



PII S0016-7037(99)00052-6

## Reply to the comment by S. T. Petsch on carbon isotope ratios of Phanerozoic marine cements: Re-evaluating global carbon and sulfur systems

SCOTT J. CARPENTER,<sup>\*,†,1</sup> and KYGER C. LOHMANN<sup>2</sup><sup>1</sup>Department of Geosciences, The University of Texas at Dallas, Richardson, TX USA<sup>2</sup>Department of Geological Sciences, The University of Michigan

(Received September 24, 1998; accepted in revised form February 10, 1999)

### 1. INTRODUCTION

Any complete model of the global carbon-oxygen-sulfur (C-O-S) systems must acknowledge the existence of seafloor hydrothermal (SFH) systems as a potential source of sulfur to the world's oceans (e.g., Edmond et al., 1979; Von Damm et al., 1985a,b; Von Damm et al., 1995; Humphris et al., 1995a and works therein). In Carpenter and Lohmann (1997), we provided a detailed description of the potential sulfur fluxes for the modern ocean. Petsch and others discount SFH systems as an important flux of sulfur to the ocean (as various sulfide minerals and H<sub>2</sub>S; e.g., Berner and Raiswell, 1983; Berner et al., 1983; Lasaga et al., 1985; Kump and Garrels, 1986; Francois and Gerard, 1986; Kump, 1989; Berner, 1987; 1989; 1990; Petsch and Berner, 1998). Although SFH system fluxes create a mass imbalance in the modern sulfur system, this is not justification for excluding these fluxes from isotope-mass balance models. We argue that Petsch's omission of SFH fluxes (of various materials capable of consuming marine O<sub>2</sub>), invalidates the subsequent discussions of marine O<sub>2</sub> levels and the link with the global carbon cycle (e.g., burial and oxidation of organic carbon).

If a model fails to include SFH fluxes (or any other documented flux), it is incumbent upon the authors of that model to explain why these fluxes do not impact their calculations and/or why published data are not used. For example, Petsch states that SFH fluxes are not needed to explain empirical data (e.g., Lindh, 1983; Figure 1), yet he does not adequately explain why these fluxes have been excluded from his calculations. To date, Petsch and others have made no attempt to refute the sulfur flux estimates associated with SFH systems (e.g., Edmond et al., 1979; Von Damm et al., 1985a,b; Von Damm et al., 1995; Humphris et al., 1995a and works therein). Instead of invoking a SFH sulfur flux, these workers have relied solely on the formation of sedimentary pyrite to account for the changes in the carbon and sulfur isotope data (e.g., Petsch and Berner, 1998). While it is possible to model the carbon-sulfur isotope systems in this manner, it is likely that their model parameters are incomplete. This omission is particularly important if their

model results do not explain the total range of empirical data and/or the empirical data in the context of other geochemical tracers (e.g., coeval <sup>87</sup>Sr/<sup>86</sup>Sr ratios).

Walker (1986) and Carpenter and Lohmann (1997) are the only studies that have incorporated sulfur fluxes from SFH systems to model/interpret the C-O-S system. As in Veizer et al. (1980), the interpretation of the secular variation presented by Carpenter and Lohmann (1997) is dependent on achieving steady-state over relatively long periods of time. Carpenter and Lohmann (1997) explicitly stated that the cycling time for sulfur is longer than that of carbon and that this may induce short-term deviations in δ<sup>13</sup>C values about a steady-state δ<sup>13</sup>C–δ<sup>34</sup>S correlation line (p. 4832). On this subject, we agree with Petsch. However, do empirical data indicate that the marine carbon-sulfur systems behave as predicted by his model (Petsch, 1999; Petsch and Berner, 1998)?

Here we examine the events of the Late Permian to provide evidence that Petsch's model falls short of predicting short-term variations observed in the rock record. Also, we present additional data supporting the concept that SFH activity is a substantial and variable flux during the Phanerozoic Eon.

### 2. GENERAL COMMENTS

Carpenter and Lohmann (1997) pointed out that previous models have used Lindh's (1983) carbon isotope data in conjunction with the Claypool's (1980) sulfur isotope data to model a δ<sup>13</sup>C<sub>carb</sub>–δ<sup>34</sup>S<sub>sulfate</sub> relation with a slope of –0.26 (as described by Lindh, 1983). However, the various authors of these models have invoked the interpretation of Veizer et al. (1980) whose interpretation was based on a slope of –0.13 and did not involve sulfur fluxes from SFH systems. As stated in Carpenter and Lohmann (1997), the steeper slope produced by the combination of the Claypool et al. (1980) data with that of Lindh (1983) or Carpenter and Lohmann (1997) yields a steady-state relation that is approximately twice that of Veizer et al. (1980). We suggest that models that fail to incorporate the significant sulfur fluxes from seafloor hydrothermal systems oversimplify the C-O-S system. For example, Petsch (1999) and Petsch and Berner (1998) exclude SFH fluxes from their calculations, suggesting that their isotope-mass balance calculations may be incomplete.

Petsch (this issue) explicitly states that the δ<sup>13</sup>C<sub>carb</sub>–δ<sup>34</sup>S<sub>sulfate</sub> relation is ~–0.25 and not –0.10. As Petsch does not dispute these data (used in Petsch and Berner, 1998), then he must discount the steady-state relation used by Veizer et al. (1980), Lindh (1983), Walker (1986), and Carpenter and Lohmann (1997). Are the δ<sup>13</sup>C<sub>carb</sub> and δ<sup>34</sup>S<sub>sulfate</sub> values of the Holocene,

\*Author to whom correspondence should be addressed (scarp@utdallas.edu).

