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Carbon Isotopic Measurements of Nanotubes to Differentiate Carbon Sources

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ABSTRACT

Stable carbon isotope ($\delta^{13}\text{C}$) analysis can provide information concerning the starting materials and the production process of a material. Carbon nanotubes (CNTs) are produced using a variety of starting materials, catalysts, and production methods. The use of $\delta^{13}\text{C}$ as a tool to infer the nature of starting materials to gain insight into the mechanics of CNT growth was evaluated. The production process of NRC's SWCNT-1 was traced via the $\delta^{13}\text{C}$ measurement of the available starting materials, intermediate products, and the final product, SWCNT-1. As isotopic fractionation is likely negligible at high temperatures, the $\delta^{13}\text{C}$ value of the starting materials were reflected in the $\delta^{13}\text{C}$ value of the final CNT product. For commercially available CNTs, the estimated $\delta^{13}\text{C}$ values of identified starting materials were related to the $\delta^{13}\text{C}$ signatures of CNTs. Using this information and the $\delta^{13}\text{C}$ values of CNTs, the nature of unknown carbon sources were inferred for some samples. The use of $\delta^{13}\text{C}$ analysis may be used as a tracer to differentiate between those processes that use relatively ^{13}C -depleted carbon source(s) such as carbon monoxide, methane or natural gas, and those that do not.

KEYWORDS

carbon nanotubes, stable carbon isotope analysis, characterization, carbon source

INTRODUCTION

Carbon nanotubes (CNTs) are a class of materials that have been extensively studied in the past three decades [1-6]. CNTs resemble seamless rolled graphene sheets, and can exist in various forms: as single-walled CNTs (SWCNTs), double-walled CNTs (DWCNTs), multi-walled CNTs (MWCNTs) and few-walled CNTs. Depending on their helicity, SWCNTs can be either metallic or semi-conducting, and have been incorporated into many everyday products such as batteries, sporting goods, electronics, sensors, household products, etc. [3, 7].

As the properties of CNTs are mainly dictated by the carbon-containing starting materials, the catalysts, and the production methods and conditions, there is an endless list of methods used to manufacture CNTs. Production methods can be classified into several broad categories, including but not limited to, electric arc discharge (EAD), laser ablation (or laser vaporization), and chemical vapor deposition (CVD) [1-6]. Further, almost any carbon-containing material can serve as a starting material for CNT production, and the choice of starting materials is somewhat dictated by the production method. For EAD or laser ablation, graphite is the most common starting material, however studies using electric arc discharge with hydrocarbons, carbon black, coal [4], and biomaterials [8] have been reported. Conversely, CVD is probably the most diverse CNT production method in terms of starting materials and catalysts, which are important parameters to control to produce large quantities of high quality, pure CNTs. Several hydrocarbons such as methane, ethene, acetylene, and benzene, alcohols including ethanol, and natural oils are frequently used as starting materials with a variety of metal catalysts [1, 6]. Other processes including the high pressure carbon monoxide method (HiPCO) [9] and the cobalt-molybdenum-catalyst (CoMoCAT) [10] process both use carbon monoxide (CO) as the starting material.

Stable carbon isotope ($\delta^{13}\text{C}$) analysis is a frequently used forensic tool for many applications, including source appropriation of pollutants, and determining provenance of samples (food, humans, etc.) [11, 12]. The $\delta^{13}\text{C}$ value of a sample can provide information concerning the starting materials and production process used to manufacture the sample, with two main factors determining the resulting $\delta^{13}\text{C}$ value: 1) the $\delta^{13}\text{C}$ values and relative proportion of the starting materials, and 2) the extent of fractionation that may occur during the manufacturing process. As the temperature of most of the CNT production processes often surpass 1000 °C, isotopic fractionation (i.e. the preferential incorporation of either the heavy or light isotope from the starting material(s) into the final product) attributed to the manufacturing process is likely negligible [13], and the $\delta^{13}\text{C}$ value of the sample would mostly reflect the $\delta^{13}\text{C}$ value(s) of the starting material(s). Since a wide range of carbon-containing starting materials are available to manufacture CNTs, it follows that the resulting range of $\delta^{13}\text{C}$ values of CNT may also be large, potentially ranging from -10 ‰ (for CNTs manufactured from C4-based materials such as ethanol) to -55 ‰ or more negative (for CNTs derived from hydrocarbons or CO) [14].

Although CNTs have been extensively studied, direct observation and measurement during CNT nucleation and growth is very challenging. Current understanding of CNT growth mechanics is largely based on numerical simulations and theories that are consistent with observations of the final CNT product. Some studies [15, 16] have used labelled compounds to further elucidate the growth mechanism of CNTs using a single material as the sole carbon source. As CNTs are produced using a variety of carbon

sources, catalysts, and under different environmental controls, it is difficult to make any generalization about growth mechanisms other than about the specific method being studied. However, by measuring both the quantity and the $\delta^{13}\text{C}$ value of (each of) the carbon-containing starting material(s), $\delta^{13}\text{C}$ analysis has the potential to estimate the relative amount the carbon-containing starting material(s) incorporated into the final product, information which may help to elucidate the growth mechanism of a particular CNT, or may be helpful in source appropriation studies.

