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Isotope shifts in the Late Permian of the Delaware Basin, Texas, precisely timed by varved sediments

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Closely spaced samples (285 in number) of varved sediments from the Upper Permian in Delaware Basin, Texas, have been analyzed for $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{13}\text{C}_{\text{org}}$, $\delta^{18}\text{O}_{\text{carb}}$, C_{org} , C_{carb} , and calcite/dolomite. $\delta^{13}\text{C}$ records a dramatic rise from -2.8 to $+5.7\%$ in only 4400 years, detected in three sections across the basin, extrapolating smoothly through a 600-year interruption by a local (west side of the basin) fresh-water inflow evidenced by low $\delta^{18}\text{O}$. This continuity and low C_{org} within the basin, both indicate that the excess net deposition of C_{org} , necessary to generate the rise in $\delta^{13}\text{C}$, took place in the ocean external to the Delaware Basin. Correlation with similar records from the Zechstein Basin suggest that the event was world-wide, although this poses obvious difficulties for the carbon cycle. The rate of rise of $\delta^{13}\text{C}$, and its sustained high level, must imply conversions of oxidized carbon to reduced carbon that are very large depending on which reservoirs were involved.

1. Introduction

Long-term shifts of isotope ratios in marine rocks were early recognized in the wide variations of $\delta^{34}\text{S}$ of evaporite sulfates (reviewed in Claypool et al. [1]), and more subtle long-term changes have been substantiated for $\delta^{13}\text{C}$ of marine carbonates [2], as well as for $\delta^{18}\text{O}$ sulfate [3]. Other sharp changes with time of isotope ratios, superimposed on these long-term swings, were detected at several specific times on the geological time scale, for $\delta^{34}\text{S}$ (e.g. [4]), and separately for $\delta^{13}\text{C}$ (e.g. [5,6]).

This is a further investigation of one such sharp rise in $\delta^{13}\text{C}$ carbonate, that was previously found near the base of the Late Permian Zechstein Series at several points in the Zechstein Basin of northern Europe [7–11]. On the far western edge of the Pangean continent, near the base of the Late Permian Ochoan Series of the Delaware Basin, we

have found a closely similar rise in $\delta^{13}\text{C}$, and in this place a previously documented varve sequence [12,13] has also enabled us to time precisely the isotopic changes.

During Late Permian time the continental plates were assembled into Pangea [14]. The Zechstein Basin was connected to the surrounding world ocean along the northern edge of Pangea [15], and the Delaware Basin had its inlet along the western edge of the continent [16], about 7000 km distant. Both cratonic basins were sites of extensive and thick deposition of sediments during the final stage of Permian time, when very little sedimentation was occurring anywhere else except on the borders of the Tethyan Sea. The basins lay at latitudes of about 5°N and 15°N , respectively [14], and the dominant sediments in both basins were evaporites. Definitive fossils are scarce, so a precise time correlation between the sections in the Zechstein

and Delaware Basins is not presently available [17–20]. The most that can be said within the limits of the evidence, is that the whole of the Zechstein Series in the Zechstein Basin is an approximate time equivalent of the whole of the Ochoan Series in the Delaware Basin.

During the Late Permian the generalized isotope age curves showed a minimum of $\delta^{34}\text{S}$ and a maximum of $\delta^{13}\text{C}$ [2,21]. Against this background a detailed study of $\delta^{13}\text{C}$ and related chemistry was made.

2. Geological setting

Subsidence of the Delaware Basin, accompanied by sustained reef growth around the margin, produced an initially deep, sediment-starved basin [22,23]. The finely laminated siltstone and claystone units of the Bell Canyon Formation (Fig. 1) were deposited in the starved basin. Partial closure of the arid basin resulted in a net water loss by evaporation and a thick sequence of Castile evaporites rapidly filled the basin. A brief break in sedimentation after Castile deposition, was followed by deposition of the overlying, shallower-water, Salado and Rustler evaporites, which overlapped and extended far into the back-reef area.

The sequence examined in this study includes the laminated siltstone and claystone of the Bell Canyon Formation, a Basal Limestone which marks the onset of evaporite conditions, and the calcite-laminated anhydrite of the Castile Formation (Fig. 1). The lateral continuity of the sediments deposited within the deeper basin is remarkable, with correlations of laminations in the Bell Canyon and Castile established over distances of 113 km [12,13]. The rocks preserve fine primary detail even within the laminae; consistently very fine grains, and compositional layering.

The entire sequence is marine in origin. The laminated siltstone and claystone of the Bell Canyon Formation contain an abundant radiolarian fauna (see Anderson et al. [12, fig. 3C], originally identified as a silicified fusulinid). The radiolarians, plus turbidite materials and structures in the upper Bell Canyon Formation, suggest a marine and deep-water environment. A marine

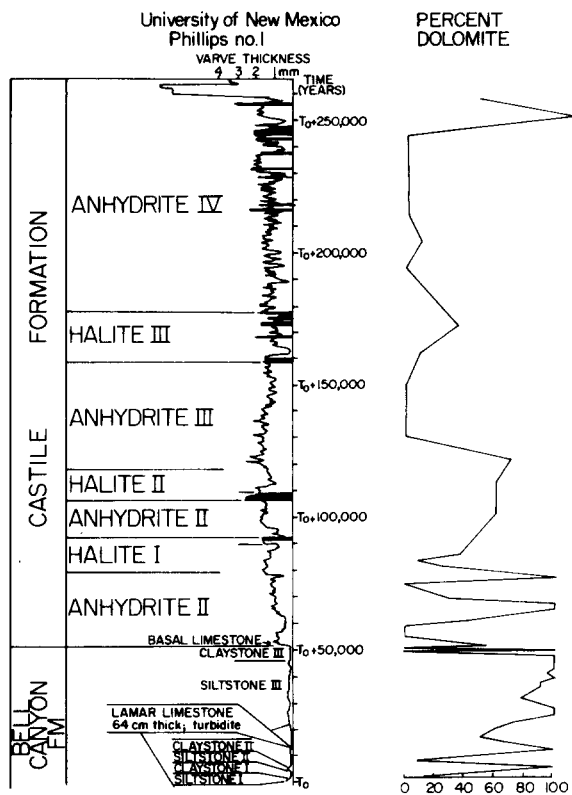


Fig. 1. Geological section in UNM Phillips 1, western Delaware Basin, Texas, showing variations of varve thickness and of dolomite/(calcite + dolomite) ratio.

source for the overlying Castile evaporite is verified by correlation of $\delta^{34}\text{S}$ with other marine Permian evaporites of the world (e.g. [1]), and by a bromide content that is only slightly lower than normal for marine salt [24,25]. In addition, the basal Castile contact is transitional [26].

