Determination of the Role of Sulfate in Initiating Ocean Anoxic Event 2

Understanding Earth’s geological history could shed light on our planet’s biogeochemical cycles, including today’s dramatic climate change. Earth’s current greenhouse conditions represent only one period in Earth’s history when the global carbon cycle was perturbed. Disruption of the carbon cycle also occurred during the Cretaceous Period, from 145 to 65 million years ago. During the Cretaceous, the oceans experienced several periods of significantly decreased oxygen levels, which are called oceanic anoxic events (OAEs). Ocean Anoxic Event 2 (OAE2) began approximately 94.5 million years ago and lasted about one million years. During OAE2, the carbon cycle changed as burial of organic carbon in sediment and volcanic out-gassing of carbon dioxide significantly increased. The carbon cycle is linked to the oxygen cycle through photosynthesis. Therefore, a change in the carbon cycle will affect the oxygen cycle, but the exact mechanism by which the carbon cycle was disrupted is unknown. Previous research has shown that the global sulfur cycle changed significantly during OAE2, which opens the possibility that sulfate affected the carbon cycle and induced the decrease in oxygen during OAE2 [6]. This possibility is under investigation in Professor Matthew Hurtgen’s laboratory. My research project will attempt to determine if sulfate directly caused ocean anoxia in OAE2 by analyzing samples from southeastern France, with the larger goal of elucidating the role of sulfate in carbon and oxygen cycles, including today’s altered carbon cycle. Alexander Kegley, another student in Dr. Hurtgen’s lab, plans to analyze samples from western Australia to help determine if sulfate caused ocean anoxia in OAE2. Taken together, the independent efforts of Alexander Kegley and myself will provide a global perspective of the role of sulfate in OAE2.

Evidence of past biogeochemical cycles can be extracted from ancient ocean chemistry. Because the oceans are normally chemically well mixed due to their immense size, changes in ocean chemistry reflect significant changes in global biogeochemical processes [2]. Therefore studying past OAEs provides important clues to past global carbon and sulfur cycles [6]. Analyzing samples from varied locations will strengthen our understanding of these global biogeochemical cycles. In my project, I will be using samples collected from a region in southeastern France that was below sea level during OAE2. The geological layering of these rocks and the presence of minute fossils have been well characterized and will aid me in creating a timeline for the biogeochemical events during OAE2 [5].

Both geological and biological processes regulate the carbon cycle. One crucial biological process is the production of organic carbon from carbon dioxide and water in photosynthesis, which at its most basic is described by the equation: $6\text{CO}_2 + 6\text{H}_2\text{O} (+ \text{light energy}) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$. This reaction occurs on the ocean surface [Figure 1, step (1)]. The products sink into the ocean, where they are consumed [Figure 1, (2)]. Microbial consumption of organic carbon leads to microbial sulfate reduction, in which microbes breathe in oxygen and break down sulfate into hydrogen sulfide, which then reacts with iron oxides to form pyrite [Figure 1, (3) and (4)]. The formation of pyrite removes iron oxides from the ocean so that phosphorous in the ocean cannot react with iron oxides. [Figure 2, Figure 1, (5)]. This enables phosphorous, a vital nutrient for photosynthesis, to be recycled more efficiently in the ocean and drive photosynthesis [Figure 1, (6)]. An increased concentration of free phosphorous produces an increase in the rate of photosynthesis, which causes this entire cycle to proceed at a greater rate and produce a greater concentration of products. As the cycle repeats, the increased microbial respiration of oxygen exceeds the supply of oxygen and drives ocean anoxia.

Biogeochemical cycles, such as the cycle described above, can be analyzed through isotopes. Isotopes are atoms of the same element with different atomic masses. The natural geological and biological separation of isotopes based on their atomic masses can be determined with an isotope ratio mass spectrometer (IRMS), which uses a magnet to separate the isotope with a heavier mass from the lighter isotope. The ratio of the isotopic masses in a sample is highly indicative of the process responsible for the formation of the sample. For example, enrichment in lighter sulfur is indicative of volcanic outgassing of sulfur because the lighter isotope can escape from a volcano more quickly than can the heavier isotope. The plot of sulfur isotope ratios over time that I will construct will elucidate the mechanisms by which sulfate was formed, which will be indicative of the role of sulfate in OAE2.

My research project will build on previous investigation into the connection between sulfate, oxygen, and carbon in OAE2. In 2004, Paytan et al. reported significant changes in sulfur isotopes in seawater during the Cretaceous and suggested that the changes in sulfate isotopic compositions could affect atmospheric
oxygen [6]. Wortmann and Chernyavsky (2007) investigated the inverse relationship between sulfur and carbon burial in the early Cretaceous in an effort to elucidate the connection between carbon and sulfur cycles in the Cretaceous [7]. Based on these results, the Hurtgen lab hypothesizes a connection between carbon, sulfur, and oxygen. In 2010, Derek Adams, a former graduate student in Prof. Hurtgen’s lab, characterized the sulfate isotope curve for samples obtained from the Western Interior Seaway, a region in North America covered with seawater during OAE2 [1, Figure 3]. I will build on these results by analyzing the heavy and light sulfur isotope ratios in samples collected from France to determine the origin of sulfur and its role in OAE2. I predict that sulfate, through its effect on nutrient cycling, directly caused global ocean anoxia during the Cretaceous.

