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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 $\delta^{34}\text{S}$ (sulfate and pyrite) and $\delta^{13}\text{C}_{\text{carbonate}}$ record from the Middle-Upper Cambrian Port au Port Group, a mixed carbonate-siliciclastic succession exposed in western Newfoundland, Canada. The results illustrate systematic $\delta^{34}\text{S}_{\text{sulfate}}$ shifts of $>15\text{‰}$ over relatively short stratigraphic intervals (10 m, likely <1 m.y.), low average $\Delta^{34}\text{S}_{\text{sulfate-pyrite}}$ (ca. 23 ‰) and a generally positive coupling between changes in $\delta^{13}\text{C}_{\text{carbonate}}$ and $\delta^{34}\text{S}_{\text{sulfate}}$. 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 $>15\text{‰}$ $\delta^{34}\text{S}_{\text{sulfate}}$ 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 $\Delta^{34}\text{S}$, driving larger $\delta^{34}\text{S}$ 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 O₂ 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 $\delta^{13}\text{C}_{\text{carbonate}}$ (assumed to reflect the $\delta^{13}\text{C}$ of DIC) and $\delta^{34}\text{S}_{\text{sulfate}}$ 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 $\delta^{13}\text{C}_{\text{carbonate}}$ and $\delta^{34}\text{S}_{\text{sulfate}}$ 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 $\delta^{13}\text{C}$ composition of DIC is susceptible to both heterogeneity among the world's ocean basins and short-term (<1 m.y.) change. In contrast, $\delta^{34}\text{S}_{\text{sulfate}}$ 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 $\delta^{34}\text{S}$ 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 $\delta^{13}\text{C}_{\text{carbonate}}$ and $\delta^{34}\text{S}$ (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 $\sim 4\text{‰}$ positive $\delta^{13}\text{C}_{\text{carbonate}}$ 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).

47

48 **2. Background**

49 *2.1 Geochemical cycles of C and S: Mass balance and isotopic considerations*

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

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

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

removed from the terminal electron acceptor (i.e., CO₂ 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 $\delta^{13}\text{C}_{\text{carbonate}}$ and $\delta^{34}\text{S}_{\text{sulfate}}$ (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 ($\delta^{13}\text{C}_{\text{carbonate}}$) is assumed to reflect the $\delta^{13}\text{C}$ of the DIC pool from which it precipitated and is represented by:

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

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, $\Delta^{13}\text{C}$ 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 ($\delta^{34}\text{S}_{\text{sulfate}}$) is assumed to reflect the $\delta^{34}\text{S}$ of the seawater from which it precipitated and is represented by:

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

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 $\Delta^{34}\text{S}$ 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 $\delta^{34}\text{S}_{\text{sulfate}}$.

Here, we consider the response of $\delta^{13}\text{C}_{\text{carbonate}}$ and $\delta^{34}\text{S}_{\text{sulfate}}$ 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 $\delta^{13}\text{C}$ but a negligible (0.3‰) shift in $\delta^{34}\text{S}_{\text{sulfate}}$. 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

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

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

The March Point Formation preserves a *Bolaspidella* trilobite fauna, which indicates an upper Middle Cambrian age. The SPICE event ($>4\text{‰ } \delta^{13}\text{C}_{\text{carbonate}}$ positive excursion) has previously been identified in this particular section by Saltzman et al. (2004) and is biostratigraphically constrained to the *Aphelaspis*, *Dunderbergia*, and *Elvinia* trilobite zones (Cowan and James, 1993; Saltzman et al., 2004), which are Upper Cambrian (Steptoean) in age. 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 ($\delta^{34}\text{S}$) notation; results were generally reproducible to within $\pm 0.2\%$. C isotope ratios are expressed as ‰ deviations relative to VPDB in the standard delta ($\delta^{13}\text{C}$) 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 ($\delta^{13}\text{C}$) 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. $\delta^{13}\text{C}$ increases from a low of $\sim -2.5\%$ 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 $\sim -0.5\%$. $\delta^{34}\text{S}_{\text{sulfate}}$ follows a similar although more exaggerated pattern, with values starting at $\sim 30\%$, falling to 15% and then increasing to values $>40\%$ (Fig. 2). The initial drop in $\delta^{34}\text{S}_{\text{sulfate}}$ precedes the decline in $\delta^{13}\text{C}$ by ~ 25 m. $\delta^{34}\text{S}_{\text{pyrite}}$ generally mimics $\delta^{34}\text{S}_{\text{sulfate}}$ through this interval; values begin around