†Present address: Department of Geosciences, University of Texas at Dallas P.O. BOX 830688 Richardson, TX 75083 USA.  
Reply to Petsch S. T. (1999). Comment on "Carbon isotope ratios of Phanerozoic marine cements: Re-evaluating global carbon and sulfur systems." [S. J. Carpenter and K. C. Lohmann (1997) *Geochimica et Cosmochimica Acta*] Comment published in *Geochimica et Cosmochimica Acta* 63(2), 307–310.

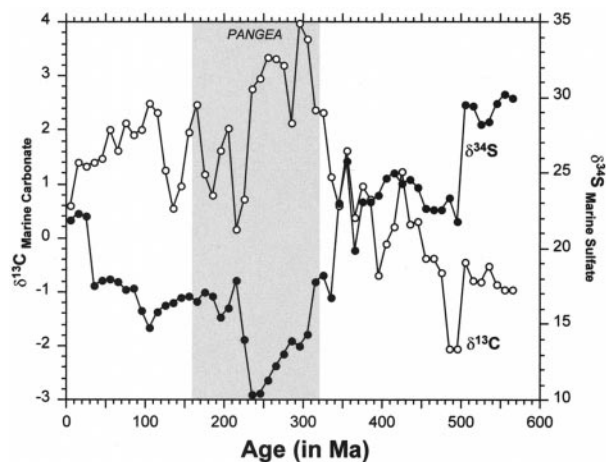


Fig. 1. Temporal distribution of marine carbonate  $\delta^{13}\text{C}$  and marine sulfate  $\delta^{34}\text{S}$  values. Data from Lindh (1983). Timing of the assembly of Pangea is represented by the gray shaded area (320 to 160 Ma). Note that  $\delta^{34}\text{S}$  values reach a Phanerozoic low and  $\delta^{13}\text{C}$  values reach a Phanerozoic high following the assembly of Pangea. Both tracers change abruptly at  $\sim 350$  Ma (the timing of a significant increase in marine carbonate  $\delta^{18}\text{O}$  values interpreted as an increase in seafloor hydrothermal activity; Walker and Lohmann, 1989; Carpenter et al., 1991).

the Permian, and the Cambrian, representative of non-steady-state conditions? Clearly, the time between each sample is greater than 50 myrs (as suggested by Petsch, 1999). Do these values (particularly the  $\delta^{13}\text{C}$  values) represent responses to short-lived perturbations of ocean chemistry? On the basis of similar  $\delta^{13}\text{C}$  values for long periods of geologic time (Cambrian-Ordovician, Pennsylvanian-Permian, the Mesozoic, etc.), it is unlikely that the marine cement data represent rapid changes in the  $\delta^{13}\text{C}$  value of marine DIC. In fact, we have attempted to avoid using data that represent non-steady-state conditions (e.g., Upper Ordovician, Upper Permian) in our calculations. As the data of Veizer et al. (1980), Lindh (1983), and Carpenter and Lohmann (1997) all have similar sampling frequencies, the potential risk of sampling non-steady-state conditions must be applied to each data set equally. That is, the Veizer et al. (1980) data set cannot represent steady-state conditions if the Lindh (1983) and Carpenter and Lohmann (1997) data set do not. As discussed by Carpenter and Lohmann (1997), it is unlikely that the differences between the Veizer et al. (1980) data and those of Lindh (1983) and Carpenter and Lohmann (1997) can be ascribed to sampling of non-steady-state conditions.

One of the important points of Carpenter and Lohmann (1997) is that our data did not match the assumptions associated with the predicted  $\delta^{13}\text{C}_{\text{carb}} - \delta^{34}\text{S}_{\text{sulfate}}$  relation with a slope of  $\sim -0.10$  as suggested by previous studies that had not incorporated SFH sulfur fluxes. Citing the difference between Cretaceous  $\delta^{13}\text{C}$  values and those reported by Veizer et al. (1980), Walker (1986) was the first to suggest that SFH sulfur fluxes should not be neglected when modeling the C-O-S system. Petsch excludes SFH systems from consideration and thereby models a system where the carbon system drives the sulfur system through burial of organic matter and subsequent sulfate reduction. In contrast, we have chosen to include SFH system

sulfur fluxes and have suggested that oxidation of reduced sulfur ( $\text{H}_2\text{S}$  and various sulfide minerals) controls  $\text{O}_2$  which in turn controls the burial and oxidation of organic matter.

The  $\text{O}_2$  levels of Phanerozoic atmospheres have been extensively studied by various authors (e.g., Berner, 1987; Berner, 1989; Petsch and Berner, 1989). The primary method of these studies is examination of the  $\delta^{13}\text{C} - \delta^{34}\text{S}$  relation described by Lindh (1983). Berner (1989), augmented Lindh's (1983)  $\delta^{13}\text{C}$  values by the addition of Popp et al.'s (1986) Carboniferous and Permian brachiopod data (producing  $\delta^{13}\text{C}$  values in excess of +6‰ at  $\sim 300$  Ma). In contrast, Petsch and Berner (1998) subsequently abandon the Popp et al. (1986) data in favor of the original Lindh (1983) data set (maximum  $\delta^{13}\text{C}$  values of +4‰; see Figure 1). Petsch and Berner (1998) provide no explanation for this significant change in their primary data set.

