In-situ chromium isotope measurement of chromium-rich fine grains in the Murchison CM2 chondrite

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Isotopic anomalies of ^{54}Cr have been reported in bulk chondrites. Stepwise dissolution experiments have suggested the presence of a carrier of the ^{54}Cr anomaly, probably of presolar origin. Although stepwise dissolution experiments and ion microprobe studies of Cr-rich grains have revealed, to some extent, the carrier of anomalous ^{54}Cr, the nature of the carrier is not yet well understood. In this study, we attempted to detect the carrier phases. We performed an *in-situ* measurement of Cr isotopic compositions of small (~1 μm or less in size) Cr-bearing grains in the Murchison CM2 chondrite using a NanoSIMS 50 ion microprobe. ^{54}Cr has an isobaric interference of ^{54}Fe, which makes the measurement of ^{54}Cr/^{52}Cr isotopic ratios difficult. In order to evaluate the contribution of ^{54}Fe, the abundance of ^{56}Fe was measured. Even after large corrections for ^{54}Fe, δ^{54}Cr values of Cr-rich grains were determined with a precision of ~30‰.

No grain out of ~200 Cr-rich grains was confirmed to be a presolar grain with a large ^{54}Cr anomaly. If the carrier of the ^{54}Cr anomaly is Cr-rich, this result implies a low abundance and a huge isotopic anomaly of the carrier, and/or its extremely fine grain size. In the former case, the maximum abundance of the presolar Cr-rich grains is roughly estimated to be ~1 ppm. In that case the minimum isotopic anomaly would be ~90‰.

Keywords: 54-chromium, isotopic anomaly, presolar grain, NanoSIMS, isobaric interference

INTRODUCTION

Isotopic anomalies found in meteorites have been one of the important issues when considering mixing processes of materials in the early solar system. They are also crucial for chronological studies of solar system objects using radioactive nuclides because they are based on homogeneities of the parent and daughter nuclides (Lugmair and Shukolyukov, 1998; Bizzarro *et al.*, 2005; Villeneuve *et al.*, 2009). Refractory inclusions in CV3 carbonaceous chondrites (Ca, Al-rich Inclusions; CAIs) have been known to display isotopic anomalies in the iron group elements such as Ca, Ti, Cr and Ni (summarized in Birck, 2004). Moreover, previous studies reported isotopic anomalies of Ti, Ni, Cu, Mo, Nd, Zr, Ba, Os, etc. in bulk samples and acid residues of chondrites and achondrites taking advantage of recent high precision (10 to 1 ppm level) isotope measurements (e.g., Yin *et al.*, 2001, 2002; Dauphas *et al.*, 2002a, b; Luck *et al.*, 2003; Ranen and Jacobsen, 2006; Carlson *et al.*, 2007; Yokoyama *et al.*, 2007; Regelous *et al.*, 2008; Trinquier *et al.*, 2009). These isotopic anomalies are generally interpreted as implying nucleosynthetic signatures, hence, incomplete mixing of diverse nucleosynthetic components in the early solar nebula.

While CAIs show isotopic anomalies in iron group elements including Cr (Birck and Allègre, 1984), isotopic anomalies of ^{54}Cr have also been reported in bulk meteorites (Shukolyukov and Lugmair, 2006; Trinquier *et al.*, 2007) and leachates in stepwise dissolution experiments of carbonaceous chondrites (Rotaru *et al.*, 1992; Podosek *et al.*, 1997; Trinquier *et al.*, 2007). According to these studies, chondrites (Shukolyukov and Lugmair, 2006; Trinquier *et al.*, 2007) and achondrites (Trinquier *et al.*, 2007) are found to be characterized by their unique ^{54}Cr/^{52}Cr ratios. In stepwise dissolution experiments (Rotaru *et al.*, 1992; Podosek *et al.*, 1997; Trinquier *et al.*, 2007), all leachates of bulk carbonaceous chondrites show ^{54}Cr excesses or deficits relative to Earth. Rotaru *et al.* (1992) and Trinquier *et al.* (2007) showed that large ^{54}Cr enrichments in HCl + HF solutions of CI, CM2 and CR2 chondrites. Podosek *et al.* (1997) and Trinquier *et al.* (2007) also reported that fractions of the Orgueil CI chondrite treated with HCl show the strongest positive anomalies of ^{54}Cr in the stepwise dissolution experiments. On the other hand, HCl + HF solutions of CV3 and CO3 chondrites do not display such large ^{54}Cr anomalies. Recently, Qin *et al.* (2010) reported Cr isotopic composi-