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

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

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

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

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

(e.g., Given and Lohmann, 1985). The absence of any correlation between $\delta^{34}\text{S}_{\text{CAS}}$ and $\delta^{18}\text{O}_{\text{carbonate}}$ suggests that post-depositional processes did not alter the S isotope composition of CAS substantially. Furthermore, to a first order, $\delta^{34}\text{S}_{\text{pyrite}}$ is dictated by seawater sulfate $\delta^{34}\text{S}$. Therefore, the large and sympathetic shifts in $\delta^{34}\text{S}_{\text{sulfate}}$ and $\delta^{34}\text{S}_{\text{pyrite}}$ (particularly in the lower part of the section) supports the contention that $\delta^{34}\text{S}_{\text{sulfate}}$ 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 ($\Delta^{34}\text{S}$) (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 $\Delta^{34}\text{S}$ (and by inference an increase in Earth surface oxygen levels) is evident in Figure 3 and marked by a substantial decline in $\delta^{34}\text{S}_{\text{pyrite}}$ through the second half of the Ediacaran Period, as recorded in sediments from Oman (Fike et al. 2006). $\Delta^{34}\text{S}$ decreases at the very end of the Ediacaran period (Fike and Grotzinger, 2008) before increasing again in the earliest

Cambrian. [Note that this composite $\delta^{34}\text{S}$ (sulfate and pyrite) and $\delta^{13}\text{C}$ 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 $\Delta^{34}\text{S}$ 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 $\Delta^{34}\text{S}$ through this interval due to a lack of previously published $\delta^{34}\text{S}_{\text{sulfate}}$ and $\delta^{34}\text{S}_{\text{pyrite}}$ generated in tandem from the same stratigraphic section.

6.2 $\delta^{34}\text{S}_{\text{sulfate}}$, $\delta^{34}\text{S}_{\text{pyrite}}$, $\Delta^{34}\text{S}$ 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 $\delta^{34}\text{S}_{\text{sulfate}}$ ($>25\text{‰}$) 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 $\Delta^{34}\text{S}$). Moreover, $\delta^{34}\text{S}_{\text{pyrite}}$ shifts in unison with $\delta^{34}\text{S}_{\text{sulfate}}$ 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, $\delta^{34}\text{S}_{\text{pyrite}}$ is dictated by seawater sulfate $\delta^{34}\text{S}$ and sympathetic changes in $\delta^{34}\text{S}_{\text{sulfate}}$ and $\delta^{34}\text{S}_{\text{pyrite}}$ supports the contention that $\delta^{34}\text{S}_{\text{sulfate}}$ 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 ($\Delta^{34}\text{S}$) 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 $\delta^{34}\text{S}$ 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 $\Delta^{34}\text{S}$.

In order to achieve $\Delta^{34}\text{S} > 46\text{‰}$, BSR must be accompanied by fractionations incurred during the disproportionation of intermediate S species (e.g., S^0 , $\text{S}_2\text{O}_3^{2-}$; 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 $\Delta^{34}\text{S}$ 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_{O_2} (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 $\Delta^{34}\text{S}$ values are not necessarily representative of a Middle to Late Cambrian average. However, the low $\Delta^{34}\text{S}$ values in combination with the rapid shifts in $\delta^{34}\text{S}_{\text{sulfate}}$ and $\delta^{34}\text{S}_{\text{pyrite}}$ over relatively short stratigraphic distances strongly support the notion that this particular basin contained low sulfate concentrations.

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

Very generally, $\delta^{13}\text{C}$ and $\delta^{34}\text{S}_{\text{sulfate}}$ 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 $\delta^{34}\text{S}_{\text{sulfate}}$ (or $\delta^{34}\text{S}_{\text{pyrite}}$). While only five $\delta^{34}\text{S}_{\text{sulfate}}$ values were determined through the SPICE event, it is important to note that one sample is coincident with the peak of the $\delta^{13}\text{C}$ 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 $\delta^{34}\text{S}_{\text{sulfate}}$ 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 $\delta^{13}\text{C}$ 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), $\delta^{34}\text{S}_{\text{sulfate}}$ does exhibit a positive excursion (>10‰) through the SPICE interval (Gill et al., 2007) and pre-SPICE event $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ are elevated relative to Newfoundland strata. These contrasting datasets from central and southern Laurentia suggest that the ocean was heterogeneous with respect to $\delta^{34}\text{S}_{\text{sulfate}}$ (and $\delta^{13}\text{C}$) 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 $\delta^{13}\text{C}$ excursions are recognized globally and $\delta^{34}\text{S}_{\text{sulfate}}$ 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 $\delta^{34}\text{S}_{\text{sulfate}}$ heterogeneity throughout the world oceans. If we assume the residence time of DIC approximated modern values (~100 k.y.), and S fluxes

