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Radiocarbon measurements of black carbon in aerosols and ocean sediments

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Abstract—Black carbon (BC) is the combustion-altered, solid residue remaining after biomass burning and fossil fuel combustion. Radiocarbon measurements of BC provide information on the residence time of BC in organic carbon pools like soils and sediments, and also provide information on the source of BC by distinguishing between fossil fuel and biomass combustion byproducts. We have optimized dichromate-sulfuric acid oxidation for the measurement of radiocarbon in BC. We also present comparisons of BC ^{14}C measurements on NIST aerosol SRM 1649a with previously published bulk aromatic ^{14}C measurements and individual polycyclic aromatic hydrocarbon (PAH) ^{14}C measurements on the same NIST standard.

Dichromate-sulfuric acid oxidation belongs to the chemical class of BC measurement methods, which rely on the resistance of some forms of BC to strong chemical oxidants. Dilute solutions of dichromate-sulfuric acid degrade BC and marine-derived carbon at characteristic rates from which a simple kinetic formula can be used to calculate concentrations of individual components (Wolbach and Anders, 1989). We show that: (1) dichromate-sulfuric acid oxidation allows precise, reproducible ^{14}C BC measurements; (2) kinetics calculations give more precise BC yield information when performed on a % OC basis (vs. a % mass basis); (3) kinetically calculated BC concentrations are similar regardless of whether the oxidation is performed at 23°C or 50°C; and (4) this method yields ^{14}C BC results consistent with previously published aromatic ^{14}C data for an NIST standard.

For the purposes of intercomparison, we report % mass and carbon results for two commercially available BC standards. We also report comparative data from a new thermal method applied to SRM 1649a, showing that thermal oxidation of this material also follows the simple kinetic sum of exponentials model, although with different time constants. *Copyright © 2002 Elsevier Science Ltd*

1. INTRODUCTION

Black carbon (BC) is a term used to describe the suite of refractory carbonaceous compounds remaining after combustion of biomass and fossil fuels. BC is not one chemical compound, but instead is best understood as a continuum of reduced carbon species of varying biological and chemical refractivities. Some terms used for compounds included in the BC spectrum are soot, charcoal, char, and elemental carbon.

Environmental measurements of BC are interesting for a number of reasons. BC aerosols have been identified as a significant forcing agent in global-scale climate; however, both the recent and geologic history of BC aerosol concentrations remain highly uncertain. Besides being an atmospheric aerosol tracer, the record of BC in sediments is also a record of paleobiomass burning. Measurements of BC in continental shelf sediments may eventually address questions related to human migratory patterns and human effects on ecosystems (Bird, 1995; Suman, 1996). Since soot BC condenses with a suite of gas-phase chemicals like polycyclic aromatic hydrocarbons, Holocene and twentieth-century sediment core data can provide information on human pollution events (Gustafsson and Gschwend, 1998).

A number of measurement techniques have been developed to quantify BC. These techniques fall into 5 classes: optical (Clarke et al., 1987), thermal (Cachier et al., 1989), chemical (Gillespie, 1990; Wolbach and Anders, 1989; Verardo, 1997), spectroscopic (Smith et al., 1975), and molecular marker (Glaser et al., 1998; Elias et al., 2001). Additionally, techniques exist which blend these four measurement types (Huntzicker et al., 1982; Kuhlbusch, 1995). Optical techniques measure the blackness of a sample and provide information useful in understanding the radiative impacts of BC aerosols. Thermal methods measure BC remaining after O_2 oxidation, and chemical techniques measure BC remaining after chemical extraction. Spectroscopic techniques pinpoint a particular infrared band or NMR region characteristic of combustion products and estimate total BC concentration based on the strength of this band or frequency, after oxidative removal of operationally defined non-BC organics. Molecular marker techniques measure the concentration of a particular compound or class of compounds associated with BC and use this information to extrapolate BC concentration. For a review of BC measurement techniques, see Kuhlbusch (1998) or Schmidt and Noack (2000).

Radiocarbon measurements hold promise for deciphering the sources, fate, and transport mechanisms for BC in the environment. BC produced by contemporary biomass burning has a $\Delta^{14}C \geq 0‰$, whereas BC produced by fossil fuel combustion has a $\Delta^{14}C$ of $-1000‰$ (for information on the reporting of ^{14}C data, see Stuiver and Polach, 1977). A $\Delta^{14}C$ measurement precision of ± 6‰ or better is standard with accelerator mass spectrometry (AMS), making it feasible to separate fossil fuel

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and biomass BC sources. Similarly, once the source of BC is constrained to biomass burning (as it is before ca. 1850 A.D.), the initial $\Delta^{14}C$ BC signature at the time of combustion can be assumed to be ~modern. Intermediate pools and transport time can then be inferred from BC age (Masiello and Druffel, 1998). Not all BC measurement techniques are compatible with ^{14}C analysis because some methods (e.g., IR or optical measurements) do not physically separate BC from its organic matrix. Because thermal and chemical measurement techniques separate some BC from all other organics, these methods are candidates for BC isotopic studies.

We have optimized the Wolbach and Anders (1989) dichromate/sulfuric acid BC measurement technique for ^{14}C analysis of abyssal Holocene marine sediments. We report data on the behavior of four characteristics during BC extraction: total mass, OC, $\delta^{13}C$, and $\Delta^{14}C$. We also show that dichromate/sulfuric acid kinetic data are more accurate when reported in terms of carbon loss instead of mass loss. Mass-loss data has been reported previously in the literature (Wolbach and Anders, 1989) as has carbon-loss data (Bird and Gröcke, 1997). We compare modeling results for dichromate/sulfuric acid oxidation to those for a thermal method. Finally, we make recommendations on the reporting of dichromate/sulfuric acid kinetics designed to simplify the intercomparison of data published by different groups.

2. MATERIAL AND METHODS

The technique used here relies on the resistance of some BC to oxidation in a dilute solution of dichromate and sulfuric acid. Other organic components (notably marine kerogens) are degraded rapidly by this oxidizing solution, allowing the separation of refractory BC from marine organics (Wolbach and Anders, 1989). Before oxidation, samples are demineralized in a solution of HF and HCl to concentrate refractory carbon.

Wolbach and Anders (1989) ran dichromate/sulfuric acid oxidations at 50°C and 0.1 M $Cr_2O_7^{2-}/2$ M H_2SO_4. We ran samples under these conditions as well as at lower temperatures and at higher dichromate concentrations. Our experimental conditions are otherwise the same as Wolbach and Anders (1989), with the modification of using Teflon tubes instead of glass for oxidation. Teflon centrifuge tubes (Nalge PFE Oak Ridge centrifuge tubes, 40 mL) are inert to HF and dichromate/sulfuric acid, allowing demineralization and oxidation in the same container. This reduces mass and isotopic errors derived from sample handling. The disadvantage of Teflon tubes is their absorption and desorption of atmospheric H_2O, which significantly affects their mass in the first 2 h after drying under vacuum. This problem can be avoided by taking measurements after tubes have been allowed to equilibrate with atmospheric water vapor for 2 h as routinely done here. All reaction temperatures reported here are ± 5°C, which was the stability of our dry bath (in the case of 50°C samples) and the variability of room temperature in our lab (in the case of 23°C samples). BC has been implicated as a component of some of the Earth's humic (base-soluble) carbon pools (Haumaier and Zech, 1995), and because of this, we chose not to add a final base rinse to this method, as has been suggested by Bird and Gröcke (1997).

