ION PROBE ANALYSIS OF ^{54}Cr ISOTOPIC COMPOSITIONS OF AN ORGANIC RESIDUE FROM MURCHISON CM2 CHONDRITE.
W. Fujiya[1], N. Sugiura[1], H. Hiyagon[1], N. Takahata[2] and Y. Sano[2], [1]Department of Earth and Planetary Science, University of Tokyo, 7-3-1 Hongo, Tokyo 113-0033, Japan (E-mail: fujiya@eps.s.u-tokyo.ac.jp), [2]Ocean Research Institute, University of Tokyo, 1-15-1 Minami-dai, Tokyo 164-8639, Japan.

Introduction: The extent of isotopic homogeneity in the solar system has been an important issue. Refractory inclusions of CV3 chondrites (CAIs) have been known to display isotopic anomalies up to 4 % in O and in iron group elements such as Ca, Ti, Cr and Ni (summarized in [1]). These isotopic anomalies are interpreted to reflect nucleosynthetic signatures, hence, incomplete mixing in the solar nebular of diverse nucleosynthetic components.

While CAIs show isotopic anomalies of iron group elements, isotopic anomalies of ^{54}Cr have been reported in bulk meteorites, including both chondrites and achondrites [2,3]. Especially, only carbonaceous chondrites show positive ^{54}Cr anomalies and the highest ^{54}Cr anomalies are found in the least metamorphosed (CI) chondrites. Stepwise dissolution experiments have suggested the presence of carriers of ^{54}Cr anomalies, probably with presolar origins [3-5]. Chemical and physical separations of carbonaceous chondrites could concentrate the anomalies up to ~20 ‰ in particular fractions [6,7]. However, these carrier phases have not been identified to date.

In this study, we measured ^{54}Cr/^{52}Cr ratios of Cr bearing grains contained in an organic residue from Murchison CM2 chondrite using the NanoSIMS 50 at Ocean Research Institute, University of Tokyo to find the carriers of ^{54}Cr anomalies. In a previous study [7], large ^{54}Cr anomalies were found in HCl leachates of organic residues. Therefore, the carrier phases appear to be in the residue.

Experimental: The organic residue was prepared using a gentle CsF technique [8]. It was deposited on a silicon wafer and analyzed with the NanoSIMS. We also prepared a powdered terrestrial chromite standard which has a ^{56}Fe$^+$/^{52}Cr$^+$ ratio of ~0.1 in the SIMS analysis.

99 grains enriched in Cr were located by ion images of ^{52}Cr and these grains are typically submicron to a few microns in size. Positive secondary ions of ^{50}Cr, ^{52}Cr, ^{54}Cr and ^{56}Fe were analyzed in an image acquisition mode using a focused (~300 nm) primary O$^-$ beam of ~10 pA. The primary ion beam was rastered over 2 x 2 – 5 x 5 µm^2 areas and number of pixels was 32 x 32 pixels. Measurement time was 5 minutes per frame, consequently irradiation time per pixel was 0.3 seconds. The abundance of each isotope contained in a Cr bearing grain was calculated by integrating the signals from the grain.

^{54}Cr has an isobaric interference of ^{54}Fe and they cannot be resolved in the SIMS analysis (mass resolution of ~73,000 is needed). Therefore it is impossible to obtain accurate ^{54}Cr/^{52}Cr ratios without corrections for ^{54}Fe. To overcome this, we measured the abundances of ^{56}Fe to estimate the abundances of ^{54}Fe and calculate ^{54}Cr/^{52}Cr ratios as follows:

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

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

where ^{54}M is total signals corresponding to the mass number of 54 (sum of ^{54}Cr and ^{54}Fe) and (^{54}Fe/^{56}Fe)$_{ref.}$ shows the terrestrial value of 0.063703 [9]. Isotopic ratios are expressed as permil deviations ($\delta(^{54}\text{Cr}/^{52}\text{Cr})$) from the value of a terrestrial chromite standard.

In this calculation, instrumental mass fractionations (IMF) of Cr and Fe were not considered. Especially, the IMF of Fe made effects on $\delta(^{54}\text{Cr}/^{52}\text{Cr})$ values of the analyzed grains indirectly through the correction for ^{54}Fe, depending on Fe/Cr ratios of the grains. The effects of IMF of ^{54}Fe ($\delta(^{54}\text{Fe}/^{56}\text{Fe})$) on calculated $\delta(^{54}\text{Cr}/^{52}\text{Cr})$ values could be evaluated as follows:

$$\Delta = \delta(^{54}\text{Cr}/^{52}\text{Cr})_{uncorrected} - \delta(^{54}\text{Cr}/^{52}\text{Cr})_{corected}$$

$$\cong 2.3 \times \delta(^{54}\text{Fe}/^{56}\text{Fe}) \times (^{56}\text{Fe}^+/^{52}\text{Cr}^+) \quad (1)$$

where Δ is the difference between $\delta(^{54}\text{Cr}/^{52}\text{Cr})$ values uncorrected and corrected for $\delta(^{54}\text{Fe}/^{56}\text{Fe})$. This equation suggests that if $\delta(^{54}\text{Fe}/^{56}\text{Fe})$ values are constant among the analyzed grains, the effects of the IMF of ^{54}Fe on calculated $\delta(^{54}\text{Cr}/^{52}\text{Cr})$ values are proportional to ^{56}Fe$^+$/^{52}Cr$^+$ ratios. Therefore, in a graph with the ^{56}Fe$^+$/^{52}Cr$^+$ ratio on the x-axis and the $\delta(^{54}\text{Cr}/^{52}\text{Cr})$ value on the y-axis, the data are expected to be plotted on a straight line.