An organic carbon (C_{org}) fraction occurs as discrete laminae in the Bell Canyon and Basal Limestone units, and as dark coloration and staining of calcite in the Castile [12]. Petrographic relations suggest that sedimentation of clastics, carbonate and calcium sulfate could have been a continuous rain of material to the bottom, punctuated by laminae of C_{org} . The carbonate in the Bell Canyon is principally dolomitic (Fig. 1), but changes to calcitic in the Castile and Basal Limestone. The dolomite has the very fine (2–8 μm) euhedral form characteristic of a direct

primary precipitate. Additional details of petrology and mineralogy are illustrated in Anderson et al. [12] and Holser [27, fig. 23 and 28].

The Basal Limestone, as defined in the Phillips core, seems to be an entirely different kind of sedimentation. Near its base, clastic deposition diminished and then essentially stopped, while calcite increased markedly to form a laminated limestone (Fig. 2). It has been recrystallized to coarse calcite, while still preserving the laminations. Some vestige remained of the marine regime of the underlying laminated siltstone, in the form

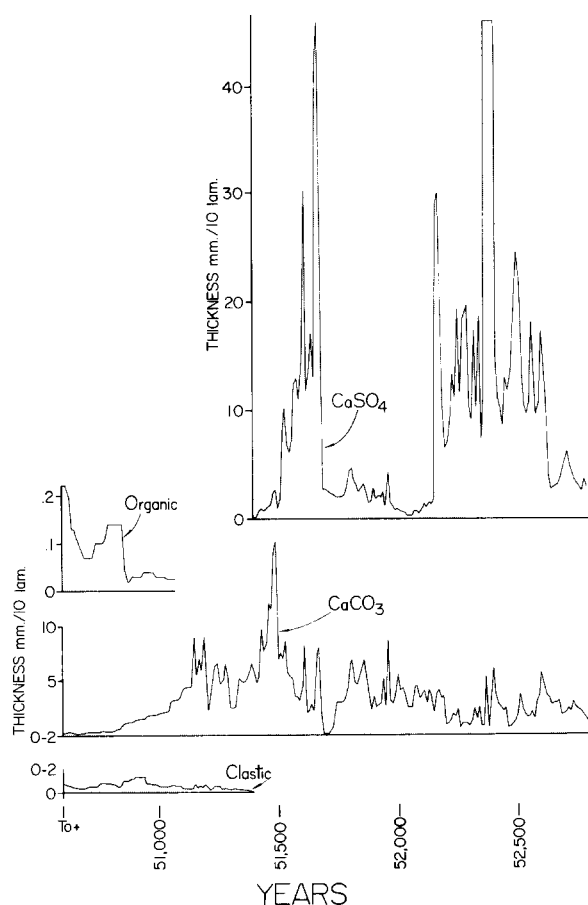


Fig. 2. Time series of the thicknesses of varve laminae of clastics, organic carbonate, inorganic carbonate, and sulfate in the transition zone from the top of the Bell Canyon Formation through the Basal Limestone Member and into the Anhydrite I Member of the Castile Formation, UNM Phillips 1. "CaCO₃" is total CO₂ calculated as CaCO₃.

of radiolarians in the first few thin organic laminae between the calcite laminae. Dolomite as the predominant carbonate mineral of the underlying Bell Canyon Formation gave way to nearly pure calcite in the Basal Limestone (Fig. 1), or to 50–90% calcite even in the overlying anhydrite. A limestone underlies the CaSO₄ facies in many evaporite basins [28], where its stratigraphic position, thinly laminated structure, and impoverished or absent fauna suggest that these limestones are an initial phase of evaporative deposition, and probably an inorganic precipitate. The relation of the Basal Limestone to evaporative precipitation is also indicated by the substantial continuity of the rate of carbonate deposition into Anhydrite I (Fig. 2).

3. Varves and calibration

Lamination pairs or couplets in both the Castile and Bell Canyon Formations are deduced to represent seasonal and annual deposition (varves). The continuity of the laminations over most of the 14,000 km² of the basin was used by Anderson [13] to establish that seasonal climatic forcing was responsible for recording the observed planetary perturbational climatic effects. Annual deposition is also indicated by the scale of the laminations, which are commensurate with annual rates of deposition: 0.1 mm in claystone and siltstone, 1.0 mm in limestone, 2+ mm in anhydrite, and 50+ mm in halite (Fig. 2). The laminations provide the basis for calibrating the rate of isotopic change in the sequence. The varves in the Castile and Basal Limestone were measured individually, and analyzed initially in units of 50. The critical "transition zone" (in Phillips 1) was then restudied in 10-year samples. The varves in the siltstone and claystone were measured and analyzed in units of 200, owing to close spacing of laminations. Time in "varve years" is designated for samples with respect to an arbitrary zero at the base of Siltstone I of the Bell Canyon Formation, assuming 3500 years for the varves of Siltstone I and Claystone I that was only estimated [12].

Geochemistry was studied on three cores that span the Delaware Basin from west to east near its midsection. Cowden 4 is near the western ero-

sional edge of the Castile evaporite, Phillips 1 is 23 km to the east of Cowden 4, and University 37 is another 96 km east of Phillips 1 and only 8 km from where the earlier Capitan reef bounds the Delaware Basin on the east. Phillips 1 was studied in the most detail, after the major features were found there, they were compared with the corresponding sections (as established by varve correlation) of the other two cores.

The inlet channel from the ocean was near the southwestern edge of the Basin, about 100 km south of the section line. The configuration of the basin and locations of the three cores are figured in Anderson, et al. [12, fig. 1].