In 2011, the National Research Council Canada (NRC) produced a high purity SWCNT certified reference material (CRM), SWCNT-1 [8]. In an effort to gain more information concerning the growth mechanism of this CNT, we measured the $\delta^{13}\text{C}$ signatures of the available starting materials, samples taken during the production and subsequent collection process, and the final product. Further, we analyzed the $\delta^{13}\text{C}$ values of several commercially available CNTs in an effort to determine if the starting material of a CNT can be predicted based on the measured $\delta^{13}\text{C}$ value. To our knowledge, only one other study has reported $\delta^{13}\text{C}$ measurements for commercially available CNTs [17], and our $\delta^{13}\text{C}$ measurements will be compared to the available literature.

EXPERIMENTAL

SWCNT-1 production

The production process of SWCNT-1 via laser vaporization is depicted in Figure 1. The principal carbon source was a biochar derived from the pyrolysis of hardwood (Ensyn Technologies Inc.), a unique and renewable starting material. A graphite adhesive and cobalt (Co) and nickel (Ni) catalysts were added to the biochar, and the mixture was pressed into a pellet, then cured at 850 °C in argon. The cured pellet was then mounted on a molybdenum stub support, heated to 1200 °C under a stream of 5% CO in argon (Ar) at 0.66 bar (500 torr), and vaporized with two 1064 nm lasers [18, 19]. The Raw SWCNT was recovered from condensation sites, and this material was homogenized and solvent washed to remove residual material, then sieved through a 400 μm sieve to produce Clean SWCNT. The Clean SWCNT was heated to 1000 °C for 30 minutes, then cooled to room temperature to produce the final product, SWCNT-1.

Several samples from this production process were analyzed, including the biochar, a cured pellet, Raw SWCNT, Clean SWCNT, and three bottles of the final product, SWCNT-1. Five samples from the pellet were obtained by snapping it by hand into pieces, and scraping the inside surface of each piece at the cleavage site.

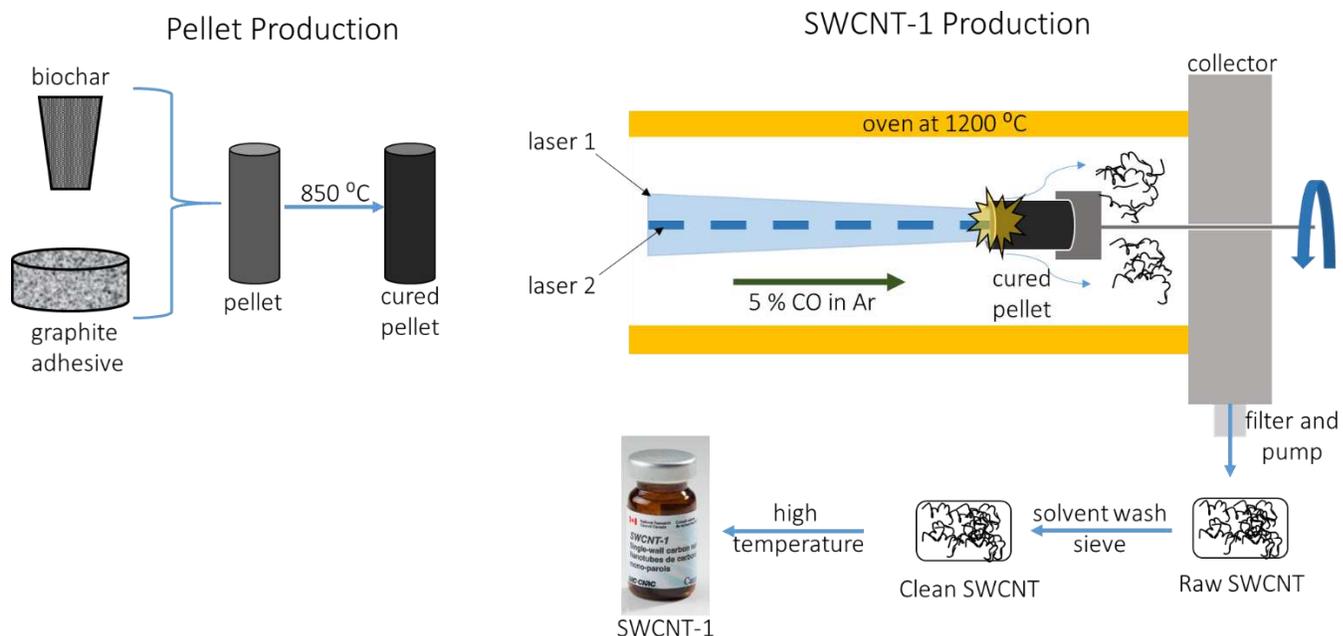


Figure 1. Production process of SWCNT-1.

