Evaluating the Relationship Between the Carbon and Sulfur Cycles in the Later Cambrian Ocean: An Example from the Port au Port Group, Western Newfoundland, Canada

Evaluating the relationship between the carbon and sulfur cycles in the later Cambrian ocean: An example from the Port au Port Group, western Newfoundland, Canada

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ABSTRACT

We present a high-resolution $\delta^{34}S$ (sulfate and pyrite) and $\delta^{13}C_{carbonate}$ record from the Middle-Upper Cambrian Port au Port Group, a mixed carbonate-siliciclastic succession exposed in western Newfoundland, Canada. The results illustrate systematic $\delta^{34}S_{sulfate}$ shifts of >15‰ over relatively short stratigraphic intervals (10 m, likely <1 m.y.), low average $\Delta^{34}S_{sulfate\text{-}pyrite}$ (ca. 23 ‰) and a generally positive coupling between changes in $\delta^{13}C_{carbonate}$ and $\delta^{34}S_{sulfate}$. Together, these results indicate that Middle to Late Cambrian sulfate concentrations were low and that the sulfate reservoir was more sensitive to change than it was in either terminal Neoproterozoic or Cenozoic oceans. However, a simple carbon (C) and sulfur (S) isotope box model of the Late Cambrian ocean illustrates that low sulfate concentrations alone fail to account for the >15‰ $\delta^{34}S_{sulfate}$ shifts recognized in Port au Port strata. Such large shifts can be generated only if fluctuating oceanic redox is invoked; marine anoxia forces reduced C/S burial and elevated $\Delta^{34}S$, driving larger $\delta^{34}S$ changes per mole of organic carbon buried. The conclusion that later Cambrian oceans featured both low sulfate levels and widespread subsurface anoxia supports hypotheses that link fluctuating marine redox conditions in the delayed recovery of skeletal animals and metazoan reefs from late Early Cambrian extinction.

Keywords: Cambrian, sulfate, anoxic, sulfur isotopes, Newfoundland, SPICE

1. Introduction

The biogeochemical cycles of carbon (C) and sulfur (S) are intimately linked through a variety of feedbacks that operate on timescales of days to millions of years. For example, under anaerobic conditions, some bacteria respire organic matter via sulfate reduction, reducing sulfate to sulfide that then reacts with iron (Fe), assuming it is available, to form pyrite. On much longer timescales, increases in organic carbon (OC) burial can drive an increase in atmospheric O_2 concentration which, in turn, facilitates an increase in the extent to which sulfides on land are oxidatively weathered and, ultimately, delivered to the oceans as riverine sulfate. These two processes impose very different relationships between the C isotope composition of dissolved inorganic carbon (DIC) and the sulfur isotope composition of sulfate in seawater. The former leads to a positive correlation between $\delta^{13}C_{carbonate}$ (assumed to reflect the $\delta^{13}C$ of DIC) and $\delta^{34}S_{sulfate}$ whereas the latter prescribes a long-term negative correlation (e.g., Veizer et al., 1980). Of course, the recognition of either a positive or negative correlation between $\delta^{13}C_{carbonate}$ and $\delta^{34}S_{sulfate}$ depends strongly on the relative residence times of seawater DIC and sulfate, neither of which is well constrained for the Cambrian Period.

In the modern ocean, the concentration of DIC is ~2 mM with a residence time of ~100 k.y. (Berner and Berner, 1996). Because of this relatively short residence time, the $\delta^{13}C$ composition of DIC is susceptible to both heterogeneity among the world's ocean basins and short-term (<1 m.y.) change. In contrast, $\delta^{34}S_{sulfate}$ is both homogenous throughout the ocean (Rees, 1978) and buffered against short-term variations due to the relatively high concentration (28 mM) and long residence time (~25 m.y.) of sulfate in the oceans (Holser et al. 1989). The large inequality in the residence times of DIC and sulfate in the recent geologic past (i.e., the Cenozoic) has made it difficult to evaluate the relationship between these two biogeochemical

cycles that play an important role in regulating Earth's climate (e.g., Kurtz et al., 2003, Paytan et al., 2004).

Recent work highlighting the $\delta^{34}S$ composition of carbonate-associated sulfate (CAS) and pyrite suggests that seawater sulfate concentrations increased near the end of the Neoproterozoic Era (Hurtgen et al., 2005; Fike et al., 2006; Halverson and Hurtgen, 2007). However, the chemical composition of fluid inclusions encased in halite (Horita et al., 2002; Lowenstein et al., 2001, 2003; Brennan et al. 2004; Petrychenko et al., 2005) and the recognition of ^{34}S-enriched CAS (Kampschulte and Strauss, 2004; Gill et al., 2007), pyrite (Strauss, 1999) and francolite-bound sulfate (Hough et al., 2006) in Lower to Middle Cambrian strata indicate that sulfate levels may have been substantially lower during this time interval relative to both the terminal Neoproterozoic and Cenozoic oceans.

Here, we present a detailed $\delta^{13}C_{carbonate}$ and $\delta^{34}S$ (sulfate and pyrite) record from the Middle-Upper Cambrian Port au Port Group, western Newfoundland, Canada. These sediments record two intervals marked by C isotope excursions, including a ~4‰ positive $\delta^{13}C_{carbonate}$ excursion that has been identified in a number of localities around the world (the SPICE event, Saltzman et al., 2004). Because of this, the Port au Port succession provides an unusual opportunity to explore the relationship between the marine geochemical cycles of C and S during a time interval when the characteristic response times of the DIC and sulfate reservoirs may have been more closely balanced than they are at present. Finally, insights gleaned from the relationship between the C and S cycles during the Cambrian Period may provide an important environmental context for biological changes during this interval, including the 40 m.y. paucity of robust skeletonized fossils in Middle Cambrian through Early Ordovician rocks (e.g., Knoll, 2003; Rowland and Shapiro, 2002; Pruss et al., in review).

2. Background

2.1 Geochemical cycles of C and S: Mass balance and isotopic considerations

The $\delta^{13}C$ and $\delta^{34}S$ composition of seawater DIC and sulfate, respectively, are dictated by the mass and isotopic compositions of C and S fluxes into and out of the ocean. For C, the primary input is riverine delivery of DIC resulting from the weathering of crustal rocks. C is removed from marine waters through photosynthesis and subsequent OC burial, as well as by carbonate precipitation and deposition. Analogous to the C cycle, the primary input of S (as sulfate) to seawater is riverine delivery resulting from the oxidative weathering of sulfides and dissolution of evaporites (principally calcium sulfates) and carbonates (e.g., CAS) on land. Sulfate is removed from the ocean via evaporite and carbonate deposition, as well as by bacterial sulfate reduction (BSR) and associated pyrite deposition.

Balanced changes in the burial of OC and pyrite have played an important role in regulating atmospheric oxygen concentrations through geologic time (Holland, 1973, 1984; Berner and Raiswell, 1983; Kump and Garrels, 1986; Berner 1987). BSR participates in, and so links, the geochemical cycles of C and S. In the presence of oxygen, OC, produced via photosynthesis in the water column, sinks and is respired aerobically. Once oxygen is consumed, either within the water column or sediments, some microbes decompose OC via BSR, reducing sulfate to sulfide that may react with available iron (Fe) to form sedimentary pyrite. Therefore, increased delivery of OC increases oxygen demand, leading to increased BSR, sulfide production and pyrite formation (Berner and Raiswell, 1983).

A kinetic isotope effect accompanies the production of both OC and sulfide during photosynthesis and BSR, respectively. The light isotope (i.e., ^{12}C and ^{32}S) is preferentially

removed from the terminal electron acceptor (i.e., CO_2 and sulfate) during the production of both OC and sulfide. Within this context, a global increase in OC production and supply to marine sediments should result in increased production of pyrite and, therefore, a positive shift in the C and S isotope compositions of the marine DIC and sulfate reservoirs, respectively. However, as noted above, the characteristic response times of DIC and sulfate strongly influence the rate and magnitude at which the isotope composition of each reservoir can shift.

