

The History of Presolar Grains, NAG5-10426
Bernatowicz, PI
Final Report
Publications Summary

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Project Description

Below we summarize the results of our investigations into the history of presolar grains that were conducted in the last year. During this time we have expended much of our effort in the development of experimental techniques and sample preparation methods that are needed to take full advantage of opportunities presented by the new NanoSIMS, which arrived in our laboratory in December, 2000. Specific information on this instrument is contained in the Full Proposal of PI Ernst Zinner and will not be repeated here. Our general strategy in the past year has been in large measure to explore novel sample handling methods for the very small (sub-micron), but more representative, presolar grains that can now be characterized isotopically in the NanoSIMS. We have developed experimental techniques that will permit NanoSIMS analyses of the very *same* ultramicrotome sections studied in the TEM, and we have developed grain dispersion, handling and mounting techniques that permit NanoSIMS isotopic analysis as well as field emission SEM, high energy TEM, and atomic force microscopy of pristine presolar grains. Although much of this has been slow and very difficult work that has no immediate payoff in terms of publishable results, we considered it absolutely necessary groundwork for future discoveries, especially in the realm of individual presolar grains that have been inaccessible to past studies due to size constraints. As discussed below, we have been largely successful in these endeavors, and expect to reap the benefits of this work in the next year. We also report on our continued morphologic studies of pristine presolar grains, on our investigations of presolar graphite grains from supernovae as well as on rarer types of presolar SiC, on the search for presolar silicates, and on our efforts to obtain direct size-distribution information on presolar SiC through X-ray mapping techniques.

Development of Sample Preparation and Analysis Procedures

Our past work (e.g., Bernatowicz *et al.*, 1996; 1998; 1999) has shown the advantages of obtaining complementary isotopic and petrologic/mineralogic data on the same presolar grains. This work has revealed the presence of internal carbides of Ti, Zr, Mo, and rarer Fe and Ru carbides, as well as kamacite, in presolar graphite. Sometimes these minerals, as well as aggregates of graphene nanocrystals, have served as nuclei for the condensation of graphite, and give direct information on condensation environments that evolve with time. It is of interest to know if the isotopic composition of the gas phase in which the grains grew also changed due to relative movement of grains and gas, especially in the case of supernova outflows, where extensive mixing has been inferred due to the inferred presence of ^{44}Ti and ^{41}Ca (synthesized deep in massive stars; cf. Amari and Zinner, 1997). Due to the small primary ion beam diameter (~50 nm) and high sensitivity of the NanoSIMS it is possible in principle to compare the isotopic composition of major and minor elements among internal grains in presolar graphite and along traverses of the graphite interiors. To gain the maximum insight, *it is crucial to get isotopic information on the very same internal grains and regions of the host presolar graphite that have been studied in ultramicrotome sections in the TEM.* The 70 nm ultrathin sections used in TEM analysis rest on a supporting holey carbon film that in turn rests on a 75 mesh 3 mm Cu grid. It may be possible to perform NanoSIMS measurements of these sections without their removal from the grids. However, a possible problem is that breaching of the delicate supporting holey carbon film, due to ablation by the primary ion beam, might result in the tearing and destruction of a section. We have explored a complementary approach: the grid (with carbon film and sections facing up) is placed on top of a small drop of ultrapure water on gold, which is allowed to evaporate very slowly under refrigeration. The water, via surface tension, seizes the exposed underside of the holey carbon film, and in the last stages of evaporation tears the film from (and pulls it through) the Cu grid and secures it to the gold. After many trials under varying conditions, we established that this method can indeed transfer a large fraction of the film to the gold, however it is crucially dependent on the flatness of the grid, and not always completely successful.

