

NANO-ESCA: A VALUABLE TOOL FOR STUDYING PRESOLAR GRAINS (AND OTHER EXTRA-TERRESTRIAL MATERIALS). U. Ott¹, Ch. Sudek¹, J. Maul², P. Bernhard², H.J. Elmers² and G. Schönhense², ¹Max-Planck-Institut für Chemie, Becherweg 27, D-55128 Mainz, Germany (ott@mpch-mainz.mpg.de); ²Institut für Physik, Staudingerweg 7, Johannes Gutenberg-Universität, D-55099 Mainz, Germany (schoenhense@uni-mainz.de).

Introduction: Besides their major structural elements, presolar grains such as silicon carbide contain a variety of diagnostic trace elements [1,2]. These contain not only important information about the nucleosynthetic sources (the s-process in AGB stars in case of the mainstream SiC grains), but potentially also about their incorporation. Based on that, they also may constrain possible modes of formation of the grains. Because the main concern in the study of presolar grains so far has been the investigation of isotopic structures, secondary ion mass spectrometry (SIMS) has been the primary method of investigation (e.g., [1], [2]). For trace element isotopic analyses, this has been supplemented by dedicated methods such as thermal ionization mass spectrometry (TIMS; e.g. [3]), noble gas mass spectrometry (e.g., [4]) and, for the study of heavy trace elements in individual grains, resonance ionization mass spectrometry (RIMS [e.g., 5, 6]). SIMS has been used also in studying trace element patterns of SiC grains [7], and the Nano-SIMS can map elemental and isotopic abundances with a lateral resolution better than 100 nm (e.g., [8]).

Nano-ESCA: In studying grains that are both small and rare the “standard” (mass spectrometric) methods listed above have the disadvantage of being destructive. It would be useful to have, before applying them for trace element isotopic analysis, information on the trace element pattern in order to help in choosing the most promising element(s). Synchrotron X-ray fluorescence (SXRF) has been explored towards this end with some success [9, 10]. SXRF is both non-destructive and more sensitive than SIMS for elements that are not easily ionized. Here we suggest application of another method, Nano-ESCA, which has additional important advantages: a) it can provide information about the spatial distribution of elements within μm -sized grains; and b) it is able to provide information about the chemical environment of the elements of interest. We also report first preliminary observations.

ESCA (Electron Spectroscopy for Chemical Analysis) is the name for X-ray induced photoelectron spectroscopy as established by Siegbahn in the 1960s (see, e.g. [11]). It comprises both, X-ray photoemission spectroscopy (XPS) and X-ray excited Auger electron spectroscopy (AES). The newly developed Nano-ESCA instrument [12] is derived from an electrostatic Photo Emission Electron Microscope (PEEM) column and a twin hemispherical analyzer (HAS). There are

three modes of operation: 1) direct non energy filtered PEEM-imaging; 2) selected area spectroscopy; and 3) energy filtered ESCA imaging for kinetic energies up to 1.6 keV. Nano-ESCA is characterized by an energy resolution of 0.1 eV and a lateral resolution in the 100 nm range.

Experiments: Analyses were performed on an acid-resistant, SiC-rich, residue from the Murchison meteorite, prepared using procedures similar to those used by [13] in the preparation of the KJ SiC separate, however without additional size separation. Material for this exploratory study was deposited on a Si wafer from an aqueous suspension. Synchrotron radiation from the BESSY II (Berlin-Adlershof) beamline UE52 SGM was used for excitation.

Observations: In the following we are going to describe some results obtained during our first beam time at BESSY II that clearly demonstrate the potential of Nano-ESCA.

Identification of submicron SiC grains. This capability is demonstrated in Fig. 1. Using energy-filtered ESCA imaging (operation mode 3 above) SiC grains are easily recognized even on a Si wafer substrate, because of the workfunction difference between the oxidized Si wafer surface and the SiC grains.

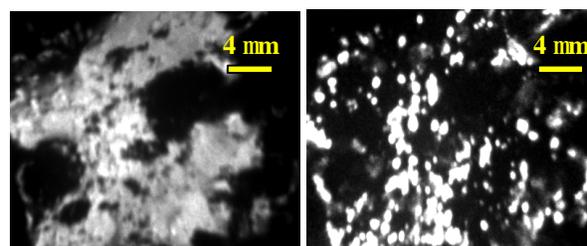


Fig. 1. Energy filtered ESCA imaging at low kinetic energies. Left (5.8 eV): Si wafer (SiO_x substrate). Right (4.4 eV): SiC grains in the same field of view. Photon energy 140 eV.