4. Analytical methods

Segments of 10, 50, or 200 varve couplets were sawed from the cores, and then ground to powder using a ball mill. An aliquot of the powder was analyzed by standard X-ray diffraction procedure. Weight percent dolomite/(dolomite + calcite) was calculated using the area under the respective peaks (Cu-K $_{\alpha}$ $2\theta = 30.8^{\circ}$ and 29.5°) and the Weber and Smith [29] formula. The major components designated approximately as C_{org}, calcium carbonate, and calcium sulfate + clastics were determined by weight differences on ignition [30], with firing temperatures of 200–550, 550–1000, and > 1000°C, respectively. Independent time series for the major components were based on the unit/time sampling procedure [13].

The carbon and oxygen isotopes in carbonate minerals were measured using the conventional phosphoric acid method. For the samples containing > 50% dolomite we used the procedure described in Magaritz and Kafri [31], measuring only the dolomitic component. The CO₂ gas was analyzed in a Varian M250 mass spectrometer and the results are given using the “ δ ” notation relative to the PDB standard as e.g.:

$$\delta^{18}\text{O} = \left[\frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}} - (^{18}\text{O}/^{16}\text{O})_{\text{st.}}}{(^{18}\text{O}/^{16}\text{O})_{\text{st.}}} \right] \times 1000\text{‰}$$

and $\delta^{13}\text{C}$ (and $\delta^{34}\text{S}$) are similarly defined. Reproducibility of duplicate samples is better than

0.15‰. The $\delta^{18}\text{O}$ values of the dolomites were corrected by -0.84‰ [32].

Samples were prepared for isotopic analysis of C_{org} as follows: Dried samples were ground to fine powder, treated with 10% HCl to remove carbonate interferences, rinsed with deionized water, centrifuged two or three times, and re-dried at 60°C in a vacuum oven. Organic carbon in the samples was converted to CO₂ in evacuated, sealed quartz tubes containing a 1:1 mixture (by weight) of CuO and Cuprox[®] by combustion at 1000°C for at least four hours. Cooled tubes were broken open in vacuo and the gas mixture circulated through dry ice-acetone cold traps to remove H₂O and over hot Cu to remove CO and O₂. Purified CO₂ was trapped in a sample bulb immersed in liquid nitrogen, and the residual non-condensable gas (N₂) was pumped away. The amount of CO₂ produced by the combustion procedure was determined manometrically, after which the sample was transferred to the inlet of the mass spectrometer. $^{13}\text{C}/^{12}\text{C}$ ratios were determined relative to two secondary standards that had been standardized against PDB. Precision of previous mass spectrometric determinations using the procedure outlined above was 0.02‰, based on 5 samples of sucrose-carbon ranging in size from 1.8 to 3.8 mg C, which gave a mean $\delta^{13}\text{C}$ value of -10.47‰ .

Sulfur isotope ratios were measured on calcium sulfate of the Castile evaporites, after precipitation as BaSO₄ [1] and thermal decomposition to SO₂ [33,34]. The resulting SO₂ was analyzed on a Micromass 602 mass spectrometer. The results are recorded as $\delta^{34}\text{S}$ relative to the CDT standard, with a reproducibility of $\pm 0.15\text{‰}$.

5. Results

Long-term variations in $\delta^{13}\text{C}$ and C_{org} in the UNM Phillips 1 core are shown in Fig. 3a. A zone (44,500–52,000 years) including the transition between the clastic cycles and the evaporitic cycles is enlarged in Fig. 3b. The lower part of the section (Bell Canyon Formation) up to year 47,000 shows “normal” $\delta^{13}\text{C}$ values ranging between -2.5 and $+1.8\text{‰}$, while C_{org} varies between 0.5 and 2.0%. Above a “transition zone” (after year 52,000) the section is characterized by fairly constant “anoma-