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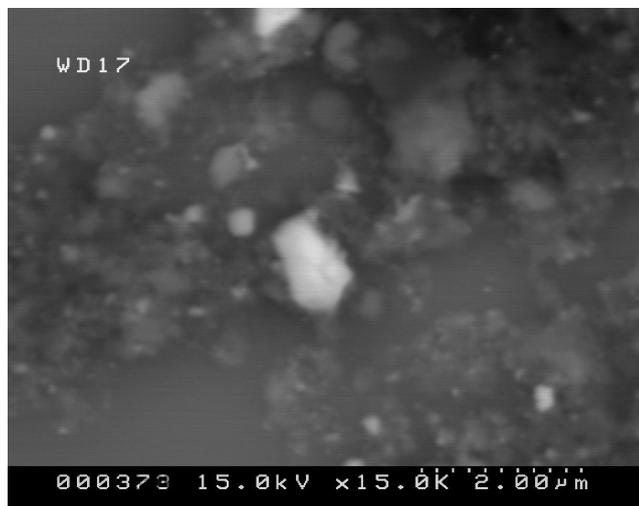*Fig. 1. SEM image of the organic rich residue. The scale bar is 2 μm. The bright grains are chromite and Cr-rich spinel grains of submicron to micron in size.*

Fig. 2. Ion images of a typical Cr-rich grain in Murchison. The field of view is 3×3 μm^2. The number of pixels is 32×32. The color scales show the ion counts. The white line indicates the region where we integrated the ion signals to calculate the elemental and isotopic ratios. The outlines were defined according to the 60% level of individual maximum values of ^{52}Cr.

tions of HCl leachates of the insoluble organic-rich residues extracted from various chondrites. They prepared the organic residue using the CsF-HF demineralization technique (Cody *et al*., 2002). While HCl leachates of the organic residues of CI, CM2 and CR2 show large excesses of ^{54}Cr, those of CV chondrites show smaller excesses. A possible explanation of these results is that a chemically refractory mineral with the ^{54}Cr anomaly in primitive meteorites was modified into a more readily dissolved phase in thermally metamorphosed meteorites. The Allende CV3 chondrite has the very low concentration of presolar SiC grains relative to Orgueil (Huss and Lewis, 1995), supporting this assumption. Therefore, stepwise dissolution experiments suggest the presence of a carrier of the ^{54}Cr anomaly probably of presolar origin, i.e., a nucleosynthetic component. Indeed, several Cr rich grains with enrichments of ^{54}Cr up to 1500‰, most likely chromite and Cr-rich spinel, were found in acid residues extracted from Orgueil (Ott *et al*., 1997; Qin *et al*., 2009; Dauphas *et al*., 2010; Nittler *et al*., 2010). However, the nature of these grains is not yet well understood. The carrier of the ^{54}Cr excess is (at least partly) soluble in HCl + HF. Hence, such a mineral is likely dissolved in conventional preparation procedures of presolar grains with harsh acids (Amari *et al*., 1994). Such nucleosynthetic components seem to be initially homogeneously distributed within the inner protoplanetary disk, inferred by the evidence from Ti isotopes of chondritic and differentiated materials (Trinquier *et al*., 2009). However, the observed isotopic heterogeneities of Cr, Ti and other elements among main meteorite groups require the existence of a secondary process imparting selective loss of these objects before the formation of solar system solids and ac-
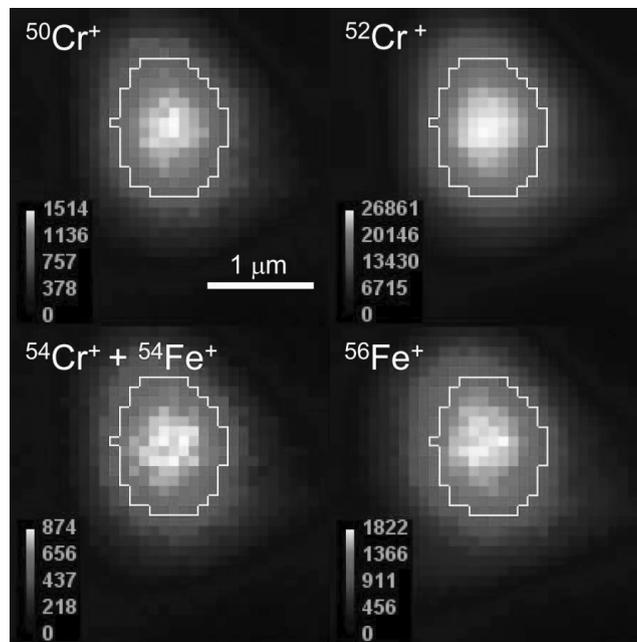
cretion of planetary bodies. Spatial dimensions of the isotope heterogeneity of the protosolar nebula should be comparable to the source regions of their parent bodies.

