CARBONATE-ASSOCIATED SULFATE: ASSESSMENT OF AND USE AS AN ISOTOPIC PROXY FOR GLOBAL SULFUR CYCLING DURING END-PERMIAN MASS EXTINCTION

A Thesis in
Geosciences
by
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Abstract

Carbonate associated sulfate (CAS) has recently become an important proxy for determining change to the global sulfur cycle through time. Variations in the isotopic composition of CAS during the late Permian have been utilized to suggest the presence of a euxinic ocean which may have helped trigger a mass extinction event. Samples from three marine sections spanning the Permian-Triassic boundary were analyzed: Meishan and Shangsi (Southern China) and Demirtas (Turkey) for CAS isotopic composition. Rapid variations in the $\delta^{34}S_{CAS}$ with extremely $^{34}S$ depleted values in the Permian were found at all three sections. A decrease in $\Delta^{13}C (\delta^{13}C_{carb}-\delta^{13}C_{org})$ was also measured at Meishan and Shangsi, but not Demirtas coincident with the largest pulse of extinction. The patterns of isotopic shift indicate a shallow unstable chemocline overlying euxinic deep water which periodically upwelled into the photic zone. This release of sulfide may have stimulated a bloom of phototrophic sulfur oxidizing bacteria. These bacteria would have produced elemental sulfur globules depleted in $^{34}S$, which were deposited in the sediment and later oxidized and incorporated as CAS. The variations in $\delta^{34}S_{CAS}$ between the three marine sections suggest intermittent euxinic conditions in the surface waters which varied by location helping to trigger the largest mass extinction of the Phanerozoic.

These rapid variations in the isotopic composition of CAS during the latest Permian associated with the Permian-Triassic boundary mass extinction event have raised concern over the susceptibility of the CAS isotopic proxy to diagenetic alteration. Chemical and spectroscopic analyses were performed on both modern and ancient samples to determine the resistance of CAS to alteration. Fourier transform infrared spectroscopy of powdered carbonate suggests CAS is present within the calcite mineral
lattice. Examinations of CAS isotopic values in a modern euxinic environment were performed at meromictic Fayetteville Green Lake (near Syracuse, NY). Lake water and sediment samples were analyzed for sulfate and sulfide concentration and isotopic composition. The isotopic values for CAS remained the same as those found in the overlying lake water for both the oxic and euxinic sediments suggesting CAS is a reliable proxy for overlying water sulfate isotopic composition under varying burial conditions.
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Let’s just get the science out of the way so I don’t have to worry about it later.

--Lee Kump, May 2003
Chapter 1

Introduction

Variations in the isotopic composition of carbon and sulfur within the ocean provide information on changes to global cycles and environmental perturbation through time. While changes to the isotopic composition of carbon and oxygen have been well documented for much of the Phanerozoic (Veizer et al., 1999), changes to sulfur have not been as well studied. Carbonate associated sulfate (CAS) has been shown to accurately record the isotopic composition of overlying seawater sulfate, and to preserve this signal in the rock record (Burdett et al., 1989). Previously, data on oceanic sulfate isotopic composition were derived from either evaporites (which are relatively rare in the rock record), or pyrite (the seawater component of which must be deconvolved). Carbonates are nearly ubiquitous within the rock record and this has greatly expanded the resolution of the available data with respect to time, and the number of locations where changes to CAS can be measured.