We continue to study "pristine grains" of presolar SiC (see below), many of which are very small ($\leq 1\mu\text{m}$). This (as well as preparation for NanoSIMS analysis) has necessitated the

development of entirely new procedures for grain picking, embedding in resin for ultramicrotome work, and mounting for atomic force microscopy. In order to pick a given grain for various analyses, it must be located by optical microscopy aided by SEM mosaics, and then manipulated at high magnification, which requires working near the limits of resolution of light microscopes without mechanical interference from the objective lens. We have accomplished this difficult task using a Nikon ME600 microscope capable of 1000x magnification at 1.4 cm working distance. Through considerable experimentation we have found that imaging in polarized, reflected light allows SiC grains to be differentiated from surrounding (e.g., silicate) grains even if these are in intimate contact with the SiC.

We have proven the feasibility of using micromanipulation in concert with this optical system to transfer individual pristine SiC grains onto carbon-film-coated grids for TEM study of their surfaces. Recently, in collaboration with T. Daulton (Stennis Naval Research Laboratory), we have successfully used high resolution TEM to image edges of a 1.0 μm pristine SiC that reveal a 1-2 nm amorphous surface layer, possibly indicating oxidation of the SiC (see below). We will continue to collaborate with Daulton on this approach to studying the surfaces of pristine SiC, and have already sent him several samples. Another approach that we are using is the compositional and crystallographic study of pristine SiC grains in cross section, which requires ultramicrotoming them. We have already shown that this is possible on SiC grains several μm in diameter (Bernatowicz *et al.*, 1992), but the extension of our standard embedding techniques for grains several μm in diameter (Bernatowicz *et al.*, 1991; 1996) to $\leq 1\mu\text{m}$ pristine grains posed difficulties that took considerable effort to surmount, exclusive of the manipulation problems mentioned earlier. Briefly, the tiny grains are essentially impossible to see once immersed in the imbedding (LR White) resin, moreover there is considerable movement from small currents, resulting in loss of grains. From the literature, we hit upon Epon-1004, which has a low melting point (104°C) and can form thin, micron-sized patches that, several degrees below the melting point, are tacky enough to secure grains without coating their surfaces (intimate contact of grain surfaces with the LR White resin is essential for successful sectioning). Using this technique, we have prepared several mounts for sectioning. We also found that we could use this Epon to affix small SiC grains to a substrate to make them suitable for atomic force microscopy, which we are carrying out in collaboration with K. Nakamura (Kobe Univ.). With this sample preparation she was able to image the surface of a pristine SiC grain to demonstrate the feasibility of this work, so we have transferred to her additional pristine grains.

Study of Pristine Presolar SiC Grains

Pristine SiC are presolar grains that have been extracted from primitive meteorites with minimal processing so that their natural surfaces can be studied to elucidate grain history, from formation to parent body processing. Scrapings of matrix material are ultrasonicated in ethanol/water and then this material is sparsely deposited on graphite plachets and X-ray mapped in the SEM to identify SiC. Bernatowicz *et al.* (2000) studied the surfaces of ~40 such grains at low voltages (1-3 keV) in a field emission SEM. Several classes of grains were discovered. Three-fourths of the grains preserve original crystal faces, indicating lack of severe fragmentation, comminution or chemical weathering in any environment since their formation. These faces are often decorated with regular, sub-micron geometrical depressions. Comparison with acid dissolution presolar SiC indicates that these are preserved primary features. The fact that such sub-micron growth features are preserved in exquisite detail suggests that these grains, at least, were likely protected by icy/organic mantles during their residence in the ISM. An interesting observation is that roughly half of the pristine SiC grains appear to be coated with a (<100 nm) layer of amorphous material. We have since doubled the number of pristine grains found in a sample of Murchison, partly to obtain a more representative sampling, and partly to provide samples for NanoSIMS, TEM (of both microtomed and whole grains), and atomic force microscopy. We are preparing a summary of this work for the upcoming Meteorological Society meeting. Our next step will be to perform isotopic and mineralogical analyses of the coatings, since these may represent silica (from oxidation in the Solar Nebula), and/or carbonaceous material (possible residues of volatile condensation and processing on grain surfaces in the ISM).