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

Alternatively, the apparent heterogeneity in $\delta^{34}\text{S}_{\text{sulfate}}$ may indicate that one or both of these environments (Newfoundland and/or Nevada) were somewhat restricted and not fully tracking the S isotope composition of the global ocean. If so, however, why is it that sediments from both localities record the $\delta^{13}\text{C}$ excursion across the SPICE event but the $\delta^{34}\text{S}_{\text{sulfate}}$ excursion is expressed only in Nevada? One explanation may be linked to carbon exchange between marine surface waters and the atmosphere. Over relatively short geologic timescales ($< 10^4$ y.r.), the $\delta^{13}\text{C}$ 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 CO₂ would have largely been dictated by equilibrium isotope fractionations associated with air-sea gas exchange between the atmosphere and ocean (Mook, 1986). If $\delta^{13}\text{C}_{\text{DIC}}$ 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 $\delta^{13}\text{C}$ composition of atmospheric CO₂ should have also increased by a corresponding, albeit offset, amount. This ¹³C-enriched atmospheric CO₂ could then influence the surface waters of basins not well connected to the open ocean and essentially transfer the $\delta^{13}\text{C}_{\text{carbonate}}$ excursion generated in the open ocean to more restricted settings. The absolute $\delta^{13}\text{C}$ 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 $\delta^{34}\text{S}_{\text{sulfate}}$ 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 CO₂ in the Cambrian atmosphere. Of course, neither the size of the DIC reservoir nor Cambrian *p*CO₂ 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 $\delta^{34}\text{S}_{\text{sulfate}}$ (and $\delta^{34}\text{S}_{\text{pyrite}}$) precedes a ~4‰ fall in $\delta^{13}\text{C}$ (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 $\delta^{34}\text{S}_{\text{sulfate}} < \delta^{13}\text{C}_{\text{DIC}}$. In other words, a decrease in OC burial may have influenced $\delta^{34}\text{S}_{\text{sulfate}}$ more

rapidly than $\delta^{13}\text{C}$ by reducing pyrite burial rates. While time constraints are poor through this interval, the lag time between the initial $\delta^{34}\text{S}$ drop and $\delta^{13}\text{C}$ 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 $\delta^{34}\text{S}_{\text{sulfate}}$ decline may not have been directly and/or immediately linked to perturbations of the C cycle. For example, $\delta^{34}\text{S}_{\text{sulfate}}$ 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 $\delta^{34}\text{S}_{\text{sulfate}}$ 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 $\delta^{34}\text{S}_{\text{sulfate}}$ 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 $\delta^{34}\text{S}$ drop that proceeds the $\delta^{13}\text{C}$ 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 $\Delta^{34}\text{S}$ on a global scale in a way that would facilitate larger $\delta^{34}\text{S}_{\text{sulfate}}$ excursions per mole of OC burial.

6.4 Modeling insights

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

The sensitivity of $\delta^{34}\text{S}_{\text{sulfate}}$ 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 $\Delta^{34}\text{S}$ (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 $\Delta^{34}\text{S}$ forces a lower steady state $\delta^{34}\text{S}_{\text{sulfate}}$ value (17.7‰) but more importantly it reduces the magnitude of $\delta^{34}\text{S}_{\text{sulfate}}$ 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 $\delta^{13}\text{C}$ as shown in Figure 1.

The model results indicate that even at very low initial sulfate concentrations (280 μM , $\tau = 0.27$ m.y.), a 50% increase in OC and pyrite burial prompts only an $\sim 5\text{‰}$ $\delta^{34}\text{S}_{\text{sulfate}}$ excursion. In three of the four runs, $\Delta^{34}\text{S}$ was held constant at 25‰. However, in run 1a (Fig. 4), we include a stepwise decrease in $\Delta^{34}\text{S}$ from 25 to 15‰ once sulfate concentrations drop to < 200 μM (e.g., Habicht et al., 2002). This forces $\delta^{34}\text{S}_{\text{sulfate}}$ to decrease abruptly within the OC burial event and ultimately bring about an $\sim 8\text{‰}$ decline over 1 m.y. This underscores an interesting aspect of S cycling in low sulfate oceans: the sensitivity of $\Delta^{34}\text{S}$ 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 $\delta^{13}\text{C}$ 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

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

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

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

Given these preliminary modeling results, it appears that $> 10\text{‰}$ global $\delta^{34}\text{S}_{\text{sulfate}}$ shifts may be generated by OC burial events (F_{org} increases by 50%) at sulfate levels approaching 1 mM if C/S and $\Delta^{34}\text{S}$ 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 $> 10\text{‰}$ $\delta^{34}\text{S}_{\text{sulfate}}$ 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 $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ (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, $\Delta^{34}\text{S}$ and ultimately $\delta^{34}\text{S}_{\text{sulfate}}$.