Here, reservoir- and time-dependent mass balance equations for $\delta^{13}C_{carbonate}$ and $\delta^{34}S_{sulfate}$ (adopted from Kump and Arthur, 1999; Kurtz et al., 2003 and Kah et al., 2004) are used to illustrate how the individual residence times of marine DIC and sulfate influence the degree to which perturbations to the coupled geochemical cycles of C and S affect the rate and magnitude of isotopic change. The C isotope composition of carbonate deposition ($\delta^{13}C_{carbonate}$) is assumed to reflect the $\delta^{13}C$ of the DIC pool from which it precipitated and is represented by:

$$\frac{d}{dt}\delta^{13}C_{carbonate} = \frac{F_{wc}(\delta_{wc} - \delta^{13}C_{carbonate}) - F_{org}\Delta^{13}C}{M_c} \quad (1)$$

where F_{wc} is the total input flux of C to the ocean-atmosphere system from weathering, δ_{wc} is the isotope composition of that weathering component, F_{org} represents the amount of OC buried, $\Delta^{13}C$ represents the average isotope fractionation incurred during the production of OC, and M_c is the mass of dissolved carbonate in the ocean. Similarly, the S isotope composition of sulfate deposition ($\delta^{34}S_{sulfate}$) is assumed to reflect the $\delta^{34}S$ of the seawater from which it precipitated and is represented by:

$$\frac{d}{dt}\delta^{34}S_{sulfate} = \frac{F_{ws}(\delta_{ws} - \delta^{34}S_{sulfate}) - F_{py}\Delta^{34}S}{M_s} \quad (2)$$

where F_{ws} is the total input flux of S to the ocean-atmosphere system from weathering, δ_{ws} is the isotope composition of that weathering component, F_{py} is the total amount of pyrite buried and $\Delta^{34}S$ is the average net isotope fractionation between seawater sulfate and pyrite resulting from the processes (e.g., BSR, disproportionation of intermediate S species, sulfide oxidation) associated with iron sulfide formation, and M_s is the mass of sulfate in the ocean. Note, sulfate removed from the oceans via calcium sulfate precipitation in evaporite settings involves minimal isotopic fractionation (0-2.4‰; Ault and Kulp, 1959; Raab and Spiro, 1991) and is excluded from this model. However, large-scale changes in evaporite deposition might significantly influence oceanic $\delta^{34}S_{sulfate}$.

Here, we consider the response of $\delta^{13}C_{carbonate}$ and $\delta^{34}S_{sulfate}$ to a 50% increase in F_{org} and F_{py} for 1 m.y. (from 2 to 3 m.y. in Fig. 1). Initial conditions were constructed using equations (1) and (2) and mass, fluxes and isotope compositions were adopted from Kurtz et al. (2003) and approximate the Cenozoic C and S cycles at steady state (Table 1). The C and S cycles are linked using a constant C/S burial ratio of 7.7 (Berner and Raiswell, 1983; Raiswell and Berner, 1985). The 50% increase in F_{org} and F_{py} manifests as a 2.8‰ positive excursion in $\delta^{13}C$ but a negligible (0.3‰) shift in $\delta^{34}S_{sulfate}$. Of course, this is a simplified model of a more complex system, but it illustrates the importance of concentration and residence time when interpreting perturbations to the coupled C and S cycles at various times in Earth history.

3. Geologic Setting

3.1 The Port au Port Group, Newfoundland, Canada

The Middle and Upper Cambrian Port au Port Group is exposed on the south-facing shore of the Port au Port peninsula in western Newfoundland. The succession records Sauk II and

113 Sauk III transgression and was deposited autochthonously on the southeastern margin of
114 equatorial Laurentia in a subtidal-peritidal setting on a mixed carbonate-clastic platform (Chow
115 and James, 1987; Cowan and James, 1993).

116 The basal unit of the Port au Port Group, the March Point Formation (~35 m),
117 disconformably overlies siliciclastic rocks of the Lower Cambrian Hawke Bay Formation.
118 March Point lithologies comprise interbedded glauconitic and phosphatic silicilcastics, along
119 with thinly-bedded nodular limestones; they include the deepest water facies preserved in the
120 Middle and Upper Cambrian succession, with some units likely deposited below storm wave
121 base. The overlying Cape Ann Member (~15 m) of the Petit Jardin Formation contains olive-
122 colored shales as well as a few thrombolitic carbonate horizons. The overlying Campbell's
123 Member (~100 m) consists largely of oolites, microbial build-ups, and fine grained carbonate
124 lithologies. The succeeding Big Cove Member, in turn, is a 40-m-thick succession of mostly
125 olive and gray shales with thin limestone beds. The shales are replaced by oolites and microbial
126 build-ups in the overlying Felix Member (50 m). The Man O' War Member (55 m) is
127 lithologically similar to the underlying Felix Member but contains a greater proportion of
128 siliciclastic sediments. Microbial build-ups are common features throughout the March Point
129 and Petit Jardin formations but skeletal limestones are rare.

130 The March Point Formation preserves a *Bolaspidella* trilobite fauna, which indicates an
131 upper Middle Cambrian age. The SPICE event (>4‰ $\delta^{13}C_{carbonate}$ positive excursion) has
132 previously been identified in this particular section by Saltzman et al. (2004) and is
133 biostratigraphically constrained to the *Aphelaspis*, *Dunderbergia*, and *Elvinia* trilobite zones
134 (Cowan and James, 1993; Saltzman et al., 2004), which are Upper Cambrian (Steptoean) in age.
135 Absolute age dates are absent from Port au Port strata, but given these broad biostratigraphic and

chemostratigraphic constraints, the section of the Port au Port Group addressed in this study was, in all probability, deposited over 5-10 million years.

4. Methods

Carbonate-associated sulfate (CAS) and pyrite were extracted using the techniques of Burdett et al. (1989) and Canfield et al. (1986), respectively. S isotope results are reported as per mil (‰) deviations from the S isotope composition of Vienna Canon Diablo Troilite (VCDT), using the conventional delta ($\delta^{34}S$) notation; results were generally reproducible to within ± 0.2‰. C isotope ratios are expressed as ‰ deviations relative to VPDB in the standard delta ($\delta^{13}C$) notation. Average external precision is estimated to be better than 0.1‰. S and C isotope data are provided in Supplementary Tables 1 and 2, respectively.

5. Results

Carbonate C isotope values ($\delta^{13}C$) shift systematically through the section, with values ranging from ~-4 to 2‰ (Fig. 2). Here, we focus on two intervals marked by sizable C isotope excursions. The first encompasses the March Point Formation and the Cape Ann and lower Campbell's members of the Petit Jardin Formation. $\delta^{13}C$ increases from a low of ~-2.5‰ at the base of the section to an average of -0.5‰ over approximately 30 m, drops to -4‰ over the next 30 m (in the Cape Ann Member) and then rises again to an average of ~-0.5‰. $\delta^{34}S_{sulfate}$ follows a similar although more exaggerated pattern, with values starting at ~30‰, falling to 15‰ and then increasing to values >40‰ (Fig. 2). The initial drop in $\delta^{34}S_{sulfate}$ precedes the decline in $\delta^{13}C$ by ~25 m. $\delta^{34}S_{pyrite}$ generally mimics $\delta^{34}S_{sulfate}$ through this interval; values begin around

158 15‰, decline to around 0‰ (one value reaches -12‰) before increasing to >25‰. Calculated
159 $\Delta^{34}S$ ($\delta^{34}S_{sulfate}$ - $\delta^{34}S_{pyrite}$) values through this interval range from 6 to 24‰.

160 The second interval includes the upper portion of the Big Cove Member, and the Felix
161 and the Man O' War members of the Petit Jardin Formation. $\delta^{13}C$ begins at -1‰, falls steadily
162 over the next 35 m to -2‰, increases to nearly 2‰ over the next 30 m and then shifts to -3‰
163 over 25 m. This positive excursion, termed the SPICE event, has been recognized in time-
164 equivalent sections globally, although absolute values vary from location to location (e.g.,
165 Saltzman et al., 2000, 2004).

