

Determination of black carbon by chemical oxidation and thermal treatment in recent marine and lake sediments and Cretaceous–Tertiary clays

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Abstract

Several sample treatments and analytical methods for the measurement of black carbon in a wide variety of sediments were considered in which the removal of organic carbon is a critical step in the procedure. A comparison between chemical oxidation and thermal treatment was conducted and the latter was shown to be inappropriate due to the polymerisation of organic matter. Using acid dichromate oxidation, reactive kerogen was separated from black carbon in a variety of lake and marine, and recent and ancient sediments with relatively small and quantifiable losses (1–6%) of black carbon under carefully controlled reaction conditions.

1. Introduction

Black carbon (BC) is uniquely generated by combustion processes such as forest fires and industrial fuel emissions. Air-borne carbonaceous particles and residual charcoal produced by such emissions can then undergo aeolian, surface runoff and fluvial transport before ultimate deposition in fresh and marine waters, and to sediments. Post-depositional changes of BC in sediments by photochemical reactions and microbiological action are generally assumed to be minor. Due to its refractory nature and its unique source signature, BC may be an excellent tracer of combustion and its preservation in sediments may therefore provide a reliable record of fire history.

The combustion of plant-derived material yields a

mixture of refractory carbonaceous products which can be classified into two broad categories, charcoal and BC which are difficult to define. Charcoal is generally formed at low (< 600°C) temperatures, the fragments are mainly super- μm and found in a wide size range (from 5 up to 100 μm) and the structure of the cell walls of the plant are sometimes recognisable under a microscope (Cope and Chaloner, 1980). BC aerosols are formed at higher temperatures (> 600°C); they often present a spherical habit (Gaudichet et al., 1995) and their size is primarily sub- μm . However, there is no absolute chemical definition of BC. There are several methods available in the literature for the determination of refractory carbon in sediments. The separation of refractory carbon from a carbonaceous matrix is by no means straightforward. Chemical treatment may separate BC and/or charcoal from organic matter but there is little information in the literature quantifying

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this process, if indeed separation is achieved. As a result of the various methodologies used to determine refractory carbon in aerosols (Wolff and Klimisch, 1982) or sediments (Clark, 1996), its definition is confusing as several terms are used, such as charcoal, BC, soot, and elemental carbon. In this paper, we present a chemical separation and the remaining refractory carbon will be called BC following a general consensus (Goldberg, 1985; Clark, 1996). This refractory carbon probably includes atmospheric BC particles and charcoal, and is defined according to the chemical method described hereafter.

Sediments contain both BC and kerogen (insoluble organic carbon derived from terrigenous or marine plant material). These compounds represent opposite end-members of a continuous spectrum of polymerised carbon compounds. The reactivity of these two carbonaceous components differ sufficiently to allow for their chemical separation by oxidation (Wolbach and Anders, 1989; Cachier and Lioussé, 1994). However, the cut-off between organic carbon and BC in the sediments will differ from method to method depending upon the sample treatment used. Hence, the most critical step of any method is the effective separation between the organic carbon and BC fractions.

The objectives of this study are to select a general method of BC determination suitable for a wide range of sediments and to optimise experimental conditions so that a satisfactory cut-off for BC can be obtained. For this purpose, experiments were conducted on a representative range of sediment matrices, namely, recent lake and marine sediments and ancient Cretaceous–Tertiary (K–T) boundary clays.

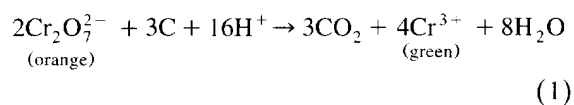
2. Experimental

2.1. Methodology

The determination of BC in sediments essentially consists of three distinct stages. First, a chemical treatment to remove carbonates and part of silicates. Second, a thermal or chemical treatment to remove organic carbon from the acid-treated sediment. Finally, analysis of the BC in the residual sediment.

For the removal of carbonates and the attack of silicates, chemical procedures are limited to acidic treatment (HCl/HF, HNO₃) (e.g., Smith et al., 1975; Herring, 1985; Winkler, 1985) whereas several methods exist for the removal of organic carbon. These methods include acidic (K₂Cr₂O₇/H₂SO₄, HNO₃) (Winkler, 1985; Wolbach and Anders, 1989) or alkaline oxidation (KOH/H₂O₂) (Griffin and Goldberg, 1975) and alkaline solvent extraction (NaOH/benzene/methanol/methyl isobutyl ketone) (Wolbach et al., 1985). With the exception of solvent extraction, separation of organic and BC rely on the differing reactivity of the two forms of carbon, the latter being more chemically refractory. The residual carbon in the treated sediments can then be analysed by: (1) infrared spectroscopy and intensity of the C=O band vibration (Smith et al., 1975), (2) loss on ignition (Winkler, 1985), (3) titration of CO_{2(g)} evolved on combustion, (4) mass spectroscopy (Wolbach et al., 1988), or (5) a counting method (planimetry) using electron microscopy (Medalia and Heckman, 1969; Wolbach et al., 1988).

