Geochemical evidence for variable redox conditions in the late Cretaceous Western Interior Seaway

Senior Thesis for Earth and Planetary Science

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Abstract

The Late Cretaceous was a period of large changes in climate in response to extreme perturbations of biogeochemical cycles. The most extreme of these perturbations culminated at Ocean Anoxic Event 2, a period of reduced oxygenation in oceans globally. Ocean Anoxic Event 2, which occurred 94 million years ago at the transition from the Cenomanian to the Turonian, is characterized by a positive excursion of both organic and inorganic carbon isotopes. This excursion is recorded in cores and outcrops around the world, indicating a global driver of the ocean anoxic event. While the occurrence of OAE2 is well documented, the biogeochemical mechanism triggering the event remains debated. This study measured carbon and sulfur isotope ratios from an outcrop in Bunker Hill, Kansas, on the eastern margin of the former Western Interior Seaway (WIS), a shallow sea stretching through western North America. The Bunker Hill organic carbon and carbon associated sulfur record are consistent with WIS and global trends of increased ocean productivity and subsequent ocean anoxia. However, $\delta^{34}$S$_{pyrite}$ records a locally distinct signal. The geographic conditions, stratigraphy and relatively enriched $\delta^{34}$S$_{pyrite}$ values suggest that the eastern margin experienced locally more intense periods of anoxia than the western margin. The pre-OAE2 organic carbon and sulfur isotope data do not refute enhanced volcanism as a driver of OAE2, but suggest that volcanic intensity may be less than previously thought. The study of the drivers and effects of perturbations to the Cretaceous carbon and sulfur cycles are relevant to understanding implications of modern day climactic responses to anthropogenic elemental perturbations.
Introduction

Climate change is one of the most significant geoscientific issues of the current century, affecting people, animals, and the environment. If human activity continues to be a high source of carbon dioxide to the atmosphere and pCO₂ passes 1000 ppmv, the climate in the next century may resemble the Cretaceous climate (Hay and Floegel, 2012). The ‘hothouse’ condition in the late Cretaceous may have helped trigger the extreme biogeochemical perturbation called Ocean Anoxic Event 2 (Kidder and Worsley, 2010). Examining the response of major reservoirs like the ocean and atmosphere to past perturbations of elemental cycles can help scientists to predict the timescale and magnitude of changes to expect due to modern, anthropogenic perturbations.

Background

Cretaceous Ocean Anoxic Events

Multiple events have been recorded in Earth’s geologic history during which there was below normal oxygen in oceans worldwide, resulting in large scale burial of organic carbon. These events are called ocean anoxic events, or OAEs, and occurred during the Cretaceous period (approximately 145-65 Ma) (Sageman, 2009). It is widely accepted that a surge in volcanism released relatively large amounts of sulfate into Cretaceous oceans, which subsequently increased phosphorus recycling (Adams et al., 2010). The increase in nutrients enhanced primary production, and the raised level of respiration initiated the Ocean Anoxic Event at the boundary of the Cenomanian and Turonian periods, also known as OAE 2 (Adams et al., 2010). The occurrence of OAE2 was dependent on a number of different factors interacting simultaneously, including carbon burial due to increased primary
production, as well as changing concentrations of atmospheric pCO$_2$ (Kump and Arthur, 1999).

Because primary production preferentially concentrates lighter carbon isotopes ($^{12}$C), the increase in production and the subsequent burial of organic material that has an increased proportion of $^{12}$C results in a positive $\delta^{13}$C excursion during Ocean Anoxic Events (Arthur et al., 1987). These widespread events are also characteristically short, likely due to some form of negative feedback loop. A negative feedback loop could include the high primary production causing a pCO$_2$ drawdown due to massive carbon burial. A decreased pCO$_2$ would lead to climactic cooling, thus decreasing terrestrial nutrient flux and lowering primary production.

Lithologically, OAEs are characterized by laminated black shales due to the high concentration of organic carbon in unperturbed sediment (Sageman, 2009). However, the lithology is not a direct representation of geologic events, and the chemical composition of the rock (a positive $\delta^{13}$C excursion) is a more reliable indicator of global ocean anoxia.

The Western Interior Seaway

This study focuses on the occurrence of OAE 2 within the Western Interior seaway. The Western Interior seaway (WIS) was a shallow inland sea in North America that connected the Arctic region to the area that is now the Gulf of Mexico, and from western Colorado to eastern Kansas during the Late Cretaceous Period (from before the Albian Age to the Maastrichtian Age) (Singerland, 1998). The characteristic black shale facies of OAE 2 are delayed in onset within the WIS compared to the global record, likely due to its shallow depth (Sageman and Lyons, 2004).
Snake in the Grass Bluff, near Bunker Hill, Kansas lies on the eastern margin of the Cretaceous Western Interior basin. The western margin of the WIS was bordered by relatively tall mountains (Sageman, 1989). The different topography between the east and west resulted in a higher input of both organic and inorganic terrestrial matter on the western margin due to the weathering of the slopes and subsequent transport of matter into the basin. In contrast, the eastern margin of the Western Interior seaway was not bordered by major uplands, and thus flux of sediment and terrestrial organic matter was lower on the eastern margin of the basin. These arguments suggest that terrestrial organic matter was preferentially on the western side of the basin, whereas the eastern margin was comparatively enriched in marine organic matter. This is experimentally confirmed by the higher H-index of organic carbon in the eastern areas of the Western Interior Seaway, specifically in Kansas (White and Arthur, 2006). The topography based hypothesis may be confirmed by regional comparison of average values of δ13Corg during Ocean Anoxic Event 2 (OAE2): the isotope record measured in Bunker Hill is more depleted than that measured in Pueblo, Colorado, which lies closer to the western margin (Adams et al., 2010). We expect Cretaceous marine organic matter to have a lighter isotopic signature than that of coeval terrestrial organic matter because the high concentration of atmospheric CO₂ in the Cretaceous and higher temperatures allowed marine primary producers to discriminate with a higher fractionation factor due to the increased solubility of CO₂ (Arthur et al., 1985).

According to Hattin (1975), nomenclature for the lithostratigraphic units of the upper Cenomanian and Turonian sections of the Bunker Hill Outcrop is as follows: the entire Greenhorn Limestone Formation consists of the Lincoln Limestone Member overlain by the Hartland Shale member (HSM), from which the lowest samples in Snake in the Grass Bluff were taken. In Kansas, the HSM is mostly calcareous shales, but contains some burrowed chalky limestones and bentonite seams (Hattin, 1975). The Jetmore chalk member overlies
the HSM, and the Pfeiffer member, which is of Turonian age, overlies the Jetmore (Hattin, 1975). The middle and upper parts of the HSM in central Kansas are equivalent to the lower part of the Bridge Creek Limestone in Colorado (Hattin, 1975).

**Carbon Cycle Geochemistry**

The marine carbon cycle consists of a number of different carbon reservoirs and pathways. The largest carbon reservoir on Earth aside from the mantle is the crust, where carbon is preserved as carbonates in sediments, or sedimentary organic carbon (Kump and Arthur, 1999). Crustal and mantle carbon can be released into the atmosphere via volcanism or fossil fuel combustion, where the CO$_2$ has a relatively shorter residence time compared to the crust. Atmospheric CO$_2$ is cycled back into the marine surface waters through diffusion and dissolution into surface water as bicarbonate, and is also incorporated by primary producers via photosynthesis (Sageman and Lyons, 2004). The primary producers act as a biological pump, preferentially incorporating isotopically light carbon in the surface waters exporting it through the water column to the sediments, where it can be incorporated into the rock record via sedimentation. Many of the processes that induce a flux of carbon between reservoirs are associated with an isotope effect that fractionates carbon in carbonate and organic carbon (See Figure 1).