Graphite Samples and Commercially Available CNTs

Three graphite samples were analyzed for this study: one sample obtained from Alfa Aesar (Ward Hill, MA, USA), and the other two were from unknown sources. Several CNT samples were procured from several suppliers (Table 1), and these samples varied with respect to the number of walls and production method. For many of these samples, information concerning the starting materials was not available.

SAMPLE ID	Sample	Production Method	Description
SW-1a, b, c	Single walled carbon nanotubes, 3 bottles	LV	SWCNT-1 produced by NRC
SW-2	Single walled carbon nanotubes	EAD	Sigma Aldrich Product # 698695
SW-3	Single walled carbon nanotubes	EAD	Sigma Aldrich Product #750492
SW-4	Single walled carbon nanotubes	EAD	CarboLex
SW-5	Single walled carbon nanotubes	EAD	Tuball 76 %, produced by OCSiAl
SW-6	Single walled carbon nanotubes	CVD	Sigma Aldrich Product # 900711 super-growth
SW-7	Single walled carbon nanotubes	CVD	Elicarb batch J8142
SW-8	Single walled carbon nanotubes	CVD	Nanocyl Lot NFL55.2
SW-9	Single walled carbon nanotubes	CVD	SouthWest Nanotechnologies (SWeNT) CoMoCAT
SW-10a, b	Single walled carbon nanotubes, 2 bottles	CVD	NIST SRM 2483 CoMoCAT
SW-11	Single walled carbon nanotubes	CVD	Carbon Nanotechnologies Inc. (Unidym) HiPCO
DW-1	Double walled carbon nanotubes	CVD	Sigma Aldrich Product # 755168
MW-1a, b	Multi-walled carbon nanotubes, lots a and b	CVD	Sigma Aldrich Product # 259258
MW-2	Multi-walled carbon nanotubes	CVD	Sigma Aldrich Product # 698849
MW-3	Multi-walled carbon nanotubes	CVD	Sigma Aldrich Product # 755117
FW-1	Few-walled carbon nanotubes	CVD	Sigma Aldrich Product # 900788 CoMoCAT
NF-1	Carbon nanofibers	CVD	Sigma Aldrich Product # 719803 floating catalyst vapour by Pyrograf Products Inc.

Table 1. Description of CNT samples analyzed for this study. LV = laser vaporization, EAD = electric arc discharge, CVD = chemical vapour deposition.

Carbon Isotope Notation and Traceability

Stable carbon isotope measurements of a sample are expressed on the VPDB scale:

$$\delta_{\text{VPDB}}^{13\text{C}} = R_{\text{SAM}} / R_{\text{STD}} - 1 \quad (\text{Eq. 1})$$

where R_{SAM} and R_{STD} are the ratio of 13-C / 12-C (i.e. $n(^{13}\text{C}) / n(^{12}\text{C})$) in the sample and standard, respectively, and VPDB refers to Vienna PeeDee Belemnite. Since 2005, the VPDB scale was realized using two modern CRMs, LSVEC (lithium carbonate) and NBS 19 (calcium carbonate), which have exact $\delta^{13}\text{C}$ values of -46.6 ‰ and $+1.95 \text{ ‰}$. IUPAC no longer recommends the use of LSVEC. However, $\delta^{13}\text{C}$ measurements must be normalized to the VPDB scale using at least two suitable reference materials selected by the analyst [20]. Throughout this work, $\delta_{\text{VPDB}}^{13\text{C}}$ is shortened to $\delta^{13}\text{C}$.

Sample Analysis

All samples received no treatment prior to $\delta^{13}\text{C}$ analysis. Approximately 100 μg of carbon nanotube samples and a micro-scoop of the combustion aid vanadium pentoxide (V_2O_5 ; Elemental Microanalysis, Okehampton, UK) were added to tin capsules (Elemental Microanalysis; Okehampton, UK) and loaded onto an 80-position autosampler carousel for $\delta^{13}\text{C}$ analysis. All analyses were performed on an elemental analyzer (EA, Vario EL III, Elementar Americas Inc., Mt. Laurel, NJ, USA) interfaced to a Delta⁺XP isotope ratio mass spectrometer (IRMS, Thermo Fisher; Bremen, Germany) via a Conflow III gas flow controller (Thermo Fisher; Bremen, Germany). The flow rate of the helium (99.999 % purity; Air Liquide; Montreal, QC, Canada) was $\sim 155 \text{ mL/min}$. The combustion and reduction reactors were held at 950°C and 500°C , respectively. No sample helium dilution was used for the analyses.