The addition of HF to samples containing any acid-soluble calcium (i.e., from $CaCO_3$ in sediments) causes the precipitation of CaF_2, a white mineral that is difficult to dissolve. To avoid the production of excessive amounts of CaF_2, samples were always treated with 6 N HCl before treatment with HF. A typical 23°C pretreatment involved three to four rinses with 6 N HCl, including at least one overnight soaking. This was followed by three to four rinses with ultrahigh purity water (to remove calcium ions brought into solution by the HCl) and then two to three rinses with 50% HF/10% HCl, again including at least one overnight soak. During the demineralization step and following oxidation, it is essential to keep the sample pH below 7, as some components of BC are soluble at neutral and basic pH.

We used four different test materials: a standard ocean sediment from the deep Northeast Pacific, lampblack to represent fossil-fuel BC, coconut charcoal (both purchased from Fisher Scientific) to represent BC produced from biomass combustion, and NIST standard 1649a, an urban atmospheric aerosol. We collected our standard sediment from Station M, a long-term oceanographic time series site (Smith et al., 1994). We recovered a box core on October 11, 1996 from 34°55.87′N, 123°1.29′W, homogenized approximately the 5- to 12-cm horizon, and stored this sample frozen at −20°C until use.

Before isotopic analysis, samples were combusted in sealed quartz tubes at 850°C with CuO and Ag (prefired to 550°C), and the resulting CO_2 was split for $\delta^{13}C$ and $\Delta^{14}C$ analysis. CO_2 for ^{14}C measurement was converted to graphite by H_2 reduction on a cobalt catalyst (Vogel et al., 1987) and ^{14}C content was measured by AMS.

3. RESULTS AND DISCUSSION

3.1. Experiments at 0.25 M $Cr_2O_7^{2-}$ and 23°C

These experiments were conducted to determine the response of organic carbon (OC) in Holocene Pacific sediments to dichromate oxidation and to determine analytical reproducibility. We demineralized and oxidized a duplicate pair of samples from the standard Pacific sediment at 23°C with 0.25 M $Cr_2O_7^{2-}/2$ M H_2SO_4. These samples were subjected to repeated oxidation with each step including the following: (1) soaking in excess oxidant for a measured length of time, (2) rinsing four times in high purity water, and (3) drying to a constant weight under vacuum. Samples were weighed and split for $\delta^{13}C$, $\Delta^{14}C$, and elemental analysis, after which the next oxidation step was begun. Care was taken to weigh samples before and after splitting for isotopic measurements so that % mass change per oxidation step could be determined accurately. Sample suspensions were centrifuged at 4000 rpm for 10 min, and the supernatant was then removed with glass pipettes (prefired at 550°C). The initial amount of sample (~10 g dry sediment) was sufficient to continue oxidation for a total of 675 h. Overall, a total of nine oxidative steps were performed on these two samples (at 0.5, 1.5, 3.5, 8.5, 49, 86.5, 127, 200, 415, and 675 h). We present these data as fractional mass recovery for intercomparison with previously published data (Wolbach and Anders, 1989).

Sample mass was constant after ~50 h of oxidation (Fig. 1a), but the fraction of carbon in the sample continued to fall throughout the 675 h of oxidation (Fig. 1b). Loss of carbon during oxidation was compensated for by ingrowth of another substance, most likely oxygen. Sample $\delta^{13}C$ dropped rapidly in the beginning of oxidation, but reached a plateau at −24 ± 2‰ between 200 and 675 h. Like the $\delta^{13}C$ profile, the $\Delta^{14}C$ profile dropped rapidly and then reached a plateau near −500‰ between 200 and 675 h. There was a slight decrease in $\delta^{13}C$ and $\Delta^{14}C$ during this time period.

Because the samples were run under duplicate experimental conditions, data from these experiments can be used to estimate the reproducibility of fractional mass, OC, $\delta^{13}C$, and $\Delta^{14}C$ measurements. Table 1 shows the data from this pair of experiments, along with average and standard deviation values for each pair of data. Because individual pairs of data are not independent from other pairs, they cannot be combined in a larger precision analysis. However, an independent calculation of precision can be made for each set of duplicate pairs. The
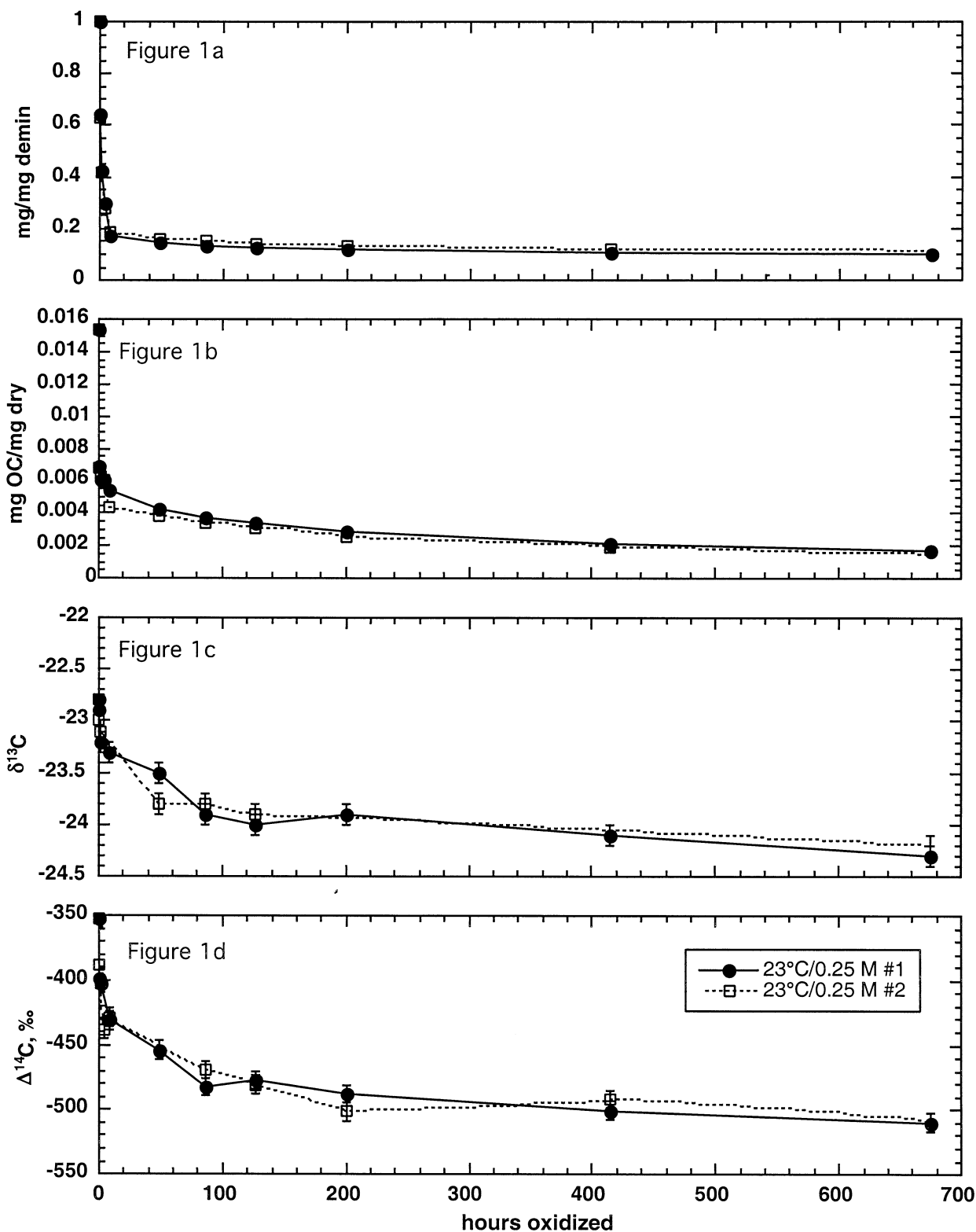
Fig. 1. (a) Fractional yield of demineralized material vs. time in oxidant solution for duplicate reactions at 23°C and 0.25 M $Cr_2O_7^{2-}$/2M H_2SO_4. Demineralized material is typically 1 to 4%; of the original dry sediment mass and is composed of refractory minerals and acid-soluble OC. (b) Yield of OC (mg) per initial dry sediment mass (mg) vs. time in oxidant solution for duplicate reactions at 23°C and 0.25 M $Cr_2O_7^{2-}$/2 M H_2SO_4. The first data point on this graph is 0.0154, because before demineralization, this sediment was 1.54% weight OC. (c) $\delta^{13}C$ of oxidized material vs. time in oxidant solution for duplicate reactions at 23°C and 0.25 M $Cr_2O_7^{2-}$/2 M H_2SO_4. (d) $\Delta^{14}C$ of oxidized material vs. time in oxidant solution for duplicate reactions at 23°C and 0.25 M $Cr_2O_7^{2-}$/2 M H_2SO_4.

