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THE POST-PALEOZOIC CHRONOLOGY AND MECHANISM OF ^{13}C DEPLETION IN PRIMARY MARINE ORGANIC MATTER

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ABSTRACT. Carbon-isotopic compositions of geoporphyrins have been measured from marine sediments of Mesozoic and Cenozoic age in order to elucidate the timing and extent of depletion of ^{13}C in marine primary producers. These results indicate that the difference in isotopic composition of coeval marine carbonates and marine primary photosynthate was ~5 to 7 permil greater during the Mesozoic and early Cenozoic than at present. In contrast to the isotopic record of marine primary producers, isotopic compositions of terrestrial organic materials have remained approximately constant for this same interval of time. This difference in the isotopic records of marine and terrestrial organic matter is considered in terms of the mechanisms controlling the isotopic fractionation associated with photosynthetic fixation of carbon. We show that the decreased isotopic fractionation between marine carbonates and organic matter from the Early to mid-Cenozoic may record variations in the abundance of atmospheric CO_2.

INTRODUCTION

Secular variations in the isotopic composition of marine dissolved inorganic carbon have been widely recognized (Veizer and Hoefs, 1976; Fischer and Arthur, 1977; Kroopnick, Margolis, and Wong, 1977; Scholle and Arthur, 1980). These variations have been interpreted in terms of changes in the sedimentation and burial of organic and inorganic carbon (Garrels and Perry, 1974; Broecker, 1974) and in terms of effects on redox balances in the cycles of sulfur and carbon (Veizer, Holser, and Wilgus, 1980; Garrels and Lerman, 1984; Lasaga, Berner, and Garrels, 1985; Kump and Garrels, 1986; Berner, 1987). Secular variations in the carbon-isotopic composition of organic matter in sedimentary rocks have also been documented (Degens, 1969; Galimov, Migdisov, and Ronon, 1975; Hayes, 1983; Arthur, Dean, and Claypool, 1985; Dean, Arthur, and Claypool, 1986; Knoll and others, 1986). Temporal resolution of these variations has been (and, for the most part, still is) inadequate to consider correlations with the carbonate record. More importantly, the origins of variations in the carbon isotopic composition of marine organic matter have been uncertain, particularly because most evidence has indicated that isotopic compositions of terrigenous organic matter have been approximately constant (Degens, 1969; Redding and others, 1980; Schoell, 1984; Dean, Arthur, and Claypool, 1986; Hayes and others, 1987).

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Maynard (1981) was the first to show that, during Devonian-Mississippian times, marine organic matter had been depleted in ^{13}C relative to terrigenous material, thus reversing the relationship found in modern systems. More recently, Arthur, Dean, and Claypool (1985) and Dean, Arthur, and Claypool (1986) concluded that a similar depletion of ^{13}C in Cretaceous marine organic matter must be of primary origin. Lewan (1986) has assembled a record of carbon isotopic compositions of amorphous kerogens (presumably representative of typical marine kerogen) that also indicates that this depletion of ^{13}C in marine organic matter occurred throughout the Mesozoic and Paleozoic. Taken together, these observations require that the carbon isotopic fractionation associated with production of marine organic matter has changed while that associated with production of terrestrial organic matter has been more nearly constant.

Hayes and others (1989) have reported carbon isotopic compositions of coexisting carbonates, geoporphyrin fractions, and total organic carbon in Greenhorn Formation sediments (Cenomanian-Turonian) from the Western Interior of the United States. The geoporphyrins in these sediments are derived from the chlorophyll of primary producers, and their isotopic analyses provide a record of the carbon isotopic composition of marine primary photosynthate improved over that of bulk organic carbon or kerogen, because the latter contain carbon derived from non-photosynthetic organisms (Hayes and others, 1989). In the sediments of the Greenhorn Formation, the geoporphyrin fractions were consistently depleted in ^{13}C relative to total organic carbon, and depleted in ^{13}C relative to modern marine photosynthate by up to ~7 permil. Thus, analysis of geoporphyrin fractions from these sediments confirmed the primary origin of the ^{13}C depletion documented by Dean, Arthur, and Claypool (1986) in total organic carbon and showed that the depletion of ^{13}C in Cretaceous primary photosynthate was even more pronounced than previously suggested (Hayes and others, 1989).

We present new isotopic analyses of geoporphyrins from marine sediments of Cenozoic and Mesozoic age to define better the magnitude and chronology of ^{13}C depletion in marine primary photosynthate. In order to interpret the isotopic records of marine and terrestrial organic materials, we review mechanisms controlling isotopic fractionation associated with photosynthetic fixation of carbon. As a result of these considerations, we show that secular variations in the isotopic composition of aquatic photoautotrophs are probably related to the abundance of CO_2 in the atmosphere.

SAMPLES AND ANALYTICAL PROCEDURES

Samples analyzed isotopically for this project range in age from Late Jurassic to Pleistocene. Specific age, depth of core sample, and type of porphyrin are given in table 1.

TABLE 1

Sample number, age, and brief description of porphyrin fractions analyzed isotopically in this study. More complete descriptions of many of these samples are available in the references cited.