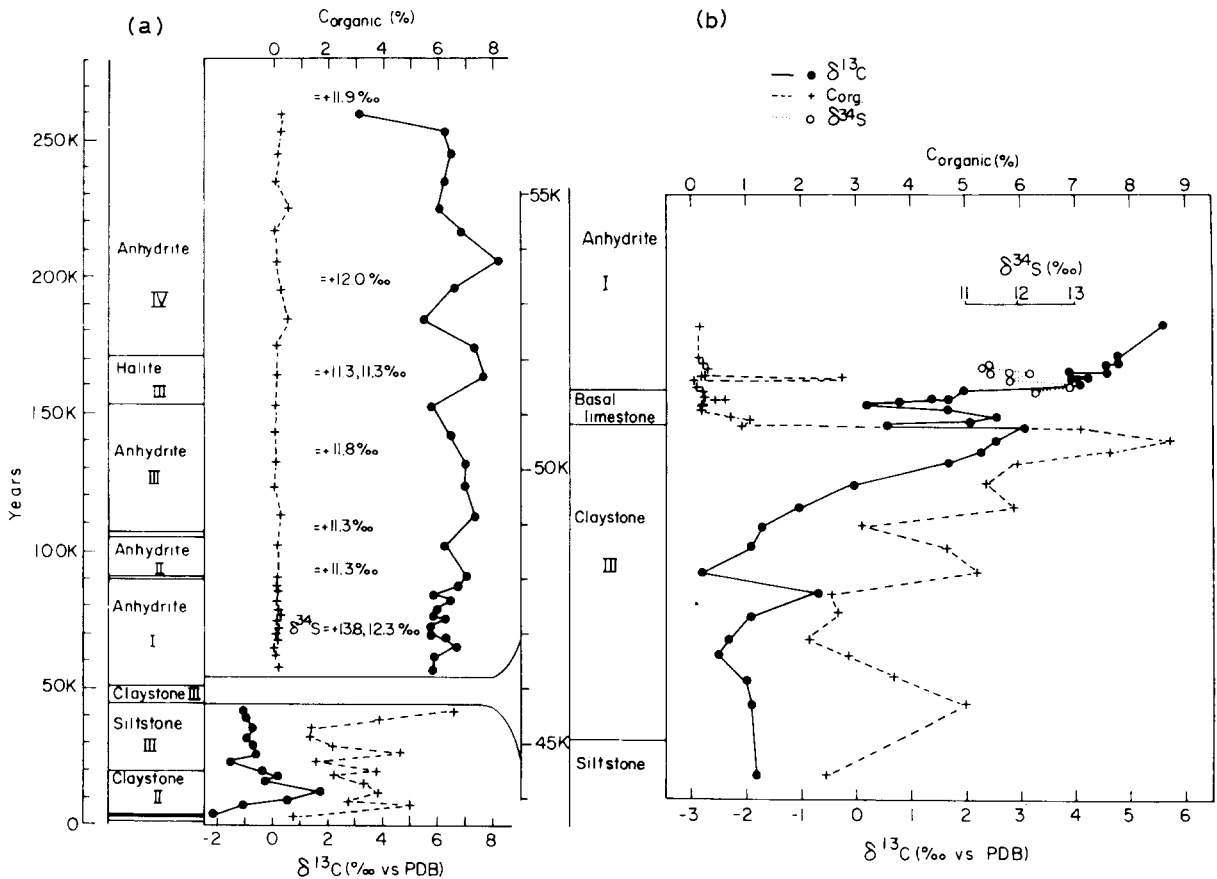


Fig. 3. $\delta^{13}\text{C}$ and C_{org} (wt.%) in UNM Phillips 1: (a) entire section; and (b) enlargement of the $\delta^{13}\text{C}$ transition zone at 44,000–54,000 years. $\delta^{34}\text{S}$ in (b) are on aliquots of the samples analyzed for $\delta^{13}\text{C}$; the $\delta^{34}\text{S}$ values listed for the overlying Castile evaporites are those reported by Claypool et al. [1] from the same core but at indeterminate levels within each member. Note that all scales are larger in (b) than in (a).

lous" $\delta^{13}\text{C}$ values ($+6.5 \pm 1\%$) and C_{org} content (about 0.1%), with fluctuations that are minor compared with the lower clastic section. The decrease in C_{org} is definitely not due to dilution by CaSO_4 : the ratio $C_{\text{org}}/(C_{\text{org}} + C_{\text{carb}})$ decreases sharply from about 0.2 in the underlying clastic section to about 0.01 in both the Basal Limestone and the overlying Castile anhydrites. The absolute rate of C_{org} deposition decreased from more than 0.01 mm a^{-1} in the claystone to about 0.0001 mm a^{-1} in the overlying Castile. The anomalously high $\delta^{13}\text{C}$ and low C_{org} continued through the rest of the Castile evaporite with only minor variations (Fig. 3a) [13,35,36], and to the very youngest

carbonates of the Permian, in the Rustler Formation [37].

In between these two parts of the core we observed a transition zone in which the carbonate became enriched in ^{13}C (Fig. 3b). In detail these changes began within Claystone III, at about year 47,000 (Figs. 1, 3). At this time a correlated upward trend began, involving both $\delta^{13}\text{C}$ and C_{org} . After a short reversal at about year 48,000 this upward trend was substantially continuous and linear to the top of Claystone III, at year 50,000, rising from $\delta^{13}\text{C} = -2.8\%$, $C_{\text{org}} = 2.5\%$, to $\delta^{13}\text{C} = +3\%$, $C_{\text{org}} = 9\%$. Just when deposition of the Basal Limestone started, $\delta^{13}\text{C}$ values temporarily de-

creased with large fluctuations, in this core, and C_{org} dropped drastically first to 1 wt.% and then immediately to 0.1%. At the top of the Basal Limestone, near year 51,400, when the first cycle of Castile evaporite deposition began, it seems that the progressive enrichment of ^{13}C continued as if it had not been interrupted by the Basal Limestone deposition. One can extrapolate the rising slope of $\delta^{13}C$ across the Basal Limestone and see a smooth continuation in the early part of the Anhydrite I cycle, up to $\delta^{13}C$ of +6‰ at about year 52,000. In contrast, C_{org} remained as low or even lower in Anhydrite I (and overlying members) than it was in the Basal Limestone Member (Fig. 3).

Fig. 4 compares the transition zone in Phillips 1 with Cowden 1 nearby to the west and University 37 far to the east. The same sharp, large rise in $\delta^{13}C$ is clearly displayed in all cores, and some finer features, such as the preliminary peak at 47,500 years, are common to the two western cores.

Measuring the rate of change of $\delta^{13}C$ values

TABLE 1

Carbon isotope analyses of organic and carbonate carbon in varve packets from the Phillips 1 core (values in ‰ versus PDB standard)

Years	$\delta^{13}C_{org}$	$\delta^{13}C_{carb}$	$\Delta^{13}C$
<i>Castile evaporite</i>			
184,695–184,744	–25.6	+5.5	31.1
		–25.1	+5.3
76,938–76,987	–24.8	+5.9	30.7
51,838–51,887	–25.0	+4.6	29.6
<i>Transition zone</i>			
51,246–51,296	–27.9	+0.8	28.7
51,100–51,149	–27.3	+1.7	29.0
50,875–50,949	–25.4	+2.1	27.5
50,625–50,824	–29.4	+3.1	32.5
<i>Bell Canyon Formation</i>			
48,075–48,274	–29.1	–2.8	26.6
47,650–47,874	–29.0	–0.7	28.3
46,049–46,249	–28.4	–2.0	26.4
		–28.8	–1.4
41,920–42,119	–28.4	–1.0	27.4
38,917–39,116	–28.7	–1.0	27.7
26,236–26,435	–28.9	–0.7	28.2