Table 1. Data accompanying Figures 1a-1d. Mass yield refers to the fractional recovery of initial demineralized material; OC yield refers to the yield of carbon per original dry sediment mass.

Hours in Oxidant	#1 Mass Yield	#2 Mass Yield	Average	Std. Error	Hours in Oxidant	#1 δ^{13}C	#2 δ^{13}C
0					0		−22.8
0.5	0.643	0.632	0.637	0.006	0.5	−22.9	−23.0
1.5	0.424	0.415	0.420	0.005	1.5	−23.2	−23.1
3.5	0.298	0.276	0.287	0.011	3.5		−25.2
8.5	0.174	0.186	0.180	0.006	8.5	−23.3	
49	0.148	0.162	0.155	0.007	49	−23.5	−23.8
86.5	0.135	0.150	0.143	0.007	86.5	−23.9	−23.8
127	0.129	0.142	0.135	0.007	127	−24.0	−23.9
200	0.118	0.131	0.124	0.007	200	−23.9	−24.7
415	0.106	0.121	0.114	0.007	415	−24.1	
675	0.098	0.114	0.106	0.008	675	−24.3	−24.2

Hours in Oxidant	#1 OC/dry	#2 OC/dry	Average	Std. Error	Hours in Oxidant	#1 Δ^{14}C	#2 Δ^{14}C
0					0		−352
0.5	0.00691	0.00680	0.0069	0.00006	0.5	−398	−388
1.5	0.00604	0.00630	0.0062	0.0001	1.5	−403	−403
3.5	0.00605	0.00608	0.0061	0.00001	3.5		−438
8.5	0.00540	0.00433	0.0049	0.0005	8.5	−431	−429
49	0.00420	0.00386	0.0040	0.0002	49	−454	
86.5	0.00373	0.00340	0.0036	0.0002	86.5	−483	−469
127	0.00338	0.00308	0.0032	0.0002	127	−477	−480
200	0.00291	0.00253	0.0027	0.0002	200	−488	−502
415	0.00216	0.00189	0.0020	0.0001	415	−501	−492
675	0.00169	0.00149	0.0016	0.0001	675	−510	−509

oxidation step to 415 h was the most relevant pair of data points, as this timestep corresponded to experimental conditions used for routine sample analysis (Masiello and Druffel, 1998). When data were not available at 415 h (as for δ^{13}C) we used the 675-h data pair because the changes in mass, %C, and isotopic properties were small between 415 and 675 h. We therefore report precisions of: (a) ± 0.007 for mass, (b) ± 0.0001 (~10%) for OC, (c) ± 0.1‰ for δ^{13}C, and ± 5‰ for Δ^{14}C.

3.2. Experiments at 0.25 $Cr_2O_7^{2-}$ and 0.10 M $Cr_2O_7^{2-}$ at 50°C

We conducted a series of experiments to compare our higher $Cr_2O_7^{2-}$ concentration (0.25 M) and lower temperature conditions with the original conditions of Wolbach and Anders (1989). Aliquots of standard Northeast Pacific sediment (~10 g dry sediment) were oxidized and split as described for the 23°C experiments, with oxidation splits taken at 0.5, 3, 9, 23, 61, 184, and 423 h. Reactions at 50°C progressed more rapidly, and as a result, there was only enough material to continue the oxidation for 423 h. In general, we observed an increase in reaction rate when reaction temperature increased, but no effect as oxidant concentration increased. An oxidant concentration effect was not expected, because all reactions were conducted in the presence of excess $Cr_2O_7^{2-}$.

While the mass recovery results (Fig. 2a) are virtually identical under all conditions, the OC results (Fig. 2b) are not the same. Sedimentary carbon oxidized more rapidly (Fig. 2b) and reached a lower C concentration at 50°C compared to 23°C at similar timesteps. The similarity of the mass results at 50 and

23°C was due to the different production rates of CaF_2 in each reaction tube during the demineralization step. This was apparent from the sample color (white mineral was visible) as well as from the initial demineralized sample %C, which varied by 3% among samples. The larger concentrations of CaF_2 in samples processed at 50°C masked differences in oxidation rates. Figure 2a,b shows the advantage of reporting data in terms of carbon concentration change.

The δ^{13}C and Δ^{14}C values dropped more rapidly at 50°C than at 23°C (Fig. 2c,d). The Δ^{14}C values of reactions at 50 and 23°C are similar at 0.25 M $Cr_2O_7^{2-}$, but appear lower at 50°C and 0.1 M $Cr_2O_7^{2-}$. This difference likely results from Δ^{14}C measurement error caused by small sample sizes for the 180- and 220-h samples at 0.1 M $Cr_2O_7^{2-}$ (0.1–0.2 mg C).

