The Influence of Sulfate on Oceanic Anoxic Event 2

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Until recently, ocean chemistry was assumed to be constant over time. Recent advances in oceanography, however, have shown that there has been substantial variation in ocean chemistry throughout Earth's history (Lowenstein et al. 2003). One example of this is the presence of dissolved oxygen. In today's ocean, and throughout much of the history of life, the ocean has had an abundance of dissolved oxygen throughout the water column, with the environment not becoming anoxic until a few centimeters into the sediment. However, there have been times where these anoxic conditions extend far into the water column in what are termed oceanic anoxic events. In this research project, we aim to look at what triggered the onset of the largest oceanic anoxic event of the Cretaceous 94.5 million years ago, termed Oceanic Anoxic Event 2 or OAE2, predicting that changes in oceanic sulfate concentrations may have played a role. This is part of a larger project continuing the work of Adams et al. 2010, which analyzed samples from the Western Interior Seaway in North America. I will be analyzing samples from the Exmouth Plateau, provided by the Ocean Drilling Program, off the coast of Western Australia, while Laura Beckerman while be analyzing samples from France, in order to make sure the data we're gathering represents a worldwide event rather than simply localized pockets of anoxia or other local anomalies.

Sulfate is processed by organisms known as sulfate-reducing bacteria. Unlike organisms that use oxic respiration to process organic carbon for energy, sulfate-reducing bacteria rely on sulfate reduction for organic carbon processing. However, oxic respiration is far more efficient than sulfate reduction, and organisms that use oxic respiration will out-compete sulfate-reducers for organic carbon in any oxic environment. This confines sulfate-reducers to anoxic environments, such as in the sediments.

In low-sulfate environments, such as lakes that only have around 1 mM sulfate, there is a direct link between increasing sulfate levels and increasing levels of primary production (Adams et al. 2010). This is because of the influence of sulfate-reducing bacteria and its relationship with phosphorus. Phosphorus is an important nutrient for primary production, often a limiting nutrient, so any increased input of phosphorus to a system will result in increased primary production. Not all phosphorus in a marine environment is available to be used by primary producers, however. Phosphorus often adsorbs to iron oxides and is deposited in the sediments. It can be released for use again by sulfate-reducing bacteria, which produce H_2S through bacterial sulfate reduction (BSR). The hydrogen sulfide reacts with iron oxides to form pyrite, in the process releasing its trapped phosphorus. So in systems with initially low sulfate concentrations, a surge of sulfate into the system will drive more BSR, releasing more trapped phosphorus, and fueling more primary production (Adams et al. 2010). If the jump in primary production is large enough, it creates a large swell of organic carbon to the system, causing increases in oxic respiration to the point where these organisms use up their oxygen supply, in what is called a productivity-anoxia feedback (Adams et al. 2010; Van Cappellan et al. 1996).

This is what we hypothesize happened in the Cretaceous oceans to produce OAE2. Sulfate levels are predicted to be initially very low, around the ~1 mM observed in lakes, from evaporite deposition caused by the opening of the South Atlantic basin. Volcanism, a large contributor of sulfate to marine systems, increased dramatically 500,000 years before the event, giving us our sulfate increase (Adams et. al 2010). From these inputs to the system, we expect to

see the same sort of situation detailed above to the extent to cause a productivity-anoxia feedback.

This mechanism can also be described in terms of changes in limiting reactants. In today's oceans, where sulfate levels are near 28 mM, the limiting reactant for BSR is organic carbon that makes its way to the sediments, not sulfate (Adams et al. 2010). Likewise, organisms that use oxic respiration are not limited by dissolved oxygen in the ocean, but by organic carbon. In this Cretaceous ocean we're observing, bacterial sulfate reduction is limited by sulfate, as its concentration is severely depleted. The substantial volcanic addition of sulfate, then, causes an increase in bacterial sulfate reduction and the production of H_2S, which releases a large amount of phosphorus from iron oxides. Primary production, being limited by phosphorus, experiences a bloom because of this. If the bloom is large enough, it can transfer enough organic carbon to the organisms using oxic respiration that they are no longer limited by organic carbon, but by oxygen, and hence the productivity-anoxia feedback.

In order to test our hypothesis, we will gather $\delta^{34}S$ and $\delta^{13}C$ isotope data from sediment core samples. The core samples will be crushed and a small portion used for $\delta^{13}C$ analysis. This data will be used to date sections of the core by comparing the $\delta^{13}C$ in carbonates of our core samples to well-documented $\delta^{13}C$ data for the Cretaceous so that we can accurately tell where each of our samples fall in relation to OAE2. More of the crushed sample will be used for carbonate-associated sulfate (CAS) extraction. Sediment accumulation here primarily consists of calcium carbonate, but sometimes sulfate ions replace carbonate ions in the calcium carbonate matrix due to a matrix defect. The incorporated sulfate is referred to as carbonate-associated sulfate. The isotope composition of CAS represents the isotopic composition of the seawater at the time of sediment deposition. We use changes of $\delta^{34}S$ in CAS (large swings in $\delta^{34}S$ in short times denotes a smaller pool of sulfate), models for volcanism (which are a source of low $\delta^{34}S$ sulfate), and fractionation from sulfate-reducing bacteria (who preferentially process ^{32}S) as a method to track changing sulfate composition throughout OAE2.