Marine carbonates are useful as a proxy for the isotopic composition of the DIC (predominantly HCO$_3^-$) in the ocean during sedimentation (Kump and Arthur, 1999). The stable isotope composition of carbon in marine carbonate depends on the flux of organic carbon to the ocean, and the difference in fractionation between organic carbon and carbonate carbon, and the isotopic composition of carbon being input by rivers from terrestrial sources. This is summarized as the lever rule:

$$\delta^{13}C_{\text{carb}} = f_{\text{org}} \Delta C_{\text{carb-org}} + \delta^{13}C_{\text{rivers}}.$$
From figure 1 we can see that steady state carbon burial has an average isotopic composition of 1‰. $\Delta C_{\text{carb-org}}$ is maintained fairly constant given a constant level of atmospheric CO$_2$. Because the amount of weathering is directly related to pCO$_2$, a constant pCO$_2$ will imply constant weathering. Weathering input is measured by the riverine $\delta^{13}C$.

Inorganic carbon weathering generally has an isotopic value of $\sim$0‰, which is not a major lever on $\delta^{13}C_{\text{carb}}$. However, the weathering of terrestrial organic carbon (such as shales) has a larger fractionation, with steady state values in the Cretaceous averaging -22‰ (Kump and Arthur, 1999).

Organic carbon is a useful proxy for the activity of primary production occurring during the period of sedimentation. Primary producers incorporate carbon via photosynthesis, which always has a large fractionation effect on organic carbon. In a steady-state system, the isotopically light carbon produced by primary producers is subsequently respired, leaving the reservoirs unaltered.
Perturbations to the carbon cycle: Elevated atmospheric carbon dioxide, primary production, and carbon burial

Volcanism and other perturbations of carbon reservoirs can release high levels of carbon dioxide into the atmosphere. Elevated pCO$_2$ allows primary producers to discriminate and increases the isotope fractionation factor, so $\delta^{13}$C$_{\text{org}}$ becomes depleted in times of high pCO$_2$. $\delta^{13}$C$_{\text{carb}}$ becomes enriched at the surface waters when light DIC is utilized for primary production and incorporated into organic matter in conditions of high pCO$_2$. The biological pump transports organic matter to the bottom waters, where the carbon is oxidized and depleted DIC is released into the low ocean, resulting in isotopically light bottom waters (Freeman, 2001). Isotopically depleted carbonates form due to vital effects of organisms preferentially incorporating $^{12}$C into their carbonate shells, and due to diagenesis. Diagenesis is the post burial alteration of sediments such that the isotope signature becomes more depleted than the original signal (Pratt et al., 1993).

A relatively high initial concentration of atmospheric CO$_2$ allows photosynthesizers to discriminate between carbon isotopes, resulting in a depleted organic $\delta^{13}$C isotope record if carbon burial is also increased (Jarvis et al., 2011). When organic material does not have access to adequate oxygen during respiration, the organic material is remineralized by microbes using other terminal electron acceptors such as nitrate and sulfate (Sageman and Lyons, 2004). These conditions are termed anoxic events, and are recorded in the rock record as periods during which the rocks are enriched in organic carbon. When the water column is sufficiently mixed, primary production during anoxic conditions turn the ocean into a carbon sink, and pCO$_2$ is drawn down the water column and removed from the atmosphere and short term carbon cycle through the sequestration of carbon into the sedimentary reservoir (Barclay et al., 2010). A drawdown of atmospheric CO$_2$ due to high primary productivity during ocean
anoxia decreases atmospheric pCO₂ and should result in a positive excursion of enriched δ¹³Corg values, in part due to a smaller fractionation factor caused by lowered pCO₂. The drawdown of CO₂ is part of a negative feedback loop that acts to naturally regulate the Earth’s climate by removing the greenhouse gas CO₂ and allowing the planet to cool until oxic conditions are restored.

Elevated CO₂ or input of other limiting nutrients will increase primary productivity. Weathering induced by high pCO₂ increases both the amount of carbon and phosphate brought into the marine system, which fuels primary production. When primary productivity is high, we expect the δ¹³Corg record to become more depleted as producers preferentially incorporate lighter isotopes and the burial of this carbon is increased. The isotopic signature of organic carbon is controlled by both primary production and organic carbon burial during the remineralization of organic matter. After a period of increased primary production, the flux of organic carbon out of the short term carbon cycle and into sediments also increases, sequestering the carbon from the available carbon pool. The amount of organic carbon that escapes decomposition as it falls down the water column will vary based on depth of the water column and on the rate of bottom water recirculation. The fraction of organic matter that reaches bottom waters and is preserved as sedimentary organic carbon will be the highest in shallow basins that experience elevated primary production rates, because there is more carbon with a smaller chance of being decomposed before burial (Suess, 1980). The sequestration of isotopically light carbon (photosynthate) results in a smaller fractionation of the remaining carbon, and subsequently a relatively enriched δ¹³Corg signal. The high organic carbon burial would increase δ¹³Ccarb, while lower rates of organic carbon burial would result in a negative δ¹³Ccarb shift (Payne et al., 2004). However, productivity is also limited by nutrients such as phosphorus. Phosphorus input to the ocean depends on weathering, which increases with pCO₂.
**Sulfur cycle geochemistry**

Because the carbon cycle is tightly coupled to the sulfur cycle, trends in sulfur isotopes are useful in determining mechanisms of perturbations in the carbon record. The changes in mass balance and fractionation of seawater sulfate are measured through the proxy of carbonate associated sulfur (CAS) isotopes, whereas pyrite isotopes are a useful proxy for organic sulfate formation and fractionation. The geologic marine sulfur cycle is controlled mainly by the mass inputs of sulfate from weathering of evaporites, such as anhydrite or gypsum, and terrestrial organic-rich shales which are rich in pyrite. Major controls also include outputs of bacterial sulfate reduction (BSR), pyrite burial, and evaporite burial in shallow settings (Strauss, 1997).

Volcanism or other hydrothermal inputs are also factors that could potentially increase the sulfate reservoir in the atmosphere and ocean, affecting the isotopic fractionation of oceanic sulfate by increasing the size of the reservoir and via input of isotopically depleted sulfate. Bacterial sulfate reduction (BSR) occurs below the sediment water interface in anoxic environments when oxygen and nitrogen can no longer act as electron acceptors (Strauss, 1997). BSR requires organic matter and sulfate, and produces reduced hydrogen sulfide and bicarbonate:

\[ 2\text{CH}_2\text{O (Organic Matter)} + \text{SO}_4^{2-} \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^- . \]

Hydrogen sulfide is very reactive with iron oxides and reacts to produce pyrite (FeS$_2$) which is preserved in the rock record. During BSR, $^{32}$S is preferentially dissociated and incorporated into H$_2$S, so greater concentrations of either reactant results in a relatively depleted $\delta^{34}$S$_{pyrite}$ record. The extent of this kinetic isotope effect depends on factors including the rate of reaction and size of the available sulfur reservoir (Strauss, 1997). Greater concentrations of seawater sulfate allow greater fractionation of sulfur during BSR,
resulting in a greater $\Delta^{34}S_{\text{sulfate-pyrite}}$ and often resulting in lighter $\delta^{34}S_{\text{pyrite}}$. The available sulfur reservoir can also be effectively increased by enhanced diffusion of sulfate to lower sediment layers as a result of bioturbation (Strauss, 1997). In contrast, the available sulfur reservoir is decreased by increasing the rate of reaction of BSR, which also depends on the other reactant: organic matter. Increased organic matter input, as in the case at the onset of OAE2, drives the BSR reaction toward the products, producing more pyrite and simultaneously reducing the available sulfate. This acts as a negative feedback loop because high rates of sulfate reduction cause a smaller fractionation of $\delta^{34}S_{\text{pyrite}}$, yielding heavier $\delta^{34}S_{\text{pyrite}}$ isotopes.

The requirement of organic matter as a reactant links the $\delta^{34}S$ record to the carbon cycle. If surface primary production increases, so does the production of organic carbon that sinks to the ocean floor via the biological pump that can subsequently be reduced by BSR to form sulfides incorporated into the sediment. This link results in a positive relationship between $\delta^{34}S_{\text{sulfate}}$ and $\delta^{13}C_{\text{carb}}$ because the process preferentially buries light fractions of both carbon and sulfur (in the forms of organic carbon and pyrite), leaving seawater (as reflected by the $C_{\text{carb}}$ and $S_{\text{CAS}}$ records) relatively enriched (Hurtgen et al., 2009). The sulfur fractionation observed in pyrite is a local signal, whereas CAS in carbonates and evaporites records fractionation in seawater sulfate, which should be consistent throughout a well-mixed basin. If the basin is predominantly stratified, the sulfur isotope signal captured in the shallow setting where evaporites are deposited may reflect only the sulfate composition of the surface water, which could be oxic despite anoxic bottom waters (Strauss, 1997).