TEM studies of Presolar Graphite from Supernovae

We continue to investigate the internal structure and composition of presolar graphite spherules that are identified as supernova condensates on the basis of isotopic composition of O and Si. We have previously reported on two such spherules from Murchison graphite separate KE3 (Bernatowicz *et al.*, 1998; 1999), shown in one case (KE3d7) to contain large internal crystals of TiC (up to 0.5 μm), and in the other (KE3d8) to contain internal crystals of two new presolar phases, kamacite and cohenite, in addition to TiC. This year we have performed a detailed study of 14 ultramicrotome sections of a new 6 μm spherule (KE3e7), which has large excesses in ^{18}O ($^{16}\text{O}/^{18}\text{O} = 100$) and ^{28}Si ($\delta^{30}\text{Si} = -290$ per mil), indicating a supernova origin. Like KE3d7, this graphite has large (~ 100 nm) internal TiC crystals that predated the formation of graphite, and these crystals imply very high minimal number densities ($>10^6$ cm^{-3}) of Ti in the supernova ejecta at the time of grain formation, and consequently very high gas pressures ($>$ several microbars). We ultramicrotomed five other KE3 supernova graphites that are now available for TEM study, and on the completion of this work we intend to follow up by NanoSIMS analyses of the internal crystals and interior graphite (pending successful demounting of the ultramicrotome slices, as outlined above).

Searches for Rare Types of Presolar SiC

To date, no TEM studies of the rarer, non-mainstream SiC grains have been performed. We wish to explore whether petrographic features might reflect different formation conditions in the various stellar sources of the non-mainstream grains. The first step is to identify grains of these types for TEM studies. Using ion mapping (with ^{12}C , ^{13}C , ^{28}Si and ^{30}Si) of a Murchison KJG separate, we have thus far located 12 X-grain and 9 Y- and Z-grain candidates, and one A+B candidate. We will confirm the identity of these grains by spot ion beam analyses, and continue mapping to locate a sufficient number of candidates of all of the SiC subtypes. Representatives from each group then will be microtomed for TEM study.

Searches for Presolar Silicates

At present we have done $^{18}\text{O}/^{16}\text{O}$ ion mapping searches (in the IMS 3f) for presolar silicates in grains from several primitive chondrites, including Acfer 094. Of 10^5 grains mapped thus far, we have identified no presolar silicates. These searches were restricted to grains $\geq 0.5\mu\text{m}$, so it may be that presolar silicates in this size range are exceedingly rare. It is also possible that the O-isotopic signature of small presolar silicates have been masked by signal from adjacent, normal silicate grains due to the relatively "large" (several μm) ion beam footprint of the IMS 3f instrument. In any event, there seems to be little point in continuing along these same lines. We intend to perform new searches among smaller grains (0.1 – 1 μm) from Acfer 094, taking advantage of the much higher sensitivity and smaller beam size of the NanoSIMS. Since automated ion mapping in the NanoSIMS is not presently implemented, initially this search will have to be done manually, but even so, it will be possible to investigate at least a hundred grains per day using all three O-isotopes.

Rapid Assessment of the Concentrations and Size Distributions of SiC in Meteorites

We proposed development of a rapid method of assessing the concentrations and size distributions of SiC grains based on our automated X-ray mapping technique originally developed for locating SiC grains *in situ*. It was estimated that one could obtain $<10\%$ precision by mapping 100:1 residues for only several hours. These residues are produced in the very first stage of a much longer total etching procedure. The size distribution would be determined by mapping at two different magnifications. However, in mapping such a 100:1 residue from Murchison, we discovered that the SiC grains apparently become covered with carbonaceous coatings during the initial etching, leading to reduced and size-dependent detection efficiencies that make it impossible to obtain accurate estimates. We are currently trying several different methods to (rapidly) remove the coatings.

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