

ATOM-PROBE TOMOGRAPHIC ANALYSES OF PRESOLAR SILICON CARBIDE GRAINS AND METEORITIC NANODIAMONDS – FIRST RESULTS ON SILICON CARBIDE.

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Introduction: The chemistry of presolar grains is studied with analytical instruments that provide very high spatial resolution, such as the NanoSIMS ion microprobe (~50 nm spatial resolution). Even this resolution is not sufficient to analyze, e.g., the isotopic composition of small subgrains (diam. of a few to tens of nm) within presolar grains or individual meteoritic nanodiamonds (avg. diam. ~3 nm). A knowledge of carbon isotope ratios in individual meteoritic nanodiamonds would help to resolve a fundamental question about the origin of nanodiamonds: What fraction of the nanodiamonds formed in the solar nebula and what fraction is presolar? Such small samples need to be studied with sub-nm spatial resolution. Chemical compositions at sub-nm resolution can be acquired with an atom probe tomograph (APT) which is basically a field-ion microscope coupled to a time-of-flight mass spectrometer [1]. The latest generation of APTs use pulsed-laser-assisted field ionization and evaporation [2,3] and have been successful in analyzing non-metallic samples [4,5]. Synthetic SiC whiskers and synthetic diamond have been already successfully analyzed by APT [6,7]. Reviews of modern atom probes are available [8,9].

Here, we present first APT results of an atom-by-atom study of several presolar SiC grains.

Samples & Experimental: We selected SiC grains from the Murchison CM2 meteorite and nanodiamonds

from the Allende CV3 meteorite, both previously extracted by acid dissolution and density separation at the University of Chicago [10,11]. We also studied synthetic SiC grains (Washington Mills Corp., Carboron). Grains suspended in an isopropanol-water solution were deposited on a Si wafer. Grain distributions were mapped with a scanning electron microscope (SEM).

For APT analyses the sample needs to be located at the apex of a sharpened needle with an apex radius <50 nm. The entire needle needs to withstand the high mechanical forces induced by the strong electric field in an APT. Before preparing tips with focused ion beam (FIB) methods [12], we sputter-coated SiC mounts with either Si or Co to protect the sample from FIB damage and to provide SEM imaging contrast. Nanodiamonds were coated with Al₂O₃ and W using atomic layer deposition (ALD) [13] to form a stable matrix. A protective Co cap was sputter-deposited on top of the ALD layers. After FIB deposition of an additional protective C or Pt layer, a wedge of the Si substrate, including the sample, was cut by FIB and lifted out with a micromanipulator. The wedge was then Pt-welded onto a tip and brought into the required shape with annular FIB milling. APT samples were prepared with FIB workstations at CAMECA France, at Argonne National Laboratory, and at Northwestern University.

APT analyses of SiC were performed with the CAMECA Laser Assisted Wide Angle Tomographic

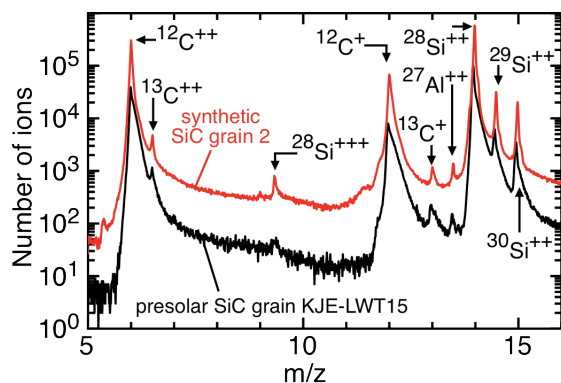


Fig. 1. Mass spectra of synthetic and presolar SiC grains. The mass-to-charge ratio (m/z) range was selected to show prominent peaks of C, Si, and Al ions.

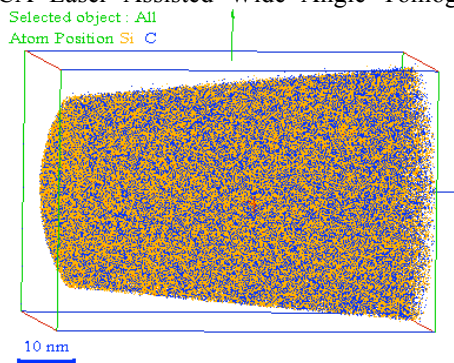


Fig. 2. Tomographic reconstruction of a selected volume ($50 \times 50 \times 72 \text{ nm}^3$) in SiC grain KJE-LWT15. Only Si and C atoms are shown. A total number of 6 million atoms were detected from this grain.