The sulfur and carbon cycles are also linked through weathering and volcanism as inputs. Weathering is expected to proportionately increase sulfate and carbonate inputs, increasing sulfate concentrations and expanding the reservoirs and enhancing fractionation, yielding a more depleted sulfate record. High marine sulfate concentrations result in large $\delta^{34}S_{\text{sulfate}}$ fractionations because the rate of sulfate reduction is reduced, and vice versa due to
the reservoir effect. Additionally, the isotope composition of the sulfate (from oxidized pyrite) inputs from weathering are depleted relative to seawater, so weathering tends to bring seawater values closer to terrestrial values.

Unresolved debates over the driving mechanisms for OAE2

While the carbon isotope record at the Cenomanian-Turonian boundary has been well studied throughout the world (Bowman and Bralower, 2005; Jarvis et al., 2011), only recently have detailed sulfur isotope analyses been applied to this event in conjunction with carbon isotope interpretations (Adams et al., 2010; Ohkouchi et al., 1999). Multiple theories have been suggested for the triggers of OAE2, including sea level transgression and flooding to enhance primary productivity and organic carbon preservation (Arthur et al., 1987), volcanism or enhanced sea-floor spreading that increased mantle input of sulfur and trace metals to the ocean (Adams et al., 2010; Jenkyns, 2003; Kerr, 1998; Snow et al., 2005), variable influx of freshwater to the oceans influencing mixing and stratification of the water masses (Floegel et al., 2005), and methane hydrate dissociation (Bowman and Bralower, 2005). While it is likely that some combination of these theories triggered OAE2, the timing and mechanism of the biogeochemical and climactic triggers of OAE2 are still debated.

Study Description

This study is a geochemical analysis of 30 samples collected from Snake in the Grass Bluff in central Kansas. This site includes a sequence of sedimentary rocks that were deposited on the eastern margin of the Western Interior Seaway, and have some of the highest levels of calcium carbonate in the basin. This study is specifically interested in comparing the stratigraphic record of carbon and sulfur isotope data to elucidate changes in redox conditions within the Western Interior Seaway during the transition into OAE2. The studied strata are late Cenomanian to early Turonian in age (C-T). OAE2 has been interpreted as a period of a
significant ocean anoxia due to globally high levels of marine primary production (Barclay et al., 2010), but not every locality shows evidence of anoxia at OAE2 onset. By examining trends in sulfur and carbon stable isotopes, this study aims to enhance the understanding of the connections and feedbacks on primary production, ocean anoxia, and volcanism in the Late Cretaceous WIS to perturbations in biogeochemical cycling.

**Methods**

*Sample Collection*

The samples were collected from an outcrop near Pfeifer, Kansas by Derek Adams and Richard Barclay from Northwestern University. The site was called Snake in the Grass Bluff. Every other sample from the original collection was chosen for analysis, to make 25 in total analyzed for inorganic carbon, while an additional five samples were analyzed for the rest of the isotope analyses to get better resolution leading up the anoxic event. The samples varied in composition from very soft, dark shale to hard chalky limestone. The samples were sawed into cubes smaller than cubic centimeters and the outer weathered surfaces were ground off to reduce post-depositional signals. These cubes were then crushed to a fine powder using a tungsten carbide shatterbox.

*Carbonate and organic carbon analysis*

Coulometry is useful in determining both the total and inorganic composition of the carbon in a sample by using acid and oven modules (Huffman, 1977). The coulometric method used in this study is based off of Huffman (1997). The samples are analyzed for inorganic carbon content using the acid module of the coulometer, which measures carbon concentrations using coulometric titration. Coulometric titration functions by testing absorbance of the solution, which is initially blue, and measuring the amount of current it
must send to titrate the solution until it is clear. The amount of current is directly proportional
to the amount of carbon in the sample. The coulometer is calibrated using a calcium
carbonate standard, and calculated the weight percent of inorganic carbon in each sample.
The total carbon content is obtained using the oven module of the coulometer, which fully
combusts all carbon present to CO₂. Total organic carbon is then derived by subtraction (TC-
TIC).

These samples are then analyzed for stable isotopic values of carbon and oxygen on an
isotope ratio mass spectrometer. Powdered samples are acidified in an airtight vial with
concentrated phosphoric acid. The calcium carbonate in the sample was given over twelve
hours to react with the phosphoric acid, producing gaseous carbon dioxide. The resulting CO₂
gas was analyzed by the gas bench IRMS to measure the mass to charge ratios of the
molecules. Reference gas was used to optimize the system for measuring CO₂, and standards
were run to check for stability and repeatability of the instrument. Outlier data were analyzed
on two separate occasions, with duplicates each time, confirming that the data was not a
result of an analytical error.

Pulverized samples are also acidified for at least 24 hours with 2N HCl on a continuous
shaker to remove inorganic carbon. These samples are analyzed for organic carbon isotope
ratios using the Elemental Analyzer. Analogous to the carbonate analysis, reference gas is
used to optimize the system and results are normalized using a standard curve. Standards
were run every ten samples to check for machine calibration.

*CAS extraction*

Carbonate Associated Sulfate (CAS) was extracted by washing out all other forms of
sulfur so that only CAS remains. The extraction method was based off of standard procedures
(Hurtgen et al., 2006). The extraction required rinsing each pulverized bulk sample in salt
(NaCl) solution overnight, followed by rinsing the sample with DI water. The samples were rinsed and allowed to soak at least overnight, then filtered using Whatman filter paper, which has been tested by this lab and does not alter the carbon or sulfur isotope signal when analyzed in the IRMS. Each sample was then rinsed three times with bleach (~6% NaOCl) and allowed to soak for at least 24 hours for the first two rinses, and 48 hours for the second rinse. The especially fine shale samples required much longer to settle out of solution in order to filter, which may have affected fractionation and allowed the CAS to oxidize during the extraction process. These five samples, which occur in the laminated shales of the Lincoln Limestone Member and Hartland Shale just before OAE2 as marked by HL-1, and just after the onset of OAE2, were not included in the CAS data analysis due to depleted $\delta^{34}\text{S}$ values not achievable without significant post-burial alteration. The samples also have a high wt% S and wt% Carbonate values less than 65%, indicating that most of the sulfur in these samples is likely in the form of pyrite or organic sulfur instead of CAS. After completing three bleach rinses, the samples were once again rinsed with DI water and then acidified with 6N HCl, but not allowed to sit for more than four hours in order to prevent oxidation. The acidification dissolved the carbonate, allowing the remaining soluble sulfur to be preserved as barite when BaCl was added. This barite (BaSO$_4$) precipitates from solution, which was then filtered out and analyzed on the Elemental Analyzer for $\delta^{34}\text{S}_{\text{CAS}}$.

**Pyrite analysis**

The procedure for pyrite extraction followed Canfield et al. (1986). This study analyzed the insoluble residue samples with CAS extractions along with the Whatman filter paper, which was measured to have no impact on $\delta^{34}\text{S}_{\text{pyrite}}$. Each sample was reacted with chromium chloride solution and 12N hydrochloric acid and heated in the extraction line, which precipitated silver sulfide (AgS) in a 3% silver nitrate and 10% ammonium hydroxide
solution (Canfield et al., 1986). The silver sulfide was filtered out and analyzed on the Elemental Analyzer for $\delta^{34}\text{S}_{\text{pyrite}}$.

**Method test: Shale vs. Insoluble Residue**

To test the reliability of the sulfur extraction method, $\delta^{34}\text{S}$ values for pyrite measured directly from three bulk shale samples were compared with values of $\delta^{34}\text{S}_{\text{pyrite}}$ from insoluble residue extracted from the same samples (M. Gomes, Personal Communication). This tested whether the multiple bleach rinse method for CAS extraction altered pyrite fractionation, especially in samples with high percent organic carbon and thereby rich in pyrite. The results showed that there was not a large difference (maximum standard deviation of ~2.4 per mil) between the two methods. More importantly, the bulk shale value could not be predicted from the insoluble residue value, revealing no trend of the shales having an enriched or depleted signal compared to their CAS extracted counterparts. The lack of predictability implies that the CAS extraction process (which included bleach treatments of varying times due to the difference in settling time for shales compared to limestones) did not greatly affect $\delta^{34}\text{S}$ fractionation.