There are a number of disadvantages associated with the above chemical methods for the removal of organic carbon (kerogen) from sediments. Although used by several researchers, alkaline peroxide oxidation (e.g., Smith et al., 1973; Griffin and Goldberg, 1975; Herring, 1985) is reported to be difficult to control due to the catalytic decomposition of the reagent during the reaction (Wolbach and Anders, 1989) and charcoal can be lost (Patterson et al., 1987). On the other hand, some mature kerogens are likely to resist peroxide oxidation (Wolbach et al., 1990) and possibly, nitric acid oxidation. The extraction of kerogen with organic solvents is likely to vary with the maturity of the sediment and is known to be erratic (Wolbach and Anders, 1989). However, dichromate oxidation appears to be a promising alternative as this method is reported to overcome most of these difficulties (Wolbach and Anders, 1989). In addition, consumption of the reactant, Cr(VI), during the reaction is accompanied with a colour change:



which provides a useful means of following the reaction since oxidation must be carried out in excess reagent to ensure complete oxidation.

Thermal treatment of aerosols has been reported as an effective means of organic carbon removal and separation from BC in carbonaceous aerosols (Wolff and Klimisch, 1982) and this method may also be suitable for sediments.

Amongst the techniques available for the quantitative determination of BC after separation from the kerogen, infrared spectroscopy is possible but this method is rather specialised for a sediment matrix (Smith et al., 1975). An alternative method of BC analysis is coulometric titration, which is both accurate and precise (Cachier et al., 1989) and can easily be adapted to the measurement of BC in sediments.

Based on the above literature review, the sequential reaction scheme for BC determination in sediments selected for evaluation in this laboratory is as follows:

(1) Removal of carbonates and silicates: acid treatment with HF/HCl;

(2) Removal of organic carbon:

(a) chemical oxidation with $K_2Cr_2O_7/H_2SO_4$, or

(b) thermal treatment, or

(c) combination of both thermal and chemical methods;

(3) Analyses: coulometric titration of $CO_2(g)$.

In the remainder of this paper, we present the results of the chemical and thermal treatment for the separation of BC from kerogen in lake and marine sediments.

2.2. Sample sites and procedures

Two lakes were sampled for lacustrine sediments. The first campaign was conducted in October 1992 in the Massif Central region in France at Lake Pavin, which is a deep volcanic crater lake. This lake was chosen because it is situated in a sparsely populated region and is likely to register background levels of BC deposition. For superficial sediments from Lake Pavin, all depths represent the level below water surface. The second campaign was carried out in July 1993 in the southwestern region of France at Lake Pareloup. This is an artificial lake created for the generation of hydroelectricity and was emptied after 30 years of use. Lake sediments were cored using a 10-cm-diameter polyethylene tube.

Marine sediment sampling was carried out at various locations in the Western Mediterranean Basin. Using a box core, two sediment cores were taken during the "PHYCEMED II" cruise in October 1983 at the SR-T ($38^{\circ}10'N-09^{\circ}00'E$) and the BO-AR ($36^{\circ}N-15^{\circ}30'E$) sites. A third sediment core was sampled November 1991 with a multicorer at the DYFAMED site ($43^{\circ}24'N-7^{\circ}51'E$) situated in the Ligurian Sea.

K-T boundary samples were taken from an exposed site at Woodside Creek (New Zealand) and provided by Dr. R. Rocchia (CFR, Gif-sur-Yvette).

2.3. Sample treatment

Individual steps for methods of sample treatment are discussed below. An overall reaction scheme is presented in Fig. 1.

2.3.1. Sample preparation

To obtain a dry homogeneous sample, lake sediments were oven-dried after sample collection and the weighed samples ground into a powder. After suspension in filtered deionised water, the resulting mixture was subjected to ultrasonic treatment at $\sim 40^{\circ}C$ for 10–15 min. The mixture was then immediately passed through a 0.1-mm-diameter mesh to

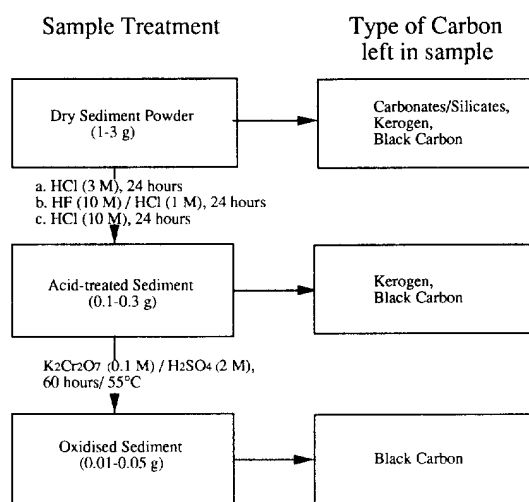


Fig. 1. Reaction scheme for the determination of kerogen and black carbon in sediments. (BC probably includes atmospheric BC particles and charcoal.)

remove stones from the sample and the slurry centrifuged at 3000–3300 rpm for 20 min. After discarding the supernatant liquid, the residual solids (350–785 g) were dried overnight at 60°C before weighing for further treatment.