For a better understanding of the relationship between planetary and mineral scale isotopic heterogeneities, there is a need for more investigations of the nature of the isotopically anomalous phases, including the chemical and isotopic composition, size, physical property and texture. These studies impose a new constraint on the models of planetary formation. Chromium-54 shows an isotopic anomaly larger than any other heavy elements in bulk meteorites. Therefore, it is the most suitable tracer to search for the mineral scale isotopic heterogeneity by an *in-situ* measurement with an ion microprobe. Here we report $^{54}Cr/^{52}Cr$ ratios of approximately 200 Cr-rich grains in an organic residue of the Murchison CM2 chondrite. We used a high sensitivity and high resolution Secondary Ion Mass Spectrometry (SIMS), NanoSIMS 50 at Atmosphere and Ocean Research Institute, the University of Tokyo.

EXPERIMENTAL

We extracted an organic residue from approximately 4 g of the Murchison CM2 chondrite by the CsF technique (Cody *et al*., 2002; Alexander *et al*., 2007) at room
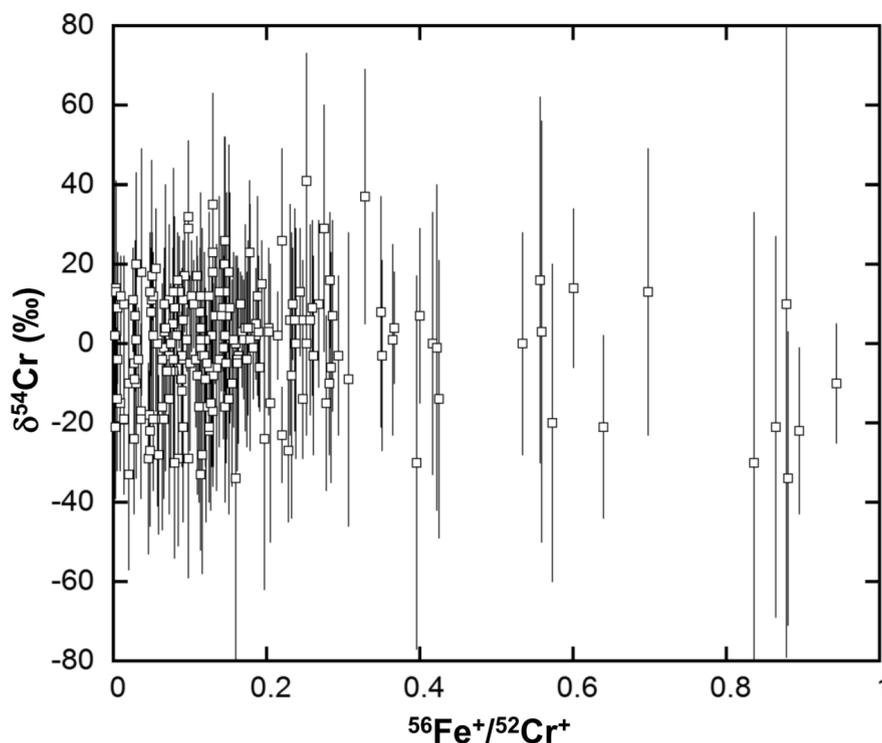
Fig. 3. $\delta^{54}Cr$ values of ~200 Cr-rich grains plotted against $^{56}Fe^+/^{52}Cr^+$ ratios, indicating the magnitudes of corrections for an isobaric interference of ^{54}Fe. Error bars are 2σ. Isotopic anomalies of ^{54}Cr were not found in analyzed ~200 Cr-rich grains within errors.