**Modeling**

The carbon cycle model used in this study was modified from Kump and Arthur (1999). Model steady state and experimental runs were set up using the program *Stella*, and were graphed in Microsoft Excel. The mass balance model follows the change in mass of oceanic carbon ($M_o$) due to inputs of carbon from weathering and volcanism, and exports from the burial of organic and inorganic carbon:

$$\frac{dM_o}{dt} = F_w + F_{volc} - (F_{b,org} + F_{b,carb})$$
The isotope balance model follows the carbon lever rule, where $\delta$ denotes the average isotopic composition of carbon from each source. Steady state values are modified from Kump and Arthur (1999). $\delta_{\text{carb}} = 0.78\%$, $\delta_{\text{volc+wr}} = -5\%$, $F_{W,\text{org}} = 10000$, $F_{W,\text{carb}} = 34000$, initial $F_{\text{volc}} = 6000$, where $W'$ indicates both organic carbon weathering and siliclastic and carbonate weathering (all fluxes in units of $10^{12} \text{ mol C/kyr}$).

$$\frac{d\delta_{\text{carb}}}{dt} = \frac{(F_W + F_{\text{volc}})(\delta_{W'} + \delta_{\text{volc}} - \delta_{\text{carb}}) - (F_{b,\text{org}}\Delta_{\text{carb-org}})}{M_O}$$

The model accounts for the feedback on weathering from changes in pCO$_2$ and the dependence of the fractionation effect on pCO$_2$ levels, but a constant concentration of phosphate is assumed. Volcanism and organic carbon burial were varied to determine the effects of these levers on the carbon isotope record.

**Limitations**

The data was acquired from bulk samples, which may include portions of sample that were diagenetically altered or contained other fossilized material. This could have been avoided by examining thin sections of the sample for recrystallization, and drilling out only unaltered sample. Another potential source of error is the assumption that organic matter all originated as photosynthate. The organic matter is likely composed of both bacterial sources and photosynthate, with possibly a small fraction of terrigeneous organic matter. To simplify analyses these relatively minor sources were ignored. These limitations have a large potential for causing analytical error for both carbonate and organic carbon isotopes. Thus, trends in the data were verified by comparison to studies of OAE2 from other sites.

Additionally, the sedimentation rate in Bunker Hill is slower than that in Pueblo, CO and in more western sites of the WIS (Hattin, 1975). Reduced sedimentation means that less time may be represented in the rock record, possibly through small hiatuses or
disconformities in the record. Even if there are no major gaps, the section will be more condensed, and both inorganic and organic constituents will have experienced a different geochemical history during deposition and early burial.
Figure 2: Sulfur and carbon lithostratigraphy and geostratigraphy from Bunker Hill, KS show isotope excursions characteristic of Ocean Anoxic Event 2. For $\delta^{13}C_{carb}$ the dark blue data were reruns of the samples one year later to corroborate the anomalous data. The blue box denotes OAE2.
Results

Carbon

The data (Figure 2) show sediments enriched in organic carbon in the upper portion of the Hartland Shale member, consistent with data previously measured from Bunker Hill and from other sites in the Western Interior Seaway (Barclay et al., 2010; Pratt et al., 1993). At -12.9 m in the section, there is a thick marker bed of limestone overlain by a thin bentonite bed, matching previously recorded locations for Limestone 1, or HL-1 in Bunker Hill, Kansas (Hattin, 1975). In Pueblo, Colorado and in other locations, there is a consistent record of the onset of OAE 2 marked by the bed HL-1 (Elder, 1985).

The carbon isotope data yielded both expected and unexpected trends. Organic carbon isotopes were expected to be enriched during the event, a trend confirmed by the data. However, the relatively large depletion of the carbonate isotope record, and thus an extreme excursion of $\Delta_{\text{carb-org}}$ (“$\Delta_B$”) after the onset of the event was not expected. The range of values and general trend of $\delta^{13}C_{\text{org}}$ from previous studies of Bunker Hill appear almost identical to the values measured here, but a bed-by-bed comparison is difficult because the previous study lacked stratigraphy (Pratt et al., 1993). The most enriched values during the event as measured by Pratt et al. (1993) are 1‰ more enriched than the values measured here.

The $\delta^{13}C_{\text{carb}}$ data records a negative excursion to -2.2‰ at HL-1, thought to be the onset of OAE2, and also a negative excursion to -2.09‰ ~300 kyrs before the event (timescale based on Meyers et al., 2012). Each of these excursions are at least a -3‰ shift from the apparent baseline before the event, which ranges between +1‰ and +1.8‰, with a mean value of +1.5‰. The intervals of depleted $\delta^{13}C_{\text{carb}}$ values are also captured by the data from Pratt et al. (1993), with a range of values from about -2‰ to 3‰ during the event,
comparable to the data here, which included a range of $\delta^{13}C_{\text{carb}}$ from -2.4‰ to 2.6‰ (Pratt et al., 1993).

The pre-excursion baseline differs from the post excursion baseline, which is more depleted and ranges from -0.6‰ to +0.4‰. A similar shift to a ~1.5‰ more depleted baseline after OAE2 is observed in Mexico (See supplementary figure S1) (Elrick et al., 2009). The change in baseline from more enriched to more depleted is especially interesting in juxtaposition with the $\delta^{13}C_{\text{org}}$ record at Bunker Hill, which has a pre-excursion baseline of ~-27.0 ‰ and a post-excursion baseline ranging from -26.3 ‰ to -27.6 ‰. This $\delta^{13}C_{\text{org}}$ record is confirmed in multiple studies of the CTB isotope record in Kansas (Bowman and Bralower, 2005; Slingerland et al., 1996).

The difference in carbonate and organic carbon isotope effects, $\Delta_B$, shows a sharp decrease right at the onset of the event, followed by a rapid recovery. Previous studies have shown a similar trend of an extreme minimum of $\Delta_B$ directly after the onset of OAE2, followed by a fairly quick recovery (Jarvis et al., 2011). This same trend is captured in unpublished data from Northwestern University measured section from Pueblo, Colorado. The unpublished data also has a range of values of $\Delta_B$ almost identical to those from this dataset, except for the one extreme point at 22 ‰ directly after the onset of the event. Jarvis et al. (2011) measured carbon-isotope data from Pont d’Issole in France, and their values are generally ~2 ‰ more enriched in $\delta^{13}C_{\text{carb}}$ and 1‰ more enriched in $\delta^{13}C_{\text{org}}$ than the values from Bunker Hill. Barclay et al (2010) found $\delta^{13}C_{\text{org}}$ from southwest Utah to follow a similar trend, but with values more than 2‰ more enriched than the data here due to the terrestrial origin of the organic matter measured.
Sulfur

The pyrite sulfur record was most robust in our analysis of sulfur isotopes, with the δ³⁴S_{pyrite} recording a pre-OAE baseline of -32 to -35‰, with a positive excursion up to -22‰ within two of the limestones at the top of the Lincoln Limestone member. A second +7‰ positive excursion to -28‰ occurs before HL-1, which marks the beginning of OAE2 in the WIS, and is sustained until HL-3 when δ³⁴S_{pyrite} returns to pre-OAE baseline levels of -38‰. The δ³⁴S_{pyrite} gradually becomes more enriched from this point on through the event, reaching -33‰ at the end of the event and gradually reaching a new post-OAE2 baseline of about -22‰, with the heaviest point at -15‰ at the base of the Pfeiffer Member.

Interestingly, all pyrite values heavier than -30‰ are from limestone or marly limestone samples, although two marly limestone samples in the middle of the anoxic event recorded δ³⁴S_{pyrite} more depleted than -30‰. The remainder of the samples recording δ³⁴S_{pyrite} < -30‰ were from laminated shales or marls with weight % carbonate of less than 75%.

