Mn-Cr isotope systematics of the D'Orbigny angrite

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Abstract–We have conducted a detailed study of the Mn-Cr systematics of the angrite D'Orbigny. Here, we report Cr isotopic abundances and Mn/Cr ratios in olivine, pyroxene, glass, chromite, and bulk rock samples from D'Orbigny. [53]Cr excesses in these samples correlate well with their respective Mn/Cr ratios and define an isochron with a slope that corresponds to an initial [53]Mn/[55]Mn ratio = $(3.24 \pm 0.04) \times 10^{-6}$ and initial [53]Cr/[52]Cr ratio of $\varepsilon(53) = 0.30 \pm 0.03$ at the time of isotopic closure. The [53]Mn/[55]Mn ratio of the D'Orbigny bulk rock is more than two-fold the [53]Mn/[55]Mn ratio of the angrites Lewis Cliff 86010 (LEW) and Angra dos Reis (ADOR) and implies an older Mn-Cr age of 4562.9 ± 0.6 Ma for D'Orbigny relative to a Pb-Pb age of 4557.8 ± 0.5 Ma for LEW and ADOR. One of the most unusual aspects of D'Orbigny is the presence of glass, a phase that has not been identified in any of the other angrites. The Mn-Cr data for glass and a pyroxene fraction found in druses indicate that they formed contemporaneously with the main phases of the meteorite. Since the Mn-Cr age of D'Orbigny is ~5 Ma years older than the angrites LEW and ADOR, D'Orbigny likely represents an earlier stage in the evolution of the angrite parent body.

INTRODUCTION

Short-lived radionuclides with half-lives of 10^5 to 10^8 yr, although now extinct, were alive when the first solids were condensing in the solar system and can serve as sensitive chronometers and tracers for early solar system processes. One of these radionuclides, [53]Mn, decays into [53]Cr with a relatively short half-life of ~3.7 Ma (Honda and Imamura 1971) and can be used to date events that took place in the first ~20 Ma of solar system history. Following the discovery of the existence of [53]Mn in the Allende refractory inclusions (Birck and Allègre 1985), other excesses of [53]Cr due to the decay of [53]Mn have been detected in a variety of solar system objects including carbonaceous chondrites (Birck and Allègre 1988; Endress et al. 1996; Shukolyukov et al. 2003), ordinary chondrites (Lugmair and McIsaac 1995; Nyquist et al. 2001; Polnau and Lugmair 2001; Glavin and Lugmair 2003), enstatite chondrites (Wadhwa et al. 1997), iron meteorites (Hutcheon et al. 1985), eucrites and SNC meteorites (Lugmair and Shukolyukov 1998; Nyquist et al. 2003), and angrites (Lugmair et al. 1992; Nyquist et al. 1994).

Since short-lived radionuclides such as [53]Mn are now extinct in the solar system, they permit us to obtain only relative ages. Thus, one important prerequisite for using the [53]Mn-[53]Cr chronometer to obtain absolute ages for solar

system objects is that the [53]Mn-[53]Cr isotope system must be tied to an absolute time scale. Mn-Cr and U-Pb investigations of the angrites Lewis Cliff 86010 (LEW) and Angra dos Reis (ADOR) have facilitated the mapping of the relative [53]Mn-[53]Cr chronometer onto an absolute time scale (Lugmair and Galer 1992; Lugmair and Shukolyukov 1998). These angrites are ideal for this purpose since they formed early in solar system history, are thought to have cooled very rapidly, and do not show any signs of later disturbance. Furthermore, the Pb-Pb ages of the angrites LEW and ADOR are accurately known $(4557.8 \pm 0.5$ Ma) and represent the time of crystallization for these two meteorites (Lugmair and Galer 1992). Due to the large range of [55]Mn/[52]Cr ratios between the various mineral components in these meteorites, a precise [53]Mn/[55]Mn ratio of $(1.25 \pm 0.07) \times 10^{-6}$ at the time of isotopic closure was determined (Lugmair et al. 1992). The fact that the angrites cooled fast (Störzer and Pellas 1977) suggests that both the U-Pb and Mn-Cr isotope systems closed approximately at the same time, therefore, the obtained value of 1.25×10^{-6} can be taken as the [53]Mn/[55]Mn ratio at 4557.8 Ma ago.

The recently classified angrite D'Orbigny, which was found in Argentina in 1979, is the largest member of the six known angrites weighing ~16.6 kg. Recent petrographic and geochemical studies indicate that D'Orbigny is an unshocked,

unmetamorphosed igneous textured rock that underwent rapid cooling and crystallization (Mittlefehldt et al. 2002). From a petrographic standpoint, D'Orbigny is a very complex rock consisting predominately of anorthitic plagioclase (39%), fassaitic clinopyroxene or Al-Ti-diopside-hedenbergite (28%), Mg-rich olivine (19%), and Ca, Fe-rich olivine (12%). In addition, ulvöspinel (0.6%), troilite (0.5%), Ca silicophosphate (0.5%), and minor modal abundances (<0.5%) of kirschsteinite, glass, and Cr-rich olivine are also present (Mikouchi and McKay 2001; Varela et al. 2001; Mittlefehldt et al. 2002). Reverse zoning in olivine-kirschsteinite and clinopyroxene suggests that D'Orbigny did not form from a single melt but, rather, crystallized from a hybrid melt with local additions of a more primitive melt during the final phases of crystallization (Mittlefehldt et al. 2002). One of the most unique features of D'Orbigny is the presence of glass, an abundant phase, which has not been previously reported in any other angrite including LEW and ADOR (Varela et al. 2001). Based on Pb isotopes, a primitive origin for the glass in D'Orbigny has been suggested (Jotter et al. 2002). However, the measured $^{207}Pb/^{206}Pb$ ratio of the glass is very high, yielding an apparent Pb-Pb age of ~4.7 Ga that is much older than the bulk rock (Jotter et al. 2003). One explanation for this unreasonably high Pb-Pb age is that the excess of ^{207}Pb in the glass originated from the decay of now extinct ^{247}Cm via excess ^{235}U (Jagoutz et al. 2003). Recently, a precise Pb-Pb age of 4557 ± 2 Ma for druse pyroxenes in D'Orbigny has been obtained (Jagoutz et al. 2002) and is consistent with Pb-Pb ages of the angrites LEW and ADOR.