temperature. Most of the silicates in the bulk sample were removed except chemically refractory phases, such as chromite, spinel and Cr_2O_3. A Scanning Electron Microscope (SEM) image of the organic residue with chemically refractory phases is shown in Fig. 1. A terrestrial chromite was used for a standard to normalize measured meteoritic $^{54}Cr/^{52}Cr$ ratios. The chromite standard was powdered so that the condition of the isotope measurement was identical for both standard and meteoritic samples. The organic residue and the powdered standard were deposited on high-purity silicon wafers.

The isotope measurement was performed with the NanoSIMS 50 at Atmosphere and Ocean Research Institute, the University of Tokyo. A primary beam of O^- with a diameter of ~0.2–0.3 μm and a beam current of ~10 pA was used. Four Electron Multipliers (EMs) were used to analyze $^{50}Cr^+$, $^{52}Cr^+$, $^{54}Cr^+$ and $^{56}Fe^+$ ions simultaneously by ion imaging. Typical count rates for $^{52}Cr^+$ and $^{56}Fe^+$ are ~15,000 and ~2500 cps, respectively. At first, the primary beam was rastered over $50 \times 50 \ \mu m^2$ areas and Cr-bearing grains were located by real-time imaging of $^{52}Cr^+$ ions. Then, the primary beam was rastered over 2×2–$5 \times 5 \ \mu m^2$ areas around the grains to measure their elemental and isotopic ratios. The acquisition time was ~5 minutes and the number of pixels was 32×32. Irradiation time

per pixel was 0.3 seconds. The dead time of each EM was 44 ns and was corrected for the calculation of isotopic compositions. The abundance of each isotope was obtained by integrating ion signals from the grain.

Typical ion images of analyzed grains are shown in Fig. 2. Grain outlines were defined according to the 60% level of individual maximum values of ^{52}Cr. No systematic change in the measured Cr isotopic ratios was observed across a single grain. The analyzed grains were observed with the SEM after the NanoSIMS analysis. Most grains were identified as spinel-chromite grains, which contained Mg, Al, Cr and Fe in varying proportions. Almost pure Cr_2O_3 grains were also found. These grains were typically submicron to a few microns in size.

^{54}Cr has an isobaric interference of ^{54}Fe, which cannot be resolved with mass resolving power of <73,000. It is difficult to measure the abundance of ^{54}Cr precisely by SIMS, and hence, a $^{54}Cr/^{52}Cr$ ratio cannot be determined easily with the analytical precision of several permil. However, because a presolar grain typically shows a large isotopic anomaly (e.g., >1500‰; Nittler et al., 2010), a precision of a few % may be sufficient to detect it.

^{56}Fe was used to correct for an isobaric interference of ^{54}Fe on mass 54 using the following equation.

