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# Blank Corrections for Ramped Pyrolysis Radiocarbon Dating of Sedimentary and Soil Organic Carbon

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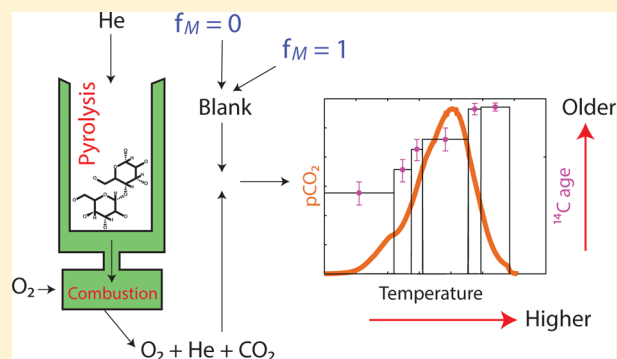
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## Supporting Information

**ABSTRACT:** Ramped pyrolysis (RP) targets distinct components of soil and sedimentary organic carbon based on their thermochemical stabilities and allows the determination of the full spectrum of radiocarbon (<sup>14</sup>C) ages present in a soil or sediment sample. Extending the method into realms where more precise ages are needed or where smaller samples need to be measured involves better understanding of the blank contamination associated with the method. Here, we use a compiled data set of RP measurements of samples of known age to evaluate the mass of the carbon blank and its associated <sup>14</sup>C signature, and to assess the performance of the RP system. We estimate blank contamination during RP using two methods, the modern-dead and the isotope dilution method. Our results indicate that during one complete RP run samples are contaminated by  $8.8 \pm 4.4 \mu\text{g}$  (time-dependent) of modern carbon (MC,  $f_M \sim 1$ ) and  $4.1 \pm 5.5 \mu\text{g}$  (time-independent) of dead carbon (DC,  $f_M \sim 0$ ). We find that the modern-dead method provides more accurate estimates of uncertainties in blank contamination; therefore, the isotope dilution method should be used with caution when the variability of the blank is high. Additionally, we show that RP can routinely produce accurate <sup>14</sup>C dates with precisions  $\sim 100$  <sup>14</sup>C years for materials deposited in the last 10 000 years and  $\sim 300$  <sup>14</sup>C years for carbon with <sup>14</sup>C ages of up to 20 000 years.



Ramped pyrolysis (RP) radiocarbon (<sup>14</sup>C) dating exploits differences in the thermochemical stability of distinct components of organic carbon to obtain the complete spectrum of <sup>14</sup>C ages that are present in a carbonaceous sample. This feature is particularly useful when we wish to isolate young constituents from older components of organic carbon within a single environmental sample. For instance, sediments typically contain autochthonous carbon that is close in age to the time of deposition, along with much older carbon that may be derived from many different sources. In the absence of <sup>14</sup>C datable macrofossils (i.e., foraminifera, seeds, etc.) a sample is treated with acid to remove carbonate minerals and the remaining organic material—termed acid-insoluble organic matter (AIOM)—is analyzed for its <sup>14</sup>C signature. Bulk AIOM dates, however, can be significantly older than the actual age of deposition of a sediment.<sup>1–4</sup> In these cases, RP offers an attractive alternative because it can provide deposition-age constraints that are up to 10 000 <sup>14</sup>C years younger than AIOM dates.<sup>5,6</sup>

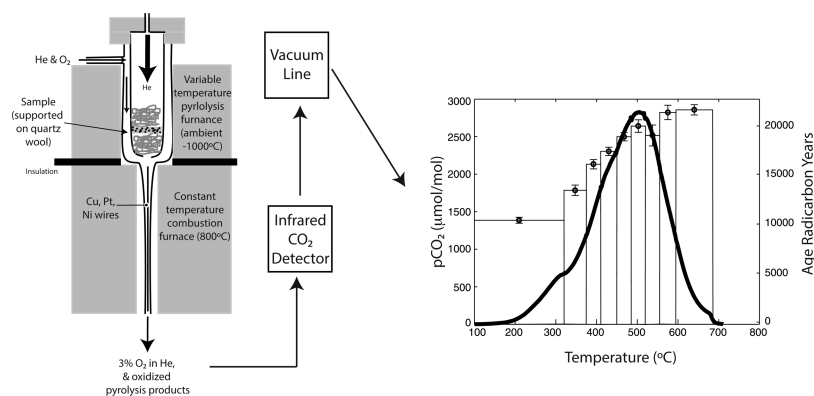
The ability of RP to distinguish between labile and refractory carbon has also been used to study the transport of organic carbon by major rivers, making use of the entire age spectrum. Rivers transport significant quantities of carbon from both the

biological and geological carbon cycles. Distinguishing between these two sources in riverine carbon has proven to be difficult; however, RP provides isotopic data on fractions of the carbon that are not otherwise extractable. For instance, Rosenheim and Galy<sup>7</sup> measured the age of the different components of particulate organic carbon (POC) transported by the Narayani tributary of the Ganges river. The authors used RP data to constrain the proportions of geologic versus biospheric carbon that are ultimately transported by the river into the ocean. In addition to riverine carbon, RP can be used to explore the dynamics of the terrestrial carbon cycle and the mechanisms responsible for the stabilization of soil organic matter (SOM). For instance, Plante et al.<sup>8</sup> used a ramped thermal analysis technique similar to RP to measure the distribution of <sup>14</sup>C ages in SOM and found that this method generates useful isotopic and chemical fingerprints that vary according to different land use practices.