Mn-Cr isotopic measurements of olivine, groundmass pyroxene, and whole rock samples of D'Orbigny have previously been carried out (Sugiura 2002; Nyquist et al. 2003). Here we report on Mn-Cr investigations of the D'Orbigny bulk rock, various olivine types, druse pyroxene, spinel, and glass separates. To our knowledge, Mn-Cr analyses of spinel, glass, druse pyroxene, and minor olivine types in D'Orbigny have not yet been reported. The goal of this study was to establish a relative Mn-Cr age for the various components in the D'Orbigny angrite and compare this age information to the angrites LEW and ADOR, for which accurate Pb-Pb ages and $^{53}Mn/^{55}Mn$ ratios at the time of isotopic closure have been determined. Preliminary results from this study were published in abstract form (Glavin et al. 2003).

EXPERIMENTAL TECHNIQUES

Sample Preparation and Chemical Procedures

A 420 mg fragment of the D'Orbigny angrite was crushed to a fine powder using a clean boron carbide mortar. In addition, several minerals in D'Orbigny, including olivine, pyroxene, and glass, were separated from the bulk rock. For the olivine samples, mineral separation was obtained on the 100–200 μm-size fraction using a clean Franz Isodynamic magnetic separator followed by hand picking under a binocular microscope. These samples were also separated into three types based on color and texture: large green olivine xenocrysts (Ol-1), brown groundmass olivine (Ol-2), and amber-colored honey olivines (Ol-3 and Ol-4). The groundmass and honey olivine separates represent the most abundant olivine phases (>99%) in D'Orbigny. Only pure idiomorphic pyroxenes (dPx) that were found inside druse-like cavities were analyzed in this study (for groundmass pyroxene, see Nyquist et al. [2003]). The glasses (Gls-1 and Gls-2) were handpicked using a binocular microscope from open druse spaces and spheres in the bulk rock and ranged in size from several tens of microns to millimeters (Varela, personal communication). Glasses found inside olivine grains were not separately analyzed.

All of the chemical procedures for the samples were performed under clean lab conditions. Before dissolution, all samples were thoroughly rinsed with distilled ethanol followed by water under ultrasonication to remove surface dust. After washing, the dried bulk rock sample and mineral separates were individually weighed and dissolved in a concentrated 2:1 HF/HNO_3 mixture under ultrasonication for 90 min and then left overnight. One of the honey olivine separates (Ol-4) was dissolved under ultrasonication in 6 N HCl and was not treated with HF or HNO_3. The following day, the solutions were dried in concentrated HNO_3 to remove HF, and the residues were redissolved in 4.5 N HCl. The acid-resistant spinel grains that remained after dissolution of the bulk rock sample were separated from the HCl silicate solution and dissolved separately in an HF/HNO_3 mixture at an elevated temperature (185 °C) overnight using a Teflon pressure bomb (Sp-1 fraction). The total rock solution was obtained by combining equal aliquots (~20%) of the spinel and silicate solutions. In addition, a large spinel grain (Sp-2, ~1 mm in diameter) that was identified by SEM analysis after dissolution of one of the glass samples (Gls-2) was rinsed several times in water, weighed, and then dissolved after several days in a Teflon bomb at 210 °C. Small aliquots (~5%) of each of the solutions were taken for the measurement of Mn and Cr concentrations using inductively coupled plasma-optical emission spectroscopy (ICP-OES). From the standard deviation of the average value of between four and six separate ICP-OES measurements, the uncertainties ($2\sigma_{mean}$) in the concentrations were found to be less than 5%. In addition, Mn and Cr concentrations in the Gls-1 and Gls-2 solutions were also measured by inductively coupled plasma-mass spectrometry (ICP-MS).

The separation procedure for Cr was similar to that previously described by Birck and Allègre (1988) and is based on the differences in ion exchange properties of various hydrated species of Cr^{3+}. The separations were performed in two steps using cation exchange chromatography. For the first step, a solution aliquot corresponding to several milligrams of

the sample was heated to a slow boil in 9.5 N HCl for 60 min, dried, dissolved in 1 N HCl, and then loaded onto a primary column containing Mitsubishi cation exchange resin AGX8 (200–400 mesh) and eluted with 1 N HCl to isolate Cr from other major matrix elements such as Fe and Mg. In some cases, especially for the olivine samples that contained high concentrations of Fe and Mg, it was necessary to repeat this step several times to obtain clean samples of chromium. After the primary column elutions, an additional clean-up column was required to remove remaining traces of Fe, alkalies, and anions. For this step, samples were first heated to a slow boil in water for several hours, loaded onto the column, and then eluted with 0.5 N HF, 1 N HCl, and 1.8 N HCl. The total yield of Cr in the chemical procedures ranged from 30% for glass to, normally, up to 85% for other phases. Blanks carried through the same chemical procedures contained only trace levels of Cr (<10 ng) and are entirely insignificant.

