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Proterozoic Sulfur Cycle: The Rise of Oxygen

Introduction

According to Anbar & Knoll (2002), the Proterozoic ocean was in a transition stage from euxinic with oxygenated shallow water to the fully oxygenated water column of the present day. Though there is no direct proxy for the concentration of oxygen in the past, carbon and sulfur isotopes help constrain these concentrations. The carbon and sulfur cycles underwent vast transitions in the Proterozoic as the concentration of oxygen rose. There is evidence for two main episodes of oxygenation in the Proterozoic eon, one around 2400-2300 Ma and one in the Neoproterozoic. This second rise likely allowed the oxidative section of the sulfur cycle to become significant and the culmination of this oxygen rise may have led to the rapid diversification of animals in the Cambrian.

Ediacaran Carbon Cycle

Fike et al. (2006) carried out a chemostratigraphic study of Ediacaran samples from the South Oman salt basin (SOSB). They show paired (from the same rock) $\delta^{13}C_{carbonate}$ (δ_a) and $\delta^{13}C_{organic}$ (δ_o) data that are uncoupled (do not track each other with a defined separation) from about 600 Ma until around 548 Ma (Figure 1). Rothman et al. (2003) proposed that the uncoupling of δ_a and δ_o during the Neoproterozoic was due to the presence of a non-steady state carbon cycle. In the Phanerozoic, where the carbon cycle is in a steady state, dissolved inorganic carbon (DIC) is the main carbon pool in the ocean. Primary producers fixed this carbon, producing organic carbon with $\delta^{13}C$ values offset from the DIC carbon isotopic composition by a biological fractionation, ε. This yields $\delta^{13}C$ isotopic signals in the sedimentary record where δ_a and δ_o are coupled. However, in parts of the Neoproterozoic, Rothman et al. (2003) suggest that DOC was two to three orders of magnitude larger in size than in the Phanerozoic and thus was a much larger contributor to the oceanic carbon pool. This large DOC pool may have allowed for intense heterotrophy. Heterotrophs used DOC, not DIC, as their carbon and energy source and the isotopic signal of the heterotrophic biomass may have masked the coupled signal of primary producers to produce sedimentary δ_a and δ_o that are not coupled (Figure 2). Around 548 Ma, the δ_a and δ_o do couple, indicating a change to a carbon cycle in steady state where DIC was the main carbon source. The large dissolved DOC pool was depleted, allowing for a significant rise in atmospheric oxygen.

The relative sizes of the boxes in Figure 2 are drawn to scale. Today, the DIC in the ocean is ~2000 μmol/kg (Ridgwell, 2005), and the OC is ~ 100 μmol/kg (Pilson, 1998). According to Rothman et al. (2003) this means that the OC concentration of the Neoproterozoic was around 10,000 μmol/kg. There are a number of ways to calculate the DIC concentrations of the Neoproterozoic, but they all give around 8000 μmol/kg. For further information about these calculations, please see Appendix 1.

A number of biological/ ecological explanations have been proposed for this draw down of the large DOM pool via the burial of organic carbon. This could have occurred through the advent of animals with guts (Logan et al., 1995) and biomineralization which may have provided ballast for organic matter (Fike et al., 2006). Additionally, the evolution of algae with recalcitrant biopolymers would have helped keep some of the organic carbon from being quickly recycled and made it easier to bury (Rothman et al., 2003). Also, Ediacara and sponge fauna present in the ocean at this time filtered and

trapped DOC (Sperling & Peterson, 2007). Tectonic forces during this time period may have created large depocenters, enhancing the burial of organic carbon and other reductants (Brasier & Lindsay, 2001). Similarly, clays are excellent at absorbing organic carbon, and an increased flux of clays at this time would have helped bury organic carbon (Kennedy et al., 2006). In any case, the burial of this large pool of organic matter would have raised the concentration of oxygen, allowing for the oxygenation of the deep ocean around 548 Ma.
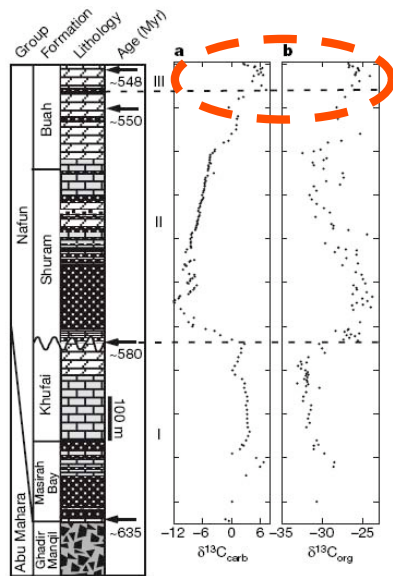