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**Figure 1.** Schematic of the RP temperature furnace and an example of RP  $^{14}\text{C}$  data. The thick black line in the plot to the right shows the pattern of  $\text{CO}_2$  evolution as a sediment sample is thermally decomposed. The opposite axis shows  $^{14}\text{C}$  age determinations of different components of organic carbon, highlighting a difference of up to 10 000  $^{14}\text{C}$  years in a sediment sample. Adapted with permission from ref 5. Copyright 2008 Wiley.

Other avenues of research where RP has been used include environmental chemistry and investigations that explore the release and transport of sedimentary organic carbon in the Arctic. For example, Pendergraft et al.<sup>9</sup> used RP to separate oil contamination ( $f_M \sim 0$ ) from background organic material ( $f_M \sim 1$ ) in marsh sediments as a rapid reconnaissance tool useful to identify the extent of oil contamination from spills. In regards to the Arctic studies, Gaglioti et al.<sup>10</sup> used RP  $^{14}\text{C}$  data to investigate the response of permafrost carbon to warmer climates. They inferred that during warm periods of the Late Quaternary (i.e., Holocene Thermal Maximum, Bølling–Allerød), significantly larger amounts of old carbon were released compared to the present.

While there has been an investigation into chemical alterations that occur during RP that can affect  $^{14}\text{C}$  results,<sup>11</sup> to this point no systematic investigation has been performed on the blank contamination that occurs during RP. Blank carbon contamination invariably occurs during the processing of samples for  $^{14}\text{C}$  analysis,<sup>12–16</sup> and its presence can significantly affect the accuracy and precision of  $^{14}\text{C}$  dates including RP, especially when measuring smaller sample sizes.

Here we explore the long-term variability of procedural blank contamination during RP. Our findings characterize the size of the carbon blank and its associated  $^{14}\text{C}$  signature, allowing us to identify the procedural steps where blank contamination can be potentially reduced. Furthermore, assessing the nominal blank value allows us to evaluate the overall performance of RP, as well as the sample size limits for which meaningful  $^{14}\text{C}$  results can be obtained. Our findings are particularly useful to laboratories that lack in-house accelerator mass spectrometers (AMS), as these laboratories face particular challenges in blank quantification. For instance, these laboratories are unable to produce sufficient blank targets to assess C contamination on a timely and effective basis. Another limitation is the cost restrictions imposed by some accelerator mass spectrometry (AMS) facilities. Nevertheless, our findings emphasize the importance of pursuing blank contamination assessments, especially over long periods of time (>3 years).

## ■ EXPERIMENTAL SECTION

**Sample Preparation Procedures.** RP was conducted following the procedures previously outlined in Rosenheim et al.<sup>5</sup> Briefly, a sample is thermally decomposed in the absence of oxygen under a ramped temperature gradient ( $5\text{ }^\circ\text{C min}^{-1}$  from room temperature to  $1000\text{ }^\circ\text{C}$ ). An ultrapure helium (ultrahigh

purity, Airgas) carrier gas is used to transfer pyrolysis products to a second furnace held at  $800\text{ }^\circ\text{C}$  where products are oxidized to  $\text{CO}_2$  (Figure 1). The concentration of  $\text{CO}_2$  that evolves is recorded using an infrared  $\text{CO}_2$  detector (Sable Systems Ca-10) before the gas is cryogenically separated and collected. Samples are then routed alternatively into two nine-loop cryogenic traps in order to split them into several temperature fractions based on temperature and/or  $\text{CO}_2$  evolution (sample decomposition) patterns (Figure 1). These different temperature fractions are referred to as “temperature splits” in the remainder of this paper.

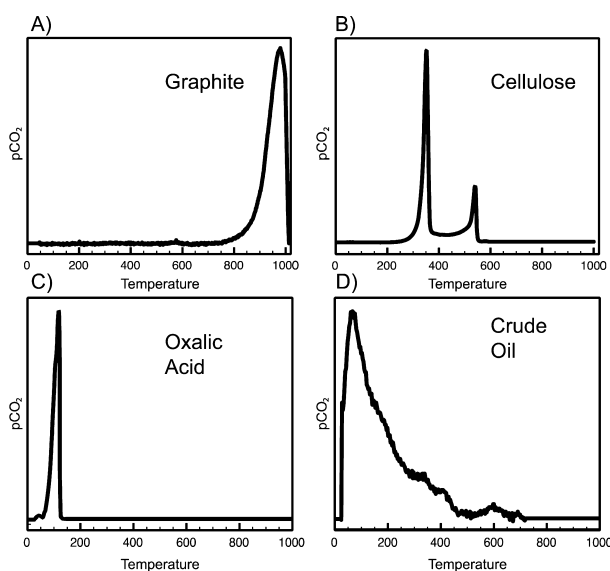
Once a  $\text{CO}_2$  gas fraction is isolated, water and non-condensable gases are removed using an additional series of traps that are cooled by liquid nitrogen or an isopropyl alcohol slush cooled to phase transition by liquid nitrogen. After this step, the mass of the gas is quantified using a capacitive diaphragm manometer and sealed into evacuated 6 mm borosilicate glass tubes with  $\sim 60\text{ mg}$  of copper oxide (Costech, part no. 11003) and  $\sim 10\text{ cm}$  of silver wire (Alfa Aesar, part no. 11470), both precombusted at  $550\text{ }^\circ\text{C}$  for 2.5 h. Finally, the sealed sample tubes are combusted at  $550\text{ }^\circ\text{C}$  for 2.5 h to remove any potential sulfur contamination,<sup>17,18</sup> and they are submitted for  $^{14}\text{C}$  measurements. The samples discussed in this paper were submitted to either the W.M. Keck Carbon Cycle Accelerator Mass Spectrometer Facility at the University of California, Irvine (KCCAMS/UCI) or to the National Ocean Sciences Accelerator Mass Spectrometry Facility at Woods Hole Oceanographic Institution (NOSAMS/WHOI).