Marine sediment cores were stored frozen, allowed to thaw at room temperature and immediately oven-dried at 60°C before further treatment and chemical analyses.

K–T boundary clays were extracted from a sediment block and pulverised into a fine powder in an agate mortar.

2.3.2. Acid treatment

Approximately 1–3 g of dried sediment were weighed into pre-cleaned polyethylene test tubes and carefully treated with 15 cm³ of 3 M HCl to remove carbonate from the sediment matrix. After the effervescence had subsided, the sediment mixture was placed in the Ultrason for 5–15 min and the reaction left to completion over 24 hr. Following repeated centrifuge and rinsing (3–6 times) with filtered deionised water, ~ 15 cm³ of 10 M HF/1 M HCl were added to the residue and the reaction allowed to continue at room temperature for a further 24 hr. The purpose of HF treatment is to liberate any superficial carbonaceous material which may be trapped between the silicate sheets (W.S. Wolbach, pers. commun.) rather than to dissolve the silicate matrix which requires higher temperature, pressure and acid volume. Thorough rinsing of the samples prior to the addition of HF is important since any Ca²⁺ ions remaining in solution will form insoluble CaF₂, thus resulting in weighing artifacts. Sediment samples were then subjected to a final 24-hr treatment of 10 M HCl after centrifuge and rinsing (3–6 times) until rinsing water pH was 4–5. It must be pointed out here that rinsing the sample until achieving a “neutral pH” is dangerous at this point as BC may form a colloidal suspension in rinse water and be easily lost during decantation of supernatant (W.S. Wolbach, pers. commun.). The washed acid-treated sediment samples were allowed to dry at 60°C until constant weight was obtained.

At all stages, the rinsings were carefully performed and number of rinsings minimised to avoid inadvertent loss of carbonaceous material on discarding the supernatant liquid, whilst ensuring that the

sample was sufficiently free from acid. In general, the greater the sample weight, the greater number of rinses (3–6 times) are needed. pH tests conducted on the oven-dried sediment indicated that any traces of HCl volatilises during the drying process to leave an acid-free sediment sample that can be directly analysed by coulometric titration without analytical artifacts.

Sediments subjected to the above treatment are henceforth referred to “acid-treated” and contain kerogen and BC. Carbon concentrations determined in acid-treated sediments are defined as total carbon (TC) (Fig. 1).

TC concentrations are likely to represent lower limits of actual organic carbon concentrations in sediments due to loss via a number of processes. These include: (1) leaching of fulvic acid (30–60% dry weight) and amino acids (< 1% dry weight) during acid-demineralisation of the sediment (Lowe et al., 1988); and (2) volatilisation of light organic matter on acidification and/or during the sediment drying step (King et al., 1996, and references therein). Such losses of organic matter during sample manipulation can have a significant bearing on global carbon flux studies, but are not important in the present study in which we focus on refractory carbon.

2.3.3. Chemical oxidation

As discussed earlier, the most delicate step in the sample treatment is separation of organic and BC. Here we describe the removal of organic carbon (kerogen) by dichromate oxidation. Since chemical oxidation of the organic component in sediments was closely based on the procedure reported by Wolbach and Anders (1989), the method used here will only be briefly described, but with sufficient detail to highlight any differences which exist between the procedures of the two laboratories.

In general, 0.1–0.3 g of dried acid-treated sediments was weighed in glass test tubes and treated with ~ 10 cm³ of 0.1 M K₂Cr₂O₇/2 M H₂SO₄. The mixture was immediately placed into an ultrasonic bath at 40°C for ~ 10 min to break up aggregates and to ensure rapid contact of the sediment with the oxidant. For the oxidation step, samples were kept in test tubes and transferred to a water bath at 55 ± 1°C. Throughout the treatment, stirring is achieved by means of a small magnetic bead

placed in the test tubes and a magnetic stirrer under the water bath. Test tubes were also periodically (once a day) subjected to additional ultrasonic treatments out of the thermostated water bath. Estimated dichromate-to-carbon ratios of the sediment/oxidant mixture were always in excess, which is monitored by the colour of the solution after ultrasonic treatment. To follow the evolution of the oxidation reaction, the sediment was allowed to be in contact with the reactant at variable reaction times from one to hundreds of hours (discussed later, Section 3.1). During long exposure times, the reaction mixture was replenished with deionised water to replace water evaporated during heating. After a specified reaction-time, test tubes were quenched in cold water for ~ 5 min and the dichromate solution was immediately separated from the sediment by centrifuge and rinsing of the sediment with deionised water (3–6 times) to prevent further oxidation. Again the number of washings were minimised to prevent accidental loss of carbonaceous material in the rinsings. Washed oxidised sediment samples were allowed to dry at 60°C.

Acid-treated sediments reacted with dichromate will henceforth be referred to “oxidised” (Fig. 1) and assumed to contain BC and perhaps some refractory kerogen depending on the extent of oxidation.