Berner (1989) and Petsch and Berner (1998) do, however, admit that the Phanerozoic extremes in  $\delta^{13}\text{C}$  and  $\delta^{34}\text{S}$  values are difficult to model given their input parameters (either producing extreme  $\text{O}_2$  levels or requiring unrealistic fluxes). It is interesting to note that in their conclusion (p. 260) Petsch and Berner (1998) explicitly state their preconceived notions about how the carbon and sulfur systems work: "Further refinement of the model is required to accommodate either the great accumulation of pyrite in the early Paleozoic (indicated by high  $\delta^{34}\text{S}$  at this time) or the minimal mass of sedimentary pyrite interpreted from the low  $\delta^{34}\text{S}$  values of the late paleozoic/Mesozoic." Unfortunately, we have been unable to find the great accumulation of pyrite in the early Paleozoic to which they refer. Perhaps Petsch and Berner's (1998) model and interpretations are made more complex by omitting SFH fluxes.

An alternative explanation of the observed changes in marine  $\delta^{34}\text{S}$  and  $\delta^{13}\text{C}$  values is that the early Paleozoic is dominated by continental weathering and the post-Devonian is dominated by SFH activity (e.g., Walker and Lohmann, 1989; Carpenter et al., 1991; Carpenter and Lohmann, 1997; Yale and Carpenter, in press). Although SFH activity and associated fluxes provide a much-needed sink for  $\text{O}_2$  and a source of mantle-derived strontium and sulfur, these fluxes are ignored. The lack of correspondence of Berner's (1989) and Petsch and Berner's (1998) model with empirical data and reasonable flux and  $\text{O}_2$  estimates suggests that their model parameters are not correct. We respectfully suggest that the first refinement of these models should be the addition of SFH fluxes and subroutine for the consumption of  $\text{O}_2$  by  $\text{H}_2\text{S}$ , sulfide minerals, methane, hydrogen, and other reduced materials emitted by hydrothermal vent systems.

Petsch argues that there is a "problem" with invoking fluxes of mantle-derived sulfur via SFH activity. He explains his decision not to use SFH sulfur fluxes in the following statement:

"There is an additional problem with a large input of mantle sulfide. To maintain an approximately constant mass of atmospheric  $\text{O}_2$ , in response to the addition and oxidation of mantle sulfide, the total mass of sedimentary pyrite and/or organic matter must increase. This would generate long-term, monotonic evolution in the  $\delta^{34}\text{S}$  and/or  $\delta^{13}\text{C}$  of seawater, or implies that the average  $\delta^{34}\text{S}$  or  $\delta^{13}\text{C}$  of the earth's crust is changing through time. Because these types of evolution are not suggested by the isotope record, it seems unlikely that a significant mantle-derived sulfide flux could be maintained on geologic time scales. To avoid these

problems any significant mantle-derived sulfide flux would require that the  $\delta^{34}\text{S}$  and mean oxidation state of subducted sulfur have the same values as the mantle-derived sulfur (pure sulfide with  $\delta^{34}\text{S} \sim 3.5\%$ ) which is unlikely. Sulfide more likely is subducted as biogenic pyrite ( $\delta^{34}\text{S} \sim -15\%$  or less)."

Carpenter and Lohmann's (1997) Figure 1 (p. 4833) indicates that there are long-term trends in the evolution of the marine  $\delta^{13}\text{C}$  and  $\delta^{34}\text{S}$  values (e.g., the Pennsylvanian through Cretaceous values are distinctly different than the pre-Pennsylvanian values; Figure 1). Given that these values respond to various fluxes, it is unlikely that any isotopic tracer would show a monotonic change over the course of 600 million years. In addition, marine  $\delta^{13}\text{C}$  values have not changed monotonically since the Cretaceous (a period of time during which SFH activity has been abundantly documented). In fact, marine  $\delta^{13}\text{C}$  values have changed very little since the Cretaceous, whereas  $\delta^{34}\text{S}$  values have increased nearly 6‰. We argue that a lack of a monotonic change in marine  $\delta^{13}\text{C}$  and  $\delta^{34}\text{S}$  values is not adequate justification for exclusion of SFH system sulfur fluxes. Given that these systems have been documented by numerous submersible dives to the sea floor, it is clear that they exist. Moreover, the sulfur flux estimates reported by Edmond et al. (1979), Von Damm et al. (1985a;b), Von Damm et al. (1995), and Humphris et al. (1995b) have never been refuted, yet Petsch and Berner (1998) continue to discount this potential contribution to the sulfur system.

Petsch incorrectly argues that subducted sulfides are more likely to have the  $\delta^{34}\text{S}$  value of biogenic pyrite ( $< -15\%$ ) than SFH system sulfides (3.5‰). Arguments about accretionary wedges aside, modern SFH systems (e.g., black smokers) occur in and on oceanic crust (basalt) and biogenic pyrite occurs in silici-clastic and carbonate sediments (sometimes overlying oceanic crust). Therefore, the likelihood of subducting dense, sulfide-rich oceanic crust is significantly greater than that of the less dense sedimentary rocks. It is quite possible that the remnants of SFH sulfides (with an initial  $\delta^{34}\text{S}$  value of  $\sim 3.5\%$ ) are consumed at subduction zones.