6.5 Relationships among sulfate levels, atmospheric O_2 and Cambrian life

The Early Paleozoic represents one of the most dynamic times in the history of complex life. Within the first 25 million years of the Cambrian Period, animals with mineralized skeletons diversified and the first metazoan reefs were established. This major diversification, known as the Cambrian Explosion, was disrupted by major extinctions near the end of the Early Cambrian (e.g., Zhuravlev and Wood, 1996). These extinctions decimated the archaeocyathids and other massively calcified reef builders and also marked the last appearances of many so-called small shelly fossils (but see Porter, 2004, for discussion of taphonomic bias). For the ensuing ~40 million years of the Middle to Late Cambrian and earliest Ordovician, the abundance of skeletons was low in marine carbonates (Li and Droser, 1997, 1999), animal reefs were absent (Rowland and Shapiro, 2002) and turnover rates were unusually high (Bambach et al., 2004). What makes this interval enigmatic is that it postdates the origins of both the major animal body plans and the evolution of calcified skeletons within many of them, but predates the major Ordovician radiation that established skeletons as major sinks for calcium carbonate.

If an increase in the oxidation state of the coupled ocean-atmosphere system paved the way for the evolution and radiation of macroscopic Metazoa in the Ediacaran (e.g., Knoll and Carroll, 1999; Canfield et al., 2007; Fike et al., 2006), it is reasonable to ask if changes in marine redox profiles during the Early to Middle Cambrian and into the Ordovician governed the demise and delayed recovery of skeletonized animals (e.g., Zhuravlev and Wood, 1996; Pruss et al., 2007). Several lines of evidence suggest that marine waters were more susceptible to episodes of anoxia during this time, including extensive black shale deposition (Berry and Wilde, 1978), increased seawater temperatures and therefore lower O₂ solubility (Berry and Wilde, 1978; Saltzman 2005; Trotter et al., 2008), and reduced C/S in Cambro-Ordovician marine shales (Raiswell and Berner, 1986). Furthermore, the C and S isotope models presented in this study

indicate that fluctuating water column anoxia in a low sulfate ocean generates the largest $\delta^{34}\text{S}$ excursions per mole of OC produced/buried consistent with the $\delta^{13}\text{C}$ and $\delta^{34}\text{S}_{\text{sulfate}}$ shifts expressed in the Port au Port carbonates of Newfoundland. Collectively, these results suggest that reduced oxygen levels in subsurface water masses may have played a significant role in late Early Cambrian extinction and the delayed recovery of animal reefs and skeletonized animals, arguably by decreasing the saturation state of surface waters with respect to carbonate minerals (Fischer et al. 2007, Higgins and Schrag, 2007; see Pruss et al., 2007, for explicit discussion of Cambro-Ordovician oceans). Continuing geochemical research will help to determine the environmental context of major events in both Cambrian and Ordovician skeletal evolution.

7. Conclusions

A significant increase in $\Delta^{34}\text{S}$, as recorded in terminal Neoproterozoic rocks, suggests that an increase in the oxidation state of the ocean-atmosphere system facilitated an increase in seawater sulfate concentrations just prior to the appearance of the Ediacaran Fauna (Fike et al., 2006). Sulfate levels, however, may have dropped substantially during the Early to Middle Cambrian (Horita et al., 2002; Lowenstein et al., 2001, 2003; Brennan et al., 2004; Kampschulte and Strauss, 2004; Petrychenko et al., 2005; Hough et al., 2006; Gill et al., 2007). S isotope results presented in this study support these findings; reduced $\Delta^{34}\text{S}$, large $\delta^{34}\text{S}_{\text{sulfate}}$ shifts over relatively short stratigraphic intervals, and a general positive coupling between $\delta^{13}\text{C}_{\text{carbonate}}$ and $\delta^{34}\text{S}_{\text{sulfate}}$ all suggest that the Middle to Late Cambrian sulfate reservoir was more sensitive to change than either terminal Neoproterozoic or Cenozoic oceans.

A simple C and S isotope box model illustrates that low sulfate concentrations alone fail to account for the $>10\text{‰}$ $\delta^{34}\text{S}_{\text{sulfate}}$ shifts recognized in the Port au Port Group strata. These

larger $\delta^{34}\text{S}$ shifts can be generated if fluctuating oceanic redox is invoked, whereby marine anoxia forces reduced C/S and elevated $\Delta^{34}\text{S}$, resulting in larger $\delta^{34}\text{S}$ 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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References Cited