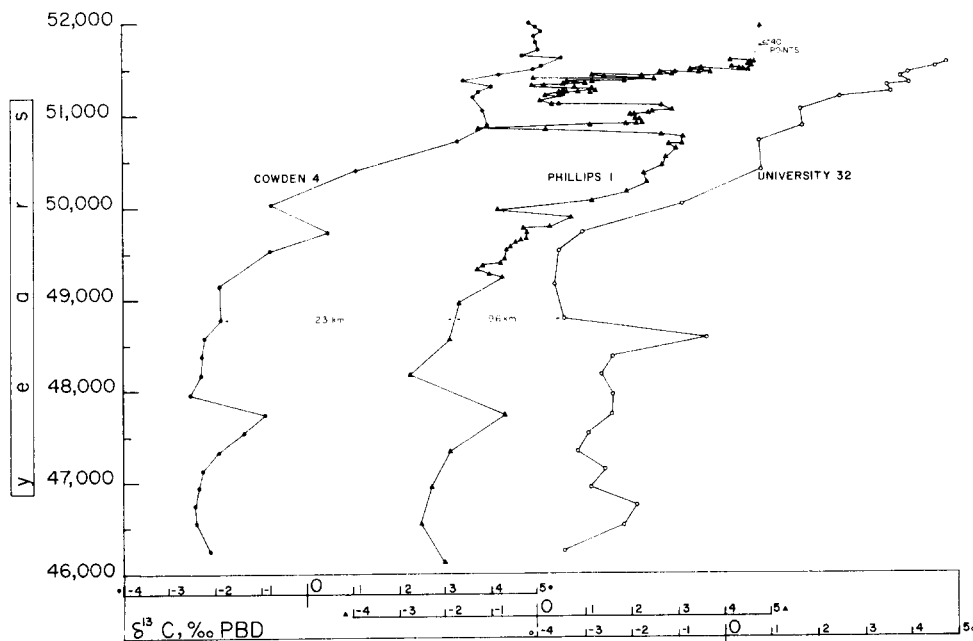


Fig. 4. Comparison of $\delta^{13}C_{carb}$ at corresponding levels of the transition zone among three cores spanning the Delaware Basin. Curves, and scales for $\delta^{13}C$, are displaced to avoid overlap confusion. Core locations are shown in fig. 1 of Anderson et al. [12].

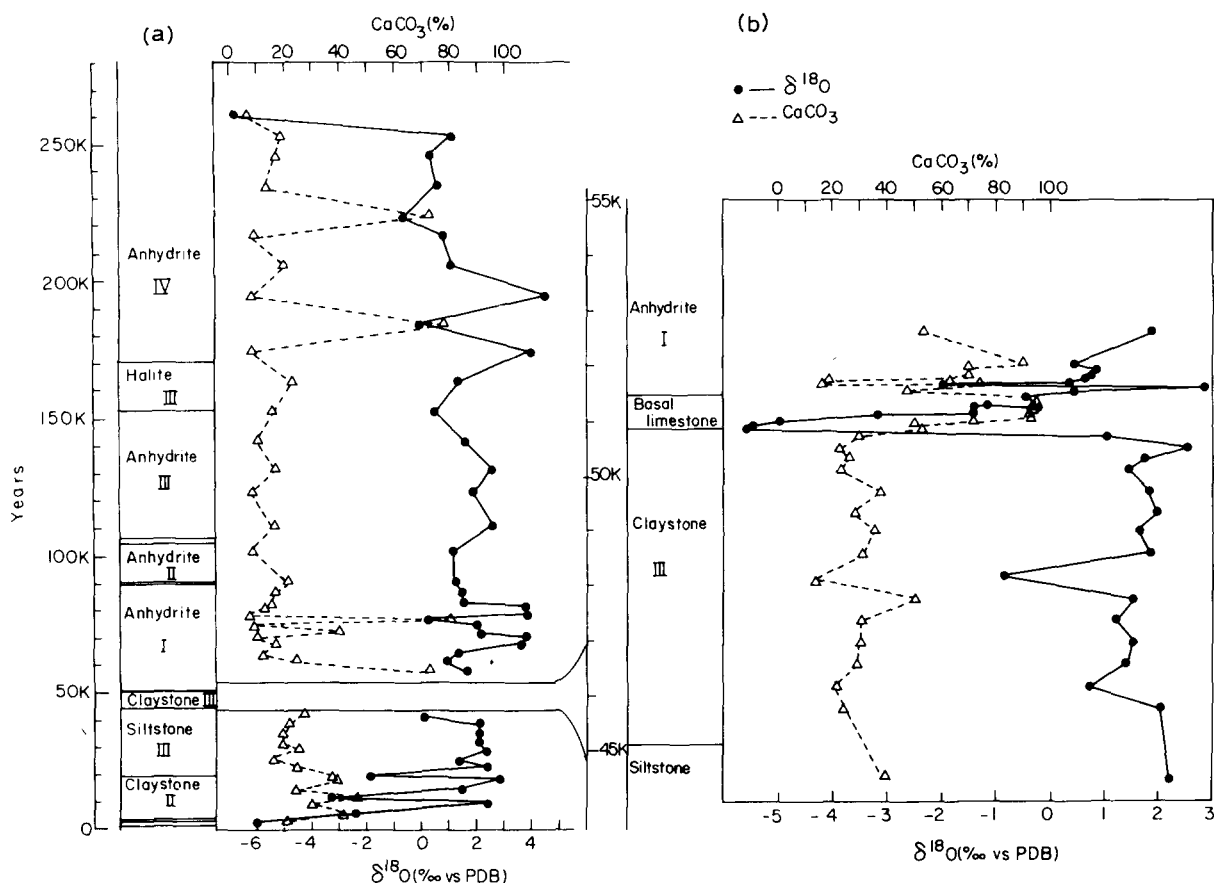


Fig. 5. $\delta^{18}\text{O}$ (‰, PDB) and C_{carb} (wt.%) in UNM Phillips 1: (a) entire section; and (b) enlargement of $\delta^{13}\text{C}$ transition zone. C_{carb} is normative CaCO_3 calculated from CO_2 weight loss, assuming all carbonate mineral is calcite. Note that all scales are larger in (b) than in (a).

through the transition zone gives 8.5% in 4500 years, or $2 \times 10^{-3}\%$ a^{-1} .

Samples of organic carbon selected to represent the range of isotopic, compositional, and stratigraphic variety in the section were analyzed for $\delta^{13}\text{C}_{\text{org}}$, and the results are compared in Table 1 with the corresponding values for $\delta^{13}\text{C}_{\text{carb}}$. Both organic carbon and carbonate carbon show enrichment in ^{13}C from the Bell Canyon Formation to the Castile evaporite, although not by the same amount.

We have supplemented the detailed work on $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ by analysis of anhydrite from the transition zone of the lowermost Anhydrite I for $\delta^{34}\text{S}_{\text{sulfate}}$. The results are shown in Fig. 3b. Previ-

ous analyses of samples from each of the overlying anhydrite and halite units [1] gave results closely similar to the new analyses of Anhydrite I (Fig. 3a). The plot of $\delta^{34}\text{S}$ in Fig. 3b suggests a possible negative correlation with $\delta^{13}\text{C}$ [2].