Figure 1. Data from Fike et al., 2006 showing paired δ_a and δ_o data. These two signals are not coupled until in area III, which is circled.
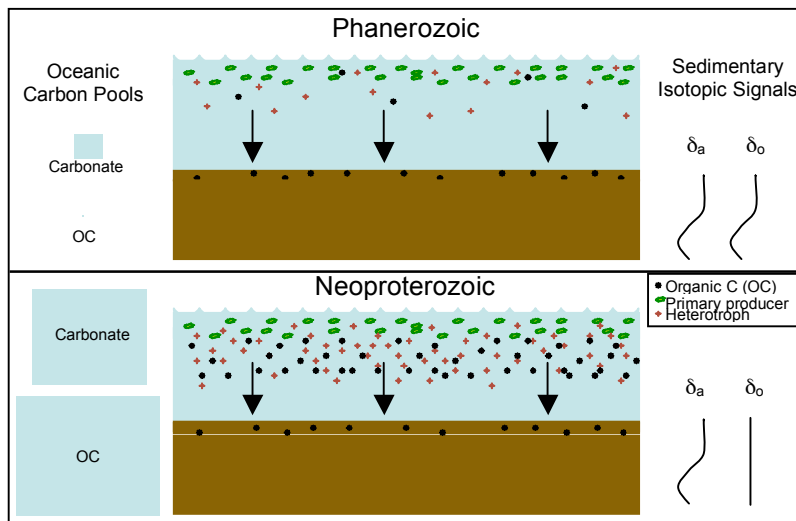

Figure 2. Figure to explain Rothman et al. (2003) hypothesis involving the changes in the size of marine carbon pools and the effect of this on the δ_a and δ_o. The DIC pool is referred to in this figure as carbonate.

Proterozoic Sulfur Cycle

Bacterial sulfate reduction (BSR) occurred throughout the Proterozoic. Of more dispute is the origin of the oxidative sulfur cycle, which includes the oxidation of hydrogen sulfide to S^0 or sulfate and bacterial sulfur disproportionation (BSD). BSD is when bacteria disproportionate S^0, or some other intermediate form of sulfur, into sulfide and sulfate (Canfield & Teske, 1996).

In 1996, Canfield and Teske proposed that the oxidative part of the sulfur cycle began between 1050 and 640 Ma. They looked at $\delta^{34}S$ in sediments and showed that though sulfate reducing bacteria can only fractionate sulfur to yield $\delta^{34}S$ sulfide values up to 46‰, marine sulfides had values up to 71‰. They suggested that the more fractionated values must have a contribution from an oxidative part of the sulfur cycle, coupled with disproportionation reactions. They provide three arguments to explain why no BSD signal (i.e. $\delta^{34}S_{sulfate} - \delta^{34}S_{sulfide} > 46$‰) was seen prior to 1050 Ma. In photosynthetic systems with low sulfide, anoxygenic photosynthetic organisms oxidize sulfide directly to sulfate, which does not allow the necessary sulfur intermediates to form. Also, when sulfide is high as it was in the oceans for much of the Proterozoic (Canfield, 1998) sulfur disproportionators are hindered because the reaction is unfavorable. Lastly, Canfield & Teske (1996) argue that the evolution of non-photosynthetic sulfide oxidizers did not occur until the late Neoproterozoic. Essentially, they argue that BSD could only occur after the Neoproterozoic rise in oxygen which lowered sulfide concentrations and allowed for the presence of sulfur intermediates. This is also when we actually see this change to larger ^{34}S fractionations due to BSD in the rock record.

