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Organic carbon $\delta^{13}C$ variations in sedimentary rocks as chemostratigraphic and paleoenvironmental tools

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Abstract

Carbon isotopic variations in marine carbonate rocks and organic matter can provide important information on stratigraphic correlations and paleoenvironments. In particular, carbon isotopic variations in marine organic materials may yield information about the concentration of oceanic dissolved CO_2 and/or the physiology of the microalgal community. This paper reviews evidence from laboratory experiments and oceanographic studies aimed at understanding controls on carbon isotopic fractionation by marine phytoplankton. We also review factors affecting carbon isotopic compositions of bulk sedimentary organic matter and individual biomarker compounds. Guidelines for analysis of isotopic compositions of organic materials and interpretations of these results for use as chemostratigraphic and paleoenvironmental tools are presented. We recommend caution in interpreting carbon isotopic variations of sedimentary organic matter because no environmental factor explains adequately variations in the carbon isotopic composition of modern phytoplankton. Studies of ancient materials should include compound-specific isotopic analyses of known phytoplankton biomarkers or organism-specific isotopic analyses with bulk isotopic results to assess the proportions of allochthonous organic materials, the degree of reworking and the extent of thermal degradation to confirm any trends present in δ-values of bulk sedimentary organic matter. © 1997 Elsevier Science B.V.

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1. Introduction

Variations in the carbon isotopic composition of marine carbonates rocks and components (fossils, marine cements) have been recognized and used for chemostratigraphic correlations and paleoenvironmental interpretations (Veizer and Hoefs, 1976; Fischer and Arthur, 1977; Scholle and Arthur, 1980; Popp et al., 1986, among others). Secular changes in the isotopic composition of carbonate materials have been well understood for over two decades (Broecker, 1974; Garrels and Perry, 1974). Variations in the carbon isotopic composition of marine organic matter have also been used for chemostratigraphic correlations (Knoll et al., 1986; Kaufman et al., 1991,

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among others) as well as environmental interpretations (Arthur et al., 1985; Dean et al., 1986; Hayes et al., 1989 and others).

Variations in the isotopic composition of modern suspended and sedimentary organic matter as well as modern phytoplankton are poorly understood. The lack of understanding results from incomplete knowledge of carbon isotopic effects associated with photosynthesis by marine microalgae and biological reworking of organic materials and our inability to distinguish primary photoautotrophic organic remains from those derived from secondary consumers in bulk samples. Recently, much effort has been directed at understanding environmental variations in the carbon isotopic composition of phytoplankton, the base of the food chain which constitutes the materials in marine organic matter. These variations have been attributed to changes in (1) the concentrations of oceanic and atmospheric CO_2 (Arthur et al., 1985; Hayes et al., 1989; Popp et al., 1989; Rau et al., 1989, among others), (2) phytoplankton productivity (Hollander and McKenzie, 1991, among others) and (3) physiology of marine phytoplankton and/or their response to one or more environmental factors (Sharkey and Berry, 1985; Rau et al., 1992; Francois et al., 1993; Goericke et al., 1994; Thompson and Calvert, 1994; Laws et al., 1995). Several authors have suggested that misinterpretation of environmental variations may result from analyses of bulk organic materials and advocate the use of compound-specific isotopic analyses (Hayes et al., 1987, 1989, 1990; Boreham et al., 1989, 1990; Ocampo et al., 1989; Popp et al., 1989; Freeman et al., 1990; Jasper and Hayes, 1990). Other workers contend that the isotopic composition of bulk suspended organic matter as well as sedimentary organic materials provides accurate average values of the isotopic composition of primary organic materials (Rau et al., 1989, 1991, 1992).

This paper reviews controls on the carbon isotopic composition of phytoplankton organic matter and presents new results of isotopic analyses of suspended organic materials from the Southern Ocean. We also review the factors which control carbon isotopic compositions of bulk sedimentary organic matter and individual biomarker compounds. Recommendations for the analysis of carbon isotopic compositions of organic materials and interpretations of these results for use as chemostratigraphic and paleoenvironmental tools are presented.

2. Methods

Selection and treatment of samples for organic geochemical analyses follows procedures outlined by Schopf (1983) and by Hurd and Spencer (1991). The interested worker is encouraged to study these detailed procedures. In this paper, we provide only a broad overview of sample collection and analysis.

2.1. Sample selection and processing

Geologic samples. Geologic field samples should be collected and packaged as to minimize contamination. For example, use of marking pens and sample containers that yield organic materials should be avoided. All surficial contamination from rock samples for organic geochemical analyses should be removed by physical separation. In addition, prior to analyses, rock samples should be fragmented (~ 2 cm^2) and the chips treated with hydrofluoric and hydrochloric acid (HF 15%, HCl 50%, by volume) to remove contamination that may have penetrated samples along fractures, cleavage and bedding planes (e.g. Schopf, 1983). We recommend each sample be mechanically powdered to homogenize the sample using either a ball mill or a ring and puck grinder that has previously been cleaned by grinding with baked (500°C for at least 8 h) quartz sand. Powdered samples and rock chips should be stored in clean vials with caps fitted with teflon liners.

A key to interpretation of secular variations in the organic geochemistry of sedimentary materials is an understanding of the sources of organic matter analyzed. Bulk geochemical analyses can yield an understanding of the source of organic matter. Common analyses include determination of the H/C and N/C ratios as well as the hydrogen and oxygen index by Rock Eval. Determination of the H/C and N/C ratios should follow recommendations of manufacturer of the CHN analysis

system. Rock-Eval analyses should follow the recommendations of Peters (1986).