Reactions at 50°C/0.25 M $Cr_2O_7^{2-}$ and 50°C/0.10 M $Cr_2O_7^{2-}$ were performed in duplicate, similar to the sample pair analyzed at 23°C/0.25 M $Cr_2O_7^{2-}$ (Table 2a,b). Precision calculated from these duplicate analyses at 50°C/0.25 M $Cr_2O_7^{2-}$ (at 423 h) were (a) ± 0.08 for mass and (b) ± 0.00003 (~6%) for OC. Corresponding precisions at 50°C/0.10 M $Cr_2O_7^{2-}$ (423 h) were (a) ± 0.03 mass and (b) ± 0.00001 (~1%) OC. Because of the expense associated with isotopic measurements, δ^{13}C and Δ^{14}C were measured on only single members of each pair of samples. However, we show below that concentration of $Cr_2O_7^{2-}$ does not influence the reaction rate in this system as long as it is present in excess (as it was in all samples here). Because of this, we can compare data pairs under different concentration conditions (i.e., OC/dry at 184 h/0.25 M $Cr_2O_7^{2-}$ and OC/dry at 184 h/0.10 M $Cr_2O_7^{2-}$). Comparisons made at 184 h (due to incomplete data at 423 h) indicate the following
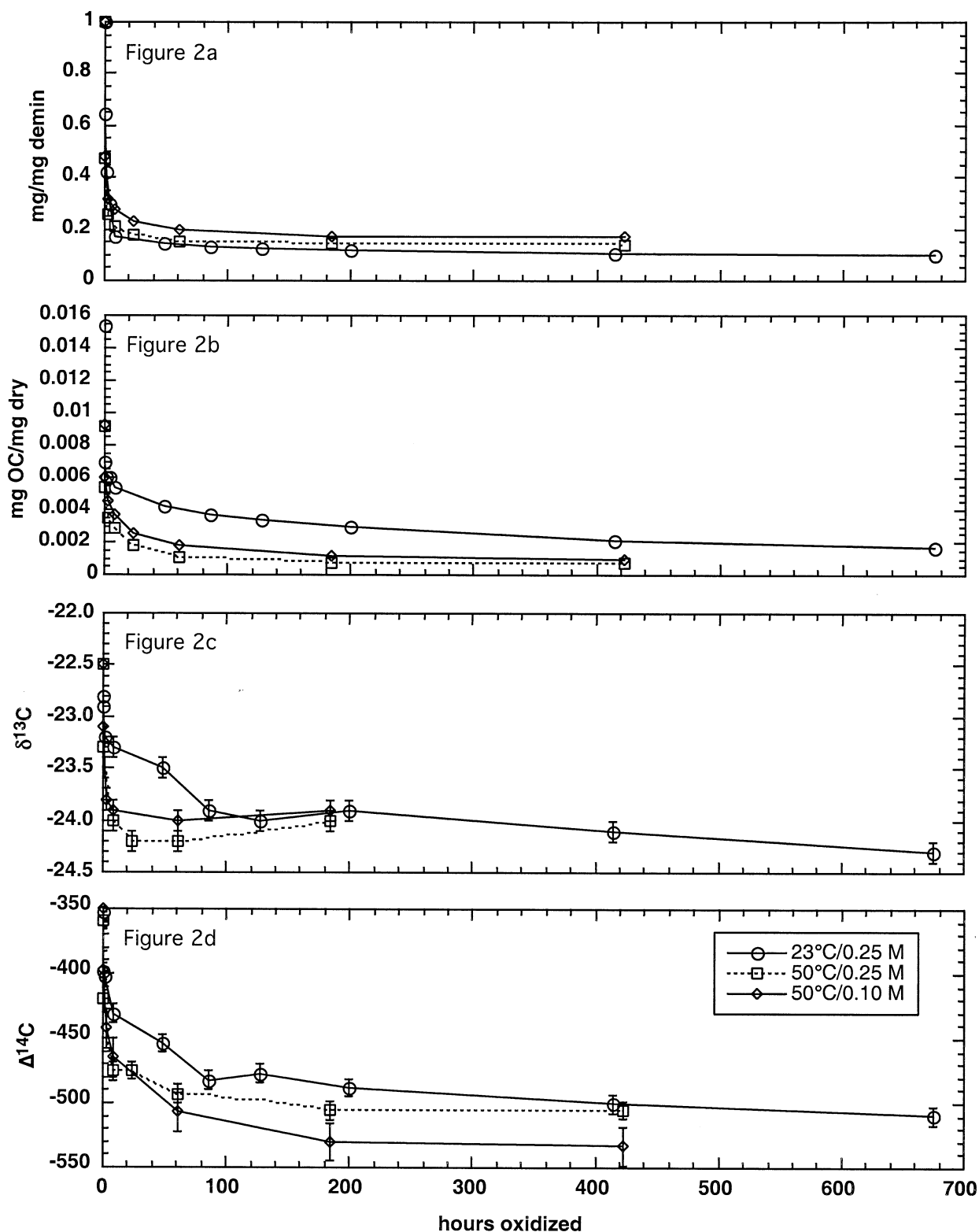
Fig. 2. (a) Fractional yield of demineralized material vs. time in oxidant solution for duplicate reactions at 23°C and 0.25 M $Cr_2O_7^{2-}$/2 M H_2SO_4, 50°C and 0.25 M $Cr_2O_7^{2-}$/2 M H_2SO_4, and 50°C and 0.10 M $Cr_2O_7^{2-}$/2 M H_2SO_4. (b) Yield organic carbon (mg) per initial dry sediment mass (mg) vs. time in oxidant solution for reactions at 23°C and 0.25 M $Cr_2O_7^{2-}$/2 M H_2SO_4, 50°C and 0.25 M $Cr_2O_7^{2-}$/2 M H_2SO_4, and 50°C and 0.10 M $Cr_2O_7^{2-}$/2 M H_2SO_4. (c) δ^{13}C of oxidized material vs. time in oxidant solution for reactions at 23°C and 0.25 M $Cr_2O_7^{2-}$/2 M H_2SO_4, 50°C and 0.25 M $Cr_2O_7^{2-}$/2 M H_2SO_4, and 50°C and 0.10 M $Cr_2O_7^{2-}$/2 M H_2SO_4. (d) Δ^{14}C of oxidized material vs. time in oxidant solution for reactions at 23°C and 0.25 M $Cr_2O_7^{2-}$/2 M H_2SO_4, 50°C and 0.25 M $Cr_2O_7^{2-}$/2 M H_2SO_4, and 50°C and 0.10 M $Cr_2O_7^{2-}$/2 M H_2SO_4.

Table 2a. Data accompanying Figures 2a and 2b; experiments at 50°C and 0.25 M $Cr_2O_7^{2-}$/2M H_2SO_4. Mass yield refers to the fractional recovery of initial demineralized material; OC yield refers to the yield of carbon per original dry sediment mass.

Hours in Oxidant	#3 Mass Yield	#4 Mass Yield	Average	Std. Error
0	1	1	1	0
0.5	0.532	0.474	0.50	0.03
3	0.380	0.256	0.32	0.06
9	0.337	0.213	0.27	0.06
23	0.321	0.175	0.25	0.07
61	0.312	0.151	0.23	0.08
184	0.303	0.146	0.22	0.08
423	0.298	0.140	0.22	0.08

Hours in Oxidant	#3 OC/dry	#4 OC/dry	Average	Std. Error
0	0.00949	0.00917	0.0093	0.0002
0.5	0.00566	0.00538	0.0055	0.0001
3	0.00396	0.00345	0.0037	0.0003
9	0.00310	0.00282	0.0030	0.0001
23	0.00172	0.00180	0.00176	0.00004
61	0.00093	0.00111	0.00102	0.00009
184	0.00073	0.00080	0.00076	0.00003
423	0.00066	0.00072	0.00069	0.00003

isotopic precisions: (a) $\delta^{13}C \pm 0.1‰$ and (b) $\Delta^{14}C \pm 20‰$ (Table 2c).

