**STATISTICAL CONSTRAINTS ON $^{13}C/^{12}C$ ANOMALIES IN ALLENDE NANODIAMONDS BY NANOSIMS ANALYSIS.** J. B. Lewis*[1], F. Podosek[2], T. Bernatowicz[1], C. Floss[1], F. Gyngard[1], L. R. Nittler[3], [1]Laboratory for Space Sciences, Physics Department, Washington University, St. Louis, MO 63130. [2]Department of Earth and Planetary Sciences, Washington University, St. Louis, MO 63130. [3]Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Rd, Washington DC, 20015. (*email: jblewis@go.wustl.edu).

**Introduction**: Nanodiamonds (characteristic size ~2.8 nm [1]) comprise a well-known phase carrying presolar isotopically anomalous components preserved in primitive meteorites [2]. It has long been puzzling that, despite hosting anomalous components of other elements (e.g. Xe, Te), the C isotopic composition of the nanodiamonds is normal in bulk [3][4]. This statement must be qualified, however, by the recognition that individual nanodiamonds contain too few atoms to allow determination of $^{13}C/^{12}C$ more precisely than several tens of percent, even under ideal circumstances (every atom counted). Moreover, analysis of individual nanodiamonds has not yet been achieved experimentally. It is possible to conjecture that individual nanodiamonds have divergent C compositions and appear normal only in aggregate. Alternatively, it has been suggested that most of the nanodiamonds have normal C, and are perhaps even local (formed in the solar system) rather than presolar [5]. In that case it would be necessary that a small subset of the nanodiamonds carry anomalous components; these nanodiamonds would presumably also have anomalous C but would have no measurable effect on bulk C isotopic compositions. In the present study we report NanoSIMS analyses of Allende nanodiamond separates, featuring analyses of tens of thousands of nanoscale aggregates, to help better define the distribution of C isotopes in the meteoritic nanodiamonds.

**Experimental:** Measurements of $^{12}C$-, $^{13}C$-, and $^{28}Si$-ions and secondary electrons from Allende DM nanodiamonds (NDs) [6], as well as a battery of standards, were carried out with the Cameca NanoSIMS 50 at Washington University in St. Louis. Our ND separates were deposited on gold foil for analysis. Standards included terrestrial detonation NDs on gold foil [7], a graphite planchet, four terrestrial kerogens on gold foil [8], and chemical vapor deposition (CVD) NDs on a TEM grid [1]. For preliminary analyses the NanoSIMS was tuned for as small a primary $Cs^+$ beam as possible (~50 nm). However, the low primary ion beam densities made collecting enough counts for statistically significant measurements impractical due to instrumental concerns (e.g. beam drift, electronics stability) over the long integration times required. For the data presented here a more typical beam current (~0.67 pA) was used, the size of which was determined by extrapolation from static-beam drilling on Si to be 150±25 nm.

Taking this beam size and the average ND size of 2.8 nm we expect to sample ~2500 NDs within the area of a single measurement, possibly more due to overlapping grains. For each sample and standard we rastered for 20 ms/pixel for 60 cycles over 5 separate 64×64 pixel, (10×10 μm) regions, giving 20,480 pixel measurements. The pixel size was larger than the beam diameter, meaning adjacent measurements did not overlap. We corrected for a deadtime of 36 nsec, discarded the first 30 presputter cycles, and summed each pixel over the remaining 30 cycles. Because we were interested in measuring only NDs and analogous (C-rich) material, pixels with anomalously high $^{28}Si$ compared to average $^{12}C$ were discarded.

The primary purpose of the standard measurements was to identify and correct for instrumental effects, which otherwise could not be distinguished from intrinsic isotopic anomalies in the Allende sample. However, topographic effects, and resultant highly variable count rates, were apparent in the data from the graphite, CVD, and detonation standards, calling into question their usefulness as standards for the Allende sample, which exhibited relatively constant count rates. We plan to conduct additional measurements with smoother samples of our standards.

The width of the distribution of $^{13}C/^{12}C$ ratios was calculated from the pixel data using the weighted mean $^{13}C/^{12}C$ ratio, where weighting was based on the $^{12}C$ and $^{13}C$ counts for each pixel. If the measured distribution is broader than the distribution predicted by the mean $^{13}C/^{12}C$ ratio and average $^{13}C$ and $^{12}C$ counts, this would indicate that we have detected intrinsic isotopic anomalies, barring other instrumental artifacts.

**Hypothesized Nanodiamond Compositions:**

*A Distribution of Isotopic Ratios:* For any hypothesized distribution of intrinsic ND compositions, the observed distribution of measured ratios will be the convolution of the (true) “native” distribution and the probability distribution of measurement errors (taken to be normal for large numbers of ions detected).