166 In the upper Big Cove Member, $\delta^{34}S_{sulfate}$ drops sharply from >40 to 27‰ with virtually
167 no change in $\delta^{13}C$. Furthermore, $\delta^{34}S_{sulfate}$ values do not shift to markedly heavier values through
168 the SPICE event, but do fall at the upper end of the C isotope excursion. The $\delta^{34}S_{pyrite}$ record is
169 sparse through this interval (limited pyrite availability) but shows values that range from 0 to
170 9‰. $\Delta^{34}S$ values begin >40‰ in the upper Big Cove Member and fall to ~20‰ in the Man O'
171 War Member.

172 While negative $\delta^{13}C_{carbonate}$ excursions in particular appear to correspond to lithologic
173 transitions in the Port au Port strata, the relationship between these two variables is not
174 systematic. For example, one negative $\delta^{13}C$ excursion is associated with relatively shallow
175 deposition within the upper Campbell's Member while another is linked with the deeper water
176 (relative to the upper Campbell's Member) facies of the Cape Ann Member.

177 The large variations in $\delta^{34}S_{sulfate}$ evident in parts of the Port au Port strata warrant
178 consideration of secondary processes that could affect the S isotope composition of CAS.
179 $\delta^{18}O_{carbonate}$ is a useful indicator of geochemical alteration as ^{18}O-depleted signatures are often
180 attributed to post-depositional alteration resulting from isotopic exchange with meteoric fluids

(e.g., Given and Lohmann, 1985). The absence of any correlation between $\delta^{34}S_{CAS}$ and $\delta^{18}O_{carbonate}$ suggests that post-depositional processes did not alter the S isotope composition of CAS substantially. Furthermore, to a first order, $\delta^{34}S_{pyrite}$ is dictated by seawater sulfate $\delta^{34}S$. Therefore, the large and sympathetic shits in $\delta^{34}S_{sulfate}$ and $\delta^{34}S_{pyrite}$ (particularly in the lower part of the section) supports the contention that $\delta^{34}S_{sulfate}$ is recording a primary seawater signal.

6. Discussion

6.1 Ediacaran and Cambrian S isotopes and marine sulfate levels

Several lines of evidence suggest that an Ediacaran increase in the oxidation state of the ocean-atmosphere system led, perhaps for the first time in Earth history, to elevated seawater sulfate concentrations. This evidence includes, but is not limited to, a shift in the abundance of redox-sensitive elements (Canfield et al., 2007; Scott et al., 2008) and a substantial rise in the S isotope difference between seawater sulfate and contemporaneously deposited sedimentary pyrite ($\Delta^{34}S$) (Canfield and Teske, 1996; Hurtgen et al., 2005; Fike et al., 2006; Halverson and Hurtgen, 2007; McFadden et al., 2008). Importantly, the extent of fractionation between seawater sulfate and co-occurring sedimentary pyrite is controlled in large part by sulfate availability. And, the amount of oxygen in the ocean atmosphere system is believed to exert a primary control on marine sulfate levels because the primary source of seawater sulfate is riverine input derived in part from the oxidative weathering of pyrite (e.g., Canfield, 2004). This increase in $\Delta^{34}S$ (and by inference an increase in Earth surface oxygen levels) is evident in Figure 3 and marked by a substantial decline in $\delta^{34}S_{pyrite}$ through the second half of the Ediacaran Period, as recorded in sediments from Oman (Fike et al. 2006). $\Delta^{34}S$ decreases at the very end of the Ediacaran period (Fike and Grotzinger, 2008) before increasing again in the earliest

Cambrian. [Note that this composite $\delta^{34}S$ (sulfate and pyrite) and $\delta^{13}C$ record does not include all available data for the terminal Neoproterozoic due to poor age constraints for some samples.]

Sulfate levels may have dropped substantially during Early to Middle Cambrian time as suggested by the chemical composition of fluid inclusions in halite (Horita et al., 2002; Lowenstein et al., 2001, 2003; Brennan et al. 2004; Petrychenko et al., 2005) and ^{34}S-enriched CAS (Kampschulte and Strauss, 2004; Gill et al., 2007), pyrite (Strauss, 1999) and francolite-bound sulfate (Hough et al., 2006) in Early to Middle Cambrian sediments. The recognition of a marked decrease in $\Delta^{34}S$ would corroborate the notion that marine sulfate levels fell at this time (see discussion below). However, as Figure 3 illustrates, it is difficult to evaluate $\Delta^{34}S$ through this interval due to a lack of previously published $\delta^{34}S_{sulfate}$ and $\delta^{34}S_{pyrite}$ generated in tandem from the same stratigraphic section.

6.2 $\delta^{34}S_{sulfate}$, $\delta^{34}S_{pyrite}$, $\Delta^{34}S$ and Middle to Late Cambrian sulfate availability

The S isotope results from this study support the fluid inclusion (Horita et al., 2002; Lowenstein et al., 2001, 2003; Brennan et al. 2004; Petrychenko et al., 2005) and previous S isotope work (Strauss, 1999; Kampschulte and Strauss, 2004; Hough et al., 2006; Gill et al., 2007) and suggest that sulfate concentrations in the Middle to Late Cambrian ocean were low relative to terminal Neoproterozoic and modern values. The large and systematic shifts in $\delta^{34}S_{sulfate}$ (>25‰) occur over relatively short geological timescales (<~2 m.y.; based on the assumption that the entire section of Port au Port Group addressed in this study was deposited over 5 to 10 million years) and are consistent with a seawater sulfate reservoir that was sensitive to relatively short-term environmental perturbations (e.g., changes in pyrite burial and/or $\Delta^{34}S$). Moreover, $\delta^{34}S_{pyrite}$ shifts in unison with $\delta^{34}S_{sulfate}$ through much of the section, but especially

through the March Point Formation and Cape Ann and Campbell's members of the Petit Jardin Formation. To a first order, $\delta^{34}S_{pyrite}$ is dictated by seawater sulfate $\delta^{34}S$ and sympathetic changes in $\delta^{34}S_{sulfate}$ and $\delta^{34}S_{pyrite}$ supports the contention that $\delta^{34}S_{sulfate}$ is changing over relatively short stratigraphic distances (at least in this particular setting).

The S isotope difference between marine sulfate and contemporaneously deposited sedimentary pyrite ($\Delta^{34}S$) provides further evidence for lower sulfate levels during this time interval. The kinetic isotope effect associated with BSR, documented through experimental studies (i.e., Detmers et al., 2001) and in natural systems (Habicht and Canfield, 1997; Habicht and Canfield, 2001), leads to a fractionation of 2-46‰. In large part, the magnitude of this fractionation is controlled by sulfate availability; larger fractionations are typically expressed under non-limiting sulfate concentrations where microbes have a large reservoir of sulfate that allows them to dissimilate ^{32}S preferentially. Smaller fractionations occur when sulfate is limiting because sulfate-reducing microbes can alter the local sulfate reservoir (water column or sediments) by extracting ^{32}S in the production of sulfide, thereby increasing the $\delta^{34}S$ composition of residual sulfate and subsequently generated pyrite. Moreover, the capacity of sulfate-reducing microbes to dissimilate ^{32}S in preference to ^{34}S decreases as sulfate concentrations fall below ~50-200 μM (Habicht et al., 2002). Therefore, the overall effect of sulfate limitation is lower $\Delta^{34}S$.

In order to achieve $\Delta^{34}S$ >46‰, BSR must be accompanied by fractionations incurred during the disproportionation of intermediate S species (e.g., S^0, $S_2O_3^{2-}$; Jørgensen, 1990) that results in sulfide depleted in ^{34}S relative to the initial reactant by an additional 7-20‰ (Canfield and Thamdrup, 1994; Cypionka et al., 1998; Habicht et al., 1998; Böttcher et al., 2001).

Through repeated sulfide oxidation and disproportionation cycles, sulfide isotope values can become depleted relative to sulfate by significantly more than 46‰.