Table 1. Chromium Isotope Measurements[1]*

Sample	^{56}Fe[2]	^{54}Cr[2]	^{52}Cr[2]	^{50}Cr[2]	Max. ^{52}Cr[3]	$^{54}Cr/^{52}Cr$[4]	$^{56}Fe^+/^{52}Cr^+$[5]	$\delta^{54}Cr$[6]
Spinel-chromite grain #1	40891	16811	522641	28197	5884	0.02718 ± 0.00050	0.078	5 ± 19
Spinel-chromite grain #2	2129028	195910	2254302	119207	12450	0.02674 ± 0.00040	0.944	−11 ± 16
Spinel-chromite grain #3	86939	26552	770963	41217	5490	0.02726 ± 0.00043	0.113	8 ± 17
Spinel-chromite grain #4	125673	27041	703580	37972	7899	0.02705 ± 0.00048	0.179	0 ± 18
Spinel-chromite grain #5	953101	88836	1064767	57004	4531	0.02641 ± 0.00057	0.895	−24 ± 22
Spinel-chromite grain #6	122974	19553	430255	22792	6026	0.02724 ± 0.00066	0.286	7 ± 25
Spinel-chromite grain #7	7277	4487	146760	7791	5826	0.02742 ± 0.00093	0.050	14 ± 35
Spinel-chromite grain #8	95902	16018	367643	19465	3042	0.02695 ± 0.00070	0.261	−3 ± 27
Spinel-chromite grain #9	52360	12024	322786	17242	8748	0.02692 ± 0.00069	0.162	−5 ± 26
Spinel-chromite grain #10	33072	17942	585560	32632	3707	0.02704± 0.00046	0.056	0 ± 18
Spinel-chromite grain #11	63778	33991	1106568	59395	14841	0.02705 ± 0.00034	0.058	0 ± 14
Spinel-chromite grain #12	14899	6406	204761	10934	10548	0.02665 ± 0.00079	0.073	−15 ± 30
Spinel-chromite grain #13	157655	38549	1072627	57524	26083	0.02658 ± 0.00037	0.147	−17 ± 15
Spinel-chromite grain #14	97492	12315	229249	12343	1568	0.02663 ± 0.00099	0.425	−15 ± 37
Spinel-chromite grain #15	16167	9958	326367	17278	3040	0.02736 ± 0.00062	0.050	11 ± 24
Spinel-chromite grain #16	157577	28137	688947	37193	5502	0.02627 ± 0.00050	0.229	−29 ± 19
Spinel-chromite grain #17	28705	7284	197700	10318	2832	0.02760 ± 0.00088	0.145	20 ± 33
Spinel-chromite grain #18	125641	48791	1504963	80955	33464	0.02710 ± 0.00030	0.083	2 ± 12
Spinel-chromite grain #19	67953	28705	901944	48653	19440	0.02703 ± 0.00038	0.075	−1 ± 15
Spinel-chromite grain #20	88678	52648	1716091	91399	11601	0.02739 ± 0.00027	0.052	13 ± 11
Spinel-chromite grain #21	202470	65443	1924073	102928	19380	0.02731 ± 0.00027	0.105	10 ± 11
Cr-oxide (Cr_2O_3) grain #1	14451	238780	8778053	471830	40726	0.02710 ± 0.00011	0.002	2 ± 9
Cr-oxide (Cr_2O_3) grain #2	17132	34428	1220029	65652	12948	0.02732 ± 0.00031	0.014	10 ± 13
Terrestrial chromite standard #1	213773	49974	1344331	71780	5202	0.02704 ± 0.00034	0.159	
Terrestrial chromite standard #2	173924	41637	1135145	60311	4795	0.02692 ± 0.00037	0.153	
Terrestrial chromite standard #3	168579	39283	1050387	55147	4723	0.02717 ± 0.00038	0.160	
Average of the standard						0.02705 ± 0.00015		

[1]: Example of analytical results obtained in one day.
[2]: Total count of each ion, i.e., summation of several pixels.
[3]: Maximum ^{52}Cr count of a pixel. Irradiation time per pixel was 0.3 seconds.
[4]: $^{54}Cr/^{52}Cr$ ratios are calculated using Eq. (1). Errors represent counting statistics (2σ).
[5]: Ratios of ion counts, not atomic ratios (see text).
[6]: Deviations from the $^{54}Cr/^{52}Cr$ ratio of the terrestrial chromite standard (0.02705). The uncertainty of that value was propagated to errors of $\delta^{54}Cr$ ratios of the sample.

