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PARALLEL TRENDS IN ORGANIC AND INORGANIC CARBON ISOTOPES ACROSS THE PERMIAN/TRIASSIC BOUNDARY

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ABSTRACT. Stable carbon isotope ratios in both inorganic and organic reservoirs have been widely applied to model environmental and sedimentological changes on a global scale. Most studies dealing with major extinction events have used the record of inorganic carbon. In this paper we report the relation between shifts in carbon-13 content of organic matter and coexisting carbonate fractions at a major extinction event, the Permian/Triassic boundary. We found that both $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ of the surface ocean varied dramatically across the boundary, but the fractionation $\Delta^{13}\text{C}$ between organic matter and carbonate remained constant. This result appreciably restricts the interpretation of changes in the carbon cycle during this critical interval. The new data are best explained by a combination of two mechanisms for variation in $\delta^{13}\text{C}_{\text{carb}}$: (1) burial and erosion of organic carbon, with a long time constant; and (2) sequestration of organic carbon into shallow and deep oceanic reservoirs, with a shorter time constant. For application to our case, the first mechanism is limited by possible buildup of marine pCO_2 , which would increase the isotopic fractionation factor. The second mechanism is limited in application to short-term transient variations in $\delta^{13}\text{C}$. Modelling of the carbon cycle and its variations of $\delta^{13}\text{C}$ must take both mechanisms into account.

INTRODUCTION

Carbon isotope composition ($\delta^{13}\text{C}$) records partition of carbon between organic and inorganic reservoirs during any specific time interval, a parameter that has been used to monitor the changes in productivity, storage of organic carbon [C_{org}], and the extinction process (Hsü, McKenzie, and He, 1982; Berner, Lasaga, and Garrels, 1983; Berger and Vincent, 1986; Holser, Magaritz, and Wright, 1986; Magaritz, 1989; Kump, 1991). To separate and study fractionation and source effects compared to secular variations of $\delta^{13}\text{C}$, it is useful to consider also the difference $\Delta^{13}\text{C} = \delta^{12}\text{C}_{\text{carb}} - \delta^{13}\text{C}_{\text{org}}$. If $\Delta^{13}\text{C}$ remains reasonably constant,

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while $\delta^{13}\text{C}_{\text{carb}}$ varies, all the shifts may be attributed to a global secular variation, whereas fluctuations in $\Delta^{13}\text{C}$ would indicate changes in origin, fractionation process (Hayes and others, 1989), or diagenesis. The groundwork for such investigations has been laid by detailed studies of the relation of $\delta^{13}\text{C}_{\text{org}}$ with $\delta^{13}\text{C}_{\text{carb}}$ in sections of Proterozoic (Knoll and others, 1986), Cambrian (Grant, 1992), and Cenomanian-Turonian age (Hayes and others, 1989; Arthur, Dean, and Pratt, 1988). The present study applies such analyses to the Permian-Triassic interval.

The Permian/Triassic [P/Tr] boundary witnessed the largest extinction event in Phanerozoic time (Raup and Sepkoski, 1984). This event was shown to be associated with a major downward shift of $\delta^{13}\text{C}_{\text{carb}}$ values (Baud, Magaritz, and Holser, 1989; Holser and others, 1989). Study of this boundary at the Gartnerkofel site [GK-1, in the Carnic Alps, Austria] showed several stages of variation in the carbon cycle, starting with a gradual decrease in $\delta^{13}\text{C}_{\text{carb}}$ (from high positive values) over several million years prior to the boundary, continuing as a fast but smooth drop across the boundary, followed by a lengthy period of $\delta^{13}\text{C}_{\text{carb}}$ minima, and ending in a gradual increase toward a Triassic value of $\delta^{13}\text{C}_{\text{carb}} \approx +1.3$ permil (Holser and others, 1989; Magaritz and Holser, 1991). The 270 m of marine carbonates in the GK-1 core provided an unusual opportunity for a parallel study of variation in $\delta^{13}\text{C}_{\text{org}}$.

