enstatite achondrites.

Sample	Weight (g)	Mn (ppm)	Cr (ppm)	⁵⁵ Mn/ ⁵² Cr (±5%)	Number of runs	ε(53)
			Peña Blanc	ca Spring		
TR 1	0.898	1052	394	3.01	15	1.16 ± 0.05
TR 2 ^a	1.62	1063 ^b	382 ^b	3.14 ^b		1.17 ± 0.08^{b}
Leach 1		205	4.0	57.9	21	1.36 ± 0.04
Leach 2		456	23.8	21.6	23	0.94 ± 0.03
Leach 3		3.1	12.1	0.289	16	1.06 ± 0.5
Leach 4		11.9	225	0.060	18	1.12 ± 0.04
Residue		387	117	3.73	16	1.30 ± 0.04
			Bishop	oville		
TR 1	0.911	916	273	3.79	17	1.31 ± 0.03
TR 2 ^a	0.860	786 ^b	218 ^b	4.07 ^b		1.36 ± 0.07^{b}
Leach 1		722	85.1	9.58	21	1.38 ± 0.04
Leach 2		4.1	113	0.041	11	1.35 ± 0.04
Residue		59.4	20.1	3.34	—	nd
			Cumberla	nd Falls		
TR	0.905	969	549	1.99	14	1.00 ± 0.05

Mn and Cr concentrations in the leaches and residues are calculated using the initial sample weight. TR-total rock. nd-not determined. *Peña Blanca Spring:* Leach 1–9 N acetic acid, Leach 2–0.6 N HCl, Leach 3–2.3 N HCl, Leach 4–8 N HNO₃.

Bishopville: Leach 1-0.6 N HCl, Leach 2-8 N HNO₃.

a -used for the leaching experiment.

^b -calculated from the mass balance.

the isotopic composition of Cr and Mn and Cr concentrations in the leaches and in another 0.911 g total rock sample. The Cr concentration in the residue was too small to facilitate a reliable measurement of the Cr isotopic composition in this phase. The results are given in Table 2. As was the case for the other enstatite meteorites the sulfides dissolved in the weaker acid have a high ⁵⁵Mn/⁵²Cr ratio (9.58, Leach 1), while the stronger acid dissolved sulfides with a very low ⁵⁵Mn/⁵²Cr ratio (0.041, Leach 2). In contrast to the other enstatite meteorites, however, the excess of ⁵³Cr in the leaches and in the total rock sample is essentially the same (Fig. 6). This indicates that this meteorite was formed (or the Cr isotopes were last equilibrated) after practically all ⁵³Mn had decayed. Thus, only an upper limit of 1.4×10^{-7} can be calculated for the ⁵³Mn/⁵⁵Mn ratio at the time of isotope closure.



Fig. 4. 53 Mn- 53 Cr isotope systematics in the aubrite Peña Blanca Spring (I). Leach 1–9 N acetic acid, Leach 2–0.6 N HCl, Leach 3–2.3 N HCl, Leach 4–8 N HNO₃. Res—residue. The 53 Cr excesses and the respective 55 Mn/ 52 Cr ratios are not correlated. The lack of a correlation suggests a disturbance of the 53 Mn- 53 Cr isotope system during a late secondary event(s) that might have caused a redistribution of the radiogenic 53 Cr and/or Mn among various mineral phases during diffusive processes.



Fig. 5. 53 Mn- 53 Cr isotope systematics in the aubrite Peña Blanca Spring (II). Lch 1–4 is the composite for all sulfides: the sum of the leaches 1, 2, 3, and 4 was calculated from mass balance. Although the range of the Mn/Cr ratios is rather small it appears that if the system Total sulfides—Total rock—Residue is considered a correlation between 53 Cr excesses and the 55 Mn/ 52 Cr ratios exists. This implies that the secondary event(s) affected only the sulfides.



Fig. 6. 53 Mn- 53 Cr isotope systematics in the aubrite Bishopville. Leach 1–0.6 N HCl, Leach 2–8 N HNO₃. The correlation line has essentially 0 slope. This indicates that the Cr isotopes were last equilibrated after practically all 53 Mn had decayed.

