

Effects of decarbonation treatments on $\delta^{13}\text{C}$ values in marine sediments

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Abstract

Three different methods for decarbonating sediment samples prior to carbon isotope analyses were compared with each other: A, treating the sample with 10% HCl; B, treating the sample with 10% HCl followed by a twofold rinse with deionized water; C, acid fuming with 36% HCl in a desiccator. Whereas, method A and method B gave comparable results, method C gave poor results, since not all of the carbonate was eliminated, especially in samples with high carbonate content, and then interfered with the isotope measurements. Therefore, it is suggested to wash the samples after a treatment with acid (Method B) to avoid deleterious effects of HCl fumes on the elemental analyser and mass spectrometer. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Carbon isotope values of marine sediments have been widely used to distinguish between marine and terrestrial organic matter contributions (Sackett, 1964; Calvert and Fontugne, 1987; Jasper and Gagosian, 1989). The rationale behind using carbon isotopes for distinguishing between both sources is that marine phytoplankton uses bicarbonate dissolved in seawater as a carbon source for photosynthesis ($\delta^{13}\text{C}$ value = 0‰ vs. VPDB), whereas

land plants use carbon dioxide from the atmosphere with a $\delta^{13}\text{C}$ value of -7‰ vs. VPDB (Degens et al., 1968; O’Leary, 1981; Sackett, 1989). This leads to ‘heavy’ values of -19‰ to -21‰ for algal material and ‘light’ values of about -25‰ to -26‰ for higher plant (terrestrial plants) material (Degens, 1969; O’Leary, 1988).

It could be shown earlier that the carbon isotopic composition of marine phytoplankton is heavily dependent on the $p\text{CO}_2$ of surface waters in the ocean (Rau et al., 1989, 1992). More recently, it has been shown by Laws et al. (1995) and Rau et al. (1997) that the fractionation of carbon isotopes by phytoplankton is also related to cell growth rate, cell size and cell membrane CO_2 permeability as well as $[\text{CO}_2(\text{aq})]$. This variability in the marine “end-member” could lead to uncertainties in the application of

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sedimentary $\delta^{13}\text{C}_{\text{org}}$ values to the interpretation of an organic matter source in the ocean.

Furthermore, two different photosynthesis pathways have to be taken into account when using carbon isotopes in sediments for reconstructions of source areas or changes in $p\text{CO}_2$. The C3 pathway using RUBP carboxylase shows values between -34‰ and -22‰ VPDB, whereas the C4 pathway used, e.g. by corn and monocots of grasslands, exhibits values between -8‰ and -16‰ VPDB and PEP carboxylase (see review by Troughton, 1979).

A prerequisite for measuring carbon isotopes of organic material in sediments is to eliminate carbonates occurring in various forms, i.e. mainly calcite and aragonite from organisms such as forams ($\delta^{13}\text{C}$ value = -0.5‰ to $+2.8\text{‰}$, Shackleton and Kennett, 1975), pteropods or molluscs, and dolomite ($\delta^{13}\text{C}$ value = -20‰ to $+60\text{‰}$, Deuser, 1970) that might be incorporated into the sediments, e.g. by river transport (weathering), since the isotopic value of the carbon atom of the carbonate would otherwise bias the isotopic signal.

In the past, several methods dissolving carbonates in sediments by acid-treatment, thereby eliminating the carbonate carbon as carbon dioxide, have been described (Froehlich, 1980; Weyliky et al., 1983; Hedges and Stern, 1984). In this study, we compare carbon isotopic values of sedimentary organic material that was treated by (1) 10% HCl, (2) 10% HCl succeeded by washing with deionized water, and (3) acid fumed in a desiccator to eliminate carbonates.

2. Experimental

For our study, we have chosen sediments from different oceans and marine shales consisting of various amounts of organic carbon (OC) and carbonate. Sediment samples were taken in the Arabian Sea (94KL and 111KL), the Arctic Ocean (PS), and the Pacific Ocean (P4). Five samples were selected from a marine shale (Late Devonian–Early Mississippian New Albany Shale). We have also included a piece of wood, which was recovered from a sediment sample of Jervis Inlet, British Columbia. Sediment samples have organic carbon and carbonate concentrations between 0.16% and 11.78% and 0.5% and 90%, respectively, and, therefore, cover a broad

range of concentrations occurring in natural sediments.