Kampschulte and Strauss (2004) have utilized CAS to expand the Phanerozoic curve for oceanic sulfate isotopic composition, providing a more detailed record of change (Fig. 1.1). When compared to the evaporite record, CAS provides more detail with smaller uncertainty. The five major mass extinction events of the Phanerozoic are marked on Fig. 1.1 and several (P-Tr, Tr/Jr, K/T) accompany changes to δ³⁴S, suggesting that changes to the sulfur cycle play a role in environmental crises. The Permian-Triassic boundary stands out with a shift from the Phanerozoic low (~12‰) to the Phanerozoic
Figure 1.1 Changes to oceanic sulfate isotopic composition for the Phanerozoic. The five major mass extinction events are marked with black arrows: L-Ord – Late Ordovician; end-Dev – End Devonian; P-Tr – Permian Triassic; Tr-J – Triassic/Jurassic; and K/T – Cretaceous/Tertiary. Image modified after Kampschulte and Strauss (2004).

high (~30‰) over a geologically brief period of time (Fig. 1.1). The Permian-Triassic boundary interval includes the largest mass extinction of the Phanerozoic, with massive extinctions in both the marine and terrestrial realms (Erwin, 1993). Changes to the oceanic sulfur cycle are invoked by a number of hypotheses for the extinction mechanism. The possibility of an anoxic deep ocean (Isozaki, 1997) has been suggested by a number of studies (Wignall and Twitchett, 2002). The long term anoxia may have led to euxinia during the late Permian as well (Kump et al., 2005) and changes to CAS
isotopic composition during the late Permian provides evidence for euxinia; however this has created concern over the integrity of CAS during burial and diagenesis under different environmental conditions.

### 1.1 Carbonate Associated Sulfate

The mechanisms underlying the incorporation of CAS are not fully known. Sulfate concentration in the depositional environment has been shown to positively correlate with CAS concentration under laboratory synthesis (Busenburg and Plummer, 1984). However, the amount of sulfate within modern carbonate on the seafloor varies considerably (200 – 24000ppm), dependent on changes in the biological component (biogenic carbonate contains more CAS) and crystal structure of the carbonate (aragonite vs. calcite vs. dolomite) (Staudt and Schoonen, 1995). The position of the CAS sulfate ion (within the carbonate mineral structure vs. separate phase) has been a subject of intense study (see Staudt and Schoonen (1995) for a summary) but remains poorly quantified. The position of the CAS is important in determining its resistance to diagenetic alteration. Previous work utilizing a number of techniques to identify the location of sulfate within carbonate bearing minerals includes Fourier transform infrared (FTIR), Raman spectroscopy (Staudt et al., 1994; Takano, 1985; Takano et al., 1980), XAFS (Staudt et al., 1994), and XANES (Pingitore et al., 1995). The results suggest CAS is present as a substitution for the carbonate anion within the calcite mineral. The possibility that sulfate is present within carbonate as a separate phase, such as sodium sulfate, has also remained a concern. To analyze the position of CAS within the samples presented here or to examine any potential changes in position associated with diagenesis, Fourier transform infrared spectroscopy was performed on a number of
ancient limestone samples from Meishan section, modern carbonate mud from Fayetteville Green Lake (see below for sample location description), and several synthetic calcite samples. The results of this study are presented in Chapter Two.

1.2 Extraction Method

A variety of extraction methodologies exists for the collection of CAS from limestone. These procedures vary by laboratory and the possibility of bias created by these procedures has led to concern when comparing results within the published literature. To address this concern, several samples from the Salona formation (near Reedsville, PA) were collected and subjected to a series of CAS extractions utilizing procedures from three different laboratories. The samples were subdivided so that each sample could be extracted multiple times. The results of this study are presented in Chapter Three.

1.3 Fayetteville Green Lake

The ability of CAS to retain its initial isotopic composition under euxinic burial conditions in modern systems has not been well documented. Previous work has focused on more normal sweater conditions and has shown CAS to be resistant to any change to its isotopic values despite ongoing sulfate reduction under oxic, iron poor conditions (Lyons et al., 2004). To further examine CAS during the early stages of burial under conditions with high sulfate reduction and ongoing iron sulfide formation, samples have been collected from Fayetteville Green Lake (FGL) near Syracuse, NY (Fig. 1.2). FGL was chosen because it is a meromictic lake that is saturated with calcium carbonate.
Figure 1.2 Fayetteville Green Lake. Modified after Brunskill and Ludlam (1969) and Thompson et al. (1990). DMP: Dead Man’s Point. Samples were collected from both the deep circular portion and shallow neck of the lake.
leading to large amounts of biologically controlled carbonate deposition with annual whiting events (Thompson et al., 1990). This allows CAS to be examined under both oxic and euxinic conditions within the same body of water. To examine if CAS retains the $\delta^{34}\text{S}$ of overlying water, lake water, pore water, and sediment samples from the oxic and euxinic portions of the lake were collected. The samples were all subject to extraction for sulfate and sulfide to determine concentration and isotopic composition, the results of which can be seen in Chapter Four.

