

MULTI-SCALE CARBON ISOTOPIC ANALYSES SHOW ALLENDE NANODIAMONDS ARE MOSTLY SOLAR WITH SOME PRESOLAR

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Introduction: Of the various presolar materials studied from meteorites, comets, and interplanetary dust particles, meteoritic nanodiamonds have the most elusive origins [1,2]. They are the only presolar material discovered to carry the Xe-HL isotopic anomaly, believed to be produced only in supernova explosions [2–6]. But when measured in bulk, the C isotopic ratios are consistent with the solar system, not supernovae [4,5,7]. We have performed a suite of experiments on different-sized aggregates of nanodiamonds from the meteorite Allende, to search for carbon isotopic heterogeneity.

Methods: Nanoscale secondary ion mass spectrometry (NanoSIMS) was utilized to perform 72,103 spot measurements, each of approximately 1000 nanodiamonds, standardized against measurements of terrestrial detonation nanodiamonds, graphite, and DAG (deflocculated Acheson graphite) carbon paint. Statistical analyses were performed on the distributions of the $^{13}\text{C}/^{12}\text{C}$ ratios produced by these measurements [8]. Atom-probe tomography (APT) was utilized to make 36 measurements of aggregates ranging in size from ~1–10 nanodiamonds. The measured $^{13}\text{C}/^{12}\text{C}$ ratios were corrected for artifacts and standardized against 26 terrestrial detonation nanodiamond standards, including some previously published data [9–11].

Results: In aggregates of different numbers of nanodiamonds: 10^6 (NanoSIMS), 10^3 (NanoSIMS), 10^2 (APT), and 10^1 (APT), most measurements are consistent with solar system values, as well as previous measurements of at least 10^{12} nanodiamonds per aggregate by stepped combustion and pyrolysis [4,5,7]. However, for aggregates of ~ 10^6 nanodiamonds, the nanodiamonds appear to be drawn from multiple isotopic reservoirs, and 5 out of 72,103 measurements of 10^3 nanodiamonds by NanoSIMS have $>4\sigma$ anomalies in $^{13}\text{C}/^{12}\text{C}$, which persist over three or more NanoSIMS analysis cycles, each apparently containing a few nanodiamonds that are ^{13}C -enriched (~10/1) compared to the solar value of 89 [12]. None of the 36 APT measurements, each of ~1–10 nanodiamonds, was conclusively anomalous in C isotopic composition, but the sensitivity was low.

Conclusions: Supernovae are the likely producers of the ^{13}C -enriched nanodiamonds, since they can also produce Xe-HL and other nucleosynthetic signatures observed in the nanodiamond acid residues, but novae, j-stars, and born-again AGB stars could also produce the magnitude of ^{13}C -enrichment implied by our NanoSIMS measurements. If only a small fraction of nanodiamonds formed in supernovae, and carry all the Xe-HL, the implantation efficiency of the Xe-HL must have been high, and raises the question why Xe-HL is not observed in other presolar materials known to form in supernovae, including some SiC X and presolar graphite grains.

If all the C isotopic anomalies, Xe-HL, and other trace elements are from supernovae, the remainder of the nanodiamonds are most simply explained as forming in the solar system, since they have solar system C isotopic values [13], although they could, in principle be formed by any source, or combination of sources that have a mean value close to that of the solar system. Further supporting a solar system formation, two pieces of evidence imply that the variation of the non-outliers is small: (1) The lack of detection of isotopically anomalous nanodiamonds in aggregates of 10^1 or 10^2 in size by APT (about 100 nanodiamonds in total). (2) The detection of only 5 out of 72,013 outliers in measurements of 10^3 nanodiamonds by NanoSIMS.

Outlook: Additional APT studies may allow the isolation and study of individual ^{13}C -enriched nanodiamonds, but these still pose significant analytical challenges. Separation of the acid residues into different sub-components, such as nanodiamonds and disordered C, could allow isolation of material from two or more isotopic reservoirs.

References: [1] Zinner E. (2014) Presolar Grains, in *Treatise on Geochemistry* 1:181–213 (Elsevier). [2] Lewis R. S. et al. (1987) *Nature* 326:160–162. [3] Lewis R. S. et al. (1989) *Nature* 339:117–121. [4] Russell S. S. et al. (1991) *Science* 254:1188–1191. [5] Russell S. S. et al. (1996) *Meteoritics and Planetary Science* 31:343–355. [6] Gilmour J. D. et al. (2005) *Geochimica et Cosmochimica Acta* 69:4133–4148. [7] Swart P. K. et al. (1983) *Science* 220:406–410. [8] Lewis J. B. et al. (2016) *79th Meteoritical Society Conference Abstract* #6367. [9] Heck P. R. et al. (2014) *Meteoritics and Planetary Science* 49:453–467. [10] Isheim D. et al. (2013) *Microanalysis* 19(Suppl 2):974–975. [11] Lewis J. B. et al. (2015) *Ultramicroscopy* 159:248–254. [12] Coplen T. B. et al. (2002) *Pure and Applied Chemistry* 74:1987–2017. [13] Dai Z. R., et al. (2002) *Nature* 418:157–159. [14] This work was supported by NASA grants NNX14AP15H (J. B. Lewis), NNX16AD26G (C. Floss), and NNX13AH08G (F. Gyngard). The LEAP tomograph at NUCAPT was acquired and upgraded with NSF DMR-0420532 and ONR-DURIP N00014-0400798, N00014-0610539, N00014-0910781 equipment grants. NUCAPT received support from the MRSEC program (NSF DMR-1121262) at the Materials Research Center, the SHyNE Resource (NSF NNCI-1542205), and the Initiative for Sustainability and Energy at Northwestern (ISEN)).