3.3. Reaction-Rate Models

$Cr_2O_7^{2-}$/H_2SO_4 solutions will eventually digest virtually all types of environmental OC, including BC. The usefulness of $Cr_2O_7^{2-}$/H_2SO_4 in BC measurement lies in its slow digestion of BC compared to other organic carbon compounds. Previously, it has been shown that fractional mass loss can be modeled as a first order, multicomponent system (Wolbach and Anders,

Table 2b. Data accompanying Figures 2a and 2b; experiments at 50°C and 0.10 M $Cr_2O_7^{2-}$/2M H_2SO_4.

Hours in Oxidant	#5 Mass Yield	#6 Mass Yield	Average	Std. Error
0	1	1	1	0
0.5	0.482	0.503	0.49	0.01
3	0.319	0.179	0.25	0.07
9	0.274	0.162	0.22	0.06
23	0.231	0.139	0.18	0.05
61	0.196	0.122	0.16	0.04
184	0.171	0.117	0.14	0.03
423	0.169	0.114	0.14	0.03

Hours in Oxidant	#5 OC/dry	#6 OC/dry	Average	Std. Error
0	0.00931	0.00948	0.00940	0.00008
0.5	0.00596	0.00639	0.00618	0.00022
3	0.00453	0.00443	0.00448	0.00005
9	0.00365	0.00352	0.00358	0.00006
23	0.00253	0.00258	0.00256	0.00003
61	0.00182	0.00170	0.00176	0.00006
184	0.00115	0.00112	0.00113	0.00001
423	0.00098	0.00099	0.00098	0.00001

Table 2c. Data accompanying Figures 2c and 2d.

Hours in Oxidant	50°C/0.25M $\delta^{13}C$	50°C/0.10M $\delta^{13}C$	Average	Std. Error
0	−22.5			
0.5	−23.3	−23.1	−23.2	0.1
3		−23.8		
9	−24	−23.9	−24.0	0.1
23	−24.2			
61	−24.2	−24	−24.1	0.1
184	−24	−23.9	−24.0	0.1
423				

Hours in Oxidant	50°C/0.25M $\Delta^{14}C$	50°C/0.10M $\Delta^{14}C$	Average	Std. Error
0	−359	−350	−355	5
0.5	−420	−398	−409	11
3		−442		
9	−475	−465	−470	5
23	−475			
61	−493	−507	−500	7
184	−506	−530	−518	12
423	−505	−533	−519	14

1989). This observation means that the demineralized material behaves as though it were composed of a number of compounds which are each digested independently according to the equation $N = N_o e^{-kt}$, where N_o is the amount of compound class N present in the system before oxidation and $t_{1/2} = \ln(2/k)$. First-order approximations dependent only on sample concentration can be used if an excess of $Cr_2O_7^{2-}$/H_2SO_4 is maintained.

We modeled the mass, OC, $\delta^{13}C$, and $\Delta^{14}C$ trends for our Northeast Pacific standard sediments with one-, two-, three-, and four-term exponential fits. This modeling was performed with Kaleidagraph software using the Levenberg-Marquardt algorithm (Press et al., 1992) to approximate curve fits. We chose not to add an initial constant term (e.g., adding an A in $N = A + N_o e^{-kt}$) as this would have required the assumption of a component in the reaction system totally inert to $Cr_2O_7^{2-}$/H_2SO_4; no environmental carbon compound has ever been shown to have this property. In the analysis below, we begin by discussing modeling results for mass data to compare our results with those published by Wolbach and Anders (1989) for Cretaceous-Tertiary clays, black carbon standards, and kerogens. Then we focus on the OC results, as this is a more meaningful way to describe our system and compare it with organic fraction data published for sediment from this site (Wang et al., 1996). It is essential to use mathematical models to fit these data, because manual fits of two or more exponential terms cannot be performed accurately (Van Liew, 1962). Exponential fits for OC and mass data produced significant values; however, it was not possible to model $\delta^{13}C$ and $\Delta^{14}C$ data in a statistically significant way.

3.3.1. Mass-based results

All Northeast Pacific sediment samples were best fit by a three-term exponential decay equation ($N = N_{o1} e^{-k1t} + N_{o2} e^{-k2t} + N_{o3} e^{-k3t}$), with R^2 values of 0.991 for 50°C/0.25 M, 0.999 for 50°C/0.10 M, and 0.999 for 23°C/0.25 M (Table

Table 3. Half-lives and fraction of original organic carbon calculated from mass yield. Half-lives are reported in hours. There are no long-lived components in the three kerogen samples. Charcoals, bone black, and norite samples were only oxidized with one step; 1st order kinetics were assumed (Wolbach and Anders, 1989).

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Sample	Reaction T	[Dichromate]	$t_{1/2}$ Long	±	Fract. Long	±
NE Pacific sediment	50°	0.25	957	591	0.18	0.04
NE Pacific sediment	50°	0.10	2270	922	0.19	0.01
NE Pacific sediment	23°	0.25	1100	173	0.142	0.005
Sample	Reaction T	[Dichromate]	$t_{1/2}$ Med	±	Fract. Med	±
NE Pacific sediment	50°	0.25	22	21	0.3	0.6
NE Pacific sediment	50°	0.10	12	2	0.15	0.01
NE Pacific sediment	23°	0.25	2.4	0.2	0.42	0.03
Sample	Reaction T	[Dichromate]	$t_{1/2}$ Short	±	Fract. Short	±
NE Pacific sediment	50°	0.25	0.2	0.1	0.6	0.6
NE Pacific sediment	50°	0.10	0.2	0.0	0.66	0.01
NE Pacific sediment	23°	0.25	0.30	0.03	0.44	0.03
Previously Published Half-Lives						
Sample	Reaction T	[Dichromate]	$t_{1/2}$ Long	±	Fract. Long	±
Woodside creek K-T clay	50°	0.10	573	39	0.20	0.01
Woodside creek K-T clay	85°	0.10	66	2	0.26	0.01
Charcoal briquette	50°	0.10	860			
Cocoanut charcoal	50°	0.10	2000			
Bone black	50°	0.10	910			
Norite	50°	0.10	810			
Sample	Reaction T	[Dichromate]	$t_{1/2}$ Med	±	Fract. Med	±
Woodside creek K-T clay	50°	0.10	52	7	0.10	0.02
Woodside creek K-T clay	85°	0.10	8	1	0.07	0.01
Kerogen type I	50°	0.10	5		0.02	
Kerogen type II	50°	0.10	41		0.59	
Kerogen type III	50°	0.10	180		0.100	
Sample	Reaction T	[Dichromate]	$t_{1/2}$ Short	±	Fract. Short	±
Woodside creek K-T clay	50°	0.10	6	2	0.71	0.02
Woodside creek K-T clay	85°	0.10	3	1	0.68	0.01
Kerogen type I	50°	0.10	1		0.98	
Kerogen type II	50°	0.10	3		0.41	
Kerogen type III	50°	0.10	8.00		0.900	

3). A three-term fit partitions the samples into three components, with short, medium, and long half-lives with respect to $Cr_2O_7^{2-}/H_2SO_4$ oxidation. Additionally, the N_o value for each component gives its percentage of the original demineralized mass.