### 3. MANTLE FLUXES AND SUPERCONTINENT ASSEMBLY

Earth processes, such as supercontinent assembly and mantle convection, occur with a periodicity of  $\sim 300$  to 500 million years (e.g., Sutton, 1963, Anderson, 1982, Gurnis, 1988, Zhong and Gurnis, 1993). The relation between supercontinents, mantle plumes and surficial volcanic activity (such as LIPs, kimberlites, carbonatites, and SFH activity) has been described by Yale and Carpenter (1998). They conclude that there is a direct relation between mantle convection changes (induced by supercontinent assembly) and Phanerozoic ocean chemistry changes (Figures 1,2).

A majority of the marine carbon isotope excursions in the more recent rock record (associated with "oceanic anoxic events") can be correlated with eruptions of LIPs and second order minima in marine  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (e.g., Scholle and Arthur, 1980; Erba, 1994; Yale, 1998). The more notable events include: Pigafetta ( $\sim 167$  Ma), Ontong-Java Plateau ( $\sim 122$  Ma), Caribbean Plateau and Broken Ridge (88–90 Ma) and the Columbia Flood Basalt ( $\sim 17$  Ma). Yale (1998) found that the volume of LIP/flood basalt correlates with the magnitude of the second order  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio variation and that

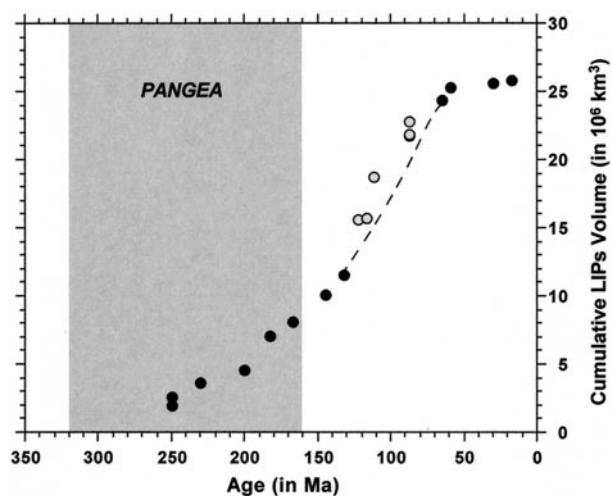


Fig. 2. Cumulative volume of LIPs (flood basalts) associated with the assembly and break-up of Pangea (data from Yale, 1998). Grey circles represent LIPs occurring between 120 and 80 Ma and represent the timing of the supposed Mid-Cretaceous superplume event. The dashed line is a 4<sup>th</sup> order polynomial fit through the data exclusive of the Mid-Cretaceous data. From Yale and Carpenter (1998).

relatively small fluxes from these basalts can induce the necessary changes in marine  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. Courtillot (1994) described a striking correlation between flood basalt eruptions (LIPs) and extinction events since the eruption of the first Pangea-related flood basalts (Siberian Traps at 250 Ma) (Figure 2). We suggest that these "mantle events" induced ocean anoxia and played an important role in these extinction events.

Although the age assignments associated with both the igneous and sedimentary rock units being described are generally poorly constrained, it is likely that second order  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio minima precede the LIP eruption (e.g., the late Permian  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio minimum and the Siberian and Emeishan flood basalts; Yale, 1998). The interaction of a large mantle plume head with both thick continental and thin oceanic crust will probably result in SFH activity (and potentially other forms of volcanic activity) preceding the flood basalt eruption. Although both can potentially add mantle-derived Sr to seawater, SFH activity is presumably a more efficient mechanism for Sr delivery to the oceans (e.g., Ingram et al., 1994; Yale, 1998). The correlation between mantle Sr fluxes and LIP eruptions is strong, but further examination of the timing of eruptions and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio minima is needed.

The relation between second order minima in marine  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and LIP eruptions strongly suggests that mantle fluxes are enhanced during these events. Conversely, the relative contribution of continental weathering (and therefore delivery of oxidized sulfur to the ocean from sedimentary pyrite) is minimized. On the basis of decreases in both marine  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and  $\delta^{34}\text{S}$  values, we conclude that the oxygen system responds to these mantle events (consuming  $\text{O}_2$ ) and thus enhances burial of organic matter. Thus, the conclusion of Carpenter and Lohmann (1997) that the sulfur system drives the carbon system (via the oxygen system) seems justified. If, however, we assume that there is no SFH flux of sulfur with these events (as suggested by Petsch), then there is no accounting for the mantle-derived strontium (and sulfur). Therefore,