- Ault, W.U. and Kulp, J.L., 1959. Isotopic geochemistry of sulphur. *Geochimica et Cosmochimica Acta* 16, 201-235.
- Bambach, R.K., Knoll, A.H. and Wang, S.M., 2004. Origination, extinction, and mass depletions of marine diversity. *Paleobiology* 30, 522-542.
- Berner, E.K. and Berner, R.A., 1996. *Global Environment*. Prentice Hall, Upper Saddle River, NJ, 376 pp.
- Berner, R.A., 1987. Models for carbon and sulfur cycles and atmospheric oxygen: application to Paleozoic geologic history. *American Journal of Science* 287, 177-196.
- Berner, R.A., 2006. GEOCARBSULF: A combined model for Phanerozoic atmospheric O₂ and CO₂. *Geochimica et Cosmochimica Acta* 70, 5653-5664.
- Berner, R.A. and Raiswell, R., 1983. Burial of organic carbon and pyrite sulfur in sediments over Phanerozoic time: a new theory. *Geochimica et Cosmochimica Acta* 47, 855-862.
- Berry, W.B.N. and Wilde, P., 1978. Progressive ventilation of the oceans-An explanation for the distribution of the lower Paleozoic black shales. *American Journal of Science* 278, 257-275.
- Böttcher, M.E., Thamdrup, B. and Vennemann, T.W., 2001. Oxygen and sulfur isotope fractionation during anaerobic bacterial disproportionation of elemental sulfur. *Geochimica et Cosmochimica Acta* 65, 1601-1609.
- Brennan, S.T., Lowenstein, T.K. and Horita, J., 2004. Seawater chemistry and the advent of biocalcification. *Geology* 32, 473-476.

537 Burdett, J.W., Arthur, M.A. and Richardson, M., 1989. A Neogene seawater sulfur isotope age
 538 curve from calcareous pelagic microfossils. *Earth and Planetary Science Letters* 94, 189-
 539 198.

540 Canfield, D.E., 2004. The evolution of the Earth surface sulfur reservoir. *American Journal of*
 541 *Science* 304, 839-861.

542 Canfield, D.E., Poulton, S.W. and Narbonne, G.M., 2007. Late Neoproterozoic deep-ocean
 543 oxygenation and the rise of animal life. *Science* 315, 92-95.

544 Canfield, D.E., Raiswell, R., Westrich, J.T., Reaves, C.M. and Berner, R.A., 1986. The use of
 545 chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales.
 546 *Chemical Geology* 54, 149-155.

547 Canfield, D.E. and Teske, A., 1996. Late Proterozoic rise in atmospheric oxygen concentration
 548 inferred from phylogenetic and sulphur-isotope studies. *Nature* 382, 127-132.

549 Canfield, D.E. and Thamdrup, B., 1994. The production of ^{34}S -depleted sulfide during bacterial
 550 disproportionation of elemental sulfur. *Science* 266, 1973-1975.

551 Chow, N. and James, N.P., 1987. Facies-specific, calcitic and bimineralic ooids from Middle and
 552 Upper Cambrian platform carbonates, western Newfoundland, Canada. *Journal of*
 553 *Sedimentary Petrology* 57, 907-921.

554 Cowan, C.A. and James, N.P., 1993. The interactions of sea-level change, terrigenous-sediment
 555 influx, and carbonate productivity as controls on Upper Cambrian Grand Cycles of
 556 western Newfoundland, Canada. *Geological Society of America Bulletin* 105, 1576-
 557 1590.

558 Cypionka, H., Smock, A.M. and Böttcher, M.E., 1998. A combined pathway of sulfur compound
 559 disproportionation in *Desulfovibrio desulfuricans*. *FEMS Microbiology Ecology* 166,
 560 181-186.

561 Derry, L.A., Brasier, M., Corfield, R., Rozanov, A. and Zhuravlev, A., 1994. Sr and C isotopes
 562 in Lower Cambrian carbonates from the Siberian craton: a paleoenvironmental record
 563 during the "Cambrian explosion". *Earth and Planetary Science Letters* 128, 671-681.

564 Detmers, J., Brüchert, V., Habicht, K.S. and Kuever, J., 2001. Diversity of sulfur isotope
 565 fractionations by sulfate-reducing prokaryotes. *Applied and Environmental Microbiology*
 566 67, 888-894.

567 Edwards, D., 1979. The early history of vascular plants based on Late Silurian and Early
 568 Devonian floras of the British Isles. In: A.L. Harris, C.H. Holland and B.E. Leake
 569 (Editors), *The Caledonides of the British Isles-reviewed*. Geological Society of London
 570 Special Publication, pp. 405-410.

571 Fike, D.A. and Grotzinger, J.P., 2008. A paired sulfate—pyrite $\delta^{34}\text{S}$ approach to understanding
 572 the evolution of the Ediacaran—Cambrian sulfur cycle. *Geochimica et Cosmochimica*
 573 *Acta* 72, 2636-2648.

574 Fike, D.A., Grotzinger, J.P., Pratt, L.M. and Summons, R.E., 2006. Oxidation of the Ediacaran
 575 Ocean. *Nature* 444, 744-747.

576 Fischer, W., Higgins, J. and Pruss, S., 2007. Delayed biotic recovery from the Permian-Triassic
 577 extinction may have been influenced by a redox-driven reorganization of the marine
 578 carbonate system, Geological Society of America, Abstracts with Programs, pp. 420.

579 Garrels, R.M. and Lerman, A., 1984. Coupling of sedimentary sulfur and carbon cycles-an
 580 improved model. *American Journal of Science* 284, 989-1007.