The gradual depletion of the δ¹³C_{org} record starting above HL-3 mirrors the gradual enrichment of the δ³⁴S_{pyrite} record for the same time period, with major differences being in the magnitude of change (+18‰ for δ³⁴S_{pyrite}, +2.5‰ for δ¹³C_{org}).

Carbonate Associated Sulfur (CAS) exhibits an isotopically light pre-OAE baseline of about +10‰, which gradually increases during the event, varying from +19‰ to +11‰, and reaching a new post-OAE2 baseline of +23‰, but with two excursions up to +30‰ (see Figure 2). These results are consistent with the findings of Adams et al (2010) in both trend of enriching δ³⁴S_{CAS} during and post-event, and in the isotopic values themselves. We expect consistency of δ³⁴S_{CAS} in the WIS because the CAS record reflects sulfur isotope values of
seawater sulfate, which should be fairly consistent throughout the well-mixed shallow inland sea for any given time.

The CAS isotope measurements yielded some anomalous results that were not included in the analysis. Six samples, five of which were the only samples with less than 65 wt% carbonate (marlstone) recorded predominantly negative $\delta^{34}S_{\text{CAS}}$ values ranging from 2‰ to -7‰. The main sources of sulfur for the sulfur cycle are the mantle, which has a sulfur value of 0‰, and weathering, which has a sulfur isotope value between 0 and 7‰. Because the anomalous values are negative, falling below possible input values, these results are likely due to experimental error caused by the oxidation of sulfur during extraction from the carbonates. Since there is comparatively low carbonate in these samples, their CAS isotope values are more sensitive to alteration.

**Discussion**

**Enriched Carbon Record**

The baseline for $\delta^{13}C_{\text{carb}}$ depends on the locality and the amount and composition of sedimentary input (Sageman and Lyons, 2004), and is therefore expected to vary across depositional environments and facies across the globe. Within the Western Interior seaway, the pre-excursion baseline at Pueblo was measured to be $\sim +1.4‰$ (Sageman et al., 2006), which is comparable to the mean $+1.5‰$ baseline observed in Bunker Hill. Also, both Rock Canyon in Colorado and Cuba in Kansas have a pre-excursion $\delta^{13}C_{\text{carb}}$ baseline of between $+1$ and $2‰$ (Bowman and Bralower, 2005), indicating that the baseline observed in Bunker Hill is in line with other sites in the Western Interior Seaway.

It is widely observed that the $\delta^{13}C_{\text{carb}}$ record in the Western Interior Seaway exhibits a $\sim 1.5$ to $2‰$ positive excursion during OAE2 (Freeman and Hayes, 1992; Hetzel et al., 2009;
Sageman et al., 2006). The observation of a ~+1‰ shift from this study in Bunker Hill is therefore slightly lower than in most sites in the Western Interior. The \( \delta^{13}C_{org} \) record exhibits a +2‰ positive excursion during the OAE, resulting in a significantly reduced \( \Delta_B \) relative to the rest of the Bunker Hill record. A carbon burial event would logically cause the same magnitude of enrichment in both the organic and carbonate C isotopes if one does not consider the effect of increased primary production on pCO\(_2\) and the influence of a change in pCO\(_2\) on the fractionation factor \( \epsilon_p \) (Kump and Arthur, 1999). To account for change in the atmospheric carbon reservoir, we expect the fractionation to decrease as the reservoir gets smaller. An organic carbon burial event would cause a drawdown of pCO\(_2\) used by primary producers, which would decrease \( \Delta_B \) by enriching \( \delta^{13}C_{org} \) due to the smaller concentration of CO\(_2\) for producers to preferentially incorporate the lighter carbon. Thus, the reservoir effect on fractionation during a carbon burial event explains why the positive \( \delta^{13}C_{org} \) excursion (~2‰) is greater than the \( \delta^{13}C_{carb} \) excursion (~1‰) (Gomes and Hurtgen, 2013; Kump and Arthur, 1999).

Although the negative pulse in carbonate isotope is not recorded uniformly across the globe, a depleted signal occurring right near the onset of the event is observed in varying magnitudes in locations in the Western Interior seaway, as well as in paleo-epicontinental seas in Italy, Crimea, and France (Hetzel et al., 2009). A composite of \( \delta^{13}C_{carb} \) records from Barclay (2011) annotated in the appendix shows at least a -2‰ shift right at the onset of the event in Aksu-dere, Crimea, as well as Monteforte Cilente and Monte Cerreto, Italy (See Supplemental Figure 1). Monte Coccovello, Italy exhibited a -4‰ shift right at the onset of the event, in addition to an almost equally negative pulse longer before the onset of the event, a pattern also seen at Monteforte Cilente and Monte Cerreto (Hetzel et al., 2009). This pattern of two negative pulses right before the onset of OAE2 is also seen in a section in the proto-
Pacific in Southern Mexico, with a pulse of -3‰ followed by a -2‰ pulse right before the onset of OAE2 (Elrick et al., 2009; Hetzel et al., 2009). In the Western Interior Basin, Rock Canyon, Colorado, exhibits a -3‰ shift at the apparent onset of the event, followed by a series of negative and positive kicks from +4‰ to -2‰ in a record measured by Bowman and Bralower (2005), but this trend is not captured in the Rock Canyon data from the composite (Hetzel et al., 2009). A -2.5 ‰ shift in δ¹³C_carb from the baseline right at the onset of the event is also observed in the #1 Portland Core from Pueblo, Colorado, but it is associated with a diagenetically altered limestone bed (Sageman et al., 2006). Further support for the global occurrence of the negative pulses in the δ¹³C_carb record comes from multiple sites in the North Atlantic Ocean where a -2 to -2.5‰ brief excursion from the baseline occurs right before the onset of OAE2 (Friedrich et al., 2012). Oddly, the record from Cuba, Kansas, which is geographically closer to Bunker Hill than any other site, does not seem to match the signal recorded in Bunker Hill, with the negative δ¹³C_carb pulse at the onset, but instead has one brief −6‰ pulse right before the Cenomanian-Turonian Boundary (Bowman and Bralower, 2005). Due to the high percentage of carbonate rich limestone beds in this record, one hypothesis for the unexpected data could be post-burial diagenesis. The litho-stratigraphy at this site has low resolution, and so it is difficult to correlate timing of the excursion in relation to the data in this study.

Additionally, multiple sites did not record any depleted δ¹³C_carb values before or during OAE2. Three separate studies from England showed no negative signal (Canfield et al., 1986; Hetzel et al., 2009), nor did Wadi Bahloul in Tunisia or Tingri in Tibet (Hetzel et al., 2009). There are multiple possible explanations for the difference in recorded signal: (1) it could be that only the sites in England, Tunisia, and Tibet avoided diagenesis and thus the records from these sites are much better proxies for global δ¹³C_carb record of the study interval. (2) Some large and brief event occurred to induce a negative pulse in the global
\[ \delta^{13}\text{C}_{\text{carb}} \] record but not the \[ \delta^{13}\text{C}_{\text{org}} \] record, and due to a widespread unconformity sites in England, Tunisia, and Tibet do not record the signal. (3) The correlation of stratigraphy and timing of the event is incorrect and the negative pulses do not actually coincide, and are thus likely due to diagenesis of limestones.