The procedure for carbonate-associated sulfate extraction starts with sodium chloride and bleach rinses and vacuum filtration to clean the sample. Next, we add hydrochloric acid to break the calcium carbonate matrix and obtain sulfate in solution, while sulfur in the form of pyrite (whose isotope data can be used for different purposes) remains insoluble and is filtered out. Next, we add barium chloride to the sample, which will react with sulfate to form insoluble barium sulfate. This precipitate is filtered with .45 micron filter paper, as the particle size is small. Barium sulfate will be analyzed for sulfur isotopes through mass spectroscopy here at Northwestern in order to determine $\delta^{34}S$ for the sample.

I worked on this project for six months last year as a work-study job. This time was mostly spent preparing samples, solidifying procedures, and testing whether or not carbonate-associated sulfate existed in this sample. Our lab results from that period confirmed that carbonate-associated sulfate can be found in the segments of our sediment core, showing that these samples can be used to obtain the data we're looking for. The next steps for the project are to test for carbon isotope data in our samples and compare to known carbon isotope information for the time period in order to date the core samples relative to OAE2. We will then select several samples from important times before, during, and after the event to test the changing sulfate levels over time. Over the course of the summer, we should be able to add enough points of data at times surrounding the event to get a good sense of the trends in sulfate concentration going into, during, and coming out of OAE2 as recorded by these Exmouth plateau samples.

Appendix

Figure 1

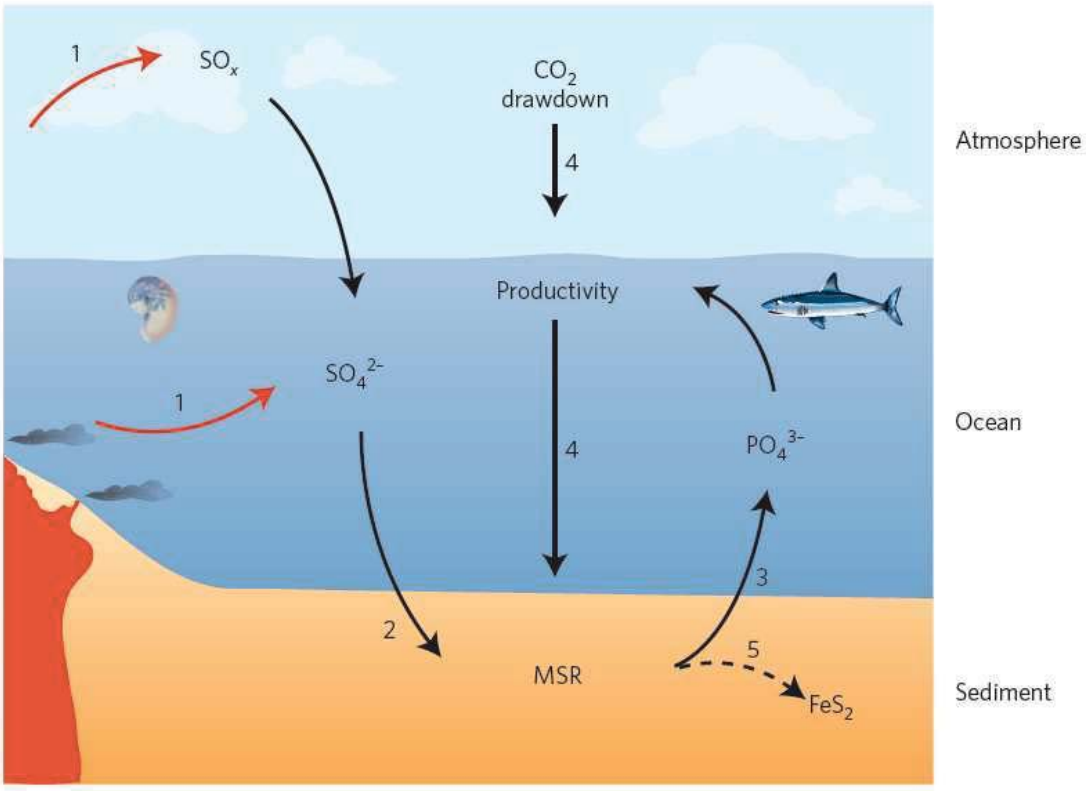

Figure 1 | The five-step evolution of Ocean Anoxic Event 2. Adams and colleagues[2] propose the following mechanism for events leading up to the Cenomanian/Turonian boundary, 93.5 million years ago. Sulphate entered the ocean through underwater volcanism or as atmospheric aerosols (1). Because pre-existing sulphate concentrations were low, the sulphate stimulated microbial sulphate reduction (MSR; 2). Concurrent degradation of organic matter released phosphate (PO_4^{3-}), making it available for primary producers (3). An increase in productivity resulted in enhanced carbon dioxide drawdown and carbon burial[10] (4). Enhanced organic matter deposition resulted in an increase in pyrite formation (FeS_2; 5), which eventually removed sufficient sulphate to halt microbial sulphate reduction and phosphorus recycling, thereby terminating Ocean Anoxic Event 2.

From Mort 2010

References

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4. Van Cappellen, P. V. & Ingall, E. D. Redox stabilization of the atmosphere and oceans by phosphorus-limited marine productivity. Science **271** , 493-496 (1996).