Mass Spectrometry

The chromium isotopic composition was determined using a Micromass Sector 54 thermal ionization mass spectrometer in single collector mode. Chromium was loaded in a mixture of silica gel and boric acid on prebaked W filaments and was analyzed as Cr^+. The loading procedure has been refined since previous work (Lugmair et al. 1992; Lugmair and Shukolyokov 1998), and loading conditions such as amounts of silica gel and boric acid, drying procedure, sample area on filament, etc. were optimized and controlled so that the Cr amount per load could be reduced. Clean samples containing 250–350 ng of Cr were loaded in a mixture of 0.5 μl silica gel (conc. ~7 μg/μl) and 0.5 μl saturated boric acid. A single measurement or run consisted of 300 ratios with typical $2\sigma_{mean}$ uncertainties on $^{53}Cr/^{52}Cr$ of 0.1–0.12 ε where $\varepsilon(53) \equiv ([^{53}Cr/^{52}Cr]_{sample}/[^{53}Cr/^{52}Cr]_{standard} - 1) \times 10^4$. In general, 18 to 36 runs of the chromium isotopic composition were made for each sample, and the results were averaged. The ion current for ^{52}Cr was held to within $(5.5 \pm 0.5) \times 10^{-11}$ A during the analyses. Before each analysis, isobaric interferences were monitored for each sample via background scans with the use of a Daly detector. Interferences from ^{50}Ti, ^{50}V, and ^{54}Fe were checked at ^{48}Ti, ^{51}V, and ^{56}Fe for each sample and were negligible for the data presented here.

All chromium isotopes were normalized to ^{52}Cr and corrected for mass fractionation using a $^{50}Cr/^{52}Cr$ ratio of 0.051859 (Shields et al. 1996) as an internal standard where an exponential fractionation law was assumed. Using this value, instrumental fractionation for sample loads typically ranged from −8.5 to −2 per mil/amu. As reported earlier by Lugmair and Shukolyokov (1998), we also observed the presence of an additional mass fractionation effect for the Micromass Sector 54 used in this study. After exponential correction, we found a strongly correlated linear variation of these residual effects on the $^{53}Cr/^{52}Cr$ versus $^{54}Cr/^{52}Cr$ ratios for the laboratory standards. These residual effects were independent of sample fractionation and seemed to depend strongly on the position of the filament or sample relative to the ion-source optics. For the D'Orbigny samples analyzed in this study, we found that the measured $^{54}Cr/^{52}Cr$ ratios were indistinguishable (within ±10 ppm) from the standard $^{54}Cr/^{52}Cr$ value of 0.0282085. Therefore, these small mass discrimination effects could be corrected by using the parameters obtained from the $^{53}Cr/^{52}Cr$ versus $^{54}Cr/^{52}Cr$ correlation line from more than 150 Cr standard measurements. This second-order fractionation correction considerably improved the reproducibility and precision of the chromium isotopic composition measurements. The $^{53}Cr/^{52}Cr$ ratios are expressed here as the deviations from the overall average standard $^{53}Cr/^{52}Cr$ in ε-units, where the standard value for $^{53}Cr/^{52}Cr$ is taken as 0.1134507.

RESULTS AND DISCUSSION

We have measured the $^{53}Cr/^{52}Cr$ and $^{55}Mn/^{52}Cr$ ratios in both major and minor mineral components of the D'Orbigny angrite including spinel (Sp), druse pyroxene (dPx), olivine (Ol), glass (Gls), and a total rock (TR) sample. The results are presented in Table 1 and Fig. 1. Occasionally, a spallation correction is necessary to account for spallogenically-produced ^{53}Cr (and ^{54}Cr) in samples with relatively low concentrations of Cr and/or those samples with long exposure ages. However, given the short cosmic ray exposure age for D'Orbigny of 12.3 ± 0.9 Ma (Eugster et al. 2002) and the relatively high levels of Cr in the samples measured in this study (see Table 1), we found that the calculated spallation correction was much smaller than the experimental error and was, therefore, negligible.

The $^{55}Mn/^{52}Cr$ ratio for the mineral separates in D'Orbigny ranged from ~0.006 for the Cr-rich spinel (Sp-2) grain up to ~28 for the honey olivine (Ol-4) sample. We found that the Mn and Cr abundances as well as the Mn/Cr ratios for both the silicate and total rock fractions were identical within error (see Table 1), which indicates that the Mn and Cr composition of the bulk rock is dominated by the silicate component. A high $^{55}Mn/^{52}Cr$ ratio of ~100 has recently been obtained for an olivine separate from D'Orbigny (Nyquist et al. 2003), similar to previous measurements of olivine in the angrites Lewis Cliff 86010 (LEW) and Angra dos Reis (ADOR), which have $^{55}Mn/^{52}Cr$ ratios of 120 and 160, respectively (e.g. Lugmair and Shukolyukov 1998). Ion probe measurements of Ca-rich olivines in D'Orbigny revealed compositions with very high $^{55}Mn/^{52}Cr$ ratios ranging from 10 to 10^5 (Sugiura 2002). The honey olivine separates (Ol-3 and Ol-4) had the highest overall Mn/Cr ratios analyzed in this study (see Table 1). We did not identify specific olivine separates from D'Orbigny with Mn/Cr ratios similar to those previously measured in olivines from the D'Orbigny, LEW,

Table 1. Mn and Cr concentrations, Mn/Cr ratios, and ^{53}Cr excesses in D'Orbigny.[a]

Sample[b]	Weight (mg)	Mn (ppm)[c]	Cr (ppm)[c]	^{55}Mn/^{52}Cr[c]	$\varepsilon(53)$[d]
TR	420	1800 ± 12	356 ± 6	5.71 ± 0.08	1.89 ± 0.04[e]
Sil	<420	1812 ± 30	359 ± 5	5.70 ± 0.11	na
Sp-1	nd	–	–	<0.011	0.30 ± 0.03
Sp-2	0.38	282 ± 50	51307 ± 3152	0.006 ± 0.001	0.35 ± 0.03
Ol-1	33	1240 ± 21	882 ± 44	1.59 ± 0.08	0.73 ± 0.03
Ol-2	21	2834 ± 26	469 ± 12	6.82 ± 0.20	2.30 ± 0.05[f]
Ol-3	50	2505 ± 13	217 ± 6	13.0 ± 0.2	4.04 ± 0.04
Ol-4	46	3595 ± 15	146 ± 2	27.8 ± 0.4	8.23 ± 0.04
dPx	24	1080 ± 3	544 ± 4	2.24 ± 0.02	0.94 ± 0.03
Gls-1	3.5	1978 ± 22	383 ± 16	5.83 ± 0.25	2.02 ± 0.08[f]
Gls-2	3.1	1702 ± 33	431 ± 16	4.46 ± 0.18	1.54 ± 0.07[f]

[a]na = not analyzed; nd = not determined.