Sample	Age	Depth (m)	Lithology	Organic carbon (% Dry wt.)	Porphyrin type	Reference§
64-479-43-1	Pleistocene	393.7	diatomaceous mud	2.6	Ni (74.8% DPEP†)	(1)
63-467-48-2	Late Miocene	445.5	silty claystone	4.6	FB (99.6% DPEP)	(2)
63-467-91-2	Middle Miocene	854.0	clayey nanno-chalk	2.3	Ni (72.2% DPEP)	(2)
63-471-69-3	Middle Miocene	650.0	silty claystone	0.8	Ni (70.3% DPEP)	(2)
Monterey Sh. A	Middle Miocene	1317.0		5.1	FB (100% DPEP)	(3)
Monterey Sh. H	Middle Miocene	2281.0		1.8	VO (88.6% DPEP)	(3)
47A-397A-16-4	Early Miocene	1072.8	calcareous mud	1.7	FB (100% DPEP)	(4)
38-346-15-4	Late Eocene	130.0		0.4	Ni	(5)
Greenhorn Fm.	mid Cretaceous*	700-711	interbedded Ls/Sh	0.3-8.8	Ni	(6)
Greenhorn Fm.	mid Cretaceous**	711-719	interbedded Ls/Sh	0.1-9.9	Ni	(6)
43-386-43-3	mid Cretaceous**	740.6	shale	7.7	Ni	(7)
43-386-43-3	mid Cretaceous**	740.6	shale	7.7	VO (100% DPEP)	(7)
50-416A-18-3	Early Cretaceous***	1266.0	calcareous shale	0.6	Ni (28.6% DPEP)	(8)
50-416A-23-3	Early Cretaceous***	1313.0	calcareous shale	1.0	Ni (58.3% DPEP)	(8)
71-511-66-4	Late Jurassic	590.5	black shale	6.3	Ni (71.3% DPEP)	(9)
71-511-66-4	Late Jurassic	590.5	black shale	6.3	VO (100% DPEP)	(9)
Treib's #1	Late Triassic				VO (90.3% DPEP)	
Treib's #2	Late Triassic				VO (84.2% DPEP)	

†DPEP = deoxophylloerythroetioporphyrin, FB = free base.
*Turonian
**Cenomanian
***Valanginian
§(1) Baker and Louda (1982)
(2) Louda and Baker (1981)
(3) Louda and Baker (1986, fig. 4, p. 110)
***Valanginian (continued)
(4) Baker and Palmer (1979)
(5) Baker, Palmer, and Parish (1976)
(6) Hayes and others (1989)
(7) Palmer, Huang, and Baker, (1979)
(8) Palmer and Baker (1980)
(9) Baker and Louda (1985)

Extraction and initial porphyrin purification procedures for samples from Deep Sea Drilling Project cores and Monterey Formation samples are described in the references listed in table 1. Final purification of these samples was achieved by HPLC (Alltech 605RPD C18 reverse-phase column, 4.6 × 250 mm, 5 μm particle size, eluted isocratically with 80/20 v/v acetonitrile/methanol at 1 ml/min). Absorbance of the eluent was monitored at 400 nm (Kratos Spectroflow 757), and the porphyrin fraction was collected from detection of the first peak until absorbance returned to baseline (approx 45–60 min). Excess solvent was removed by rotary evaporation at <30°C. The purified fraction was taken up in a minimum quantity of methylene chloride (~5 ml) and transferred to a quartz tube (9 × 150 mm). Excess solvent was removed by rotary evaporation at 25°C. Approx 0.3 mg of pre-combusted cupric oxide was added, and tubes were evacuated, sealed, and heated to 850°C for 8 hr. Tubes were opened under vacuum, and the CO_2 produced by combustion of the porphyrin fractions was purified by cryogenic distillation. Nonporphyrin materials remaining on the column were eluted with 30 percent hexanes in acetonitrile/methanol (80/20 v/v), followed by reequilibration of the column with acetonitrile/methanol prior to introduction of a new sample. Isotope ratios were determined using a Nuclide 6-60 mass spectrometer. Results of repeated analyses of samples and of a synthetic porphyrin standard indicated that overall isotopic uncertainties associated with purification and analysis of porphyrins was less than 0.3 permil.

The procedures for extraction, purification, and analyses of porphyrins and carbonates from samples of the Greenhorn Formation are given in Hayes and others (1989).

Cretaceous organic materials known to be derived from terrestrial plants were collected from surface exposures in Russell County (Linnenberger's Ranch, near Bunker Hill), central Kansas, and Jefferson County (near Fairbury), southeastern Nebraska. These claystone samples are from non-marine portions of the Middle Cretaceous (Albian-Cenomanian) Dakota Formation and are rich in leafy material and other remains of terrestrial plants. Samples of Cretaceous woody material (presumably now mostly lignite) were removed from their matrix by hand picking under a binocular microscope and decalcified using 20 percent (v/v) HCl for ~1 hr at 25°C. The acid insoluble material was transferred to a quartz tube, sealed, combusted, and purified as described for the other samples.