On a mass basis, the long-lived component has a half-life of between 957 and 2200 h with respect to $Cr_2O_7^{2-}/H_2SO_4$ oxidation. Published half-lives for four black carbon samples range from 860 to 2000 yr (Table 3) in excellent agreement with our data. In contrast, three previously studied kerogen samples (Table 3) had no long-lived components. Their most-resistant components (under $t_{1/2}$ medium, Table 1) exhibit half-lives of 5 to 180 h, depending on kerogen type. We conclude that our longest-lived component is not kerogen because it reacts at least an order of magnitude more slowly than kerogens (Wolbach and Anders, 1989).

3.3.2. Comparison of experiments at different temperatures and oxidant concentrations

Isotopic reproducibility is improved when $Cr_2O_7^{2-}/H_2SO_4$ oxidations are performed at room temperature (23°C) (see Table 1 and section 1); it is also more convenient to work at 23°C. Additionally, excess oxidant can be maintained with fewer rinses if reactions are performed at higher concentrations. This reduces sample handling and experimental error. To insure that our lower temperature and higher oxidant experiments gave valid results, we analyzed our Northeast Pacific standard sediment at 0.10 M $Cr_2O_7^{2-}/H_2SO_4$ and 50°C, at 0.25 M $Cr_2O_7^{2-}/H_2SO_4$ and 50°C, and at 0.25 M $Cr_2O_7^{2-}/H_2SO_4$ and 23°C (Table 3). Within error, there is no difference in the calculated half-life of the longest-lived component under this range of conditions. Additionally the yield of the longest-lived

Table 4. Reproducibility of half-life calculations at 23°C/0.25 M based on OC yield data. Half-lives are reported in hours.

Sample	$t_{1/2}$ Long	±	Long-Lived Fraction of SOC	±
#1	527	60	0.25	0.01
#2	421	69	0.25	0.02

Sample	$t_{1/2}$ Medium	±	Medium-Lived Fraction of SOC	±
#1	24	5	0.15	0.01
#2	4	1	0.21	0.04

Sample	$t_{1/2}$ Short	±	Short-Lived Fraction of SOC	±
#1	0.142	0.001	0.60	0.01
#2	0.07	0.05	0.54	0.04

component is quite similar under all three conditions (14–19%). We conclude from this that 0.25 M $Cr_2O_7^{2-}/H_2SO_4$ at 23°C is an acceptable substitute for 0.10 M $Cr_2O_7^{2-}/H_2SO_4$ at 50°C.

3.3.3. Reproducibility of 0.25 M $Cr_2O_7^{2-}$, 23°C experiments

In this section, we discuss the reproducibility of OC data at 0.25 M $Cr_2O_7^{2-}$, 23°C, and compare the breakdown of carbon compounds with organic fractions results from sediment collected at the same site. Although mass-based kinetics data are useful for comparison with previously published results, we prefer to use the OC-based results to analyze this system for three reasons: OC-normalized data (1) are not affected by production of CaF_2 during demineralization, (2) are not affected by ingrowth of oxygen during oxidation, and (3) provide a breakdown of sedimentary OC classes that can be compared to organic fractions data.

Table 4 shows duplicate modeling results for samples oxidized at 23°C and 0.25 M. A three-term exponential curve best fits these samples, with an R^2 of 0.999 for sample #1 and an R^2 of 0.997 for sample #2. As described previously, a three-term exponential fit partitions the samples into carbon classes with short, medium, and long reaction half-lives.

The short-lived component makes up 54 to 60% of the total sedimentary OC and has a half-life of 0.07 to 0.14 h (4.0–8.5 min). The medium-lived component makes up 15 to 21% of sedimentary OC and has a half-life of 4 to 24 h, whereas the long-lived component composes 25% of sedimentary OC and had a half-life of 421 to 527 h. The reproducibility in measurement of the half-life and sample fraction of the long-lived component (BC) is excellent, with both samples giving the same results, within error. The short- and medium-lived components have half-lives more than 20 times shorter than the long-lived, BC fraction, making possible physical separation of the sample into BC and non-BC OC components.

Half-life and kinetic data for sample #1 listed in Tables 3 and 4 are not the same. Table 3 half-lives are calculated on a mass basis whereas Table 4 half-lives are calculated based on OC. Results in Tables 3 and 4 are different because the ingrowth of oxygen during BC oxidation masks the slow loss of carbon in

mass-based analysis. Although this ingrowth is highly reproducible and does not affect the ability of this method to distinguish BC from non-BC components, it does interfere with the accurate calculation of half-lives on a mass basis; mass-based half-lives and kinetic fractions are an underestimate of BC in the system. Following organic fraction discussion, data will be OC-normalized.

3.3.4. Comparison with organic fractions data from the same site

The three kinetic classes of OC in Station M sediment can be compared with organic fraction data from this site (Wang et al., 1996). Wang et al. (1996) found that Station M sediment was composed of 14% carbohydrates, 17% amino acids, 3% lipids, and 49% acid-insolubles (components sum to 83%, the total %C recovery in these organic fractions experiments). BC, the long-lived component in this sediment, is 25% of the SOC and falls within the acid-insoluble class. Our unidentified medium-lived component is also acid-insoluble and averages 17% of the SOC. These two component classes sum to 43% of the SOC, close to the Wang et al. (1996) finding of 49% acid-insoluble carbon. The strength of the $Cr_2O_7^{2-}/H_2SO_4$ oxidation method lies in its ability to cleanly separate BC from the rest of the acid-insoluble SOC. Our short-lived component (average of 57% of the sample, half-life of 4–8 min) may be a mixture of acid-soluble carbon compounds, such as carbohydrates, lipids, and amino acids.

3.4. Soot, Charcoal, and NIST Standard Reference Material 1649a Results

While oxidation of marine environmental samples produced data best fit by three-term exponential decay equations, soot, charcoal, and an atmospheric standard produced data better fit by less complex equations. For BC standards, we chose lampblack soot and activated coconut charcoal because these materials are similar to those used in previous studies (Wolbach and Anders, 1989). The other advantage of these materials is their low cost and commercial availability. The major disadvantage of coconut charcoal and lampblack soot as standards is that their commercial preparation does not correspond to environmental BC production conditions. Ultimately, BC standards better representative of biomass burning conditions need to be developed, ideally through the collaboration of researchers measuring BC in soils, ocean sediments, the atmosphere, and the cryosphere. We regard our soot and charcoal standards as provisional and anticipate that more environmentally representative materials will be developed.