While variable, Port au Port Group $\Delta^{34}S$ values average 23‰; all but three of the values fall between 15 and 30‰ and none exceed 46‰. This average is both lower than the assumed modern average value (35‰; Garrels and Lerman, 1984) and average values published for the latest Neoproterozoic (~35‰; Fike et al., 2006). However, <46‰ values do not necessarily indicate that S disproportionation was absent (i.e., Hurtgen et al., 2005, Johnston et al. 2005); rather, they may relate to the efficiency with which sulfide is removed by reaction with Fe^{2+}, itself a function of seawater P_{O2} (Hurtgen et al., 2005). It is important to note that the S isotope composition of sedimentary pyrite is strongly influenced by local conditions and therefore these modest $\Delta^{34}S$ values are not necessarily representative of a Middle to Late Cambrian average. However, the low $\Delta^{34}S$ values in combination with the rapid shifts in $\delta^{34}S_{sulfate}$ and $\delta^{34}S_{pyrite}$ over relatively short stratigraphic distances strongly support the notion that this particular basin contained low sulfate concentrations.

6.3 Relationship between $\delta^{13}C$, $\delta^{34}S$, and sulfate concentrations

Very generally, $\delta^{13}C$ and $\delta^{34}S_{sulfate}$ are positively correlated through the Port au Port strata, which suggests that the residence times of DIC and sulfate may have been roughly comparable, at least in this basin. These positively correlated C and S isotope shifts may have been driven by changes in OC burial and subsequent sympathetic changes in pyrite burial. However, two deviations from the positive correlation exist and suggest, not surprisingly, that the relationship between these two elemental cycles is more complex than outlined above.

The most obvious deviation occurs during the SPICE event, where the ~4‰ positive C isotope excursion that straddles the Felix and Man O' War members is not accompanied by a significant shift in $\delta^{34}S_{sulfate}$ (or $\delta^{34}S_{pyrite}$). While only five $\delta^{34}S_{sulfate}$ values were determined through the SPICE event, it is important to note that one sample is coincident with the peak of the $\delta^{13}C$ excursion. This pattern is very similar to that generated by the model we used to ascertain changes in the coupled C and S system for the Cenozoic (Fig. 1); it would seem to suggest that the residence time of sulfate in the ocean was much greater than that of DIC and perhaps not drastically different from the modern ocean. However, the rapid $\delta^{34}S_{sulfate}$ shifts that are present throughout this section (Fig. 2) are consistent with a sulfate reservoir more sensitive to isotopic modification and it is unlikely that sulfate levels would increase through the SPICE event given that the positive $\delta^{13}C$ excursion is thought to have been driven by an increase in OC burial (Saltzman et al., 2004), providing more fuel for BSR. Moreover, in a separate section of equivalent age deposited in an epicontinental sea elsewhere in Laurentia (Nevada), $\delta^{34}S_{sulfate}$ does exhibit a positive excursion (>10‰) through the SPICE interval (Gill et al., 2007) and pre-SPICE event $\delta^{13}C$ and $\delta^{34}S$ are elevated relative to Newfoundland strata. These contrasting datasets from central and southern Laurentia suggest that the ocean was heterogeneous with respect to $\delta^{34}S_{sulfate}$ (and $\delta^{13}C$) and so further supports the contention that Cambrian seawater sulfate concentrations were low relative to modern values.

If marine sulfate concentrations were substantially lower in the Cambrian, why is it that positive $\delta^{13}C$ excursions are recognized globally and $\delta^{34}S_{sulfate}$ excursions are not? One possible explanation is that the residence time of seawater sulfate through this interval was significantly lower than that of DIC, allowing for greater $\delta^{34}S_{sulfate}$ heterogeneity throughout the world oceans. If we assume the residence time of DIC approximated modern values (~100 k.y.), and S fluxes

294 into and out of the ocean were similar to Cenozoic estimates (~1.5 x 10^{18} moles/m.y.; Kurtz et
295 al., 2003), then sulfate levels must have been substantially < ~100 µM. If S fluxes into and out
296 of the ocean scaled proportionally with the marine sulfate reservoir and were lower during the
297 Cambrian, sulfate concentrations would have been even lower. Conversely, if the residence time
298 of DIC in the Cambrian ocean were higher than modern values (e.g., Berner, 2006), sulfate levels
299 could have been higher. For example, if the residence time of DIC in the Cambrian ocean was
300 500 k.y. (~5x modern levels) and S fluxes into and out of the ocean were similar to Cenozoic
301 estimates, then sulfate levels must have been < 525 µM in order for the residence time of sulfate
302 to be less than the residence time of DIC. Again, if S fluxes into and out of the ocean scaled
303 proportionally with sulfate levels and were lower, sulfate concentrations would have been
304 substantially < 525 µM. These sulfate concentrations are well below those estimated from fluid
305 inclusions encased in Cambrian halite (e.g., ~5 - 12 mM; Horita et al., 2002; Lowenstein et al.,
306 2003, Brennan et al. 2004, Petrychenko et al., 2005). However, given the number of unknowns
307 (e.g., DIC residence time, S fluxes into and out of the ocean) we cannot rule out the possibility
308 that the residence time of seawater sulfate was less than the residence time of DIC during this
309 time.

310 Alternatively, the apparent heterogeneity in $\delta^{34}S_{sulfate}$ may indicate that one or both of
311 these environments (Newfoundland and/or Nevada) were somewhat restricted and not fully
312 tracking the S isotope composition of the global ocean. If so, however, why is it that sediments
313 from both localities record the $\delta^{13}C$ excursion across the SPICE event but the $\delta^{34}S_{sulfate}$ excursion
314 is expressed only in Nevada? One explanation may be linked to carbon exchange between
315 marine surface waters and the atmosphere. Over relatively short geologic timescales (< 10^4 y.r.),
316 the $\delta^{13}C$ composition of bulk atmospheric CO_2 is governed by carbon exchange with the

terrestrial biosphere and DIC in marine surface waters (e.g., Indermühle et al. 1999). Since vascular land plants had not evolved in the Cambrian (e.g., Edwards 1979), the C isotope composition of atmospheric CO_2 would have largely been dictated by equilibrium isotope fractionations associated with air-sea gas exchange between the atmosphere and ocean (Mook, 1986). If $\delta^{13}C_{DIC}$ of marine surface waters were driven to substantially higher values for hundreds of thousands of years—as they were during the SPICE event (Saltzman et al. 2004)—the $\delta^{13}C$ composition of atmospheric CO_2 should have also increased by a corresponding, albeit offset, amount. This ^{13}C-enriched atmospheric CO_2 could then influence the surface waters of basins not well connected to the open ocean and essentially transfer the $\delta^{13}C_{carbonate}$ excursion generated in the open ocean to more restricted settings. The absolute $\delta^{13}C$ values of carbonates surrounding the SPICE event in Newfoundland and Nevada are not the same but the magnitude of the C isotope excursion is remarkably similar (~4‰). No similar mechanism is known for expressing $\delta^{34}S_{sulfate}$ excursions generated in the open ocean to more restricted settings. However, in order for the C isotope composition of DIC in an isolated basin to be buffered to the atmosphere, the amount of C residing as DIC in the restricted basin must have been substantially lower than the amount of CO_2 in the Cambrian atmosphere. Of course, neither the size of the DIC reservoir nor Cambrian pCO_2 levels is known, and therefore, it is difficult to evaluate the reasonableness of this explanation.

The second instance where C and S isotopes appear to deviate from positively correlated changes is in the March Point Formation where a 15 ‰ decrease in $\delta^{34}S_{sulfate}$ (and $\delta^{34}S_{pyrite}$) precedes a ~4‰ fall in $\delta^{13}C$ (Fig. 2). This is an intriguing result and again may indicate that sulfate levels were sufficiently low in this basin and that the characteristic response time for $\delta^{34}S_{sulfate} < \delta^{13}C_{DIC}$. In other words, a decrease in OC burial may have influenced $\delta^{34}S_{sulfate}$ more

rapidly than $\delta^{13}C$ by reducing pyrite burial rates. While time constraints are poor through this interval, the lag time between the initial $\delta^{34}S$ drop and $\delta^{13}C$ fall is represented by ~25 m of section and likely represents too much time (>10^4 y.r.) for this to be reasonable if the residence time of DIC was between 100 and 500 k.y. Alternatively, the $\delta^{34}S_{sulfate}$ decline may not have been directly and/or immediately linked to perturbations of the C cycle. For example, $\delta^{34}S_{sulfate}$ variations are typically attributed to changes in pyrite burial rates facilitated by changes in OC availability. However, in the modern ocean, pyrite burial efficiency is quite low; as much as 95% of sulfide generated during BSR is reoxidized to sulfate and intermediate S species (Jørgensen et al., 1990). Within this context, pyrite burial rates may oscillate substantially if the percentage of BSR-generated sulfide that is oxidized to sulfate and intermediate S species varies—even if global rates of BSR remain constant.