The $\delta^{18}\text{O}$ values of the carbonate minerals generally show minor fluctuation (Fig. 5a). These $\delta^{18}\text{O}$ values range from -1.0 to $+4.4\%$, but 70% of the data have values of $\delta^{18}\text{O} = +1 \pm 1\%$. The only large and significant variation (with the exception of the depleted $\delta^{18}\text{O}$ values in the bottommost and uppermost samples) occurred in the Basal Limestone Member of the Phillips 1 core (Fig. 5b). Highly depleted $\delta^{18}\text{O}$ in limestone (as low as -5.5%) coincided with the change from clastic to

evaporitic sedimentation in the basin. Together with the negative $\delta^{18}\text{O}$ values, we observed a depletion in C_{org} (Fig. 3b) and an increase of carbonate minerals in the rocks (Fig. 5b). In this zone $\delta^{13}\text{C}$ was depleted and variable, compared to the period before and after. These large variations in $\delta^{18}\text{O}$ were not observed in the other two cores. However, depletion of $\delta^{18}\text{O}$ in the carbonate, correlative with a decrease in $\delta^{13}\text{C}$ and an increase in carbonate mineral content, also occurred on a much smaller scale in Anhydrite IV (Fig. 5a). A similar relation with other salinity cycles was reported by Dean and Anderson [35], and elaborated by Burdett et al. [36].

6. Discussion

6.1. Chemical changes in the Delaware Basin

The aim in the following discussion is to describe and try to relate the change in carbon isotope (and accompanying chemical changes) detected in the Delaware Basin cores, and to speculate on its global significance. A provisional interpretation of the entire sequence is summarized in Fig. 6.

Below the transition of $\delta^{13}\text{C}$, the marine clastic Bell Canyon Formation contains carbonate with

Years (non-linear scale)	Period	Stage	Formation	Phases of isotope transition	Delaware Basin Conditions	Oceanic Conditions	
X00,000	Triassic	Skythian	Dockum		non-marine (marine in Great Basin)	normal carbon cycle: $\delta^{13}\text{C}$ low	
260,000	Permian	Ochoan	Rustler, etc.	restricted/evaporative	CaSO_4 facies, marine water dominant $\delta^{18}\text{O} > 0$	anomalous carbon cycle: $\delta^{13}\text{C}$ high, constant	
53,000			Salado				
51,400			Castlie			Early Castlie Zone	anomalous carbon cycle: $\delta^{13}\text{C}$ quickly rising -2 to $+6$ ‰
50,800						Basal Limestone	
47,000-48,000	Guadalupan	Bell Canyon	Bell Canyon Zone		marine $\delta^{18}\text{O} > 0$	normal carbon cycle: $\delta^{13}\text{C}$ low	
0							

Fig. 6. Diagrammatic sketch of the essential features of a provisional interpretation of stable isotope results in the Delaware Basin. Note that the time scale is non-linear and that its zero is arbitrarily at the base of the core from UNM Phillips 1, within the Bell Canyon Formation.

isotopic characteristics normal for present-day marine carbonate.

In the transition section, commencing at the same time in the three studied sections (Fig. 4) a steady rise in $\delta^{13}\text{C}$ began in the Bell Canyon and continued or resumed along the same trend in the early Castlie. An increase in the removal of C_{org} from the active system, beyond that normally balanced by oxidative erosion of old C_{org} , could account for the correlated rise. Considering only the Bell Canyon alone, this reservoir could have been confined to the basin itself, or it could have included the surface layers of the ocean with which the basin had communication. One can simply calculate, for example, that inasmuch as up to 30% of the carbon in the varves of the Bell Canyon zone is C_{org} (Figs. 3b, 4), that this deposition itself could account for a $\delta^{13}\text{C}$ shift of $0.3 \times 25\text{‰} = 7.5\text{‰}$ in that zone, assuming no buffering of $\delta^{13}\text{C}_{\text{carb}}$ by atmospheric interaction.

However, the same trend of increase of $\delta^{13}\text{C}$ continued after the Basal Limestone, and into the base of Anhydrite I of the Castlie evaporite. The fact that the increase continued in the same linear fashion while conditions of sedimentation were radically changed within the basin, leads us to believe that the rise was generated in the ocean outside the basin.

Another good reason for thinking that the rise was derived from outside the basin, is that during Basal Limestone and Castlie time the deposition of organic carbon within the basin was extremely low, both in weight fraction (Figs. 1, 3), and in actual sedimentation rate. Whether the C_{org} was rising (Bell Canyon), or consistently very low (lower Castlie), did not seem to make any difference in the rate of rise of $\delta^{13}\text{C}$ in the carbonate deposited from the surface waters of the basin. The rise continued after the beginning of CaSO_4 precipitation, and the latter required inflow of surface seawater into the basin and a reflux of about 10% by volume out of the basin ([27]; R.Y. Anderson, unpublished modelling calculations). Consequently the water mass that was responsible for rising $\delta^{13}\text{C}$ must have included at least the surface zone of the nearby ocean.

We do not believe that the rise in ^{13}C can be explained by local or intrabasinal processes such

as diagenesis or evaporation. Diagenesis, including post-depositional methanogenesis and sulfate reduction, dolomitization, or later alteration by circulation of fresh waters, are each capable of changing $\delta^{13}\text{C}_{\text{carb}}$ on a local scale [38]. For example Irwin, et al. [39] found in Kimmeridge (Jurassic) carbonates values of $\delta^{13}\text{C}$ up to +9‰ that they attributed to bacterial fermentation of organic matter producing CO_2 and CH_4 . However, as might be expected, those variations were very irregular in a stratigraphic sense. In the Delaware Basin, $\delta^{13}\text{C}_{\text{carb}}$ rises smoothly and simultaneously throughout the basin (Fig. 4). A normal fractionation between $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ has been preserved (Table 1). The fine grains and lamellae are preserved in exquisite detail, showing none of the recrystallization and textural degradation expected during diagenesis. Apparently early diagenetic processes were not important in this basin, and the section was protected from later changes by the overlying evaporites.

The mineralogy of the carbonate phase in this study has almost no effect on the carbon isotope variation. Nearby samples of dolomite and calcite show only insignificant variations in $\delta^{13}\text{C}$ (Figs. 1, 3), as was known from previous studies in other areas. The Bell Canyon Formation in Phillips 1 is all dolomitic but nevertheless has large variations of $\delta^{18}\text{O}$, whereas in the Castile Formation both dolomitic samples and calcitic samples have only minor fluctuations ($\pm 1\%$).