Modern samples. Modern materials are filtered from seawater collected using a Niskin bottle or by large volume filtration from the ship uncontaminated seawater supply or by in situ filtration. Filtration of seawater from a Niskin bottle may allow direct comparison with other parameters measured at sea (temperature, salinity, nutrients, total dissolved inorganic carbon, alkalinity, pigment distributions, etc.) however the volume available is limited (~10's liters). Large volume filtration allows collection of materials from several hundred liters of seawater, however results obtained on the filtrate must be correlated with those of waters collected via a Niskin bottle which may have been collected at a different time and location. In situ filtration allows samples to be collected from distinct horizons in the water column (i.e., chlorophyll or particle maximum) or, if several pumps are available, profiles within the mixed layer. Prefilters, usually of 10–50 μm Nitex mesh, should be solvent washed prior to use whereas glass fiber filters (1–2 μm) should be ashed at high temperature (400°C for 8 h). All items in contact with filters (filter holder, forceps, etc.) should be solvent rinsed or ashed. Care should be taken whenever the filters are exposed to air to avoid atmospheric contaminants (e.g., boat exhaust, particulates from air conditioning, etc.). Filtered samples should be wrapped in clean (solvent rinsed or ashed) aluminum foil and immediately frozen. Samples on which pigment analyses are to be performed should be stored in liquid nitrogen to prevent pigment breakdown (Hurd and Spencer, 1991 and references therein).

Modern material used for this study was collected as large volume samples of suspended particulate organic matter (SPOM) along the WOCE SR-3 line (Hobart to Antarctica) and across the Princess Elizabeth Trough (northeast of Prydz Bay, Antarctica) on the *RSV Aurora Australis* (Jan–Mar 1994). The sections were sampled to the sea floor about every 30 nautical miles to study the dynamics of the Antarctic Circumpolar Current and samples were taken at nearly all stations. In addition to physical oceanographic measurements, carbon analyses ($[CO_2(aq)]$, δ_{DIC}, alkalinity) and biological studies (nutrient analyses, plankton counts and pigment analyses) were also performed. Samples for this study were collected on precombusted glass fiber filters (143 mm diameter Gelman A/E) from the ship's uncontaminated seawater system. Surface water fCO_2 was continuously monitored from the system and $[CO_2(aq)]$ calculated from fCO_2, temperature and salinity, after Weiss (1974). The fCO_2 measurements were made by circulating air, that had equilibrated with a shower of water from the uncontaminated seawater line, through an infrared gas analyser (LICOR 6252). The air was dried prior to analysis and standards referenced to the WMO X85 mole fraction scale were used to calibrate the analyser. The fCO_2 data were corrected for warming between the seawater inlet in the ship's bow (water depth ~5 m) and the equilibration chamber after Copin-Montegut (1988); Copin-Montegut (1989). Along the WOCE SR-3 line, 42 SPOM samples were collected at stations between 45°S and 65°S whereas across the Princess Elizabeth Trough (PET), 17 samples were collected at stations between 58°S and 67°S. All SPOM samples were filtered from 160–200 l of water. A subsample of each filter was prepared for bulk $\delta^{13}C$ analyses using methods of Wedeking et al. (1983) after acid fuming (HCl 50% v/v for 12 h).

3. Controls on the $\delta^{13}C$ of phytoplankton

In order to fully utilize the information contained in stable isotope data on sedimentary organic carbon, it is necessary to understand the factors which affect the photosynthetic isotope fractionation during the initial production of that material. Phytoplankton discriminate strongly against ^{13}C and the magnitude of that fractionation has been related to factors including temperature, availability of $CO_2(aq)$, light intensity, nutrient availability, species composition, pH, as well as phytoplankton cell size and growth rate (e.g., O'Leary, 1981; Rau et al., 1992; Francois et al., 1993; Hayes, 1993; Goericke et al., 1994; Thompson and Calvert, 1994; Laws et al., 1995). In particular, the relationship between carbon iso-

topic composition of phytoplankton (δ_P) and concentration of oceanic dissolved CO_2 ($[CO_2(aq)]$) has been the subject of considerable attention (e.g., Arthur et al., 1985; Popp et al., 1989; Rau et al., 1989; Freeman and Hayes, 1992; Goericke and Fry, 1994; Hinga et al., 1994). If δ_P is dominantly influenced by the concentration of ambient $CO_2(aq)$ (e.g., Degens et al., 1968; Pardue et al., 1976; Mizutani and Wada, 1982, among others), and if the relationship between isotopic fractionation associated with photosynthesis ($\epsilon_P \equiv 1000[(\delta^{13}Cco_2 - \delta^{13}Cp)\ (1000 + \delta^{13}Cp)^{-1}]$) and $[CO_2(aq)]$ can be quantified (e.g., Freeman and Hayes, 1992), then the prospect exists of using isotopic compositions of ancient sedimentary organic matter to investigate ancient oceanic and atmospheric pCO_2 variations. Understanding relationships between the carbon isotopic composition of marine flora and plant physiology is also important if variations in the $\delta^{13}C$ of organic matter are to be used for stratigraphic correlations and paleoenvironmental interpretations.

