New Homogeneous Standards by Atomic Layer Deposition for Synchrotron X-ray Fluorescence and Absorption Spectroscopies. A. L. Butterworth[1] N. Becker[2,3], Z. Gainsforth[1], A. Lanzirotti[4], M. Newville[4], T. Proslier[2], J. Stodolna[1], S. Sutton[4,5], T. Tyliszczak[6], A. J. Westphal[1] and J. Zasadzinski[3], [1]University of California, Berkeley, Space Sciences Laboratory, 7 Gauss Way, Berkeley, CA, 94720-7450 [2]Material Sciences Division, Argonne National Laboratory, [3]Illinois Institute of Technology, Chicago, IL, [4]CARS, University of Chicago, [5]Dept. Geophys. Sci., University of Chicago, [6]Advanced Light Source, Lawrence Berkeley National Laboratory.

Introduction: Quantification of synchrotron XRF analyses is typically done through comparisons with measurements on the NIST SRM 1832/1833 thin film standards. Unfortunately, these standards are inhomogeneous on small scales at the tens of percent level. We are synthesizing new homogeneous multi-layer standards using the Atomic Layer Deposition technique [1] and characterizing them using multiple analytical methods, including ellipsometry, Rutherford Back Scattering at Evans Analytical, Synchrotron X-ray Fluorescence (SXRF) at Advanced Photon Source (APS) Beamline 13-ID, Synchrotron X-ray Absorption Spectroscopy (XAS) at Advanced Light Source (ALS) Beamlines 11.0.2 and 5.3.2.1 and by electron microscopy techniques.

Our motiviation for developing much-needed cross-calibration of synchrotron techniques is borne from coordinated analyses of particles captured in the aerogel of the NASA Stardust Interstellar Dust Collector (SIDC) [2]. The Stardust Interstellar Dust Preliminary Examination (ISPE) team have characterized three sub-nanogram, ~1µm-sized fragments considered as candidates to be the first contemporary interstellar dust ever collected, based on their chemistries and trajectories [2, 3].

The candidates were analaysed in small wedges of aerogel in which they were extracted from the larger collector, using high sensitivity, high spatial resolution >3 keV synchrotron x-ray fluorescence spectroscopy (SXRF) and <2 keV synchrotron x-ray transmission microscopy (STXM) during Stardust ISPE. The ISPE synchrotron techniques have complementary capabilities. Hard X-ray SXRF is sensitive to sub-fg mass of elements Z ≥20 (calcium) and has a spatial resolution as low as 90nm. X-ray Diffraction data were collected simultaneously with SXRF data [3]. Soft X-ray STXM at ALS beamline 11.0.2 can detect fg-mass of most elements, including cosmochemically important oxygen, magnesium, aluminum and silicon, which are invisible to SXRF in this application. ALS beamline 11.0.2 has spatial resolution better than 25 nm. Limiting factors for Stardust STXM analyses were self-imposed limits of photon dose due to radiation damage concerns, and significant attenuation of <1500 eV X-rays by ~80µm thick, ~25 mg/cm^3 density silica aerogel capture medium.

In practice, the ISPE team characterized the major, light elements using STXM (O, Mg, Al, Si) and the heavier minor and trace elements using SXRF. The two data sets overlapped only with minor Fe and Ni (~1% mass abundance), providing few quantitative cross-checks. New improved standards for cross calibration are essential for consortium-based analyses of Stardust interstellar and cometary particles, IDPs. Indeed, they have far reaching application across the whole synchrotron-based analytical community.

Methods: Atomic Layer deposition (ALD) is a sequential, self-limiting synthesis technique that has the crucial advantage over classical deposition techniques of conformally coating arbitrarily large areas and complex substrates. The uniformity of the grown film properties (density, thickness and chemical composition) is controlled down to the atomic scale on surface areas up to 100 m^2. As the ALD technique has matured, a large number of synthetic routes have been developed over the last 20 years (reviewed [1]), allowing combinations of compatible alloys of many different elements to be grown into multi-layer structures. Typically, a number of different substrates are included in the reactor at Argonne, taking advantage of the uniform large area growth. The new homogeneous standards may be optimized for different beamline capabilities, accurately synthesizing layers tens of nanometers thick.

Silicon nitride substrate: In this work, ALD layers have been grown on silicon nitride membranes (30 or 50 nm thick, Norcada, Inc.). These homogeneous, mechanically robust membranes have been used extensively in Stardust synchrotron analyses and are compatible with all ISPE synchrotron techniques, including STXM, XRF and XRD. ALD coatings grown on Norcada holey silicon nitride mebranes provide STXM the necessary regions for signal normalization at every energy.