581 Gill, B.C., Lyons, T.W. and Saltzman, M.R., 2007. Parallel, high-resolution carbon and sulfur
 582 isotope records of the evolving Paleozoic marine sulfur reservoir. *Palaeogeography,*
 583 *Palaeoclimatology, Palaeoecology* 256, 156-173.

584 Given, R.K. and Lohmann, K.C., 1985. Derivation of the original isotopic composition of
 585 Permian marine cements. *Journal of Sedimentary Petrology* 55, 430-439.

586 Gorjan, P., Veevers, J.J. and Walter, M.R., 2000. Neoproterozoic sulfur-isotope variation in
 587 Australia and global implications. *Precambrian Research* 100, 151-179.

588 Habicht, K.S. and Canfield, D.E., 1997. Sulfur isotope fractionation during bacterial sulfate
 589 reduction in organic-rich sediments. *Geochimica et Cosmochimica Acta* 61, 5351-5361.

590 Habicht, K.S. and Canfield, D.E., 2001. Isotope fractionation by sulfate-reducing natural
 591 populations and the isotopic composition of sulfide in marine sediments. *Geology* 29,
 592 555-558.

593 Habicht, K.S., Canfield, D.E. and Rethmeier, J., 1998. Sulfur isotope fractionation during
 594 bacterial reduction and disproportionation of thiosulfate and sulfite. *Geochimica et*
 595 *Cosmochimica Acta* 62, 2585-2595.

596 Habicht, K.S., Gade, M., Thamdrup, B., Berg, P. and Canfield, D.E., 2002. Calibration of sulfate
 597 levels in the Archean ocean. *Science* 298, 2372-2374.

598 Halverson, G.P., Hoffman, P.F., Schrag, D.P., Maloof, A.C. and Rice, A.H., 2005. Towards a
 599 Neoproterozoic composite carbon isotope record. *Geological Society of America Bulletin*
 600 117, 1181-1207.

601 Halverson, G.P. and Hurtgen, M.T., 2007. Ediacaran growth of the marine sulfate reservoir.
 602 *Earth and Planetary Science Letters* 263, 32-44.

603 Hayes, J.M., Strauss, H. and Kaufman, A.J., 1999. The abundance of ^{13}C in marine organic
 604 matter and isotopic fractionation in the global biogeochemical cycle of carbon during the
 605 past 800 Ma. *Chemical Geology* 161, 103-125.

606 Higgins, J. and Schrag, D., 2007. CaCO_3 cycling in anoxic oceans, Geological Society of
 607 America, Abstracts with Programs, pp. 420.

608 Holland, H.D., 1973. Systematics of the isotopic composition of sulfur in the oceans during the
 609 Phanerozoic and its implications for atmospheric oxygen. *Geochimica et Cosmochimica*
 610 *Acta* 37, 2605-2616.

611 Holland, H.D., 1984. *The Chemical Evolution of the Atmosphere and Oceans*. Princeton
 612 University Press, Princeton, NJ, 582 pp.

613 Holser, W.T., Maynard, J.B. and Cruikshank, K.M., 1989. Modelling the Natural Cycle of
 614 Sulphur Through Phanerozoic Time. In: P. Brimblecombe and A.Y. Lein (Editors),
 615 Evolution of the Global Biogeochemical Sulphur Cycle. John Wiley & Sons Ltd, pp. 21-
 616 56.

617 Horita, J., Zimmermann, H. and Holland, H.D., 2002. Chemical evolution of seawater during the
 618 Phanerozoic: Implications from the record of marine evaporites. *Geochimica et*
 619 *Cosmochimica Acta* 66, 3733-3756.

620 Hough, M.L. et al., 2006. A major sulphur isotope event at c. 510 Ma: a possible anoxia-
 621 extinction-volcanism connection during the Early-Middle Cambrian transition? *Terra*
 622 *Nova* 18, 257-263.

623 Hurtgen, M.T., Arthur, M.A. and Halverson, G.P., 2005. Neoproterozoic sulfur isotopes, the
 624 evolution of microbial sulfur species, and the burial efficiency of sulfide as sedimentary
 625 pyrite. *Geology* 33, 41-44.

626 Hurtgen, M.T., Arthur, M.A., Suits, N.S. and Kaufman, A.J., 2002. The sulfur isotopic
 627 composition of Neoproterozoic seawater sulfate: Implications for a snowball Earth? *Earth*
 628 and *Planetary Science Letters* 203, 413-430.

629 Hurtgen, M.T., Halverson, G.P., Arthur, M.A. and Hoffman, P.F., 2006. Sulfur cycling in the
 630 aftermath of a 635-Ma snowball glaciation: Evidence for a syn-glacial sulfidic deep
 631 ocean. *Earth and Planetary Sciences* 245, 551-570.

632 Indermühle, A. et al., 1999. Holocene carbon-cycle dynamics based on CO₂ trapped in ice at
 633 Taylor Dome, Antarctica. *Nature* 398, 121-126.

