FIRST ANALYSIS OF GENTLY SEPARATED PRESOLAR GRAPHITE. A. King[1], T.Henkel[1], S. Chapman[1], D. Rost[1] and I. Lyon[1], [1]School of Earth, Atmospheric and Environmental Sciences, The University of Manchester, Oxford Road, Manchester, M13 9PL, U.K. (ashley.j.king@student.manchester.ac.uk, torsten.henkel@manchester.ac.uk).

Introduction: Presolar graphite grains were first isolated from the Murchison (CM2) meteorite by [1]. Analysis of their major and trace element isotopic compositions indicates that they are condensates from AGB-stars, Wolf-Rayet stars and Type II Supernovae [2-4].

To date all studies of presolar graphite have been carried out on grains extracted using acid dissolution techniques [5,6]. Recent evidence has suggested that the use of harsh acids may significantly alter the outer surface of presolar SiC grains extracted in this way [e.g. 7]. Also, as graphite is less chemically resistant than SiC, its separation through acid dissolution is a more complex procedure. We have previously described a technique for "gently separating" presolar SiC grains from host meteorites (i.e. isolate without the use of acids) [8] and have now adapted this procedure in order to isolate presolar graphite, providing us with pristine grains with which to study stellar environments.

Samples: The Murchison meteorite, with a presolar graphite abundance of ~5ppm [9], was selected as the source of graphite grains. Approximately 116mg of CAI- and chondrule-free matrix material was crushed using a stainless steel mortar and pestle. To further break down the sample it was then subjected to 138 freeze-thaw cycles, whereby it was alternately dipped between liquid nitrogen and an ultrasonic bath containing hot water (~45°C). Electron microscope analysis of a small deposit of the disaggregated sample confirmed grains were typically <20μm, with most being ~1μm in diameter.

The sample was separated according to size using a fixed angle rotor centrifuge. Sedimentation rates were calculated using Stokes' Law . Grain size fractions were chosen as A = >20μm, B = 7-20μm, C = 1-7μm and D = <1μm. At the end of each size separation the suspended grains were siphoned from the tube, leaving behind only the sedimented grains.

A series of organic heavy liquids were used to separate the size fractions according to density. The density of presolar graphite ranges between 1.6-2.2 gcm^{-3} [5], so density boundaries of 1.6, 2.05, 2.15 and 2.26 gcm^{-3} were applied. As presolar graphite grains are typically 1-10μm in diameter [5] only size fractions B and C were density separated.

Experimental Procedure: A small aliquot of separation B.4 (7-20μm, 2.15-2.26 gcm^{-3}) was distributed over a cleaned, ultra-pure gold foil. Prior to this a copper finder-grid had been imprinted onto the foil. Using the grain search feature of the electron microscope we located candidate graphite grains. Their origin as presolar needed to be confirmed by isotope analysis. High resolution images of candidate grains were taken and their locations relative to the finder-grid noted.

Sample B.4. was then transferred to a Time-of-Flight Secondary Ion Mass Spectrometer (TOFSIMS) for sub-micron spatial resolution and high mass resolution analyses (m/dm ~3000) of the isotopic and elemental compositions of candidate grains. A grain was analysed by rastering a Au^+ primary ion beam over its surface and detecting positive secondary ions. The field-of-view of the resulting secondary ion image reflected the size of the grain and each image contained 64 x 64 pixels, with each pixel containing a complete mass spectrum. The raw data was collected for offline analysis where it could be corrected for instrumental drift and spectra obtained from only the region of interest. To obtain C isotope ratios a peak deconvolution technique, as described by [10], was used to separate the ^{13}C-peak from the $^{12}C^{1}H$ interference.

Results: So far only 1 presolar graphite grain (B4-J0-1) has been analysed using TOFSIMS, although this is ongoing work and we expect to report results for more grains. Figure 1 shows that the grain is ~10μm x 9μm in size. It is within close proximity to a second grain, which from EDX spectra is likely $MgSiO_3$. The spatial resolution of the primary ion beam allows the two grains to be resolved in the secondary ion images and only spectra from the graphite have been analysed.
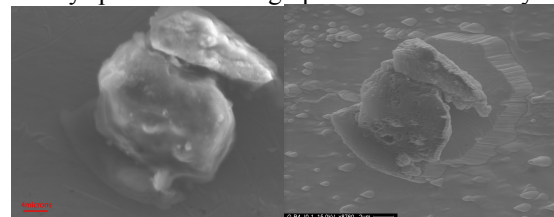

FIGURE 1. **High resolution ESEM images of presolar graphite grain B4-J0-1. On the left, an image of the grain before sputtering with the Au^+ primary ion beam. The grain is irregular in shape and lies in close proximity to a smaller grain (top right). An EDX spectrum was taken from the centre of this smaller grain and confirmed it as a silicate. Right, B4-J0-1 after sputtering. The grain is sat upon a**

pedestal created by sputtering of the surrounding gold foil.

