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CARBON ISOTOPE SHIFTS IN PENNSYLVANIAN SEAS

MORDECKAI MAGARITZ* AND WILLIAM T. HOLSER**

ABSTRACT. A section at Big Hatchet Peak, southwestern New Mexico, which provides a nearly complete sequence of Pennsylvanian marine carbonate rocks, was analyzed for carbon isotopes as a proxy for variations in the world surface ocean chemistry. The profile of δ¹³C is mainly high — +2 to +4 permil — confirming previous findings of δ¹³C in marine rocks of that age. Three or four short and sharp negative excursions (to δ¹³C = −1 to −3 permil) are also judged to be oceanic, as confirmed by a high-resolution profile through one of these minima in another, distant marine basin at Arrow Canyon, Nevada. Minima are apparently correlated with interstage regressions such as those marking the beginnings of the Atokan and Desmoinesian stages. The excursions to low δ¹³C may be a direct consequence of regression, which allowed erosion of organic carbon from paralic coal basins, or shelves, where it had accumulated during the general Carboniferous transgression. The consequent high levels of atmospheric oxygen modelled by Berner and Canfield (1989) must have been interrupted by brief returns to near PAL.

INTRODUCTION

Chemical events, especially those with isotopic signatures, are being increasingly recognized in the marine record (Arthur, 1979; Holser, 1984). Specifically, carbon isotope ratios in marine rocks have been shown to vary in response to geological events: if the event corresponds to a high proportion of carbon deposited as organic carbon relative to carbonate, ¹³C will be enriched in the depositing marine carbonate and vice versa. The events occur on several time scales. At glacial to interglacial transitions in the Pleistocene, δ¹³C increases sharply in several thousands of years (Shackleton, 1977; Shackleton and Hall, 1984). Episodes of organic-rich sedimentary deposition in the deep sea generate high δ¹³C values for periods of several million years over all the oceans, for example, in the Miocene (Vincent and Berger, 1985), in the Cenomanian-Turonian (Cretaceous) (Jenkyns, 1985; Arthur, Dean, and Pratt, 1988), and in the Toarcian (Jurassic) (Jenkyns, 1985, 1988). Very sharp drops of δ¹³C are associated with mass extinction events, for example, at the Cretaceous-Tertiary boundary (Zachos and Arthur, 1986: Margolis and others, 1987: Zachos, Arthur, and Dean, 1989) and several other boundaries.

* Isotopes Research Department, The Weizmann Institute, 76100 Rehovot, Israel
** Department of Geological Sciences, University of Oregon, Eugene, Oregon 97403
Fig. 1. Paleogeographic situations of the sampled Pennsylvanian sections at Big Hatchet Peak, Pedregosa Basin, New Mexico, and Arrow Canyon, Bird Spring Basin, Nevada, 600 km to the northwest. After Greenwood, Kottlowski, and Thompson (1977) and Webster and Langenheim (1984), respectively.

It seems reasonable therefore to expect that carbon isotope shifts might also be associated with the vast deposition of coal and other types of organic carbon during the Permo-Carboniferous interval. Indeed, a general high in $\delta^{13}C$ for this interval was established by statistics on a variety of carbonate samples (Veizer, Holser, and Wilgus, 1980; Lindh, ms), and more recently supplemented by extensive analyses of fossils (Popp, Anderson, and Sandberg, 1986; Veizer, Fritz, and Jones, 1986) and cements (Given and Lohmann, 1985). (An alternative interpretation by Beauchamp, Oldershaw, and Krouse, 1987, is discussed below.) Geochemical modelling of the carbon and sulfur cycles has confirmed the connection between coal accumulations and the periods of high $\delta^{13}C$ (Berner and Raiswell, 1983; Berner, 1987); the model also implies a significantly higher level of atmospheric oxygen for this interval (Berner, 1987; Berner and Canfield, 1989).