3.3. ⁵³Mn-⁵³Cr Systematics in the Bulk Samples of Aubrites

In addition to the PBS and BISH total rock samples, we have measured the Cr isotopic composition and Mn and Cr concentrations in a large (0.905 g) bulk sample of the aubrite Cumberland Falls (CF) (Table 2). The Mn/Cr ratio in CF is significantly smaller than in the other two aubrites and the ⁵³Cr excess is also lower. The ⁵³Cr excesses in all bulk samples are correlated with the respective Mn/Cr ratios and form a straight line (Fig. 7). The open symbols designate samples for which the Mn/Cr ratios and the ⁵³Cr excesses were calculated from mass balance of the dissolved fractions. (Although the 53Cr/52Cr ratio in BISH Residue has not been measured, its contribution to bulk Cr is negligible. In addition, the Cr isotopes in this meteorite are essentially equilibrated). If this correlation line is taken as an isochron its slope dates the last Cr equilibration and the final large scale Mn/Cr fractionation on the aubrite PB. The 53 Mn/ 55 Mn ratio at this time was (2.0 ± 0.5) $\times 10^{-6}$ and the initial 53 Cr/ 52 Cr is $+0.63 \pm 0.12 \epsilon$. The existence of the correlation in Figure 7 suggests that the source reservoirs of these meteorites were formed contemporaneously and that the ⁵³Mn-⁵³Cr systems of the bulk samples remained effectively closed since the time of their formation. In addition, the bulk aubrite isochron results are within error the same as those of PBS (see Fig. 5). Thus, PBS itself must have formed very close to the time of this last planetary differentiation episode.

In contrast to the HED bulk meteorite isochron (Lugmair and Shukolyukov, 1998), the slope and initial of the bulk aubrite isochron are less well defined since low Mn/Cr differentiates (analogous to the diogenites in the HED PB) are so far lacking. The other striking and more important difference is that the isochron passes far above both the ordinary and enstatite chondrite data points. This clearly indicates an evolution of the Mn-Cr isotope system in an environment with a substantially elevated Mn/Cr ratio for several million years before the formation of the aubrite reservoirs. Therefore, the evolution of the Mn-Cr isotope system in the aubrite PB is more complex than that in the HED PB, which still reflects an ordinary chondrite Mn/Cr ratio.



Fig. 7. ⁵³Mn-⁵³Cr isotope systematics in the bulk samples of the aubrites Bishopville (BISH), Cumberland Falls (CF), and Peña Blanca Spring (PBS). The open squares designate samples for which the Mn/Cr ratios and the ⁵³Cr excesses were calculated from mass balance of individually measured fractions. The bulk ordinary and enstatite chondrite data points are shown for comparison by opened circles. The ⁵³Cr excesses in the bulk samples are correlated with their respective Mn/Cr ratios. This suggests that the source reservoirs of these meteorites were formed contemporaneously and that the ⁵³Mn-⁵³Cr systems of the bulk samples remained essentially closed since the time of their formation. The isochron passes far above the ordinary and enstatite chondrite data points. This implies that due to the Mn/Cr fractionation within the aubrite parent body the Mn-Cr isotope system in the aubrite precursor material evolved in an environment with an elevated Mn/Cr ratio (relative to ordinary chondrites) for several millions of years.

4. ⁵³Mn-⁵³Cr ISOTOPE SYSTEMATICS IN THE E-CHONDRITES AS AN ARGUMENT FOR ⁵³Mn HETEROGENEITY AND PLACE OF THEIR ORIGIN

In Lugmair and Shukolyukov, 1998 and Shukolyukov and Lugmair (2000a) we have shown that the ⁵³Mn-⁵³Cr isotope systematics in all meteorite classes studied in the earlier work are consistent with the same original abundance of ⁵³Mn and essentially the same chondritic Mn/Cr ratio in materials from which these meteorites formed. This is made evident by several examples presented in Figure 8. The internal isochrons for angrites, pallasites, and for Brachina (Wadhwa et al., 1998) pass through the bulk ordinary chondrite data point. At the chondritic 55 Mn/ 52 Cr ratio of ~0.76 the 53 Cr excesses are the same as measured for the bulk ordinary chondrites ($\sim 0.48 \epsilon$). The line labeled "Chondrule" is a bulk chondrule isochron obtained by Nyquist et al. (2001) based on the study of Bishunpur and Chainpur chondules. The isochron passes close to the chondritic data point, illustrating general agreement between JSC and our data.

In contrast, the isochrons for all three studied E-chondrites pass well below the chondritic data point (Fig. 8). While these isochrons intersect very close to the chondritic 55 Mn/ 52 Cr ratio of ~0.76, the 53 Cr excesses at the chondritic Mn/Cr ratio are considerably lower (~0.16 ε) than for ordinary chondrites. Why are the characteristic 53 Cr/ 52 Cr ratios of the E-chondrites so different?