Goericke and Fry (1994) showed that variation between ϵ_P and $[CO_2(aq)]$ in contemporary oceanic samples was weak, although significant. They suggested that poor covariance resulted from biological and environmental factors distinct from effects of $[CO_2(aq)]$. The weak covariance may also have resulted from the temporally and spatially disparate data used for this compilation. No data compiled by these workers was from research cruises in which all parameters (i.e., $[CO_2(aq)]$, δ-CO_2, δ_P, sea surface temperature, etc.) were synoptically collected. In some instances, isotopic results were correlated with $[CO_2(aq)]$ collected on cruises that occurred in different seasons and different locations. We have reduced the consequences of disparate sampling by using only results of isotopic analyses of SPOM where these parameters were synoptically sampled. Following the convention adopted by Rau et al. (1992) and Jasper et al. (1994) we have plotted isotopic fractionation (ϵ_P) versus $1/CO_2$ (Fig. 1). In these samples, we assumed that the carbon isotopic composition of SPOM is equal to that of phytoplankton and that, for the Southern Ocean samples, the carbon isotopic composition of total dissolved inorganic carbon was constant and equal to $+1.7‰$ vs. PDB (see Francois et al., 1993).

Results of analyses of samples from the Southern Ocean show reasonably good correlation between ϵ_P and $1/CO_2$ (Fig. 1). However, there is a noticeable divergence from this trend in samples from lower latitudes, with results from the equatorial Pacific marking the region of greatest divergence. These trends confirm the suggestion of Goericke and Fry (1994) that there is no simple relationship between the carbon isotopic composition of SPOM and $[CO_2(aq)]$ for the worlds oceans. To determine if such differences result from changes in plant physiology, Laws et al. (1995) have recently explored plant physiological parameters which may control ϵ_P using growth experiments in a continuous culture system (chemostat).

Several authors (Rau et al., 1992; Francois et al., 1993; Goericke et al., 1994) have speculated that the concentration of CO_2 inside phytoplankton cells (C_i) is an important parameter controlling ϵ_P. Francois et al. (1993) suggested that C_i is controlled by the flux of CO_2 across a cell membrane which is a function of cell permeability, surface area and growth rate. Laws et al. (1995) formulated the relationship between growth rate (μ) and C_i and tested the controls of μ on ϵ_P using a marine diatom grown in a chemostat system.

Phaeodactylum tricornutum CCMP 1327 was grown in a nitrate-limited chemostat culture at $\mu = 0.5$ to 1.4 d^{-1} on either continuous light or a 12 h light:12 h dark cycle and constant supply of CO_2. Laws et al. (1995) measured daily cell density, fluorescence, concentration of total dissolved inorganic carbon (DIC) and total alkalinity (allowing calculation of $[CO_2aq]$) and the $\delta^{13}C_{DIC}$ in the growth chamber. Samples of phytoplankton organic matter were taken for carbon isotopic analysis only after each of these parameters reached steady state.

In continuous culture systems, growth rate is accurately set ($\mu \pm 0.01$ d^{-1}) so that effects of μ can be directly related to ϵ_P using a modification of the equation of Farquhar et al. (1982):

$$\epsilon_P = \epsilon_t + (\epsilon_f - \epsilon_t)\left(\frac{K_1}{K_2} - \frac{\mu}{K_2 CO_2}\right) \quad (1)$$