Coal deposition in the Carboniferous was strikingly cyclic, reflecting a transgressive-regressive sedimentary rhythm ("cyclothem") which is emphasized by the sensitivity of sedimentation in this paralic regime (Heckel, 1977; Klein and Willard, 1989). Cyclothsms have been grouped into a hierarchy of longer-term cycles (Busch and Rollins, 1984; Fischer, 1986; Ramsbottom, 1979), although the reality of discrete groupings has been questioned (Heckel, 1986), and their time scale is debated (Klein, 1990). At mid-levels of this hierarchy the transgressive-regressive cycles can be correlated among sections from North America, northwestern and eastern Europe and, consequently, are attributed to eustasy (Ross and Ross, 1985, 1987a, 1988). Glaciation was prevalent in the southern hemisphere during this interval (Caputo and Crowell, 1985), and estimated periods of 100 to 400 ka in some orders of the cycles led some to conclude that the eustasy was glacial, forced by
Milankovitch orbital eccentricity (Busch and Rollins, 1984; Fischer, 1986; Heckel, 1986; Veevers and Powell, 1987).

The question therefore arose as to whether any of the cycles that had been widely recognized in Pennsylvanian paralic sedimentation, including the widespread but episodic deposition of coal, might also be reflected in the marine carbon cycle as analogous episodic excursions of $\delta^{13}C$. That is, if deposition (and erosion) of peat/coal (plus disseminated non-marine organic matter) was controlled by worldwide cycles of various orders, and if the variation in the rate of carbon deposited (or eroded) was sufficient to shift significantly the marine $\delta^{13}C$, then excursions of $\delta^{13}C$ should be found in the marine record. The previously available data of $\delta^{13}C$ in the Pennsylvanian were for the most part measured on samples not tied explicitly to cycle stratigraphy but did nevertheless show a scatter of values below the general level of $\delta^{13}C = +4$ to +6 permil, down to as low as −1 permil (Lindh, ms; Popp, Anderson, and Sandberg, 1986; Veizer, Fritz, and Jones, 1986), as might have been expected by a chance sampling of negative excursions of $\delta^{13}C$.

In order to map out any such excursions, it is necessary to measure profiles of $\delta^{13}C$ in closely spaced samples along stratigraphically controlled, preferably fully marine sections. In a careful study done for another purpose, Adlis and others (1988) measured isotope profiles through two separate single cycles in the Virgilian (Pennsylvanian) of the Midland Basin, west Texas. Their measurements were restricted to brachiopod shells from a central shale member, a few meters thick, of each section. Each showed “subtle decreases upward” (of about 1 permil $\delta^{13}C$), but for this tantalizing result they had “no simple explanation.” Stemmerik and Magaritz (1989) analyzed three partial sections of Pennsylvanian limestones in northeastern Greenland. Their results are consistent with a rise of $\delta^{13}C$ correlated with each of three major transgressive sequences in the lower Moscovian (~Atokan), upper Moscovian (~Desmoinesian), and middle Gzhelian (~Virgilian).

The present study attempts a more comprehensive analysis of variations in carbon isotopes during the Pennsylvanian. It has two parts: (1) a profile in moderate detail of a section from upper Mississippian through Pennsylvanian and into the lower Permian, at Big Hatchet Peak (BHP), New Mexico; and (2) a very detailed profile through a single negative excursion in the lower Pennsylvanian (Morrowan-Atokan boundary), at Arrow Canyon (AC), Nevada (fig. 1).

**GEOLOGICAL BACKGROUND**

The geology of Pennsylvanian rocks in the United States of America is summarized by the U. S. Geological Survey (1979): corresponding subsurface relations had previously been described by McKee and Crosby (1975). In the Midcontinent region shallow seas inundated the craton in many cycles of transgression-regression, leaving a record of alternating marine, paralic, and non-marine lithofacies complex in both time and
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space. In contrast to such complexity, along the southern and western borders of the craton slowly subsiding basins recorded a continuous marine sequence through most of the Pennsylvanian, in which one can still trace much of the history of transgressions through biostratigraphic correlation with the type stages of the Midcontinent (Ross and Ross, 1987b). These fully marine sections are most appropriate for our purposes.