634 Johnston, D.T. et al., 2005. Active microbial sulfur disproportionation in the Mesoproterozoic.
 635 *Science* 310, 1477-1479.

636 Jørgensen, B.B., 1990. A thiosulfate shunt in the sulfur cycle of marine sediments. *Science* 249,
 637 152-154.

638 Kah, L.C., Lyons, T.W. and Frank, T.D., 2004. Low marine sulphate and protracted oxygenation
 639 of the Proterozoic biosphere. *Nature* 431, 834-838.

640 Kampschulte, A. and Strauss, H., 2004. The sulfur isotopic evolution of Phanerozoic seawater
 641 based on the analysis of structurally substituted sulfate in carbonates. *Chemical Geology*
 642 204, 255-286.

643 Knoll, A. and Carroll, S., 1999. Early animal evolution: emerging views from comparative
 644 biology and geology. *Science* 284, 2129-2137.

645 Knoll, A.H., 2003. Biomineralization and evolutionary history. In: P.A. Dove, J.D. Yoreo and S.
 646 Weiner (Editors), *Biomineralization*. Mineralogical Society of America, Washington,
 647 DC, pp. 329-356.

648 Kump, L.R. and Arthur, M.A., 1999. Interpreting carbon-isotope excursions: carbonates and
649 organic matter. *Chemical Geology* 161, 181-198.

650 Kump, L.R. and Garrels, R.M., 1986. Modeling atmospheric O₂ in the global sedimentary redox
651 cycle. *American Journal of Science* 286, 337-360.

652 Kurtz, A.C., Kump, L.R., Arthur, M.A., Zachos, J.C. and Paytan, A., 2003. Early Cenozoic
653 decoupling of the global carbon and sulfur cycles. *Paleoceanography* 18.

654 Leventhal, J.S., 1983. An interpretation of carbon and sulfur relationships in Black Sea
655 sediments as indicators of environments of deposition. *Geochimica et Cosmochimica*
656 *Acta* 47, 133-137.

657 Li, X. and Droser, M.L., 1997. Nature and distribution of Cambrian shell concentrations:
658 Evidence from the Basin and Range Province of the Western United States (California,
659 Nevada, and Utah). *Palaaios* 12, 111-126.

660 Li, X. and Droser, M.L., 1999. Lower and Middle Ordovician shell beds from the Basin and
661 Range province of the western United States (California, Nevada, and Utah). *Palaaios* 14,
662 215-233.

663 Lowenstein, T.K., Hardie, L.A., Timofeeff, M.N. and Demicco, R.V., 2003. Secular variation in
664 seawater chemistry and the origin of calcium chloride basinal brines. *Geology* 31, 857-
665 860.

666 Lowenstein, T.K., Timofeeff, M.N., Brennan, S.T., Hardie, L.A. and Demicco, R.V., 2001.
667 Oscillations in Phanerozoic seawater chemistry: Evidence from fluid inclusions. *Science*
668 294, 1086-1088.

669 Lyons, T.W., 1997. Sulfur isotopic trends and pathways of iron sulfide formation in upper
 670 Holocene sediments of the anoxic Black Sea. *Geochimica et Cosmochimica Acta* 61,
 671 3367-3382.

672 McFadden, K.A. et al., 2008. Pulsed oxidation and biological evolution in the Ediacaran
 673 Doushantuo Formation. *Proceedings of the National Academy of Science* 105, 3197-
 674 3202.

675 Mook, W.G., 1986. ^{13}C in atmospheric CO_2 . *Netherlands Journal of Sea Research* 20, 211-223.

676 Paytan, A., Kastner, M., Campbell, D. and Thiemens, M.H., 1998. Sulfur isotopic composition of
 677 Cenozoic seawater sulfate. *Science* 282, 1459-1462.

678 Paytan, A., Kastner, M., Campbell, D. and Thiemens, M.H., 2004. Seawater sulfur isotope
 679 fluctuations in the Cretaceous. *Science* 304, 1663-1665.

680 Petrychenko, O.Y., Peryt, T.M. and Chechel, E.I., 2005. Early Cambrian seawater chemistry
 681 from fluid inclusions in halite from Siberian evaporites. *Chemical Geology* 219, 149-161.

682 Porter, S.M., 2004. Closing the phosphatization window: testing for the influence of taphonomic
 683 megabias on the pattern of small shelly fossil decline. *Palaios* 19, 178-183.

684 Pruss, S., Finnegan, S., Fischer, W. and Knoll, A., submitted. Carbonates in skeleton-poor seas:
 685 New insights from Cambrian and Ordovician strata of Laurentia. *Palaios*.

686 Raab, M. and Spiro, B., 1991. Sulfur isotopic variations during seawater evaporation with
 687 fractional crystallization. *Chemical Geology* 86, 323-333.