RESULTS AND DISCUSSION

Results of isotopic analysis.—Isotopic compositions of geoporphyrin fractions from samples of marine origin are shown in table 2. These average about −25 permil prior to the Late Eocene, then shift to about −21.5 permil in samples of Late Miocene or younger age. This shift roughly coincides with that observed in isotopic compositions of amorphous kerogens. Younger, "h-amorphous kerogens" (h = isotopically

TABLE 2

Carbon isotopic compositions of geoporphyrin fractions analyzed in this study. Carbon isotopic values of carbonates were obtained from the compilation of Lindh (1983), except from the Greenhorn Formation where isotopic compositions of micritic carbonates are given (Hayes and others, 1989). Values for ϵ_P were calculated using eq 6 (see text).

Sample	Age	Porphyrin Type	$\delta^{13}C_{por}$	$\delta^{13}C_{carb}$	ε_P
64-479-43-1	Pleistocene	Ni	-22.00	+0.81	-12.64
63-467-48-2	Late Miocene	FB	-20.10	+0.60	-10.51
63-467-91-2	Middle Miocene	Ni	-20.88	+1.33	-12.03
63-471-69-3	Middle Miocene	Ni	-21.80	+1.33	-12.95
Monterey Sh.A	Middle Miocene	FB	-23.14	+1.33	-14.03
Monterey Sh.H	Middle Miocene	VO	-21.51	+1.33	-12.66
47A-397A-16-4	Early Miocene	FB	-21.99	+1.70	-13.51
38-346-15-4	Late Eocene	Ni	-27.02	+1.53	-18.42
Greenhorn Fm.†	mid Cretaceous*	Ni	-27.30±0.93	+1.52±0.43	-18.61±0.90
Greenhorn Fm.‡	mid Cretaceous**	Ni	-26.54±2.25	+1.83±1.54	-18.22±1.18
43-386-43-3	mid Cretaceous**	Ni	-25.83	+2.03	-17.72
43-386-43-3	mid Cretaceous**	VO	-24.36	+2.03	-16.23
50-416A-18-3	Early Cretaceous***	Ni	-27.03	+2.09	-18.98
50-416A-23-3	Early Cretaceous***	Ni	-27.60	+2.09	-19.56
71-511-66-4	Late Jurassic	Ni	-25.23	+0.51	-15.60
71-511-66-4	Late Jurassic	VO	-29.12	+0.51	-19.53
Treib's #1	Late Triassic	VO	-23.96	+2.00	-15.80
Treib's #2	Late Triassic	VO	-24.99	+2.00	-16.84

*Turonian
**Cenomanian
***Valanginian

†uncertainty = 2 s. d.; n = 37
‡uncertainty = 2 s. d.; n = 24

heavy) have isotopic compositions close to that of modern marine organic material, and Lewan (1986) has suggested that these derive from phytoplankton that grew in the mixed layer of the ocean. Older, "l-amorphous kerogens" (l = isotopically light) were interpreted as related to "phytoplankton growing in the photic zone of shallow (<200 m) restricted epicontinental seas where the carbon source is dominated by organic-derived CO_2" (Lewan, 1986). Such significant perturbation of the isotopic composition of dissolved inorganic carbon is commonly associated with stratification. Moreover, limited equilibration with atmospheric carbon dioxide is inevitably associated with limited access to atmospheric oxygen—anaerobic conditions are common in such zones. Finally, the magnitude of the shift in the isotopic composition of dissolved inorganic carbon in these settings is usually variable, being dependent on local conditions. Excluding the two lightest and two heaviest examples, the remaining 40 l-amorphous kerogens range in isotopic composition from −30.6 to −26.7 permil (Lewan, 1986). These materials are broadly representative of most of the marine sedimentary organic material preserved from an interval of 500 Ma. Is it plausible that all these derive from bodies of water "dominated by organic-

derived CO_2"? If so, it is required that conditions of stratification leading to a 7 ± 2 permil depletion in the isotopic composition of dissolved inorganic carbonate in the marine photic zone were not the exception but, instead, the rule during most of the Phanerozoic.

An alternative interpretation has been offered by Arthur, Dean, and Claypool (1985) and Dean, Arthur, and Claypool (1986). These workers observed that carbon-isotopic compositions of bulk marine organic material in sediments of Cretaceous age (incidentally including sites other than restricted epicontinental seas) fell in the same range as those of l-amorphous kerogens. They systematically considered possible interpretations and concluded that the isotopic fractionation associated with photosynthetic fixation of carbon must have been larger during Cretaceous and earlier times. They specifically associated this larger fractionation with a greater "concentration or availability of CO_2." (Dean, Arthur, and Claypool, 1986.)

Fractionation of isotopes during photosynthetic fixation of carbon.— Processes of two kinds are involved in the fixation of carbon by autotrophs: (1) transport of inorganic carbon to the C-fixing enzyme ("mass transport") and (2) formation of a chemical bond ("fixation"). O'Leary (1981) and Farquhar, O'Leary, and Berry (1982) have shown that isotopic compositions of most plants could be understood in terms of a combination of isotope effects associated with these processes. The simplified scheme below depicts the relevant carbon flows:

$$CO_2 \text{ (environment)} \underset{\phi_o,\ \delta_o}{\overset{\phi_i,\ \delta_i}{\rightleftharpoons}} CO_2 \text{ (at site of fixation)} \xrightarrow{\phi_f,\ \delta_f} R{-}CO_2 \quad (1)$$

where ϕ's designate carbon fluxes (moles/time) and δ's designate carbon isotopic compositions. At steady state, the following mass balance equations apply:

$$\phi_i = \phi_o + \phi_f \quad (2)$$

$$\phi_i\delta_i = \phi_o\delta_o + \phi_f\delta_f \quad (3)$$

Rearrangement of eq 3 yields:

$$\delta_i = (\phi_o/\phi_i)\delta_o + (\phi_f/\phi_i)\delta_f \quad (4)$$

In the absence of active transport, $\phi_i = p_a/r$ and $\phi_o = p_i/r$, where p_a and p_i are the atmospheric and internal partial pressures of CO_2, and r is the resistance to diffusion of CO_2 along the pathway linking the atmosphere and the site of fixation. Thus $\phi_o/\phi_i = p_i/p_a$, and $\phi_f/\phi_i = 1 - p_i/p_a$.

The δ values can be related in terms of isotopic fractionation factors. Specifically,

$$\alpha_t = \frac{1000 + \delta_a}{1000 + \delta_i} = \frac{1000 + \delta_s}{1000 + \delta_o} \quad (5)$$

$$\alpha_f = \frac{1000 + \delta_s}{1000 + \delta_f} \tag{6}$$

Where α_t denotes the isotope effect associated with mass transport, α_f denotes the isotope effect associated with carbon fixation, δ_a is the carbon-isotopic composition of the atmosphere (or CO_2 source), and δ_s is the isotopic composition of CO_2 at the site of fixation. Substitution of these fractionation factors and pressure ratios in eq 4 yields, without approximation:

$$\alpha_P = \alpha_t + (\alpha_f - \alpha_t)p_i/p_a \tag{7}$$

where α_p is the overall isotope effect associated with photosynthetic carbon fixation. In terms of ϵ values; where $\epsilon \equiv (\alpha - 1)10^3$:

$$\epsilon_P = \epsilon_t + (\epsilon_f - \epsilon_t)p_i/p_a \tag{8}$$

Values of the ϵ terms can be specified quite precisely. For emergent plants, the most important isotope effect associated with mass transport is that of diffusion in air. The isotopic fractionation associated with mass transport of CO_2 in air is proportional to the square root of the ratio of reduced masses (Mason and Marrero, 1970) and thus given by $\epsilon_{ta} = -4.4$ permil (the subscript ta referring to mass transport in air). For plants that grow under water, the corresponding fractionation is much lower ($\epsilon_{tw} = -0.7$ permil; the subscript tw referring to mass transport in water), in accordance with the smaller isotope effect associated with the slower diffusion of CO_2 in an aqueous solution (O'Leary, 1984). The isotope effect associated with fixation of carbon depends upon the specific C-fixing reactions and mechanisms. For marine primary producers and most land plants (C-3 plants or those that use the Calvin-Benson Cycle), the critical reaction is that catalyzed by ribulose bisphosphate carboxylase-oxygenase ("rubisco"). Recent determinations of the isotope effect associated with that reaction indicate $\epsilon_f = -29.0$ permil at 25°C (Roeske and O'Leary, 1984, 1985; M. H. O'Leary, 1988, personal commun.). Measurements of ϵ_P, p_i and p_a in living plants show, however, that the effective value of ϵ_f is approx -27 permil (Farquhar, O'Leary, and Berry, 1982; Evans and others, 1986), possibly due to low levels of carbon fixation by phosphoenol pyruvate carboxylase, an enzyme that discriminates against ^{13}C less strongly than does rubisco (Farquhar and Richards, 1984).

The relationship between the overall isotopic fractionation, ϵ_P, and p_i/p_a for emergent and aquatic plants is summarized in figure 1. The overall fractionation is large when the rate of C-fixation is controlled by kinetics of the bond-forming reaction itself (when p_i/p_a approaches 1) and small when mass transport controls the rate of C-fixation (when p_i/p_a approaches 0). The observation that most terrestrial vascular

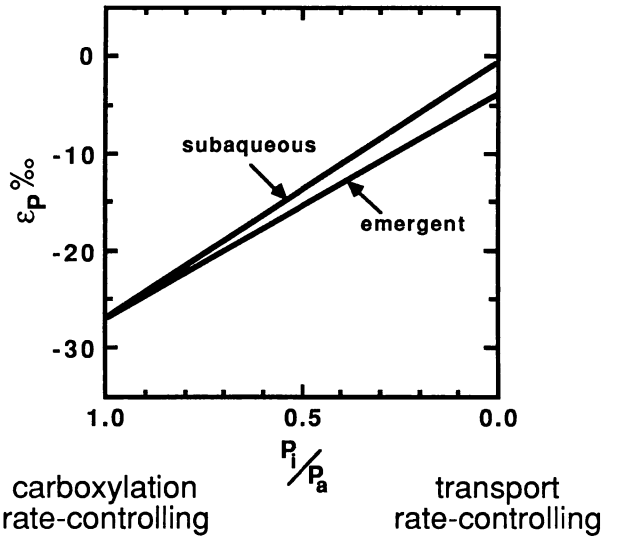

Fig 1. ϵ_P plotted as a function of p_i/p_a (see text, eq 8). The slopes result from differences in the kinetic isotope effect associated with transport of CO_2 in air (ϵ_{ta}) and in water (ϵ_{tw}).

plants display $\epsilon_P \approx -19$ permil indicates that, for most plants, $p_i/p_a \approx 0.69$ (Wong, Cowan, and Farqahar, 1979, 1985).