[b]Total rock (TR), silicate (Sil), spinel (Sp), olivine (Ol), druse pyroxene (dPx), and glass (Gls).

[c]The uncertainties ($2\sigma_{mean}$) are based on the standard deviation of the average value of between four and six separate ICP-OES measurements. In addition, the errors in the absolute concentrations of Mn and Cr take into account an uncertainty in the mass measurements of approximately ±0.02 mg.

[d]$\varepsilon(53) = ([^{53}Cr/^{52}Cr]_{sample}/[^{53}Cr/^{52}Cr]_{standard} - 1) \times 10^4$; the uncertainties on $\varepsilon(53)$ are $2\sigma_{mean}$.

[e]For TR, 36 runs were made. To measure Sil as well was deemed unnecessary based on similar Mn and Cr concentration results.

[f]Only five to twelve runs for the Cr isotopic composition could be made because of limited sample amounts or partial loss during chemistry.
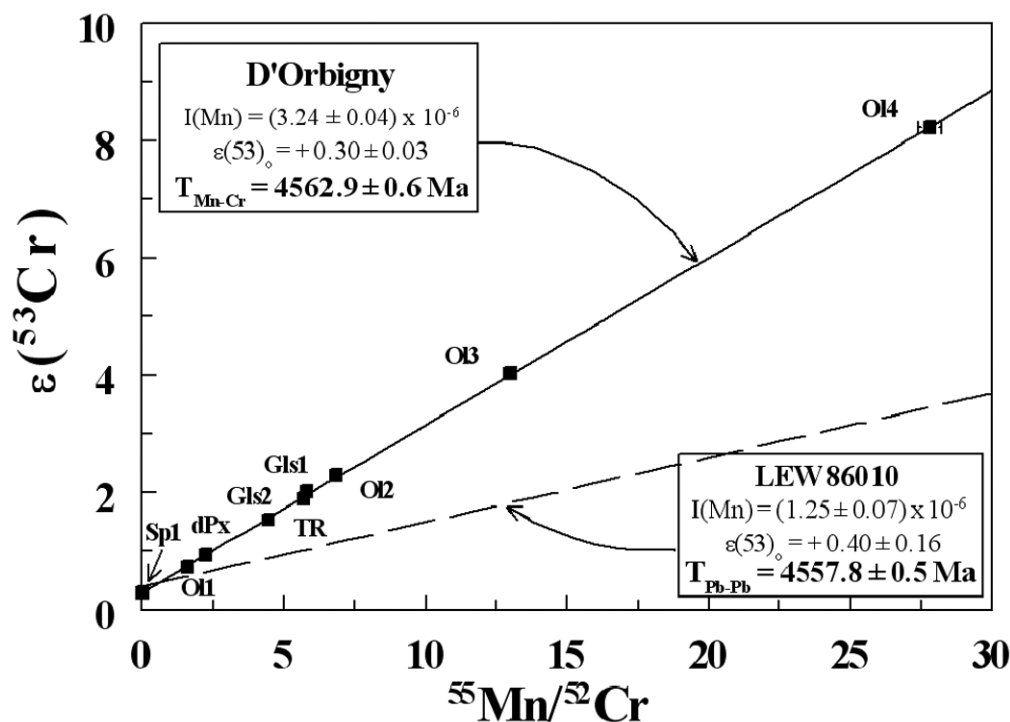

Fig. 1. ^{53}Mn-^{53}Cr systematics of the D'Orbigny angrite (solid line). The ^{53}Cr/^{52}Cr excesses relative to the terrestrial value are expressed in ε-units (1 part in 10^4). The isochron for the angrite LEW 86010 (LEW), taken from Lugmair and Shukolyukov (1998) is shown for comparison (dashed line). The calculated age of D'Orbigny relative to LEW (4557.8 ± 0.5 Ma) is $\Delta T = 5.1 \pm 0.3$ Ma, resulting in an absolute Mn-Cr age of 4562.9 ± 0.6 Ma. A spallation correction for cosmic ray-produced ^{53}Cr was not necessary given the relatively short exposure age for D'Orbigny (Eugster et al. 2002).

and ADOR angrites (i.e., ≥100). It should be noted here that small acid-resistant grains (probably spinel and/or pyroxene) were found in our honey olivine separates after acid dissolution. Since the average ^{55}Mn/^{52}Cr ratio for the 6 N HCl resistant grains found in the Ol-4 sample was measured to be ~1, the presence of these grains in our dissolved honey olivine separates may have lowered the Mn/Cr ratio. Large Cr-rich xenocrystic olivine grains (Ol-1) that have been previously identified in samples of D'Orbigny (Kurat et al. 2001) but are very rare in the bulk meteorite (<0.5% modal abundance) had a very low ^{55}Mn/^{52}Cr ratio of ~1.6. The variations in ^{55}Mn/^{52}Cr for our olivine samples are likely produced both by Cr

zoning in single olivine crystals as well as element partitioning among olivine types.

Two separate Cr-rich spinel samples from D'Orbigny were analyzed in this study: (Sp-1) small (<100 μm) fines separated from the bulk rock sample, and (Sp-2) one large (~900 μm) spinel grain isolated from the D'Orbigny glass separate. Large rounded spinel grains (~300 μm) have previously been identified in thin sections of D'Orbigny (Mittlefehldt et al. 2002). In the past, due to the difficulty in obtaining an accurate mass of tiny acid-resistant spinel fines isolated from bulk rock meteorite samples, Mn and Cr concentrations for the spinel fraction were not determined, only Mn/Cr ratios (Lugmair and Shukolyukov 1998). However, in the present study, the mass of the large Cr-rich spinel grain (Sp-2) could be measured (0.38 ± 0.02 mg), and the concentrations of Mn and Cr for the Sp-2 are given in Table 1. The ^{53}Cr excesses for the Sp-1 and Sp-2 fractions are indistinguishable from one another within the uncertainty of the measurements.