SAMPLES AND ANALYSIS

Coring and sampling protocols are detailed in Holser and others (1989) and Holser, Schönlaub, and Klein (1991). Isotope analyses of organic carbon were performed at the California Institute of Technology and Global Geochemistry Corporation. Samples from the core were ground and reacted with 10 percent HCl to remove carbonate. The sample was then reacted with CuO in sealed Vycor tubes at 900°C for 3 hrs. Isotope ratios were determined after purification on the CO_2 produced. Kerogen and bitumen fractions were separated and analyzed from three samples. The kerogen was concentrated by acid treatment as above, whereas the bitumen was first extracted from the untreated powder with methylene chloride followed by evaporation to remove the solvent. Isotope results are reported in the conventional “ δ ” notation as permil deviation from the PDB standard. Data were previously available for these same samples, for $\delta^{13}\text{C}_{\text{carb}}$ (Magaritz and Holser, 1991) and for the content of total C_{org} (Klein, 1991). All these data are collected in table 1, together with calculated values of $\Delta^{13}\text{C}$.

RESULTS

The contents of C_{org} in this section are low—most are between 0.06 and 0.15 percent C_{org} , which is within the range usually found in platform carbonates. Knoll and others (1986) showed in a similar study that anomalous $\delta^{13}\text{C}_{\text{org}}$ values were found only in rocks with $\text{C}_{\text{org}} < 0.02$ percent. Most of our measured values of $\delta^{13}\text{C}_{\text{org}}$ lie in the range expected for organic matter (−23 to −30 permil), and no correlation is observed

TABLE 1

Carbon isotope data from the Gartnerkofel-1 core samples

Depth in core (m)	C _{org}	$\delta^{13}\text{C}_{\text{carb}}$ ‰	$\delta^{13}\text{C}_{\text{org}}$ ‰	$\Delta^{13}\text{C}_{\text{carb-org}}^{\dagger}$ ‰	$\delta^{13}\text{C}_{\text{kerogen}}^{**}$ ‰	$\delta^{13}\text{C}_{\text{bitumen}}^{**}$ ‰
74.4	0.06	1.70	-25.4	27.1		
75.9	0.07	1.66	-29.1	(30.76)		
76.3	0.08	1.59	-25.2	26.79		
82.6	0.10	1.48	-24.9	26.38		
90.3	0.15	1.49	-25.0	26.49		
95.9	0.12	1.35	-25.2	26.55		
103*	0.09	1.20	-26.9	<u>28.10</u>		
140*	0.11	1.35	-27.6	<u>28.95</u>		
177*	0.08	0.88	-27.4	<u>28.28</u>		
183*	0.14	-0.61	-26.2	25.59		
185*	0.10	-1.33	-26.6	25.27		
187	0.06	-0.45	-26.3	25.85		
188*	0.25	-0.17	-29.3	<u>29.13</u>		
193*	0.11	-0.40	-27.9	<u>27.5</u>		
202	0.09	0.58	-26.0	26.58		
220	0.17	-1.39	-29.9	<u>28.51</u>		
224	0.07	-0.88	-27.1	26.22		
229	0.07	1.21	-25.7	26.91		
234	0.08	1.74	-25.2	26.94		
235	0.06	1.64	-24.3	25.94		
236	0.15	1.79	-24.5	26.29		
240	0.06	1.92	-24.1	26.02		
241	0.06	1.98	-26.6	<u>28.58</u>		
243	0.07	1.86	-24.1	25.96		
244	0.10	1.75	-24.7	26.45		
251	0.31	2.27	-37.6	(39.87)		
252	0.08	2.69	-39.0	(41.69)		
254	0.11	2.12	-24.5	26.62		
267	0.07	2.83	-23.9	26.73		
268	0.34	2.13	-32.5	(34.63)	-33.6	-27.3
270	0.09	2.03	-23.8	25.83	-23.4	-25.9
285*	0.09	2.68	-31.5	(34.18)	-31.3	-29.6
301	0.06	2.94	-24.8	<u>27.74</u>		
306	0.08	2.95	-24.6	<u>27.55</u>		
310	0.07	3.02	-25.3	<u>28.32</u>		
320	0.08	2.66	-23.1	25.76		

* These samples represent a mixture of samples analyzed for $\delta^{13}\text{C}_{\text{carb}}$ values. Depth and $\delta^{13}\text{C}_{\text{carb}}$ and C_{org} values are means for the core segment.

