

A COORDINATED SEARCH FOR THE CARRIER OF ^{54}Cr ANOMALIES IN METEORITES. N. Dauphas^{1,2}, L. Remusat^{2,3}, J.H. Chen^{2,4}, J. Stodolna⁵, M. Roskosz⁵, Y. Guan², J.M. Eiler², D.A. Papanastassiou^{2,4}, ¹Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, USA (dauphas@uchicago.edu), ²Division of Geological and Planetary Sciences, Caltech, USA, ³Museum National d'Histoire Naturelle, Paris, France, ⁴Science Division, Jet Propulsion Laboratory, USA, ⁵Université des Sciences et Technologies de Lille, France.

Introduction: Acid leachates and residues of primitive meteorites have revealed large variations in ^{54}Cr relative to terrestrial composition [1-8]. The largest anomalies ($\sim +260 \epsilon$) correspond to excesses in ^{54}Cr most likely of nucleosynthetic origin. Smaller anomalies have also been found in bulk meteorites (~ -0.7 to $+1.5 \epsilon$) [5-7]. Despite two decades of research, the carrier of ^{54}Cr excesses has not been identified. It is partially dissolved in HCl and survived aqueous alteration in the parent bodies of Orgueil and Tagish Lake, where the largest Cr isotopic anomalies have been found. The carrier also seems to be very fine grained, most likely less than 200 nm in size [3]. Ion probes offer the opportunity to address directly the question of the nature of the carrier of ^{54}Cr anomalies by measuring $^{54}\text{Cr}/^{52}\text{Cr}$ ratios in individual grains. An exploratory study revealed hints for the presence of excess ^{54}Cr in several grains from Orgueil but the analytical uncertainties were large [9]. Two recent studies took advantage of the high spatial resolution and high transmission efficiency of the NanoSIMS to reinvestigate the question of the carrier of ^{54}Cr anomalies [10,11]. Fujiya et al. [10] did not detect any departure from terrestrial composition in a residue from Murchison while Qin et al. [11] measured grains in Orgueil and reported the detection of positive 100-300 ϵ anomalies. Here, we present a NanoSIMS search for the carrier of ^{54}Cr anomalies in residues from Orgueil and Murchison. In bulk, those residues display the highest ^{54}Cr -excesses ever reported in solid residues of meteorites.

Samples and methods: The sequence of chemical and physical separation used to prepare ^{54}Cr -enriched residues is most similar to that described by Nichols et al. [3]. Because we wanted to identify the potential carrier grains of ^{54}Cr anomalies, leaching was stopped after the acetic acid and nitric acid steps and prior to the HCl steps. Historically, the HCl leachates show the largest excesses in ^{54}Cr in Orgueil. Approximately 1.4 g each of Orgueil and Murchison were disaggregated by the freeze-thaw technique. The samples were then leached in acetic acid and nitric acid. A magnetic fraction was removed in sodium hydroxide using a Teflon coated magnetic stirring bar. A colloidal non-magnetic fraction was recovered by flocculation of the super-

natant. The non-magnetic fraction that readily sedimented was further leached with nitric acid. The residue was finally separated into 3 size fractions using differential sedimentation rates (<0.2 , $0.2-0.8$, and $>0.8 \mu\text{m}$). These are nominal size fractions as density and shape also play roles in sedimentation rates. Sample preparation was done at the University of Chicago in 2002.

Aliquots of the four size fractions (colloidal, <0.2 , $0.2-0.8$, and $>0.8 \mu\text{m}$) were dissolved under high pressure and temperature for bulk Cr isotopic analyses by TIMS at the JPL Cosmochemistry Labs (Fig. 1). The data are discussed in more detail in a companion abstract (Chen et al. 2010).

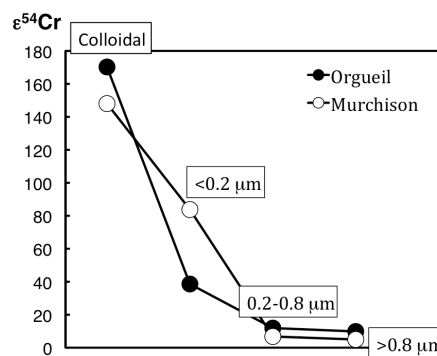


Fig. 1. $\epsilon^{54}\text{Cr}$ in bulk acid residues from the Orgueil and Murchison meteorites. $\epsilon^{54}\text{Cr} = [(^{54}\text{Cr}/^{52}\text{Cr})_{\text{sample}} / (^{54}\text{Cr}/^{52}\text{Cr})_{\text{SRM979}} - 1] \times 10^4$, where $^{54}\text{Cr}/^{52}\text{Cr}$ was corrected for mass fractionation by internal normalization to constant $^{50}\text{Cr}/^{52}\text{Cr}$ and SRM979 is a terrestrial isotopic standard. The error bars (~ 0.1 to 0.2ϵ) are smaller than the symbols.

Additional aliquots of the residues were mounted on gold foils by deposition of sample slurries suspended in water-isopropanol. The carrier of ^{54}Cr anomalies is presumably fine-grained [3] and particular care was taken to ensure that the grains were well dispersed (Fig. 2), so that identification of individual grains would not be limited by the size of the primary ion beam. SEM imaging confirmed that the nominal sizes based on differential sedimentation rates corresponded to the actual granulometry of the samples.