The ^{55}Mn/^{52}Cr ratio of ~5.7 for our D'Orbigny bulk rock (TR) is lower than the whole rock value given by Nyquist et al. (2003). This suggests that the D'Orbigny angrite is quite heterogeneous in its mineral distribution. The olivine separate from the D'Orbigny sample measured by Nyquist et al. (2003) has a very high ^{55}Mn/^{52}Cr ratio (~100). Our lower total rock ^{55}Mn/^{52}Cr ratio may be due to a lower olivine content in our sample, more olivines with "low" Mn/Cr as reflected by our olivine separates (^{55}Mn/^{52}Cr ≤28), or both. However, as we did not measure groundmass pyroxene, a proper mass balance estimate cannot be performed. Nyquist et al. (2003) report ^{55}Mn/^{52}Cr ~15 for a high density pyroxene separate from D'Orbigny; interestingly, their low density groundmass pyroxene separate (Px-1) has a very similar ^{55}Mn/^{52}Cr ratio (~2.2) to the druse pyroxene sample (dPx) measured in this study.

In addition to the druse pyroxene, we also investigated two separate glass samples that were handpicked from the open druse spaces and pockets within the D'Orbigny bulk rock sample. Glasses have not been reported in any of the other angrites including LEW and ADOR (Varela et al. 2001). Since a non-shock origin for the glasses in D'Orbigny has recently been suggested (Varela et al. Forthcoming), the Mn-Cr isotope systematics for this phase most likely have not been disturbed. The ^{55}Mn/^{52}Cr ratios of the Gls-1 and Gls-2 samples were measured by ICP-OES and ICP-MS and are ~5.8 and ~4.5, respectively. These ratios are well-correlated with their respective ^{53}Cr excesses. The Mn/Cr ratio of Gls-1 is nearly identical to that of the TR, which is not surprising since previous analyses have shown that the major and trace elemental content of the glass is indistinguishable from the bulk rock (Mittlefehldt et al. 2002; Varela et al. Forthcoming). However, Gls-2 has a slightly lower than expected ^{55}Mn/^{52}Cr ratio. Since, after dissolution, a large Cr-rich spinel grain was identified in this sample, it is possible that some Cr from the

spinel dissolved into the Gls-2 fraction during the acid dissolution procedure. It should also be noted that, due to the limited amount of glass sample available for this study (~3 mg each), only 5 to 10 runs for the Cr isotopic composition could be made.

Due to the wide range of ^{55}Mn/^{52}Cr ratios for the various mineral components of D'Orbigny, a very precise ^{53}Mn/^{55}Mn ratio could be determined. The data points for the spinel, total rock sample, the olivines, and the minor druse phases form a well-defined isochron with a slope that corresponds to an initial ^{53}Mn/^{55}Mn, I(Mn) = (3.24 ± 0.04) × 10^{-6} and an initial ^{53}Cr/^{52}Cr, ε(53)$_0$ = 0.30 ± 0.03 at the time of isotopic closure (Fig. 1). These values are slightly higher than those obtained by Nyquist et al. (2002): (2.83 ± 0.25) × 10^{-6} and 0.15 ± 0.26 ε, respectively. Sugiura (2002) inferred a much lower initial ^{53}Mn/^{55}Mn ratio of ~(1.9 ± 0.1) × 10^{-6} for Ca-rich olivines in D'Orbigny. Our value of ε(53)$_0$ for D'Orbigny overlaps that of LEW within error limits (Fig. 1). Nevertheless, it should be noted that the two isochrons intersect close to the chondritic ^{55}Mn/^{52}Cr ratio. The ^{53}Mn/^{55}Mn ratio for D'Orbigny is more than two and a half times larger than the ^{53}Mn/^{55}Mn ratio of (1.25 ± 0.07) × 10^{-6} previously obtained for LEW (Lugmair and Shukolyukov 1998). Therefore, the Mn-Cr isotope system in D'Orbigny must have closed much earlier than in LEW.

The "Mn-Cr age" for D'Orbigny relative to LEW can be determined from the ratio of their respective ^{53}Mn/^{55}Mn ratios using the equation:

$$\Delta T = 1/\lambda \cdot \ln([^{53}Mn/^{55}Mn]_{D'Orbigny}/[^{53}Mn/^{55}Mn]_{LEW}) \qquad (1)$$

where λ is the decay constant for ^{53}Mn, taken to be 1.87 × 10^{-7} yr^{-1} (Honda and Imamura 1971). From Equation 1, the ^{53}Mn/^{55}Mn ratio for the D'Orbigny bulk rock translates into an age relative to LEW of ΔT = 5.1 ± 0.3 Ma. The errors in the ^{53}Mn/^{55}Mn ratios for D'Orbigny and LEW were propagated through the equation for ΔT, but the uncertainty in the decay constant of ^{53}Mn was not taken into account. With the precise Pb-Pb age of LEW of 4557.8 ± 0.5 Ma (Lugmair and Galer 1992), we calculate an absolute Mn-Cr age of 4562.9 ± 0.6 Ma for D'Orbigny, where the uncertainty in the Mn-Cr age includes the uncertainty in the Pb-Pb age of LEW. Our value agrees reasonably well with the Mn-Cr age of 4561.6 ± 0.5 Ma calculated by Nyquist et al. (2003).