Recent radiometric measurements in the Late Carboniferous of western Europe (Hess and Lippolt, 1986) have led to a proposed revision of the time scale, which we adopt here. On the revised scale (Klein, 1990) the whole Pennsylvanian Period is contracted to 19 Ma: each of the 5 North American stages lasts 3 to 5 Ma.

*Big Hatchet Peak.*—The southern face of Big Hatchet Peak, in the Big Hatchet Mountains, New Mexico, exposes a long and apparently complete section of Pennsylvanian carbonate rocks (Armstrong and others, 1979). The Pennsylvanian section here is conformable on the underlying Chesterian (uppermost Mississippian) and conformable with the overlying Wolfcampian (lowermost Permian) (fig. 2). In most of New Mexico the upper Mississippian is incomplete, with evidence of major unconformities. However, at BHP the Mississippian section is relatively continuous except for part of the last microfossil zone (Armstrong and others, 1979, 1984), corresponding to a nearly worldwide hiatus (Saunders and Ramsbottom, 1986).

The Pennsylvanian sections change southward in New Mexico from mixed nonmarine-marine clastic facies to a predominantly shallow-marine shelf facies at BHP. South of BHP, in the subsurface of the central part of the Pedregosa Basin in Chihuahua (fig. 1), the facies changes to thin, dark deep-marine limestones and mudstones (Greenwood, Kottlowski, and Thompson, 1977). Thus the BHP section is clearly from a marine environment near the shelf-basin margin, at the southern edge of the continent.

Stratigraphy in the Big Hatchet Mountains is based on the pioneering work of Zeller (1965). The section at BHP was measured and described by Thompson and Jacka (1981), who subdivided the strata into 78 lithostratigraphic units and interpreted depositional and diagenetic features from petrographic studies of each unit. We were able to take advantage of their basic study by analyzing the same samples, through the courtesy of Sam Thompson, III. Figure 2 summarizes their section.

The samples, and most of the described section at BHP (fig. 2), are micritic to richly fossiliferous limestones. The lower part of the section,

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Fig. 2. Sedimentary section at Big Hatchet Peak, using customary lithological symbols (after Thompson and Jacka, 1981). Sample horizons that we analyzed are marked by short lines.
Fig. 3. Profiles of the entire section at Big Hatchet Peak, for (A) $\delta^{13}C$, (B) $\delta^{18}O$, and (C) Sr.
Morrowan to Desmoinesian, contains much oolitic and coated grain material. The upper part, Missourian to Wolfcampian, is dominated by skeletal packstones and wackestones. Chert nodules are common in the lower part of the section and dolomite in the uppermost, but these were avoided in most of our sampling. The rate of deposition is calculated at 40 ± 20 m/Ma.

**Arrow Canyon.**—This section, 600 km northwest of BHP, exposes a sequence of shallow-water limestone facies, on the eastern edge of the Bird Spring Basin and west of interfingerling clastic deposits that crop out in the Grand Canyon area (fig. 1). The region around AC seems to be relatively free of disconformities in the Pennsylvanian, compared with the shoreline facies to the east and the eugeosynclinal facies farther west in central Nevada (fig. 1; Larsen and Langenheim, 1979; Webster and Langenheim, 1984). In the AC section, the stratigraphy, microfacies, and paleontology of various taxa have been intensively studied by R. L. Langenheim, Jr., and his colleagues, as well as others. Many of these studies have been tied to a series of brass markers placed at 1.5-m stratigraphic intervals by Amoco geologists and pinpointed on a series of photographs of the continuous outcrop, relative to the numbered beds of several of the previous workers. Our samples were located in the field on a set of these photographs, furnished through the courtesy of Ralph Langenheim, Jr., relative to both the numbered Amoco markers and the paleontology summarized by Langenheim and others.