** Analyses performed by Global Geochemistry Corporation.

† Group A: unmarked; Group B: underlined.

between $\delta^{13}\text{C}_{\text{org}}$ and C_{org}, indicating a predominantly endogenic origin. Five samples (in parentheses in table 1) are anomalously depleted in ^{13}C , with $\delta^{13}\text{C}_{\text{org}}$ values as low as -39 permil and $\Delta^{13}\text{C}$ over 30 permil. Knoll and others (1986) suggested that similarly deviate samples may have been altered and gave them little weight in discussion; lacking other criteria for our smaller group of samples, we will do likewise.

The main set of samples shows a bimodal distribution of $\Delta^{13}\text{C}$ (fig. 1): 21 samples of group A with low $\Delta^{13}\text{C} = 26.3 \pm 0.5$ permil, and 10 samples of group B (underlined in table 1) with relatively greater $\Delta^{13}\text{C} =$

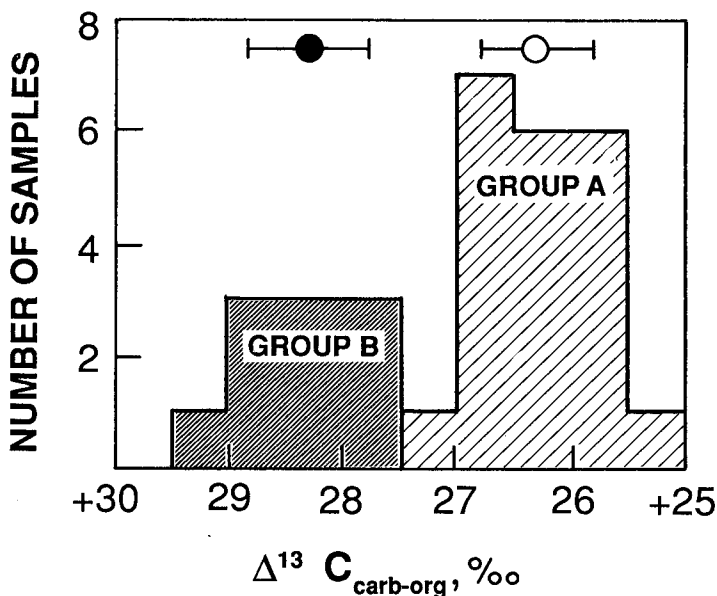


Fig. 1. Distribution of values of the fractionation $\Delta^{13}\text{C}$ between inorganic and (total) organic carbon in the Gartnerkofel core, including both Permian Bellerophon and Triassic Werfen Formations. The distribution is bimodal, with the means ($\pm\sigma$) of the two groups indicated.

28.3 ± 0.6 permil. These two populations are significantly different at a level of $\alpha = 0.001$, with $t = 9.57$ (15 *d.f.*). When plotted in figure 2, the $\delta^{13}\text{C}$ of each of these groups parallels (separately) the more detailed profile of $\delta^{13}\text{C}_{\text{carb}}$. Both show the high values in the Permian Bellerophon Formation, a steep drop across the P/Tr boundary, two minima in the Griesbachian Stage, and a return to intermediate values in the overlying section of later Lower Triassic. $\Delta^{13}\text{C}$ remains constant for each of the two groups throughout the major excursions of $\delta^{13}\text{C}_{\text{carb}}$ across the P/Tr boundary. These characteristics of the data argue for a primary source for both inorganic and organic signals, as no secondary process is known to shift $\delta^{13}\text{C}$ ratios of both carbonate and organic reservoirs in the same direction at the same time (Knoll and others, 1986). The lack of a shift in $\Delta^{13}\text{C}$ is further evidence that the variations of both organic and inorganic isotope ratios are primary signals. In cases where the $\delta^{13}\text{C}$ values of either the carbonate or organic fraction are altered during diagenesis, one would expect that the system (inorganic or organic) that suffered the alteration would show correlation with $\Delta^{13}\text{C}$. Such is the case for the data presented by Grant (1992) of a profile in the Cambrian of Newfoundland, in which $\delta^{13}\text{C}_{\text{carb}}$ (and consequently $\Delta^{13}\text{C}$) has been altered owing to the low carbonate content of the clastic section.