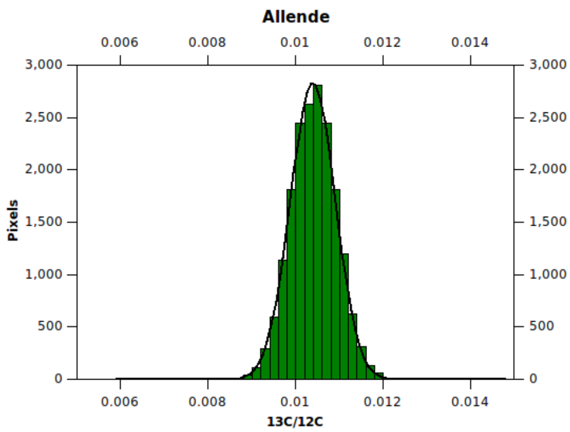


*Figure 1: Binned Data for Allende DM nanodiamonds. The bin size is 0.0002 in $^{13}C/^{12}C$ ratio.*

As a limiting case, it can be posited that the native distribution is normal, with some mean $\mu_d$ and variance $\sigma_d^2$. Samples of N NDs, i.e. the number in the beam area, will also be a normal population with the same mean and with variance $\sigma_d^2/N$. Convolution with the distribution of analytical errors will yield another normal distribution, with mean $\mu_o = \mu_d$ and variance $\sigma_o^2 = \sigma_d^2/N + \sigma_i^2$. Thus, an intrinsic variation characterized by standard deviation $\sigma_d$ would not become evident in the data until $\sigma_d$ approaches $\sigma_i\sqrt{N}$. For measurement errors on the order of 5%, and $N \approx 1000$, $\sigma_d$ would have to approach 150%.

*Normal with a Few Anomalous Grains:* Alternatively, we hypothesize that only a tiny fraction of the NDs are isotopically anomalous. It only requires 1 in a million grains to carry the observed anomalous Xe, and we assume that each such grain is isotopically heavy, $^{13}C/^{12}C = 0.2$, the maximum expected from low density graphite grains in supernovae [4]. The number of such grains in a measurement of 2,500 NDs would be dominated by Poisson statistics: For 2,500 NDs per measurement, 1-in-400 measurements should contain an isotopically heavy grain, so in 20,000 measurements we would predict 50 measurements with one isotopically heavy grain and 19,950 measurements with all normal grains and no isotopically heavy grains. We calculate for such a case that the distribution of $^{13}C/^{12}C$ ratios would be $\sim 4\times10^{-7}$ broader than the case of a sample with no isotopically anomalous material. Taking the precision of our data to be on the same order as the standard error of the mean, which is on the order $10^{-6}$, we conclude that we are not capable of detecting this fairly extreme scenario with these data.

**Results and Discussion:**

Integrated data for the Allende NDs were plotted in a histogram and fitted to a Gaussian distribution (see Fig. 1).

The weighted mean $^{13}C/^{12}C$ ratio for the Allende NDs was 0.010386. The weighted standard deviation was calculated from the data to be 4.95% of the mean. The width predicted by the measured mean and average counts is also 4.95% of the mean, so to our level of significance we detect no broadening of the $^{13}C/^{12}C$ distribution. Nor do we detect significant broadening in our standards, despite the presence of topographic effects and variable counts. The current Allende measurements reflect a compromise between high counts and low number of NDs per beam spot. With sufficient sensitivity and comparable instrumental effects between our samples and standards we would expect the broadening of the Allende $^{13}C/^{12}C$ ratio distribution to be greater than that of the normal standards if the Allende sample contained any NDs with anomalous $^{13}C/^{12}C$ ratios. However, given the sensitivity of the current measurements we do not expect to detect any broadening at all even given the extreme anomalies hypothesized in the previous section. Therefore, although our results are derived from the most sensitive measurements of the smallest aggregates of NDs carried out to date, the lack of detection of any broadening in the $^{13}C/^{12}C$ ratio distribution for Allende cannot rule out the presence of a subpopulation or distribution of subpopulations with highly isotopically anomalous grains.

We plan to measure additional Allende samples, ND separates from CM2 Murray, and smoother standards. SRIM simulations suggest $Cs^+$ implants to a depth of ~14 nm in C, deeper than our presputter depth, so by increasing our presputtering to that depth should improve our useful yield, allowing us to improve sensitivity by decreasing beam size without compromising counting statistics and integration times [9].


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