**Blank Determination.** We estimated the mass and isotopic composition of the RP procedural blank by repeated measurements of different target sizes from two reference materials: a  $^{14}\text{C}$ -free graphite and the IAEA-C3 standard. These reference materials were used for repeat measurements over a 3 year period, so the results are useful for exploring the long-term variability of blank contamination in our laboratory. The graphite is powdered synthetic graphite from Alfa Aesar (CAS no. 7782-42-5; part no. 14734), which was baked for 2 h at  $550\text{ }^\circ\text{C}$  before each use. We confirmed its uncorrected background value at  $47\,670 \pm 2320\text{ }^{14}\text{C}$  years BP ( $n = 4, \pm 1\sigma$ ; fraction modern ( $f_M$ ) =  $0.0026 \pm 0.0013$ ) by measuring large aliquots of this sample (>0.75 mg) using the conventional sealed tube combustion method. It should be noted that we assume that the graphite is free of  $^{14}\text{C}$  and any measured quantity is, thus, the result of RP procedures and/or the closed tube combustions. Thus, the  $f_M$  value of the graphite presented

above includes the  $^{14}\text{C}$  blank that occurs during closed tube combustions. The implications of this blank assumption are discussed in the Blank Correction Procedures section. The IAEA-C3 standard is a cellulose sample distributed by the International Atomic Energy Agency (IAEA); it has a consensus  $f_M$  value of  $1.2941 \pm 0.0006$ .

Different sized aliquots of Alfa Aesar graphite and IAEA-C3 cellulose were weighed to obtain a range of  $\text{CO}_2$  pressures to produce a large array of graphitized sample masses. To minimize extraneous carbon during sample preparation, all tools used to process these samples were precombusted at  $550\text{ }^\circ\text{C}$  for 2 h. A clean pyrolysis reactor was used for every sample. Prior to each use, the quartz reactors were cleaned by rinsing with acetone and DI water and then baked at  $900\text{ }^\circ\text{C}$  for 2 h. The same preparation procedures are also used for “unknown” samples.

The  $\text{CO}_2$  that evolved during pyrolysis of Alfa Aesar graphite was collected and submitted for  $^{14}\text{C}$  analysis as single samples. The  $\text{CO}_2$  trapping started at room temperature and was stopped at the end of the pyrolysis reaction when the temperature reached  $1000\text{ }^\circ\text{C}$ . Cellulose, on the other hand, decomposes into two discrete peaks and has a markedly different pyrolysis reaction profile (Figure 2B). One peak



**Figure 2.**  $\text{CO}_2$  concentration that evolves during RP of a graphite (A), cellulose (B), oxalic acid (C), and crude oil (D). These graphs provide qualitative information on the pyrolysis kinetics of different materials, and they are used to select the location of the different temperature splits.

occurs at low temperature ( $\sim 350\text{ }^\circ\text{C}$ ) and the other at higher temperatures ( $\sim 550\text{ }^\circ\text{C}$ ). In some cases the  $\text{CO}_2$  was split into two samples, one from each peak. In other cases both peaks were combined into a single sample. One or both fractions were submitted for analysis.

The blank was quantified by two different methods. In the first approach, which was originally developed by Santos et al.,<sup>13</sup> the blank is treated as a mixture of two C components of very distinct  $^{14}\text{C}$  signatures. The first component is devoid of  $^{14}\text{C}$  (or dead), and the second component has a  $f_M$  value equal to the Ox-I standard (or modern). We refer to this approach as the “modern-dead” method in the rest of this paper. To estimate the procedural mass of the modern carbon (MC)

blank of our methods, we used several Alfa Aesar graphite  $^{14}\text{C}$  measurements, which are almost unresponsive to dead carbon (DC) contaminants but extremely sensitive to the presence of any MC inputs.