Table 1 summarises the chosen analytical protocol. The main differences with the Wolbach and

Anders (1989) method lie in the acid treatment and the drying step. In this study, a milder HCl treatment is used to minimise efferversence during decarbonisation and drying is carried out a lower temperature (60°C) to reduce the loss of light organics. For sediments containing elevated concentrations of kerogen (e.g., > 18% C w/w bulk dry sediment), higher concentrations of dichromate may be needed to ensure that oxidation is complete. Section 3 shows that the duration of oxidation was carefully optimised.

2.3.4. Thermal treatment

About 0.01–0.03 g of acid-treated or oxidised sediments was directly weighed into clay combustion boats, previously cleaned by heating to 1200°C. The thinly-spread layer of sediment was then subjected to thermal treatment in a 2-cm-diameter insulated tubular furnace with exposure times varying from 15 min to several hours (see later, Section 3.2). Furnace conditions (temperature, carrier flow gas) were carefully controlled and oxidation was performed using parameters previously optimised for the determination of BC in aerosols (Cachier et al., 1989). Then the carrier gas used was pure oxygen and burn-off temperature was $340 \pm 1^\circ\text{C}$. Combustion boats were placed into predetermined heating zones of the furnace where sample temperatures reached 340°C within 2 min of heating.

After thermal treatment, sediments are henceforth referred to as “thermally-treated” (Fig. 1) and assumed to contain BC and perhaps some refractory kerogen depending on the extent of separation.

2.4. Analytical procedures

The various sediments were weighed into combustion boats and directly analysed using standard coulometric titration of CO₂ gas evolved from sediment samples combusted at 1200°C under pure O₂, using a Ströhlein Coulomat 720C Instrument. Analytical efficiency of the instrument was routinely monitored by the combustion of graphite standards (Carbone-Lorraine, Inc.) at the beginning of each sample run and results were generally within $\pm 5\%$ of certified values using amounts of standard carbon 2–10 higher than that found in samples. Instrumental blanks were routinely determined between every five

Table 1
A comparison of experimental conditions of chemical oxidation of sediments with dichromate

	Wolbach and Anders (1989)	This study
Acid	(1) HCl (9 M) (2) HF (10 M)/HCl (1 M) (3) HCl (9 M)	(1) HCl (3 M) (2) HF (10 M)/HCl (1 M) (3) HCl (9 M)
Oxidant	K ₂ Cr ₂ O ₇ (0.1 M) H ₂ SO ₄ (2 M)	K ₂ Cr ₂ O ₇ (0.1 M) ^o H ₂ SO ₄ (2 M)
Temperature	50°C	55°C
Drying	120°C/2 hr	60°C/1–2 days
Sample mass	1 mg–30 g	100–300 mg

Higher concentrations of K₂Cr₂O₇ (about 0.5 M) were used for lake sediments with high organic matter.

or six samples during each analytical run and sample concentrations were typically 10–100 times greater than instrumental blanks ($< 12 \mu\text{g}$). Carbon concentrations presented in this work are blank corrected and expressed as percentage w/w of the dry bulk sediment.

3. Experimental results

The most critical step of the protocol is the separation of the two refractory carbonaceous components in the acid-treated sediment matrix, kerogen and BC. This separation is particularly difficult to control as there is no clear physical or chemical cut-off between these two end-members of the carbonaceous spectrum. Below, we present the results of kerogen removal from BC using chemical oxidation and thermal treatment.

3.1. Chemical oxidation

3.1.1. Loss in mass (experiment 1)

Since the only component of the sediment matrix which can undergo oxidation is the carbonaceous matter, the rate of change of sample weight during oxidation should be analogous to the loss of kerogen. The objective of experiment 1 was to monitor the rate of oxidation of kerogen in the acid-treated sedi-

ments as a function of dry sediment mass loss during the course of reaction.

Reactions were carried out over a duration of ~ 100 hr with dichromate and a few typical results are presented in Table 2 for each type of sediment. Similar curves were observed for all sediments despite the differing amounts and concentrations of organic matter in samples, with sample masses decreasing exponentially during the initial few hours of reaction, followed by a gradual decline of sample mass (Fig. 2). These results are in agreement with those reported by Wolbach and Anders (1989) who suggested, using electron microscopy, that the initial exponential decrease in sample mass was probably due to the removal of reactive kerogen from the sediment matrix, and that the gradual decline over longer reaction times was likely to be due to the oxidation and subsequent loss of BC. Over such reaction times, it is estimated that between 75% and 92% of TC (kerogen plus BC) is oxidised.

To a first approximation, initial amounts of BC in the sediment can be estimated by extrapolation of the quasi-horizontal slope of the graph (Fig. 2A) to the intercept of the y-axis. From the graph it may be inferred that oxidation of kerogen is complete when the carbon concentration in the residual sediment remains constant within analytical uncertainties (i.e. less than $\sim 10\%$). All reactions were performed for

Table 2
Dichromate oxidation of lake, marine and Cretaceous–Tertiary sediments at 55°C as a function of mass over time

Depth	Lake		Cretaceous–Tertiary	Marine	
	Pavin – 20 m	Pareloup 1–2 cm	Woodside Creek + 25 cm	DYFAMED 15–20 cm	PHYCEMED (BOAR) 0–10 cm
Time (min)	Fraction of initial mass				
0	1.000	1.000	1.000	1.000	1.000
90	0.749	0.685	0.986	0.767	0.854
270	0.643	0.622	0.977	0.672	0.795
690	0.559	0.583	0.947	0.637	0.752
910	0.528	0.562	0.927	0.627	0.736
1830	0.508	0.511	0.916	0.610	0.714
3000	0.358	0.465	0.914	0.610	0.709
5720	0.307	0.412	0.903	0.595	0.679
6900	(^a)	(^a)	(^a)	0.597	0.677

Results are means of duplicate sample runs.