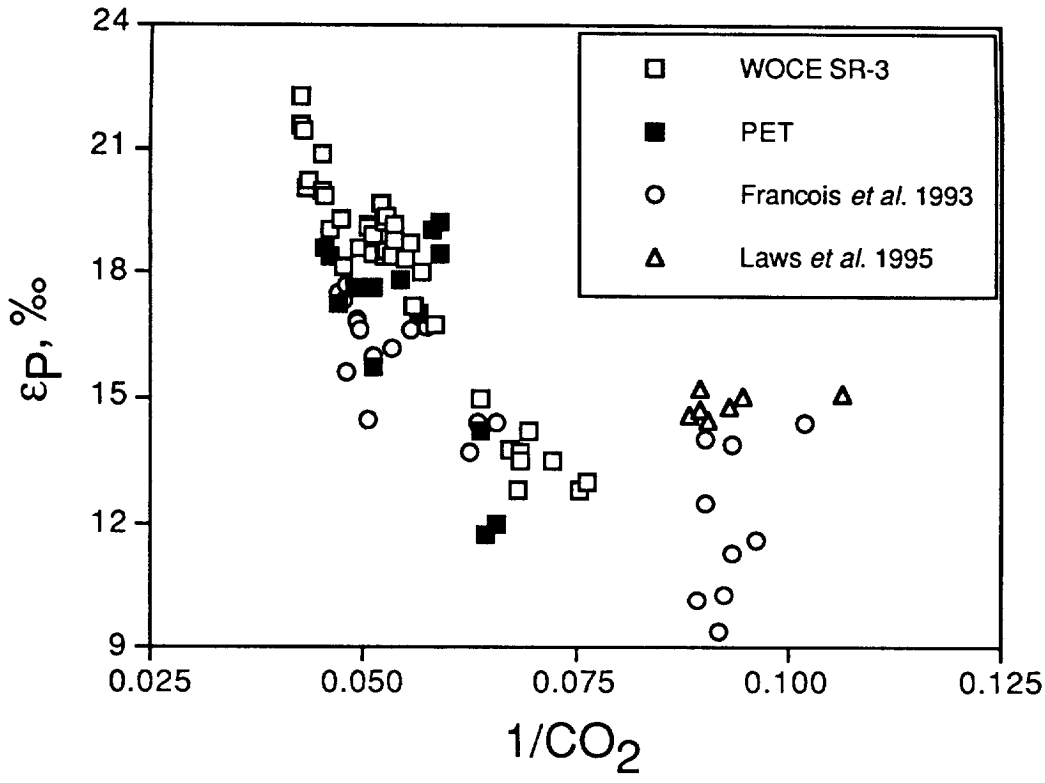

Fig. 1. Isotopic fractionation (ϵ_P) plotted as a function of reciprocal of the ambient CO_2(aq) concentration. Isotopic analyses are from bulk suspended organic matter collected at less than 10-m water depth and at oceanic stations where [CO_2(aq)] was determined synoptically. The Southern Ocean samples were collected from the WOCE SR-3 line south of Tasmania, Australia (this study), across the Princess Elizabeth Trough (PET) just northeast of Prydz Bay, Antarctica (this study) and from the Southern Indian Ocean (Francois et al., 1993). Samples from the equatorial Pacific were collected between 3°N and 12°S, 140°W (Laws et al., 1995).

where CO_2 is the concentration of CO_2(aq) external to the cell, ϵ_t and ϵ_f are the discrimination factors associated with diffusion of CO_2 into the plant and fixation of CO_2 within the plant, respectively, and K_1 and K_2 are diffusive flux constants for CO_2 into and out of the cell, respectively. Inherent in this expression is the assumption that:

$$\mu = k(C_e - C_i) \quad (2)$$

where C_e is the [CO_2(aq)] outside the cell membrane, C_i is the [CO_2(aq)] inside the cell and k is a constant (see Laws et al., 1995). If isotope discrimination effects due to respiration and photorespiration are negligible, then ϵ_P is expected to be a linear function of μ/CO_2. If $K_1 \cong K_2$, then ϵ_P should approach ϵ_f in the limit as $\mu/CO_2 \rightarrow 0$. ϵ_f is the combined fractionation due to Rubisco and β-carboxylase carboxylations, and its likely value is 25–28‰ (see review by Goericke et al., 1994).

Laws et al. (1995) applied equation 1 to laboratory data and found a linear relationship between ϵ_P and μ/CO_2. Linear regression lines were fit to continuous light and the 12h light:12h dark data from *P. tricornutum*. In the latter experiments, $\delta^{13}C_{P.\ tricornutum}$ showed no temporal trend during the 12h dark period indicating little isotopic fractionation was associated with respiration and isotopic fractionation was expressed only during the photoperiod. The value of ϵ_P predicted by the linear regressions at $\mu/CO_2 = 0$ is 25.0 ± 0.2‰, an ϵ_P value consistent with the expected fractionation of 25–28‰ due to Rubisco and β-carboxylase carboxylations.

Application of the empirical relationship

between ϵ_P and μ/CO_2 for *P. tricornutum* to results of analyses of samples collected during the spring 1992 Equatorial Pacific (EqPac) Study allowed estimates of in situ growth rates of natural phytoplankton populations. Laws et al. (1995) combined the comprehensive suite of analyses performed by EqPac investigators with isotopic analyses of total dissolved inorganic carbon and chlorophyll *a*. Calculated phytoplankton μ based on the *P. tricornutum* relationship agreed with community μ measured independently during the 1992 EqPac study (Laws et al., 1995).

To determine if growth rates significantly alter the correlation found between $[CO_2(aq)]$ and ϵ_P for antarctic phytoplankton, we estimated maximum growth rates during the photoperiod for our WOCE SR-3 samples using a modification of the μ-temperature equation of Eppley (1972). A μ-temperature relationship has been shown to accurately describe the dependence of Antarctic phytoplankton photosynthesis rates on temperature (Neori and Holm-Hansen, 1982). We used the relationship of Eppley (1972) modified to yield specific growth rates (rather than doublings per day):

$$\mu_{MAX} = 0.590(1.066)^T \quad (3)$$

where μ_{MAX} is the maximum growth rate and T is temperature (°C). Growth rates predicted by this equation assume that sea surface temperature is the factor that limits growth. This latter assumption may be unrealistic as other authors (e.g., de Baar et al., 1995) have suggested that growth rates in Antarctic phytoplankton may be limited by micronutrients such as iron. Certainly more work is needed to understand the controls of growth rates in antarctic as well as other phytoplankton species especially those flora living in high nutrient, low chlorophyll regions (e.g., Martin et al., 1994). However, when our calculated temperature-dependent maximum growth rates of antarctic phytoplankton are considered, a linear relationship is obtained for the WOCE SR-3 samples which is more consistent with the laboratory and field results of Laws et al. (1995). Specifically, the slope of the line describing μ, $[CO_2(aq)]$ and ϵ_P for these samples (Fig. 2) is closer to that found by Laws et al. (1995), however it is certainly not identical.

Reworking of primary materials by heterotrophic organisms can cause shifts in the carbon isotopic composition of bulk organic materials (e.g., Hayes, 1993). A shift of ~1.5‰ to lower ϵ_P values in the WOCE samples may have resulted from incorporation of heterotrophic biomass in bulk SPOM samples. A similar difference between bulk SPOM and phytoplankton carbon isotopic values was observed by Laws et al. (1995) in the equatorial Pacific samples. This potential diagenetic shift in ϵ_P is minor however compared to the change in the slope of the regression lines characterizing the Southern Ocean samples (compare Figs. 1 and 2).