Turchyn and Schrag (2004) argued that fluctuations in the oxygen isotope composition of seawater sulfate over the last 10 m.y. can be attributed to changes in the extent and means by which sulfide has been reoxidized on continental margins. These high frequency changes in pyrite burial efficiency have had little to no effect on $\delta^{34}S_{sulfate}$ over the last 10 m.y. due to the large residence time of sulfate over this time interval (e.g., Paytan et al., 1998). However, if the Cambrian ocean had much lower sulfate concentrations, changes in the balance between sulfide production (via BSR) and reoxidation could have affected $\delta^{34}S_{sulfate}$ considerably on shorter (<1 m.y.) geological timescales. An important control on the extent of sulfide reoxidation is oxygen availability in the marine system and it has been argued that globally extensive black shale deposition in the Middle and Upper Cambrian resulted from poor ventilation of the deep oceans during a greenhouse climate (Berry and Wilde, 1978). The $\delta^{34}S$ drop that proceeds the $\delta^{13}C$ fall in the March Point Formation may have been induced by changes in pyrite burial efficiency

facilitated by subtle changes in Cambrian marine redox that influenced the S cycle before (and/or to a greater extent than) the C cycle. This discussion is expanded below. More specifically, we explore how oceanic redox might influence the C/S burial ratio and $\Delta^{34}S$ on a global scale in a way that would facilitate larger $\delta^{34}S_{sulfate}$ excursions per mole of OC burial.

6.4 Modeling insights

Here, we utilize the simple reservoir- and time-dependent mass balance equations for $\delta^{13}C$ and $\delta^{34}S_{sulfate}$ (equations 1 and 2) to understand better the relationship between sulfate residence time and $\delta^{34}S_{sulfate}$ response to perturbations to the Cambrian C cycle. More specifically, how low must sulfate concentrations have been (assuming Cenozoic inputs and outputs of S to and from the marine system) to generate the >10‰ $\delta^{34}S_{sulfate}$ shifts expressed in the Cambrian data presented in Figure 2 and yet remain consistent with the modest, but not negligible, $\Delta^{34}S$ values? In the following simulations, we assume the >10‰ $\delta^{34}S_{sulfate}$ variations were global in extent; however, as already discussed, it is possible that the Newfoundland $\delta^{34}S$ signal records local perturbations not necessarily linked to the global ocean. Nonetheless, this exercise highlights important aspects of the relationships among $\delta^{13}C$, $\delta^{34}S$, and $\Delta^{34}S$ in a low sulfate ocean.

The sensitivity of $\delta^{34}S_{sulfate}$ to a stepwise, 50% increase in F_{org} and F_{py} for 1 m.y. (during the interval 2 to 3 m.y., represented by gray band) is explored under varying initial sulfate concentrations (Fig. 4). As earlier, initial conditions were constructed using mass, flux and isotope compositions believed to represent Cenozoic C and S cycles (Kurtz et al., 2003). However, here we prescribe lower initial sulfate levels (0.28 mM, 1.9 mM and 3.5 mM) and a lower $\Delta^{34}S$ (25‰ rather than 35‰) that approximates the average recorded in Port Au Port

Group sediments and is more consistent with a low sulfate ocean. The reduced $\Delta^{34}S$ forces a lower steady state $\delta^{34}S_{sulfate}$ value (17.7‰) but more importantly it reduces the magnitude of $\delta^{34}S_{sulfate}$ excursions generated per mole of OC buried. The C and S cycles are again linked using a constant C/S burial ratio of 7.7. [Raiswell and Berner (1986) challenged constant C/S and we explore the consequences of relaxing this assumption below.] Although not shown in Figure 4, the 50% increase in F_{org} forces a 2.8‰ positive excursion in $\delta^{13}C$ as shown in Figure 1.

The model results indicate that even at very low initial sulfate concentrations (280 µM, τ = 0.27 m.y.), a 50% increase in OC and pyrite burial prompts only an ~5‰ $\delta^{34}S_{sulfate}$ excursion. In three of the four runs, $\Delta^{34}S$ was held constant at 25‰. However, in run 1a (Fig. 4), we include a stepwise decrease in $\Delta^{34}S$ from 25 to 15‰ once sulfate concentrations drop to < 200 µM (e.g., Habicht et al., 2002). This forces $\delta^{34}S_{sulfate}$ to decrease abruptly within the OC burial event and ultimately bring about an ~8‰ decline over 1 m.y. This underscores an interesting aspect of S cycling in low sulfate oceans: the sensitivity of $\Delta^{34}S$ to fluctuating ocean chemistries and its influence on the S isotope evolution of seawater sulfate.

Previous work suggests that the Middle to Upper Cambrian ocean may have been more susceptible to at least regional anoxia. Berry and Wilde (1978) argued that extensive black shale deposition in the Cambrian resulted from poor ventilation of the deep oceans due to minimal sea ice formation at high latitudes. Similarly, Saltzman (2005) suggested that extended (>10^7 y.r.) periods of relative $\delta^{13}C$ stability found in much of the Middle and Upper Cambrian resulted from nitrogen limitation in a greenhouse climate that promoted reduced O_2 solubility in marine waters and increased denitrification as result of water column anoxia. Furthermore, Raiswell and Berner (1986) found that C/S ratios in Cambrian aged marine shales were lower (~0.5) than

408 those recorded during any other period during the Phanerozoic (modern = 2.8). They attributed
409 reduced C/S to euxinic conditions.

410 If the chemocline were raised into the water column during times of enhanced OC
411 production in the Cambrian, syngenetic (water column) pyrite formation may have occurred.
412 This has important implications for evaluating the relationship between the Cambrian C and S
413 isotope record for two reasons. First, sediments deposited under euxinic conditions are
414 characterized by reduced C/S as result of syngenetic pyrite formation that is decoupled from the
415 amount of OC buried in the sediments (Leventhal, 1983; Raiswell and Berner, 1985). Under
416 these circumstances, Fe is often the limiting factor in pyrite formation rather than OC (Raiswell
417 and Berner, 1985). Second, if a significant fraction of pyrite ultimately buried in the sediments
418 formed syngenetically, $\Delta^{34}S$ values may have shifted to significantly higher values. This is
419 because sulfate-reducing bacteria have a much larger reservoir of sulfate from which to
420 dissimilate the lighter ^{32}S versus ^{34}S (e.g., Lyons, 1997; the effect is seen in mid-Proterozoic S
421 isotope data of Shen et al., 2003). Within this context, if the Cambrian ocean was susceptible to
422 periods of euxinia, C/S ratios likely decreased and $\Delta^{34}S$ may have increased (assuming sulfate
423 levels were not brought too low during the event), permitting much larger S isotope shifts in
424 seawater sulfate per mole of C buried.

425 As earlier, the sensitivity of $\delta^{34}S_{sulfate}$ to a stepwise, 50% increase in F_{org} for 1 m.y. is
426 explored under varying initial sulfate concentrations (Fig. 5). However, in order to account for
427 an increase in syngenetic pyrite formation resulting from anoxia, F_{py} increases 100% through the
428 OC burial event and $\Delta^{34}S$ increases from 25 to 30‰. As a result, larger $\delta^{34}S_{sulfate}$ excursions are
429 expressed per mole of OC buried. A ~13‰ $\delta^{34}S_{sulfate}$ increase is generated over 1 m.y. when
430 initial sulfate levels are set at 700 μM (τ = 0.67 m.y.).