Results and discussion: An example of ^{50}Cr, ^{52}Cr, ^{54}Cr and ^{56}Fe ion images is shown in Fig.1. The data of obtained $\delta(^{54}\text{Cr}/^{52}\text{Cr})$ values are plotted in a graph with the ^{56}Fe$^+$/^{52}Cr$^+$ ratio on the x-axis and the $\delta(^{54}\text{Cr}/^{52}\text{Cr})$ value on the y-axis (Fig.2).
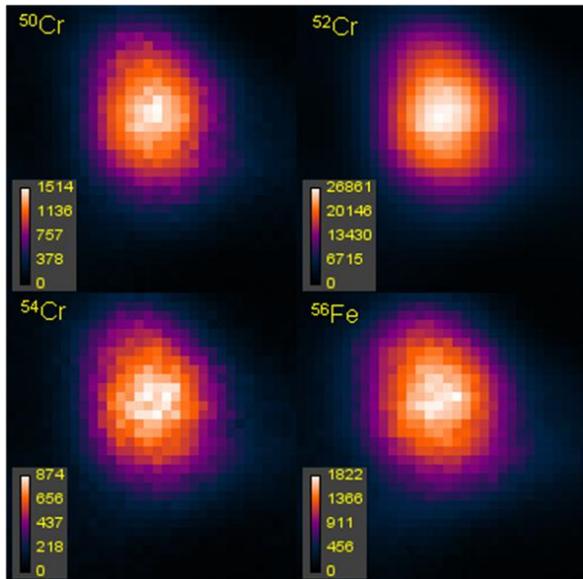
Fig.1: An example of ^{50}Cr, ^{52}Cr, ^{54}Cr and ^{56}Fe ion images. Field of view is 3 x 3 μm^2. Number of pixels is 32 x 32 pixels.
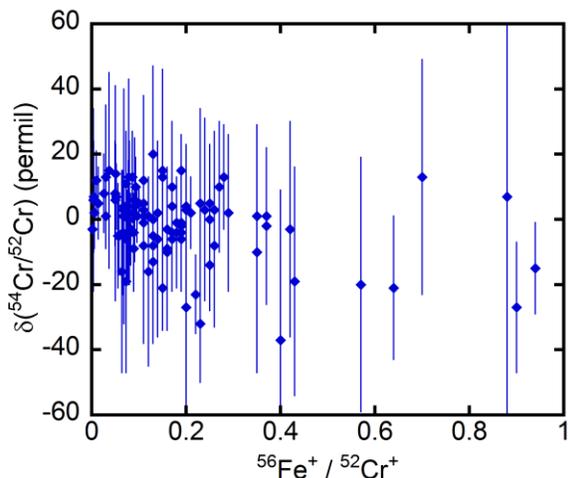

Fig. 2: Obtained $\delta(^{54}Cr/^{52}Cr)$ values of Cr bearing grains in the organic residue. X-axis represents the $^{56}Fe^+/^{52}Cr^+$ ratio. Errors are 2σ.

As shown in Fig.2, most data points are within a range of ±20 ‰ and no grain has a large positive isotopic anomaly expected from the result of [7]. This result also shows that if $^{56}Fe^+/^{52}Cr^+$ ratios of the grains are less than ~1, $^{54}Cr/^{52}Cr$ ratios can be determined with uncertainties of ±20 ‰ in spite of the presence of the IMFs of Cr and Fe. This seems sufficient for the detection of large isotopic anomalies. Although we didn't correct the IMF of Fe, this might affect obtained $\delta(^{54}Cr/^{52}Cr)$ values. According to the equation (1), the influences of the IMF of Fe on $\delta(^{54}Cr/^{52}Cr)$ values of the grains increase in proportion to $^{56}Fe^+/^{52}Cr^+$ ratios.

In this study, this trend might be seen but it is negligible and not important when analyze large isotopic anomalies. However, it appears difficult to determine $^{54}Cr/^{52}Cr$ ratios of grains with higher $^{56}Fe^+/^{52}Cr^+$ ratios with reasonable uncertainties.

In a previous study using the ion probe [10], significantly large (up to ~800 ‰) isotopic anomalies were found for the grains which belonged to the population with the lowest total counts of $^{52}Cr^+$. Unfortunately, carrier phases of the anomalies were not identified. Since the IMF of Fe was not considered in the study, maybe the anomalies would be derived from the IMF if the grains with the anomalies had high $^{56}Fe^+/^{52}Cr^+$ ratios.

In our analysis, the analyzed 99 grains were dominated by spinel-chromite and Cr_2O_3 grains. These phases are not sufficiently soluble in HCl and unlikely the carriers of ^{54}Cr anomalies found in [7]. However, stepwise dissolution experiments suggested that more acid resistant phases were also anomalous [3-5]. With uncertainties of ±20 ‰ in this study, no presolar phase was identified. In previous analyses of Orgueil organic residues using the NanoSIMS [11-13], several presolar chromite and spinel-magnesiochromite grains out of ~3000 O-rich grains were identified by oxygen isotopic anomalies and the abundance of Orgueil presolar chromite of ~50 ppb was estimated [12]. Therefore it is plausible that of 99 grains analyzed in this study, no presolar grain was identified.

The carriers of large ^{54}Cr anomalies soluble in HCl contained in the organic residue have been unknown. It is possible that very minor phases and/or very fine grains expected to form in the ejecta of supernovae as suggested by [14] have large anomalies.

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