The value of 3.24 × 10^{-6} obtained from our isochron would then represent the ^{53}Mn/^{55}Mn ratio of the D'Orbigny parent body at ~4562.9 Ma ago. Störzer and Pellas (1977) inferred, for ADOR, that the angrites cooled rapidly. This conclusion was also adopted for LEW 86010 by Lugmair and Galer (1992) who obtained the same Pb-Pb age for both meteorites. On this basis, Lugmair and Shukolyukov (1998) argued that, in these rapidly cooled objects, the U-Pb and the Mn-Cr systems closed contemporaneously, and the obtained ^{53}Mn/^{55}Mn ratio for these meteorites could then be tied to their Pb-Pb age. However, for druse pyroxenes in D'Orbigny

a Pb-Pb age of 4557 ± 1 Ma has recently been measured (Jagoutz et al. 2003). This age is comparable to the Pb-Pb ages of LEW and ADOR (Lugmair and Galer 1992) but is significantly younger (~6 Ma) than the Mn-Cr age for D'Orbigny. This discrepancy is clearly reflected in Fig. 1, where the Mn-Cr data point for the druse pyroxene (dPx) falls precisely on the D'Orbigny correlation line and clearly above the LEW isochron.

The disagreement between Pb-Pb and Mn-Cr ages for D'Orbigny suggests that the U-Pb and Mn-Cr isotope systems probably did not close at the same time in this meteorite, at least in some mineral phases. Mittlefehldt et al. (2001) originally suggested a two-stage cooling history for D'Orbigny based on the sharp boundary observed between the homogeneous core and strongly zoned rims in olivine grains. But the time interval required by this process may not be relevant to our age problem. On the other hand, if one assumes that the Mn-Cr system closes at a slightly higher temperature than the U-Pb system, a sufficiently slow cooling rate for D'Orbigny through the intermediate temperature range could explain the approximately 6 Ma yr difference we observe in closing times between the Mn-Cr and U-Pb isotope systems. (To be sure, accurate relative closure temperatures for the U-Pb and Mn-Cr systems and relevant diffusion coefficients for these elements in pyroxene would be necessary to substantiate this hypothesis.) However, Mittlefehldt et al. (2002) later argued that the sharp boundary between the cores and zoned rims in olivine reflects the onset of (groundmass) pyroxene crystallization and not a change in the cooling environment. This would negate the previous scenario, and the problem of the age difference would not be resolved. It should also be pointed out that the closure of the Mn-Cr and U-Pb systems may date separate events in D'Orbigny. The Mn-Cr system may have closed during the last spinel-olivine equilibration, while the U-Pb system dates the retention of Pb in druse pyroxene. Another distinct possibility for the older Mn-Cr age relative to LEW is that, unlike D'Orbigny, prolonged thermal metamorphism at intermediate but sufficiently high temperatures may have equilibrated the Cr isotopes and the olivine composition in both LEW and ADOR (Mittlefehldt et al. 2002; Nyquist et al. 2003). At ~4558 Ma, LEW (and ADOR) then cooled rapidly to below the Pb closure temperature, and both the U-Pb and Mn-Cr systems closed contemporaneously.

With regard to time scales, a radically different scenario may be constructed for the case where D'Orbigny cooled rapidly and the U-Pb and Mn-Cr systems closed contemporaneously, as could be inferred from the latest arguments of Mittlefehldt et al. (2002). Since the measured Pb-Pb ages for LEW 86010 (Lugmair and Galer 1992) and D'Orbigny (Jagoutz et al. 2003) are identical (~4558 Ma), the $^{53}Mn/^{55}Mn$ ratio of D'Orbigny (~3.24×10^{-6}) would then correspond to the Pb-Pb age of ~4558 Ma. The low $^{53}Mn/^{55}Mn$ ratio of LEW 86010 (~1.25×10^{-6}; Lugmair and Shukolyukov

1998) would, thus, indicate prolonged subsolidus reequilibration of the Mn-Cr system in LEW 86010 (in sharp contrast to the above scenario, where Mn-Cr closes before U-Pb). Thus, this scenario would radically change presently inferred Mn-Cr time scales by anchoring the $^{53}Mn/^{55}Mn$ ratio of D'Orbigny to the absolute age of ~4558 Ma, in contrast to the much lower $^{53}Mn/^{55}Mn$ ratio of LEW 86010. As a consequence, all inferred absolute "Mn-Cr" ages of Lugmair and Shukolyukov (1998) would be shifted downward by ~5 Ma. However, this would, in fact, increase enormously the existing, but generally small, discrepancies between various chronometers. In addition, the time difference of about 2 Ma between CAI formation (~4568 Ma) and chondrule fractionation/formation (Amelin et al. 2002) for the U-Pb system, which is in good agreement with the Al-Mg system (e.g. Mostefaoui et al. 2002), would be extended by a factor of ~2 if the $^{53}Mn/^{55}Mn$ ratio (~9.5×10^{-6}) measured for chondrules by Nyquist et al. (2001) is considered. Overall, this scenario is not very appealing, and we are left with our preferred scenario where slow cooling of D'Orbigny through an intermediate temperature range is invoked.

Based on petrographic and geochemical evidence, it has recently been suggested that the glasses in D'Orbigny were formed contemporaneously with the other phases in the meteorite rather than as a result of impact shock melting of the bulk rock or incorporation from an external source by injection once the rock was formed (Varela et al. Forthcoming). This is supported by the observations that the D'Orbigny glasses have a chemical composition that is very similar to the bulk rock (Mittlefehldt et al. 2002), are also present as inclusions in olivines, do not form any interconnecting veins or networks crosscutting the rock, and lack any of the shock features in D'Orbigny (Varela et al. Forthcoming). Since our Mn-Cr analysis indicates that the glasses formed contemporaneously (within ~0.3 Ma) with the major phases of the meteorite at ~4563 Ma, a shock origin for the glasses is highly improbable and would require the Mn-Cr age of the glass to be younger than the major phases of the bulk rock. The majority of the glass in D'Orbigny is found in open druse spaces or hollow shells and may have been formed by a vapor-liquid-solid condensation process during olivine formation (Varela et al. Forthcoming). Large quantities of liquid that condensed from the vapor may have coagulated and then filled open spaces and pockets in the olivine. Our Mn-Cr data is consistent with formation of these glasses up to ~0.3 Ma after the crystallization of the D'Orbigny bulk rock components.