^a No data.

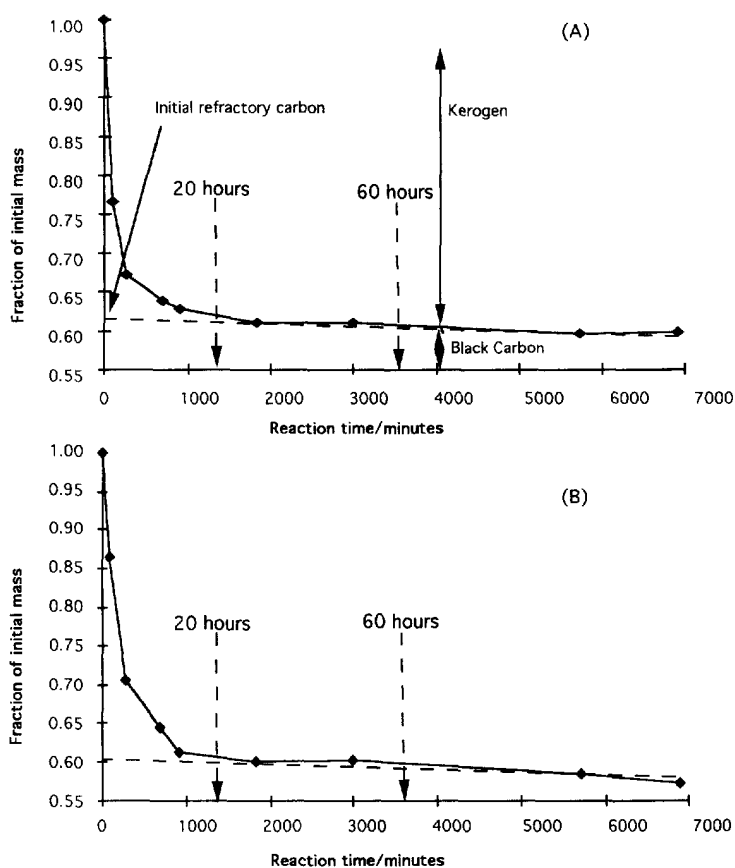


Fig. 2. Dichromate oxidation of Mediterranean sediments at 55°C as a function of fraction of initial mass over time. Sediments were sampled at the DYFAMED site and represent sediment layer depths from the sediment surface of: (a) 15–20 cm; and (b) 30–35 cm.

~ 100 hr. Average reaction times required to oxidise kerogen are shown in Table 3 for various sediments. They were found to be in the range of 10–20 hr. This range of oxidation times is likely to reflect the variability of composition of kerogen and its reactivity (Durand, 1980). All factors related to the origin,

age and physical nature of sediment grains (such as aggregate size, organic coatings) may play an important role in retarding the oxidation of kerogen.

Half-lives obtained from the graphs may provide an indication of the chemical reactivity of the carbonaceous matter which undergoes oxidation. Half-

Table 3

Mean reaction times and half-lives of chemically-oxidised lake, marine and Cretaceous–Tertiary sediments

Type of sediment	lake	marine	K–T
Number of sediments	6	4	3
Reaction time (hr)	13 (11–18)	21 (17–29)	19 (14–28)
Half-life, $t_{1/2}$ (short) (hr)	4 (1.5–7)	6 (3.5–10)	2 (1.9–2.5)
Half-life, $t_{1/2}$ (long) (hr)	215 (123–388)	410 (390–445)	1992 (1863–1982)

Reaction time is the time estimated to remove kerogen without attacking black carbon (see text). Half-life, $t_{1/2}$, is the time taken in hours for the mass of the sediment sample to fall to half its initial mass; short- and long-lived components refer to kerogen and black carbon components, respectively.

lives, $t_{1/2}$, of the short-lived carbon component (kerogen) are similar for all sediment types, with average values ranging from 2 to 6 hr (Table 3). Conversely, for all sediments the half-lives of the long-lived (BC) component are 2–3 orders of magnitude higher than those for short-lived (kerogen) component, underlining the difference between the reactivity of kerogen and BC. However, notable differences in the half-lives of the long-lived (BC) component are found between lake (215 hr) and marine (410 hr) compared to K–T sediments, for which a higher average value of ~ 2000 hr is observed. The much lower half-lives of the long-lived kerogen in lake sediments again suggest differences in the physical and chemical nature of the organic matter. Such differences should primarily be related to both sediment age and origin and an interesting test would reside in the parallel determination of kerogen polymerisation degree (as reported by H/C elemental ratio).