The lower bulk ⁵³Cr/⁵²Cr ratios in Earth, Moon, and Mars can in principle be explained by lower Mn/Cr ratios in their



Fig. 8. ⁵³Mn-⁵³Cr isotope systematics in various solar system objects. The internal isochrons for the angrites, pallasites, the primitive achondrites Brachina, the enstatite chondrites Indarch, Abee and Khairpur and the bulk chondrule isochrion (Nyquist et al., 2001) are shown schematically by the dashed lines. "Angrites" stands for ADOR and LEW 86010. The filled squares indicate the ⁵³Cr/⁵²Cr and ⁵⁵Mn/⁵²Cr ratios for bulk ordinary and enstatite chondrites. The isochrons form two families: most isochrons pass close to the data point for the bulk ordinary chondrites (0.48 \pm 0.03 ε at ⁵⁵Mn/⁵²Cr of ~0.76) while the enstatite chondrite isochrons intersect at a chondritic Mn/Cr ratio but pass well below the ordinary chondrite data point. The characteristic $^{53}\text{Cr}/^{52}\text{Cr}$ ratio in the bulk E-chondrites of 0.16 \pm 0.03 ϵ is clearly lower than in the bulk ordinary chondrites and other "asteroid belt" bodies (~0.5 ε). Because the Mn/Cr ratios in the ordinary and Echondrites are essentially the same, this difference cannot be explained by a Mn/Cr fractionation. This most likely reflects lower original ⁵³Mn abundance in the formation regions of E-chondrites and suggests that the original ⁵³Mn distribution in the nebula was heterogeneous (see text for details). Data are from this work, Lugmair and Shukolyukov (1998) and Wadhwa et al. (1998).

precursor planetesimals. The bulk Mn/Cr ratios of these (and the other) *differentiated* bodies, however, cannot be determined experimentally. Theoretical models are not precise enough to provide an adequate resolution. For example, Drake et al. (1989) calculated a ⁵⁵Mn/⁵²Cr ratio for bulk Earth of as low as 0.40 while data by Allègre et al. (1995) suggest a value almost as high as 0.68, very close to 'chondritic'. Thus, the model Mn/Cr ratios for bulk Earth do not provide an unambiguous indication of the existence or absence of a Mn depletion in its precursors. The model Mn/Cr ratio of Mars, although estimated with a large uncertainty, is chondritic (Dreibus and Wänke, 1979, 1980; Drake et al., 1989).

A comparative study of ordinary and enstatite chondrites helps to avoid these difficulties. The 55 Mn/ 52 Cr ratio in bulk EH-chondrites (~0.79) is practically indistinguishable from the solar (CI) value (~0.81) (data from Wasson and Kallemeyn, 1988) and from the ordinary chondrite value (~0.76, see section 2.1). Because they originate from relatively small and undifferentiated planetary objects, there was no planet-wide, or worse, open-system Mn/Cr fractionation during the evolution of these chondrite parent planetesimals. Therefore, any variations in 53 Cr/ 52 Cr ratios in large *bulk* samples of chondrites should be characteristic for the whole parent bodies and for the region where these parent bodies formed. Although the Echondrites are characterized by the same primitive chondritic



Fig. 9. Relative abundance of radiogenic ⁵³Cr in solar system objects vs. their heliocentric distance (after Fig. 2) in Shukolyukov and Lugmair, 2000a). The dependence is linear, however, the shape of this dependence outside the 1 AU–2.4 AU range is not known. The observed gradient is most likely due to an original heterogeneous radial distribution of ⁵³Mn (see text). Using this gradient and a characteristic ⁵³Cr excess in the bulk enstatite chondrites of ~0.16 ε , their parent bodies appear to have formed at ~1.4 AU. If the earth's precursors were somewhat depleted in Mn compared to ordinary and enstatite chondrites, the place of origin of the enstatite chondrites would be closer to the Sun (shown by the arrow) and the dependence would become non-linear.

Mn/Cr ratio, their characteristic 53Cr/52Cr ratios are much lower than in ordinary chondrites. Because this difference cannot be explained by a Mn/Cr fractionation we suggest that the original ⁵³Mn abundance in the regions where the Echondrite PBs formed was lower and, thus, the ⁵³Mn distribution in the nebula most likely was heterogeneous. An alternative scenario would require a separation of Cr from Mn in E-chondrite precursor material for several millions of years at an early stage of solar system history followed by re-mixing to result in a chondritic Mn/Cr ratio. We consider this possibility as unlikely, particularly in view of the metamorphic type (EH4) of this meteorite. Further, we note that taking into account the uncertainties and shallow slopes of the E-chondrite isochrons their intersection is surprisingly close to the chondritic data point and not to a "primary" solar nebula (chondrule) isochron. One of the reviewers suggested that the E-chondrite parent body could have formed from material of generally low Mn/Cr ratio that acquired a "late veneer" of more volatile material enriched in ⁵³Mn towards the end of its accretion. However, to explain the E-chondrite data this "last veneer" had to be equilibrated with the rest of the body, which is unlikely taking into account the fact that the E-chondrite parent body(ies) is undifferentiated. It appears, therefore, that the ⁵³Mn-⁵³Cr isotope systematic is consistent with the hypothesis that the observed radial gradient in the relative ⁵³Cr abundance is due to initial ⁵³Mn heterogeneity. From this it can be inferred that the Echondrites formed in zones closer to the sun than the asteroid belt. The characteristic ${}^{53}Cr/{}^{52}Cr$ ratio of $\sim 0.16 \epsilon$ for both the bulk EH- and EL-chondrites may either indicate the same PB or different PBs that, however, originated at the same heliocentric distance. What is this distance? Figure 9 illustrates the observed gradient in the relative ⁵³Cr abundance (Lugmair and Shukolyukov, 1998). The Earth-Moon system is characterized by a ⁵³Cr/⁵²Cr ratio of 0 ε , Mars (SNC meteorites) ~ +0.24 ε , and the asteroid Vesta ~ 0.5 ε . Placing a characteristic ⁵³Cr/⁵²Cr ratio for the E-chondrites of ~0.16 ε on the correlation line yields a heliocentric distance of ~1.4 AU. Obviously this does not imply that the E-chondrite PBs are presently located at 1.4 AU: after formation at 1.4 AU these PBs were presumably perturbed by close planetary encounters into new orbits in the asteroid belt region where these meteorites now come from. The estimated heliocentric distance of 1.4 AU is consistent with the assumption that the E-chondrites formed much nearer to the Sun than the other meteorites, as was discussed by Baedecker and Wasson (1975). These authors, however, suggested formation even closer to the Sun: in the Mercury-Venus region.