Finally, one additional point is worth mentioning. It was suggested by Mittlefehldt and Lindstrom (1990) that the angrite parent body may be similar in bulk composition to one of the more primitive carbonaceous chondrite groups. In particular, they suggested that the angrites were formed by partial melting of carbonaceous chondrite-like source regions. However, it has been shown (Shukolyukov et al.

2003, and references therein) that, especially, the more primitive carbonaceous chondrite types (CI-CM-CO) exhibit well-resolved excesses on $^{54}Cr/^{52}Cr$. As mentioned above, the $^{54}Cr/^{52}Cr$ ratios in all analyzed D'Orbigny samples agree with the terrestrial standard value within ±10 ppm. Thus, any affinity of this meteorite (and previously measured angrites) with carbonaceous chondrites is not supported by the Cr isotopic system.

CONCLUSIONS

One aim for studying the Mn-Cr isotopic systematics of the angrites was to tie the relative ^{53}Mn-^{53}Cr chronometer to an absolute time scale. The angrites LEW 86010 (LEW) and Angra dos Reis (ADOR) are believed to be ideal for this purpose, since they are early planetary differentiates, which cooled fast through the respective isotopic closure temperatures, do not show any signs of later disturbance, and their ages are precisely known. Mn-Cr isotopic investigations of an additional angrite, D'Orbigny, reveal an initial $^{53}Mn/$ ^{55}Mn, I(Mn) = (3.24 ± 0.04) × 10^{-6}, indicating cooling ~5 Ma before LEW and ADOR. This translates into an absolute age for D'Orbigny of 4562.9 Ma compared to the Pb-Pb age of 4557.8 Ma reported for LEW and ADOR. However, the Pb-Pb age of ~4557 Ma for druse pyroxenes in D'Orbigny is in close agreement with the Pb-Pb ages of the LEW and ADOR angrites. Thus, cooling of the D'Orbigny material in the intermediate temperature range may have proceeded slowly, with the Mn-Cr system closing ~6 Ma before the U-Pb system. Since LEW and ADOR appear to be more thermally metamorphosed than the D'Orbigny angrite, it is possible that the lower $^{53}Mn/^{55}Mn$ ratios in LEW and ADOR are due to the equilibration of the Cr isotopes at moderate temperatures in both of these angrites. Thus, considering some alternatives, our preferred scenario, still, is that the U-Pb and Mn-Cr systems have closed contemporaneously in LEW and ADOR.

One of the most unusual aspects of D'Orbigny is the presence of glass, a phase that has not been found in any of the other angrites. Mn-Cr analyses of the D'Orbigny druse glasses reveal that this phase formed contemporaneously with the main assemblage at ~4563 Ma years ago. It appears that this glass solidified from a melt of primary origin and did not result from impact shock melting of the bulk rock or incorporation of a melt by injection from an external source after the rock had formed.

The $^{53}Mn/^{55}Mn$ ratio of 3.24 × 10^{-6} of the D'Orbigny bulk rock at the time of isotopic closure is more than twice the initial $^{53}Mn/^{55}Mn$ ratio of 1.25 × 10^{-6} previously measured for the LEW and ADOR angrites. The relative Mn-Cr age difference between D'Orbigny and LEW of 5.1 ± 0.3 Ma suggests that D'Orbigny represents an earlier stage in the evolution of the angrites.

The normal terrestrial $^{54}Cr/^{52}Cr$ ratio in D'Orbigny and other angrite samples does not support the hypothesis that angrites may have any direct link to carbonaceous chondrite material.

REFERENCES

Amelin Y., Krot N. K., Hutcheon I. D., and Ulyanov A. A. 2002. Lead isotopic ages of chondrules and calcium-aluminum-rich inclusions. *Science* 297:1678–1683.

Birck J. L. and Allègre C. J. 1985. Evidence for the presence of ^{53}Mn in the early solar system. *Geophysical Research Letters* 12:745–748.

Birck J. L. and Allègre C. J. 1988. Manganese-chromium isotope systematics and the development of the early solar system. *Nature* 331:579–584.

Endress M., Zinner E. K., and Bischoff A. 1996. Early aqueous activity on primitive meteorites parent bodies. *Nature* 379:701–703.

Eugster O., Busemann H., Kurat G., Lorenzetti S., and Varela M. E. 2002. Characterization of the noble gases and CRE age of the D'Orbigny angrite. *Meteoritics & Planetary Science* 37:A44.

Glavin D. P. and Lugmair G. W. 2003. Mn-Cr isotope systematics in the LL type ordinary chondrite St. Séverin. (abstract #1276). 34th Lunar and Planetary Science Conference. CD-ROM.

Glavin D. P., Jagoutz E., and Lugmair G. W. 2003. Mn-Cr isotope systematics of the D'Orbigny angrite. *Meteoritics & Planetary Science* 38:A40

Honda M. and Imamura M. 1971. Half-life of ^{53}Mn. *Physical Review C* 4:1182–1188.

Hutcheon I. D., Teshima J., Armstrong J. T., and Wasserburg G. J. 1985. The chromium isotopic composition of phosphates in IIIA iron meteorites: A search for ^{53}Mn (abstract). *Meteoritics* 20: 668–669.

Jagoutz E., Jotter R., Varela M. E., Zartmann R., Kurat G., and Lugmair G. W. 2002. Pb-U-Th isotopic evolution of the D'Orbigny angrite. (abstract #1043). 32nd Lunar and Planetary Science Conference. CD-ROM.

Jagoutz E., Jotter R., Kubny A., Varela M. E., Zartman R., Kurat G., and Lugmair G. W. 2003. Cm?-U-Th-Pb isotopic evolution of the D'orbigny angrite (abstract). *Meteoritics & Planetary Science* 38:A81.

Jotter R., Jagoutz E., Varela M. E., Zartman R., and Kurat G. 2002. Pb isotopes in glass and carbonates of the D'Orbigny angrite. *Meteoritics & Planetary Science* 37:A73.