Conversely, the mass of the DC blank can be estimated by similar  $^{14}\text{C}$  measurements of reference materials with  $^{14}\text{C}$  concentrations close to the MC contamination. This is the strategy taken by Santos et al.<sup>13</sup> who used the primary oxalic acid standard Ox-I, which has a  $^{14}\text{C}$  signal very close to  $f_M = 1$ . Oxalic acid decomposes at very low temperatures ( $<150\text{ }^\circ\text{C}$ ), making it an ideal material when studying aerosol organic carbon fractions from thermal optical analysis of particulate matter on filters. Here, during RP (Figure 2C), the oxalic acid thermal decomposition was unpredictable and often very sensitive to the temperature settings of the combustion furnace. For instance, we generally observe an increase from ambient laboratory temperature to around  $80\text{--}100\text{ }^\circ\text{C}$  in the pyrolysis furnace approximately 30 min after the combustion furnace is heated to  $800\text{ }^\circ\text{C}$ . The result is that if the combustion furnace has reached  $800\text{ }^\circ\text{C}$  prior to loading the sample in the quartz reactor insert, the oxalic acid tends to partially decompose at lower temperatures. However, this does not impact environmental samples because these samples do not produce pyrolysis products at temperatures  $<100\text{ }^\circ\text{C}$ .

Cellulose, unlike oxalic acid, has a very predictable decomposition reaction that is used to verify reproducibility in the RP reactor set up. We used the IAEA-C3 cellulose reference material despite its bomb-pulse  $f_M$  value ( $f_M > 1$ ) to calculate the DC blank contamination. Thus, our measurements of IAEA-C3 are affected by both the DC and MC blank contaminant components. To estimate the mass of the DC component the cellulose results were first corrected for modern blank contamination. The remaining mismatch between the measured and consensus values were used to calculate the DC blank.

The second method used to estimate the pyrolysis blank was isotope dilution. In this method the blank is calculated by solving a set of two linear equations that are constructed using repeated measurements from two standards.<sup>12,19</sup> For instance, we can rearrange an isotope mass balance equation that describes the mixture of a sample with blank contamination into the following equation:

$$f_{m_T} = f_{m_s} - \frac{m_b(f_{m_s} - f_{m_b})}{m_T} \quad (1)$$

where  $f_{m_T}$  is the measured fraction modern,  $f_{m_s}$  is the actual (blank free) fraction modern of the sample,  $f_{m_b}$  is the fraction modern of the blank,  $m_b$  is the mass of the blank, and  $m_T$  is the total mass (sample plus blank). The variables in this equation are either known or can be calculated when two similar equations exist. In our case, this was accomplished by linear regression of the graphite and cellulose  $^{14}\text{C}$  results against the reciprocal of their sample sizes ( $1/m_T$ ). This resulted in two linear equations, one built from the graphite data and the other one from the cellulose data. The intercepts ( $f_{m_s}$ ) in these equations are an estimate of the true value of each standard. The slopes [ $m_b(f_{m_s} - f_{m_b})$ ], on the other hand, depend on the mass and  $^{14}\text{C}$  composition of the blank. These quantities were estimated by simultaneously solving the two equations.

**Uncertainties in the Blank Determination.** Uncertainties in the mass and the isotopic composition of the blank propagate directly into  $^{14}\text{C}$  age determinations and associated

uncertainties, so it is important to understand how the blank contamination varies for a specific measurement and sample preparation method. The most straightforward way to estimate the variability in the blank is by several independent estimates of its value. This is the approach we use to estimate the uncertainties in the mass of the MC and DC blank, which were obtained using the modern-dead method.

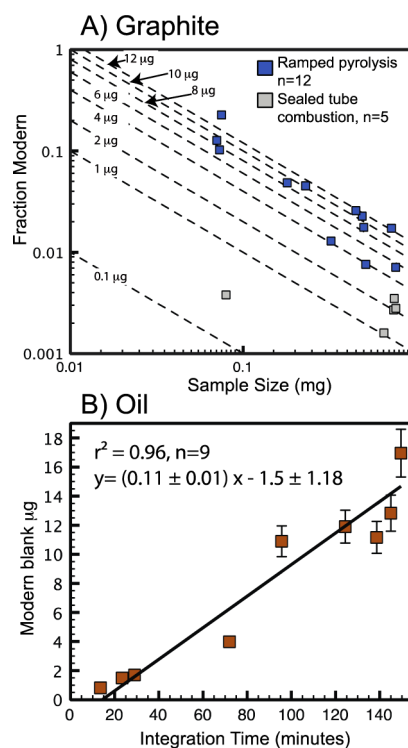
In contrast, estimating uncertainties in the isotope dilution calculated blank is not as straightforward as expected, because this method results in a single estimate. In this case, we used a Monte Carlo simulation to estimate its uncertainty. The simulation randomly resamples half of the data set and uses the resampled data to build two linear models (eq 1) that are subsequently solved to recalculate the blank. The simulation is repeated 10 000 times to obtain an average value and associated confidence intervals.

**Time Dependence of Blank.** During RP some samples begin to decompose at lower temperatures while other samples react quantitatively at much higher temperatures (Figure 1). The result is that CO<sub>2</sub> is collected for longer periods of time in some unknown samples and in some of the most thermally resistant blanks for contamination determinations. For instance, if modern contamination is the result of atmospheric leaks into the pyrolysis system, it is possible that a higher blank contamination occurs in samples integrated over a longer period of time. To test this hypothesis, we estimated the time dependence of the modern blank contamination during RP using crude oil instead of just Alfa-Aesar graphite. The refractory nature of the Alfa-Aesar graphite places its pyrolysis decomposition kinetics at much higher temperatures (Figure 2A). Conversely, crude oil collected directly from the Macondo well-head<sup>9</sup> during the 2010 BP Deepwater Horizon oil spill and provided by BP (reference material ID: SOB-20100617-032; source sample ID: ENT-052210-OL-041/043) decomposes at low temperatures (Figure 2D), similar to oxalic acid (Figure 2C). Despite the inherent difficulties in generating an RP profile for a material that starts evaporating at room temperature, the crude oil's lack of detectable <sup>14</sup>C and decomposition at low temperatures makes it an effective material to test whether blank contamination in the system is time-dependent or not.