It is important to consider whether some of the carbon isotope anomaly that we find in this isolated basin (as well as in the Zechstein Basin) may be ascribed to evaporative processes within the basin, rather than to input from the surface ocean, as we have postulated above.

In general one might expect that CO_2 would be lost during the evaporation of seawater, and that such loss would leave the brine enriched in ^{13}C . In a putative equilibrium CO_2 degassing during evaporation, the drastic reduction in volume of liquid would in itself tend to cause a substantial loss of CO_2 . The loss would be increased by the considerable decrease of CO_2 solubility with increasing ionic strength. Precipitation of carbonate minerals, although not in itself accompanied by large carbon isotope fractionation, would never-

theless add to CO_2 loss through the conversion of bicarbonate to carbonate. Kinetic fractionation could modify these equilibrium tendencies, particularly in the evaporative mechanism, where the departure from equilibrium is influenced by the differentials of CO_2 pressure and of $\delta^{13}\text{C}$ between brine and atmosphere, by the wind speed, etc. Of course equilibrium with atmospheric CO_2 would erase evaporation effects.

Wigley et al. [40] have developed a comprehensive theory of the equilibrium changes of carbon isotopes in aqueous systems, including in particular a model for (non-evaporative) degassing of CO_2 with simultaneous precipitation of calcite. Previously Hendy [41] considered many factors controlling isotope ratios in groundwaters, including kinetic fractionation due to fast loss of CO_2 . Both of these models were for relatively dilute waters, in which activity coefficients and fractionation factors were well known. In response to our interest, Creighton Yapp (personal communication, 1982) has developed a more comprehensive model that includes a variety of kinetic effects, and at high concentrations. Such modelling shows in principle that $\delta^{13}\text{C}$ in the residual brine may rise by say 8‰ from degassing of CO_2 through evaporation and calcite precipitation.

However, it seems that this expected rise is not a normal result in the development of natural evaporite basins. Sabkhas in the Persian Gulf [42], Baja California [43], and the Afar Depression [44] have carbonates with negative to slightly positive $\delta^{13}\text{C}$, while sections in other evaporite basins that range from deep water to sabkha conditions in Pleistocene Lake Lisan [45], Miocene Mediterranean [43], Triassic of southern Israel (Magaritz and Druckman, unpublished), and Pennsylvanian Paradox (Magaritz, unpublished) have $\delta^{13}\text{C}$ that are all generally negative. Furthermore, $\delta^{13}\text{C}$ in the Delaware Basin started going positive thousands of years before evaporative concentration began (Fig. 3). In the correlative case of the Zechstein Basin, referred to in the introduction, the rise of $\delta^{13}\text{C}$ started an even longer time before the first evaporite [7–11] and continued through returns to carbonate facies in subsequent depositional cycles [46,47]. Furthermore, as one moves across the Delaware Basin from west to east (Fig. 4), the corre-

sponding increase in salinity indicated by thickness of the overlying Halite I [12, fig. 13] is not reflected in changes of $\delta^{13}\text{C}$.

In a somewhat analogous situation measured equilibrium and kinetic fractionations for $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ give a theoretical rise of up to 6‰ during evaporation of seawater, but natural systems show only a fractional or sometimes negligible increase [48].

One major departure from the regularities described above occurs in the Basal Limestone of Phillips 1, as a sharp shift to negative $\delta^{18}\text{O}$, as low as $\delta^{18}\text{O} = -5.5\text{‰}$ (Fig. 5). During the next 600 years $\delta^{18}\text{O}_{\text{carb}}$ gradually returned, with the onset of calcium sulfate deposition, to weakly positive values ($\delta^{18}\text{O} = +1.0 \pm 0.5\text{‰}$) characteristic of evaporites [28,42], and thereafter only varied by about 1‰ during salinity cycles. The negative excursion of $\delta^{18}\text{O}_{\text{carb}}$ was accompanied by a similar excursion in $\delta^{13}\text{C}$, although that never dropped as low as the pre-transition levels (Fig. 3b). These anomalies are less dramatically developed in Cowden 4, and are absent in University 37 (not illustrated). They probably reflect a major influx of meteoric water in at least the surface of the western part of the basin. A similar type of influx of meteoric water was recorded in Holocene sapropelic sediments of the Eastern Mediterranean [49], and was also suggested in the North Pacific during the last phase of the Pleistocene [50].

From about year 52,000 and continuing for the rest of the Castile section (Fig. 3a) (and indeed for the rest of the Permian—see below), $\delta^{13}\text{C}$ remained abnormally high. The changeover from a rising $\delta^{13}\text{C}$ to a high but level $\delta^{13}\text{C}$ seems to be abrupt in the data so far available, but definition of the precise form of this discontinuity will require further analyses. If, as the previous discussion indicates, the anomalously high level of $\delta^{13}\text{C}$ was derived from the surface ocean outside the basin, then its continuation at a high level was also from that source.

The worldwide statistical compilations of Veizer et al. [2], Lindh et al. [51], and Saltzman et al. [21] indicated a high in $\delta^{13}\text{C}$ lasting through the Pennsylvanian and Permian, and the finer time divisions of the latter compilations also demonstrated a low in the Triassic. However, very little published data for these times was available from the

western U.S.A. (e.g. [52]). The dissertation by Wilgus [37] included a few analyses of the overlying Rustler Formation in the back-reef area of West Texas that indicated high $\delta^{13}\text{C}$ continuing through the latest Permian in North America, except for the Phosphoria Formation. The earliest Triassic (in the Western Interior) was again of low $\delta^{13}\text{C}$.

In contrast to the anomaly of $\delta^{13}\text{C}$, the low values in $\delta^{34}\text{S}$ that we determined in the Castile evaporite are only a short-term manifestation of a well-documented low that began in the Early Permian and continued through most of Early Triassic time [1]. This comparison points up the independence of the carbon and sulfur cycles on a short time scale, in contrast to a general anticorrelation on a long time scale [2].

