NANO-SYNCHROTRON XRF AND XRD: A POWERFUL NON-DESTRUCTIVE TECHNIQUE FOR IN-SITU CHEMICAL AND STRUCTURAL ANALYSES OF PRESOLAR GRAINS. M. Jadhav[1], S. Schmitz[2], T. K. Croat[3], F. E. Brenker[2], M. Schmitt[2], B. Vekemans[4], L. Vincze[4], T. Schoonjans[4], G. Wellenreuther[5], B. De Samber[5], G. Falkenberg[5], M. Burghammer[6], G. R. Huss[1]. [1]University of Hawai'i at Mānoa, Hawai'i Institute of Geophysics and Planetology, Honolulu, USA. manavi@higp.hawaii.edu [2]Goethe University, Dept. of Geosciences, Frankfurt/M., Germany; [3]Laboratory for Space Sciences, Washington University, USA; [4]Gent University, Dept. Anal. Chemistry, Gent, Belgium; [5]DESY, Hamburg, Germany; [6]ESRF, Grenoble Cedex 9, France.

Introduction: Multi-technique, correlated analyses of individual presolar grains are the most effective way to constrain the stellar sources of these grains and gain information about their stellar environments. Graphite grains tend to be larger (1-15 μm) than other presolar grain types, and so far it has been possible to do multi-element NanoSIMS measurements, resonant ionization mass spectrometry (RIMS) for heavy element isotopic data, transmission electron microscopy (TEM), Raman analysis, and noble gas measurements on single graphite grains. Most of these techniques are destructive that lead to the loss of precious stardust material. Taking advantage of new generation synchrotron sources at the European Synchrotron Radiation Facility (ESRF) and the Deutsches Elektronen-Synchrotron (DESY) facility, high resolution, non-destructive synchrotron XRF and XRD can be added to the suite of techniques employed to identify and study the stellar sources of presolar grains. Chemical, structural, and tomographic information obtained by this technique for the grains and their nm-sized refractory subgrains (TiC, SiC, Fe-Ni metals, etc.), will provide a wealth of information on the physical and chemical conditions in the circumstellar environments where these grains condensed. Such *in situ* measurements can reconstruct temporal evolution of the physical, chemical and isotopic properties of the circumstellar environment.

To demonstrate some of the capabilities of this technique, we present here some preliminary results from SXRF/SXRD measurements of presolar graphite grains from Orgueil.

Methods: Two low-density (LD) graphite grains from Orgueil (OR1d: ρ = 1.75 – 1.92 g cm^{-3}) were mounted on sharp borosilicate capillaries using a nano-manipulating set-up at Goethe University. No adhesive was used in this step ensuring that the grains can be remounted for future analytical studies. XRF and XRD measurements were performed at two synchrotron beamlines, Microfocus ID13 (150 × 200 nm; 13 keV) and PETRA III (~ 100 nm; 15 keV) at ESRF and DESY, respectively. In addition, small- and wide-angle x-ray scattering (SAXS and WAXS) measurements were also made at ESRF. We reported detailed experimental methods and some preliminary results earlier in [1].

Results: *Grain #1*: Figure 1 shows the distribution of Fe, Ti, and V in an 11 μm graphite grain. While the Fe signal appears to be concentrated on the surface, the correlated Ti and V signals are heterogeneously distributed throughout the interior. From previous TEM studies, we know Ti and V exist in the form of (Ti,V)C subgrains in presolar graphites (e.g., [2]). A 3-dimensional view of grain #1 (obtained by rotating the grain) establishes that the center has smaller carbides (< 100 nm beam size) while larger subgrains (~ 1 μm) are found towards the outside. The Fe image outlines the shape of the grain, which makes it clear that no (Ti,V) carbides are present in the outermost layers of the grain. A radial trend in Ti/V ratios of TiCs was observed by TEM studies of supernova (SN) graphites by [2]. Such chemical trends versus radial distance are an indication of the temporal evolution of the chemical environment in which the graphite condensed. Trends in grain sizes can provide clues to varying gas number density as the grain moves through varying physical conditions under the influence of a cooling stellar wind.

Figure 1

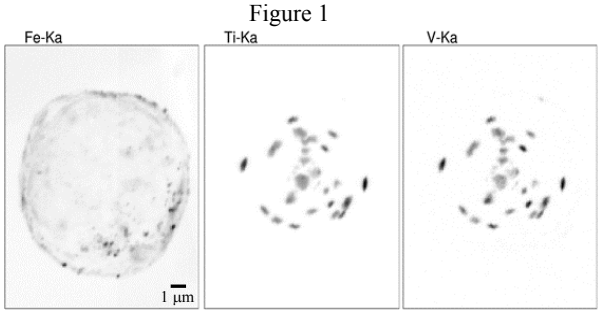
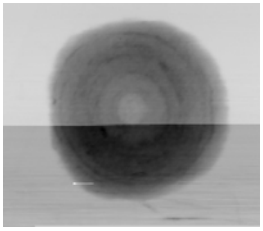


Figure 2



The SAXS signal from the grain (Figure 2) shows the mean value of diffuse scattering in the sample, which is an indicator of the internal density distribution. The grain has a very low-density core coinciding

with the same area in which the smallest carbides are visible in Figure 1. Concentric layers of alternating low- and high-density regions surround the core. The low-density core in this grain is similar to nano-crystalline cores that have been observed in onion-type Murchison graphites [3]. These cores consist of randomly oriented graphene sheets, which suggest that the carbon in such presolar graphites started out condensing rapidly from supersaturated gas and then transitioned to well-graphitized shells as partial pressures dropped in the circumstellar environment. The alternating high-density layers could be tightly packed graphite (indicating fluctuations in physical condensation conditions) or TiC subgrains that condensed on the surface of the graphite layers (chemical changes). Future XRD measurements of the different layers will be able to confirm the growth phase and its structure in the different layers.