Samples were analyzed in four sequences. To minimize any potential carryover due to incomplete combustion, an empty space was included after every blank, sample, and CRM. In all cases, the total area of the empty space was similar in magnitude to blank samples, suggesting complete conversion of the carbon sample to CO_2 . Blank samples, both with V_2O_5 and without, were included at the beginning and end of the sequences, and comprised $\leq 2 \%$ of the total area signal. All analyses were blank corrected, using either the blanks with no V_2O_5 (for CRMs with no added V_2O_5), and blanks with V_2O_5 (for all samples and USGS24). No drift corrections were applied to any of the analysis sequences. The IUPAC recommended algorithm for correction of the oxygen-17 contribution to the ion beam at m/z 45 was applied to all analyses [21].

All samples were normalized to 4 CRMs: a suite of three sugar CRMs from NRC [22]: BEET-1 ($\delta^{13}\text{C} = -26.02 \text{ ‰}$), GALT-1 ($\delta^{13}\text{C} = -21.41 \text{ ‰}$) and FRUT-1 ($\delta^{13}\text{C} = -10.98 \text{ ‰}$), and NBS-22 ($\delta^{13}\text{C} = -30.03 \text{ ‰}$ [23]). Two quality control (QC) samples were included with each set of reference materials: USGS24, graphite ($\delta^{13}\text{C} = -16.05 \text{ ‰}$ [23]), and an internal QC material ($\delta^{13}\text{C} = -22.95 \text{ ‰}$). A micro-scoop of V_2O_5 was added to USGS24, but no combustion aids were added to BEET-1, GALT-1, FRUT-1, NBS-22 or the internal QC sample. The coefficients of determination (R^2) for each normalization curve was ≥ 0.998 . The average $\delta^{13}\text{C}$ values \pm standard deviation (SD) of USGS24, which is the closest matrix-matched QC to the samples, were $-15.94 \pm 0.09 \text{ ‰}$ (N=5), $-15.90 \pm 0.23 \text{ ‰}$ (N=4), $-16.14 \pm 0.18 \text{ ‰}$ (N=3), and $-16.09 \pm 0.17 \text{ ‰}$ (N=3) for the four analysis runs, respectively. As these average $\delta^{13}\text{C}$ values are within the accepted $\delta^{13}\text{C}$ value of USGS24, -16.05 ‰ , with a standard uncertainty of 0.07 ‰ , [24] we are confident that the use of organic

CRMs with no addition of V_2O_5 to normalize carbon-only samples did not introduce any appreciable bias on the measured $\delta^{13}C$ values. The average $\delta^{13}C$ values \pm SD of the second QC material were -22.92 ± 0.06 ‰ (N=5), -22.97 ± 0.16 ‰ (N=4), -23.03 ± 0.21 ‰ (N=5) and -22.99 ± 0.38 ‰ (N=3), and were similar the known value of -22.95 ‰. All samples were analyzed in at least duplicate, and the SD was < 0.50 ‰ for all replicate measurements.

RESULTS AND DISCUSSION

$\delta^{13}C$ Measurements of SWCNT-1 CRM and its production intermediates

The $\delta^{13}C$ value of a product can provide insight into the nature of the starting materials used, and/or the manufacturing process. To trace the $\delta^{13}C$ values throughout the production of NRC's CRM SWCNT-1, the biochar and various samples collected at different stages throughout the production process (Figure 1) were analyzed (Figure 2).