The Morrowan-Atokan part of the section, with which we are concerned here (fig. 4), is illustrated with outcrop photographs, a detailed columnar section, and a consolidated faunal list published by Langenheim and others (1984); microfacies are described by Heath and others (1967). This interval is a very fine-grained calcitic limestone, supporting an assortment of bioclasts varying from nearly zero ("microfacies 0" of Heath and others, 1967) to 40 ("microfacies 2") percent of the rock. Silt-sized angular grains of detrital quartz are common, particularly in the upper Morrowan; mica is rare. Sparitization or spar cement is uncommon, except for millimeter-scale calcite veins that are easily avoided. The calcite is stained dark by a small percentage of organic matter and fine pyrite. Nodular or bedded chert is prominent in the AC section. Our sampling was at intervals of 0.5 to 2 m.

**SAMPLING AND ANALYSIS**

Sample selection emphasized micritic limestones and attempted to minimize sparry cements and vein material. We checked the petrographic character of the selected samples in new thin sections.

Billets from the thin sections were powdered for isotope measurements. X-ray diffraction showed that, with one exception, dolomite was less than 4 percent in the samples chosen. The powder was reacted with phosphoric acid (McCrea, 1950), and the generated CO₂ was measured on a Varian 250 mass spectrometer. The result was calculated using a standard calibrated against NBS-19 (δ¹³C = +1.96 permil, δ¹⁸O = +2.02
permil PDB) and presented using the conventional "δ" notation, relative to the PDB standard. Reproducibility on replicated samples is better than 0.15 permil for δ¹⁸O and 0.1 permil for δ¹³C. In the BHP section, strontium and other trace elements were determined by atomic absorption spectroscopy.

RESULTS

Carbon and oxygen isotopic data together with Sr concentration of the BHP section are presented in figure 3. δ¹⁸O values range from −3.8 to −9.6 permil but do not show any regular pattern and lack correlation with δ¹³C (r = 0.06, for n = 49). Oxygen isotope ratios in ancient
limestones are subject to diagenetic alteration much more easily than the carbon, and these data will not be considered further here. Sr concentration at BHP shows large variations—from 1590 to 380 ppm. Most of the Sr values range from 250 to 750 ppm, similar to other ancient marine carbonates, which are presently low Mg-calcite (Veizer, 1978). Sr lacks correlation (r = 0.23, for n = 38) with \( \delta^{13}C \), consequently any diagenetic rock alteration indicated by low values of Sr did not substantially affect \( \delta^{13}C \).

The same samples were also analyzed for Fe, K, Mg, Mn, Na, and P: the results are filed with the New Mexico Bureau of Mines and Mineral Resource, Socorro, N.M.

Carbon isotope values through the whole section at BHP range from \( \delta^{13}C = -3.0 \) to +4.4 permil, but in most of the section they fluctuate from about −2 to +3 permil. Two major negative excursions in \( \delta^{13}C \) values occurred at the boundaries between the Morrowan and the Atokan stages and between the Atokan and the Desmoinesian (about 5 Ma apart). The \( \delta^{13}C \) values remained depleted through the early Desmoinesian (about 40 m) and increased to values of about +3.2 permil within the following 50 m of section. A third excursion occurred in mid-Desmoinesian (about 2 Ma later) and comprises a considerable part (80 m) of the series. The upper Desmoinesian shows moderate \( \delta^{13}C \) values of about +1.5 permil. The density of samples was less in the upper part of the BHP section, and the main feature one sees (with the exception of a single sample of 0 permil at the top of the Desmoinesian) is a consistent level of about +2.5 permil into the Wolfcampian (Permian).