Diffraction measurements of the grain indicate that it is dominated by well-graphitized carbon with a d_{002} spacing of 3.35; similar to Murchison onion graphites rather than LD graphites [3, 4].

Grain #2: We measured another ~ 7 μm graphite grain that shows completely different internal features compared to grain #1. Silicon, Ca, and Ti distributions in the whole grain can be seen in Figure 3a. The grain boundary is defined by the Ca signal. Calcium appears to be uniformly distributed in the whole grain (it could also be surface contamination) but there is also a Ca hotspot at the center that coincides with the Si and Ti signals seen at the center of the grain. Figure 3b is a higher-resolution measurement of this central hotspot region. The exact correlation of the Si and Ca signals suggest that a Si- and Ca-rich phase (~ 1 μm) was the nucleation site for the graphite grain. The Ti (and V, not shown) signal arises from smaller regions in the same area as the Si and Ca hotspot. No 3-d information for grain#2 exists but it is likely that these Ti hotspots are TiC subgrains that condensed on a pre-existing Si and Ca-rich phase.

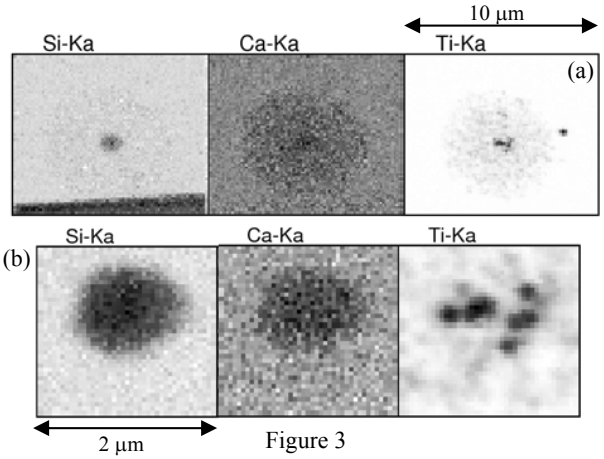


Figure 3

Given the lack of any other information on grain #2 and based on past TEM studies, we assume the grain has a TiC or SiC subgrain in the center. We speculate on 3 possible scenarios: (1) TiCs are the most common subgrains in LD graphites (e.g., [2]) and most Orgueil LD grains show signatures of SN origins [5]. If this central inclusion condensed in type II SN ejecta and received most of its material from the Si/S zone then it could have condensed as a ^{44}TiC grain. The Si/S zone synthesizes the short-lived radioisotope, ^{44}Ti, which is the most abundant Ti isotope in this zone. The ^{44}Ti decayed to ^{44}Ca ($\tau_{1/2}$ = 60 a) in the subgrain and is the source of the strong Ca signal in Figure 3b. The Si/S zone also contains almost pure ^{28}Si which could have been incorporated in the TiC giving rise to the correlated Si and Ca signals in Figure 3b. If this scenario is accurate, isotopic measurements on the subgrain will yield simultaneous ^{28}Si and ^{44}Ca excesses, similar to those found in SiC-X and other SN graphite grains. (2) Some SiC inclusions have also been found in LD Orgueil graphites [e.g., 6]. The subgrain could be a SiC-X grain with ^{28}Si and ^{44}Ti from the Si/S zone. The Ca signal in Figure 3b, in this case, will be from the decay of ^{44}Ti to ^{44}Ca, similar to scenario 1. (3) Another scenario for this graphite is a SiC central subgrain with no contribution from the Si/S zone. Croat et al. [7] recently found rare SiC inclusions within high-density Murchison graphite grains with large ^{29,30}Si excesses. This study claims the grains contain some material from O-rich zones in a SN that are highly enriched in ^{29,30}Si. These zones are also enriched in ^{42,43}Ca. Such a scenario, albeit less likely for a LD graphite, can also explain the Si and Ca signals in Figure 3b. Large ^{29,30}Si excesses from SIMS analysis can verify this case.

Our ideas can easily be tested by coordinated SIMS and TEM measurements of this grain that we intend to carry out in the near future. In case scenarios 1 or 2 are correct, Figure 3 could be an *in situ* view of correlated ^{28}Si and extinct ^{44}Ti from the Si/S zone of a SN.

Conclusions: Preliminary results of nano-SXRD and SXRF measurements of presolar graphite grains demonstrate the advantages of using this method before employing destructive analytical techniques. Future work on these grains will include trace elemental abundance calculations of the grains and large subgrains, whole grain tomography, structural information of the subgrains, etc.

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