Because diffusion of CO_2 in water is about 10^4 times slower than diffusion of CO_2 in air, the balance between rates of diffusion and carboxylation is often different in aquatic plants. Values of p_i/p_a (eq 8, fig. 1) can be significantly less than 0.7, and the magnitude of ϵ_P will be strongly dependent on factors that influence mass transport. For example, increased rates of stirring or agitation facilitate the delivery of CO_2 to the cell and lead to larger isotopic fractionations (Osmond and others, 1981; Raven, Beardall, and Griffiths, 1982). Further, because the rate of diffusion of CO_2 into a C-fixing cell will be enhanced by steeper concentration gradients, high concentrations of CO_2 in the environment should decrease the extent to which the rate of fixation is limited by mass transport. As shown in figure 1, this should lead to an increase in isotopic fractionation. Numerous reports of relationships between ϵ_P and pCO_2 observed in laboratory studies have appeared (Pardue and others, 1976; Mizutani and Wada, 1982). In an experiment that most closely represents natural systems McCabe (1985) found that ϵ_P became more negative with increased concentration of dissolved CO_2 for laboratory cultures of zooplankton-free, mixed algal populations from several New Zealand lakes. Results of twenty-two different observations of ϵ_P by McCabe (1985) at varying concentrations of CO_2 (aq) (from equilibrium

with the atmospheric pCO_2 to ~7-fold higher and ~6-fold lower) are summarized by:

$$\epsilon_P = (-17.0 \pm 2.2) \log [CO_2(aq)] + 3.4$$
$$2 \leq [CO_2(aq)] \leq 74\ \mu mol/L \quad (9)$$

where $CO_2(aq)$ refers specifically to that solute (the substrate for rubisco), not total dissolved carbonate, and the uncertainty indicated in the slope is the 95 permil confidence interval.

Reconstruction of isotopic fractionations associated with photosynthesis.— Even if ϵ_P and pCO_2 in aquatic environments have been related by eq 9 throughout geologic time, the use of this relationship for determining ancient pCO_2 levels could not proceed until some way of measuring ϵ_P had been developed (however, see Mizutani and Wada, 1985). This is problematic because the total organic carbon (TOC) commonly analyzed in sedimentary isotopic studies is derived not only from primary producers but also from a wide range of other organisms. Accordingly, the isotopic composition of TOC reflects not only ϵ_P, but also isotope effects associated with a variety of secondary processes (Hayes and others, 1989).

In order to determine more accurately the isotopic composition of primary producers, we have analyzed sedimentary geoporphyrins. Geoporphyrins are derived from the heteroaromatic tetrapyrrole nucleus of chlorophyll and can be considered "isotopic biomarkers" for primary producers. In modern plants, tetrapyrroles are enriched in ^{13}C relative to total biomass by approx 0.5 permil (Hayes and others, 1987), and presently available evidence indicates that isotopic compositions of geoporphyrins differ little, if at all, from those of the biological tetrapyrroles from which they are derived (Hayes and others, 1989). Therefore, in order to estimate the composition of ancient primary photosynthate, we employ the relationship

$$\delta_P \approx \delta_{por} - 0.5 \quad (10)$$

where δ_P is the isotopic composition of the total biomass of primary photosynthate, δ_{por} is the isotopic composition of the related porphyrins, and 0.5 permil is the characteristic isotopic difference between these two carbon pools. Similarly, for the isotopic composition of carbon dioxide (the substrate in the carbon-fixing reaction), one can write

$$\delta_d = \delta_{carb} - 10.8 \quad (11)$$

where δ_d is the isotopic composition of dissolved carbon dioxide, δ_{carb} is the isotopic composition of calcite in equilibrium with that carbon dioxide, and 10.8 (assuming no diagenetic alteration or vital effect) is the equilibrium isotopic difference between calcite and dissolved CO_2 at 25°C (Vogel, Grootes, and Mook, 1970; Mook, Bommerson, and

Staverman, 1974; Deines, Langmuir, and Harmon, 1974; O'Leary, 1984). The values of δ_{por} and δ_{carb} can then be used to compute ϵ_P:

$$\begin{aligned}\epsilon_P &\equiv([(\delta_P + 1000)/(\delta_d + 1000)] - 1)1000 \\ &= ([(\delta_{por} + 999.5)/(\delta_{carb} + 989.2)] - 1)1000 \qquad (12)\end{aligned}$$

Fractionations calculated from the results of isotopic analyses of geoporphyrins are given in the last column of table 2 and are summarized graphically in figure 2. Although errors are inevitably introduced by using values of δ_{carb} averaged over intervals of ~5 to 10 my, it is evident that ϵ_P was approx -18 permil in the Late Cretaceous and Eocene but became significantly smaller in magnitude more recently, reaching values as small as -11 permil in the Miocene (fig. 2).