Graber and Lohmann (1989) published a carbon-isotope profile from the Pennsylvanian in the Big Hatchet Mountains, showing variations from −0.6 to 2.0 permil, but this was an isolated 6-m section of dolostone from an unspecified locality and undetermined stratigraphic level in the Desmoinesian to Virgilian part of the section, so their results cannot be correlated with ours.

One of the negative excursions was also studied in the AC section. As illustrated in figure 4, this detailed profile covers about 25 m on each side of the Morrowan/Atokan boundary out of total thicknesses for these stages of 250 and 100 m, respectively. Values of \( \delta^{13}C \) in the Morrowan are nearly +4 permil, decreasing sharply to below +1 permil exactly at the boundary (first appearance of Profusulinella) and rising, again sharply, to about +3 permil in the Lower Atokan. This anomaly at AC, while very distinct, is about half the depth and much narrower (in time) than the corresponding excursion at BHP (fig. 3).

**DISCUSSION**

Absence of diagenetic modification of carbon.—Carbon isotopes of ancient rocks reflect both the environment of deposition and the subsequent history of diagenetic and epigenetic carbonate phases. In general one can use petrographic study to determine the proportions of primary material, early marine cement, and meteoric diagenetic cement. The
first two sources give a marine carbon isotope signature, but one must carefully avoid the third source in sampling and interpretation. Studies of other limestone sections of geological age comparable to the one in this study have reached varying conclusions regarding the importance of meteoric diagenetic cement with respect to the carbon isotope ratio of the whole rock. Allan and Matthews (1982) found decreases of 2 to 4 permil in whole-rock analyses within a few meters of old erosion surfaces. The decrease was logically attributed to infilling or replacement of the original carbonate mineral by sparry calcite that had taken up an appreciable fraction of soil-gas derived CO₂ of organic origin. But in a detailed study of a similar occurrence Meyers and Lohmann (1985) separately sampled several cycles of cement calcite and found little difference (mostly less than 1 permil) between the carbon isotope ratios of early cements and the original carbonate rock.

The carbon isotope system is dominated by the carbon of the carbonate rock, as shown in several case studies (Magaritz, 1975). In a model calculation assuming typical isotope parameters for marine and freshwater calcite, Magaritz (1983) found that although oxygen isotope ratios were affected at even very low water/rock ratios, carbon isotope ratios were not appreciably decreased until the water/rock ratio was raised to 1000 or more. These considerations have encouraged us to use analyses of carefully selected whole rocks to define significant fluctuations of marine δ¹³C with time.

The results bear out these expectations. At least one of the excursions is duplicated in two sedimentary basins 600 km apart, which would not be expected if local diagenesis dominated the signal. The low values are continuous for a greater thickness than the deepest soil profiles so far observed (Allan and Matthews, 1982; Goldstein, 1988). On petrographic evidence, none of those samples with low δ¹³C is any more recrystallized than others nearby in the section that have high δ¹³C values. At BHP, a few of those depleted in δ¹³C also have lower Sr content (fig. 3). But these samples are δ¹³C-depleted more (up to −3 permil) than any cement separated from the Mississippian rocks studied by Meyers and Lohmann (1985): their lowest value of δ¹³C from their “Zone 3” cement, was only −1 permil. Consequently the excursions at BHP are also provisionally assigned a primary marine origin.