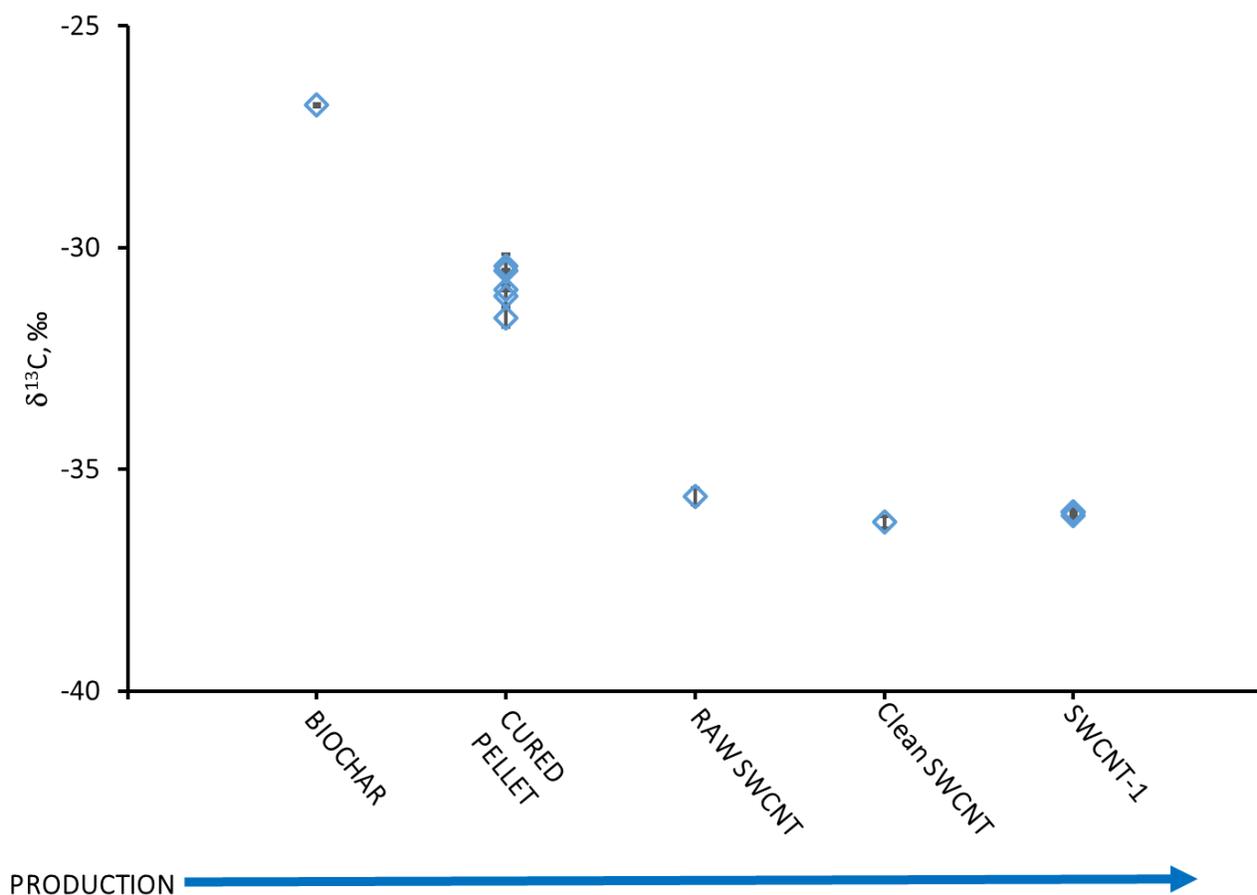


Figure 2. $\delta^{13}\text{C}$ values of samples taken during the production of SWCNT-1. Error bars represent the SD on replicate analyses. For details on the production process, see text.

The biochar had a measured $\delta^{13}\text{C}$ value of $-26.78 \pm 0.03 \text{ ‰}$ (N=4), and is consistent with hardwood trees with a C3 photosynthetic pathway [25]. Graphite adhesive, and cobalt (Co) and nickel (Ni) catalysts, were added to the biochar, pressed into a pellet, and the pellet was cured at $850 \text{ }^\circ\text{C}$ in Ar. The graphite adhesive is a viscous paste comprised of graphite powder in furfuryl alcohol. During curing, the furfuryl alcohol polymerizes and graphitizes, leaving only graphitic carbon in the pellet. A sample of graphite adhesive was attempted to be measured for $\delta^{13}\text{C}$ values; however, the sample was old and had tar-like consistency, suggesting that the sample was likely compromised, and the measured $\delta^{13}\text{C}$ value may not be reflective of the graphite adhesive used in the pellet making process.

The average $\delta^{13}\text{C}$ value obtained from five different sampling sites of one pellet, with four sites analyzed in duplicate and one in triplicate, was $-30.86 \pm 0.47 \text{ ‰}$ (N=11), with individual measurements ranging from -30.25 ‰ to -31.73 ‰ . With a sample size of only $100 \text{ }\mu\text{g}$, it is possible that the pellet was not homogenous at this small scale, resulting in a 1.5 ‰ difference between sampling sites. Regardless, the pellet is ~ 4 to 5 ‰ more negative than the biochar. The curing process incorporates carbon from both the graphite powder and the furfuryl alcohol, with a net result of incorporation of carbon atoms with a more negative $\delta^{13}\text{C}$ value than the biochar.

The cured pellet was then vaporized with two lasers under a stream of 5 ‰ CO in Ar in a $1200 \text{ }^\circ\text{C}$ oven [18, 19]. The $\delta^{13}\text{C}$ value of the recovered Raw SWCNT was $-35.62 \pm 0.18 \text{ ‰}$ (N=4), which is ~ 4 to 5 ‰ more negative than the cured pellet from which it was derived. As this process occurred at $1200 \text{ }^\circ\text{C}$, isotopic fractionation during the manufacturing process is expected to be very small or negligible [13], and the $\delta^{13}\text{C}$ value of final product should reflect the relative proportion of all sources of carbon incorporated into its structure. The CO in the CO+Ar gas stream was not directly measured. CO is typically derived from the oxidation of methane, and the $\delta^{13}\text{C}$ of methane can range between -50 ‰ to -110 ‰ for biogenically formed methane, and from -20 ‰ to -50 ‰ for thermogenic processes [26]. Two commercial tanks of methane of unknown origin were measured to be -38 ‰ and -51 ‰ [14]. NRC obtained a CO reference gas with a calibrated $\delta^{18}\text{O}$ value of -6.2 ‰ , and an estimated $\delta^{13}\text{C}$ value of -55.5 ‰ . As the estimated $\delta^{13}\text{C}$ value of the CO used in SWCNT-1 production was most likely more negative than the pellet, carbon from the CO was likely incorporated into the Raw SWCNT structure.