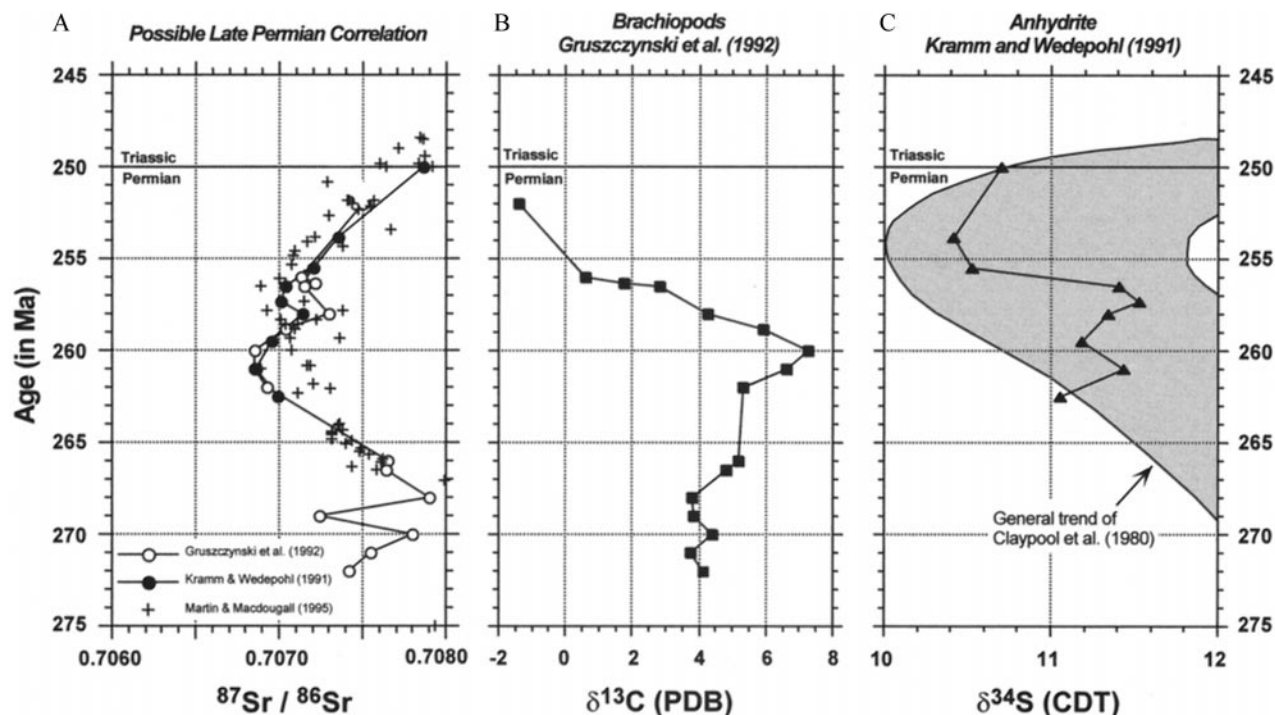


Fig. 3. Summary of selected Late Permian strontium, carbon and sulfur isotope data. A. Correlation of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios from Zechstein Fm. anhydrite (Kramm and Wedepohl, 1991) and Kapp Starostin Fm. brachiopods (Gruszczynski et al., 1992), and biogenic phosphates from various Formations (Martin and Macdougall, 1995). All data are normalized to an NBS-987 value of 0.710238. B.  $\delta^{13}\text{C}$  values of the Gruszczynski et al. (1992) samples plotted in Fig. 3A. C.  $\delta^{34}\text{S}$  values of the Kramm and Wedepohl (1991) samples plotted in Fig. 3A. The general trend of the Claypool et al. (1980) data for the same time period is represented by the shaded area.

we must conclude that the isotopic chemistry of the ocean responds to large-scale changes in mantle convection and modification of SFH systems.

#### 4. EVENTS NOT EXPLAINED BY WEATHERING OF SEDIMENTARY SULFIDES

Several carbon isotope excursions in the marine record are worthy of further modeling. Three quickly come to mind: 1) The Late Ordovician (Hirnantian) where there is as much as a 6‰ increase in marine  $\delta^{13}\text{C}$  values in ~1 million years but relatively little change in  $\delta^{34}\text{S}$  values (e.g., Claypool et al., 1980; Brenchley et al., 1994; Gibbs et al., 1997; Kump et al., 1995; see Carpenter and Lohmann, 1997 for discussion); 2) The Late Permian (e.g., Gruszczynski et al., 1989; Mii et al., 1997; Bowring et al., 1998); and 3) The oceanic anoxic events of the Mesozoic (e.g., Scholle and Arthur, 1980; Ingram et al., 1994; Yale, 1998).

Given that Petsch (1999) and Petsch and Berner (1998) provide a model that potentially constrains the effects of non-steady-state perturbations in the C-O-S system, it is reasonable to compare their model with available empirical data. We have chosen data from the Late Permian as a test of their model. Figure 3 describes the correlation between the high  $\delta^{13}\text{C}$  values of marine carbonates of this period and the occurrence of voluminous sulfate deposits with very low  $\delta^{34}\text{S}$  values and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. It is difficult to reconcile the Phanerozoic maximum  $\delta^{13}\text{C}$  value and the Phanerozoic minimum  $\delta^{34}\text{S}$

value and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios with enhanced weathering of sedimentary pyrite and burial of organic matter alone. While these phenomena may potentially explain the C and S isotope data, they have no bearing on marine  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. In contrast, processes associated with an increase in mantle fluxes and seafloor hydrothermal systems can accommodate all three systems simultaneously.

Clearly there can be large and rapid perturbations of the carbon system without a significant change in the sulfur system. The model described by Petsch (1999) fails to explain documented empirical data (Figure 4). Petsch's model indicates that a 20% change in the burial of organic carbon produces a 1‰ change in marine carbonate  $\delta^{13}\text{C}$  values. Given these input parameters, the carbon isotope variation observed in the Upper Permian would require a 60% increase in  $C_{\text{org}}$  burial followed by a 170% decrease in  $C_{\text{org}}$  burial between 268 and 252 Ma. These results strongly suggest that the model parameters used by Petsch (1999) and Petsch and Berner (1998) are not correct.