$$\left(^{54}Cr/^{52}Cr\right) = \frac{^{54}M - ^{54}Fe}{^{52}Cr}$$

$$= \frac{^{54}M - ^{56}Fe \times \left(^{54}Fe/^{56}Fe\right)_{ref.}}{^{52}Cr} \quad (1)$$

where ^{54}M is the total ion signal at mass 54 (sum of ^{54}Cr and ^{54}Fe) and $(^{54}Fe/^{56}Fe)_{ref.}$ represents the solar $^{54}Fe/^{56}Fe$ ratio of 0.063703 (Lodders, 2003). In this calculation, mass fractionation of Fe (irrespective of instrumental and intrinsic) was not considered for the reasons described below: 1) A presolar grain is likely to have a large isotopic anomaly of Cr according to previous results (e.g., Nittler *et al.*, 2010), and as a result, the uncertainty of

$^{54}Fe/^{56}Fe$ ratio seems negligible; 2) The leach fractions with the greatest ^{54}Cr anomalies in the stepwise dissolution experiment have no isotopic anomaly of other elements including Fe (Rotaru *et al.*, 1992); 3) The presolar grains are likely enriched in Cr (Podosek *et al.*, 1997). Obtained $^{54}Cr/^{52}Cr$ ratios of analyzed samples are expressed as a deviation from that of the terrestrial standard in permil:

$$\delta^{54}Cr = \frac{\left(^{54}Cr/^{52}Cr\right)_{sample} - \left(^{54}Cr/^{52}Cr\right)_{std.}}{\left(^{54}Cr/^{52}Cr\right)_{std.}} \times 1000 \quad (2)$$

where $(^{54}Cr/^{52}Cr)_{sample}$ and $(^{54}Cr/^{52}Cr)_{std.}$ are $^{54}Cr/^{52}Cr$

ratios of a meteoritic sample and the terrestrial standard, respectively. The reproducibility of $^{54}Cr/^{52}Cr$ ratios of the terrestrial chromite standard ranged 6‰ to 25‰, which varied from day to day. The uncertainties of $(^{54}Cr/^{52}Cr)_{std.}$ were propagated to the errors of $\delta^{54}Cr$.

^{50}Cr also has irresolvable isobaric interferences of ^{50}Ti and ^{50}V, and $^{50}Cr/^{52}Cr$ ratios could not be corrected for their contributions because other isotopes of Ti and V were not measured. Therefore, the $^{50}Cr/^{52}Cr$ ratios are not referred to in the following discussion.

RESULTS AND DISCUSSION

Data for approximately 200 Cr-rich grains are plotted in a $\delta^{54}Cr$ vs. $^{56}Fe^+/^{52}Cr^+$ diagram (Fig. 3) and some of the data obtained in one day are given in Table 1. $^{54}Cr/^{52}Cr$ ratios are also shown in a histogram (Fig. 4). The relative sensitivity factor for Fe/Cr is not fully understood. Therefore, $^{56}Fe^+/^{52}Cr^+$ values do not represent true $^{56}Fe/^{52}Cr$ atomic ratios. Data for grains with high $^{56}Fe^+/^{52}Cr^+$ ratios have large corrections for ^{54}Fe; e.g., if $^{56}Fe^+/^{52}Cr^+$ = 1, ions at mass 54 consists of ~70% $^{54}Fe^+$ and 30% $^{54}Cr^+$.

As illustrated in Figs. 3 and 4, most grains showed the terrestrial Cr isotopic composition within the 2 standard deviation of ~30‰. No grain was confirmed to be a presolar grain with a large ^{54}Cr anomaly expected from the results of previous studies (e.g., Qin et al., 2010). This result also indicates that if $^{56}Fe^+/^{52}Cr^+$ ratios of the grains are less than ~1, $\delta^{54}Cr$ values can be determined with uncertainties of ±30‰ in spite of the possible presence of (instrumental and/or intrinsic) mass fractionation of Cr and Fe. Although mass fractionation of Cr and Fe affects calculated $\delta^{54}Cr$ values, it is found to be negligible when large isotopic anomalies are searched for. However, it appears difficult to determine $\delta^{54}Cr$ values of grains with higher $^{56}Fe^+/^{52}Cr^+$ ratios (>1) with a precision of 30‰.