It should be noted, however, that a distance of 1.4 AU is actually an upper limit. Although the gradient in the relative ⁵³Cr abundance among solar system objects is based on experimental data only, assuming normal 50Cr/52Cr and experimentally determined ⁵⁴Cr/⁵²Cr ratios, placing the E-chondrite parent bodies at 1.4 AU is model dependent. If theoretical models that reconstruct the bulk Earth composition with a lower than chondritic Mn/Cr ratio are correct and the Earth's precursors were indeed depleted in Mn relative to Cr, then the true characteristic ⁵³Cr/⁵²Cr ratio for a body with a chondritic Mn/Cr at 1 AU would be larger than 0 ε ; this hypothetical body would plot in Figure 9 somewhere above the Earth-Moon data point. In this case the place of origin of E-chondrites would be somewhat closer to Earth's orbit as indicated by the arrow in Figure 9. Similarly, if due to subsequent radial mixing at the planetary embryo stage the ⁵³Cr gradient at present is less steep than it initially was then the origin of the E-chondrites would have been also closer to 1 AU. Thus, we infer from the Mn-Cr isotope systematics that the E-chondrites formed somewhere in the range of >1 AU to 1.4 AU.

As was noted by Shukolyukov and Lugmair (2000a) a nonchondritic Mn/Cr ratio for Earth would imply that the actual gradient in the initial ⁵³Mn abundance is non-linear. Obviously, this would not influence the validity of the observed linear gradient in the ⁵³Cr abundance but would imply that the observed linearity is coincidental and is a result of the superposition of the initial ⁵³Mn heterogeneity and Mn depletion in Earth's precursors. Moreover, there is no a priori reason to suggest that the radial distribution of ⁵³Mn *should* be linear. The observed linearity is either a riddle or a trivial coincidence. In addition, we do not know the form of this dependence outside the 1 AU-2.4 AU range (Fig. 9). We do not know why the "asteroid belt" bodies reveal the same characteristic ⁵³Cr excess ($\sim 0.5 \epsilon$): either all studied bodies formed in the same. relatively narrow region (or feeding zones) with no detectable ⁵³Mn heterogeneity or the whole asteroid belt is characterized by similar ⁵³Cr/⁵²Cr ratios. This would imply a thorough radial mixing in the asteroid belt region. What one can assume, however, is that the abundance of the radiogenic ⁵³Cr obviously cannot increase continuously and there should be a maximum in the radial dependence and a subsequent decrease of the ⁵³Cr abundance. This maximum may be located within the asteroid belt or further outside. The recent studies of carbonaceous chondrites (Shukolyukov and Lugmair, 2001) have shown that the primitive (CI) carbonaceous chondrites with chondritic Mn/Cr ratios of ~ 0.8 are characterized by a slightly lower ⁵³Cr excess of ~0.4 ε . If the parent bodies of the carbonaceous chondrites were formed in the outer regions of the asteroid belt (as is suggested by the astronomical observations on the location of C-type asteroids, Bell et al., 1989), this may imply that this difference is due to a lower initial ⁵³Mn in these outer regions. This difference, however, is too small to draw unequivocal conclusions at present. Moreover, carbonaceous chondrites contain an anomalous presolar Cr component (e.g., Papanastassiou, 1986; Rotaru et al., 1992; Podosek et al., 1997), thus making the interpretation of these data additionally complicated.