The high  $\delta^{13}\text{C}$  values for the Upper Permian reported by Gruszczynski et al. (1989; 1992) have been confirmed by Mii et al. (1997). Therefore, the marked increase in  $\delta^{13}\text{C}$  values from ~+4 to +8‰ during the Late Permian has been replicated in two independent studies. The subsequent decrease in  $\delta^{13}\text{C}$  values near the Permian-Triassic boundary was not observed by Mii et al. (1997). However, carbon isotope data from China indicate that  $\delta^{13}\text{C}$  values decrease abruptly (to values as low as -6‰) near the Permian-Triassic boundary

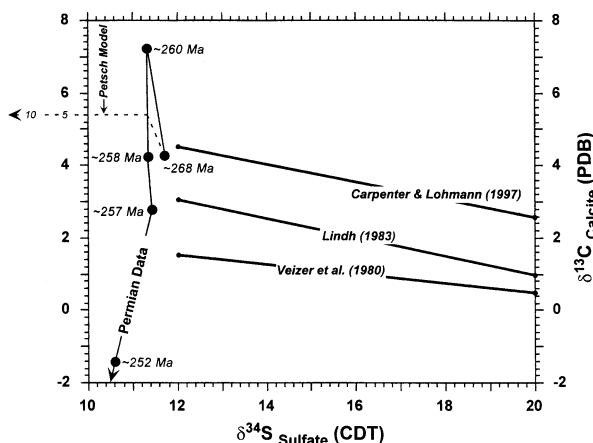


Fig. 4. Schematic diagram of  $\delta^{13}\text{C}$  and  $\delta^{34}\text{S}$  values for Permian data plotted in Figure 3.  $\delta^{13}\text{C}$ – $\delta^{34}\text{S}$  relations of Carpenter and Lohmann (1997), Lindh (1983), and Veizer et al. (1980) are plotted for reference (from Carpenter and Lohmann, 1997). Dashed arrow represents the  $\delta^{13}\text{C}$  and  $\delta^{34}\text{S}$  values as predicted by Petsch's (1999) model. The numbers 10 and 5 represent approximate locations on the trend that represent 10 and 5 million years following perturbation of the C and S systems (here started at 268 Ma).

(Bowring et al., 1998). Irrespective of the casual links between the  $\delta^{13}\text{C}$  value decreases and the Permian-Triassic extinction event, the Petsch model cannot accommodate the 4‰ increase during the Late Permian. Given that these data are at the time scale described by Petsch (1999), it is clear that this model does not account for such non-steady-state changes. Moreover, it is unclear whether the changes that the Petsch model describes exist or are to be found in the rock record.

The initiation of enhanced mantle convection and flood basalt volcanism (and likely SFH activity) at the same time as the secular variation of the late Permian is not fortuitous. Yale and Carpenter (1998) have shown that there is a direct relation between plume-related igneous activity and insulation of the mantle resulting from the assembly of Pangea. An example of this is the increase in the eruptive volume of LIPs (flood basalts) following the assembly of Pangea (320 to 160 Ma; Figure 2). The Late Permian is the time just prior to the eruption of the first Pangea-related LIPs (Siberian Traps and Emeishan Flood Basalt). In addition, the correlation of these Phanerozoic extremes in the C, S, and Sr isotope ratios coincide with exceptionally large deposits of marine sulfates that are not uniquely interpreted as evaporites (e.g., Zechstein and Castille Formations). If these sulfate deposits are the result of direct precipitation from seawater, then it is likely that this period is marked by elevated marine  $\text{Ca}^{2+}$  and/or  $\text{SO}_4^{=}$  concentrations. Conversely, if this sulfate is the result of weathering of sedimentary pyrite, then continental weathering should be enhanced during the Late Permian. Although Benison et al. (1998) have suggested that Permian lakes and groundwater in central North America were acidic, marine  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and  $\delta^{34}\text{S}$  values (both unequivocally mantle-derived) suggest that continental weathering fluxes are low, relative to mantle fluxes.

##### 5. PROTEROZOIC $\Delta^{13}\text{C}$ – $\Delta^{34}\text{S}$ RELATIONS

Petsch's model also fails to explain the marked difference in the slope of the Phanerozoic and Proterozoic  $\delta^{13}\text{C}$ – $\delta^{34}\text{S}$  rela-

tions (slopes of  $-0.24$  and  $0.50$ , respectively; Strauss, 1993; Carpenter and Lohmann, 1997). We stand by our interpretation that the Proterozoic  $\delta^{13}\text{C}$ – $\delta^{34}\text{S}$  relation is the result of significantly higher SFH fluxes.

##### 6. CONCLUSION

Seafloor hydrothermal systems exist. Sulfur flux estimates from these systems are significant. Without any evidence suggesting that reported sulfur flux estimates from these systems are invalid or grossly overestimated, incorporation of these fluxes and isotope ratios into models is justified. Empirical data from Upper Permian rocks indicate that the model presented by Petsch (1999) and Petsch and Berner (1998) fails to account for non-steady-state perturbations of the marine carbon and sulfur systems. A preponderance of evidence suggests that ocean chemistry responds to long-term changes in mantle activity. Only by using mantle-fluxes can a satisfactory explanation of marine  $\delta^{13}\text{C}$  and  $\delta^{34}\text{S}$  values and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios be achieved.