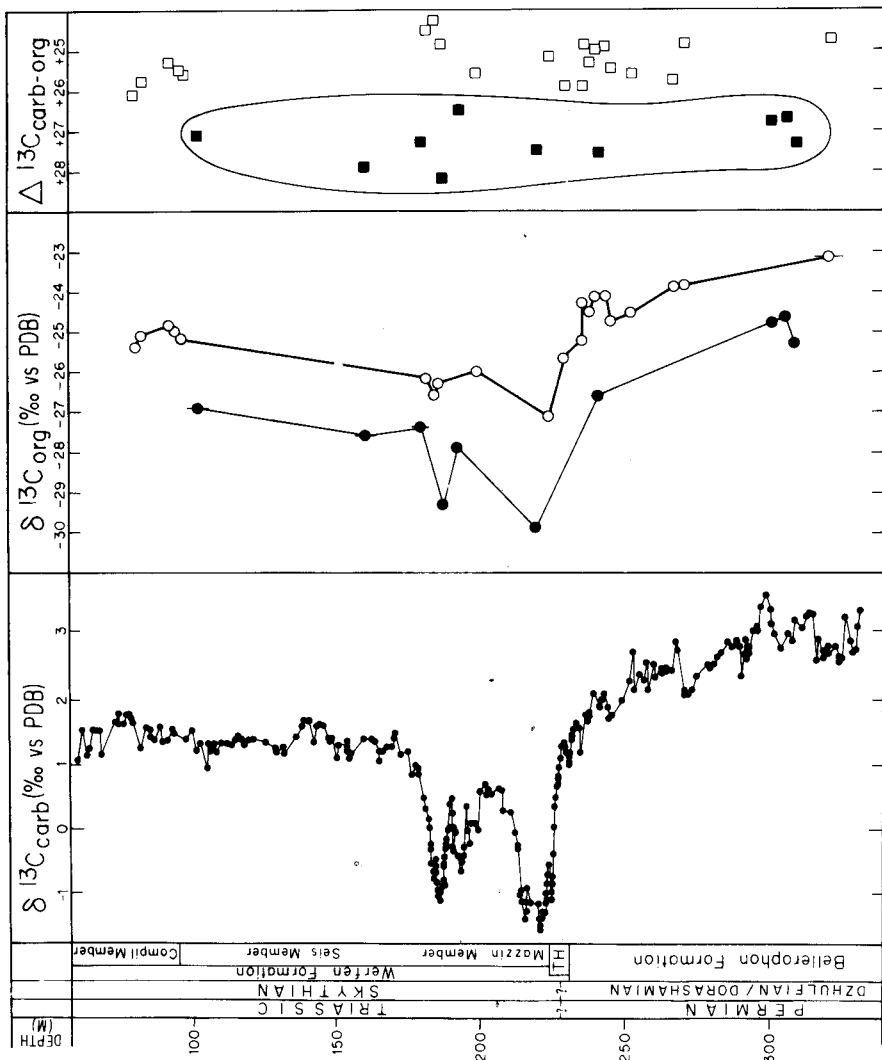


Fig. 2. Carbon isotope composition of the carbonate (Magaritz and Holser, 1991) and the organic fraction in the Gartnerkofel core across the Permian/Triassic boundary. The fractionations $\Delta^{13}\text{C}$ form two groups (fig. 1) for which $\delta^{13}\text{C}_{\text{org}}$ values are charted separately: group A in open symbols, and group B in solid symbols Each group tracks $\delta^{13}\text{C}_{\text{carb}}$. Five samples with $\Delta^{13}\text{C} > 30$ percent are not considered. TH = Tesero Horizon of the Werfen Formation.

The reality of a worldwide parallel shift of $\delta^{13}\text{C}_{\text{org}}$ (and $\delta^{13}\text{C}_{\text{atmosphere}}$) has recently been verified for the late Permian by new data on $\delta^{13}\text{C}_{\text{org}}$ in terrestrial vegetation, as measured in apatite of reptilian teeth (Thackeray and others, 1990).

DISCUSSION

The bimodal distribution of $\Delta^{13}\text{C}$.—The reason for the two groups of $\Delta^{13}\text{C}$ (figs. 1 and 2) is not yet apparent. The parallel behavior of the two curves indicates that in the two cases $\delta^{13}\text{C}_{\text{org}}$ is behaving similarly, presumably in response to environmental changes. Some nearby samples belong to different groups, as at the 241 and 180 m intervals. No differences in carbonate microfacies are evident between horizons in the two groups (K. Boeckelmann, personal communication, 1990).