3.1.2. Loss in kerogen carbon (experiment 2)

Objectives of experiment 2 were two-fold: (1) to verify that the rate of oxidation of organic matter was analogous to the rate of sediment rate loss by directly analysing the carbon concentration in the sediment; and (2) to evaluate the resistance of BC to prolonged reaction times. Results of experiment 1 (Table 3) suggest that the vast majority of kerogen is removed from all sediments within ~ 20 hr of exposure time. It was therefore decided to carry out experimental trials over 20 hr of reaction time with intervals at 5–6 hr. For this purpose, marine sediments from the Mediterranean DYFAMED site were selected for further study for a number of reasons. First, the study of BC in marine sediments is one of the axes of future research in our laboratory. Second, the dichromate oxidation method was originally developed for the analyses of BC in K–T sediments, and to our knowledge, this oxidation method has not previously been tested on recent marine sediments.

Results of experiment 2, in which two sets of marine sediments have been simultaneously taken through the oxidation procedure, are shown in Table 4. In both cases, the reaction was monitored by sample mass as well as by the measurement of carbon concentrations. A comparison between the two data sets shows that the rate of loss of sediment

mass appear to broadly reflect the change in carbon concentrations (Table 4), indeed confirming the earlier assumption that the rate of carbon oxidation could be monitored by sample mass. Furthermore, both sediment mass and carbon concentrations reach near-stable values after 11 hr of reaction time, indicating that all the kerogen has been removed from this sample during this period. However, at longer exposure times (e.g., 20 hr), results show that slight loss of carbon can occur, but always in the order of $< 1\%$ C relative to initial carbon concentrations. The progressive loss of BC during prolonged reaction times is not surprising since the BC component, although refractory, is not completely inert and undergoes slow oxidation. This BC loss is measurable by coulometric titration which is a more sensitive method of monitoring the reaction than by sediment mass.

A suitable standard reaction time should ensure that the kerogen is removed from the sediment whilst attacking as little of the BC as possible. Results in Table 4 show that the decrease in carbon concentrations is relatively minor up to 20-hr reaction time. Although trial runs showed that 20 hr were sufficient to oxidise the kerogen in most sediments, longer

Table 4

A comparison of change of carbon concentrations and fraction of initial mass of Mediterranean sediments subjected to dichromate oxidation over time (g/100 g)

Reaction time (hr)	Carbon concentration (g/100 g)		Sample mass (g)	
	sample 1	sample 2	sample 1	sample 2
0	1.214 \pm 10% (1.00)	1.344 \pm 15% (1.00)	0.241 (1.00)	0.339 (1.00)
5	0.211 \pm 29% (0.17)	0.308 \pm 20% (0.23)	0.211 (0.88)	0.308 (0.91)
11	0.096 \pm 3% (0.08)	0.127 \pm 6% (0.09)	0.100 (0.41)	0.132 (0.39)
15	0.090 \pm 1% (0.07)	0.127 \pm 6% (0.09)	0.100 (0.41)	0.131 (0.39)
20	0.086 \pm 1% (0.07)	0.125 (0.09)	0.100 (0.41)	0.158 (0.39)

Sample 1 DYFAMED 25–30 cm; sample 2 DYFAMED 20–25 cm; numbers in parenthesis are carbon concentrations or sample weights expressed as ratios of initial concentrations or weights of acid-treated sediments; carbon concentrations are averages of triplicate analyses.

oxidation times of 60 hr appear to be generally necessary for ancient K–T boundary clays (Wolbach et al., 1988). Since one objective of this study was to develop a standard method for all sediments, tests were carried out to evaluate the loss of BC over 60 hr. Results showed that increasing the reaction time from 20 to 60 hr results in only a relatively small loss of BC (1%) in marine sediments (Fig. 2). Similar decay curves were also obtained for lake sediments, pointing out a mean loss of 5%. It was therefore decided to adopt a standard reaction time of 60 hr for all sediments.

3.2. Thermal treatment (experiment 3)

The thermal treatment of aerosols and particulates in precipitation (e.g., rain, snow) is a standard procedure used to separate the organics from refractory BC and has been successfully used in this laboratory for several years (Ducret and Cachier, 1992). The objective of experiment 3 was to test the suitability of this thermal method for BC determination in sediments using experimental parameters previously optimised for aerosols (Cachier et al., 1989).

Acid-treated sediments from the DYFAMED site were subjected to thermal treatment over time intervals of several hours and the carbon concentrations were measured. Results showed that carbon concentrations in thermally-treated sediments were rather erratic by contrast to the well-behaved exponential decay of sample mass of chemical oxidised sediments (Fig. 3). This type of behaviour is thought to be typical of polymerisation of organic matter during heating which may occur when the oxygen flow over the sediment granules is unevenly distributed.