The shape of the gradient in the region inside 1 AU is not known either. Based on the observed gradient one can expect 53 Cr/ 52 Cr ratios lower than 0 ε . An extrapolation of the correlation line to 0 AU yields a $^{53}\text{Cr}/^{52}\text{Cr}$ ratio of $\sim -0.4~\epsilon$. This value, when taken as the initial solar system ⁵³Cr/⁵²Cr ratio, was used to estimate an initial 53 Mn/ 55 Mn ratio of 1.4 imes 10 $^{-5}$ (Lugmair and Shukolyukov, 2001). This then would imply no addition of ⁵³Mn to the Sun. However, the assumption of linearity inside 1 AU is rather speculative. The exploration of the gradient inside 1 AU is complicated by the fact that at present there is no clear identification of material, which would have originated inside of Earth's orbit. The recent study of Cr implanted by the solar wind into lunar grains by Nichols et al. (2002) is very interesting but also confusing and does not seem helpful in solving our problem. The unusual Cr isotopic composition most likely does not characterize the bulk Sun but probably can be explained by spallation reactions in the solar atmosphere (Nichols et al., 2002).

Is the ⁵³Mn-⁵³Cr isotope systematics of the E-chondrites consistent with the idea that these materials are a substantial constituent of the inner planets? One can argue that their Cr isotopic composition is rather similar to that of bulk Mars and therefore suggest that the E-chondrite materials were important building blocks for this planet. However, such an approach is most likely an oversimplification and may be incorrect. At least it does not work in the case of the Earth. Bulk samples of all meteorite classes studied so far reflect clear ⁵³Cr excesses relative to the Earth. This indicates that any mixing of known materials cannot reconstruct the terrestrial Cr isotopic composition because of a lack of meteorites (except of CAI) with relative ⁵³Cr deficits. Thus, although the Earth's precursors could be chemically similar to known meteorite classes in general, and to the E-chondrites in particular, these materials were isotopically different (at least for Cr). If in the future no meteorites with clear relative ⁵³Cr deficits can be identified then one has to assume that the 'missing materials' were essentially fully consumed during assembly of the inner planets and may not exist at present within the asteroid belt (or have not been sampled because of their low abundance).

In summary, the ⁵³Mn-⁵³Cr systematics in the E-chondrites is a strong argument in favor of an original radial ⁵³Mn heterogeneity. Although we cannot completely exclude a volatilitydriven scenario as an explanation of the observed gradient, it is difficult to perceive another reason than ⁵³Mn heterogeneity that can be responsible for the differences in the ⁵³Cr abundance in primitive meteorites with the same 'chondritic' Mn/Cr ratio.

5. CHRONOLOGICAL IMPLICATIONS

5.1. Enstatite Chondrites

An important prerequisite for using any short-lived radionuclide as a relative chronometer is the same original relative abundance of this radionuclide in the various objects that are dated. We have shown earlier (Lugmair and Shukolyukov, 1998; Shukolyukov and Lugmair, 2000a) that for ⁵³Mn most of the 'asteroid belt' objects appear to meet this requirement. This, of course, holds true also for obtaining absolute ages, where ⁵³Mn/⁵⁵Mn ratios are compared with an object whose absolute age is precisely known. This method was demonstrated with the angrite LEW 86010 (Lugmair and Shukolyukov, 1998), whose Pb-Pb age of 4557.8 \pm 0.5 Ga (Lugmair and Galer, 1992) and 53 Mn/ 55 Mn ratio ((1.25 ± 0.07) × 10⁻⁶) are known. Enstatite chondrite material, however, has a lower original abundance of ⁵³Mn than the previously measured 'asteroid belt' objects. Under these circumstances, is it then possible to obtain any meaningful chronological information for E-chondrites?

Obviously, their ⁵³Mn-⁵³Cr ages cannot be obtained in a straightforward way, that is, by comparing their ⁵³Mn/⁵⁵Mn values directly with that of LEW 86010. However, using the available Mn-Cr isotope systematics in ordinary and enstatite chondrites and some reasonable assumptions we can deduce the relationship between their original ⁵³Mn abundances and calculate the absolute ages of the E-chondrites. The present day ⁵³Cr/⁵²Cr ratios are determined by

$${}^{53}\text{Cr}/{}^{52}\text{Cr}_{\text{ord.chond}} = ({}^{53}\text{Cr}/{}^{52}\text{Cr})_0 + ({}^{55}\text{Mn}/{}^{52}\text{Cr})({}^{53}\text{Mn}/{}^{55}\text{Mn})_{0, \text{ ord.chond}}$$
(1)

$${}^{53}\text{Cr}/{}^{52}\text{Cr}_{\text{enst.chond}} = ({}^{53}\text{Cr}/{}^{52}\text{Cr})_0 + ({}^{55}\text{Mn}/{}^{52}\text{Cr})({}^{53}\text{Mn}/{}^{55}\text{Mn})_{0,\text{ enst.chond}}.$$
 (2)

where subscript 0 indicates the initial ratios; the solar system initial ⁵³Cr/⁵²Cr ratio, although unknown, is assumed to be the same in the inner solar system while the original ⁵³Mn abundances differ. Subtracting (2) from (1) and using the measured present day ⁵³Cr/⁵²Cr ratios for ordinary and enstatite chondrites (+0.48 and +0.16 ε , respectively, translated into absolute values) at a chondritic ⁵⁵Mn/⁵²Cr of 0.76, gives the relationship between their original ⁵³Mn abundances:

$$({}^{53}\text{Mn}/{}^{55}\text{Mn})_{0, \text{ enst.chond.}} = ({}^{53}\text{Mn}/{}^{55}\text{Mn})_{0, \text{ ord.chond.}}$$

