A SEARCH FOR PRESOLAR CHROMIUM-OXIDE (Cr_2O_3) GRAINS IN ORGUEIL.
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Introduction: Isotopic anomalies of ^{54}Cr have been reported in bulk carbonaceous chondrites, especially least metamorphosed CI chondrites [1-4]. A Cr rich carrier(s) that has (have) ^{54}Cr excess was (were) found by step dissolution of carbonaceous chondrites [1,2,4]. Presolar grains are suggested to be potential carriers of the Cr isotopic anomalies. Actually, transmission electron microscopy (TEM) studies revealed the presence of Cr bearing-phases in Orgueil (CI): magnesiochromite ($MgCr_2O_4$), ureyite ($NaCrSi_2O_6$) and chromium-oxide (Cr_2O_3), in addition to chromite ($FeCr_2O_4$) [5]. Spinel grains ($MgAlCrO_4$ and $FeCr_2O_4$) were studied with Nano-SIMS and found to have oxygen and magnesium isotopic anomalies, and hence of presolar origin [6,7]. But the isotopic studies of chromium-oxide grains have not yet been performed. In this study, we report Cr isotopic composition of a chromium-oxide grain in Orgueil.

Experimental: A polished shin section of Orgueil was used in this study.

Cr rich grains were identified by EDS (energy dispersive X-ray spectroscopy) elemental mapping using a scanning electron microscope (SEM). The analyzed fields covered approximately 57600 μm^2. We found about 20 Cr rich grains which range from submicron to a few micron in size. Subsequently we performed spot EDS analyses and detected one almost pure chromium-oxide grain with irregular and polygonal shape (Fig. 1) and some spinel grains.

This chromium-oxide grain was analyzed by the SIMS ion microprobe (ims-6f) in image acquisition mode using a resistive anode encoder (RAE). A primary beam of O^- with a diameter of 15 μm was used and the beam current was ~0.1 nA. The O^- beam of 12.8 keV was irradiated on the sample surface of ~70 μm in diameter and spatial resolution of images was ~0.4 μm. We obtained secondary ion images of ^{52}Cr, ^{53}Cr, ^{54}Cr, ^{56}Fe and ^{57}Fe. Their acquisition times were 600 seconds, respectively, except for ^{54}Cr whose acquisition time was 3000 seconds to reduce the counting error. The maximum count rate of the RAE was limited to ~$2x10^4$ cps. The ^{56}Fe count rate was the highest, mainly from the matrix of Orgueil. The field of view of the images was limited to ~10 μm in diameter, in order to exclude extra signals of ^{56}Fe, resulting in high Cr count rate.

Isotopic fractionation of Cr and isobaric interference of ^{54}Fe were taken into account for estimating ^{54}Cr count rate. Fractionation of $^{54}Cr/^{52}Cr$ was estimated based on $^{53}Cr/^{52}Cr$ ratio. ^{54}Fe was estimated based on ^{56}Fe and ^{57}Fe. Dead time correction of the RAE detector was applied to ^{56}Fe.

It was assumed that Fe has the solar isotopic composition. We thought this assumption was valid because the grain was an almost pure chromium-oxide, so the Fe signals were attributed to the matrix around the grain.

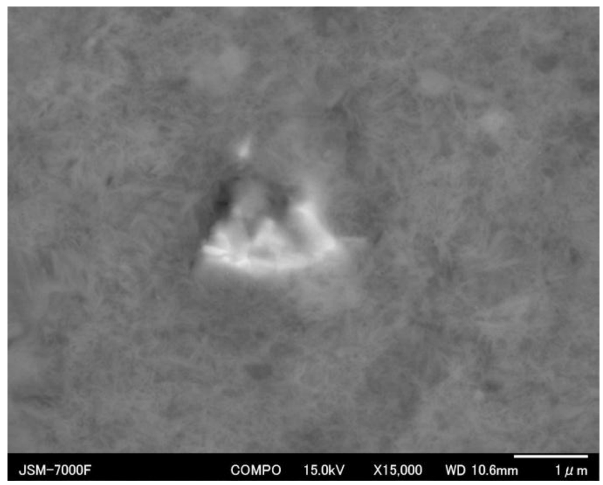

Figure 1. Backscattered FE-SEM image of a chromium-oxide grain (Cr_2O_3). This grain has irregular and polygonal shape.

Results and discussion: An example of obtained images is shown in Fig.2. In this case, the field of view is ~20 μm in diameter. (Actually we measured isotopic composition with the field of view ~10 μm in diameter.) The color shows counting rates in logarithmic scale. The Cr rich phase seems to be poor in Fe. The grain size appears to be a little large because of aberration of secondary ion optics.

For calculating isotopic compositions of Cr and Fe using the isotopic images by RAE, we integrated signals of the grain across 3x3 pixels. The maximum count rate of the RAE was $1.43x10^4$ of ^{56}Fe. Considering dead time of the RAE detector was $4x10^{-6}$ second, dead time correction of 5.72% was applied to ^{56}Fe. Cr and Fe isotopic compositions of this grain were obtained to be 15 ± 8‰ for $\delta(^{53}Cr/^{52}Cr)$ and -5.6 ± 2.3‰ for $\delta(^{57}Fe/^{56}Fe)$ (errors are 1σ). Mass dependent fractionations of Cr and Fe were calculated to be 30‰ for ^{54}Cr and 11.2‰ for ^{54}Fe. Total signals of the grain (3x3 pixels) were $1.6x10^5$ counts for ^{52}Cr,

8.5×10^4 counts for ^{56}Fe and 5.0×10^4 counts for ^{54}Cr. Therefore $\delta(^{54}Cr/^{52}Cr)$ was calculated to be -33 ± 15‰. This indicates the grain has small deficit or almost terrestrial value of $^{54}Cr/^{52}Cr$.