Given these preliminary modeling results, it appears that > 10‰ global $\delta^{34}S_{sulfate}$ shifts may be generated by OC burial events (F_{org} increases by 50%) at sulfate levels approaching 1 mM if C/S and $\Delta^{34}S$ are allowed to fluctuate as a result of water column anoxia. Of course, this is a crude estimate that assumes we have some control on the residence time of DIC in the Cambrian as well as S fluxes into and out of the ocean—which we do not. In fact, if S fluxes into and out of the ocean were scaled proportionally with the marine sulfate reservoir and were lower in the Cambrian, the residence time of sulfate would have been higher (similar to Cenozoic values), making it more difficult to generate > 10‰ $\delta^{34}S_{sulfate}$ excursions (e.g., Fig. 1). We are not necessarily advocating a particular sulfate concentration for Late Cambrian seawater. Rather, we are suggesting that sulfate levels were low relative to modern values, that decreased residence time for S and, possibly, increased residence time for C are necessary to understand the relationships between C and S isotopes, and perhaps most importantly, basinal anoxia must be invoked in the models to reproduce the geochemical signatures preserved in the Port au Port strata. Furthermore, the interpretations developed in this study are only based on two sections in relatively shallow seas bordering Laurentia (Newfoundland and Nevada; Gill et al., 2007). Future work should focus on reconstructing the temporal and spatial evolution of $\delta^{13}C$ and $\delta^{34}S$ (sulfate and pyrite) through multiple sections of early Paleozoic strata in order to constrain the mechanistic details underpinning the geochemical evolution of the C and S cycles. Nonetheless, these two data sets, coupled with simple modeling results, do highlight some interesting dynamics relating OC burial, sulfate concentrations, ocean redox, $\Delta^{34}S$ and ultimately $\delta^{34}S_{sulfate}$.

6.5 Relationships among sulfate levels, atmospheric O_2 and Cambrian life

453 The Early Paleozoic represents one of the most dynamic times in the history of complex
454 life. Within the first 25 million years of the Cambrian Period, animals with mineralized
455 skeletons diversified and the first metazoan reefs were established. This major diversification,
456 known as the Cambrian Explosion, was disrupted by major extinctions near the end of the Early
457 Cambrian (e.g., Zhuravlev and Wood, 1996). These extinctions decimated the archaeocyathids
458 and other massively calcified reef builders and also marked the last appearances of many so-
459 called small shelly fossils (but see Porter, 2004, for discussion of taphonomic bias). For the
460 ensuing ~40 million years of the Middle to Late Cambrian and earliest Ordovician, the
461 abundance of skeletons was low in marine carbonates (Li and Droser, 1997, 1999), animal reefs
462 were absent (Rowland and Shapiro, 2002) and turnover rates were unusually high (Bambach et
463 al., 2004). What makes this interval enigmatic is that it postdates the origins of both the major
464 animal body plans and the evolution of calcified skeletons within many of them, but predates the
465 major Ordovician radiation that established skeletons as major sinks for calcium carbonate.
466 If an increase in the oxidation state of the coupled ocean-atmosphere system paved the
467 way for the evolution and radiation of macroscopic Metazoa in the Ediacaran (e.g., Knoll and
468 Carroll, 1999; Canfield et al., 2007; Fike et al., 2006), it is reasonable to ask if changes in marine
469 redox profiles during the Early to Middle Cambrian and into the Ordovician governed the demise
470 and delayed recovery of skeletonized animals (e.g., Zhuravlev and Wood, 1996; Pruss et
471 al.,2007). Several lines of evidence suggest that marine waters were more susceptible to
472 episodes of anoxia during this time, including extensive black shale deposition (Berry and Wilde,
473 1978), increased seawater temperatures and therefore lower O_2 solubility (Berry and Wilde,
474 1978; Saltzman 2005; Trotter et al., 2008), and reduced C/S in Cambro-Ordovician marine shales
475 (Raiswell and Berner, 1986). Furthermore, the C and S isotope models presented in this study

476 indicate that fluctuating water column anoxia in a low sulfate ocean generates the largest $\delta^{34}S$
477 excursions per mole of OC produced/buried consistent with the $\delta^{13}C$ and $\delta^{34}S_{sulfate}$ shifts
478 expressed in the Port au Port carbonates of Newfoundland. Collectively, these results suggest
479 that reduced oxygen levels in subsurface water masses may have played a significant role in late
480 Early Cambrian extinction and the delayed recovery of animal reefs and skeletonized animals,
481 arguably by decreasing the saturation state of surface waters with respect to carbonate minerals
482 (Fischer et al. 2007, Higgins and Schrag, 2007; see Pruss et al., 2007, for explicit discussion of
483 Cambro-Ordovician oceans). Continuing geochemical research will help to determine the
484 environmental context of major events in both Cambrian and Ordovician skeletal evolution.
485
486 **7. Conclusions**
487 A significant increase in $\Delta^{34}S$, as recorded in terminal Neoproterozoic rocks, suggests
488 that an increase in the oxidation state of the ocean-atmosphere system facilitated an increase in
489 seawater sulfate concentrations just prior to the appearance of the Ediacaran Fauna (Fike et al.,
490 2006). Sulfate levels, however, may have dropped substantially during the Early to Middle
491 Cambrian (Horita et al., 2002; Lowenstein et al., 2001, 2003; Brennan et al., 2004; Kampschulte
492 and Strauss, 2004; Petrychenko et al., 2005; Hough et al., 2006; Gill et al., 2007). S isotope
493 results presented in this study support these findings; reduced $\Delta^{34}S$, large $\delta^{34}S_{sulfate}$ shifts over
494 relatively short stratigraphic intervals, and a general positive coupling between $\delta^{13}C_{carbonate}$ and
495 $\delta^{34}S_{sulfate}$ all suggest that the Middle to Late Cambrian sulfate reservoir was more sensitive to
496 change than either terminal Neoproterozoic or Cenozoic oceans.
497 A simple C and S isotope box model illustrates that low sulfate concentrations alone fail
498 to account for the >10‰ $\delta^{34}S_{sulfate}$ shifts recognized in the Port au Port Group strata. These

larger $\delta^{34}S$ shifts can be generated if fluctuating oceanic redox is invoked, whereby marine anoxia forces reduced C/S and elevated $\Delta^{34}S$, resulting in larger $\delta^{34}S$ changes per mole of OC buried. The emerging environmental picture of the later Cambrian Earth system suggests that the delayed recovery of organisms with carbonate skeletons and animal reefs following late Early Cambrian extinction may have been due in part to fluctuating marine redox and reduced oxygen levels in the coupled ocean-atmosphere system.

Ultimately, the relationship between the geochemical cycles of C and S represent a complex set of feedbacks that operate on a variety of timescales. The Middle to Late Cambrian ocean presents an opportunity to investigate the driving forces behind C and S isotopic change in oceans unlike those we know today (i.e., through most of Earth history).

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Figure 1. The response of $\delta^{13}C_{carbonate}$ and $\delta^{34}S_{sulfate}$ to a 50% increase in organic carbon and pyrite burial for 1 m.y. As a result of increased pyrite burial, sulfate concentrations fell from 28.0 to 27.8 mM. Pre-perturbation mass and isotope compositions were adopted from Kurtz et al. (2003) and approximate the Cenozoic C and S cycles at steady-state.

Figure 2. Stratigraphic column and geochemical data for the March Point and Petit Jardin Formations of the Port au Port Group, Newfoundland, Canada.

Figure 3. Compilation of Ediacaran-Ordovician $\delta^{13}C_{carbonate}$ (Halverson et al., 2005; Derry et al., 1994; Hayes et al., 1999; Saltzman 2005) and $\delta^{34}S_{sulfate}$ (Hurtgen et al., 2002; Kampschulte and Strauss, 2004; Fike et al., 2006) and $\delta^{34}S_{pyrite}$ (Canfield and Teske, 1996; Gorjan et al., 2000; Schöder et al., 2004; Hurtgen et al., 2006; Fike et al., 2006).