Aluminum in different chemical environments. Relevant observations are shown in Fig. 2. In the upper part on the left (a) an area is shown imaged via the Al 2p electrons at 75 eV, which corresponds to Al bound to oxygen. The bright circled dot in all likelihood represent a corundum grain. On the right (b) the same area is shown imaged at an electron energy of 77.5 eV. The grain from (a) is not seen in (b), but there are other bright spots, which we believe to correspond to Al in-SiC grains. This is substantiated in Figs. 2c, 2d below,

which are local spectra for the microareas indicated in the images; they were extracted from the (x,y,E) data stack after acquisition of the images. The spectrum in Fig. 2d clearly has a major peak for Al 2p that is shifted relative to Al 2p in Al_2O_3 , in accordance with the images. Al has often been assumed to be contained within the SiC grains in the form of AlN in subgrains or in solid solution in the SiC lattice structure (e.g., [14]); this can be investigated in detail in future work based on data as in Fig. 2.

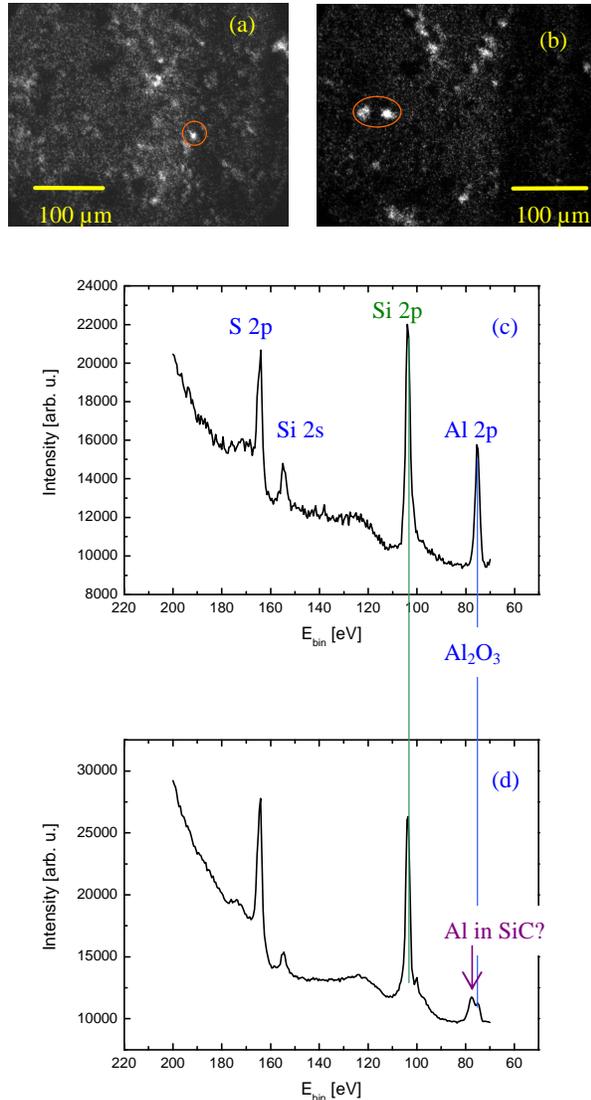


Fig. 2. (a) and (b) Energy-filtered ESCA imaging for Al 2p electrons at binding energies of 75 eV (a) and 77.5 eV (b). (c) and (d) show the energy spectra extracted from the microareas indicated in (a) and (b). Photon energy 250 eV. See text for discussion.

Trace elements. Apart from major (Si, C) and minor (N, Mg, Al, Fe) elements, our imaging has revealed the presence of a variety of heavy trace elements: Sr, Y, Zr, Nb, Mo, Ba and, interestingly the Rare Earth Elements Dy, Er and possibly Tm. Ba and the REE had not been seen in the SXRF work of [9, 10]. Among REE, the only abundance data reported for single grains are for Ce and, in a few cases, Nd [7]. Our preliminary Nano-ESCA results indicate relative abundances to be quite non-uniform, in accordance with the variable Ce/Nd ratio observed in [7].

Summary: While there is still a need for quantification, Nano-ESCA is likely to be a valuable tool for screening presolar grains from meteorites for trace element contents. It is a surface analysis, though, providing information about the outermost ~nm of a grain only. Nano-ESCA is also capable of determining the chemical environments in which various elements occur within these grains. As such it is superior to SXRF. X-ray absorption near edge structure (XANES; e.g., [15]) and electron energy loss spectroscopy (EELS; e.g. [16]) can provide some of the same information, with possibly somewhat better energy and /or spatial resolution; however, compared to Nano-ESCA these techniques require the preparation of thin samples because they operate in transmission. Hence they do not leave the grain of interest intact. Application of Nano-ESCA needs not be restricted to presolar grains, but can be a valuable approach also in studying other fine-grained extraterrestrial materials such as interplanetary dust particles (IDPs) and possibly cometary material caught and returned to Earth by the Stardust mission [17].

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