Samples were all freeze-dried and homogenized by grinding, before treatment with the procedure as follows.

(A) The first sample set material was several times (usually 3–5 times) acid treated in glass vials with 10% HCl until no further gas bubbling was recognized. The dried (40°C) samples were then transferred into tin cups (20–30 mg dry weight). One has to be careful at this step because it is not possible to pack the samples long in advance since the tin foil will be damaged by the acidic sediments.

(B) The second set of samples was acidified with 10% HCl in glass test-tubes until no further carbon dioxide formation evolved. The supernatant was centrifuged and the samples were twice washed with deionized water. After drying at 40°C samples were weighed (20–30 mg dry weight) in tin cups.

(C) The third sample set was weighed in test-tubes and transferred in a desiccator containing a bowl with 36% HCl. The ungreased (!) lid was closed immediately. Since there might be, depending on the carbonate content of the samples, a strong carbon dioxide formation, one has to make sure that this gas can escape, i.e. the lid should not be closed hermetically. After 24 and 48 h, the acid was renewed and after 72 h in total the samples were dried at 40°C and transferred in tin cups.

All samples were combusted in a Fisons NA1500 element analyzer and the evolved CO_2 was passed online to a VG PRISM isotope-ratio mass spectrometer in a continuous flow of helium. Results are reported in the δ notation:

$$\delta^{13}\text{C} (\text{‰}) = \left\{ R_{\text{sample}} / R_{\text{standard}}^{-1} \right\} \times 1000,$$

where R_{sample} and R_{standard} are the $^{13}\text{C}/^{12}\text{C}$ ratios of the sample and standard, respectively. VPDB is the reference standard for $\delta^{13}\text{C}$ and the external measurement precision was better than $\pm 0.2\text{‰}$.

3. Results and discussion

Measured values range between -19.23‰ and -30.24‰ for sediment samples treated by method A, -19.45‰ and -30.21‰ for method B, and

–4.07‰ and –30.26‰ for method C (Table 1). Values measured by the first two methods are in a range characteristic for organic material in marine sediments (e.g. Jasper and Gagosian, 1989; Prahl and Muehlhausen, 1989; Fischer, 1991).

For all three methods, lightest values (–28.90‰ to –30.24‰) are measured for sediment samples with high TOC content (3.09% to 11.78%). Heaviest values are measured for Arabian Sea sediment samples for method A and B, whereas samples with high carbonate content (Pacific Ocean samples) lead to heaviest values using method C (see Fig. 1). Methods A (treated by acid) and B (treated by acid and rinsed with deionized water) give relatively similar results with the greatest difference between pairs being 0.70‰, the mean difference between all sample pairs was only 0.27‰. There is no general trend in that one or the other method would lead to heavier or lighter values (Fig. 2), but method B produces 20 values to be lighter and only 6 values to be heavier than method A. Also, the heavier values are only

slightly heavier (0.03–0.47‰, mean = 0.17), whereas the lighter values are strongly lighter (0.01–0.70‰, mean = 0.29). No correlation between the OC or carbonate content of a sample and the size of the difference of the carbon isotopic value could be observed.

Deviation of water-rinsed samples suggests that during the rinsing process, organic matter that was hydrolyzed during the acidification step was lost as dissolved organic matter by decanting the deionized water. Since most isotopic values were shifted to lighter values, it is assumed that the more ‘labile’ marine organic matter is hydrolyzed and lost. It is, therefore, suggested not to rinse the sediment samples after acidification if exact values are necessary. If, depending on the requirement of precision, small deviations of the isotopic values due to a rinsing step could be accepted, washing the sample may be better since, e.g. halogenated compounds (mainly chloride) can be deleterious for the measuring unit over a longer timespan. Using method B would protect the

Table 1
 $\delta^{13}\text{C}$ values organic carbon and carbonate concentrations of the investigated values (n.d. means not determined)