General trend of δ¹³C.—An envelope of peak values of δ¹³C at BHP (fig. 3) may be taken as an estimate for long-term variations of marine values. Starting at +2 permil at the base of the Pennsylvanian, this base line rises to over +4 permil in the Atokan Stage (also evident at AC, fig. 4), drops to +2 permil in the Desmoinesian, and peaks again at nearly +4 permil at the Pennsylvanian-Permian boundary before dropping back to +2 permil at the top of the BHP section (sometime in the Wolfcampian). The time between the envelope peaks is about 10 Ma; in this respect it resembles the curve of synthesized “second-order” long-term high stands of the sea (Vail, Mitchum, and Thompson, 1977; Ross and Ross, 1987a), but the two curves do not seem to be correlated.
These carbon-isotope values lie somewhat below the best previous estimates of marine $\delta^{13}C$ based on marine cements (Given and Lohmann, 1985) and minimally-altered brachiopods (Popp, Anderson, and Sandberg, 1986), which however were dated no more precisely than their geological period. Beauchamp, Oldershaw, and Krouse (1987) also found values in the range $+4$ to $+7$ permil in limestones of Pennsylvanian and Permian age in the Sverdrup Basin of Arctic Canada. However, they found $\delta^{13}C = +1$ to $+3$ permil farther south in eastern British Columbia, particularly in an Atokan limestone; they published only aggregate data without profiles. Intermediate values occur in the northern Yukon. To explain this seeming latitudinal gradient, they postulated that the low values in eastern British Columbia represented the true value of $\delta^{13}C$ for the Paleopacific Ocean, and that the high values in the Sverdrup Basin were a local effect of evaporative fractionation in a semi-closed basin, which also supplied some mixture of higher $\delta^{13}C$ to southerly longshore currents in the ocean. Our results contradict this proposal: AC lies 2000 km farther south along the Pacific edge (and BHP even farther)—yet they still show high $\delta^{13}C$, as do many of the brachiopods from various latitudes analyzed by Popp, Anderson, and Sandberg (1986).

*Short-term variations of $\delta^{13}C$.—Although the course of the excursions is not completely delineated, the data presented in this paper indicate that the marine carbon isotope value did oscillate in the Pennsylvanian, as in later periods (Cretaceous, Scholle and Arthur, 1982; and Tertiary, Shackleton, 1986).*

*Minima of $\delta^{13}C$, stage boundaries and regression cycles.—If the excursions of $\delta^{13}C$ represent real marine fluctuations, we should look for correlative cycles in the geological record. The earliest two excursions occurred at boundaries between stages of the Pennsylvanian. Why at stage boundaries? The North American standard stages of the Pennsylvanian were formalized in Midcontinent America by Moore (1944), based on a variety of criteria — “marker species,” faunal “breaks,” and regional unconformities (R. M. Jessup in Sutherland and Manger, 1984, p. 3). In the intervening half century, biozonation (fusulinids, conodonts) has been progressively refined and adapted to these somewhat arbitrarily defined stage boundaries. During the same period, detailed study of sedimentary sequences developed a hierarchy of cycles of onlap-offlap sedimentation along the marine to non-marine transition in the Midcontinent, which also seemed to fit into the previously defined stages. Ross and Ross (1985, 1988 [written 1985]) counted five “third-order” depositional sequences in the Morrowan and two or three in the Atokan; further consideration (Ross and Ross, 1987a) led them to raise these to seven and five depositional sequences, respectively—but in any case the stage boundary and its biozone boundary coincide with maximum offlap in one of the depositional sequences. This is the global view, although locally, as at AC, the Atokan/Morrowan boundary is at a maximum-depth facies (Heath, Lumsden, and Carozzi, 1967).*
Ross and Ross (1985) also found that their sedimentary sequences correlated with similar sequences in northwestern Europe and in the Soviet Union and deduced that they represented eustatic shifts of sealevel.

The Morrowan/Atokan and Atokan/Desmoinesian boundary regressions correlate with two of our major carbon-isotope excursions (figs. 3, 4). Since resolution of biozones in the BHP sequence is not sharp, we can only guess which (if any) of the many Desmoinesian intrastage events (Ross and Ross, 1987b) are represented by the excursion of $\delta^{13}$C that we see in the Desmoinesian (fig. 3).