3.4.1. Soot and charcoal results

Coconut charcoal and lampblack soot oxidation experiments were run in duplicate similar to the previous standard sediment samples. Oxidations were performed at 23°C in 0.25 M $Cr_2O_7^{2-}/H_2SO_4$. Initial oxidation steps produced an increase in total system mass for all four samples. This effect was most pronounced in the charcoal samples, which increased to 160% of their initial mass after 25 h of oxidation (Fig. 3). The mass of the lampblack soot samples also peaked at 25 h (not shown), although only at ~104% of the initial mass. Increases in mass
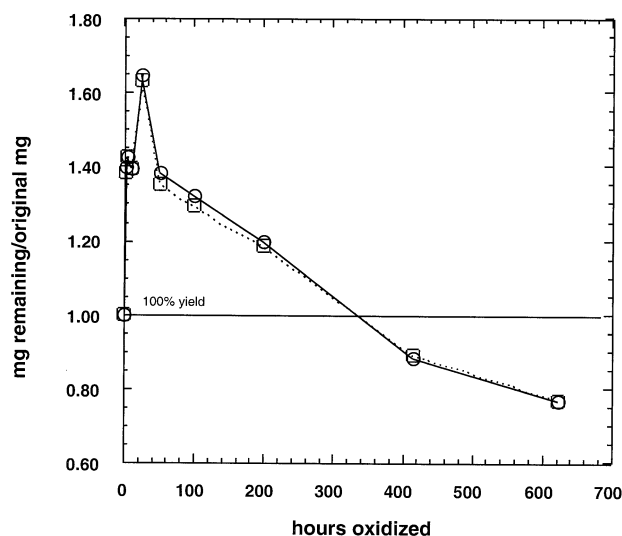
Fig. 3. Fractional yield by mass of coconut charcoal vs. hours oxidized. The line at the y-axis value of 1.00 represents 100%; of the initial mass.

were accompanied by decreases in weight percent carbon. The total carbon mass in each sample was either constant or decreased with oxidation time. The increase in sample mass and a concurrent decrease in sample %C is consistent with the ingrowth of oxygen as surface groups become functionalized during oxidation. Like the formation of CaF_2 during demineralization, ingrowth of oxygen seriously compromises the accuracy of mass-based kinetics calculations but has no effect on the accuracy of carbon-based calculations. Kinetic data for coconut charcoal and lampblack soot are presented in carbon terms only.

Both coconut charcoal and lampblack soot were best fit by single-term exponential decay equations ($N = N_o e^{-kt}$). The half-life of the major component of the coconut charcoal carbon (95–96% of the sample's total carbon) was 547 to 637 h (Table 5). Lampblack soot was much more resistant to dichromate oxidation, displaying only a 10% drop in sample mass after 622 h of oxidation. Because our experiments lasted far less than one half-life of this material, it is not possible to produce a well-constrained estimate of its half-life. We report only that the half-life of this material is on the order of 4000 to 5000 h in dichromate/sulfuric acid.

3.4.2. SRM 1649a results, dichromate oxidation

NIST SRM 1649a is an urban atmospheric aerosol standard collected for more than 1 yr (1973) in the parking lot at the Washington, DC Navy Yard (for more information on 1649a, see Currie et al., 1997). This material has been analyzed for a number of organic carbon components, including polycyclic aromatic hydrocarbons (PAH), which condense with soot during combustion processes and are likely a chemical tracer for some BC forms. 1649a has been radiocarbon dated and Δ^{14}C values are known for bulk aliphatics, bulk aromatics, bulk polar carbon (Currie et al., 1984) and individual PAH fractions (Currie et al., 1997; NIST, 2001). The analytical history of this sample makes it an excellent candidate for preliminary BC method comparisons and for studying the relationships between BC and other C components.

1649a was oxidized for a total of 406 h during which we made isotopic measurements (δ^{13}C and Δ^{14}C) on aliquots reacted for 2, 15, 50, 198, and 406 h. Oxidations were performed at 23°C and 0.25 M $Cr_2O_7^{2-}$/H_2SO_4. The carbon oxidation kinetics of this sample were best fit by a two-term exponential decay equation ($N = N_{o1}e^{-k1t} + N_{o2}e^{-k2t}$). The shorter-lived component of 1649a made up 39.7 ± 8.4% of the carbon in the sample and had a half-life of 0.85 ± 0.31 h, whereas the longer-lived component (BC) made up 54.6 ± 4.6% of the sample and had a half-life of 1000 ± 430 h (Table 5). The 1000 h half-life value for BC falls within the range of half-lives of the coconut charcoal and lampblack soot.

The Δ^{14}C values for dichromate/sulfuric-acid-extracted BC can be compared with previously published Δ^{14}C values for 1649a organic fractions and specific PAHs (Currie et al., 1997). The final (406 h) Δ^{14}C value for 1649a BC is −832 ± 7‰, in excellent agreement with the previously reported aromatic fraction Δ^{14}C of −830 ± 40‰ (Currie et al., 1984). This is also similar to previously reported values for the Δ^{14}C of PAHs proposed as combustion tracers, specifically benzo[*ghi*]perylene, reported at −860 ± 3–6‰ (Currie et al., 1997), and more recently at −914 ± 9‰ (NIST, 2001). These results are consistent with the theory that a fraction of BC, including soot, cocondenses with PAH out of the hot, reduced combustion gases. This result bodes well for the use of aromatic fractions, and specifically PAHs, as combustion tracers. There was no dramatic change in the δ^{13}C of 1649a throughout the oxidation: δ^{13}C began at −25.6‰ and dropped 0.4‰ to −26.0‰.

Because the half-life of the short-lived component of 1649a was 0.85 ± 0.31 h, the influence of this component on the

Table 5. Half-life data for charcoal, soot, and NIST SRM 1649a based on OC yield data. Half-lives are reported in hours.

Sample	$t_{1/2}$	±	Fract. Total C	±
Coconut charcoal A	637	66	1.0	0.1
Coconut charcoal B	547	51	0.9	0.1
Lampblack soot A	~4000		1.01	0.02
Lampblack soot B	~5000		1.01	0.01

	$t_{1/2}$	±	Fract. Total C	±	$t_{1/2}$, Hours	±	Fract. Total C	±
NIST SRM 1649a	1000	430	0.55	0.05	0.8	0.3	0.40	0.08
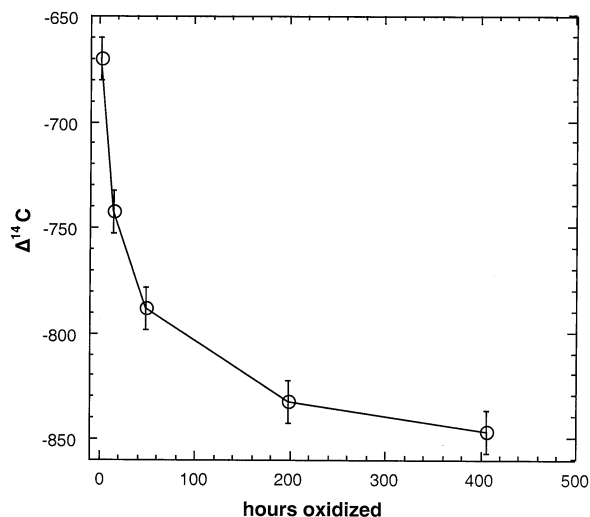
Fig. 4. Δ^{14}C of sample 1649a vs. hours oxidized.

Table 6. BC content of NIST SRM 1649a.