- 4.7 × 10⁻⁶ (3)

Using our current "best estimate" for the age of the solar system of 4571 Ma, as was recently discussed in Lugmair and Shukolyukov (2001), and the corresponding ⁵³Mn/⁵⁵Mn ratio for the "asteroid belt" meteorites of 1.4×10^{-5} we obtain an original ⁵³Mn abundance in enstatite chondrite materials of 9.3 $\times 10^{-6}$. This value can then be used for the determination of the enstatite chondrite absolute ages. Strictly speaking, this calculation is warranted if the contribution of co-produced Cr isotopes in non-solar proportions can be neglected. Since the

⁵⁴Cr/⁵²Cr ratios in E-chondrites are indistinguishable within uncertainties from the terrestrial standard value (see section 2) we argue that this is the case.

Using the ⁵³Mn/⁵⁵Mn ratios in the EH-chondrites and in KHA we calculated the relative ages of these meteorites (Table 3). Because the original abundance of ⁵³Mn in the EH- and EL-chondrites was the same, the ⁵³Mn-⁵³Cr age of KHA can be obtained by direct comparison of its ⁵³Mn/⁵⁵Mn ratio with that of IND and Abee. This comparison yields a 4-5 Ma younger age for the EL6-chondrite KHA than the EH4-chondrites. This may indicate that the younger ⁵³Mn-⁵³Cr age of this meteorite with its higher metamorphic grade represents the cooling age of KHA. These results are in good agreement with the ¹²⁹I-¹²⁹Xe data by Kennedy et al. (1988) that suggest a ~ 4 Ma time difference between KHA and the EH4-chondrites. Further, using the calculated initial ⁵³Mn abundance in the E-chondrites of 9.3×10^{-6} at 4571 Ma, the ⁵³Mn abundances at the time of isotope closure in IND, Abee and KHA, and a ⁵³Mn half-life of 3.7 Ma, we obtain an estimate for their absolute ages of \sim 4565 Ma, \sim 4565 Ma, and \sim 4560 Ma, respectively. These ages are very similar to absolute ages for IND, Abee and KHA based on the results of Kennedy et al. (1988) as noted by Nichols et al. (1994). The old ages of EH-chondrites, which are the same as the time of the last Mn/Cr fractionation in the HED PB, indicate that the EH-chondrite PB also formed in the early stages of solar system evolution.

5.2. Enstatite Achondrites

We have shown above that the original ⁵³Mn abundance in the enstatite chondrites was lower than in ordinary chondrites and the other "asteroid belt" objects. Is this also the case for the enstatite achondrites? Peña Blanca Spring (PBS) is a differentiated meteorite with a bulk Mn/Cr ratio very much higher than the chondritic value. Its 53Mn/55Mn ratio shows that it had chemically differentiated while ⁵³Mn was still extant. We cannot, therefore, directly compare the measured ⁵³Cr excesses in bulk PBS and in bulk ordinary chondrites to ascertain if the initial ⁵³Mn abundance in the aubrite parent body was indeed lower than in the "asteroid belt" objects. However, considering the chemical, O isotope and other data as arguments for a probable genetic relationship of the enstatite chondrites with the aubrites, and thus a probable formation of their PB materials in common regions of the solar nebula, one may assume the same original relative abundances of ⁵³Mn and the same (chondritic) Mn/Cr ratios for their parent bodies. Consequently, we can deduce the time of the isotope closure in PBS from the relationship between the original ⁵³Mn abundances in ordinary chondrites and in the aubrite PB: $({}^{53}Mn/{}^{55}Mn)_{0, \text{ enst. chond.}} =$ $({}^{53}Mn/{}^{55}Mn)_{0, \text{ Aubrite PB.}} = ({}^{53}Mn/{}^{55}Mn)_{0, \text{ Ord. Chon.}} - 4.7 \times$ 10^{-6} and the inferred original ⁵³Mn/⁵⁵Mn in the "asteroid belt" bodies of $\sim 1.4 \times 10^{-5}$ (see above). This time is ~ 4564 Ma. If

Table 3. Relative ⁵³Mn-⁵³Cr ages of E-chondrites.