The CsF technique used for extraction of the organic residue removes silicates. Therefore it is unlikely that silicates are candidates for the carriers of ^{54}Cr anomalies in the organic residues of carbonaceous chondrites. Incomplete dissolution of presolar SiC grains may be a possible candidate for the ^{54}Cr anomaly, as suggested by Dauphas et al. (2002b) for the Mo isotopic anomaly in Orgueil. However, the measured $\delta^{54}Cr$ values of SiC grains were indistinguishable from the terrestrial value (Savina et al., 2010). Therefore, they concluded that incomplete dissolution of presolar SiC grains is not the source of the ^{54}Cr anomalies in leachates of carbonaceous chondrites. They also suggested that SiC doesn't contain a significant amount of Cr (~1 ppm; Knight et al., 2008), so even if the SiC had a large anomaly of ^{54}Cr the effect of incomplete dissolution seems small. Isotope data on refractory inclusions (Birck, 2004) and nucleosynthetic

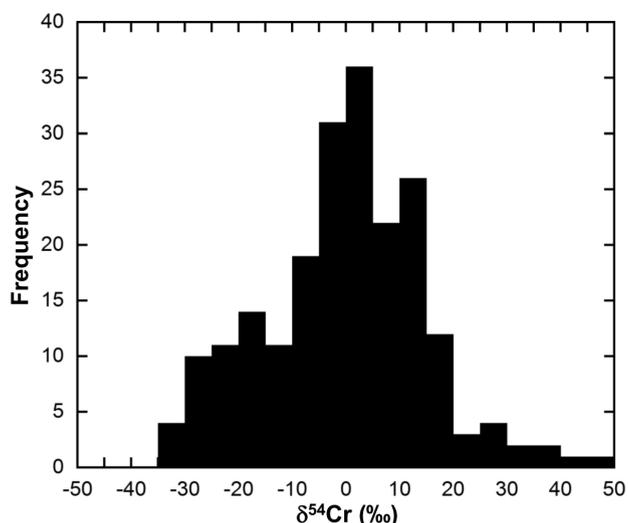Fig. 4. Histogram of $\delta^{54}Cr$ values of Cr-rich grains. Most grains show $\delta^{54}Cr$ ~ 0, i.e., identical to the terrestrial isotopic composition. The 2 standard deviation of $\delta^{54}Cr$ values is ~30‰.

calculations (Woosley et al., 2002) indicate that ^{54}Cr anomalies should be associated with detectable effects on the other heavy isotopes of the iron peak elements. However, no correlative anomaly of any other elements, including iron group elements, has yet been found in the fractions by the stepwise dissolution of bulk meteorites (e.g., no anomaly was found in Ni isotopes for the fractions with Cr isotopic anomalies; Rotaru et al., 1992). The absence of correlative anomalies in other elements suggests that the carriers of ^{54}Cr anomalies are chemically enriched in Cr (Podosek et al., 1997).

The number of grains analyzed in this study was about 200 and they are dominated by spinel-chromite and almost pure Cr_2O_3 grains. Although these phases are generally thought to be not sufficiently soluble in HCl, it is not impossible that due to their small grain sizes, these phases are soluble in HCl and are the carriers of ^{54}Cr excesses in the organic residues of carbonaceous chondrites. Qin et al. (2010) reported that both the HCl leachates and residues of the Murchison organic-rich separates show ^{54}Cr excesses, supporting the idea that there could be ^{54}Cr-rich oxide grains in the organic residues of carbonaceous chondrites (at least Murchison). In fact, chromite and Cr-rich spinel grains of <200 nm with large ^{54}Cr enrichments were recently reported in the organic residue of Orgueil, although the nature of these grains is not yet well understood (Qin et al., 2009; Dauphas et al., 2010; Nittler et al., 2010). In a previous NanoSIMS analysis of an organic residue from Orgueil (Nittler et al., 2005), 5 presolar chromite grains and one Al_2O_3 grain out of ~2700 O-rich grains were identified based on oxygen isotopic anoma-

lies. Chemical analyses by SEM-EDS indicated that the residue consisted of ~33% $MgAl_2O_4$, ~15% TiO_2, ~14% Cr_2O_3, ~13% $MgCr_2O_4$ and ~12% other Cr-rich oxides with varying amounts of Fe, Mg, Al, and/or Mn. Minor amounts of Al_2O_3, hibonite and contamination phases make up the remainder (Nittler and Alexander, 2003). This is the case for Orgueil, and we assume that it is also the case for Murchison. Then, ~40% of the oxide grains were Cr-rich oxides, hence, about 1100 grains out of 2700 grains were Cr-rich. The ratio of presolar chromites to all Cr-rich oxides was found to be ~1/220 (=5/1100). Therefore, it may be reasonable to assume that no presolar grain was identified among the ~200 Cr-rich grains analyzed in this study.