So the collective intuition and experience of R. C. Moore and his committee wrought a framework of stratigraphic units that has turned out to be congruent with evolutionary biozones, with the physical development of sedimentary sequences, with worldwide rhythms of sealevel, and now here with variations in ocean chemistry. One should look to the underlying physical reality of sealevel shifts to connect these diverse phenomena. Some, but not all, of these shifts (as determined by sedimentary packaging) coincide with biozone boundaries, with stage boundaries, and with negative excursions of $\delta^{13}$C. As Ross and Ross (1987b, p. 164) suggest, “In part, these sea-level fluctuations themselves may be one of the main contributing causes of the rapid evolution that aids in the zonation.” Whether a particular phenomenon is manifest at a given regression of sealevel may be a function of the relative magnitudes, at present only guessed at, of the regressions, but more likely they are a consequence of other modulating parameters.

*Glaciation, regressions, and carbon.*—Glaciation lowers sealevel, and some regressions lower $\delta^{13}$C. So the question arises as to whether there is a more direct connection between glaciation and the carbon cycle. For example, are both controlled by climatic cycles?—are they all run by the same clock?

Late Paleozoic glaciation is discussed in detail in Hambrey and Harland (1981) and Veevers and Powell (1987). The strongest and final of three glacial “episodes” began in the late Mississippian, peaked in the Missourian, and died quickly in the early Permian, overall encompassing somewhat more time than the entire BHP section. Veevers and Powell (1987) postulate that these long-period episodes are set off internally by incidents of mountain building. The entire interval is also marked by cyclic deposition (“fifth order”). Their period has been estimated at 0.3 to 0.4 Ma, in the major cyclothems of the Midcontinent (Heckel, 1986) and in glaciogenic boulder beds of Australia (Veevers and Powell, 1987), but these limits may be substantially shortened by revision of the Pennsylvanian time scale (Klein, 1990). Whether this corresponds to the longest Milankovitch period of orbital eccentricity is debatable (Heckel, 1986; Veevers and Powell, 1987; Klein, 1990).

Thus the interval of 3 to 5 Ma between excursions of $\delta^{13}$C is much shorter than that between glacial episodes but much longer than the longest astronomical cycle. Apparently the carbon isotope excursions
are related to some intermediate order of regression cycle. But there
seems to be no agreement on the various "orders" of cycles, on the
criteria for their recognition, or on their timing by the various authors
who have described them in the Pennsylvanian (Vail and others, 1977;
Busch and Rollins, 1984; Ross and Ross, 1985, 1987a; Heckel, 1986;
Furthermore, we are at a loss for a cause of large shifts of sealevel at
periods longer than the longest glacial-interglacial cycles (0.1–0.5 Ma)
but shorter than shifts of the oceanic thermal regime (10–30 Ma). The
reviews by Donovan and Jones (1979) and Hallam (1984) do not seem to
have discovered a satisfactory ultimate cause of sealevel shifts of the size,
speed, and duration that we find associated with carbon shifts in the
Pennsylvanian.

Origin of the carbon-isotope shifts.—Whatever the origin of the sea-
level changes, they may be a direct cause of the carbon isotope shifts.
The erosion of organic carbon, depleted in $\delta^{13}C$, during a regression
from shelves on which it had been accumulating during the previous
transgression, was postulated by Loutit and Keigwin (1982) to connect
the end-Miocene carbon isotope shift and regression, and Broecker
(1982) proposed erosion of organic carbon (and associated phospho-
rus) from shelves during the Pleistocene glacial low stands. A similar
model would apply to carbon accumulated in paralic coal-forming swamps
(Berner, 1987; Berner and Canfield, 1989). Thus the Carboniferous and
Permian saw a generally large accumulation of organic carbon, forcing
marine $\delta^{13}C$ to generally high positive values, punctuated at intervals of
a few million years by strong regressions during which a substantial
fraction of this new organic carbon was reoxidized and returned to the
surface ocean, resulting in lower marine $\delta^{13}C$. Large, recently deposited
accumulations of organic carbon would have been especially vulnerable
to fast erosion, resulting in the rapid drops of $\delta^{13}C$ observed.

