INDIGENOUS POLYCYCLIC AROMATIC HYDROCARBON MOLECULES IN CIRCUMSTELLAR GRAPHITE GRAINS; S. J. Cleemtt1, S. Messenger1, X. D. F. Chiiller1, X. Gao2, R. M. Walker3, R. N. Zare1; 1Department of Chemistry, Stanford University, Stanford CA 94305; 2McDonnell Center for the Space Sciences, Department of Physics, Washington University, One Brookings Drive, St. Louis MO 63130.

Exotic carbon isotope ratios observed in some graphite grains extracted from primitive meteorites point to a circumstellar origin [1]. We have used microprobe two-step laser desorption/laser ionization mass spectrometry (μL2MS) [2,3] to analyze individual circumstellar graphite grains for organic matter in the form of polycyclic aromatic hydrocarbons (PAHs). To date, we have studied 124 graphite grains, extracted from the Murchison CM2 (105 grains), Tieschitz H3 (8 grains), Indarch E4 (6 grains), and Acet 094 (5 grains) meteorites. Approximately 70% of the grains showed appreciable concentrations of PAHs. Molecule specific isotopic analyses show that most of the PAHs are isotopically normal and could have been added to the grains at various stages in their evolution. However, there is a significant number of molecules that are isotopically similar to the parent grains and are hence indigenous to the circumstellar grains themselves.

Individual grains were first investigated by μL2MS, which has been demonstrated to be a sensitive (~10,000 molecule detection limit) and highly selective method for the detection of aromatic species [4]. Grains were then analyzed by ion microprobe to determine their bulk carbon isotopic compositions [5]. A total of 89 grains were studied by both techniques, of which 38 grains were found to be depleted in 13C and 20 grains enriched in 13C. In general, the grains studied have an extensive suite of PAHs, spanning the mass range of 100-600 amu, comprising both parent and alkylated homologs at an estimated total concentration of 500-5000 ppm. Large variations in both signal intensity and mass distribution were observed between individual grains with no apparent correlation to grain size, morphology, or bulk carbon isotope ratio as determined by ion microprobe. The lack of a common PAH signature strongly argues against terrestrial contamination or formation of PAH species during the chemical digestion process used to prepare the residue from which the grains are isolated.

We performed molecule specific isotopic analyses of the aromatic molecules to investigate whether their isotopic compositions reflected those of the parent grains. Carbon isotopic ratios are determined from the measurement of the relative signal intensities of a 12C parent ion peak and its first 13C isotopomer peak [6]. Accuracy at the small signal limit is determined primarily by the limited number of ions detected. In many of the grain spectra only the dominant peaks are amenable to isotopic analysis. Given the number of ions observed in a given 12C parent peak the number of ions expected in the corresponding first 13C isotopomer peak can be calculated for a given carbon isotopic composition. Isotopomer peaks in samples with isotopically normal carbon show intensities that lie close to the predicted values. While most molecules measured in graphite grains depleted in 13C appear proximate to isotopically normal, strong deficits from the number of ions expected in the first 13C isotopomer peak are observed in several cases. In Figure 1 we summarize the isotopic analysis of 79 peaks from graphite grains depleted in 13C and 61 peaks from normal carbon samples, including bulk acid residue spectra and normal carbon graphite grains. Nearly all peaks from the isotopically normal samples fall within 2 standard deviations of the expected number of isotopomer peak ions. The apparent excesses in some isotopomer peaks (13C rich) arise from chemical interferences, as discussed later. While most peaks from graphite grains depleted in 13C appear isotopically normal, several peaks have strong depletions (>4σ) relative to normal values. In all, 6 13C depleted grains show strong evidence of 13C depletions in one or more of the dominant PAHs, and in several cases both a parent PAH and one or more of its alkylated homologs share the effect. The correlated isotopic anomalies observed in these molecules and their parent grains demonstrate that they are truly indigenous, and may be circumstellar in origin. In addition to 13C depleted PAHs, 3 grains enriched in 13C show strong evidence of 13C excesses in one or more of the dominant PAHs. Identification of further examples of 13C enrichments is complicated, however, by chemical interferences and spectral spreading of the signal across multiple isotopomer peaks.

As a self consistency check, Figure 2 shows the molecule-specific isotopic measurements for the five most abundant parent PAH species (naphthalene, C10H8; phenanthrene, C14H10; pyrene, C16H10; chrysene, C20H12; benzopyrene, C22H12) and their alkylated homologs from eleven bulk acid residue samples (Cl, CM, L, LL and H classes). All the residues have a solar carbon isotope composition and contain a complex mixture of aromatic
species of comparable intensity and distribution to that observed from the individual grains. The integrated peaks of the parent $^{12}\text{C}$ ions are plotted against the first $^{13}\text{C}$ isotopomer peaks. In such a plot, molecules of solar isotope composition ($^{12}\text{C}^{13}\text{C} = 89$) will lie along a diagonal line of slope $^{13}\text{C}/^{12}\text{C}$. In Figure 2 this behavior is seen to be the limiting case with a spread of points appearing to show a first $^{13}\text{C}$ isotopomer peak enrichment relative to the solar line. This is an unavoidable consequence of measurements of samples that contain a wide range of organic species, where chemical interferences from heteroaromatic species can contribute to the intensity of the first isotopomer peak. For example, both the first isotopomer peak of phenanthrene ($^{12}\text{C}_{13}^{13}\text{C}_{10}; 179.082 \text{amu}$) and the parent peak of phenanthridine ($^{12}\text{C}_{18}\text{H}_{13}N; 179.073 \text{amu}$) overlap at the mass resolution of our $\mu$L$^2$MS instrument. Therefore, any observations of $^{13}\text{C}$ isotopic enrichments within circumstellar grains are interpreted with caution. However, the observation of $^{13}\text{C}$ depletions cannot be exaggerated by chemical interferences, and in none of the acid residues studied does an indication exist of $^{13}\text{C}$ depleted PAH species beyond the uncertainties associated with instrumental and measurement effects.

This study shows that PAHs are quite generally associated with circumstellar graphite grains. Most of the PAHs are isotopically normal and could have been added to the grains at various times during their evolution. However, there is a significant component of the PAHs whose isotopic compositions reflect those of their parent grains. These isotopically anomalous molecules must have either formed with the grains in a circumstellar environment or from the grains themselves at some later stage, and we suggest this work represents the first direct sampling of PAHs formed in circumstellar or interstellar environments.

Figure 1. Isotopic analysis of molecules from $^{13}\text{C}$ light graphite and normal C samples. The number of ions observed in a given peak is used to estimate the statistical significance of deviations from the expected number of ions.

Figure 2. Isotopic analysis of PAHs from eleven bulk acid residue samples.