**Validation of Blank Results.** To validate the results of the blank assessment we subjected samples with consensus <sup>14</sup>C ages to RP. Two different wood samples from the Fourth International Radiocarbon Intercomparison (FIRI) experiment were used (FIRI-H and FIRI-F with  $f_M = 0.7574 \pm 0.0002$  and  $0.5705 \pm 0.0004$ , respectively<sup>20</sup>). A portion of the wood samples was processed by an acid–base–acid (ABA) treatment involving a three-step protocol of dilute hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions. Later, both treated and untreated aliquots were subjected to RP. In addition to the FIRI samples, we processed several aliquots of the OX-I ( $f_M = 1.040 \pm 0.0020$ ) and IAEA-C7 ( $f_M = 0.4953 \pm 0.0012$ ) oxalic acid standards by RP. These samples cover a large range in <sup>14</sup>C activities, so they are suitable for accuracy and precision tests for RP dates.

## RESULTS AND DISCUSSION

**Modern Blank Estimated Using the Modern-Dead Method.** The Alfa Aesar graphite samples were contaminated with  $8.8 \pm 4.4 \mu\text{g}$  ( $1\sigma$ ) of MC during the pyrolysis runs (Figure 3A). This value is an order of magnitude larger than values observed during traditional sealed tube combustion and



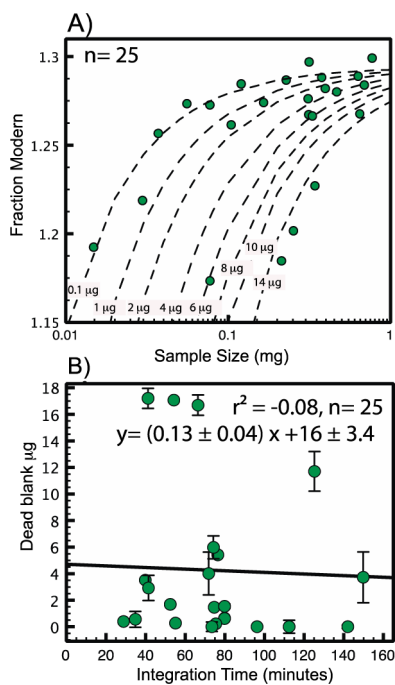
**Figure 3.** (A) Radiocarbon results from RP and conventional closed tube combustion of Alfa Aesar graphite samples (note the log–log axis in this plot). The lines show the effect of constant amounts of MC contamination. (B) MC contamination during RP of crude oil plotted against total CO<sub>2</sub> integration time. Linear model in panel B is the result of a model II linear regression model.

graphitization at other laboratories.<sup>13</sup> This is not surprising given the additional processing that samples are subjected to during RP. However, it is important to note that this value reflects blank contamination that occurs during a complete run (i.e., 25–1000 °C, with all CO<sub>2</sub> collected in a single fraction), and it may not be representative of typical samples. For instance, in previous work<sup>5–10,21</sup> generally more than five splits from one RP run were analyzed; therefore, assigning the full amount of MC blank to these samples may not be appropriate.

This possibility is what prompted us to examine the blank contamination that occurs during RP of crude oil. In these samples, we observe a strong correlation between MC contamination and the time of collection along the temperature ramp (Figure 3B). This observation coupled with the present <sup>14</sup>C composition of the atmosphere<sup>22</sup> ( $\sim f_M = 1$ ) strongly supports our suspicion that the MC blank is the result of atmospheric leaks into the pyrolysis system. There are, however, other plausible sources of MC that would result in a similar time-dependency effect. For instance, contaminants in the He carrier gas (organic compounds, CO<sub>2</sub>) can also explain our observations. However, this possibility was not directly investigated. Regardless of the source, we show that MC accumulates with time at a more or less constant rate (Figure 3B); thus, each temperature split does not contain the total blank amount that occurs during a complete run. Instead, the amount of MC each split contains depends on how long the CO<sub>2</sub> of a particular fraction spends within the pyrolysis apparatus. The time of CO<sub>2</sub> integration can be easily calculated using the known temperatures of collection over a constant temperature ramp; we use this quantity to estimate actual

amounts of MC in the different temperature splits. This approach was taken to correct the IAEA-C3 cellulose samples that were used to quantify the DC blank component.