In the present study, we searched for the carriers of the ^{54}Cr anomalies in the organic residue based on the assumption that they are enriched in Cr. Carriers of ^{54}Cr anomalies were not detected among ~200 grains. This indicates either (1) the carriers are extremely fine grains (the size of dust grains in the ejecta of supernovae is estimated to be <10 nm; Kozasa *et al*., 1991) which cannot be detected even by the NanoSIMS, and/or (2) the abundance of the carriers is low and they carry huge isotopic anomalies sufficient to explain the anomalies reported in bulk meteorites.

If (2) is the case, the maximum abundance of the carriers and their minimum isotopic anomaly can be roughly estimated. A previous study reported that the organic residue from Murchison contained 6.0% of the total Cr (Qin *et al*., 2010). Within 6.0% of the total Cr, 5.8% was insoluble in HCl, while 0.2% of the total Cr is soluble in HCl and shows a large ^{54}Cr enrichment of 137ε. In this study, the analyzed ~200 Cr-rich grains were all acid resistant phases and showed the terrestrial $^{54}Cr/^{52}Cr$ ratio. Therefore, the maximum abundance of presolar Cr can be estimated to be ~0.03 (=6.0/200)% of the total Cr in Murchison. As the isotopic anomaly of 137ε is diluted by <0.03/0.2, the minimum isotopic anomaly of the carrier phases is ~90 (=0.2/0.03 × 137ε)‰. Given the bulk Cr concentration of Murchison to be ~3300 ppm (Jarosewich, 1990), presolar Cr appears to be less than ~1 (3300 × 0.03/ 100) ppm.

Another possibility ((1) mentioned above) is that very fine grains are responsible for the observed ^{54}Cr anomalies. Indeed, Qin *et al*. (2009) reported a few chromite and Cr-rich spinel grains of <200 nm with positive $^{54}Cr/$ ^{52}Cr anomalies of 100‰ to 300‰. Astrophysical simulations have suggested that ^{54}Cr associated with other neutron-rich isotopes of the iron-group elements is produced in a neutron-rich environment at or near nuclear statistical equilibrium in massive stars prior to the supernova stage (Woosley *et al*., 2002). Fine grains of <10 nm are expected to form in the ejecta of supernovae as suggested by Kozasa *et al*. (1991). If this is the case, an iso-

tope measurement with spatial resolution of the nanometer scale will be needed for identification of the carriers, and that is impossible at present.

CONCLUSIONS

In this study, $^{54}Cr/^{52}Cr$ ratios of approximately 200 Cr-bearing small grains (~1 μm in size) in a Murchison organic residue were determined with a precision of ~30‰ using the NanoSIMS ion microprobe. No grain was confirmed to be a presolar grain with a ^{54}Cr anomaly. The analyzed grains were dominated by spinel-chromite and almost pure Cr_2O_3. Based on the Cr isotopic compositions of the HCl leachates and residues of the Murchison organic-rich separates, there could be ^{54}Cr-rich oxide grains in the organic residues of carbonaceous chondrites. Considering one previous report on the abundance of presolar oxide grains, however, it may be reasonable to assume that no presolar grain was identified in the 200 grains analyzed in this study.

If the carriers of ^{54}Cr anomalies are enriched in Cr, the fact that no grain out of ~200 grains was confirmed to show a ^{54}Cr anomaly indicates their low abundances associated with huge isotopic anomalies, and/or their extremely fine grain sizes. According to the results of this study, the maximum abundance of presolar Cr can be estimated to be ~1 ppm. This means that the minimum isotopic anomaly is ~90‰.

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