**Diagenesis**

The short negative excursions observed in the \[ \delta^{13}\text{C}_{\text{carb}} \] data before and at the onset of OAE2 could potentially be explained by diagenetic alteration of the sediment. If this is the case, then the diagenetically altered facies are not representative of changes in the carbon cycle because the isotope concentration was chemically altered after sedimentation occurred. Diagenetic alteration implies that the \[ \delta^{13}\text{C}_{\text{carb}} \] isotopic signal will be depleted in relation to the original signal (Pratt et al., 1993). Diagenesis is most likely to occur in facies that formed under a high water to rock ratio, and is identifiable by a strong covariance between \[ \delta^{13}\text{C}_{\text{carb}} \] and \[ \delta^{18}\text{O} \] (Preto et al., 2009). Because the eastern margin exhibited a slow sedimentation rate which allowed organic matter to decompose before sedimentation, the high water to rock characteristic supports the hypothesis of diagenetic alteration leading to the negative

![Figure 3: Carbonate and Oxygen isotope record shows evidence of possible diagenesis, with the most anomalous samples from the carbonate record circled in red. \( R^2 = 0.4474 \)](image)
excursions, because all four anomalously light values correspond to limestone beds of ~90 weight percent carbonate. However, the correlation of carbonate and oxygen isotopes is less apparent in the Bunker Hill data. Figure 3 shows that there is some covariance between $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}$, but the correlation is not tight. However, Preto et al. (2009) have shown that the characteristic potentially unaltered $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}$ relationship in Triassic micrites is an asymmetrical distribution with most values clustered at relatively positive values of $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}$. If the anomalously depleted facies (circled in red) are not considered, the Bunker Hill record yields a mirror image of the potentially unaltered distribution, with most values clustered at relatively positive values of $\delta^{13}\text{C}_{\text{carb}}$, but relatively low values of $\delta^{18}\text{O}$. This trend is puzzling, and is a point that requires further investigation. The mirror image effect may be due to different isotope fractionation in different climates of Triassic and Cretaceous time periods.

Diagenesis in the limestone facies prior to OAE2 is supported by the magnitude of the negative excursion. From carbon mass balance models based on Kump and Arthur (1999), I observed that changes in flux do not lead to significant (-1 ‰ or greater) shifts in the $\delta^{13}\text{C}_{\text{carb}}$ record, especially not without also affecting the $\delta^{13}\text{C}_{\text{org}}$ record, so diagenesis provides a more plausible explanation for this pattern. Additionally, a simple carbon cycle model (Figure 4) shows that increased volcanism followed by carbon burial can account for the general isotopic trend between pre-OAE baseline and the positive excursions, but cannot account for the depleted $\delta^{13}\text{C}_{\text{carb}}$ outliers at the onset of the event. The extreme difference in value from the model implies that an independent factor changed the isotopic composition of carbonate only in a very specific location in the rock record, suggesting diagenesis. However, because diagenesis is a post-sedimentation alteration, the effect is generally local so one would not expect to observe the pattern in locations across the globe. The observation of the negative
\(^{\delta^{13}}\text{C_{carb}}\) signal at the onset of OAE2 across the Western Interior Basin (Sageman et al., 2006), Italy, Crimea (Hetzel et al., 2009), and the North Atlantic (Friedrich et al., 2012) point toward the signal being global, indicating that diagenesis may not be the driver of these trends.
Figure 4: (A) Overlay of modeled values of $\delta^{13}$C with measured values from Bunker Hill. Model imposes a 200 kyr increase in carbon burial by 40%. Blue is measured $\delta^{13}$C_{carb}, purple is modeled $\delta^{13}$C_{carb}, red is measured $\delta^{13}$C_{org}, orange is modeled $\delta^{13}$C_{org}. (B) depicts the overlay of $\delta^{13}$C_{carb} values with model response to a 500 kyr at 7x increased volcanism (from Adams et. al, 2010) followed by rapid increase in C burial to 1.5x, peaking at 1.58x carbon burial and then gradually reducing back to steady state over a period of 600 kyr. (C) depicts the $\delta^{13}$C_{org} response to the same perturbation.
Volcanism

A second hypothesis that should be considered for the anomalously depleted $\delta^{13}C_{\text{carb}}$ values is the occurrence of a volcanic pulse associated with the onset of the event. There is mounting evidence that increased volcanism prior to the OAE2 onset was a driver for the major increase in organic matter burial (Adams et al., 2010; Barclay et al., 2010), so it is valuable to consider volcanism as a possible mechanism for the negative $\delta^{13}C_{\text{carb}}$ pulses. However, this hypothesis for depleted $\delta^{13}C_{\text{carb}}$ values is difficult to support because a volcanic pulse should be recorded globally due to the atmosphere being well mixed, but the signal is not observed in all sites around the globe (Hetzel et al., 2009). If the sites not recording the signal have disconformities, then volcanism may actually be considered as a possible driver of the negative $\delta^{13}C_{\text{carb}}$ pulse. Jarvis et al. (2011) observed a negative shift in carbonate isotopes prior to OAE2 onset at Pont D’Issole, which provides some evidence for the volcanism hypothesis. However, a pulse of volcanism would drive a decrease in $\delta^{13}C_{\text{carb}}$, but would also drive a larger decrease in $\delta^{13}C_{\text{org}}$ values (Kump and Arthur, 1999). Such a change in the $\delta^{13}C_{\text{org}}$ record was not observed in this study of Bunker Hill, nor was it noticeable in any of the previously mentioned studies that included both $\delta^{13}C_{\text{carb}}$ and $\delta^{13}C_{\text{org}}$ records (Bowman and Bralower, 2005; Hetzel et al., 2009; Sageman et al., 2006). Thus, volcanism could not have been the sole driver of the negative $\delta^{13}C_{\text{carb}}$ pulses. If other fluxes of carbon mass are changing at the same time as volcanism (e.g. carbon burial) it is possible that the $\delta^{13}C_{\text{org}}$ is balanced by the negative driving of volcanism and the positive driving of carbon burial, while the $\delta^{13}C_{\text{carb}}$ is more sensitive to volcanism than to carbon burial and thus exhibits a brief negative pulse (Kump and Arthur, 1999). Volcanism seems like an unlikely driver of the dramatic changes in the $\delta^{13}C_{\text{carb}}$ record before OAE2, but the hypothesis cannot be completely refuted.
A time scale is necessary to use the biogeochemical model to test hypotheses for possible explanations of measured data. The most updated dating of the beds in the Western Interior uses radioisotope analysis of bentonite layers that span the entire seaway, biozones, and astrochronology to provide the most accurate dating of the Cenomanian-Turonian Boundary interval (Meyers et al., 2012). Meyers et al. (2012) provide new radioisotope age data (both Ar-Ar and U-Pb) from multiple sites across the basin as and employ an astrochronologic framework to more accurately interpolate stage and biozone boundary ages. The biozone boundary ages can be correlated to the Bunker Hill, Kansas section, allowing local development of a high resolution timescale (Figure 6). The relative locations of major limestone beds and bentonite beds recorded for the Bunker Hill site analyzed in this paper correspond to the high resolution lithostratigraphy reported by Hattin and Elder at the same site (Elder, 1985; Hattin, 1975). The biozones of *Pseudaspidoceras flexuosum*, *Neocardioceras judii*, and *Dunveganoceras pondi* corresponding with the lithostratigraphy of Hattin and Elder were used to relate bentonite and limestone beds in Bunker Hill to dated beds across the basin. Bentonite bed D, in the *P. flexuosum* biozone, was dated using the astronomically recalibrated age of 93.66 +0.31/-0.16 Ma, while Bentonite bed B in the *N. judii* biozone was dated in the same way to 94.07 +0.16/-0.15Ma (Meyers et al., 2012). At the contact with the Graneros Shale, the division between the middle and upper Cenomanian, the Western Interior Ammonite taxon range zone for *D. pondi* identified by Hattin in...
combination with radioisotope analysis dates the strata to 94.71 ± 0.49 Ma (Cobban et al., 2006; Hattin, 1975). These three specific dates allow the extrapolation of a timescale for the entire section, assuming a relatively constant sedimentation rate. This timescale places the first bed of the 23.05 m Bunker Hill section at 94.7 Ma, and the top of the section at 93.2 Ma (Figure 6).

The control of Bacterial Sulfate Reduction on the Sulfur Record

Both the overall trend in $\delta^{34}S_{\text{CAS}}$, going from more depleted values before the event, becoming suddenly (and variably) enriched during the event and becoming even heavier post-event, and the absolute values of $\delta^{34}S_{\text{CAS}}$, are consistent with the sulfur geochemistry measured in Pueblo, CO, which is expected from two sites within the same basin (Adams et al., 2010) (See Error! Reference source not found.). Compared to the $\delta^{34}S_{\text{sulfate}}$ record of Bonarelli, Italy, the Bunker Hill $\delta^{34}S_{\text{CAS}}$ record is larger by about 3‰ across the OAE2 onset (Ohkouchi et al., 1999). Because the positive isotope shift is apparent and simultaneous in

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Figure 6: Three different sites across the world exhibit a shift in sulfate isotopes from depleted pre-OAE2 to enriched post-OAE2
North America and in Italy, the WIS shift was likely driven by a global event instead of the opening of an oceanic gateway to the Atlantic.