3.3. Reproducibility of carbon determinations

In order to evaluate the reproducibility of the method, marine sediment samples were taken through the reaction scheme (Fig. 1) and analysed for TC and BC at each stage of the treatment. The standard error of BC measurements (Table 5) of both within and between batches of sediment samples, are surprisingly good (means 5%, 12% respectively). However, the reproducibility of TC determinations was poorer (± 3 to $\pm 23\%$) for triplicate analyses of sediment samples. Moreover, standard errors of TC concentra-

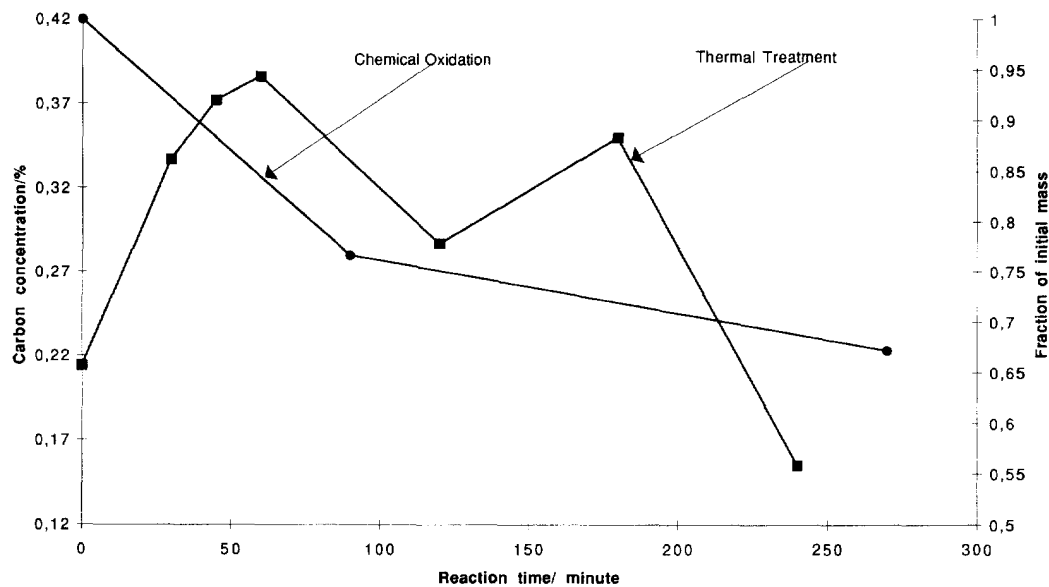


Fig. 3. Carbon concentrations of Mediterranean sediment subjected to thermal treatment at 340°C over time (squares). Fraction of initial mass of Mediterranean sediment oxidised with dichromate over time (circles). The marine sediment used was sampled from the DYFAMED site (15–20 cm).

tions between batches of sediments are much higher ($\pm 35\%$ to $\pm 23\%$ for samples 1 and 2, respectively). The lower reproducibility of TC measurements on acid-treated sediments may be due to the heterogeneous partition of kerogen on sediment grains and irreproducible loss of volatile organics during sediment drying.

Whilst it is recognised that the few reproducibility tests on a limited number of sediment samples cannot be used to evaluate the reproducibility of the method, they indicate that within and between batch variabilities of BC are minor. For simplicity, in our standard protocol, a single sediment sample was taken through the reaction scheme and analysed in triplicate. Results for the various sediments analysed in this study are given in Table 6.

We estimated the cumulative errors of BC determinations for all steps of the sample manipulation to be minor ($< 0.1\%$) and that these errors were primarily due to weighing uncertainties (± 0.05 mg) which were generally much less than 0.1% of sample masses.

3.4. Accuracy of black carbon measurements

Having established a standard method for the determination of BC by chemical oxidation, the accuracy of the protocol was evaluated. One approach is the use of standard addition of a known quantity of BC to a sediment. But this technique is rather difficult to apply in the case of BC because surface hydrophilic nature of BC in aerosols (Ducret and

Table 5
Reproducibility of replicate analyses of black and total carbon in marine sediments

	Total carbon (g/100 g)	Black carbon (g/100 g)
Sample 1	0.23 + 8%	0.15 ± 4%
	0.26 + 3%	0.16 ± 4%
	0.43 + 18%	0.15 + 7%
Sample 2	0.48 + 10%	0.17 ± 6%
	0.65 ± 23%	0.18 ± 3%
	0.78 + 13%	0.26 ± 18% ^a

Samples 1 and 2 are from DYFAMED (over the 0–10-cm core interval); standard errors are expressed as standard deviation of triplicate analyses divided by mean values.

^a Suspect data.