The extent of CO incorporation into the Raw SWCNT (Table 2) can be theoretically estimated by varying an assumed $\delta^{13}\text{C}$ value for the CO, and using the mass balance equation:

$$(a_{\text{pellet}})(\delta^{13}\text{C}_{\text{pellet}}) + (b_{\text{CO}})(\delta^{13}\text{C}_{\text{CO}}) = (1)(\delta^{13}\text{C}_{\text{Raw SWCNT}}) \quad [2]$$

where a_{pellet} and $\delta^{13}\text{C}_{\text{pellet}}$ are the mass fraction and $\delta^{13}\text{C}$ value of the pellet, respectively, b_{CO} and $\delta^{13}\text{C}_{\text{CO}}$ are the mass fraction and $\delta^{13}\text{C}$ value of the CO, respectively, $\delta^{13}\text{C}_{\text{Raw SWCNT}}$ is the $\delta^{13}\text{C}$ value of the Raw SWCNT, and $a_{\text{pellet}} + b_{\text{CO}} = 1$.

Assumed $\delta^{13}\text{C}$ of CO ($\delta^{13}\text{C}_{\text{CO}}$), ‰	Mass fraction of carbon from pellet (a_{pellet})	Mass fraction of carbon from CO (b_{CO})
-40	0.48	0.52
-45	0.66	0.34
-50	0.75	0.25
-55	0.80	0.20
-60	0.84	0.16
-70	0.88	0.12
-80	0.90	0.10

Table 2. Estimated amount of carbon from CO incorporated into the Raw SWCNT. The $\delta^{13}\text{C}$ values of the pellet and Raw SWCNT were -30.86 ‰ and -35.62 ‰, respectively.

Using this method, the theoretical estimated percentage of carbon incorporated into the final product can vary between 10 % and 52 %, with decreasing amount of carbon from CO incorporation with increasingly negative assumed $\delta^{13}\text{C}$ CO values. In order to fully understand the distribution of carbon from all starting materials, future experiments will include the $\delta^{13}\text{C}$ measurement of all starting materials and potential sources of carbon, intermediate products from various steps in the production process, and the resulting CNT sample.

The subsequent homogenization and solvent washes of the Raw SWCNT to remove residual material did not significantly alter the $\delta^{13}\text{C}$ value (Clean SWCNT $\delta^{13}\text{C} = -36.20 \pm 0.13$ ‰ (N=2)), and the average $\delta^{13}\text{C}$ values of the three bottles of the final product SWCNT-1 were very similar: -35.96 ± 0.17 ‰ (N=4), -35.97 ± 0.04 ‰ (N=2), and -36.04 ± 0.01 ‰ (N=2). The average $\delta^{13}\text{C}$ value of the three bottles of SWCNT-1 was -35.98 ± 0.11 ‰ (N=8), and little variation in the $\delta^{13}\text{C}$ value between the three bottles was observed. Although this material was not originally intended to be used as a $\delta^{13}\text{C}$ CRM [8], these initial measurements may serve as an informative $\delta^{13}\text{C}$ value for SWCNT-1. Additional analyses are planned to provide a more robust $\delta^{13}\text{C}$ value assignment to SWCNT-1, and to evaluate $\delta^{13}\text{C}$ measurement uncertainty. Further, although most CNTs are produced at high temperatures where fractionation of the starting materials is likely negligible, CNTs produced at lower temperatures [27] should be evaluated for fractionation of the carbon source material during the production process.

$\delta^{13}\text{C}$ survey of CNTs

The $\delta^{13}\text{C}$ values of commercially available CNTs are presented in Figure 3. The CNTs varied with respect to the number of walls and production method. For many of these samples, information concerning the starting materials were not available. As these processes usually involve high temperatures, the measured $\delta^{13}\text{C}$ values of the samples are assumed to reflect that of the starting material(s). Based on the $\delta^{13}\text{C}$ values of the CNTs, inferences concerning the source of the starting materials can be made, and may be used as a tool to differentiate between CNT sources.