The possibility exists that results from experiments using *Phaeodactylum tricornutum* may be inappropriate for estimating growth rates of antarctic phytoplankton. Although *P. tricornutum* is easy to handle in laboratory cultures, it is not a typical open ocean diatom and does not grow at temperatures less than 10°C. As suggested by Francois et al. (1993) and Laws et al. (1995), there is no reason to anticipate that the relationship between ϵ_P and μ/CO_2 will be the same for all phytoplankton. Recent measurements performed in the Ross Sea (Dunbar and Leventer, 1992; Rogers and Dunbar, 1993), Prydz Bay (Kopczynska et al., 1995) and the Bransfield Strait (Fischer, 1991) have documented large species-dependent variations in the carbon isotopic composition of SPOM. The ϵ_P–μ/CO_2 relationship Laws et al. (1995) found for *P. tricornutum* may be representative of phytoplankton living only in limited regions in the Southern Ocean. However, phytoplankton growth rates are variable in the Southern Ocean (e.g., Sakahaug and Holm-Hansen, 1986; Spies, 1987; Tilzer and Dubinsky, 1987) and these changes likely affect ϵ_P. Use of the ϵ_P vs. $1/CO_2$ relationship assumes that growth rate is constant (Fig. 1). The greater similarity in the *slope* of the regression lines characterizing the field data and laboratory results in which growth rates are allowed to vary imply that phytoplankton growth rates can influence the carbon isotopic composition of photoautotrophs. However, in order to understand the isotopic biogeochemistry of Southern Ocean phytoplankton it will be necessary to determine the relationship between growth

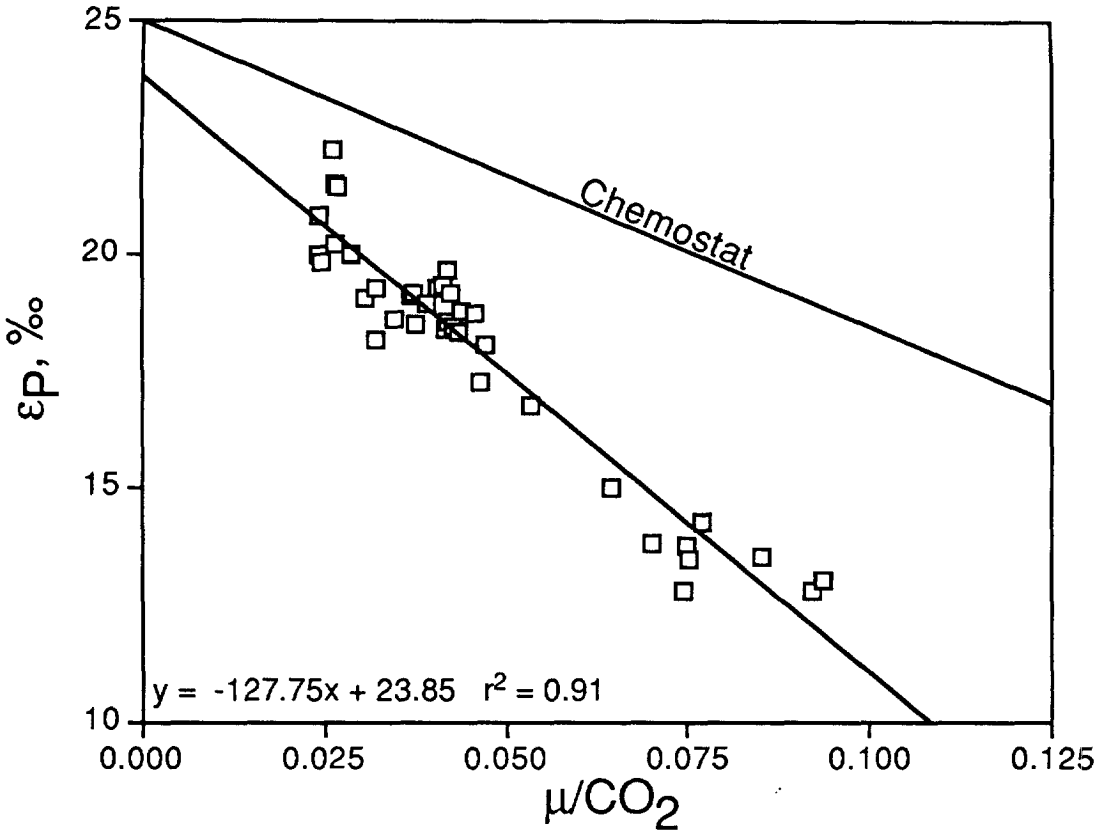

Fig. 2. Relationship between ϵ_P and μ/CO_2 for samples collected along the WOCE SR-3 line. Growth rates were determined using Eq. (3) which is a modification of the μ_{MAX}–temperature relationships of Eppley (1972) and Neori and Holm-Hansen (1982). The line pasing through the data is a linear regression for all the WOCE SR-3 results whereas the *chemostat* line is the ϵ_P–μ/CO_2 relationship Laws et al. (1995) obtained for *P. tricornutum*. The equation describes the results for the WOCE SR-3 data.

rate, $[CO_2(aq)]$ and ϵ_P for representative antarctic species using a combination of laboratory and field studies.