In pre-Miocene sediments terrestrial $\delta^{13}\text{C}_{\text{org}}$ is several permil more enriched in ^{13}C than marine $\delta^{13}\text{C}_{\text{org}}$ (Dean, Arthur, and Claypool, 1986; Maynard, 1981; Popp and others, 1989), and alternation of two such differing sources is a possible explanation. The sediments at Gartnerkofel were deposited on a shallow marine shelf (Buggisch, 1978; Boeckelmann, 1991), and elsewhere in the region they have a varying content of acritarch (marine phytoplankton), terrestrial plant, and even fungal palynomorphs (Visscher and Brugman, 1988), but identifiable organic material was not found in the GK section itself (R. Zetter, personal communication, 1989). One would expect a marine-terrestrial alternation of carbon sources to give a continuous spectrum of $\delta^{13}\text{C}_{\text{org}}$ analyses rather than two groups. It seems more likely that the two groups of $\delta^{13}\text{C}$ represent bistable states of an oscillating system of non-linear variables, analogous to models for oscillations of $\delta^{13}\text{C}_{\text{carb}}$ in the Quaternary (Saltzman and Sutera, 1987). Until we know the temporal and geographic extent of this bimodal system, it is premature to speculate on the controlling parameters.

Interpretation of $\delta^{13}\text{C}_{\text{carb}}$ shifts.—Whatever the origin of the two groups of $\Delta^{13}\text{C}$, and whichever one (or both) represents original C_{org} , the data indicate no substantial and consistent change in $\Delta^{13}\text{C}$ through the studied interval. This observation constrains the possible interpretations of the radical drop of $\delta^{13}\text{C}_{\text{carb}}$ from a Permo-Carboniferous high documented through the late Permian in many sections around the globe (Popp, Anderson, and Sandberg, 1986; Beauchamp, Oldershaw, and Krouse, 1987; Holser and Magaritz, 1987; Magaritz and others, 1988; Baud, Magaritz, and Holser, 1989; Gruszczynski and others, 1989, 1990; Holser and others, 1989; Magaritz and Holser, 1991).

Two fundamentally differing mechanisms may underlie these shifts in $\delta^{13}\text{C}_{\text{carb}}$, and indeed both may contribute in a particular case (Broecker and Peng, 1984; Berger and Vincent, 1986; Weissert, 1989; Kump, 1991). Mechanism I (Garrels and Lerman, 1984; Holser, Magaritz, and Wright, 1986; Berner, 1987; Holser and others, 1988)—called “external fractionation” by Berger and Vincent (1986)—involves a net relative flux of carbon from the total organic reservoir to the total carbonate reservoir,

either by a decrease of burial and storage of new C_{org} (relative to C_{carb}) in sediments or by an increase of oxidation of older C_{org} . This shift is smoothed over a long term relative to the residence time of carbon in the ocean-biosphere system (10^5 yr). Such a shift moves ^{13}C -depleted carbon from the overall C_{org} reservoir to the overall C_{carb} reservoir (including the ocean) and is marked by a decrease in the mean $\delta^{13}\text{C}_{\text{carb}}$ of the whole ocean. All else being equal, this also results in an increase of atmospheric (plus dissolved) CO_2 and a decrease of O_2 . "All else" would *not* be equal if the global system reacted by reducing sulfate (or ferric iron), but even if the system included such a compensating feedback, it would be on a much longer time constant (Kump and Garrels, 1986; Berner, 1987) and would not appreciably affect our short-term conclusion.

Mechanism II ("internal fractionation" or the "biological pump": Berger and Vincent, 1986; Holser, Magaritz, and Wright, 1986; Kump, 1981) depends upon the division of the ocean into a small shallow subreservoir where productivity extracts C_{org} and drops it downward into a larger deep-sea subreservoir where most of it is re-oxidized. Such a process generates a gradient of dissolved $\delta^{13}\text{C}_{\text{carb}}$ between higher values in the surface ocean $\delta^{13}\text{C}_{\text{carb/shal}}$ and lower values in the deep ocean $\delta^{13}\text{C}_{\text{carb/deep}}$. This gradient is a measure of "new productivity" (productivity not immediately re-oxidized in the surface waters). So a drop in $\delta^{13}\text{C}_{\text{carb/shal}}$ may be explained in Mechanism II by a decrease or cessation of previous high productivity (Magaritz, 1989) but with no shift of the mean ocean $\delta^{13}\text{C}_{\text{carb}}$ (which is dominated by $\delta^{13}\text{C}_{\text{carb/deep}}$), no long-term net transfer of C_{org} out of the sedimentary reservoir, and no putative increase of atmospheric CO_2 or decrease of O_2 .

