

IMPROVED TECHNIQUES FOR AUGER QUANTITATIVE ANALYSIS AND SPECTRAL IMAGING APPLIED TO STARDUST TRACKS AND METEORITE THIN SECTIONS.

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Introduction: In this abstract we describe numerous improvements to the sample preparation and data collection and processing techniques for Auger Electron Spectroscopy [1] as well as to the algorithms for quantitative analysis. We are developing a gold grid coating technique for meteorite thin sections that ensures good conductivity while also preserving open areas for Auger surface measurements. We also describe elemental mapping and processing techniques that allow collection of a true Auger spectral image, which preserves the underlying spectra for each pixel in the map. Finally we present results from direct integration of Auger spectral peaks which have some advantages over the conventional derivative methods for quantitative analysis.

Methods: Auger spectra were collected using a PHI 700 Auger Nanoprobe and quantitative analyses were performed using both derivative and direct integration methods. The Auger spectral imaging technique uses PHI multiplex mode which allows scans over narrow energy windows around major peaks of interest (S, C, Ca, O, Fe, Mg, Si). A user-defined array of spatial areas (such as the 10x10 array in Fig. 2) is loaded using PHI Autotool and the defined multiplex scans are run serially on each pixel in the array. The python scripts used for data acquisition and analysis are available at github.com/tkcroat/Augerquant.

Results and Discussion: Due to the surface sensitivity of Auger electron spectroscopy, gold or carbon coatings cannot be used. The absence of conductive coatings for insulators or semiconductors can impair Auger measurements, including significant shifts in the peak position which are sometimes time-dependent. These properties make it difficult to correlate useful Auger data with prior SIMS, SEM or other measurements of coated samples. We are developing a gold grid coating technique for meteorite thin sections that will better enable correlated Auger and conventional SIMS measurements. A meteorite thin section is first sputtered coated with gold to a depth of ~30-50 nm using an Argon plasma in an Anatech Hummer coating system. Then a fine mesh gold grid (18 μ m hole and 7.4 μ m gridbar from SPI) is overlaid on the surface and the sample is etched (by reversing the polarity) to remove the gold coating in the open areas but preserve the gold coating beneath the gridbars. Once the gold grid is lifted, the resulting thin sections contain uncoated areas amenable to Auger analysis along with sufficient net conductivity to enable other correlated meas-

urements. The sputter coating and etching conditions are still being optimized, but the Auger spectra from open areas (Fig 1) show strong and quantifiable Mg, Fe and Si Auger peaks.

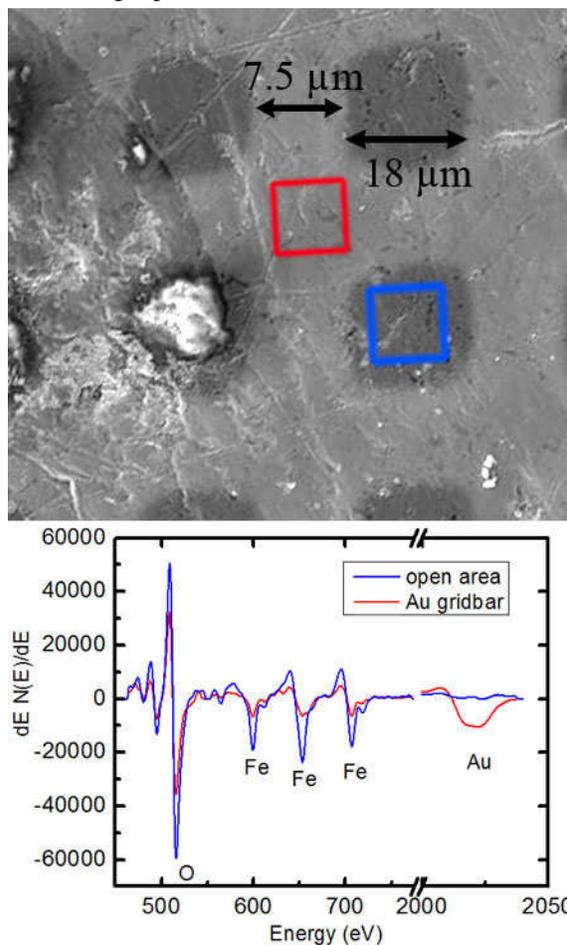


Fig. 1. Meteorite thin section [Plainview (c)] with overlaid, sputtered-deposited gold coating in a grid pattern. Auger spectra collected from the two indicated areas (red on Au gridbar and blue in open area) showed strong cometary peaks (Fe and O) from the open areas and strong Au from the gridbars.

A significant limitation of PHI Auger elemental maps is the absence of quantifiable spectra data (a PHI .map file returns only a single scaled image). We have developed an Auger spectral imaging technique that preserves the underlying spectral data for each map pixel, which allows quantitative compositional determinations for major elements. Furthermore, regions of interest around cometary grains can be defined after ac-

quisition, and the Auger data from the adjacent pixels in the selected ROI can then be combined, resulting in a more accurate compositional determination with longer total acquisition time. Fig. 2 demonstrates the Auger spectral imaging technique applied to the task of locating cometary grains in an indium-embedded Stardust aerogel track [2].