**Dead Blank Estimated Using the Modern-Dead Method.** The IAEA-C3 cellulose samples were contaminated with  $4.2 \pm 5.5 \mu\text{g}$  ( $1\sigma$ ) of DC during the pyrolysis runs (Figure 4A). Our estimate for this component of the blank is both



**Figure 4.** (A) Radiocarbon results from RP of the IAEA-C3 cellulose. The dashed lines show the effect of  $4.6 \mu\text{g}$  of MC (the average amount present in these samples) and different amounts of DC contamination (note the log  $x$ -axis in this plot). (B) DC blank estimated with the IAEA-C3 cellulose plotted against  $\text{CO}_2$  integration time. The DC was calculated after samples were corrected for MC contamination. The MC contamination was estimated using  $\text{CO}_2$  integration times (see the Blank Correction Procedures section).

highly variable and an order of magnitude larger than what is typically observed during combustion/graphitization.<sup>13</sup> In this case, however, we do not observe a correlation between the amount of DC and  $\text{CO}_2$  integration time (Figure 4B). Instead, DC appears to be independent of the pyrolysis system, and, as a consequence, the same amount is likely present in all temperature splits from one run. Additional evidence that this is indeed the case comes from comparison of the amounts of DC in cellulose runs where the  $\text{CO}_2$  was split into two temperature splits ( $n = 20$ ) versus cases where all of the  $\text{CO}_2$  was collected together in a single split ( $n = 3$ ). The same amount of DC is present in both groups (two-sample  $t$  test,  $p = 0.61$ ); thus, the complete mass of DC contamination should be assigned to every temperature split regardless of where it was collected along the temperature ramp.

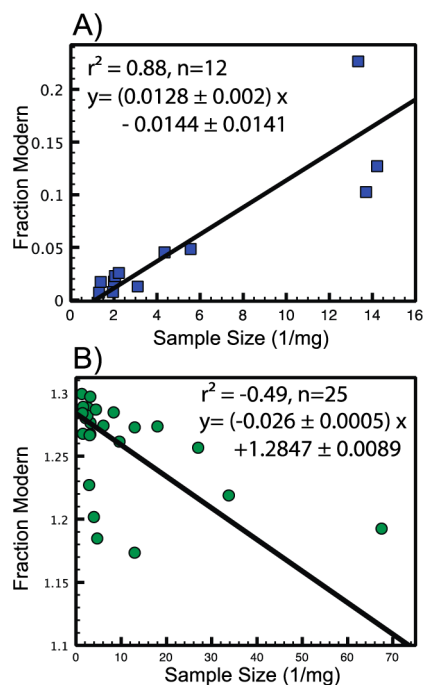
We have not yet identified a definitive source for the DC blank. The observation that it is independent of pyrolysis, however, points to the reagents used during the redundant combustion as a possible source. Other possibilities include carbon derived from the vacuum grease that is used in the various fittings throughout the pyrolysis system, and refractory (old) carbon from previous runs that may be left adhering to the high-temperature furnace between runs. Both of these

sources represent sporadic inputs of DC that may occur at any time along the temperature ramp; thus, they have the same probably of affecting one particular temperature split as all the others. Regardless of where the blank is ultimately coming from, its variability in the pyrolysis system is well-constrained by multiple independent estimates that span a 3 year period.

As previously discussed, one disadvantage of using the IAEA-C3 cellulose standard to estimate the DC blank is that both MC and DC contamination can affect the  $^{14}\text{C}$  value measured. The result is that uncertainties in the MC estimate propagate into the DC calculation. This can, however, be avoided by altering the definition given to the  $f_M$  value of the  $^{14}\text{C}$ -enriched blank component. If that component is set to equal the value of the IAEA-C3 standard, the blank is then a mixture of DC ( $f_M = 0$ ) and postmodern carbon ( $f_M = 1.2941$ ). We recalculated the blank using these constraints to check the accuracy of our initial calculation (see the Supporting Information for details). In that case, the postmodern component was estimated at  $7.1 \pm 3.5 \mu\text{g}$  ( $1\sigma$ ) and the DC component at  $5.0 \pm 5.6 \mu\text{g}$  ( $1\sigma$ ). These values correspond to a mixed (DC plus postmodern)  $f_M$  value of  $0.6 \pm 0.4$  and a total mass of  $12.1 \pm 6.1 \mu\text{g}$ . These values are nearly equal to the corresponding mixed values obtained for the modern-dead calculation ( $f_M = 0.69 \pm 0.5$  and  $13.2 \pm 7 \mu\text{g}$ ).

#### Blank Estimated Using the Isotope Dilution Method.

Using the isotope dilution method we estimate a blank contamination with a  $f_M$  value of  $1.15 \pm 0.18$  ( $1\sigma$ ) and a mass of  $9.9 \pm 4 \mu\text{g}$  ( $1\sigma$ ) (Figure 5). The  $f_M$  value of this blank is more enriched in  $^{14}\text{C}$  than the estimate obtained using the modern-dead method. The uncertainty in the mass is roughly equal to the errors estimated using the modern-dead method,



**Figure 5.** (A) Results from the graphite standard. (B) Results from the IAEA-C3 cellulose standard. The linear models (model II regressions) were used to estimate the measured  $f_M$  (blank included) value for a specific sample size. The  $f_M$  values are used to construct two equations in the form of eq 1. These two equations are then solved simultaneously to obtain the mass and the isotopic composition of the blank.