There are, however, a few problems with these arguments. The first two address the inhibition of sulfur disproportionators due to lack of sulfur intermediates and high sulfide concentrations. Canfield & Teske's (1996) arguments were based on the current knowledge of γ-proteobacteria. There are also sulfate reducing δ-proterobacteria that disproportionate sulfur (Fuseler & Cypionka, 1995; Habicht et al., 1998). Also, BSD could have occured by any sulfur disproportionator in shallow water at the chemocline, where S^0 can be found. Lastly, sulfur intermediates may have formed via reactions with inorganic oxides. The oxides of both Mn(IV) and Fe(III) can oxidize H_2S. When H_2S reacts with $Fe(OH)_3$ or MnO_2, the main product is elemental sulfur (Yao & Millero, 1996). Canfield & Teske's (1996) last argument is an evolutionary one. They did not, however, consider ε-proteobacteria, which not only oxidize sulfur, but may be genealogically older than γ-proteobacteria (Sievert, 2007; Sievert et al., 2008).

In 2006, Fike et al. measured the $\delta^{34}S$ values for carbonate associated sulfate (CAS) and pyrite in several samples throughout the SOSB. They constrained the timing for BSD to be significant as after ~548 Ma, which is the age of the oldest stratum where they found $\Delta^{34}S$ ($\delta^{34}S_{CAS} - \delta^{34}S_{pyrite}$) values greater than 45‰ (Figure 3). Though Hurtgen et al. (2005) agree that $\Delta^{34}S$ did not exceed 46‰ before 580 Ma, they propose that BSD "likely occurred at least since the Early Proterozoic, and that $\Delta^{34}S$ values remained relatively low as a consequence of efficient pyrite burial in an ocean with few oxidants and a low sulfate concentration." Thode et al. (1953) also suggest that isotopic fractionation of sulfur between sulfide and sulfate began to be fully expressed 700-800 Ma and that autotrophic organisms that oxidize H_2S did not become significant before this time. More substanitively, Johnston et al. (2005) suggest that sulfur disproportionation was a significant part of the sulfur cycle by 1300 Ma. Using plots of $\Delta^{33}S$ ($\delta^{33}S - [(\delta^{34}S / 1000 + 1)^{0.515} - 1] * 1000$) vs. $\delta^{34}S$ of several sections, he developed a model of the regions in which purely BSR falls and where BSD is needed (Figure 4). Points fall into the BSD zone as early as 1300 Ma.

However, the Mesoproterozoic sections in which Johnston found BSD to occur are the Society Cliffs Fm. and the Dismal Lakes Group, which are shallow platform

environments (Horodyski & Donaldson, 1983; Cook et al., 1992; Kah & Knoll, 1996). So, Johnston shows that BSD did occur by the Mesoproterozoic, but it may not have occurred throughout the water column. Most likely, BSD was occurring on a small scale before the Mesoproterozoic and we just have not studied samples that show this fractionation or they have been buried in the intervening billion years. Fike et al.'s (2006) data is also from a shallow marine environment, so though BSD may have been occurring for some time in the Proterozoic, it may not have led to global Δ^{34}S signatures above 45‰ until the late Ediacaran.
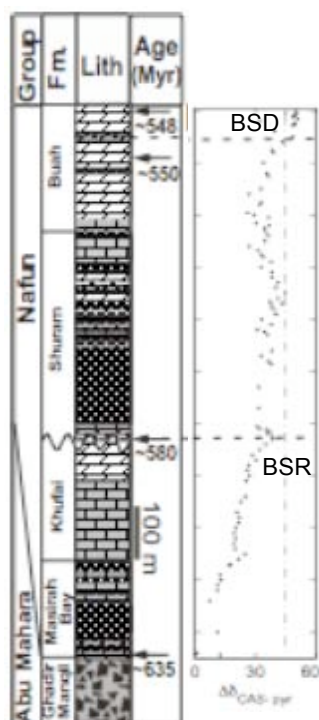

Figure 3. Data from Fike et al., 2006 showing Δ^{34}S through a stratigraphic column of Oman. The vertical dotted line is at 45‰, the maximum value for purely BSR. At the top where the isotopic signature crosses that line, BSD must contribute.

Figure 4 removed due to copyright restrictions. Citation: Johnston, D. T.; Wing, B. A.; Farquhar, J.; Kaufman, A. J.; Strauss, H.; Lyons, T. W.; Kah, L. C.; Canfield, D. E. 2005. *Science* **310**, 1477-1479.