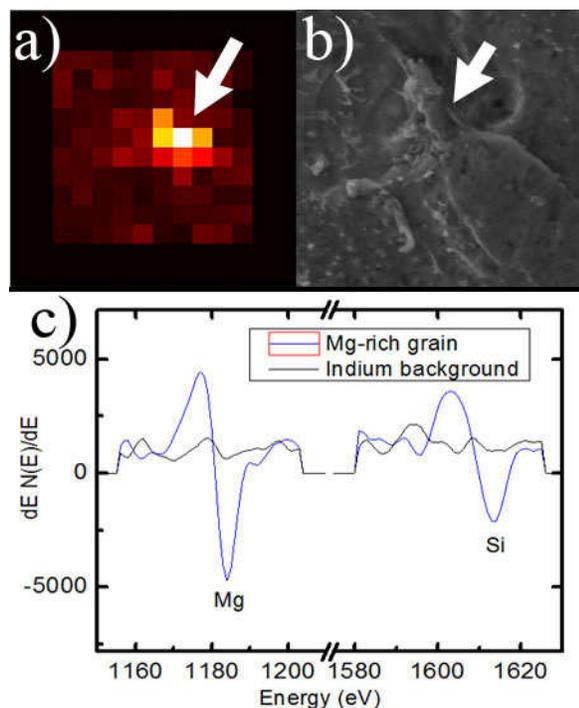


Fig. 2. a) Auger Mg elemental spectral image and b) SE image of a region within Stardust track 184 after indium embedding, in which a Mg-rich cometary grain was detected (arrows). c) Differentiated Auger spectrum from the most Mg-rich pixel (white pixel indicated by arrow in 2a), along with a spectrum from a typical nearby background pixel in the indium-rich region.

We have also developed reliable algorithms for Auger quantitative analysis based on direct peak integration, as opposed to the derivative methods (Savitsky-Golay smoothing and differentiation) that are normally employed [1]. As the peak amplitude in the differentiated Auger spectrum approaches the noise level of the backscattered electron background, there is no reliable criterion for peak detection which is problematic for minor elements and for weaker spectra. With a direct integral approach, however, there are straightforward statistical criteria for determining peak significance (i.e. peak intensity $>2\sigma$ of background counts). The direct method does require adaptive background fitting that is sufficiently robust to handle shifts in the Auger peak energy, and considerable difficulties in fitting the backscattered electron background (variable noise levels, slope changes and peaks, etc.). Linear fits to back-

ground regions above and below each peak (adjusted for any peak shift) with spline interpolation work well (see Fe and Mg plots in Fig 3a). After background fitting and subtraction, Auger peak counts are determined by integration over the Auger peak (~ 10 eV width). Fig. 3b compares the elemental peak strengths of the derivative method (peak-to-peak amplitude using methods of [1]) with the direct peak integration (electron counts/sec under Auger peak) on a set of ~ 300 spectra from Stardust C2010W craters [3]. The good agreement between the two methods demonstrates that background subtraction and direct peak integration are a practical method for quickly determining the elemental compositions of geological samples. This method has the further advantage of straightforward statistical thresholds for peak detection and error analysis (e.g. 2σ error bars on Y axis in Fig. 3b), whereas error determination methods from differentiated data are less clear. In practice, both quantification methods are run together in batch processing mode and comparison of these separately derived compositions can be illustrative. Taken together, these improvements in sample preparation, data collection, and quantification of Auger Electron spectra will help enable elemental characterization of primitive solar system materials at higher spatial resolutions than is possible with x-ray spectrometry.

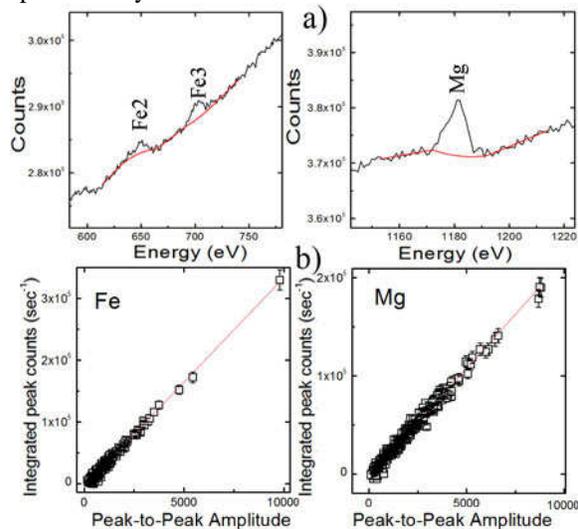


Fig. 3. Direct Auger spectra and background fits for Fe and Mg peaks of a Stardust foil crater and b) comparison of Fe and Mg Auger peak strengths as determined using two different methods from the same spectra: 1) Savitsky-Golay smoothed and differentiated peak-to-peak amplitude and 2) direct integration of Auger peak counts after secondary electron background subtraction.

References: [1] Stadermann et al. (2009) *Met. Planet Sci.* 44, 1033-49. [2] Ogliore et. al (2015) *GCA* 166, 74-91. [3] Croat et al. (2016) *LPSC* 47, #2204.