Method	1649a BC Mass Fraction (mg/mg)	Citation
Dichromate/sulfuric acid oxidation	0.098 ± 0.008	This paper
Thermal-optical FID	0.046 ± 0.005	Birch & Carey, 1996
Nitric acid-combustion-NDIR	0.052 ± 0.006	Klouda et al., 1996

system's isotopic values can be assumed to be trivial beyond 20 half-lives (~17 h), at which point it is only 1 part in 10^6. According to this model, the ^{14}C of the remaining material should only reflect the ^{14}C of BC beyond ~20 h of oxidation. Indeed, the most dramatic drop in the ^{14}C of the system occurred in the first 50 h, when the Δ^{14}C decreased from −671 to −788‰, as shown in Figure 4. However, as the oxidation progressed beyond 50 h, the isotopic signature of the sample continued to decrease, reaching a value of −847‰, a drop of 59‰ from the 50-h value. Possible explanations for this decrease center on the chemical heterogeneity of BC.

The variable resistance of different kinds of BC to chemical oxidation has been well documented, both in simple coconut charcoal and lampblack experiments presented here and in previous studies (Bird and Gröcke, 1997). Although the method presented here may be able to distinguish grossly between BC and non-BC within samples, it may not be able to distinguish among BC fractions of different chemical reactivity and different molecular signatures. One possible explanation for the continued decrease in 1649a Δ^{14}C, well beyond the time when nonblack organic matter has been oxidized, is the inability of this method to distinguish regions in the BC spectrum in an environmental sample matrix. For example, in our laboratory experiments on coconut charcoal and soot, the modern, biomass-derived coconut charcoal is much more chemically labile than the ^{14}C-free, fossil fuel-derived lampblack soot. If environmental charcoal is more chemically labile than environmental soot, the ^{14}C signature of charcoal should become an increasingly smaller component of the BC ^{14}C signature of 1649a. Whereas biomass burning produces charcoal and soot, fossil fuel combustion produces only soot. The effect of this heterogeneity would be a slow decrease in the ^{14}C signature of BC during dichromate oxidation like the trend observed in our 1649a experiments.

The BC content of NIST SRM 1649a has been measured previously by two groups, providing an opportunity to compare results (Birch and Cary, 1996; Klouda et al., 1996). The three measurements for 1649a (Table 6) agree within a factor of 2, and compare well with previous BC methods studies. In one

study conducted in 1986 (Countess, 1990), the variation between laboratories measuring BC/OC ratios was 10 to 67%. An intercomparison of thermal techniques among European laboratories reported variations of 8 to 44% (Guillemin et al., 1997). Both studies report improved agreement as sample size increased, with reliably reaching 10% for the largest samples analyzed. When the BC content of a suite of soil samples was recently intercompared using a broad range of methods, BC concentration values varied over two orders of magnitude (Schmidt et al., 2001).

Although the data presented in Table 6 are consistent with previous intercomparison studies, they are by no means satisfactory. As noted in all previous comparisons, lack of commonly used standards limits development of consistent BC methods. Another hindrance is the use of operational definitions of BC (i.e., BC is the material that survives oxidation under specific thermal or chemical oxidant conditions). Because BC is a continuum of materials (slightly charred wood through highly condensed soot), the choice of standards implicitly constrains the window of the BC spectrum to be analyzed. For example, the thermal-optical method used by Birch and Cary (1996) (data in Table 6) uses a diesel soot standard to represent black carbon. The choice of diesel soot as a black carbon standard implicitly restricts this analysis tool to the most thermal, chemical, and microbiologically refractory components of the BC spectrum. This restriction is appropriate for the intended atmospheric uses of this technique, because larger, less refractory charcoal and char particles do not remain airborne long enough to become an air pollution problem or a health hazard. The dichromate/sulfuric acid technique described here, however, was optimized to a broader range of the BC spectrum, including both soot and the more refractory biomass-burning charcoal components. Because none of the methods described above have been developed using the same standards (other than NIST SRM 1649a), we cannot be sure that they all measure the same components in the BC spectrum. Indeed, given how different these techniques are, it is encouraging that all results are the same within a factor of 2. The data in Table 6 point to the need for the development of common BC standards useful to scientists studying BC in natural settings.

3.5. Comparison of 1649a dichromate oxidation results with thermal oxidation kinetic results

Our results can also be compared to a developing thermal optical kinetic (TOK) method for BC and ^{14}C BC speciation (Currie and Kessler, 1999). In common with the chemical oxidation method reported here, the thermal oxidation method

showed a decrease in 1649a Δ^{14}C with time, supporting the conclusion that the more refractory BC has a larger fossil carbon component. The isothermal oxidation rate could also be fit with a sum of exponentials, although with the inclusion of a constant term.

Some preliminary data have been obtained for ^{14}C and time constants for isothermal oxidation of carbonaceous species in SRM 1649a. Oxidation takes places at 560°C in a stream of He (5% O_2) for periods up to 700 s. The oxidizable carbon can be described as a rapidly lost labile fraction, and a more refractory fraction having time constants of 39, 225, and > 1000 s (constant). The labile/refractory carbon ratio (42/58%) is similar to that of the dichromate-sulfuric acid technique (40/55%), although that refractory endmember (intercept) is smaller (11%). Radiocarbon behavior also is similar for the two methods, with the most refractory component displaying the largest fossil carbon content. Because of the very large difference between chemical and thermal time constants, the thermal technique is interesting for isolating the most refractory soot component of atmospheric aerosol for isotopic measurements.

4. CONCLUSIONS

The dichromate/sulfuric acid oxidative method for BC measurement developed by Wolbach and Anders (1989) can be used to produce reliable BC Δ^{14}C data from samples collected in marine environments and works equally effectively at 23°C and higher dichromate concentrations (0.25 M). We recommend reporting oxidative kinetics data in terms of %C loss vs. oxidation time, instead of % mass loss vs. oxidative time. Reporting kinetics data as %C vs. time eliminates measurement errors introduced to some samples by ingrowth of oxygen due to BC functionalization and in addition, provides data useful for comparison with measurements on other carbon components. Our ^{14}C measurements on BC in NIST SRM 1649a are similar to some previously published ^{14}C measurements on the molecular fractions of this SRM, providing an order-of-magnitude external check on the isotopic measurements reported here.

For marine sediments, we prefer oxidation conditions of 23°C, a dichromate concentration of 0.25 M, and oxidation times of ~400 h (~1 half-life). The precision of our measurements of BC on deep, Northeast Pacific sediments conducted at 23°C, 0.25 M $Cr_2O_7^{2-}$/2 M H_2SO_4 was ± 0.00019 mg BC/mg dry sediment (~10%), ± 0.1 ‰ δ^{13}C, and ± 5% Δ^{14}C (when normalized to modern, this is < 14‰). We compared our BC mass results with previous mass results for NIST SRM 1649a, and found the three measurements consistent within a factor of 2, with our measurements producing the highest yield of BC. This is consistent with the optimization of the dichromate/sulfuric acid oxidative technique for a broader range of types of BC. We recognize BC to be composed of a spectrum of combustion products ranging from slightly charred biomass to fully recondensed, highly aromatic soot. Currently, the scientific community lacks realistically produced BC standards that span this combustion continuum and as a result, it is not possible to identify what windows of the BC continuum individual measurement techniques isolate. This lack of a broad range of easily accessible BC standards is serious: The consequence is that methods cannot be accurately compared, and it is not currently possible to report true error values for any BC

measurement technique. The development of a suite of commonly available and/or easily produced BC standards that span the continuum of combustion products is a necessary next step for the BC measurement community.

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