Figure 4. $\delta^{34}S_{sulfate}$ response to a stepwise, 50% increase in F_{py} for 1 m.y. (from 2 to 3 m.y. and represented by gray band) under varying initial sulfate concentrations (0.28 mM, τ = 0.27 m.y.; 1.9 mM, τ = 1.80 m.y.; and 2.5 mM, τ = 3.33 m.y.).

Figure 5. $\delta^{34}S_{sulfate}$ response to a stepwise, 100% increase in F_{py} and 10‰ increase in $\Delta^{34}S$ (from 25 to 35‰) for 1 m.y. (from 2 to 3 m.y. and represented by gray band) under varying initial sulfate concentrations (0.70 mM, τ = 0.67 m.y.; 2.1 mM, τ = 2.00 m.y.; and 3.5 mM, τ = 3.33 m.y.).

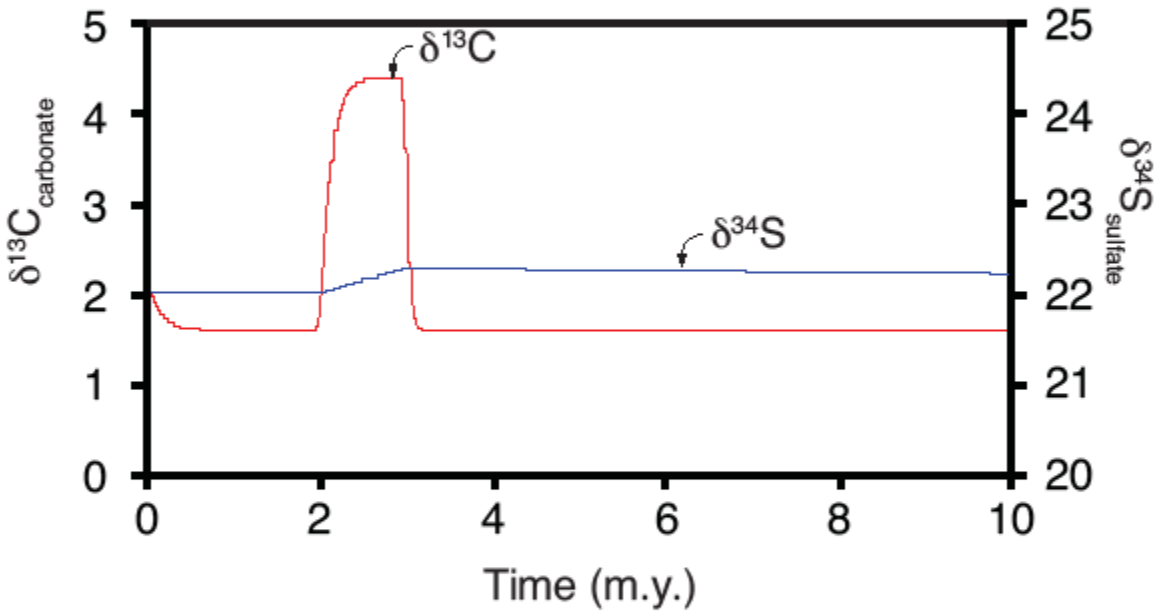

Figure 1, Hurtgen et al.

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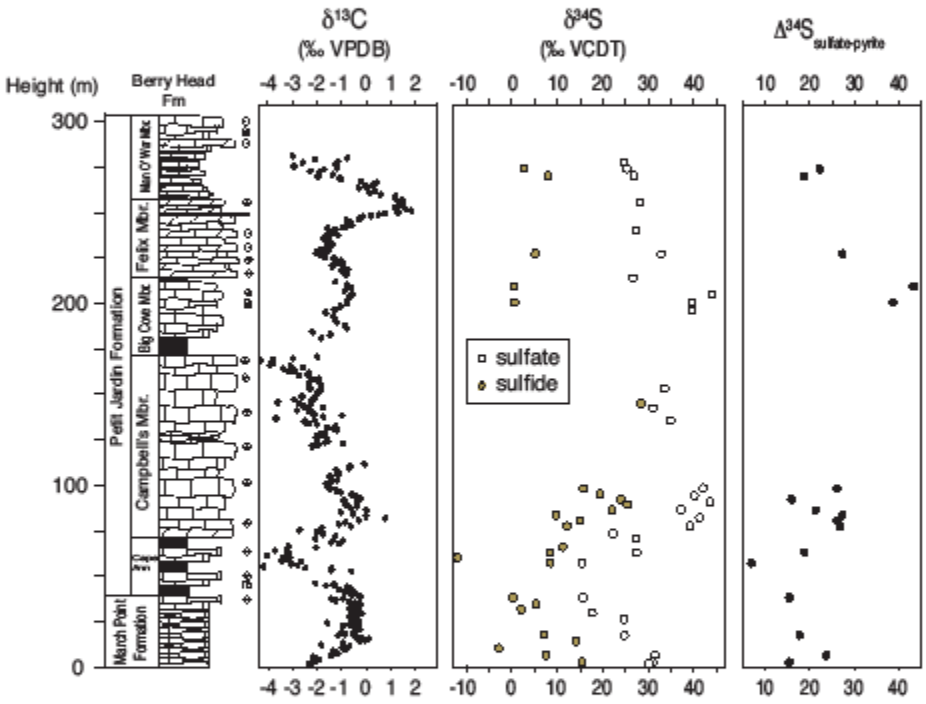

Figure 2, Hurtgen et al.

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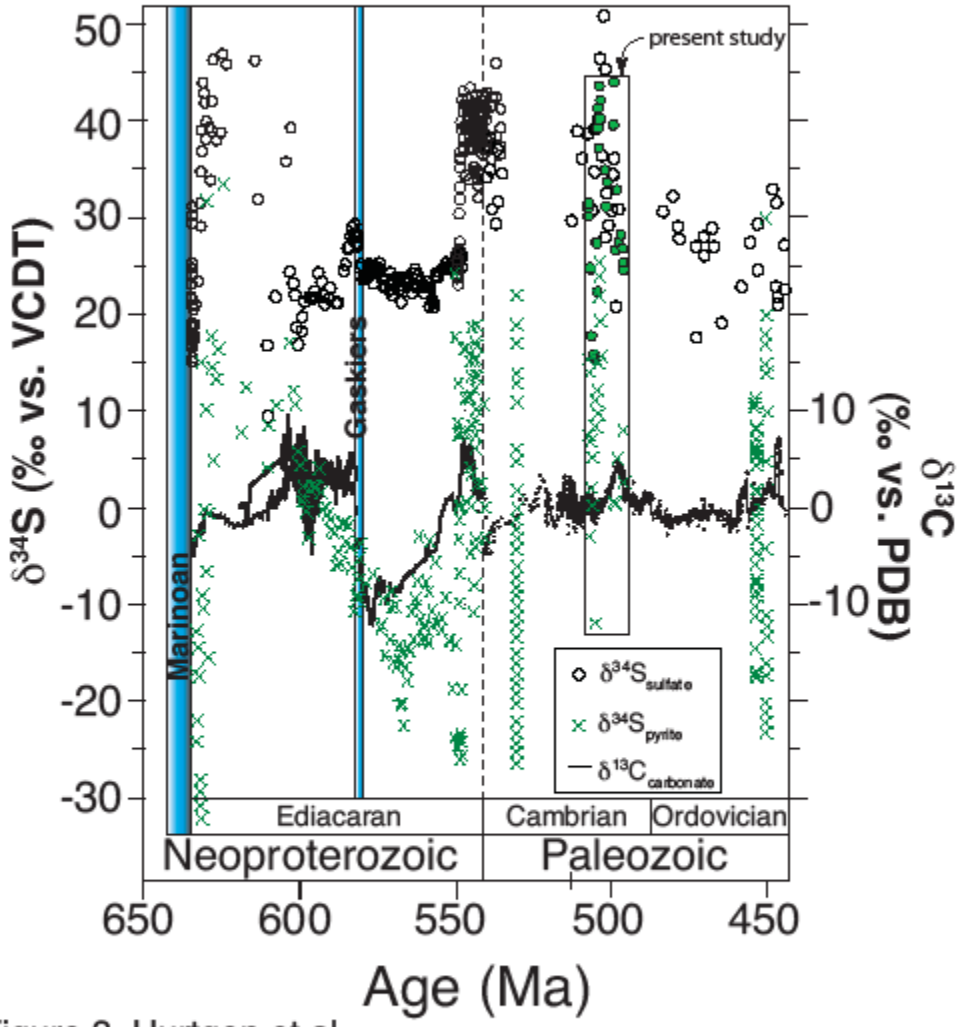

Figure 3, Hurtgen et al.