Several authors have related ϵ_P to changes in productivity (Hollander and McKenzie, 1991; among others). It should be noted that the rate of phytoplankton growth (μ, d^{-1}) is related to the rate of primary production (dC/dt, mg C m^{-3} d^{-1}) according to the following equation:

$$\mu = \frac{1}{C}\frac{dC}{dt} = \frac{Chl}{C}\frac{1}{Chl}\frac{dC}{dt} \quad (4)$$

where, C is phytoplankton carbon biomass (mg C m^{-3}) and Chl is chlorophyll a concentration (mg Chl m^{-3}). This equation implies that equivalent production rates can be achieved under conditions of high algal biomass/low growth rate (e.g. post-bloom waters) and low algal biomass/high growth rate (e.g. open-oceanic waters). Algal growth and primary production rates can only be related if the standing stock of phytoplankton carbon is known. Phytoplankton carbon biomass can be estimated from Chl concentration and knowledge of the *C:Chl* ratio. The *C:Chl* ratio expressed by phytoplankton is dependent upon both growth irradiance and the rate of nutrient supply (Laws and Bannister, 1980). Consequently, this ratio is highly variable in natural waters, with most values typically ranging from 10 to 200 mg mg^{-1}. Alternatively, phytoplankton carbon biomass can by estimated from cell counts, biovolumes and published carbon-to-biovolume rela-

tionships. While cellular carbon quotas vary considerably, cellular carbon content varies predictably as a function of cellular volume (Montagnes et al., 1994). Thus, in the case of, for example, diatoms, which leave behind quantifiable amounts of inorganic fossil remains in the sedimentary record, it should be possible to estimate cellular carbon concentrations. While this information is useful, estimation of paleoproduction rates from μ (derived from the ϵ_P–μ/CO_2 relationship; cf. Laws et al., 1995) still requires knowledge of the original cellular abundances (cells m^{-3}) in the overlying water column.

Lastly, under conditions of low [CO_2(aq)], cells may obtain inorganic carbon via active transport. Many marine phytoplankton are known to be able to utilize bicarbonate as a source of inorganic carbon (Burns and Beardall, 1987; Raven and Johnston, 1991, 1994). Because of the equilibrium isotope effect between bicarbonate and CO_2(aq), utilization of the former by phytoplankton can alter the carbon isotopic composition of fixed carbon (e.g., Sharkey and Berry, 1985). However, the mechanisms of inorganic carbon active transport and its affect on ϵ_P are currently a matter of speculation (Raven and Johnston, 1991, 1994; Laws et al., 1995). Laws et al. (1995) concluded that active transport may only be an issue when phytoplankton growth rates are very rapid and/or when [CO_2(aq)] is less than 10 μmol kg^{-1}. Active transport of inorganic carbon thus may not have affected the carbon isotopic composition of most Paleozoic phytoplankton when, presumably, the concentration of atmospheric CO_2 was much higher than it is today (e.g., Berner, 1990).

4. Factors influencing the $\delta^{13}C$ of bulk organic matter and of individual compounds

When considering the sources of organic matter in sediments and rocks, we commonly think in terms of derivation from only marine primary producers with perhaps some allochthonous terrestrial organic matter inputs. The structures of some sedimentary organic compounds indicate that they are algal in origin, but much of the organic matter characterized in sediments cannot easily be distinguished from the products of the remainder of an ecosystem which is devoted to the consumption, not preservation, of phytoplanktonic organic material. The average isotopic composition of total organic carbon will depend on the proportions of these inputs and on post-depositional processes of alteration. For example, zooplankton can significantly modify the structure of molecular biomarkers and can affect isotopic compositions of organic matter in the ocean (e.g., Altabet and McCarthy, 1985; Altabet, 1988; Lee and Wakeham, 1988; Fischer, 1991). Critical to our understanding of secular isotopic variations in organic carbon is the extent to which we can understand isotopic shifts due to herbivory, post-depositional alteration and the influence of allochthonous inputs.

Carbon- and nitrogen-isotopic compositions of marine particles, the primary source of sedimentary organic matter, may be related to the trophic level of those organism from which it is derived (see recent review by Hayes, 1993). Several studies of modern macro-organisms in the laboratory and in nature have documented ^{13}C enrichments of 1–1.5‰ and ^{15}N enrichments of 3–5‰ (in total biomass) per trophic level (e.g., DeNiro and Epstein, 1978; McConnaughy and McRoy, 1979; Monson and Hayes, 1980; Monson and Hayes, 1982a,b; Fry et al., 1983, 1984; Fry and Sherr, 1984; Fry, 1988). Fry (1988) found that nitrogen-isotopic compositions were robust measures of trophic position in a variety of vertebrate and invertebrate organisms collected on Georges Bank. In addition, McConnaughy and McRoy (1979) report ^{13}C enrichments of up to 8‰ relative to that of phytoplankton in organisms in the Bering Sea. The magnitude of ^{13}C enrichments commonly correlated with known or probable feeding habits (McConnaughy and McRoy, 1979). When interpreting geochemical secular variations it is important to keep in mind that biological inputs derive from multiple trophic levels, and the assortment and prominence of specific organisms can change in response to environmental variations and, thus, can strongly affect particularly the isotopic composition of bulk sedimentary organic matter. Isotopic compositions of phytoplankton (based on analyses of their biomarker compounds) can be one to several permil different from bulk organic matter $\delta^{13}C$ in ancient sediments (Hayes

et al., 1987, 1989; Freeman et al., 1990; Kenig et al., 1994) as well as modern suspended organic matter (Laws et al., 1995).