Optimizing ALD Standards for STXM: In STXM, Optical Density (OD) at one energy is the normalized measure of absorption of incident photons (I_0) transmitted through a sample, resulting in detector signal intensity (I) such that $OD = -ln(I/I_0)$. The intensity of absorption depends on the absorption cross section at that energy (μ, cm^2/g), density (ρ, g/cm^3) and thickness (*t,* cm) of the sample:

$$OD = \mu\rho t$$

Ideal STXM samples result in measured OD values between 0.1 and 2.0; they are neither too thick or optically dense, nor too thin or of very low element abundance. The column density, g/cm^2, of an element present is determined by measuring the difference in OD – the edge jump – across a sharp absorption edge within the STXM energy range 180 eV to 1900 eV (Beamline ALS 11.0.2) or 700 eV to 2500 eV (Beamline ALS 5.3.2.1). We use absorption cross section values tabulated at CXRO *http://henke.lbl.gov/optical_constants/*, which are generally accepted to have 10% accuracy or better.

The theoretical edge jump, ΔOD for a column density of 10 pg/μm^2 for all elements suitable for ALD, and with absorption edges between 150 eV and 2.5 keV are plotted in Fig 1. Detection sensitivity can be up to 10 times higher than plotted due to resonance enhancements at the absorption edge, depending on the element and chemical bonding.

Elements heavier than Ca are all compatible with SXRF, subject to spectral overlap.

Results: We have synthesized three ALD multilayers simultaneously on silicon nitride membranes and silicon and characterized them using RBS (on Si), XRF (on Si3N4) and STXM/XAS (holey Si3N4). The systems we have started to work with are Al-Zn-Fe and Y-Mg-Er.

We have found these ALD multi-layers to be uniform at μm- to nm scales (Fig 2.), and have found excellent consistency between four analytical techniques so far. The ALD films can also be used as a standard for e-beam instruments, eg., TEM EELS or EDX.

After some early issues with the consistency of coatings to the back-side of the membrane windows, we are confident to be able to show multi-analytical agreement to within 10%. As the precision improves, we can use the new standards to verify or improve the tabulated cross-sections.

References: [1] R. L. Puurunen, *J. Appl. Phys.* 97, 121301 (2005). [2] Westphal A. J. et al (2011) *LPS, XLII,* Abstract #2083. [3] Westphal A.J. et al. (2012) *LPS, XLIII.* [4] Gainsforth Z. et al.(2012) *LPS, XLIII.*

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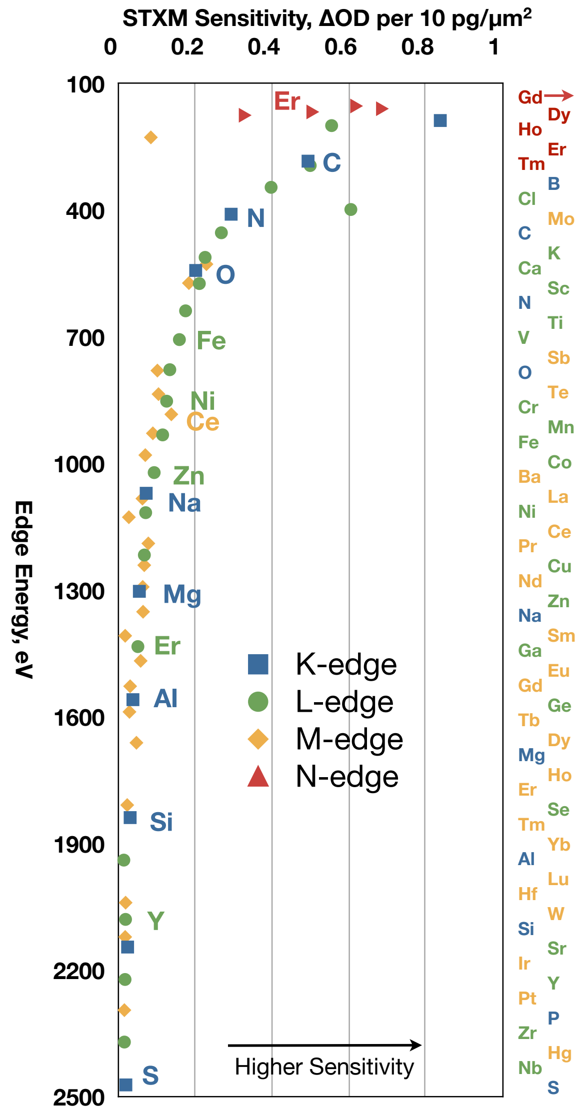

Figure 1: Theoretical edge jump for 10 pg/μm^2 column density of all elements suitable for ALD with an absorption edge within range of ALS STXM beamlines 11.0.2 or 5.3.2.1. Important Stardust ISPE elements are labeled, plus Er which has 2 edges in the energy range.

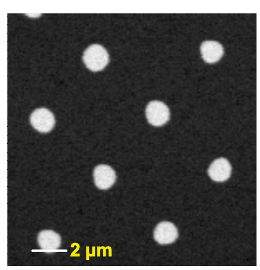

Figure 2: STXM Absorption image (740 eV) of 29nm-Fe_2O_3 and 95nm-Al_2O_3 ALD layers on holey Si_3N_4 membrane, showing nm-scale homogeneity of Fe distribution.