Kump (1991) described a simple numerical model that included both Mechanisms I and II and applied it to the carbon isotope data of Zachos, Arthur, and Dean (1989) across the K/T boundary; Caldeira and others (1990) calculated a more elaborate model that explicitly specified weathering reactions.

The time constant that limits the rate of Mechanism I is of the order of 10^5 yrs, whereas Mechanism II (which involves a much smaller reservoir) can change in hundreds of yrs (Kump, 1991). Any changes in $\delta^{13}\text{C}_{\text{carb/shal}}$ by Mechanism II will in the longer term be overwhelmed by the slowly implemented dominance of Mechanism I.

For pre-Cretaceous time there is little if any opportunity to sample $\delta^{13}\text{C}_{\text{carb/deep}}$ and $\delta^{13}\text{C}_{\text{carb/shal}}$ separately, and hence to measure the productivity-induced gradient, for a couple of reasons: (A) most deep-sea sediments of that age have been subducted, and few are exposed on the continents; and (B) these older sediments are generally well lithified, making it difficult to separate the rarer deep-water fossils for isotope analysis. Consequently in analyzing whole rocks (or fossils) in these older sections we are for the most part measuring $\delta^{13}\text{C}_{\text{carb/shal}}$, both because the samples are generally from shallow water deposits, and because even in deeper water sediments the bulk of the carbonate is pelagic in origin. The changes of $\delta^{13}\text{C}_{\text{carb}}$ we are measuring in these whole rocks are essentially

the sum of any changes owing to both Mechanisms I and II, although in the long term Mechanism I dominates. For example, based on the rates of isotope shifts exhibited in the profile of $\delta^{13}\text{C}_{\text{carb/shal}}$ in figure 2, we suggest that Mechanism I is dominant both during slowly decreasing $\delta^{13}\text{C}$ in the Late Permian (Bellerophon Formation, below 231 m) and during the very slowly increasing $\delta^{13}\text{C}$ in the Early Triassic (above 175 m). Mechanism II is cryptically superimposed on the slow change in the Bellerophon until its abrupt decrease (or cessation) generates the sharp negative excursions of the earliest Triassic (beginning in the Tesero Horizon: "TH" in fig. 2).

Relation of isotopic fractionation between the reservoirs to shifts in carbonate carbon isotope composition.—A possible connection between the above modelling of variations in $\delta^{13}\text{C}_{\text{carb}}$ and our new finding of constant $\Delta^{13}\text{C}$ across the period boundary lies in the level of atmospheric pCO_2 . Deines (1980), Mizutani and Wada (1982), Popp and others (1989), and Rau and others (1991) have reviewed laboratory and limited ecological data that indicate an increased fractionation $\Delta^{13}\text{C}$ with an increasing supply of dissolved $\text{CO}_2(\text{aq})$, levelling off at a "maximum fractionation barrier" that has been variously determined from -28 permil (Deuser, Degens and Guillard, 1968) to a "rarely realized" -39 permil (Estep and others, 1978). Some determinations of the relationship between $\Delta^{13}\text{C}$ and CO_2 supply have been described by Estep (1984), Rau, Takahashi, and Des Marais (1989, 1990), Arthur and others (1990), and Hollander and McKenzie (1991). The fractionation is fairly sensitive to changes in $\text{CO}_2(\text{aq})$. Rau and others (1991) substantially explained the decrease of 1 to 2 permil in $\delta^{13}\text{C}_{\text{org}}$ (and increase in $\Delta^{13}\text{C}$) across the last glacial-interglacial transition of the Quaternary by the measured increase in $\text{CO}_2(\text{aq})$ and pCO_2 . But it is not yet clear how high a concentration of $\text{CO}_2(\text{aq})$ [or pCO_2] is needed to reach maximum fractionation, where this sensitivity disappears.