Characterization of sedimentary organic matter by Rock Eval pyrolysis is commonly used to determine the source and thermal maturity of sedimentary organic matter. Extensive review of the Rock Eval methods and correlations between hydrogen index and oxygen index with H/C and O/C ratios can be found in Tissot and Welte (1984). An excellent discussion of the use of pyrolysis data to characterize the source and thermal maturity of sedimentary organic matter and their effects on the carbon isotopic composition of bulk sedimentary organic matter can be found in Dean et al. (1986). Briefly, the hydrogen index obtained through Rock Eval pyrolysis is a function of the elemental H/C ratio of the kerogen and is believed to reflect the relative amount of lipid-rich, sapropelic organic matter preserved in rocks (Espitalie et al., 1977; Tissot and Welte, 1984). The oxygen index is an indicator of the oxygen content of organic matter (Espitalie et al., 1977). In their original description of this type of analysis, Espitalie et al. (1977) showed that the hydrogen index and oxygen index could be used like a van Krevelen diagram to facilitate the identification of the source of organic matter and the extent to which it has been thermally altered.

Pratt (1984) found that the Rock Eval hydrogen and oxygen index corresponded to extent of bioturbation in the Greenhorn Formation from central Colorado. Pratt (1984) showed in this unit that a decrease in hydrogen index and increase in oxygen index was correlated with increased evidence for bioturbation and was not the result of increased relative abundance of terrestrial organic matter. The distribution of *n*-alkanes in all lithologies was essentially smooth without significant odd-carbon preference and only small amounts of long chain paraffinic compounds were present indicating low abundance of terrestrial organic matter (see Pratt, 1984). Kenig et al. (1994) provided evidence that the extent of reworking by infaunal organisms can influence the carbon isotopic composition of bulk sedimentary organic materials. Kenig et al. (1994) documented a relationship between infaunal biofacies, hydrogen index and enrichment of ^{13}C in sedimentary organic matter in the marine Jurassic Oxford Clay. Cautious interpretation of Rock Eval analyses can lend insights to the source of organic materials, the extent of reworking by epifaunal and infaunal organisms as well as the thermal maturity of organic matter all of which can affect the carbon isotopic composition of sedimentary organic matter.

Although chemical characterization of organic matter provides insight into its origin and can be used to understand the environmental processes responsible for that chemical signature, Rock Eval analysis can lack the specificity required to fully characterize many natural mixtures. Stable isotopic compositions of bulk organic matter and Rock Eval data can be difficult to interpret due to indistinct boundaries between sources and an inadequate understanding of the isotopic compositions of the source materials (Fry and Sherr, 1984; Gearing et al., 1984; Altabet and McCarthy, 1985; Kennicutt et al., 1987). To resolve this complexity, determinations of stable isotopic compositions of individual compounds have been investigated, including amino acids (Macko et al., 1987), photosynthetic pigments (Bogacheva et al., 1980; Katase and Wada, 1990; Bidigare et al., 1991; Kennicutt et al., 1992), fatty acids (Monson and Hayes, 1980, 1982a,b), aliphatic and aromatic hydrocarbons (Summons and Powell, 1986; Hayes et al., 1987, 1990; Freeman et al., 1990; Kennicutt and Brooks, 1990), alkenones (Jasper and Hayes, 1990; Jasper et al., 1994), and geoporphyrins (Hayes et al., 1987, 1989, 1990; Boreham et al., 1989; Ocampo et al., 1989; Popp et al., 1989; Chicarilli et al., 1993; Keely et al., 1994).

Stable isotopic signatures of individual photosynthetic pigments ($\delta^{13}C$, $\delta^{15}N$) and steroidal biomarkers ($\delta^{13}C$) offer unique means of monitoring biosynthetic strategies and fates of phytoplankton production. Chlorophyll-related compounds, in particular, are ideal for a molecular, stable isotope approach because (a) porphyrins and chlorins are abundant in nature, (b) early diagenetic reactions are well defined, (c) tetrapyrroles contain two elements amenable to stable isotope analysis and (d) chlorophylls are the basis of the photosynthetic process that produces biomass. Furthermore, tetrapyrrole-based diagenetic alteration products, geoporphyrins, are ubiquitous and stable in the geosphere. Molecular and stable isotopic composi-

tion of individual geoporphyrins has been extremely useful in delineating precursor-product relationships for this class of compound in geological samples (Hayes et al., 1987, 1989; Boreham et al., 1989; Ocampo et al., 1989; Callot et al., 1990; Chicarilli et al., 1993; Keely et al., 1994).

An alternative to compound-specific isotopic analyses (CSIA) for understanding specifically the isotopic composition of phytoplankton is analyses of matrix-bound organic materials. Shemesh et al. (1993) produced coherent carbon and nitrogen isotopic records from sediment cores in the Atlantic sector of the Southern Ocean by analyzing organic matter preserved in the insoluble fraction of diatom opal. These authors used carbon and nitrogen isotopic analyses of the HNO_3–$HClO_4$–insoluble organic matter in diatom frustules to record changes in isotopic compositions of diatoms during the last 80,000 yr. The relative abundance of amino acids in the matrix organic fraction taken from samples at the LGM is similar to that in living diatoms, suggesting excellent preservation of primary material (see fig. 1 in Shemesh et al., 1993). One advantage of this isotopic method is that if sufficient numbers of diatoms are available in a sedimentary deposit, most laboratories have the capabilities to determine carbon and nitrogen isotopic compositions of the matrix-bound organic material. Potentially, this method could provide a relatively easy measurement of the carbon isotopic composition of organic matter in specific groups of organisms. Like the CSIA approach, it has source specificity and is relatively immune to diagenetic shifts in isotopic compositions. As a matter of fact, the source specificity of matrix-bound organic matter analysis may be greater than CSIA because an individual compound can come from a group of organisms whereas origins of matrix organic materials can be constrained using the morphology of the organism test.