Oxygen and magnesium isotopic measurements of three spinel grains were previously performed by spot analyses with Nano-SIMS [6]. In the study, presolar spinel grains were identified but they had moderate depletions of ^{54}Cr or almost solar Cr isotopic compositions.

Grains in residues from treatments with acetic and nitric acids were studied by SIMS [8]. Some grains were found to show large isotopic anomalies of ^{54}Cr up to ~800‰. The chromium-oxide grain in our study and some spinel grains studied previously [6] are not potential carriers of very large anomalies of ^{54}Cr isotope. Ott et al. suggested that Cr rich grains with large grain size (high total ^{52}Cr count) had low ^{54}Cr anomalies [8]. In our study, the Cr rich grain is relatively large and the high total count of ^{52}Cr suggests that it belongs to the population of large grains of Ott et al. . Therefore, the lack of a large isotope anomaly is consistent with [8]. Although we have not detected plausible candidates of Cr rich phases with large excesses of ^{54}Cr so far, they are expected to be detected in the population of relatively small grains.

Stepwise dissolution of Orgueil showed that the largest excess (~100ε, 1ε is 1 part in 10^4) of ^{54}Cr did not occur in the most chemically resistant phases [1,2,4]. Spinel is one of the most chemically refractory phases. Therefore we think spinel grains are not the carriers with isotopic anomalies of ^{54}Cr, and chromium-oxide grains might be the candidates.

Stepwise dissolution also showed a deficiency of ~6ε in the most easily dissolved (acetic and nitric acids) fractions [1,2,4]. The fractions accounted for alteration phases and most (>80%) of Cr in the whole rock. Isotopic composition of ^{54}Cr in bulk Orgueil appears to be a mixture of the materials that have excess or deficit of ^{54}Cr. Bulk Orgueil has ^{54}Cr excess of ~1.5ε and its Cr concentration is ~2500 ppm [3]. Considering the data above, if we assume that there are grains with very large ^{54}Cr excesses of 800‰ in Orgueil, the grain's concentration is calculated to be ~2.3 ppm.

It is noteworthy that ^{54}Cr is more homogeneously distributed in various phases in more metamorphosed chondrites [1,4]. Generally, presolar grains seem to have survived nebular processes and heating events in the early solar system. Therefore ^{54}Cr homogeneity in more metamorphosed chondrites appears to be somewhat strange. Anomalous Cr might be provided by late stellar input.

For future works, we will obtain more data about chromium-oxide and other Cr rich grains, and try to detect presolar Cr-bearing grains with ^{54}Cr excesses. We expect Cr isotopic heterogeneity in meteorites to help our understanding of primordial materials of planetary bodies and constrain planetary formation processes in the early solar system.

References: [1] Rotaru M. et al. (1992) *Nature* 358, 465. [2] Podosek F. A. et al. (1997) *Meteorit. Planet. Sci.* 32, 617. [3] Shukolyukov A. & Lugmair G. W. (2006) *Earth Planet. Sci. Lett.* 250, 200. [4] Trinquier A. et al. (2007) *Astrophys. J.* 655, 1179. [5] Greshake A. et al. (1996) *Lunar Planet. Sci. XXVII*, 461-462. [6] Zinner E. et al. (2005) *Geochim. Cosmochim. Acta* 69, 4149. [7] Nittler C. M. et al. (2005) *68th Annual Meteorit. Society Meeting*, abstract #5208. [8] Ott U. et al. (1997) *Lunar Planet. Sci. XXVIII*, abstaract #1278.

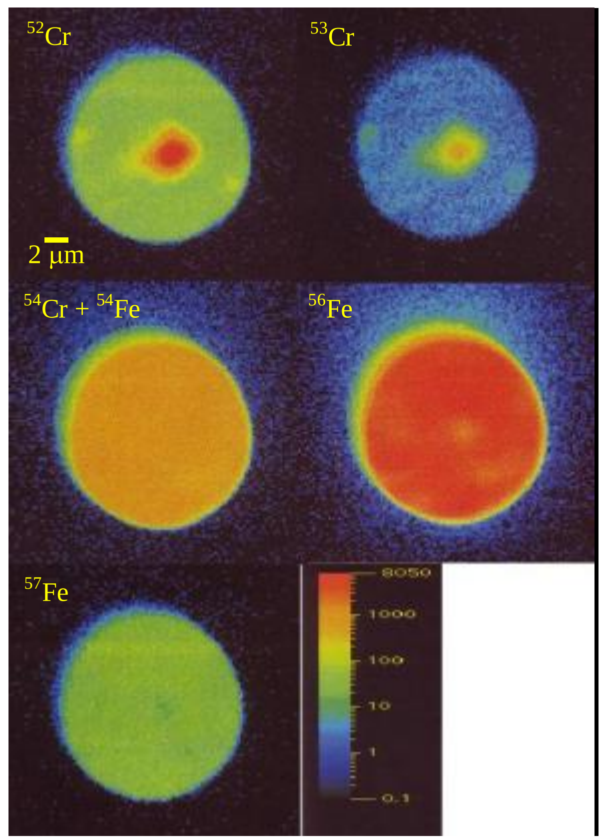

Figure 2. An example of obtained isotope images. The scale bar is 2 µm. The field of view is ~20 µm in diameter. Actually, we measured isotopic compositions with the field of view ~10 µm in diameter in order to exclude extra signals of ^{56}Fe in the matrix. For calculating isotopic compositions of Cr and Fe, we integrated signals of the grain across 3x3 pixels.