This discussion and the relationship described by eq 9 suggest that the increase in ϵ_P from the Cretaceous to the Miocene (fig. 2) may have resulted from a decrease in the partial pressure of CO_2 in the atmosphere. The present study of ϵ_P thus supports and adds detail to the interpretation offered earlier by Arthur, Dean, and Claypool (1985) and Dean, Arthur, and Claypool (1986) on the basis of their study of bulk organic carbon. Decreases in oxygen isotope paleotemperatures from nannofossils and planktic and benthic foraminifera (Shackleton and Kennett, 1975; Douglas and Savin, 1975; Savin, 1977, 1982) have indicated global cooling during this interval of time that several authors (Berner, Lasaga, and Garrels, 1983; Arthur, Dean, and Schlanger, 1985; Barron and Washington, 1985; Lasaga, Berner, and Garrels, 1985) have linked to decreased concentration of atmospheric CO_2. Elevated atmospheric pCO_2 during the Mesozoic and early Cenozoic is also consistent with (1) the transition from a "greenhouse" to an "icehouse" state (based on the stratigraphic, faunal, and floral records; Fischer, 1981, 1982), (2) the mineralogy of nonskeletal marine carbonates (Sandberg, 1983; 1985a, b), (3) increased volcanism (Vogt, 1972, 1979; Kennett and Thunell, 1975; Arthur, Dean, and Schlanger, 1985), (4) the results of climate modeling (Barron and Washington, 1982; 1984, 1985; Schneider, Thompson, and Barron, 1985), (5) the results of isotope mass balance calculations (Garrels and Lerman, 1981, 1984; Berner, Lasaga, and Garrels, 1983; Berner and Raiswell, 1983; Lasaga, Berner, and Garrels, 1985), and (6) estimates of atmospheric CO_2 levels based on the preservation and carbon isotopic composition of foraminifera (Berger and Spitzy, 1988). If the slope of the CO_2 versus ϵ_P relationship (eq 9) observed by McCabe (1985) can be applied to the marine realm, then the change in ϵ_P from the Cretaceous to Miocene (fig. 2) is consistent with a two to three-fold decrease in pCO_2. This estimated change is significantly smaller than that suggested by Lasaga, Berner, and Garrels (1985) but is in agreement with the lower estimates by Barron and Washington (1985), who suggested that CO_2 levels from two to ten-fold higher than present would have been consistent with inferred Cretaceous climates.