The range of values of $\delta^{34}S_{CAS}$, which increase from 10 to 30‰, indicates the sensitivity of the sulfur record to changes in seawater sulfate concentration. The sudden, relatively large isotopic shifts seen in the WIS $\delta^{34}S_{CAS}$ record would not be possible in a high sulfate ocean due to the reservoir isotope effect. Adams et al. (2010) demonstrated this reservoir effect using a simple mass balance model to show that the same increase in sulfate concentration due to external (volcanic) input would cause a -4‰ excursion in an initially low sulfate ocean (1.4 mM) compared to a -1‰ excursion if the initial sulfate concentration was higher (9 mM).

The Bunker Hill $\delta^{34}S_{CAS}$ values exhibit a +6‰ shift over the time period of ~100 kyr at the onset of OAE2 (Figure 2). Such a dramatic shift would require a low initial sulfate concentration, or else an extremely large shift in seawater sulfate, and the latter seems unlikely in the context of the $\delta^{34}S_{pyrite}$ and $\delta^{13}C_{carb}$ records (Adams et al., 2010). Instead, the data suggest a combination of the two factors influenced the Bunker Hill isotope record: (1) an increase in sulfate upon a (2) low sulfate reservoir. Isotope fractionation, represented by $\Delta^{34}S_{sulfate-py}$, is strongly dependent on the size of the sulfate reservoir (Habicht et al., 2002).

The $\Delta^{34}S$ values increase from ~30‰ at the base of the sample site before OAE2, to a maximum of 54‰ during OAE2, high above modern fractionation levels (~35‰) (see Figure 2). This large increase in fractionation, which is often proportional to sulfate concentration, in unison with an increase in organic carbon burial evidenced by a positive excursion in $\delta^{13}C_{org}$, indicates a dramatic increase in relative seawater sulfate concentration local to Bunker Hill.

Hypotheses for the increase in available seawater sulfate and the resulting enriched $\Delta^{34}S$ include: 1) sea level rise resulting in flooding and a higher proportion of oceanic water mass in the WIS, 2) variable redox conditions that caused differences in sediment exposure to
seawater sulfate through bioturbation, or 3) increased input of organic matter due to prolonged and enhanced primary production.

**Late Cretaceous sea level transgressions**

One possible explanation for the initial enrichment of $\delta^{34}\text{S}_{\text{CAS}}$ in the Bunker Hill Hartland Shale member compared to the Lincoln member is the influx of relatively enriched (~19‰) sulfate from the ocean into the Western Interior Seaway. For an initially low sulfate seaway, an influx of seawater sulfate from either the north or from the Tethys Sea to the south would affect sulfur isotope values in seawater and in pyrite. $\delta^{34}\text{S}_{\text{CAS}}$, which has a baseline of ~10‰ in the Lincoln Limestone Member before the event (Figure 2), would be expected to become enriched if an influx of isotopically heavier seawater sulfate flooded the WIS. Arthur and Sageman (2005) have demonstrated a rise in sea level throughout the late Cretaceous,
culminating in peak flooding during the early Turonian (see Error! Reference source not found.) (Sageman and Lyons, 2004). Transgressive periods may have been associated with increased input of nutrients to the WIS from the Atlantic, enhancing primary productivity (Arthur and Sageman, 2005). However, enrichment beyond 19‰ in the Turonian cannot be explained by flooding because the isotopic value of seawater sulfate during this time is estimated to be 19‰ (assuming this stays constant, which is a risky assumption if large scale volcanic events are occurring). Alternatively, primary productivity could be enhanced by increased input of nutrients from weathering or volcanic events (Kerr, 1998). It is likely that the δ²⁴S_CAS trend is due to the dominance of the reservoir isotope effect of sulfate over the influx of heavier seawater sulfate. As high rates of primary production during OAE2 increased the intensity of BSR and thereby the mineralization of organic matter and sulfate in the form of sulfide burial, the seawater sulfate concentration diminished, resulting in a negative feedback loop that left δ²⁴S_CAS more enriched (Ohkouchi et al., 1999).

_varying redox conditions in the WIS_

Compared to the Portland Core and other sites in the WIS, sites in Kansas on the eastern margin are thought to have lower levels of oxygenation near the Cenomanian Turonian boundary (Savrda, 1998). The eastern margin, specifically the Bounds Core in Kansas, has a much higher percent of laminated fabrics than Portland core in the time period represented by the lower Hartland Shale Member at Bunker Hill (Savrda, 1998). Laminated fabrics indicate anoxic bottom water conditions. In contrast, bioturbated fabrics represent periods with burrowing organisms, which require oxic conditions. Bioturbation affects not only the lithological preservation, but also geochemical conditions in the sediment. During oxic conditions, bioturbation of the sediment occurs, exposing below-surface sediment to seawater. An increase in bioturbation during periods of oxygenation low enough to allow for
BSR will effectively increase the concentration of seawater sulfate available to be reduced via BSR. Figure shows that the extent of fractionation during pyrite formation can be increased by increasing one or both of the following factors: 1) available sulfate concentrations (through influx of high sulfate waters or through bioturbation) and 2) input of organic matter.

Given unlimited organic matter, higher effective sulfate concentrations should increase the extent of fractionation of $\delta^{34}S_{\text{pyrite}}$ in a given locality, leading to a lighter isotope signature. Anoxic conditions should isolate the sediment from bioturbation, effectively decrease available sulfate concentrations and yield an enriched $\delta^{34}S_{\text{pyrite}}$ record. This Bunker Hill record provides geochemical evidence for the difference in local redox conditions between the eastern and western margins of the WIS. At the onset of OAE2, $\delta^{34}S_{\text{pyrite}}$ is more than 10‰ more enriched in the lower Bridge Creek Limestone in Bunker Hill than in Pueblo, CO. This is consistent with the Savrda (1998) observation that the Portland core has a higher percentage of bioturbated fabrics in the lower Bridge Creek (87% compared to 52% at Bounds core in Kansas). The seawater-sediment conditions were therefore more anoxic on the eastern margin than the center of the WIS in the initial part of OAE2. However, as the ocean anoxic event progresses, $\delta^{34}S_{\text{pyrite}}$ values at Bunker Hill once again become depleted, and are consistent with the trend from the Portland Core as $\delta^{34}S_{\text{pyrite}}$ becomes more enriched throughout and past the OAE2 (Adams et al., 2010).

*Figure 9: The relative input of organic matter to the sediments indirectly affects the isotope composition of seawater sulfate by limiting bacterial sulfate reduction*
Figure 10: All sites exhibit a ~8‰ depletion of $\delta^{34}\text{S}_{\text{pyrite}}$ during OAE2 and a rebound to enriched values after the event. The differing background levels between sites is a result of varying local conditions, with Demarara Rise exhibiting depleted values in comparison to the sites in the WIS.
Primary Production leaves $\delta^{34}S_{\text{sulfate}}$ enriched

Theoretically, we might expect a mass demise of primary producers due to an anoxic event to reduce the input of organic matter to the sediments, limiting BSR and resulting in a relatively light $\delta^{34}S_{\text{CAS}}$ record. Once the input of organic matter increases again, BSR can increase and preferentially incorporate light seawater sulfate into pyrite, leaving a relatively enriched $\delta^{34}S_{\text{CAS}}$ record (Strauss, 1997). The Bunker Hill $\delta^{34}S_{\text{CAS}}$ data exhibit this enrichment of CAS as the ocean anoxic event is ending at the onset of the Turonian, indicating an increase in sulfate reduction, likely due to increased organic matter input from high primary productivity. Enhanced primary productivity during OAE2 is corroborated by the enriched $\delta^{13}C_{\text{org}}$ record measured in this study and at localities around the world (Jarvis et al., 2011; Sageman, 2009). Additionally, evidence for increased BSR at the onset of the event is provided by the correlation between $\delta^{34}S_{\text{sulfate}}$ and $\delta^{13}C_{\text{carb}}$ (Figure 1111). This positive correlation is indicative of BSR because the process discriminates against heavy isotopes of both sulfate and carbon during remineralization leaving seawater (as reflected by the $C_{\text{carb}}$ and