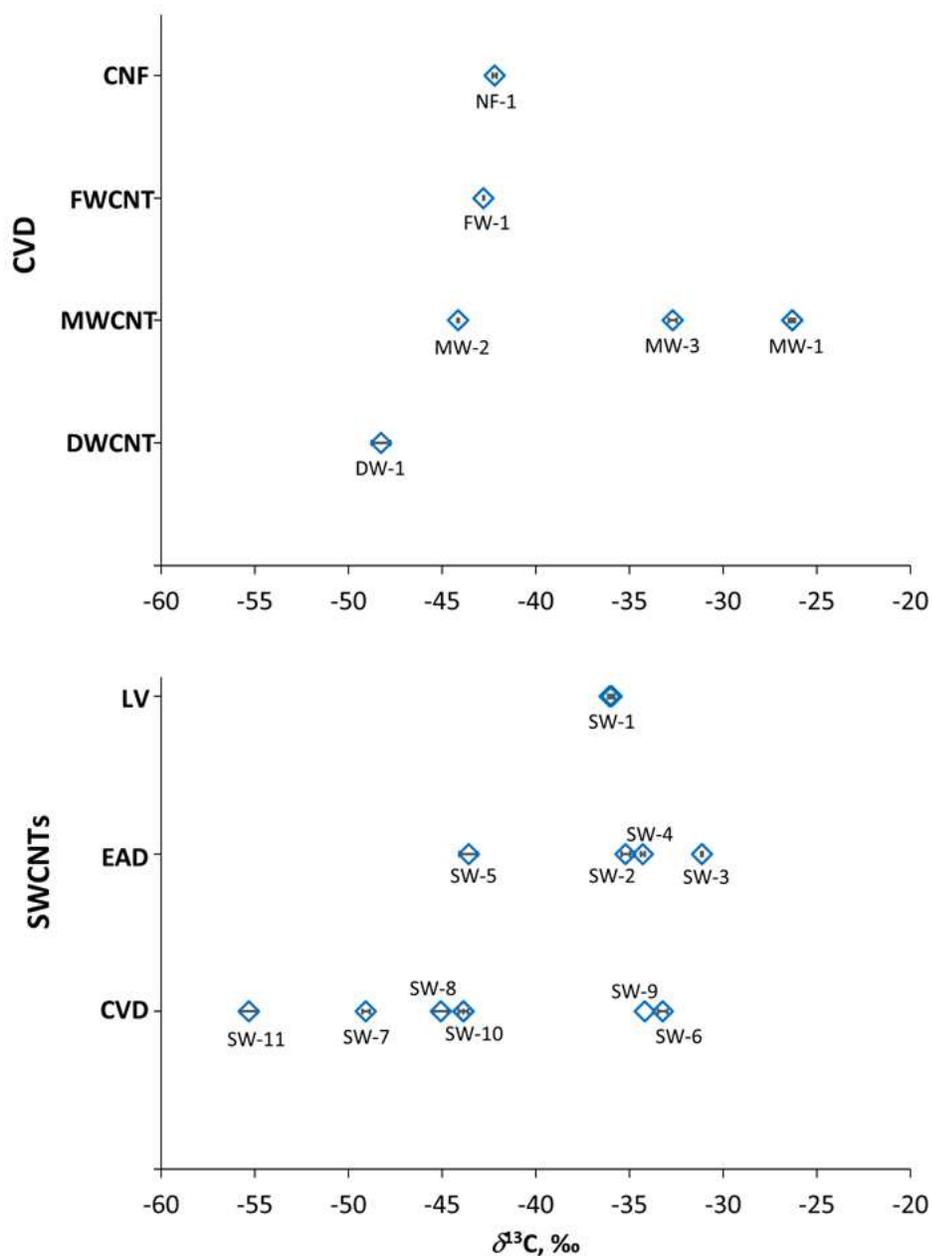


Figure 3. $\delta^{13}\text{C}$ values of single walled carbon nanotubes (SWCNTs; bottom) manufactured by different production processes (CVD = chemical vapor deposition, EAD = electric arc discharge, LV = laser vaporization), and $\delta^{13}\text{C}$ values of nanotubes with more than one wall (top) produced via the CVD method (DWCNT = double walled carbon nanotubes, MWCNT = multi-walled carbon nanotubes, FWCNT = few-walled carbon nanotubes, CNF = carbon nanofiber). Error bars represent the SD on replicate analyses.