The question then arises as to why only some of the sedimentary
sequences (third order of Ross and Ross, 1987a) and none of the highest
order cycles (cycloths) are evident in the carbon isotope profiles (figs,
3, 4; Adlis and other, 1988). Of course we are sampling a marine section,
looking for a (worldwide) marine signal that corresponds to the sedimentary
cycles so dramatically exposed in the cycloths of the continental
interior. The reason may be that the marine section is only a partial
record punctuated by paraconformities (Sadler, 1981); it may be that the
waxing and waning of organic carbon storage is not strictly correlative
worldwide on short time scales; or it may be that the marine carbon cycle
is otherwise buffered and does not faithfully follow faster fluctuations of
organic carbon storage. Only further detailed profiling under the best
available biostratigraphic control can hope to answer this question.

Modelling of atmospheric oxygen, consequent on the variations of
carbon storage that are evidenced by the shifts of marine $\delta^{13}C$, indicates
that not only was the Pennsylvanian-Permian an interval of generally
high levels of atmospheric oxygen (Berner, 1987; Berner and Canfield,
1989), but that this interval also witnessed several sharp excursions of oxygen to approximately present atmospheric level. Berner (1987) found that a simple box model of the C–S–O system (Garrels and Lerman, 1984), with input from the generally high $\delta^{13}C$ outlined in the data of Popp, Anderson, and Sandberg (1986), resulted in extremely high oxygen (nearly twice the present mass): by more rapid recycling of new carbon he reduced the calculated oxygen peak to about $1.5 \times$ present mass. Based on C/S ratios, Berner (1987) calculated that most of the excess carbon production was on land, and that the site and rate of sedimentation strongly affected atmospheric oxygen accumulation (Berner and Canfield, 1989). Kump (1988) proposed that the feedback mechanism between land carbon and atmospheric oxygen was fire, and this was tied to marine carbon through the phosphorous cycle. Our carbon isotope profiles suggest that, whatever the site and rate of carbon deposition, the accumulation of organic carbon, hence of atmospheric oxygen, was intermittently reversed during Pennsylvanian time.

Furthermore, the abruptness of the drops in $\delta^{13}C$ suggests to us that the buildup may have been allowed to proceed metastably until equilibrium was restored by catastrophic or nearly catastrophic oxidation, with positive rather than negative feedback. This would be another example of a non-linear system with discontinuous bimodal response, as has been modelled in general and applied to glacial ice cap formation (North and Crowley, 1985; Crowley and North, 1988). To return to the question posed in a previous paragraph, sealevel regressions may have been effective only in extensive re-oxidation of stored organic carbon when the previous accumulation of carbon and oxygen had reached critical metastable levels. Not a single but several episodes of carbon deposition may have been required to reach such levels.

**CONCLUSIONS**

1. A profile of carbon isotopes in a completely marine section through the entire Pennsylvanian Period verifies the generally high level of $\delta^{13}C$ previously determined from individual analyses of fossils.
2. This high level of $\delta^{13}C$ is punctuated by at least three sharp excursions to low values of $\delta^{13}C$.
3. The global nature of these negative excursions is supported by a detailed sampling of a second profile in another basin 600 km distant.
4. Two of these drops (and possibly the third) correlate with worldwide eustatic drops in sealevel, which are also coincident with stage boundaries.
5. The rises and falls of $\delta^{13}C$ are interpreted as increases and decreases of storage of organic carbon, related to eustatic rises and falls of sealevel.
6. The consequent rise of atmospheric oxygen modelled by Berner (1987) and Kump (1988) was probably interrupted by short intervals of re-oxidation.
7. The abruptness of the drops of $^{13}C$ suggests that the accumulation of organic carbon and oxygen was a metastable non-linear system, and that re-oxidation may have been catastrophic or nearly so.

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