6.2. A worldwide event in the carbon cycle?

The previous documentation of a sharp rise in $\delta^{13}\text{C}$ throughout the Zechstein Basin [7–11] had led one of us to speculate that it might be representative of a worldwide event [8]. This led to a search for similar anomalies in other basins of stratigraphically equivalent age, which has here been abundantly confirmed for the Delaware Basin. Preliminary data from several profiles in the correlative Bellerophon Formation of the Alpine Tethyan facies indicate a similar rise (Holser and Magaritz, unpublished). We are therefore convinced that a very high $\delta^{13}\text{C}$ is indeed a characteristic of the world ocean (at least its surface layer) during the last stage of Permian time.

Not only the size, but especially the rate of rise of this shift of $\delta^{13}\text{C}$ is extraordinary. In the studied section of the Marl Slate in the Zechstein Basin [9,10], the whole carbon isotope transition zone is represented by 60 cm of the core. At a rate of deposition of $80 \mu\text{m a}^{-1}$ roughly estimated from mean varve thickness [9], this part of the sequence represents 7500 years. The total rise time in the Zechstein is therefore about twice that in the Castile, but is nevertheless very fast in a geological sense.

Evidently a large shift of the carbon cycle toward excess deposition of organic carbon is involved here, but the large amount and high rate of

the $\delta^{13}\text{C}$ increase raise many difficulties of interpretation. These difficulties are aggravated by the probable large size of the reservoirs of carbon involved.

An oceanic accumulation of C_{org} was previously postulated to explain rises of $\delta^{13}\text{C}$ during Cretaceous anoxic events [53]. Those rises were both smaller and slower but more crudely timed than the one in the Delaware Basin. A rise of over +8‰ in $\delta^{13}\text{C}$ was previously recorded by Schidlowski et al. [54] from the Lomagundi carbonates of mid-Precambrian ages. They assumed that it was due to excess deposition of C_{org} within a closed basin, but $\delta^{13}\text{C}$ and % C_{org} stratigraphy was not available in sufficient detail (as it is from the Delaware Basin) to make a clear distinction between basinal and oceanic sources.

It seems unlikely that the surface layer of the ocean could sustain its $\delta^{13}\text{C}_{\text{HCO}_3^-}$ at levels in greater disequilibrium with $\delta^{13}\text{C}_{\text{CO}_2}$ of the atmosphere for any appreciable length of time (e.g. [55]) consequently the reservoir that was in communication with the evaporite basins probably included the atmosphere as well as the surface ocean waters. Furthermore, the present time for mixing of the surface ocean waters with the deep ocean is a few thousand years, and while vertical mixing may have been very much less effective in a possible stratified ocean, we still must consider the possibility that the carbon reservoirs of the deep ocean might also have been involved in the shift of $\delta^{13}\text{C}$ that was recorded in the two basins. If the surface/atmosphere reservoir were first involved, and then only slowly mixed with the large deep-ocean reservoir, we might have expected an initial rise in $\delta^{13}\text{C}_{\text{carb}}$, followed by a reversal and slow return to normal values. In fact what we observe is a steady rise and then a long-sustained high.

We have made a series of model calculations, as to how the present carbon cycle might be distorted to generate the kind of carbon isotope record that we have found in the Permian. As might be expected, the above considerations are so restrictive that none of our calculations give a satisfactory answer. For example, if only the surface ocean and atmospheric reservoirs of carbon were involved, and only the very small fraction of organic carbon productivity were deposited without being bal-

anced by oxidation of old C_{org} , then the calculated rate of rise of $\delta^{13}\text{C}$ is of the right order of magnitude to explain the Permian anomaly. But if the whole ocean reservoir of C_{carb} is involved, then one would need to deposit a very much larger fraction of the photosynthesized C_{org} in order to generate such a large and fast rise in $\delta^{13}\text{C}$. But such large rates of burial could not be sustained for long unless the reflux to surface waters of phosphorous nutrient were much more efficient than it is today.

The carbon isotope anomaly in these Permian basins is unprecedented in magnitude and rate. As more and more geochemical and geological data have accumulated, the worldwide nature of the anomaly has become empirically established. At the same time, theoretical calculations have so far failed to give a satisfactory model explaining how the anomaly was generated. As one anonymous referee of this paper pointed out, "...It seems likely that [the] shifts reflect a global change in the $\delta^{13}\text{C}$ distribution. This result is very significant in that it cannot be explained without violating hypotheses of how the modern $\delta^{13}\text{C}$ balance is achieved."

7. Conclusions

The isotopic record in the varved sediments of the Upper Permian of the Delaware Basin, Texas, when combined with similar records already published from rocks of the same stratigraphic stage in the distant Zechstein Basin, has important implications for the geochemical cycle of carbon during that time interval:

- (1) The main event is a continuous rise of $\delta^{13}\text{C}_{\text{carb}}$, documented from three cores across the Delaware Basin, from $\delta^{13}\text{C} = -2.8$ to $+5.7\text{‰}$ in only 4400 years, or at a rate of $2 \times 10^{-3}\text{‰ a}^{-1}$.
- (2) The recording (but not the progress) of this carbon event is interrupted, for a few hundred years, by an influx of fresh water in the western side of the basin, depositing the Basal Limestone with variably light $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$, and low C_{org} .
- (3) The rise of $\delta^{13}\text{C}$ and the excess of C_{org} deposition which must have generated it, took place in the surface ocean external to the Delaware

Basin, as shown by its continuity and by a lack of C_{org} within the Delaware Basin.

(4) Correlation of some details of the Delaware carbon event with that previously recorded in the Zechstein Series in northwestern Europe suggests that these sites probably record a single event, that therefore was pervasive in the world surface ocean.

(5) While it is theoretically possible that the rise of $\delta^{13}C$ in the two basins might have been separately generated either by CO_2 degassing during evaporation, or by addition of $\delta^{13}C$ -rich CO_2 added by diagenetic fermentation of C_{org} -rich sediments into CH_4 and CO_2 , such a rise has not been observed in other evaporites.

(6) Ready equilibration of surface ocean water with the atmosphere makes it likely that at least the combined atmosphere-surface ocean reservoirs of carbon were involved in the carbon transfer.

(7) The persistence of high $\delta^{13}C$ for at least a few hundred thousand years after its rise, in both the Delaware and Zechstein Basins, suggests that the deep ocean reservoir of carbonate may also have been involved, even if mixing was inhibited by oceanic stratification.

(8) Calculations based on reservoirs and fluxes of carbon in the modern ocean do not satisfactorily model the Permian anomaly.

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