Sample no.	Method A	Method B	Method C	Contamination grease	TOC	CaCO ₃	Sample name	Location
1	–19.63	–19.79	–19.29	–25.09	0.31	35.40	94KL 60	Arabian Sea
2	–19.28	–19.45	–13.99	–22.00	0.57	42.89	94KL 155	Arabian Sea
3	–19.41	–19.62	–13.41	–22.51	0.51	40.07	94KL 810	Arabian Sea
4	–20.12	–20.41	–8.5	–26.71	0.24	33.05	94KL 860	Arabian Sea
5	–28.89	–28.99	–29.03	–29.60	11.78	0.50	64	New Albany Shale
6	–30.24	–30.21	–30.26	–30.65	8.60	1.58	6	New Albany Shale
7	–27.41	–27.27	–27.62	–38.08	0.16	29.08	35	New Albany Shale
8	–28.43	–28.25	–28.21	–36.06	0.31	12.83	9	New Albany Shale
9	–29.45	–29.42	–29.46	–30.99	3.09	19.58	33	New Albany Shale
10	–19.96	–19.49	–16.62	n.d.	1.26	54.31	111KL 689	Arabian Sea
11	–19.84	–19.88	–19.64	–28.46	1.58	40.08	111KL 200	Arabian Sea
12	–19.58	–20.25	–19.72	n.d.	4.88	10.95	111KL 1169	Arabian Sea
13	–19.83	–19.84	–19.34	n.d.	3.11	34.90	111KL 1299	Arabian Sea
14	–21.44	–21.28	–7.91	–22.67	n.d.	90.00	P4 50–55	Pacific Ocean
15	–20.49	–20.78	–4.07	–23.24	n.d.	90.00	P4 90–95	Pacific Ocean
16	–21.38	–21.57	–22.35	–32.30	0.47	8.30	PS2163-2	Arctic Ocean
17	–21.26	–21.71	–22.29	–29.19	0.58	10.00	PS2186-1	Arctic Ocean
18	–22.20	–22.90	–22.91	–29.45	1.15	13.70	PS2212-5	Arctic Ocean
19	–21.08	–21.76	–23.26	–32.75	0.31	23.30	PS2200-2	Arctic Ocean
20	–21.50	–21.78	–21.69	–33.80	0.55	5.80	PS2170-1	Arctic Ocean
21	–21.39	–21.77	–21.78	–33.48	0.40	5.80	PS2178-2	Arctic Ocean
22	–22.08	–22.25	–22.97	–32.13	0.75	10.40	PS2159-4	Arctic Ocean
23	–21.56	–21.94	–22.29	–30.67	0.91	3.30	PS2190-3	Arctic Ocean
24	–22.86	–23.05	–23.07	–27.58	0.65	3.60	PS2215-2	Arctic Ocean
25	–26.26	–26.68	n.d.	–26.39	n.d.	n.d.	wood	Jervis Inlet

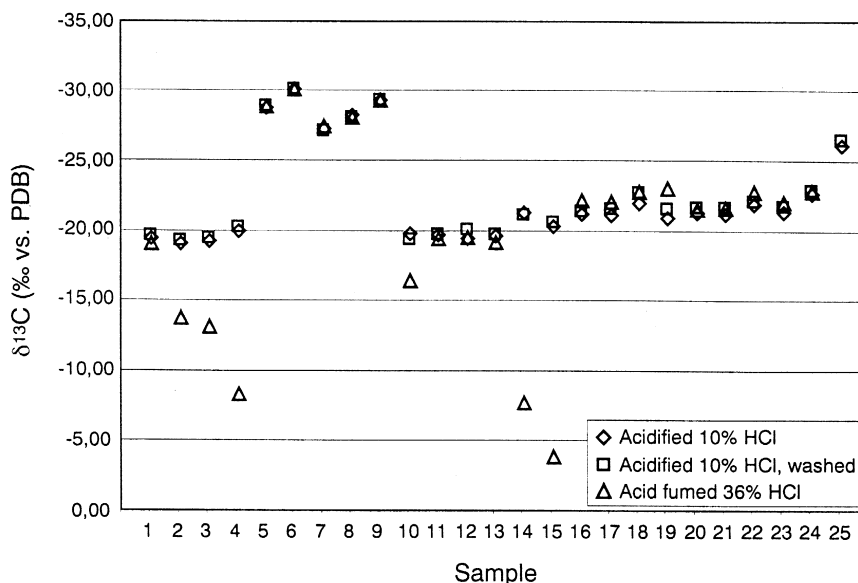


Fig. 1. $\delta^{13}\text{C}$ values of the investigated samples. Sample numbers of sediments are listed in Table 1. Note the large difference for method C for samples with high carbonate content.