If Mechanism I were operative during the major drop of $\delta^{13}\text{C}_{\text{carb}}$ in the late Permian, then the reduction in the reservoir of C_{org} and the probable consequent increase in pCO_2 should have increased $\Delta^{13}\text{C}$ —unless pCO_2 already had been so high (throughout the Permian) that the CO_2 added at the P/Tr boundary could not further increase $\Delta^{13}\text{C}$. Berner's (1987, 1989, 1991) modelling of the C–S–O system through this period indicates that even with the most conservative parameters (especially erosion rate constants) the late Permian witnessed a record high rate of C_{org} burial and a high atmospheric pO_2 , and correspondingly low levels of inorganic carbon burial and pCO_2 . Taken together, the above considerations question the customary dependence of modelling on Mechanism I.

Even with Mechanism I active it is possible that the CO_2 released across the P/Tr transition did not accumulate as a higher atmospheric (and oceanic) pCO_2 , owing to some presently unidentified feedback process. The experience of recent years indicates that about half the CO_2 released by the burning of fossil fuel has not remained in the atmo-

sphere + ocean, although a debate still continues as to the deposition site (or other fate) of the remainder (Sabine and Mackenzie, 1991; Tans, Fung, and Takahashi, 1990). When this presently undefined site has been more clearly identified by study of the recently perturbed carbon cycle, we may be able better to define the importance of Mechanism I in the P-Tr interval.

Suppose that Mechanism II was responsible for some of the changes in $\delta^{13}\text{C}_{\text{carb}}$ during the P-Tr. Kump (1991) modelled the K/T drop with this mechanism, showing that the isotopic gradient between surface and deep ocean is controlled by the relative fluxes of organic (F_{sd}°) and inorganic carbon (F_{sd}) from surface to deep:

$$\delta^{13}\text{C}_{\text{carb/shal}} - \delta^{13}\text{C}_{\text{carb/deep}} = -\Delta(F_{\text{sd}}^{\circ}/[F_{\text{sd}}^{\circ} + F_{\text{sd}}]).$$

In this model the only change is in the fluxes from the surface to the deep reservoir and the return flux back to the surface, and one does not face the problem of the large oxidation of organic matter required in Mechanism I. Kump (1991) notes that if changes in productivity affect these surface-to-deep fluxes, such changes will be recorded isotopically, at least in the short term. The disappearance at the K/T boundary of the surface-to-deep gradient of +2 permil was at least partially explained by a collapse of Cretaceous new productivity (Zachos, Arthur, and Dean, 1989; Kump, 1991). But to account for the much larger drop across the P/Tr by this mechanism would require a somewhat different regime of surface-to-deep fluxes to generate the very high $\Delta^{13}\text{C}_{\text{carb/shal}}$ in the Permian, before collapse of this system. For example, with a $\Delta^{13}\text{C}$ of 26.3 (group A), to gain a surface-to-deep gradient of even 4 permil, the factor $F_{\text{sd}}^{\circ}/(F_{\text{sd}}^{\circ} + F_{\text{sd}})$ would have to be boosted to 0.15, nearly double the value of 0.08 suggested by Kump (1991) for the late Cretaceous. Such a system might involve, for example, halving the carbonate surface-to-deep flux while leaving the organic output constant. Across the P/Tr boundary this regime of new productivity would have precipitously collapsed to result in the sharp negative excursions of surface $\delta^{13}\text{C}$.

Complete decoupling of surface-to-deep fluxes from the corresponding marine burial fluxes seems unlikely, that is, high productivity may be one cause (although not the only cause) of massive burial. Consequently we may expect both mechanisms to be operative at one time or another. The general agreement found through years of modelling (premised on Mechanism I) between the separate geological records of carbonate carbon isotopes, organic carbon burial, and paleoclimatology indicates that for long periods ($\geq 10^6$ yr) Mechanism I has been widely effective. However, the record of fractionation in the present instance, with its implications for a possible contribution of Mechanism II to the fast variations of $\delta^{13}\text{C}_{\text{carb}}$, suggests an added complexity that future modelling should try to encompass. Perhaps this objective may be attained by further detailed study of the nature and extent of coupling between surface-to-burial fluxes and surface-to-deep fluxes, that is, between Mech-