	ΔT in Ma
Indarch-Khairpur Abee-Khairpur	$4.5 \pm 0.4 \\ 4.9 \pm 1.0$

the assumption of an originally lower than ordinary chondritic ⁵³Mn in the PBS PB material is not correct, a direct use of the original ⁵³Mn/⁵⁵Mn ratio for the "asteroid belt" bodies of ~1.4 $\times 10^{-5}$ gives an age of ~4562 Ma. Whichever the case may be, the large uncertainty in the ⁵³Mn/⁵⁵Mn ratio obtained for PBS is the limiting factor. Nevertheless, a relative I-Xe age for PBS of 3.2 ± 1.2 Ma after Bjurböle (Podosek, 1970, 1972) and using an absolute age for Shallowater of 4566 ± 2 (Brazzle et al., 1999) would yield a consistent age of ~4563 Ma (see also Nichols et al., 1994).

In section 3.2 and Figure 6 we have shown that Bishopville (BISH) was formed (or the Cr isotopes were last equilibrated) after practically all ⁵³Mn had decayed and, thus, only an upper limit of 1.4×10^{-7} can be calculated for the ⁵³Mn/⁵⁵Mn ratio at the time of isotope closure. This implies that BISH is at least ~10 Ma younger than PBS. This is also consistent with the result that the ¹²⁹I-¹²⁹Xe isotope system in BISH closed ~16 Ma after PBS (Podosek, 1970, 1972).

In section 3.3 we discussed the fact that the evolution of the Mn-Cr isotope system in the aubrite PB is more complex than that in the HED PB, which still reflects an ordinary chondrite Mn/Cr ratio. This complexity does not allow a direct estimate of the original ⁵³Mn abundance in the aubrite PB or its evolutionary time scale. Nevertheless, to illustrate the influence of various parameters on possible evolutionary paths we will give some examples using reasonable model assumptions.

Based on a probable genetic link between aubrites and enstatite chondrites we assume that the original ⁵³Mn in the aubrite PB was similar to that of the enstatite chondrites. We then can deduce the time of the last Mn/Cr fractionation in the aubrite PB from the relationship between their original ⁵³Mn abundance, $({}^{53}Mn/{}^{55}Mn)_{0, \text{ E-chond.}} = ({}^{53}Mn/{}^{55}Mn)_{0, \text{ Ord. Chond.}} - 4.7 \times 10^{-6}$, and a ${}^{53}Mn/{}^{55}Mn$ ratio of $\sim 2.1 \times 10^{-6}$ as obtained from the bulk meteorite isochron. This time is ~ 4563 Ma ago. If, instead, the original ${}^{53}Mn$ abundance in the aubrite PB was similar to that in ordinary chondrites, a straightforward calculation yields an age of ~ 4561 Ma. Thus, these times would indicate the end of planet-wide fractionation processes in the aubrite PB but the planetesimal must have melted and differentiated several million years earlier. At what time did this global differentiation/fractionation occur?

To attempt an answer to this question we have to make additional assumptions. We use $T_0 = 4571$ Ma as the starting time of ⁵³Mn decay (Lugmair and Shukolyukov, 1998) and a time of global fractionation of Mn/Cr at $T_1 = 4569$ Ma—a period of intense thermal processing of inner solar system material (Lugmair and Shukolyukov, 2001). We can then estimate the ⁵³Cr/⁵²Cr evolution from a solar system initial value of -0.42ε and using an E-chondrite initial ⁵³Mn/⁵⁵Mn = 9.3×10^{-6} and the obtained aubrite ⁵³Mn/⁵⁵Mn = 2.1×10^{-6} with

$$\begin{split} ^{53}\mathrm{Cr} / ^{52}\mathrm{Cr}(\mathrm{T}_{1}) &= {}^{53}\mathrm{Cr} / {}^{52}\mathrm{Cr}(\mathrm{T}_{0}) \, + \, {}^{55}\mathrm{Mn} / {}^{52}\mathrm{Cr} \times \, {}^{53}\mathrm{Mn} / {}^{55}\mathrm{Mn}(\mathrm{T}_{1}) \\ & \times \{ \exp[\lambda(\mathrm{T}_{0} - \mathrm{T}_{1})] - 1 \}. \end{split} \tag{4}$$

From T₀ to T₁ the material evolved with an ordinary chondritic or E-chondritic ⁵⁵Mn/⁵²Cr ratio of 0.76; at T₁ the ⁵³Cr/ ⁵²Cr ratio will be -0.27ε while ⁵³Mn/⁵⁵Mn = 6.4×10^{-6} . From this time on the primary source reservoir of aubrites evolved with an elevated Mn/Cr ratio in the mantle. At ~4563 Ma the outer layers of the aubrite PB were re-melted (residual heat and/or collisional energy) and isotopic equilibration and Mn/Cr fractionation formed the final aubrite sources. Using the obtained initial ⁵³Cr/⁵²Cr ratio of 0.62 ε for bulk aubrites and the equation above we can calculate the ⁵⁵Mn/⁵²Cr ratio in the primary source reservoir of aubrites as ~ 2.3. This value is similar to the average of 2.9 from our three aubrites and literature values. If, for example, we were to move the time of global differentiation T₁ to 4566 Ma, one would derive a ⁵⁵Mn/⁵²Cr ratio in the primary source reservoir of 5.1, which seems unreasonably high.