The methods that I will use for my project are based on those outlined by Gill et al. (2011) and Burdett et al. (1989) [2, 4]. In the formation of the rocks at Pont d’Issole, a rock deposition in southeastern France, a small amount of sulfate replaced carbonate in the structure and became trapped within the rocks. To isolate this sulfate, samples must first be crushed into a fine powder, which I have already completed in preparation for my project. The next step is to remove any sulfate not associated with carbonate through a series of washes with sodium chloride, deionized water, and bleach. Then I will dissolve the carbonate in acid to release trapped carbon-associated sulfate into solution. I will then add barium chloride, a source of barium ions. Barium ions are highly reactive with sulfate; therefore the two will precipitate as barium sulfate. I will isolate the barium sulfate precipitate from the solution and determine the isotopic composition of the sulfate using IRMS. I will plot my results to form a sulfate isotope curve, such as the one produced by Adams et al. [Figure 3.]

Each of the six washes for a sample requires 24 to 48 hours to complete, and sulfate extraction and analysis of a sample takes an additional day. I expect to analyze the sulfate fractionation of approximately 60 samples during the eight-week period, which will be enough samples to construct an accurate model of the sulfate cycle in France during OAE2. Comparison of the sulfate isotope curve to the oxygen isotope curve will provide a basis for determining whether sulfate directly caused ocean anoxia. Furthermore, comparison of the sulfate isotope curve that I obtain for samples from Pont d’Issole to that produced by Alexander Kegley for samples from western Australia will strengthen evidence for or against the role of sulfate in OAE2. Our analyses, when combined with that of Adams et al. for samples from North America, will provide a global picture of the role of sulfate in OAE2.

My strong academic background and past research experience have prepared me to undertake this project. I have taken the General Chemistry, Organic Chemistry, and General Biology sequences and will have completed the General Earth and Planetary Sciences and General Physics sequences by this summer. I have taken Biological Sciences (Bio) 315: Cell Biology and Earth and Planetary Sciences (Earth) 340: Paleobiology and am currently taking Earth 300: Earth and Planetary Materials and Bio 309: Principles of Biochemistry, both of which directly apply to my research project. Last summer, I conducted independent research at NASA Goddard Space Flight Center as an undergraduate research associate of Dr. Jennifer Stern. I analyzed carbon isotopes in Mars analog materials and presented my research on two sites analogous to two craters on Mars for scientists of the NASA Astrobiology Institute. My research experience at NASA taught me many of the skills and methods needed for this research project, such as acidification of samples for carbonate analysis. In Fall 2011, I received additional Northwestern laboratory training, which including training in techniques needed for this project such as cutting, crushing, and powdering rock samples and the procedure for sulfate extraction. During Winter 2012, I drilled the samples from Pont d’Issole to obtain and analyze the carbonate and to construct a timeline for the biogeochemical events within OAE2. After drilling the samples for carbonate analysis, I also prepared samples for sulfate analysis by crushing the remaining material of each sample into fine powder.

I plan to continue conducting research in Dr. Hurtgen’s laboratory through my senior year and to write a senior honors thesis on my work, including my research this summer. Following graduation from Northwestern University, I intend to earn my doctorate in geological science with a focus in astrobiology. This summer research project will prepare me for research at a graduate level, and I will use the skills developed this summer throughout my career as a research scientist. Furthermore, my project will help elucidate the role of sulfur in OAE2 and could have profound implications on our understanding of Earth’s geological history and Earth’s current climate change.
Figure 1: Photosynthesis occurs on the ocean surface (1). The products sink into the ocean, where they are consumed (2). The hydrogen sulfide reacts with iron oxides to form pyrite and therefore prevents free phosphorous from reacting with iron oxides. An important nutrient for photosynthesis, free phosphorous drives photosynthesis and the cycle repeats. Microbial consumption of organic carbon leads to microbial sulfate reduction (3), in which microbes breathe in oxygen and break down sulfate into hydrogen sulfide, which then reacts with iron oxides to form pyrite (4). The formation of pyrite removes iron oxides from the ocean so that phosphorous in the ocean cannot react with iron oxides. (5). This enables phosphorous, a vital nutrient for photosynthesis, to be recycled more efficiently in the ocean and drive photosynthesis (6). An increased concentration of free phosphorous produces an increase in the rate of photosynthesis, which causes this entire cycle to proceed at a greater rate and results in a greater concentration of products. As the cycle repeats, the increased microbial consumption of oxygen drives ocean anoxia.
Figure 2: An increase in sulfate reduction is correlated with an increase in phosphorous concentrations and to a decrease in iron concentrations in the deep ocean. An increase in phosphorous produces an increase in photosynthesis and in the rates of the cycle described above. Adapted from Caraco et al. (1993).

Figure 3: Adams et al. (2010) constructed a sulfate isotope curve for samples from the Western Interior Basin. On the y-axis (not shown), time increases from 94.99 to 93.19 million years ago. OAE2 is shaded in gray. On the x-axis, sulfate isotopic composition is plotted relative to a standard (VCDT). I will construct similar isotope curves for samples. Adapted from Adams et al. (2010).
References


