IRON–L_3 SPECTROSCOPIC ANALYSIS OF STARDUST INTERSTELLAR DUST CANDIDATE I1043,1,30 (ORION). Anna L. Butterworth[1], Tolek Tyliszczak[2], Andrew J. Westphal[1] and Zack Gainsforth[1], [1]Space Sciences Laboratory, University of California, Berkeley, CA USA, [2]Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA USA.

Introduction: An international consortium recently completed the Stardust Interstellar Preliminary Examination (ISPE) [1], providing characterizations of impacts detected in approximately one half of the Stardust Interstellar Dust Collector aerogel and ~3% of the foils [2]. Detailed synchrotron X-ray analyses were performed on two 3–4 pg particles captured in aerogel [3-6] which were likely to have an interstellar origin [7]. The candidate particles were I1043,1,30 "Orion" and I1047,1,34 "Hylabrook". A third interstellar candidate detected in aerogel contained no discernible residue.

Determination of the phase and oxidation state of Fe in an interstellar particle provides important comparisons with astronomical observations. For example, is Fe present in silicates or in reduced phases? What are the grain sizes and crystallinity of Fe-bearing phases?

During ISPE, the consortium discovered a number of unexpected challenges, including some unexplained modification of Orion and Hylabrook, the effects of which were described in [8, 3]. In light of these challenges, we have re-evaluated the Fe-L_3 edge data collected on Orion during ISPE.

Experimental: X-ray absorption data were collected at the Fe L_3-edge during ISPE at the Scanning Transmission X-ray Microscopy (STXM) endstation of Beamline 11.0.2 at the Advanced Light Source, Lawrence Berkeley National Laboratory, acquisition details are given in [3]. Multispectral image stacks of Orion were collected at the Fe L-edge, Mg and Al K-edges using 0.2 eV for the finest energy steps, and with spatial resolutions in the range 15 nm to 133 nm. The data were analyzed using the aXis2000 suite (http://unicorn.mcmaster.ca/aXis2000.html).

All of the ISPE STXM analyses were carried out on particles in small volumes of aerogel called "picokeystones", that were extracted from the original aerogel tiles so that the terminal particles were contained in 60-100 µm thick sections of aerogel [2]. Prepared in this way, aerogel around Orion was 100 µm thick and 27±2 mg/cm^3 in density, which was of sufficiently low column density to allow STXM measurements to be made at the Fe L-edge (~700 eV).

During an unexpected, modifying event before the STXM analyses, most Fe from Orion (800±100 fg Fe previously measured by XRF [4]) had been redeposited in a newly formed crack, along the track walls, on a second particle "Sirius" and into the surrounding aerogel up to a radius ~3 µm from the terminal particle, Fig. 1 [3].

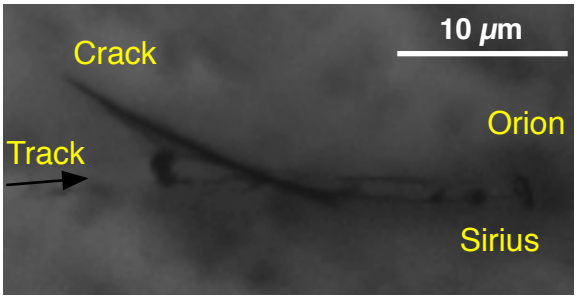

Figure 1. 708 eV X-ray absorption image of modified I1043,1,30 (Track 30) containing Orion, a newly formed second particle "Sirius" and a dark crack.

Results:. Fig. 2 is an (LRGB) image of Orion using a 704 eV optical density image for the luminosity channel and Al-Fe-Mg for the R, G, and B channels respectively.

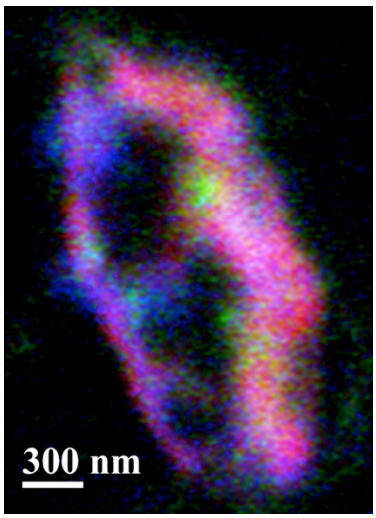

Figure 2. LRGB image of Orion as imaged by STXM: red is Al, green is Fe, blue is Mg and the luminosity channel is a 704 eV optical density map.

The dispersed Fe had contaminated the background aerogel surrounding Orion, which was necessary to normalize the X-ray absorption measurements of the particle, though we did not know this at the time of acquisition. We manually scrubbed the Fe contamination by assuming the background spectrum was linear

over the small energy range (20 eV). We then extracted Fe-L_3 XANES (X-ray Absorption Near-Edge Structure) spectra from each pixel of the original Fe stacks on Orion and Sirius, Fig. 3, for principle component analysis.