Isotopic measurements were made on a Cameca NanoSIMS-50L at the Caltech Center for Microanalysis. A ~ 500 nm O^+ primary ion beam of ~ 15 pA was rastered over 5×5 to $40 \times 40 \mu m^2$ areas at a grid spacing of ~ 13 px/ μm integrated for 20 ms/px over several frames. Positive secondary ion beams of ^{52}Cr , ^{53}Cr , ^{54}Cr , ^{56}Fe , and ^{57}Fe were measured simultaneously on 5 electron multipliers. The colloidal fraction was too fine-grained to be analyzed by SIMS.

Results and discussion: The four residues prepared for this study contain the largest ^{54}Cr anomalies measured so far in a bulk solid sample (~ 150 and 170ϵ in the colloidal fractions of Murchison and Orgueil, respectively, Fig. 1). This is much higher than previously reported values of ~ 10 to 20ϵ in bulk residues of carbonaceous chondrites [5,11]. This indicates that our sample treatment is efficient at concentrating the carrier of ^{54}Cr anomalies. The values measured in our residues approach those measured in HCl leachates [1-8]. In both Orgueil and Murchison, the magnitudes of the anomalies are larger in smaller size fractions (Fig. 1). This confirms the conclusion of [3] that the carrier of ^{54}Cr anomalies is smaller than $0.2 \mu m$.

Approximately ~ 700 regions of interest (ROIs) corresponding to Cr-rich grains were measured in Orgueil and Murchison. This is more than the 99 grains measured by Fujiya et al. [10] but it is much less than the tens of thousands of grains analyzed by Qin et al. [11]. Our analyses (Fig. 1) clearly shows that the ^{54}Cr -rich grains are smaller than 200 nm, which is below the spatial resolution of the NanoSIMS-50L with a primary O^+ beam of sufficient intensity. It is, therefore, critical to prepare mounts with sufficient dispersion to identify single 200 nm grains (Fig. 2, top).

No clear anomalies were detected in the 700 Cr-rich ROIs that we analyzed. The smallest grains have very large error bars (up to $\sim 300 \%$) but their $^{54}Cr/^{52}Cr$ are still normal within uncertainties. Another strategy that we adopted was to generate maps of $\delta^{54}Cr$ corrected for ^{54}Fe interference and mass fractionation. The $\delta^{54}Cr$ values of each pixel were normalized to the $^{54}Cr/^{52}Cr$ of the bulk image, excluding regions where ^{54}Fe correction exceeded $1,000 \%$. Most images show no departure from the terrestrial composition. However, a map generated on a mount of Orgueil $< 0.2 \mu m$ shows a region with positive $\delta^{54}Cr$ anomaly at $\sim +260 \%$ (Fig. 2, bottom). This is similar to what was reported by Qin et al. [11]. This region, however, does not correspond to a clearly identifiable grain, which supports the view that the carrier phase of ^{54}Cr anomalies is very small.

Conclusion: Colloidal fractions of Orgueil and Murchison show the largest ^{54}Cr anomalies yet re-

ported in bulk solid residue (150 - 170ϵ). This indicates that the carrier of ^{54}Cr anomalies is most likely much smaller than 200 nm. NanoSIMS Cr isotopic analyses of single grains did not reveal significant anomalies, except for one region not associated with any identifiable grain. Work is currently under progress to characterize the mineralogy of ^{54}Cr -rich residues.

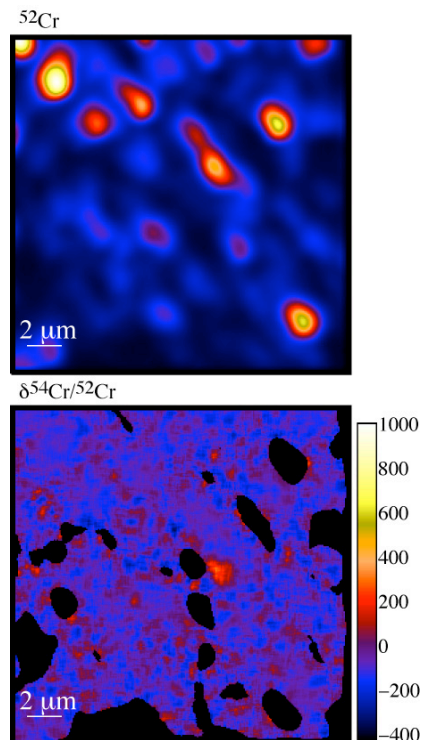


Fig. 2. $20 \times 20 \mu m^2$ (256×256 px 2) NanoSIMS images of $< 0.2 \mu m$ grains from Orgueil. Top panel: $^{52}Cr^+$ ion image. Bottom panel: calculated $\delta^{54}Cr$ image ($\delta^{54}Cr = \epsilon^{54}Cr/10$). Regions where the $^{54}Fe^+$ correction on $^{54}Cr^+$ exceeded $1,000 \%$ or which contained less than 5% of the maximum ^{52}Cr intensity were excluded from the map.

References: [1] Rotaru M. et al. (1992) *Nature*, 358, 465-470. [2] Podosek F. et al. (1997) *Meteoritics & Planet. Sci.*, 32, 617-627. [3] Nichols Jr R.H. et al. (1998) *LPSC XXXI*, #1748. [4] Alexander C.M.O'D. (2002) *LPSC XXXIII*, #1872. [5] Shukolyukov A. & Lugmair G.W. (2006) *EPSL*, 250, 200-213. [6] Trinquier A. (2007) *ApJ*, 655, 1179-1185. [7] Qin L. et al. (2009) *GCA*, in press. [8] Birck J.-L. et al. (2009) *LPSC 40*, #1683. [9] Ott U. et al. (1997) *LPSC XXVIII*, #1278. [10] Fujiya W. et al. (2009) *LPSC 40*, #1486. [11] Qin L. et al. (2009) *Meteoritics & Planet. Sci.*, 44, A71.