688 Raiswell, R. and Berner, R.A., 1985. Pyrite formation in euxinic and semi-euxinic sediments.
 689 *American Journal of Science* 285, 710-724.

690 Raiswell, R. and Berner, R.A., 1986. Pyrite and organic matter in Phanerozoic normal marine
 691 shales. *Geochimica et Cosmochimica Acta* 50, 1967-1976.

692 Rees, C.E., Jenkins, W.J. and Monster, J., 1978. The sulphur isotopic composition of ocean
693 water sulphate. *Geochimica et Cosmochimica Acta* 42, 377-381.

694 Rowland, S.M. and Shapiro, R.S., 2002. Reef patterns and environmental influences in the
695 Cambrian and earliest Ordovician. In: W. Kiessling, E. Flügel and J. Golonka (Editors),
696 *Phanerozoic Reef Patterns*, Tulsa, pp. 95-128.

697 Saltzman, M.R., 2005. Phosphorus, nitrogen, and the redox evolution of Paleozoic oceans.
698 *Geology* 33, 573-576.

699 Saltzman, M.R. et al., 2004. The Late Cambrian SPICE event and the Sauk II-Sauk III
700 regression: New evidence from Laurentian basins in Utah, Iowa and Newfoundland.
701 *Journal of Sedimentary Research* 74, 366-377.

702 Saltzman, M.R. et al., 2000. A global carbon isotope excursion (SPICE) during the Late
703 Cambrian: relation to trilobite extinctions, organic-matter burial and sea level.
704 *Palaeogeography Palaeoclimatology Palaeoecology* 162, 211-223.

705 Schröder, S., Schreiber, B.C., Amthor, J.E. and Matter, A., 2004. Stratigraphy and environmental
706 conditions of the terminal Neoproterozoic-Cambrian Period in Oman: evidence from
707 sulphur isotopes. *Journal of the Geological Society, London* 161, 489-499.

708 Scott, C. et al., 2008. Tracing the stepwise oxygenation of the Proterozoic ocean. *Nature* 452,
709 456-459.

710 Shen, Y., Knoll, A.H. and Walter, M.R., 2003. Evidence for low sulphate and anoxia in a mid-
711 Proterozoic marine basin. *Nature* 423, 632-635.

712 Strauss, H., 1999. Geological evolution from isotope proxy signals-sulfur. *Chemical Geology*
713 161, 89-101.

714 Trotter, J.A., Williams, I.S., Barnes, C.R., Lécuyer, C. and Nicoll, R.S., 2008. Did cooling
 715 oceans trigger Ordovician biodiversification? Evidence from conodont thermometry.
 716 Science 321, 550-554.

717 Turchyn, A.V. and Schrag, D.P., 2004. Oxygen isotope constraints on the sulfur cycle over the
 718 past 10 million years. Science 303, 2004-2007.

719 Veizer, J., Holser, W.T. and Wilgus, C.K., 1980. Correlation of $^{13}\text{C}/^{12}\text{C}$ and $^{34}\text{S}/^{32}\text{S}$ secular
 720 variations. Geochimica et Cosmochimica Acta 44, 579-587.

721 Zhuravlev, A. and Wood, R., 1996. Anoxia as the cause of the mid-early Cambrian (Botomian)
 722 extinction event. Geology 24, 311-314.

Figure 1. The response of $\delta^{13}\text{C}_{\text{carbonate}}$ and $\delta^{34}\text{S}_{\text{sulfate}}$ 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 $\delta^{13}\text{C}_{\text{carbonate}}$ (Halverson et al., 2005; Derry et al., 1994; Hayes et al., 1999; Saltzman 2005) and $\delta^{34}\text{S}_{\text{sulfate}}$ (Hurtgen et al., 2002; Kampschulte and Strauss, 2004; Fike et al., 2006) and $\delta^{34}\text{S}_{\text{pyrite}}$ (Canfield and Teske, 1996; Gorjan et al., 2000; Schöder et al., 2004; Hurtgen et al., 2006; Fike et al., 2006).

Figure 4. $\delta^{34}\text{S}_{\text{sulfate}}$ 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, $\tau = 0.27$ m.y.; 1.9 mM, $\tau = 1.80$ m.y.; and 2.5 mM, $\tau = 3.33$ m.y.).

Figure 5. $\delta^{34}\text{S}_{\text{sulfate}}$ response to a stepwise, 100% increase in F_{py} and 10‰ increase in $\Delta^{34}\text{S}$ (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, $\tau = 0.67$ m.y.; 2.1 mM, $\tau = 2.00$ m.y.; and 3.5 mM, $\tau = 3.33$ m.y.).

Figure 1, Hurtgen et al.

Figure 2, Hurtgen et al.

Figure 3, Hurtgen et al.

Figure 4, Hurtgen et al.

Figure 5, Hurtgen et al.