A presolar origin for this grain is indicated by a $^{12}C/^{13}C$ ratio of 19.8 ± 2.4 (1σ) (see Table 1). This value is consistent with previous measurements of presolar graphite [1-4] and suggests an origin in a Type II SNe or AGB star. Further isotopic measurements, with both positive and negative secondary ions, are required in order to determine a definite stellar source.

Measurement Depth (nm)	$^{12}C/^{13}C$
28	22.6 ± 5.9
108	17.9 ± 1.8
459	17.8 ± 1.5
719	20.8 ± 2.4
	19.8 ± 2.4

TABLE 1. $^{12}C/^{13}C$ ratio with depth in grain B4-J0-1. Errors are 1σ.

Figure 2 shows a depth-profile of total secondary ions/C for trace elements within the outer region of B4-J0-1. The element ratios relative to carbon are as measured as we do not yet have an accurate calibration of ionisation efficiencies of elements in graphite relative to carbon. As carbon forms positive ions very poorly, the measured elemental ratios to carbon therefore appear very high. At present we therefore look at changes within the grain with depth and are calibrating elemental ionisation efficiencies appropriate for graphite in order to calculate absolute elemental abundances. The elements Mg, Na, Al, K, Ca and Fe appear to be the most abundant within the outer part of the grain. The elements Cr, Ti Mn, Li and B are lower in abundance. The grain has been sputtered to a depth of 1μm but no significant variation in elemental abundance is yet observed.
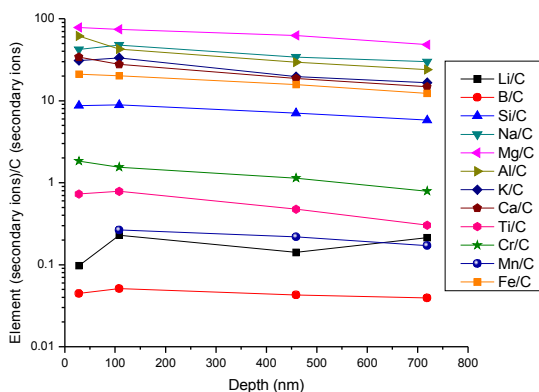

FIGURE 2. Elemental abundance depth-profile through the outer rim of grain B4-J0-1. Abundances are given as the number of secondary ions of

an element relative to the number of C secondary ions.

Discussion: The $^{12}C/^{13}C$ ratio of grain B4-J0-1 confirms it as presolar in its origin. This shows that the gentle separation procedure, originally developed for the isolation of presolar SiC grains, has been successfully adapted for the extraction of pristine presolar graphite. Although only 1 gently separated presolar graphite grain is reported here, several other candidate grains have been located in sample B.4. However, isotopic analyses have not yet been undertaken to confirm their origin as presolar.

Previous studies have shown that presolar graphite grains with large $^{12}C/^{13}C$ anomalies in acid separations are predominantly spherical in shape [2]. In contrast grains B4-J0-1 appears to be irregularly shaped. Also, Figure 1 shows that as the interior of B4-J0-1 has become exposed through sputtering, small hollows (<600nm) have appeared which were not present before analysis. Potentially the grain has a "cauliflower" structure as seen in other presolar graphite grains [11], which was not initially recorded due to any coating that may have existed on the grain surface.

Initial analysis of B4-J0-1 by TOFSIMS has provided a preliminary insight into its trace element composition. Although no variations in trace element abundances are observed within the outer part of grain B4-J0-1, TOFSIMS enables us to depth-profile through the grain and study any potential internal variations, such as those seen in presolar SiC [12]. Carbide sub-grains, common within presolar graphite [13], could also be studied but have not been found so far.

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