If we turn the argument around and start with the assumption that the 55 Mn/ 52 Cr ratio in the primary source reservoir is 2.9, the average from the three measured aubrites, we can estimate the time of global Mn/Cr fractionation using the following equation:

$$\begin{split} ^{53}\mathrm{Cr}/^{52}\mathrm{Cr}(\mathrm{T}_2) &= {}^{53}\mathrm{Cr}/{}^{52}\mathrm{Cr}(\mathrm{T}_0) \,+\, {}^{55}\mathrm{Mn}/{}^{52}\mathrm{Cr}_{\mathrm{CH}} \times\, {}^{53}\mathrm{Mn}/{}^{55}\mathrm{Mn}(\mathrm{T}_0) \\ & \times \left\{1 \,-\, \exp[-\lambda(\mathrm{T}_0 - \mathrm{T}_1)]\right\} \,+\, {}^{55}\mathrm{Mn}/{}^{52}\mathrm{Cr}_{\mathrm{AUB}} \\ & \times\, {}^{53}\mathrm{Mn}/{}^{55}\mathrm{Mn}(\mathrm{T}_2) \times \left\{\exp[\lambda(\mathrm{T}_1 - \mathrm{T}_2)] - 1\right\}. \end{split} \tag{5}$$

Here again $T_0 = 4571$ Ma; the time of isotopic closure in the final aubrite source reservoirs $T_2 = 4563$ Ma and T_1 is the time of global Mn/Cr fractionation. From T_0 to T_1 the original material to form the aubrite PB evolves with a 'chondritic' 55 Mn/ 52 Cr_{CH} ratio of 0.76 and, after global differentiation, the mantle evolves between T_1 and T_2 with 55 Mn/ 52 Cr_{AUB} = 2.9. In addition, we use 53 Mn/ 55 Mn(T_0) = 9.3 × 10⁻⁶, 53 Mn/ 55 Mn(T_1) = 2.1 × 10⁻⁶, and 53 Cr(T_0) = -0.42 ε . From this a time of primary planetary differentiation of $T_1 = 4568$ Ma can be estimated.

As already pointed out above, the available Mn-Cr data on samples originating from the aubrite PB do not permit a more quantitative assessment of its evolutionary time scale at present. It certainly appears to be desirable to further pursue this work in the future.

6. SUMMARY

- The ⁵³Mn-⁵³Cr isotope systematics was extended to the EH4 chondrites Indarch and Abee, the EL6 chondrite Khairpur, and to three enstatite achondrites Peña Blanca Spring, Bishopville, and Cumberland Falls.
- The relative abundance (compared to terrestrial Cr) of the radiogenic ⁵³Cr in the enstatite chondrites is three times smaller than in the ordinary chondrites while the enstatite chondrites have essentially the same Mn/Cr ratio as the ordinary chondrites.
- This finding suggests that the ⁵³Mn-⁵³Cr isotope systematic is consistent with the hypothesis that the observed radial gradient in the relative ⁵³Cr abundance is due to an initial ⁵³Mn heterogeneity, although alternative scenarios are still possible.
- From the enstatite chondrite data and the observed radial gradient in the relative ⁵³Cr abundance it can be inferred that the E-chondrites formed in zones closer to the Sun than the asteroid belt (i.e., >1.0–1.4 AU).
- From internal isochrons obtained with the use of a differential dissolution procedure the ages of the enstatite chondrites were calculated. The "absolute" ⁵³Mn-⁵³Cr ages of the EH4-

chondrites Indarch and Abee are ~ 4565 Ma. The EL6chondrite Khairpur is ~4.5 Ma younger. This is in good agreement with the ¹²⁹I-¹²⁹Xe data from the literature. The age of the aubrite Peña Blanca Spring is similar to that of EH4 chondrites. Bishopville, with equilibrated Cr isotopes, is at least 10 Ma younger. This is also in good agreement with the ¹²⁹I-¹²⁹Xe data.

The results from bulk aubrite samples indicate that the evolution of the aubrite parent body was more complex than that of the HED parent body and imply an evolution of the ⁵³Mn-⁵³Cr isotope system in an environment with an higher than chondritic Mn/Cr ratio for several million years. Calculations suggest that the last Mn/Cr fractionation in the aubrite parent body occurred ~4563 Ma ago.

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