Atom Probe (LA-WATAP) at CAMECA France. Samples with meteoritic nanodiamonds were run with the Imago Local Electrode Atom Probe (LEAP) tomograph at Northwestern University. Both atom probes are equipped with pulsed ultraviolet lasers and use channel plate and delay-line detection systems. The mass-to-charge ratio and three-dimensional spatial coordinates are determined for each detected ion.

Results & Discussion: Two synthetic SiC grains and three presolar SiC grains from the KJE fraction from Murchison were successfully analyzed with the LA-WATAP instrument. One to ten million ions per sample were detected. In the obtained mass spectra, ion peaks from the isotopes of major elements Si and C, compounds thereof, and an Al peak can be identified (Fig. 1). Very preliminary raw data (Tab. 1) show that peak ratios corrected for background but not for instrumental bias for the two synthetic grains are different from normal but consistent within uncertainties. All isotope data are preliminary and need to be corrected for apparent instrumental bias in the future. We observe that preliminary $\delta^{29}\text{Si}$ data of two presolar grains (KJE-LWT15 and 20) are different from the synthetic SiC (Tab. 1).

Tomographic models of samples with signals of interest were reconstructed (Fig. 2). Data from selected regions of the analyzed volume were evaluated independently. This is useful to obtain depth profiles over volumes of interest or search for heterogeneities with isosurface concentration threshold functions. Such a function has been applied to a presolar Murchison SiC grain, where a region with an enhanced silicon dicarbide (SiC_2) signal was found (Fig. 3). SiC_2 occurs in the gaseous phase after heating synthetic SiC [14]. SiC_2 is also observed astronomically in spectra of carbon stars [15], the stellar sources of most presolar SiC grains. It is not clear what condensation conditions lead to the formation of SiC_2 .

APT analyses of nanodiamonds have failed so far during analysis due to weak interfaces between diamonds and the substrate, and presumably also due to porosity between the diamond grains, which reduces the

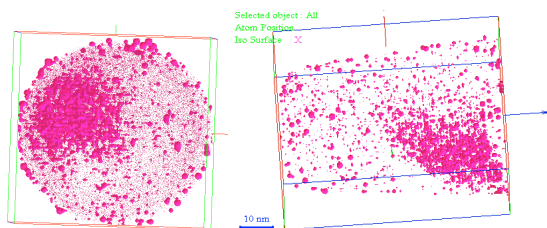


Fig. 3. Bottom and side view of a volume of enhanced SiC_2 concentration that was found in presolar Murchison SiC grain KJE-LWT15 by performing an isosurface concentration threshold function analysis on the SiC_2 signal.

Sample	$^{12}\text{C}^{++}/^{13}\text{C}^{++}$	$^{12}\text{C}^{+}/^{13}\text{C}^{+}$	$\delta^{29}\text{Si}^{++}$	$\delta^{30}\text{Si}^{++}$
Syn. Gr. 1	160±16	127±20	-149±16	-174±16
Syn. Gr. 2	142±6	157±12	-144±6	-132±8
LWT15	124±10	67±6	-245±14	-170±14
LWT20	154±10	106±12	-296±10	-184±12
LWT23	109±18	77±16	-120±32	-106±36

Table 1. Preliminary raw background-corrected peak ratios not corrected for instrumental bias. Errors based on counting statistics (2σ). Raw δSi -values in ‰ normalized to solar system Si isotope ratios.

stability of the tip and leads to tip fracture in the strong electric field [16].

Conclusions & Outlook: Our preliminary results show that the new generation of a laser-assisted APTs can be successfully used to analyze presolar SiC at a scale previously not accessible. The current development allows us to find and characterize chemical heterogeneities within individual grains at the sub-nm scale. APT software is currently optimized for studying elemental concentrations in materials. In addition to elemental data, isotopic compositions are essential in presolar grain cosmochemistry. We are currently improving the robustness of our data reduction and correction methods for the small mass peaks of minor isotopes. This will hopefully provide us with accurate isotope ratios, which are crucial for cosmochemical interpretations.

Besides analyzing more SiC grains, we continue to improve our sample preparation techniques in order to improve tip stability for meteoritic nanodiamonds, and also to extend our effort to presolar graphites, oxides, and silicates.

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