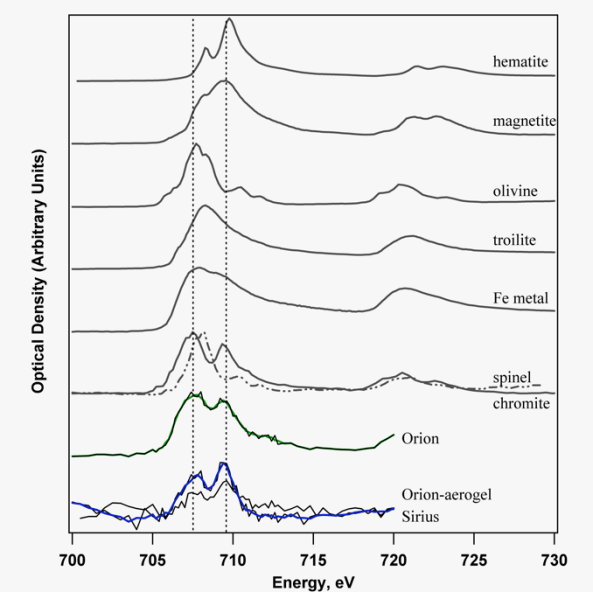

Figure 3. Fe L-edge spectra of Orion (smoothed spectrum in green) and Fe in the surrounding aerogel of Orion (smooth spectrum in blue) and Sirius, with standards also measured at the Advanced Light Source Beamline 11.0.2 (STXM).

Discussion: The spectrum of the remaining few femtograms of Fe in Orion (2 fg Fe hotspots in Fig. 2) resembles that of Stillwater chromite (~$FeCr_2O_4$), which is consistent with the remaining spinel-like mass of Orion (200 fg Mg in partially crystalline $MgAl_2O_4$) [3,5]. Fe can occur as Fe^{2+} or Fe^{3+} in the spinel group of minerals, which may explain the difference between our measured chromite and spinel standards spectra. Fe with this signature spectrum was mapped in several ~50 nm hotspots, and accounts for <5% total Orion Fe.

In the surrounding aerogel, the Fe spectrum was different, possibly showing greater Fe^{3+} characteristics than the chromite. The signal-to-noise ratio was low because this iron was diffuse; we detected no Fe-particle sizes greater than the 50 nm STXM Fe map pixel resolution. A second particle, Sirius, characterized as amorphous Mg-silicate (300 fg Mg), was postulated to be the result of the track modification, originating as forsteritic olivine in the captured Orion particle [3]. The Fe L-edge XANES spectrum for Sirius is similar to the Fe-contaminated Track 30 aerogel and there is no evidence for a silicate residue matching an Fe-bearing olivine standard, or similar amorphous silicate.

We concluded that >95% Orion's Fe now occurs as very fine-grained material, which is most likely altered in oxidation state compared to the pristine captured particle. We note the Fe L-edge spectrum of Fe hotspots in Orion is also consistent with spectra (from EELS) of metallic nano-particles [9] but there are insufficient data to be certain.

The re-evaluation of Fe in I1043,1,30 confirms that >95% Fe in the likely interstellar particle Orion was originally in a different phase from the major elements Al and Mg, and suggests that Fe was not present as silicate. The Fe-phase was likely present as an outer shell surrounding olivine and partially crystalline spinel.

In the case of Hylabrook, the column density of the I1047,1,34 aerogel was too high (SiO_2 density = 35±14 mg/cm^3 and 85 µm thickness) to allow any direct Fe L-edge measurement by STXM, but we know the particle is also Fe rich from XRF (1300 fg Fe [4]) and that it also had suffered a minor modification during XRF/XRD analysis [3], but the Hylabrook Fe phase and oxidation state is unknown. Hylabrook has a similar shell-like morphology to Orion, both have a seemingly fine-grained Fe-phase surrounding olivine cores. Characterization of Hylabrook Fe is therefore one of the highest priorities post-ISPE (next to oxygen isotope measurements), but we must be particularly cautious in order to avoid damage similar to that experienced byOrion. The ISPE reports describe meticulous measurements and care, Orion was not damaged during any analysis, and the explanation for the modification remains a mystery. We suggest that the composition, morphology and collection method of Orion and Hylabrook resulted in samples that are more fragile than other extraterrestrial materials.

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References: [1] Westphal A. J. et al. (2013) *Meteoritics & Planet. Sci.,* in press. [2] Frank, D. et al. (2013) *Meteoritics & Planet. Sci.,* in press. [3] Butterworth A. L. et al. (2013) *Meteoritics & Planet. Sci.,* in press. [4] Brenker, F. et al. (2013) *Meteoritics & Planet. Sci.,* in press. [5] Gainsforth et al. (2013) *Meteoritics & Planet. Sci.,* in press. [6] Simionovici A et al. (2013) *Meteoritics & Planet. Sci.,* in press. [7] Westphal A. J. et al. (2014) *LPS XLV* Abstract #2269. [8] Simionovici A. (2011) *LPS XLII* Abstract #2812. [9] Wang F. et al. (2006) *Micron* 37, 316-323.