

Distinguishing Meteoritic Nanodiamonds from Amorphous Carbon Using Atom-probe Tomography

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Meteoritic nanodiamonds are of interest because they may have formed prior to the solar system [1]. These 3 nm diameter, crystalline sp^3 -bonded diamond particles are extracted from carbonaceous chondrites by acid dissolution. The resulting acid residue also contains a fraction, estimated to be one-half [2,3] of amorphous, sp^2 -bonded C. Various models about the formation of the nanodiamonds have different implications for this fraction – whether it formed independently from the nanodiamonds, formed at the same time from carbonaceous precursor material [3] or formed prior to the nanodiamonds. To better establish the origins of the nanodiamonds and amorphous material, measurements of the ratio of the stable carbon isotopes, $^{12}C/^{13}C$, in individual nanodiamonds have been performed utilizing atom-probe tomography (APT) [4–6]. We present a method herein that allows us to distinguish the amorphous and diamond components of the acid residues utilizing APT.

To fabricate APT nanotips we dispersed the acid residue onto a Pt substrate thin-film deposited by ion-beam sputtering (IBS), coated the residue with an additional IBS-Pt layer, and conducted cross-sectional focused ion beam (FIB) liftouts [5]. APT was performed utilizing the LEAP 4000X Si at Northwestern University, with experimental conditions described in detail in references [4–6]. We reanalysed regions of interest in 10 APT datasets from [4] and 15 from [6], focusing on the nanodiamond deposition layer. We utilized updated background correction [6] and peak selection [7] methods, and standardized the $^{12}C/^{13}C$ isotopic ratios relative to a suite of measurements of terrestrial nanodiamonds [8]. APT reconstructions from 11 new nanotips were also analysed using these techniques.

There are two distinct carbon phases observable in adjacent regions of the atom-probe tomographic reconstructions of the acid residues. Excluding the Pt from APT nanotip preparation, one phase can be identified by the presence of Na (average ion concentration in a data set is 1.4% with a $\pm 3.3\%$ one standard deviation) and NaO ($0.2\pm 0.6\%$) from contamination during the acid separation, as well as the presence of PtCO ions ($1.1\pm 0.8\%$). The other phase is richer in C_1 ($4.6\pm 6.4\%$), C_2 ($0.2\pm 0.3\%$), and C_3 ($0.2\pm 0.3\%$) ions. The quantity of these ions detected in each nanotip is approximately inversely proportional between these two phases; that is, the higher PtCO+Na+NaO correlates with the lower $C_1+(2\times C_2)+(3\times C_3)$, and vice versa. The (PtCO, Na, NaO)-rich phase we identify as sp^2 amorphous C at the surfaces of the nanodiamonds, where there is substantial surface roughness and surface defects for Pt and Na to bond during acid dissolution and the APT preparation steps. The (C_1 , C_2 , C_3)-rich phase we identify as the interiors of the nanodiamonds, where sp^3 bonds dominate. Transmission electron microscopy studies of the acid residues demonstrate that the nanodiamonds contain small amounts of nitrogen (N) ($0.3\pm 0.5\%$), and that oxygen ($3.7\pm 2.6\%$) is present in the amorphous sp^2 -bonded C [3].

Figure 1 details the results of our analysis. N does not correlate with the $C_1+(2\times C_2)+(3\times C_3)$ atoms in our samples, probably because of low concentrations of N in the nanodiamonds, and the presence of N-contamination from the sputter-deposited Pt. Oxygen content, on the other hand, does correlate, albeit

weakly, with the number of PtCO+Na+NaO ions, adding credence to our assignment of these regions to the sp^2 amorphous C phase in the acid residues. The $^{12}\text{C}/^{13}\text{C}$ isotopic ratios measured in the nanotips do not depend strongly on the fraction of the acid residue that is amorphous sp^2 -bonded carbon relative to nanodiamonds, at least within the sensitivity limits of our method. This result suggests that the two phases did not originate from two different presolar sources.

References:

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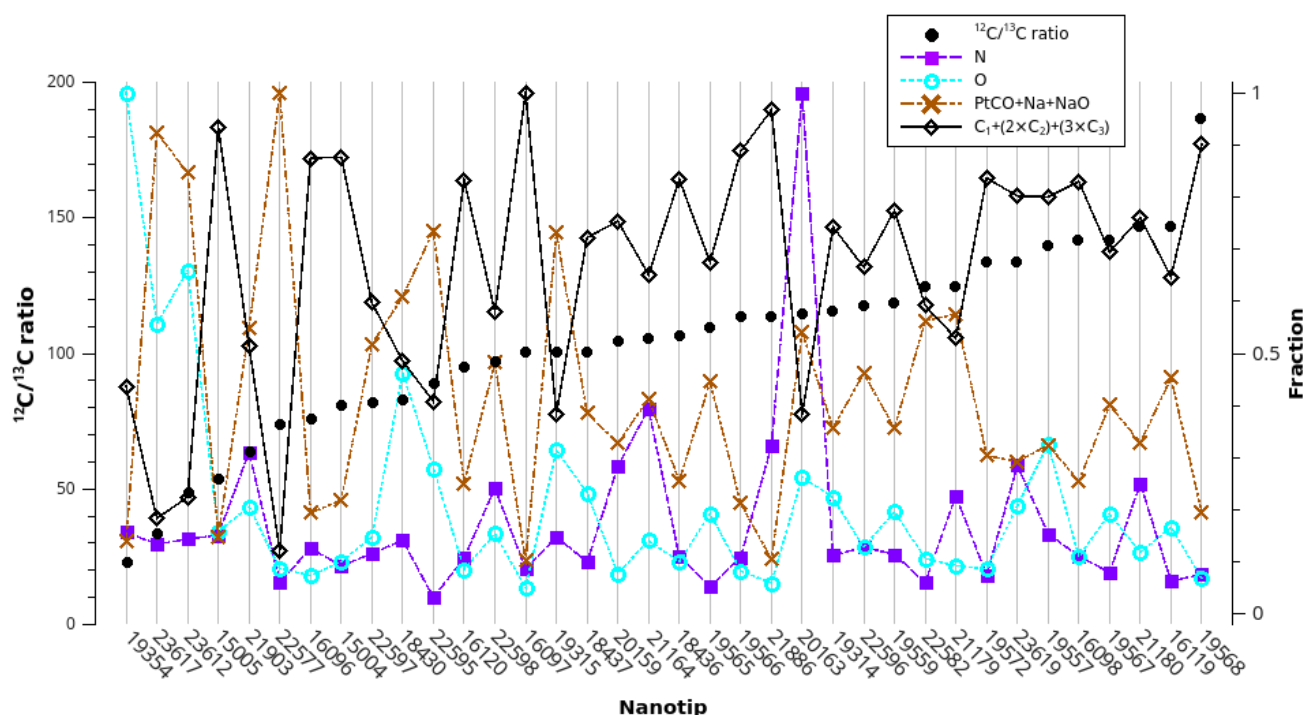


Figure 1. Corrected, standardized $^{12}\text{C}/^{13}\text{C}$ isotopic ratios of meteoritic nanodiamonds for different nanotips (solid black circles, left-hand axis), in order of increasing $^{12}\text{C}/^{13}\text{C}$ isotopic ratio. The four other quantities plotted are each divided by the sum of the ions associated with the deposition layer and then normalized to the maximum atomic concentration observed, to emphasize relative variations (see legend and right-hand axis).