*Acknowledgments*—This research was supported in part by funds from Marathon Oil Company, National Science Foundation Grant EAR-8115840 to KCL and by Texas Advanced Research Program Grant #009741-064 to SJC.

##### REFERENCES

- Anderson D. L. (1982) Hotspots, polar wander, Mesozoic convection and the geoid. *Nature* **297**, 391–393.
- Benison K. C., Goldstein R. H., Wopenka B., Burruss R. C., and Pasteris J. D. (1998) Extremely acid Permian lakes and ground waters in North America. *Nature* **392**, 911–914.
- Berner R. A. (1987) Models for carbon and sulfur cycles and atmospheric oxygen: Application to Paleozoic geologic history. *Am. J. Sci.* **287**, 177–196.
- Berner R. A. (1989) Biogeochemical cycles of carbon and sulfur and their effect on atmospheric oxygen over Phanerozoic time. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **75**, 97–122.
- Berner R. A. (1990) Atmospheric carbon dioxide levels over Phanerozoic time. *Science* **249**, 1382–1386.
- Berner R. A. and Canfield D. (1989) A model for atmospheric oxygen over Phanerozoic time. *Am. J. Sci.* **289**, 333–361.
- Berner R. A. and Raiswell R. (1983) Burial of organic carbon and pyrite sulfur in sediments of Phanerozoic time: A new theory. *Geochim. et Cosmochim. Acta* **47**, 855–862.
- Berner R. A., Lasaga A. C., and Garrels R. M. (1983) The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. *Am. J. Sci.* **283**, 641–683.
- Bowring S. A., Erwin D. H., Jin Y. G., Martin M. W., Davidek K., and Wang W. (1998) U/Pb zircon geochronology and tempo of the end-Permian mass extinction. *Science* **280**, 1039–1045.
- Brenchley P. J., Marshall J. D., Carden G. A. F., Robertson D. B. R., Long D. G. F., Meidla T., Hints L., and Anderson, T. F. (1994) Bathymetric and isotopic evidence for a short-lived Late Ordovician glaciation in a greenhouse period. *Geology* **22**, 295–298.
- Carpenter S. J. and Lohmann K. C. (1997) Carbon isotope ratios of Phanerozoic marine cements: Re-evaluating the global carbon and sulfur systems. *Geochim. Cosmochim. Acta* **61**, 4831–4846.
- Carpenter S. J., Lohmann K. C., Holden P., Walter L. M., Huston T., and Halliday A. N. (1991)  $\delta^{18}\text{O}$  values,  $^{87}\text{Sr}/^{86}\text{Sr}$  and Sr/Mg ratios of Late Devonian abiotic marine calcite: implications for composition of ancient seawater. *Geochim. Cosmochim. Acta* **55**, 1991–2010.
- Claypool G. E., Holser W. T., Kaplan I. R., Sakai H., and Zak I. (1980) The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. *Chemical Geology* **28**, 199–260.
- Courtillot V. (1994) Mass extinctions in the last 300 million years: One impact and seven flood basalts? *Israeli J. Earth Sci.* **43**, 255–266.
- Edmond J. M., Measures C., McDuff R. E., Chan L. H., Collier R., Grant B., Gordon L. I., and Corliss J. B. (1979) Ridge crest hydro-

