

UNDILUTED ISOTOPIC MEASUREMENTS OF METEORITIC NANO-OXIDES THROUGH ATOM PROBE TOMOGRAPHY

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Introduction: Due to their small sizes, analytical challenges have impeded fine-grained, extraterrestrial materials and their nanoscale components from being fully characterized. Presolar oxides can range in size from a few micrometers down to <30 nm and have been found to be the carriers of ⁵⁴Cr isotopic anomalies, with the smallest grains carrying the largest anomalies [1–3]. Unfortunately, even with the spatial resolution afforded by NanoSIMS, measurements of the isotopic compositions of grains <100 nm across can suffer from significant dilution effects from nearby material and are, therefore, only lower limits and the amount of dilution must be modelled to obtain better estimates [3]. Although frequently used in materials science, atom probe tomography (APT) has only recently begun to be applied in planetary science and cosmochemistry (e.g., [4, 5]). While NanoSIMS has a much higher mass resolving power, APT generates quantitative atom-by-atom elemental and isotopic distributions in 3D with a high sensitivity (~80% detection efficiency) at near-atomic spatial resolution. APT also detects all mass/charge-state ratios <600 Da, allowing for the possibility of additional correlated anomalies to be discovered within a grain, which may have been previously missed. APT is therefore a powerful technique for studying fine-grained materials, such as presolar oxides by providing undiluted local elemental and isotopic compositions of each grain with nm-scale spatial resolution, so that subgrains, inclusions, and other compositional heterogeneities (e.g., gradients) can be detected.

Samples and Methods: APT analyses require laborious sample preparation, particularly for site-specific sub-μm grains. For this study, we have developed protocols adapted from traditional APT sample preparation methods [6] for lifting out and preparing nano-tips that target sub-μm grains for APT analyses. Samples were prepared with the TESCAN LYRA3 FIB-SEM at the University of Chicago. The nano-tips were analyzed with the LEAP5000XS tomograph at Northwestern University. Prior to analyzing *bona fide* presolar oxides, we have analyzed a ~1.5 μm meteoritic chromite from the CI chondrite Orgueil. This grain was also analyzed by energy dispersive spectroscopy (EDS) prior to APT. Presolar oxides were previously identified in this residue by NanoSIMS [2]. We also analyzed three nano-tips prepared from a natural chromite reference material, UWCr-3, from a South African chromitite [7].

Results and Discussion: APT confirms that the UWCr-3 chromite standard is homogenous in all elements at the nm-scale as confirmed by a nearest-neighbor statistical analysis. Cr²⁺, CrO^{+,2+}, CrO₂^{+,2+}, and CrO₃⁺ molecular ions were detected, but no peaks associated with Cr₃O⁺ or Cr₂O₅⁺ were observed as seen in synthetic chromite [8]. In NanoSIMS, Cr isotopic ratios must be corrected for isobaric overlaps from Fe, where ⁵⁴Fe⁺ overlaps with ⁵⁴Cr⁺ can be corrected by assuming a fixed ⁵⁴Fe/⁵⁶Fe ratio. This can be mitigated in APT, where the formation of molecular ion species is element-dependent. While ion species with different isotopes of the same element will have the same field evaporation behavior (e.g., ⁵³CrO vs ⁵⁴CrO), ion species of the same mass but from different elements may not (e.g., ⁵⁴CrO vs ⁵⁴FeO). Notably, we found that the peaks due to CrO₂⁺ ions in the 82–86 Da mass region of UWCr-3 correspond to the terrestrial abundances in all isotopes, allowing for measurements of ⁵⁴Cr/⁵²Cr ratios. Peaks due to CrO₂⁺ ions in the 33–35 Da mass region also correspond to natural abundances in all peaks when areas with Ga ion implantation are removed from the mass spectrum. Some mass regions have isobaric overlaps in only one or two Cr peaks, so the remaining peak ratios can be used for verification.

The meteoritic chromite from Orgueil is also homogenous in all elements at the nm-scale and has a nearly identical mass spectrum to the UWCr-3 chromite, sharing all peaks with only minor differences in relative peak intensities and peak shapes, likely due to their small differences in elemental abundances (UWCr-3 is more Cr- and Mg-rich and more Fe-, Al-, and Ti-poor) and different operating conditions, respectively. As with UWCr-3, the peaks due to CrO₂⁺ and CrO⁺ ions correspond to natural abundances in all peaks. We were also able to confirm the Orgueil chromite is isotopically normal in Mg, Ti, and Fe. This is not unexpected for a meteoritic chromite of this size. Preparations of meteoritic chromites <200 nm in size are currently underway.

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