NANOSIMS MEASUREMENTS OF SMALL AGGREGATES OF ALLENDE NANODIAMONDS.

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Introduction: Meteoritic nanodiamonds have the potential to trace supernova, interstellar medium, and solar system processes, if their origins can be determined [1,2, and references therein]. It is essential to measure smaller numbers of nanodiamonds to discover if the nanodiamonds were produced from more than one reservoir of C with different $^{12}C/^{13}C$ ratios. To date, only aggregates of 10^{10} or greater nanodiamonds have been studied, with the exception of ongoing atom-probe studies of single nanodiamonds [3–5] and initial steps in this study [6]. Here we report the first results of nanoscale secondary ion mass spectrometry (NanoSIMS) studies of aggregates of no more than 10^3 nanodiamonds, which we have analyzed for their isotopic compositions.

Experimental: The Allende DM separate [7], deposited on gold foil, was analyzed using the Cameca NanoSIMS 50 at Washington University. For standards, we used detonation-produced nanodiamonds [8], as well as C paint and graphite. To minimize and estimate the number of nanodiamonds analyzed, we tuned to a small beam. We measured the Cs^+ primary beam to be < 70 nm in diameter by line scanning over a sharp edge of the sample and calculating the full width, half maximum, assuming a Gaussian beam shape. After presputtering at a high current, thousands of measurements were made, with 1s integration time for each. Extremely low beam current and count rates lead us to believe we did not sputter away more than one layer of nanodiamonds (3 nm thick [9]) in each measurement. However, the implantation depth of the 8 kV Cs^+ primary ions is ~14 nm [10], so atomic mixing may have led to the sampling of more nanodiamonds. The detonation diamonds yielded the lowest count rates, so we summed fewer cycles of the Allende nanodiamonds and C paint measurements, to yield the same average counts per measurement. We used the approximate analysed volume and C counts to estimate that the fraction of C atoms from the sample that were detected was 0.3–2%.

Results and Discussion: We averaged results from three different data sets of 256 analysis locations each to create a "bulk" measurement (as many as $5x10^6$ nanodiamonds) for comparison to previous studies. The Allende nanodiamond $\delta^{13}C$ is calculated as -21±42‰, normalized to the detonation nanodiamond standards. This is consistent with previous bulk measurements of Allende, where $\delta^{13}C$ = -32 to -38‰ [11], and $\delta^{13}C$ = -32.7±0.1‰ normalized to Pee Dee belemnite [12].

We then tested to see if individual measurements contained statistically significant isotopic anomalies. Given the properties of our beam and sample, we estimate that 100–500 nanodiamonds are sampled in each measurement. Of 9983 measurements of the $^{12}C/^{13}C$ ratio on Allende separates, two had isotopic ratios that were > 4σ away from the bulk $^{12}C/^{13}C$ ratio (0.11 such outliers are expected given Gaussian statistics). Both of these measurements have $\delta^{13}C$ ~ 800, or $^{12}C/^{13}C$ = 51, normalized to the detonation nanodiamond standards. Measurements with fewer than 10 counts of the least abundant isotope (^{13}C) were not included, as the approximation to a Gaussian distribution breaks down for small numbers. If we assume that the nanodiamonds are composed of two isotopic reservoirs, one with a solar ratio of $^{12}C/^{13}C$ = 89.9, then at least 43% of the carbonaceous material in these two measurements is required to be composed of the ^{13}C-heavy material, with a ratio greater than 51. Because outliers as high as 4.5σ are detected in our graphite and C paint standards (albeit with higher expectation, due to much higher numbers of measurements) these two outliers do not necessarily represent a detection of presolar nanodiamonds. Given our experimental conditions and the assumption of a bimodal solar/presolar composition, a 5σ outlier would represent an aggregate of 100–500 nanodiamonds of which at least 49% are presolar. This is our detection limit for aggregates of this size. A range of detectable $^{12}C/^{13}C$ ratios and anomalous percentages are: 5 and 52%; 10 and 55%; 20 and 63%; 30 and 73%.

We are continuing to test our data set for isotopic anomalies by searching for statistically significant deviations from the expected shape of the distribution of isotopic measurements.

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