$\delta^{13}\text{C}$ values of samples with identified carbon sources

Sample SW-1 (discussed above) had three possible carbon sources: biochar, graphite adhesive and CO, all of which likely contributed carbon to the final product. Both the HiPCO and CoMoCAT processes use CO as the starting material [9, 10] and other researchers have reported $\delta^{13}\text{C}$ values ranging from -49.8‰ to -51.7‰ from SWCNT samples produced using these methods [17]. Sample SW-11 was produced using the HiPCO method, and yielded the most negative measured $\delta^{13}\text{C}$ value measured in this study, -55.32‰ , consistent with previously published data [17]. Samples SW-9, SW-10, and FW-1 were manufactured using the CoMoCAT process. While SW-10 and FW-1 showed relatively negative $\delta^{13}\text{C}$ values of -43.86‰ and -43.85‰ (for two separate bottles of SW-10) and -42.78‰ (for FW-1), SW-9 measured a relatively more positive $\delta^{13}\text{C}$ value of -34.16 , which may reflect the extent of variation in the $\delta^{13}\text{C}$ values of the CO used in the manufacturing process.

Sample SW-5, with a $\delta^{13}\text{C}$ value of -43.59‰ , was obtained from OcSiAl, with the brand name Tuball. While the production process of this particular sample was not verified, the manufacturing process used by this company involves the use of EAD to produce plasma, and hydrocarbons between C1 and C10 can be the carbon source [28]. $\delta^{13}\text{C}$ values of methane (C1), ethane (C2), and propane (C3) in natural gas samples can range from -26‰ to -73‰ [29], and methane between -20‰ to -110‰ [26], which is consistent with natural gas as a carbon source for SW-5.

$\delta^{13}\text{C}$ values of samples with inferred carbon sources

Three other samples (SW-2, SW-3, and SW-4) were produced via the EAD method, with $\delta^{13}\text{C}$ values ranging between -31.13‰ and -35.19‰ , a similar range to that reported by other researchers (-23.5‰ to -36.7‰ [17]). The most common source material for this process is graphite [4]. For this study, three graphite samples were analyzed, with $\delta^{13}\text{C}$ values of -24.57‰ , -26.15‰ , and -27.07‰ , and graphite samples as negative as -41‰ have been reported [14]. The measured $\delta^{13}\text{C}$ values for SW-2, SW-3 and SW-4 are consistent with graphite as a source material.

Inferring Carbon Sources Based on $\delta^{13}\text{C}$ Measurements

Reliable information concerning the source materials could not be found for nine CNT samples produced via the CVD method. This method can use a wide variety of catalysts, carbon sources, and operating conditions to produce CNTs [1, 6]. Based on the measured $\delta^{13}\text{C}$ values from the samples with known or inferred carbon sources, the type of carbon source(s) were anticipated.

Both MW-3 and SW-6 had similar $\delta^{13}\text{C}$ values of -32.69‰ and -33.21‰ , respectively. SW-6 was produced via a super-growth CVD method, and previous research using this method reported the use of ethylene as the source material [30]. The $\delta^{13}\text{C}$ value of SW-6 and MW-3 is consistent with a reported $\delta^{13}\text{C}$ value of -35.2‰ for a SWCNT sample with a known ethylene source [17], which may be a likely source material for these two samples. Two different lots of sample MW-1 both had average $\delta^{13}\text{C}$ values of -26.32‰ , which were the most positive $\delta^{13}\text{C}$ values measured from this study. This relatively more positive $\delta^{13}\text{C}$ value is consistent with being derived from a plant source with a C3-based photosynthetic pathway, with a range of -21‰ to -35‰ [25].

Samples SW-7, SW-8, MW-2, DW-1 and NF-1 all demonstrated relatively negative $\delta^{13}\text{C}$ values between -42.20‰ and -49.06‰ . Of the CNTs with known carbon sources measured in this study and in the literature [17], only CNTs using CO, or perhaps methane or natural gas, had $\delta^{13}\text{C}$ values more negative than -40‰ . Therefore, we suggest that CNTs with relatively negative $\delta^{13}\text{C}$ values (for instance, those with $\delta^{13}\text{C}$ values more negative than -40‰) may use CO (or methane or natural gas) as either the sole starting material, or as was observed with SW-1, as at least one of the carbon-containing components that is incorporated into the CNT structure.

CONCLUSIONS

Stable carbon isotope analysis of both the starting materials and the final product can provide insight into the nature of the starting materials, and the mechanics of the production process. For the NRC CRM SWCNT-1, $\delta^{13}\text{C}$ measurements of the carbon-containing starting materials and samples collected at different stages throughout the production process demonstrated that three sources of carbon were likely incorporated into the final product. For some commercially available CNTs, the carbon source material was known, or could be inferred based on the production method, and in most cases were related to the source material. The $\delta^{13}\text{C}$ values of commercially available CNTs with unknown starting materials were used to infer the carbon sources of these products. Given that the starting materials, exact quantities and nature of catalysts, and production conditions used in the production of CNTs is proprietary, we suggest the use of $\delta^{13}\text{C}$ analysis may be used as a tracer to differentiate between those processes that use CO (or similarly ^{13}C -depleted carbon source(s) such as methane or natural gas), and those that do not.

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CONFLICT OF INTEREST STATEMENT

The authors declare no competing financial interest.

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