Table 6
Black and total carbon concentrations in lake and marine sediments (g/100 g)

	Total carbon, TC (%)	Black carbon, BC (%)	BC/TC (×100%)
Lake Pavin 0.1 cm	0.28 ± 8	0.01 ± 11	4
Lake Pavin – 4 m (C)	0.42 ± 14	0.01 ± 25	2
Lake Pavin – 4 m (F) ^a	5.08	0.95 ± 9	19
Lake Pavin – 20 m	7.80 ± 4	0.42 ± 14	5
Lake Pareloup 1–2 cm	3.40 ± 4	0.23 ± 8	7
Lake Pareloup 10–30 cm	2.62 ± 6	0.19 ± 25	7
DYFAMED 0–10 cm	0.41 ± 12	0.16 ± 5	38
DYFAMED 15–20 cm	0.31 ± 35	0.08 ± 4	25
DYFAMED 30–35 cm	0.63 ± 24	0.06 ± 4	9
PHYCEMED BA-OR 1–10 cm	0.44 ± 8	0.02 ± 5	5
PHYCEMED SR-T 1–10 cm	0.79 ± 13	0.08 ± 28	10

C and F are the coarse and fine sediments fractions, respectively, separated by centrifuge; standard errors are expressed as standard deviation divided by mean of triplicate analyses.

^a Insufficient sample for triplicate analyses.

Cachier, 1992) and sediments cannot not be faithfully reproduced in standard graphitic carbon which may float and be lost during the rinsing steps of the sample manipulation. The difference between artificial BC and aerosol particles therefore complicates the interpretation of standard addition experiments. Laboratory tests that were performed suggest that BC recovery was reasonable (nearly 100%) over 20-hr oxidation times. However, results were more variable and on average a little less satisfactory (60–110%) during longer oxidation exposures of ~ 60 hr. This is probably due to the slow chemical attack of functional groups residing at the BC particle surface (Smith et al., 1989; Wolbach and Anders, 1989) and the tendency of BC to form a colloidal suspension (W.S. Wolbach, pers. commun.) as its composition gets closer to purely elemental carbon (see Section 2.3.2).

A second, but indirect, approach to evaluate the accuracy of measurements, is the intercomparison of literature results. Table 7 lists published data of carbon concentrations found in coastal and open Pacific ocean sediments. The range of BC concentrations in the Mediterranean Sea (this study) are higher

Table 7
Comparison of black carbon concentrations in sediments reported in the literature (g/100 g)

Site	Carbon concentrations (%)	Method	Reference
Pacific Ocean	0.044 ^a	H ₂ O ₂ /IR	Smith et al. (1973)
Pacific Ocean	0.0001–0.01	H ₂ O ₂ /IR	Herring (1985)
Santa Barbara, coastal	0.03 ^a	H ₂ O ₂ /IR	Griffin and Goldberg (1975)
Lake Michigan	0.37 ^a	H ₂ O ₂ /IR	Griffin and Goldberg (1983)
Lakes Pavin and Pareloup	0.01–0.95 (0.30 ^a)	Cr ₂ O ₇ ²⁻ /Coul	this study
Mediterranean Sea	0.02–0.08 (0.06 ^a)	Cr ₂ O ₇ ²⁻ /Coul	this study

IR = infrared spectroscopy; Coul = coulometric titration.

^a Average concentrations.

than those found in Pacific deep-sea sediments (Table 7) but appear reasonable given the proximity to polluted aeolian inputs of the Western Mediterranean basin (Cachier and Brémond, 1988). Although it is recognized that BC concentrations in lake sediments can vary widely according to important variability in lake depositional processes (Winkler, 1985), the BC concentrations found in the superficial sediments of Lakes Pavin and Pareloup (this study), which may contain both charcoal and BC, compare well with those reported for Lake Michigan (Griffin and Goldberg, 1983). Such an agreement might be coincidental but indicates that data are reasonable.

For K–T sediments, 0.21% TC and 0.06% BC were determined in a sample 25 cm above the K–T boundary at Woodside Creek, New Zealand. For a similar distance above the boundary layer at the same site and for the same oxidation time, Wolbach et al. (1988) report comparable values of 0.15% TC and 0.06% BC. BC concentrations of K–T sediments from other sites will be reported elsewhere (manuscript in prep.).

4. Conclusions

We evaluated for all sediment types, the dichromate oxidation method originally intended for the separation of kerogen and BC in K–T sediments (Wolbach et al., 1985). Our tests were carried out on a variety of recent lake and marine sediments under modified experimental conditions. Results showed that typical reaction times of 20 hr (average) were required to remove the organic matter from lake and recent marine sediments, but up to 60 hr were neces-

sary in some cases. Given that relatively small amounts of BC (1–6%) are lost by oxidation during prolonged oxidation times (e.g., 60 hr), it is considered prudent to use standard oxidation times of 60 hr for the separation of organic and BC in sediments. However, due to the complex and variable refractory chemical nature of kerogen in sediments, we recommend that measurements of BC are also determined at longer reaction times (e.g., 100 hr), where practical, to ensure that attack of kerogen is complete.

We recognise the need to resolve the differences that exist between experimental approaches of BC determination in sediments. An interlaboratory comparison would be invaluable but is beyond the scope of this study. Such a comparison may help distinguish between various forms of particulate carbon in sediments. Further studies to investigate the different half-lives of kerogen in sediments of various origin and age might yield additional information on the chemical nature and maturity of kerogen in such sediments. Work is currently underway to separate charcoal debris from aerosol-derived BC in sediments which could be more refractory and stable over geological time. Improved separation of refractory BC from other carbonaceous matter in sediments is important to estimate the particulate carbon flux from the biosphere to the sediment sink.

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