- thermal activity and the balances of major and minor elements in the ocean: The Galapagos data. *Earth and Planet. Sci. Lett.* **46**, 1–18.
- Erba E. (1994) Nannofossils and superplumes: The early Aptian “nannoconid crisis.” *Paleoceanography* **9**, 483–501.
- Francois L. M. and Gerard J.-C. (1986) A numerical model of the evolution of ocean sulfate and sedimentary sulfur during the last 800 million years. *Geochim. Cosmochim. Acta* **50**, 2289–2302.
- Gibbs M. T., Barron E. J., and Kump L. R. (1997) An atmospheric pCO<sub>2</sub> threshold for glaciation in the Late Ordovician. *Geology* **25**, 447–450.
- Gruszczynski M., Hoffman A., Malkowski K., Zawidzka K., Halas S., and Zeng Y. (1989) A brachiopod calcite record of the oceanic carbon and oxygen isotope shifts at the Permian/Triassic transition. *Nature* **337**, 64–68.
- Gruszczynski M., Hoffman A., Malkowski K., and Veizer J. (1992) Seawater strontium isotopic perturbation at the Permian-Triassic boundary, West Spitsbergen, and its implications for the interpretation of strontium isotopic data. *Geology* **20**, 779–782.
- Gurnis M. (1988) Large-scale mantle convection and the aggregation and dispersal of supercontinents. *Nature* **332**, 695–699.
- Humphris S. E., Zierenberg R. A., Mullineaux L. S., and Thomson R. E. (eds.) (1995a) Seafloor Hydrothermal Systems. *Amer. Geophys. Union Monograph* **91**, 466 p.
- Humphris S. E., Herzig P. M., Miller D. J., Alt J. C., Becker K., Brown D., Brugmann G., Chiba H., Fouquet Y., and others (1995b) The internal structure of an active sea-floor massive sulfide deposit. *Nature* **377**, 713–716.
- Ingram B. L., Coccioni R., Montanari A., and Richter F. M. (1994) Strontium isotopic composition of mid-Cretaceous seawater. *Science* **264**, 546–550.
- Kramm U. and Wedepohl K. H. (1991) The isotopic composition of strontium and sulfur in seawater of Late Permian (Zechstein) age. *Chem. Geol.* **90**, 253–262.
- Kump L. R. (1989) Alternative modeling approaches to the geochemical cycles of carbon, sulfur, and strontium isotopes. *Amer. Jour. Sci.* **289**, 390–410.
- Kump L. R. and Garrels R. M. (1986) Modeling atmospheric O<sub>2</sub> in the global sedimentary redox cycle. *Amer. Jour. Sci.* **286**, 337–360.
- Kump L. R., Gibbs M. T., Arthur M. A., Patzkowsky M. E., and Sheehan P. M. (1995) Hirnantian glaciation and the carbon cycle. In *Ordovician Odyssey: 7th International Symposium on the Ordovician System* (ed. J. D. Cooper et al.), pp. 299–302. SEPM.
- Lasaga A. C., Berner R. A., and Garrels R. M. (1985) A geochemical model of atmospheric CO<sub>2</sub> fluctuations over the last 100 million years. In *The Carbon Cycle and Atmospheric CO<sub>2</sub>: Natural Variations Archean to Present*. (ed. E. T. Sunquist and W. S. Broecker), Geophysical Monograph 32, pp. 397–411. Washington, D.C., American Geophysical Union.
- Lindh T. B. (1983) *Temporal variations in <sup>13</sup>C and <sup>34</sup>S and global sedimentation during the Phanerozoic* [M.S. thesis]: Miami, University of Miami, 98 p.
- Martin E. E. and Macdougall J. D. (1995) Sr and Nd isotopes at the Permian/Triassic boundary: A record of climate change. *Chem. Geol. (Isotope Geoscience Sect.)* **125**, 73–99.
- Mii H.-S., Grossman, E. L., and Yancey, T. E., 1997. Stable carbon and oxygen isotope shifts in Permian seas of West Spitsbergen-global change or diagenetic artifact? *Geology* **25**, 227–230.
- Petsch S. T. (1999) Comment on “Carbon isotope ratios of Phanerozoic marine cements: Re-evaluating global carbon and sulphur systems.” [S. J. Carpenter and K. C. Lohmann (1997) *Geochimica et Cosmochimica Acta* **61**, 4831–4846], 307–310.
- Petsch S. T. and Berner R. A. (1998) Coupling the geochemical cycles of C, P, Fe, and S: The effect on atmospheric O<sub>2</sub> and the isotopic records of carbon and sulfur. *Am J Sci.* **298**, 246–262.
- Popp B. N., Anderson T. F., and Sandberg P. A. (1986) Brachiopods as indicators of original isotopic compositions in some Paleozoic limestones. *Bull. Geol. Soc. Amer.* **97**, 1262–1269.
- Scholle P. A., and Arthur M. A. (1980) Carbon isotope fluctuations in Cretaceous pelagic limestones: Potential stratigraphic and petroleum exploration tool. *Bull. Amer. Assoc. Petroleum Geol.* **64**, 67–87.
- Strauss H. (1993) The sulfur isotopic record of Precambrian sulfates: New data and a critical evaluation of the existing record. *Precambrian Research* **63**, 225–246.
- Sutton J. (1963) Long-term cycles in the evolution of continents. *Nature* **198**, 731–735.
- Veizer J., Holser W. T., and Wilgus C. K. (1980) Correlation of <sup>13</sup>C/<sup>12</sup>C and <sup>34</sup>S/<sup>32</sup>S secular variation. *Geochim. Cosmochim. Acta* **44**, 579–587.
- Von Damm K. L., Edmond J. M., Grant B., Measures C. I., Walden B., and Weiss R. F. (1985a) Chemistry of submarine hydrothermal solutions at 21°N East Pacific Rise. *Geochim. Cosmochim. Acta* **49**, 2197–2220.
- Von Damm K. L., Edmond J. M., Measures C. I., and Grant B. (1985b) Chemistry of submarine hydrothermal solutions at Guaymas Basin, Gulf of California. *Geochim. Cosmochim. Acta* **49**, 2221–2237.
- Von Damm K. L., Oosting S. E., Kozlowski R., Buttermore L. G., Colodner D. C., Edmonds H. N., Edmond J. M., and Grebmeler J. M. (1995) Evolution of the East Pacific Rise hydrothermal vent fluids following a volcanic eruption. *Nature* **375**, 47–50.
- Walker J. C. G. (1986) Global geochemical cycles of carbon, sulfur, and oxygen. *Marine Geology* **70**, 159–174.
- Walker J. C. G. and Lohmann K. C. (1989) Why the oxygen isotopic composition of seawater changes through time. *Geophysical Research Letters* **16**, 323–326.
- Yale L. B. and Carpenter S. J. (1998) Large Igneous Provinces and Giant Dike Swarms: Proxies for Supercontinent Cyclicity and Mantle Convection. *Earth and Planetary Sci. Letters* **163**, 109–122.
- Yale L. B. (1998) *Petrogenetic considerations regarding the 87Sr/86Sr ratio of seawater, super-continent cyclicity, and mid-Atlantic ridge basalts*. The University of Texas at Dallas, 136 p.
- Zhong S. and Gurnis M. (1993) Dynamic feedback between a continentlike raft and thermal convection. *J. Geophys. Res.* **98**, 12,219–12,232.