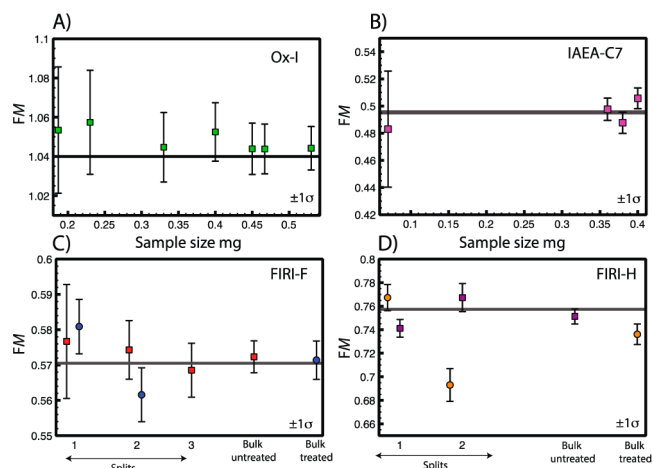
but the associated error we estimated for its isotopic composition is significantly smaller.

To reach an uncertainty estimate this method assumes that the blank was constant across multiple samples over long periods of time. This is not the case during RP, as observed using the modern-dead method. For instance, the variability seen around the linear models presented in Figure 5 is a direct result of variability in the blank. The fit of both models affects the accuracy and precision of the blank estimate. A better fit is obtained for the graphite data ( $r^2 = 0.88$ ) than the cellulose results ( $r^2 = 0.49$ ). Additionally, the intercept of the cellulose model does not accurately reflect the consensus value of the IAEA-C3 standard, and it is biased toward higher blank concentrations. Thus, the blank estimate obtained using this method is suspect because outliers significantly affect its value. The end result is that this method does not necessarily produce accurate blank estimates when the variability of the blank is high. For this reason we use the blank estimated using the modern-dead method to correct unknown samples for blank contamination.

Although our results show that the isotope dilution method is not appropriate when the variability of the  $^{14}\text{C}$  blank is high, in some cases isotope dilution may offer some advantages over the modern-dead method. For instance, it allows workers to better match the matrix of standards with samples.<sup>12</sup> However, the decision whether to use the isotope dilution method or not should be undertaken after a careful examination of the potential variability of the  $^{14}\text{C}$  blank.

**Blank Correction Procedures.** We show that the MC blank contamination during RP is time-dependent. Therefore, we use a linear model that is constrained at time zero (25 °C) and at the end of the temperature ramp (1000 °C, 195 min) to estimate the MC blank at each temperature split. The MC blank that occurs in a full pyrolysis run ( $8.8 \pm 4.4 \mu\text{g}$ ) is used for the point at 195 min, and the MC blank that occurs during closed tube combustion of graphite is used as the point at time zero. This is necessary because all RP samples are processed through a redundant combustion step. The MC blank during closed tube combustions was estimated at  $1.95 \pm 0.7 \mu\text{g}$  of C using the graphite data presented in the Blank Determination section.  $\text{CO}_2$  integration times are calculated using the known temperatures of collection, and the uncertainties in the blank concentration at 195 min is propagated to the blank estimates so that errors are in the order of  $\pm 50\% \mu\text{g}$  of C ( $1\sigma$ ). For the DC, a constant mass of  $4.2 \pm 5.5 \mu\text{g}$  ( $1\sigma$ ) was added to each temperature split because this quantity is independent of the pyrolysis system. The formulas presented by Santos et al.<sup>13</sup> were used for the blank correction, and all of the uncertainties (i.e., from blank concentrations and  $^{14}\text{C}$  analysis) were propagated into the final result using standard error propagation formulas.

**Validation of Blank Results.** Radiocarbon determinations from both oxalic acid standards (OX-I and IAEA-C7) are statistically indistinguishable from consensus values. This is true for a range of sample sizes (0.07–0.53 mg of C) that bracket typical RP samples (Figure 6, parts A and B). Similarly, after blank correction the  $^{14}\text{C}$  ages for the five temperature splits of the FIRI-F sample are indistinguishable from each other (Figure 6C), and the weighted bulk ages for both treated and untreated samples are within error from the consensus age. Moreover, the weighted bulk  $^{14}\text{C}$  age for the untreated FIRI-H aliquot is also within analytical error from the consensus value,



**Figure 6.** Blank-corrected  $^{14}\text{C}$  results from reference materials used to verify the blank estimates. The horizontal blank lines are the consensus  $^{14}\text{C}$  ages; the thickness of the line is approximately equal to the  $1\sigma$  uncertainties of the reference materials. Colored dots represent chemically treated or untreated samples subject to either closed sealed combustions and/or RP splits. The data shown here are already corrected for the blank estimated by the modern-dead method.

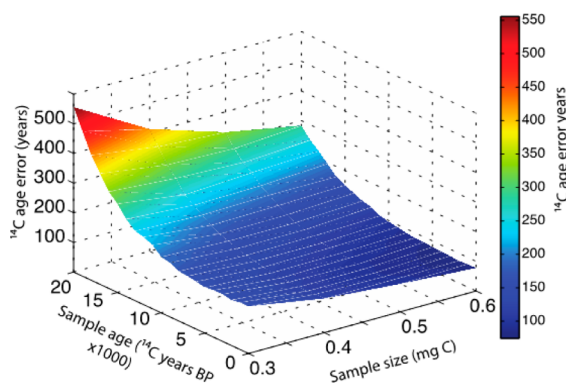
and so are the low- and high-temperature fractions of this sample (Figure 6D).