Widespread applications of CSIA or matrix organic matter analyses in natural environments are currently limited by our lack of understanding of processes affecting distributions of the isotopic composition of individual compounds in organisms. Lipids and pigments are useful molecular biomarkers because they are present in unique distributions and/or possess structural features indicative of their biological source. However, relatively few studies exist which document isotopic composition of individual compounds in modern microorganisms. Recently, Summons et al. (1994) reported that the carbon isotopic composition of individual compounds from a methanotrophic bacterium grown in culture can differ by as much as 10–14‰. In addition, carbon isotopic fractionation varied with growth stage. Because fractionations are greatest when single carbon compounds are involved, the variation Summons et al. (1994) documented may be viewed as maximum. However, knowledge of distributions of isotopic values of potential biomarker compounds in producer organisms grown under controlled conditions is crucial for the continued utilization of CSIA in interpretations of origins and fates of organic materials.

A second issue pertinent to the use of compound or organism-specific isotopic analyses in natural environments is related to biological diversity. Since compounds isolated from marine particles and sedimentary organic matter represent only a fraction of primary biomass, estimates of the isotopic composition of that primary biomass (and, thus, of the food source for any community) must be derived by applying a correction to observed, single-compound δ-values. For example, Jasper and Hayes (1990) found that isotopic compositions of diunsaturated, long-chain alkenones were depleted by 3.8‰ relative to total biomass of prymnesiophyte algae grown in a single laboratory batch culture. However, it is not known whether the same isotopic difference is species specific or whether the same isotopic difference prevails under conditions of varying temperature, growth rate, nutrient availability, pH, or under stress of predation. This baseline information needs to be obtained to clarify the limits of interpretation of compound-specific isotopic analyses of organic matter.

5. Conclusions and recommendations

Results of analyses of algae grown in continuous culture and of suspended marine organic matter suggest that the carbon isotopic composition of sedimentary marine organic matter is strongly

affected by the concentration of dissolved CO_2 and the growth rate of phytoplankton. These results imply that carbon isotopic variations in sedimentary organic materials are not expected to be as globally representative as variations in carbonate rocks because factors controlling [CO_2(aq)] and phytoplankton growth rate can be influenced by local environmental factors. Thus, the carbon isotopic composition of photosynthetic organic matter and the magnitude of their stratigraphic variations should vary from basin to basin. Although intrabasinal correlations in the carbon isotopic composition of organic matter may be possible, interbasinal chemostratigraphic correlations may be difficult.

Extreme caution must be taken in relating variations in carbon isotopic fractionation by marine phytoplankton to rates of primary production. Field and laboratory results indicate that ϵ_p is influenced by the growth rate of phytoplnkton. Because equivalent rates of primary production can be achieved under conditions of high algal biomass/low growth rate and low algal biomass/high growth rate, algal growth and primary production rates can only be related if the standing stock of phytoplankton carbon is known.

We recommend caution in interpreting carbon isotopic variations of sedimentary organic matter. No single environmental factor explains adequately variations in the carbon isotopic composition of phytoplankton. Furthermore, isotopic analyses of ancient bulk organic materials should be used cautiously and in combination with ancillary analyses to determine the proportions of allochthonous organic materials, the degree of reworking and the extent of thermal degradation. Although the few studies which compare the carbon isotopic composition of modern marine suspended organic matter with that of phytoplankton indicate only small differences between these phases, the studies are too few in number and from a limited variety of environments to suggest a reliable correction for predicting the isotopic composition of phytoplankton from bulk isotopic results. No studies currently exist in which the carbon isotopic compositions of suspended and phytoplanktonic organic matter have been traced from their origins in the water column to deposition and preservation in sediments. Large and nonsystematic differences have been observed between the isotopic composition of total organic carbon and algae (determined by analyses of phytoplankton biomarkers, e.g., see Hayes et al., 1989 and Kenig et al., 1994) in the same ancient deposit. Therefore, the assumption that the carbon isotopic composition of marine sedimentary organic matter reflects directly or indirectly the carbon isotopic composition of phytoplanktonic organic matter must be used cautiously.

We recommend that studies which rely heavily on the carbon isotopic compositions of bulk materials for chemostratigraphic and environmental interpretations confirm isotopic trends using compound-specific or organism-specific isotopic analyses. Such analyses should aid in distinguishing primary variations from those imposed by secondary alteration. Even though isotopic analyses of individual compounds and matrix-bound organic matter are more source-specific than bulk isotopic results, there are uncertainties in the relationship between the isotopic composition of biomarkers(s) and their source organisms. No study to date has tested the assumption that differences between the isotopic composition of biochemicals and the source organism remains constant under varying conditions of algal growth. Continued research on algae grown in laboratory cultures and collected under well-characterized conditions in the modern ocean are still a prerequisite to quantitative interpretations of variations in Phanerozoic algal physiology (e.g., growth rate) and physical environments (e.g., [CO_2(aq)]) from isotopic compositions of organic materials.

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