Figure 4. Figure from Johnston et al., 2005 indicating regions of BSD occupied by samples from the Mesoproterozoic. The smaller area can be explained by BSR alone.

A complete history of these pieces of the sulfur cycle is shown on a timeline (Figure 5). The start of the BSD and BSR colored boxes indicate the latest point at which these processes could have started. Throughout the Archean, the only Δ^{34}S fractionations seen can be explained by abiological processes (blue region). This does not mean it is all volcanogenic in origin, since biological fractionation is minimal if there is less than 1

mM sulfate present (Shen et al., 2001). The global sulfate concentrations grew above 1 mM around 2.3 Ga (Canfield & Raiswell, 1999). Though evidence for BSR is present before this time in isolated areas, there is no global oceanic signature until around 2.4 Ga (Canfield, 1998; Canfield & Raiswell, 1999; Anbar & Knoll, 2002). Early in the Proterozoic, the $\Delta^{34}S$ values regularly become greater than 20‰ and the presence of BSR must be invoked (yellow region). Though Johnston et al. (2005) finds evidence of BSD by the Meoproterozoic, there is little global evidence for the values of $\Delta^{34}S$ to be consistently greater than 45‰ until the Neoproterozoic (pink region).
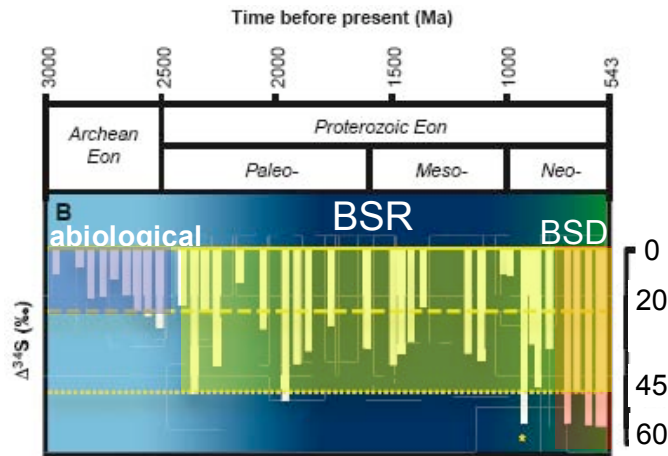

Figure 5. Figure adapted from Anbar and Knoll, 2002 showing the range in both time and values of $\Delta^{34}S$ of abiological sulfur fractionation, BSR and BSD. The start of the BSR and BSD boxes is the latest point at which that process could have begun.

Future Directions

Future work includes identifying whether or not the signal in Oman is representative of the entire world at that time. Preliminary carbon and sulfur isotopic evidence from Kathleen McFadden who is studying the Doushantuo Fm. in China shows at least one more area where a stepwise oxidation is found in the Ediacaran. More importantly, it needs to be understood whether BSD began when $\Delta^{34}S$ values become greater than 45‰ or if it could have been earlier. Most likely, the biological ability was present long before it showed up in the rock record. Johnston et al.'s more sensitive $\delta^{33}S$ data moves the observance of a BSD signal back to the Mesoproterozoic, but only for shallow formations. The next step should be to analyze Paleo- and Mesoproterozoic sections both from shallow areas and from depth using $\delta^{33}S$.

APPENDIX 1

The calculations of DIC assume that the concentration of Ca was the same in the Neoproterozoic as it is today, but this is a reasonable assumption. According to Horita et al. (2002) the Ca concentration today and in the Ediacaran is around 10 mmol/kg. Ridgwell (2005) states that the current DIC is 2000 μmol/kg and calculates the Ediacaran value to be around 8000 μmol/kg. According to Kasting (1993) the Ediacaran concentration of CO_2 was between 0.5 and 30 PAL. Hotinski et al. (2004) utilize a model (developed by Broecker & Peng, 1982) in which the DIC concentration increases as the

square root of the atmospheric levels of CO_2 increase. Using Kasting's (2003) values, this puts the Ediacaran DIC values in the range of 1-7 times that of today. The calculated value of Ridgewell (2005) fits within that range.

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