The  $^{14}\text{C}$  age obtained for the low-temperature split of the treated FIRI-H aliquot is also accurate. The same is not true, however, for the high-temperature split where the consensus age falls outside the reported  $2\sigma$  error. This temperature split is an outlier among the 19 other accurate age determinations presented in this paper. Its presence in our results underscores the importance of replicate analyses for accurate high-resolution chronology work. In sum, these results suggest that our calculated blank amounts are reasonable estimates of the actual amounts of carbon contamination that occur during RP.

**Implications for Natural Samples.** Uncertainties in the mass of blank contamination propagate directly into  $^{14}\text{C}$  determinations and result in a loss of analytical precision. The significance of larger error bars depends, of course, on the particular scientific question. For instance, in questions of  $^{14}\text{C}$  age spectrum, where the range of ages (geologic or environmental uncertainty of a bulk organic  $^{14}\text{C}$  age) is of importance, the current blank determinations are suitable. In general, previous work has shown ranges of ages in the  $10^3$  years magnitude.<sup>7,23</sup> Blank contamination that increases the error bars of a  $^{14}\text{C}$  determination to  $\sim 100$   $^{14}\text{C}$  years can almost be considered negligible. On the other hand, for questions of  $^{14}\text{C}$  chronology the blank contamination determined herein are more significant.

Several approaches can be taken to minimize the impact of blank contamination to samples of chronological importance. For instance, larger sample masses can be used (Figure 7). In most cases it is possible to routinely obtain final analytical uncertainties of  $\sim 100$   $^{14}\text{C}$  years for samples deposited in the last 10 000 years and  $\sim 300$  years for samples with  $^{14}\text{C}$  ages of 20 000 years (Figure 7); however, in cases where the percentage of organic carbon in soil/sediment is very low ( $<1\%$ ) it may not always be possible to obtain large enough temperature splits.

Therefore, when dealing with samples with  $<1\%$  C, a potentially helpful approach is to combine very small samples from multiple consecutive runs to take advantage of the time



**Figure 7.** Effect of sample  $^{14}\text{C}$  age and size on RP  $^{14}\text{C}$  age errors. The calculation assumes that a sample is contaminated with an amount of MC equal to that expected for a typical RP temperature split (one of five total splits; 20% RP temperature ramp,  $3.3 \pm 1.7 \mu\text{g}$  of MC and  $4.2 \pm 5.5 \mu\text{g}$  of DC). For a typical sample size ( $\sim 0.5 \text{ mg}$  of C) RP results in age errors of  $\sim 100$   $^{14}\text{C}$  years for sediments deposited in the last 10 000 years and  $\sim 300$   $^{14}\text{C}$  years for sediments deposited 20 000 years ago.

dependency of the MC blank, so long as combination is carried out prior to combustion of the samples over reagents and catalysts that potentially carry intrinsic blank contamination. To illustrate this situation, consider the effect of RP in sediment that was buried 8000  $^{14}\text{C}$  years ago. The carbon in this sample is a mixture of younger autochthonous carbon (representative of the time of burial) along with older allochthonous carbon of various ages. To obtain an estimate of the burial age the lowest temperature RP split is submitted for  $^{14}\text{C}$  analysis to target the youngest carbon present in the sediment sample. This split is relatively small at  $100 \mu\text{g}$  of C and represents 20% of the temperature ramp ( $\sim 40 \text{ min}$  of  $\text{CO}_2$  collection) so that the amount of MC in this fraction is just  $3.3 \pm 1.7 \mu\text{g}$  along with  $4.2 \pm 5.5 \mu\text{g}$  of DC. After blank correction this sample would have an uncertainty of  $\pm 320$   $^{14}\text{C}$  years ( $1\sigma$ ) associated with its  $^{14}\text{C}$  age. If instead, samples from five different runs were combined before the recombustion step (for a total mass of  $500 \mu\text{g}$  of C), the composite sample would contain  $10.8 \pm 5.4 \mu\text{g}$  of MC and  $4.2 \pm 5.5 \mu\text{g}$  of DC. In this case the error bars would be approximately  $\pm 180$   $^{14}\text{C}$  years ( $1\sigma$ ) years, assuming no additional contamination during mixing. In this way, altering processing techniques can mitigate the effects of blank contamination on small samples.

## CONCLUSIONS

We examined the carbon contamination that occurs during RP using the modern-dead and isotope dilution methods. Taking into account blank contamination and its uncertainties, we find that RP can routinely provide accurate  $^{14}\text{C}$  ages with uncertainties of  $\sim 100$  years for materials deposited in the last 10 000 years and  $\sim 300$  years for materials up to 20 000 years old. Additionally, our results suggest that the modern-dead method provides more realistic estimates of the uncertainties in blank contamination; thus, in cases where the variability of the blank is high the isotope dilution method should be used with caution.

## ASSOCIATED CONTENT

### Supporting Information

Formulas to calculate the blank using the IAEA-C3 cellulose and a  $^{14}\text{C}$ -dead material as the two blank components. This

material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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