Jotter R., Jagoutz E., Varela M. E., Zartman R., and Kurat G. 2003. Lead isotopic study of glasses from the D'Orbigny angrite (abstract). *Meteoritics & Planetary Science* 38:A53.

Kubny A., Banerjee A., Jagoutz E., Varela M. E., Brandstätter F., and Kurat G. 2002. Some properties of glass in the D'Orbigny angrite (abstract). *Meteoritics & Planetary Science* 37:A84.

Kurat G., Varela M. E., Brandstätter F., Wäsch E., and Nazarov M. A. 2001. D'Orbigny; A new window into angrite genesis (abstract #1737). 32nd Lunar and Planetary Science Conference. CD-ROM.

Kurat G., Varela M. E., Brandstätter F., Weckwerth G., Clayton R., Weber H. W., Schultz L., Wäsch E., and Nazarov M. A. Forthcoming. D'Orbigny: A non-igneous angritic achondrite? *Geochimica et Cosmochimica Acta*.

Lugmair G. W. and Galer S. J. C. 1992. Age and isotopic relationships among the angrites Lewis Cliff 86010 and Angra dos Reis. *Geochimica et Cosmochimica Acta* 56:1673–1694.

Lugmair G. W., MacIsaac C., and Shukolyukov A. 1992. The ^{53}Mn-^{53}Cr isotope system and early planetary evolution (abstract). 23rd Lunar and Planetary Science Conference. pp. 823–824.

Lugmair G. W. and MacIsaac C. 1995. Radial heterogeneity of ^{53}Mn in the early solar system? (abstract). 26th Lunar and Planetary Science Conference. pp. 879–880.

Lugmair G. W. and Shukolyukov A. 1998. Early solar system timescales according to ^{53}Mn-^{53}Cr systematics. *Geochimica et Cosmochimica Acta* 62:2863–2886.

Mikouchi T. and McKay G. 2001. Mineralogical investigation of D'Orbigny: A new angrite showing close affinities to Asuka-881371, Sahara 99555, and Lewis Cliff 87051 (abstract #1876). 32nd Lunar and Planetary Science Conference. CD-ROM.

Mittlefehldt D. W. and Lindstrom M. M. 1990. Geochemistry and genesis of the angrites. *Geochimica et Cosmochimica Acta* 54: 3209–3218.

Mittlefehldt D. W., Killgore M., and Lee M. T. 2001. Petrology and geochemistry of the new angrite D'Orbigny (abstract #2057). 32nd Lunar and Planetary Science Conference. CD-ROM.

Mittlefehldt D. W., Killgore M., and Lee M. T. 2002. Petrology and geochemistry of D'Orbigny, geochemistry of Sahara 99555, and the origins of angrites. *Meteoritics & Planetary Science* 37:345–369.

Mostefaoui S., Kita N. T., Togashi S., Tachibana S., Nagahara H., and Morishita Y. 2002. The relative formation ages of ferromagnesian chondrules inferred from their initial ^{26}Al/^{27}Al ratios. *Meteoritics & Planetary Science* 37:421–438.

Nyquist L. E., Bansal B., Wiesmann H., and Shih C. Y. 1994. Neodymium, strontium, and chromium isotopic studies of the LEW 86010 and Angra dos Reis meteorites and chronology of the angrite parent body. *Meteoritics* 29:872–885.

Nyquist L., Lindstrom D., Mittlelfehldt D. W., Shih C. Y., Wiesmann H., Wentworth S., and Martinez R. 2001. Manganese-chromium formation intervals for chondrules from the Bishunpur and Chainpur meteorites. *Meteoritics & Planetary Science* 32:281–292.

Nyquist L. E., Shih C. Y., Wiesmann H., and Mikouchi T. 2003. Fossil ^{26}Al and ^{53}Mn in D'Orbigny and Sahara 99555 and the timescale for angrite magmatism (abstract #1388). 34th Lunar and Planetary Science Conference. CD-ROM.

Nyquist L. E., Reese Y., Wiesmann H., Shih C. Y., and Takeda H. 2003. Fossil ^{26}Al and ^{53}Mn in the Asuka 881394 eucrite: Evidence of the earliest crust on asteroid 4 Vesta. *Earth and Planetary Science Letters* 214:11–25.

Polnau E. and Lugmair G. W. 2001. Mn-Cr isotope systematics in the two ordinary chondrites Richardton (H5) and Ste Marguerite (H4) (abstract #1527). 32nd Lunar and Planetary Science Conference. CD-ROM.

Shields W. R., Murphy T. J., Cantanzaro E. J., and Garner E. L. 1966. Absolute isotopic abundance ratios and the atomic weight of a reference sample of chromium. *Journal of Research of the National Bureau of Standards* 70A:193–197.

Shukolyukov A., Lugmair G. W., and Bogdanovski O. 2003. Manganese-chromium isotope systematics of Ivuna, Kainsaz, and other carbonaceous chondrites (abstract #1279). 34th Lunar and Planetary Science Conference. CD-ROM.

Störzer D. and Pellas P. 1977. Angra dos Reis: Plutonium distribution and cooling history. *Earth and Planetary Science Letters* 35:285–293.

Sugiura N. 2002. Mn-Cr chronology of olivine in some meteorites (abstract #1435). 33rd Lunar and Planetary Science Conference. CD-ROM.

Varela M. E., Kurat G., Brandstätter F., Bonnin-Mosbah M., and Métrich N. 2001. Glasses in the D'Orbigny angrite. (abstract #1803). 32nd Lunar and Planetary Science Conference. CD-ROM.

Varela M. E., Kurat G., Zinner E., Métrich N., Brandstätter F., Ntaflos T., and Sylvester P. Forthcoming. Glasses in the D'Orbigny angrite. *Geochimica et Cosmochimica Acta*.

Wadhwa M., Zinner E. K., and Crozaz G. 1997. Manganese-chromium systematics in sulfides of unequilibrated enstatite chondrites. *Meteoritics & Planetary Science* 32:281–292.