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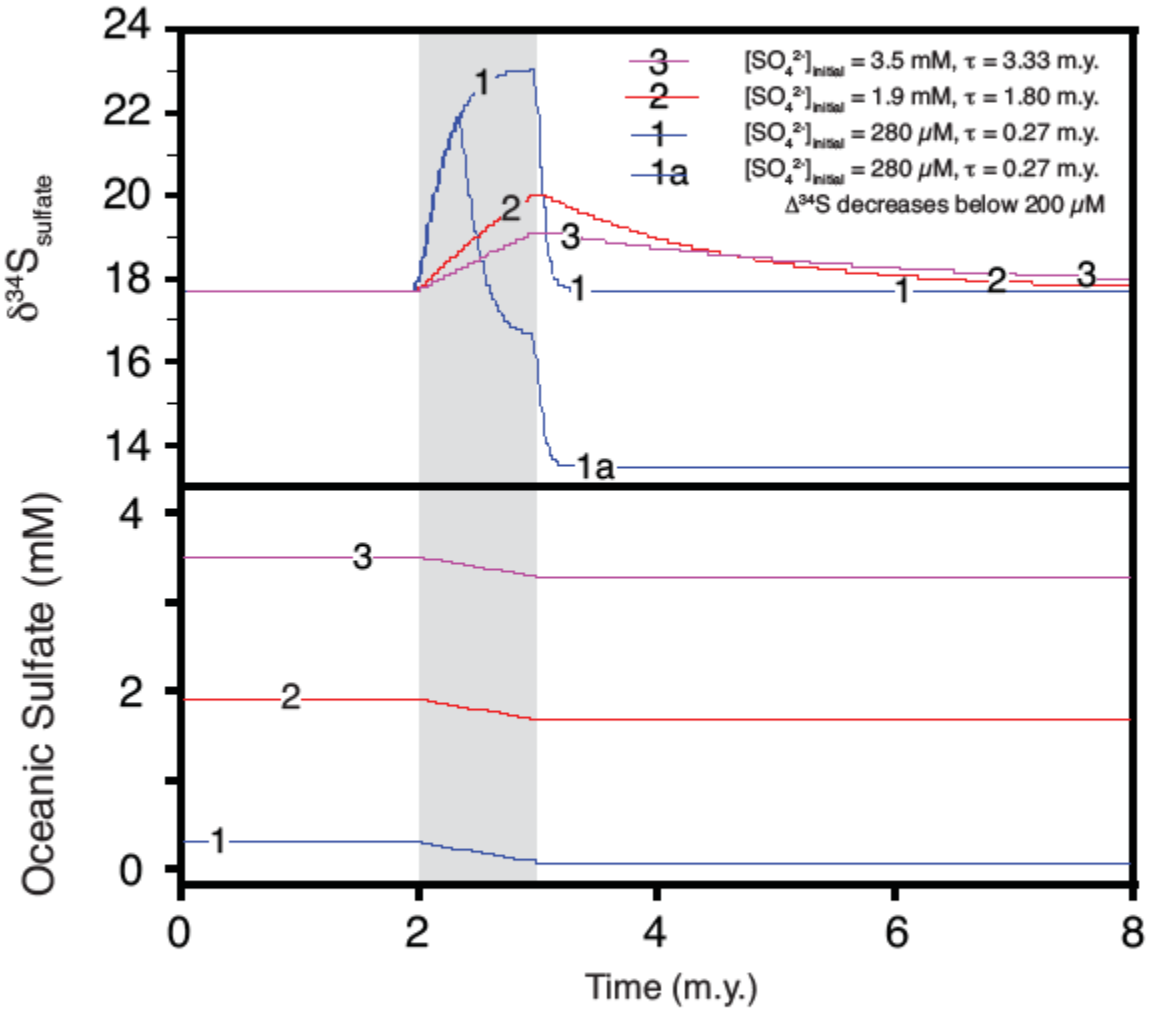

Figure 4, Hurtgen et al.

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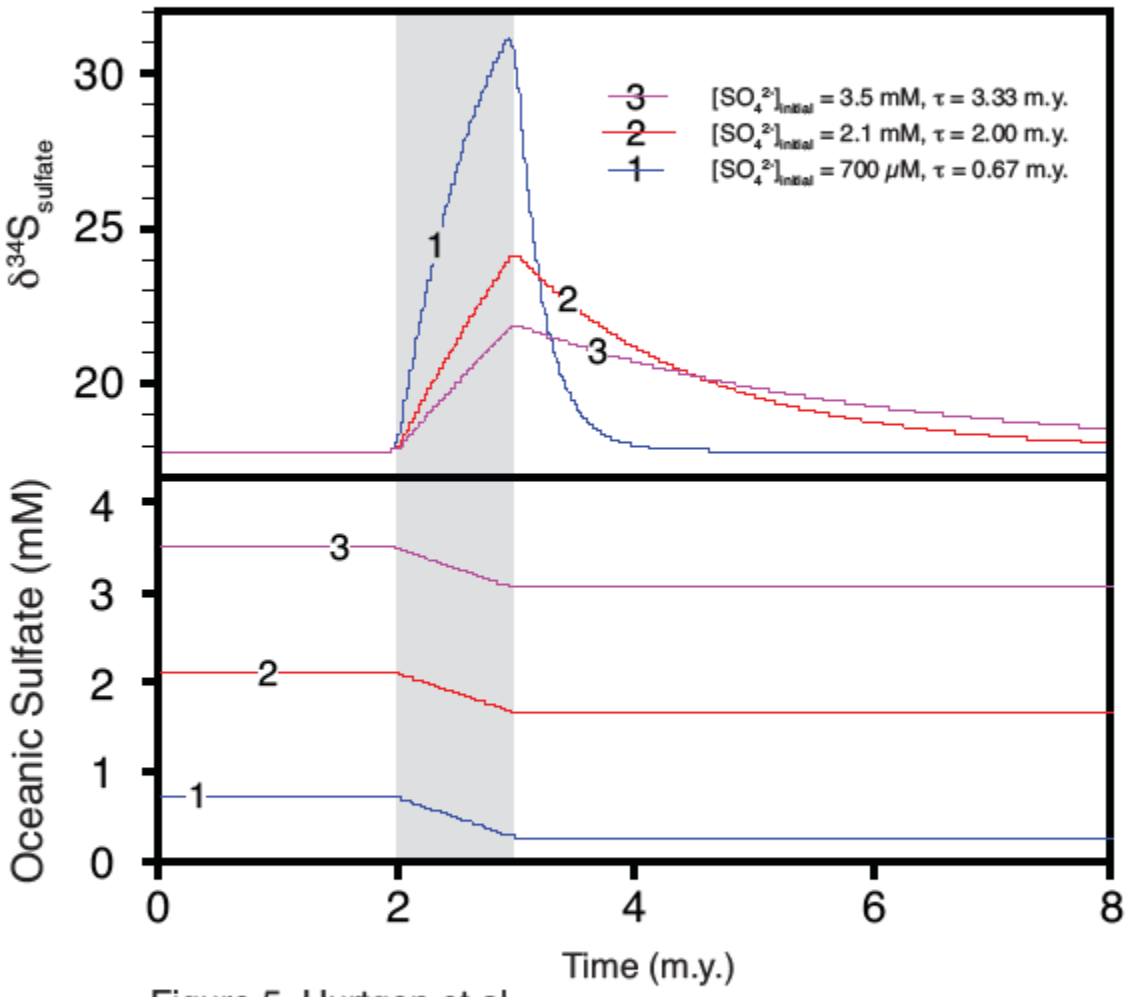

Figure 5, Hurtgen et al.

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