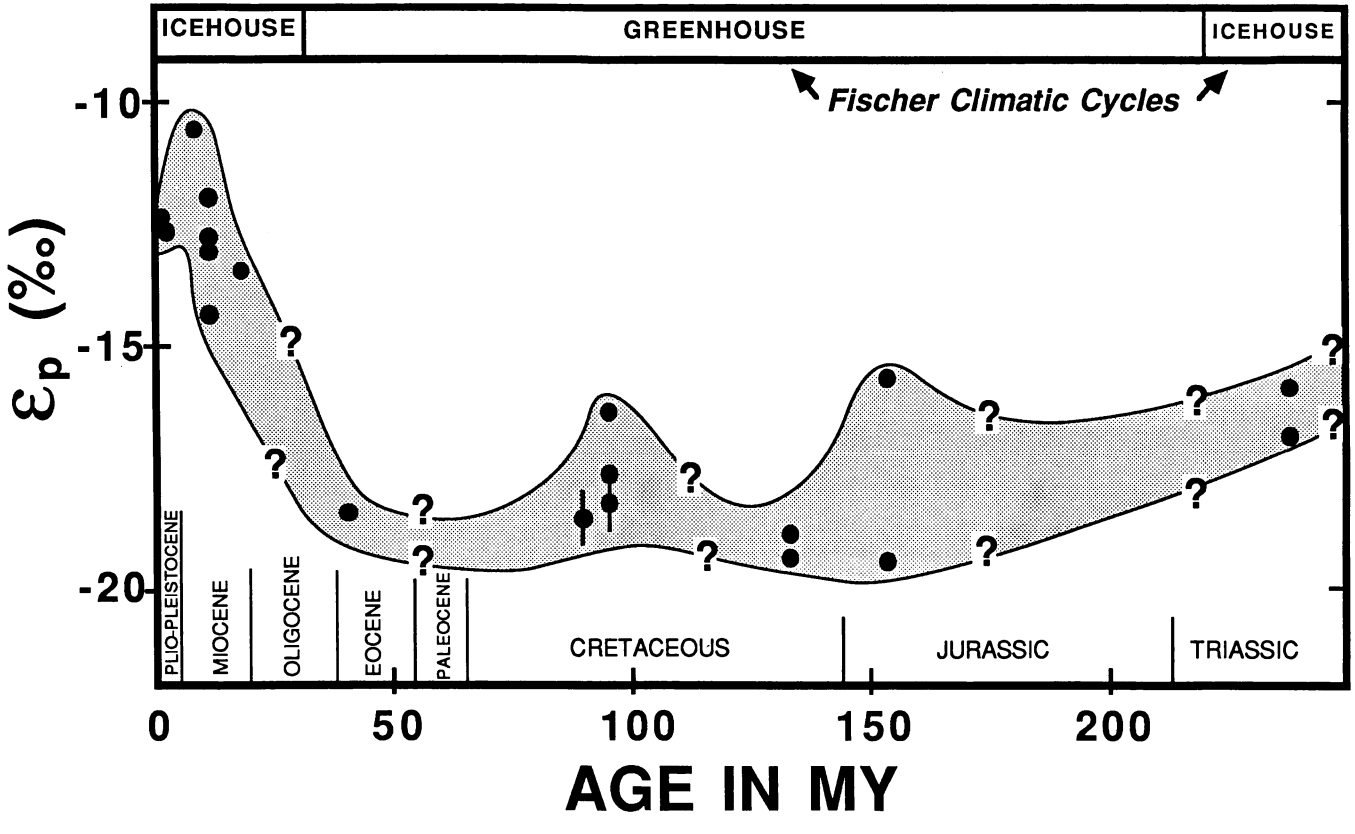

Fig. 2. Values of ϵ_P calculated from eq 12 and the isotopic compositions of porphyrins (table 2) and of primary marine carbonates (Lindh, 1983; for samples from the Greenhorn Formation see Hayes and others, 1989).

Care must be taken in relating variations in ϵ_P to changes in the concentration of atmospheric CO_2. The modern atmospheric level of CO_2 is apparently low enough to induce transport and assimilation of bicarbonate in some photoautotrophs, such as *Synechococcus* sp. (Badger and Andrews, 1982; Sharkey and Berry, 1985). Because there is a +9 permil enrichment of ^{13}C in HCO_3^- versus CO_2 at equilibrium and 25°C (Mook, Bommerson, and Staverman, 1974), dehydration of bicarbonate and fixation of the resulting CO_2 yields ^{13}C-enrichment of that organism relative to a typical C-3 autotroph (Badger, Kaplan, and Berry, 1980; Beardall, 1981; Beardall and Raven, 1981; Kaplan, Badger and Berry, 1980; Beardall, Griffiths, and Raven 1982; Lucas, 1983). In modern oceans, marine blue-green algal picoplankton like *Synechococcus* sp. are responsible for 50 to 80 percent of primary production in oligotrophic open oceans and 2 to 25 percent in coastal waters (Stockner, 1988). If such organisms presently are assimilating bicarbonate actively, at least 30 percent of modern marine photosynthate might be expected to be enriched appreciably in ^{13}C relative to photoautotrophs without such capability. Therefore, it is logical to suggest that, if atmospheric pCO_2 was high during the Mesozoic and early Cenozoic, the impact of bicarbonate usage on the average isotopic composition of marine primary photosynthate would have been lower (see also, Sharkey and Berry, 1985). Both bicarbonate assimilation and reduced mass transport of CO_2 result from lower levels of pCO_2, and both lead to enrichment of ^{13}C in organic matter. However, because the relative importance of each mechanism is unknown at this time, the isotopic records of porphyrins and pristine carbonates cannot be used to quantify the absolute concentration of atmospheric CO_2. We are exploring possible calibration of this record by analysis of primary photosynthetic products in sediment cores covering the time span for which pCO_2 values are available from ice cores.

Isotopic compositions of terrigenous organic matter.—The range of isotopic compositions of terrestrial organic material during the Cenozoic and early Mesozoic is not well known. Cretaceous organic matter with low hydrogen indices and high oxygen indices has been interpreted as refractory, predominantly terrestrial debris, presumably derived from lignin (Arthur, Dean, and Claypool, 1985; Dean, Arthur, and Claypool, 1986). The isotopic composition of bulk organic matter with these characteristics was found to be ~ -24 permil (Dean, Arthur, and Claypool, 1986).

In an effort to determine a range of isotopic compositions for Cretaceous terrestrial organic matter, a specific, exclusively terrestrial, biomarker was sought. Although macrofossil litter of Cretaceous leaves and other debris of higher plants is available, it was concluded that, for these materials, geoporphyrins were not the biomarker of choice for two reasons. (1) During autumn, when leaves are apt to fall, lysing enzymes often destroy chlorophyll, rupturing the tetrapyrrole ring system before the leaves detach from their branches (Sanger, 1971a,b; Gorham and Sanger, 1967). (2) Surfaces of decaying leaves may serve as substrates for

algae that will furnish secondary sources of chlorophyll (Sanger and Gorham, 1970). To avoid these problems, samples rich in the macromolecule lignin were analyzed. This biomarker is associated exclusively with terrestrial plants and expected to maintain structural integrity through geologic time, being particularly resistant to both chemical and microbial breakdown. Isotopic compositions of the remains of (lignin-rich) stems hand-picked from samples of strata of middle Cretaceous age (Albian-Cenomanian) are ~ -26 permil. For comparison, isotopic compositions of modern beech bark fragments also are ~ -26 permil. These few data from plant debris are consistent with the isotopic record of coals. Compilations of $\delta^{13}C$ values of Phanerozoic coals (Degens, 1969; Redding and others, 1980; Schoell, 1984) show essentially no depletion of ^{13}C relative to modern C-3 vascular plants regardless of age or degree of coalification.

Mechanism producing constant isotopic compositions in vascular plants.—Dean, Arthur, and Claypool (1986) suggested that enhanced availability of CO_2 as a consequence of increased CO_2 partial pressure (Berner, Lasaga, and Garrels, 1983; Lasaga, Berner, and Garrels, 1985; Arthur, Dean, and Schlanger, 1985; Barron and Washington, 1985) and/or from decreased productivity (Bralower and Thierstein, 1984) resulted in the depletion of ^{13}C in Cretaceous marine organic matter. But results summarized above show that elevated pCO_2 (if present) did not lead to similar depletion of ^{13}C in terrestrial plants. This different response to the same environmental stimulus can be attributed to factors controlling delivery of CO_2 to carbon-fixing enzymes in land plants.