![Graph](image)

Figure 8: Carbonate Associated Sulfate and carbonate isotope are coupled post-OAE2 with an R-squared value of 0.69 (clearly diagenetically altered samples removed from analysis). As CAS continues to be enriched with time, carbonate isotopes shift heavier at the onset but then return to lighter values.
The redox conditions are closely coupled to the input of organic matter to the sediments, another factor that visibly controls the local $\delta^{34}\text{S}_{\text{pyrite}}$ record. Total organic carbon (TOC) has limited use in analysis of the redox conditions within a basin because TOC depends not only on oxygenation but also on changes in inputs of organic matter and siliclastics to the system, which impacts the sedimentation rate (Sageman and Lyons, 2004). On the Eastern margin of the WIS, weathering and runoff are minimal due to the very shallow nature of the margin and lack of orogeny (Arthur and Sageman, 2005), so Bunker Hill would be more sensitive to change in the already low sedimentation rate. This lower sedimentation rate allows enhanced oxygen consumption, making the locality more pervasively anoxic. Before OAE2, our coulometric data show an increase in TOC chronologically associated with relatively depleted (~-35‰) $\delta^{34}\text{S}_{\text{pyrite}}$ (see Supplementary Figure S4). This period of high organic matter preservation is consistent with a period of euxinia, and the high OM input resulted in a large fractionation effect during BSR.

At the onset of OAE2, anoxic conditions on the eastern margin of WIS cause a decrease in primary production and the input of organic matter to the sediment. Additionally, anoxia eventually reduces bioturbation of sediment, decreasing the exposure of seawater sulfate to the sulfate reducers below the sediment. The decrease in reactants necessary for BSR (organic matter and available sulfate) reduces the extent of fractionation during BSR and enriches $\delta^{34}\text{S}_{\text{pyrite}}$. This isotope excursion is reversed at the Cenomanian Turonian boundary, as the total organic matter increases in the local sediments on the eastern margin, and enhanced BSR forms pyrite depleted in $\delta^{34}\text{S}$ (Figure 2).

An alternative hypothesis explaining the enrichment of both the $\delta^{34}\text{S}_{\text{CAS}}$ and $\delta^{13}\text{C}_{\text{org}}$ records at the onset of OAE2 is a large-scale increase in volcanism leading up to the event,
followed by enhanced BSR (Adams et al., 2010). Higher volcanism before the event could explain the relatively depleted values of both organic carbon and sulfur before the event, followed by an enrichment of CAS and organic carbon as a result of increased pyrite and organic carbon burial. However, if volcanism is the driver we expect to see a negative excursion before the event in both $\delta^{34}$S$_{CAS}$ and $\delta^{13}$C$_{org}$ (see supplementary figures S2 and S3), but this trend is not strongly developed in the data. If the beginning of the volcanic pulse is not recorded because the data do not go far back enough, the model predicts that such a prolonged and extensive event (7x the background level of volcanism) should cause at least a 5‰ negative shift in $\delta^{13}$C$_{org}$, which is unlikely because that would assume pre-volcanism baseline that is 3‰ more enriched than the peak of OAE2, which is well shown to be the max value of $\delta^{13}$C$_{org}$ for millions of years (Leckie et al., 2002). However, a smaller, yet still prolonged event may explain the trigger for OAE2.

**Conclusions**

The eastern margin of the Western Interior Seaway records a $\delta^{34}$S of seawater consistent with other sites across the entire basin, but records locally unique $\delta^{34}$S$_{pyrite}$. Savrda (1998) has documented greater periods of laminated sediments isolated from bioturbation on the eastern margin of the WIS compared to the west. The more enriched pyrite isotopes in Bunker Hill provide geochemical evidence of higher levels of anoxia on the eastern margin than in Pueblo, Colorado on the western margin. In addition to changes in oxygenation, variable sedimentation rates may have also influenced the sulfur isotope record (Gautier, 1986). Periods of relatively enriched $\delta^{34}$S$_{pyrite}$ at the onset of the event occurred during a period of anoxia and the excursion may have been enhanced by a higher sedimentation rate.
\( \delta^{34}\text{S}_{\text{pyrite}} \) records a primarily local signal of isotope fractionation, therefore the consistency of trends in \( \delta^{34}\text{S}_{\text{pyrite}} \) exhibiting a \( \sim 8\% \) negative excursion at the Cenomanian-Turonian boundary throughout the WIS and Demarara Rise implies a regional if not global driver of the change affecting each locality within 300 kiloyears of one another.

Prolonged primary production during OAE2 increased the transport of organic matter to the sediment floor, enhancing bacterial sulfate reduction and increasing the extent of fractionation during pyrite formation. Enhanced BSR preferentially incorporates light seawater sulfate, leaving the remaining seawater increasingly enriched in sulfate as the event progressed.

Enhanced volcanism prior to OAE2 remains a plausible hypothesis for explaining the trigger of OAE2 in the WIS, though likely not as intense volcanism as suggested by Adams et al. (2010). This study was not conclusive in determining the drivers of the event, but more complicated models, in combination with more sulfur/carbon datasets from this period, should provide insight to the most likely triggers of OAE2.

Future studies should measure the variance of sedimentation rates across the WIS during this period to observe the effect of sedimentation rate on local redox conditions, and thus the isotopic composition of the sediment. Additionally, a comprehensive model linking the mass balance of carbon and sulfur through BSR, volcanism, weathering and sea level changes would provide insight to the significance of each of these levers on the biogeochemistry of seaway sediments and the resulting climactic and biological effects during the Cretaceous. A greater understanding of these connections will allow scientists to better predict the biological response of marine organisms to modern and future anthropogenic and natural biogeochemical perturbations.
Acknowledgements

I am immensely grateful to Professor Brad Sageman for guiding this study and for mentoring me through my journey into the world of sedimentary geology. Thank you to Professor Sageman and Professor Matt Hurtgen for providing background and analytical discussion for understanding the data, in addition to funding the laboratory analyses. I am also grateful to Maya Gomes and Young Ji Joo for their patient assistance and for teaching laboratory techniques and running samples on the IRMS. Alexa Socianu, Petra Sheaffova, and the lab managers Kelly and Koushik assisted and taught laboratory techniques for sample processing and coulometer and IRMS data collection. Thanks also to Jenny Mills for assisting with stella modeling. Derek Adams collected the samples from Snake in the Grass Bluff in Bunker Hill. All laboratory analyses were performed in the Integrated Laboratory for Earth and Planetary Science (ILEPS) at Northwestern University.

References

Cobban, W. A., Obradovich, J. D., Walaszczk, I., and McKinney, K. C., 2006, USGS zonal table for the Upper Cretaceous Middle Cenomanian - Maastrichtian of the Western


Gomes, M. L., and Hurtgen, M. T., 2013, Sulfur isotope systematics of a euxinic, low-sulfate lake: Evaluating the importance of the reservoir effect in modern and ancient oceans: Geology.


Sageman, B. B., and Lyons, T., 2004, Geochemistry of fine-grained sediments and sedimentary rocks, Treatise on Geochemistry: Amsterdam Boston, Elsevier/Pergamon, p. 115-158.


Appendix

Figure S1: Composite of carbonate isotope excursions adapted from dissertation of Richard S Barclay (2011). Red arrows annotate pre-OAE2 negative excursions comparable to the ones observed in Bunker Hill Kansas in this study.
Figures S2 and S3: Results of carbon cycle perturbation of 500 kyr 7x increase in volcanism followed by a 50% increase in carbon burial
Figure S4: $\delta^{34}$S$_{pyrite}$ is most depleted in Bunker Hill during periods of high total organic carbon levels, indicating a link between primary production and bacterial sulfate reduction and anoxic conditions.
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**δ¹³C_carb**

**δ¹³C_org**

**Total Organic Carbon**

**Wt% CO₃**

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**KEY OF LITHOLOGIC SYMBOLS**

- Chalky Limestone
- Concretionary Limestone
- Shaly Limestone
- Marly Limestone

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