combustion and reduction columns in the CN analyzer. They are of quartz or silica and break quite easily if they are weakened by some interaction between the quartz/silica and sample material. However, nothing should get into the mass spectrometer since these compounds are being trapped by the reagents in the combustion column or pumped away before CO_2 are led into the mass spectrometer.

Carbon isotopic values of samples treated with method C (acid fuming succeeded by drying at 30°C) show considerable deviations from the acid rinsed (method A) samples. There is no general trend comparing samples values from both methods, instead, some values of samples treated by method C are very heavy -4.0‰ to -8.0‰ , whereas others are slightly lighter than values of samples treated by method A. Such heavy isotopic values for organic material in sediments are unrealistic; therefore, a dilution of the organic material by carbonate has likely occurred. This is especially obvious for samples with very high carbonate content, e.g. the samples from the Pacific (90%) but also samples with lower carbonate concentrations (33%, Arabian Sea) have not been totally decarbonated. Although 36% hydrochloric acid was used and exchanged after 24 h twice, this treatment is not effective enough to elimi-

nate high concentrations of calcium carbonate or dolomite (incorporated by rivers) in sediment samples so that the carbon isotopic value of the carbonate is mixed with the organic carbon isotope value. Nevertheless, this method might be well applied for filters on which phytoplankton from the water column has been sampled since those usually include only a small amount of carbonate that is easily eliminated.

Accidentally, we have also fumed samples in a desiccator of which the lid has been greased with

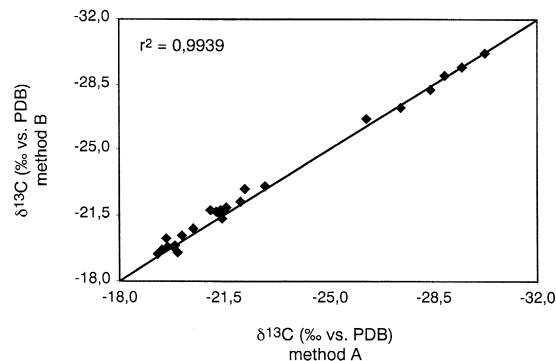


Fig. 2. Correlation of $\delta^{13}\text{C}$ values of sediments that were treated with method A and B, respectively. There are only slight shifts in the values, as also expressed by the correlation coefficient.

silicone grease (Dow Corning; “high vacuum grease” silicone-based, from Dow Corning, Midland, MI, USA). Whereas here, samples with high organic carbon (8–12%) show only minor effects in the carbon isotopic values (-0.6% at most), samples with lower organic carbon contents are heavily biased (up to -12%). It turned out that the HCl has reacted with the silicone grease ($\delta^{13}\text{C} = -50\%$) that, in turn, then has contaminated the samples during the fuming process. Therefore, whenever applying the fuming technique, the lid should be cleaned from silicone grease very thoroughly with acetone and dried before being used.

4. Conclusion

Whenever sediment samples are prepared for carbon isotopic measurements, it is suggested to apply method A that includes the dissolution of carbonates with 10% HCl and no further treatment with deionized water. However, to treat the CN-Analyzer and, in some cases, the mass spectrometer more carefully, the samples should be treated by method B, which includes several rinses with deionized water and drying before measuring. This might lead to small deviations of the carbon isotopic values; using this method, therefore, is dependent on the precision needed for the analyses and interpretation of the results.

Method 3 (fuming the samples in a desiccator) seems not be a very useful technique for sediments and should be avoided. To eliminate carbonates from filters that have been used for filtering sea water, however, this method is spread widely and seems to work fine, also it has not been tested in this study. In any case, and this should be obvious for any user, the use of vacuum/silicone grease on the seal of the desiccator must be avoided at any time.

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