In terrestrial environments, normal metabolic processes in C-3 plants can be affected by excessive evaporative loss of water. To minimize this loss, leaves are coated with waxy layers, and gases (H_2O, CO_2) are gained and lost primarily through stomatal apertures. Two points arise in connection with the fact that water is transpired as CO_2 is absorbed through stomata. First, it has been found that the density of stomata on a leaf surface varies with the concentration of CO_2 in ambient air (Woodward, 1987). Presumably because losses of water can be limited while still obtaining adequate quantities of CO_2, plants grown under high pressures of CO_2 have fewer stomata than those grown under low pressures of CO_2. Thus, as pCO_2 rises, the internal airspaces of leaves are less well connected to the atmosphere. Because the inside of a leaf constitutes a sink for CO_2, this phenomenon, if general, creates a situation in which pressures of CO_2 inside the leaves will vary much less strongly than those of ambient air. Second, there is now evidence (Farquhar, O'Leary, and Berry, 1982) that the ratio P_i/P_a (eqs 7, 8) tends to remain constant as P_a changes, at least in the short term (Wong, Cowan, and Farquhar, 1979; Farquhar and Wong, 1984). These results indicate that the effect of increased atmospheric pCO_2 was offset by the decrease in stomatal conductance (presumably to limit loss of water). The applicability of this finding to the geologic record remains to be tested. Other reports (Park and Epstein, 1960; Vogel,

1980; Enoch and others, 1984) suggest that isotopic compositions of higher plants *do* depend on pCO_2. But mechanisms predicting ^{13}C content independent of the concentration of atmospheric CO_2 in higher plants appear highly plausible and lead to exactly the result required to explain the isotopic biogeochemical record: strong variations can occur in the isotopic compositions of subaqueous photoautotrophs at the same time little variation is observed in the isotopic compositions of terrestrial higher plants.

Implications of the results for geochemical models.—Although variations in atmospheric pCO_2 have been proposed based on various observations (Budyko and Ronov, 1979; MacKenzie and Pigott, 1981; Fischer, 1982; Barron, 1983; Sandberg 1983, 1985; Barron and Washington, 1985; Arthur, Dean, and Claypool, 1985), only recently have numerical models been constructed that calculate the atmospheric concentration of CO_2 from the carbon-sulfur-carbonate-silicate geochemical cycles (Berner, Lasaga, and Garrels, 1983; Lasaga, Berner, and Garrels, 1985). These models are particularly sensitive to changes in spreading rates at mid-ocean ridge systems (and the subsequent degassing of CO_2 from the mantle) and the rate of burial of organic carbon (a major sink for atmospheric CO_2). For example, Lasaga, Berner, and Garrels (1985) have shown that their numerical model is sensitive to the mean isotopic composition of carbon in sediments (carbonate-carbon and marine- and terrestrial-carbon). Spreading rates are estimated from changes in the area of sea floor through time, whereas fluxes of organic carbon are inferred from secular variations in the isotopic composition of marine carbonates and organic matter (Garrels and Perry, 1976; Garrels and Lerman, 1981, 1984; Berner, 1987). Several compilations of the isotopic composition of Phanerozoic marine limestones and fossils exist (Veizer and Hoefs, 1976; Lindh, 1983; Veizer, Fritz, and Jones, 1986; Popp, Anderson, and Sandberg, 1986), and numerical models have been constructed from these compilations. The isotopic record of organic carbon in these models is calculated from that of marine carbonates by assuming that the isotopic composition of organic matter has always been depleted in ^{13}C relative to that of carbonate by a constant value (typically 25 permil). Although a constant isotopic difference predicts the isotopic variations of terrestrial organic materials reasonably well, we have shown here that it is inappropriate for estimation of the isotopic composition of marine organic carbon. Although our results are preliminary, we suggest that consideration of variable isotopic fractionation between organic materials and carbonates may explain currently calculated, unreasonably high CO_2 levels (on the order of 13-times modern atmospheric CO_2 levels for the mid-Cretaceous; Lasaga, Berner, and Garrels, 1985; see also Kump, 1989).

CONCLUSION

The observation that the isotopic difference between carbonate and primary organic material during the Mesozoic and early Cenozoic

was 7 permil greater than at present directly supports earlier suggestions that photosynthetic fractionation of carbon isotopes during the Cretaceous was enhanced by a "greater availability of CO_2" (Dean, Arthur, and Claypool, 1986). Our review of mechanisms of photosynthetic fractionation of carbon isotopes shows that this can result from higher atmospheric partial pressures of CO_2, and that calibration of this "CO_2 paleobarometer" may be possible.

At present we cannot determine if the change in $\delta^{13}C$ values of primary photosynthate resulted from only the effect of pCO_2 on mass transport in subaqueous organisms or if a presumed lowering of pCO_2 from the Mesozoic to the Cenozoic induced bicarbonate assimilation in some aquatic photoautotrophs.

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