1.4 The Permian-Triassic Boundary

Changes in the isotopic composition of sulfate in the ocean during periods of environmental stress, such as the Permian-Triassic mass extinction, have the potential to provide information as to the mechanism which led to the extinction. The Permian-Triassic mass extinction occurred ~251 Ma, and was the largest of the Phanerozoic mass extinctions (Erwin, 1993). The cause of mass extinction remains unknown, but many of the hypotheses rely on mechanisms internal to the biosphere, particularly on the possibility of an anoxic deep ocean (Wignall and Twitchett, 1996). Numerical modeling has shown that the anoxic deep ocean could have become euxinic (Kump et al., 2005). Euxinia is defined here as conditions where the water is both anoxic and contains free sulfide. This euxinic deep water would have created an unstable chemocline resulting in the upwelling of sulfide to the surface environment and possibly the atmosphere triggering the extinction event (Kump et al., 2005). These changes to the global sulfur cycle could have altered the isotopic composition of oceanic sulfate in a way that would be preserved by CAS. Changes in $\delta^{34}\text{S}_{\text{CAS}}$ are examined for three marine sections
spanning the paleo-Tethys ocean, the Meishan and Shangsi sections, both located in southern China, and the Demirtas section, located in Turkey (Fig. 1.3). The results of the CAS studies are detailed in Chapter Five for the south China sections and Chapter Seven for Demirtas.

**Figure 1.3** (A) Modern day locations for the Meishan, Shangsi, and Demirtas sections. (B) Approximate paleo-locations for the three sections. World maps modified after Scotese (2002), South China insert modified after Wignall et al. (1995), Turkey insert modified after Groves et al. (2005).
The potential change to the dominant marine biota brought about by prolonged sulfidic conditions in the surface waters created by the chemocline upward excursions would have created a favorable environment for phototrophic sulfur oxidizing bacteria. Green phototrophic sulfur oxidizing bacteria fractionate carbon utilizing the reverse TCA cycle. The reverse TCA cycle fractionates carbon less than the Calvin cycle used by cyanobacteria/algae presumed to be present during oxic marine conditions creating a smaller $\Delta^{13}C$ (Van der Meer et al., 1998). Therefore, a decrease in $\Delta^{13}C$ ($\delta^{13}C_{\text{carb}}-\delta^{13}C_{\text{org}}$) across the Permian-Triassic would suggest a change to the dominant biota of the surface ocean. Changes to inorganic and organic carbon were measured at all three sections to determine if a change to $\Delta^{13}C$ was present. The changes to the carbon isotopic compositions are presented in Chapter Six for the south China sections and Chapter Seven for Demirtas.

Overall, CAS is shown to be a reliable proxy for sulfate isotopic composition of the overlying water under both oxic and euxinic conditions. The variations in carbon and sulfur isotopic composition measured at these three marine sections suggest that euxinic conditions were present during the end-Permian and may have continued into the Triassic.
Chapter 2

Fourier Transform Infrared Spectroscopy of Carbonate Associated Sulfate in Modern and Ancient Samples

2.1 Abstract

Carbonate associated sulfate (CAS) has become an important proxy for the isotopic composition of oceanic sulfate through time. The controls on the incorporation and the placement of sulfate within carbonate minerals have not been completely determined. The sulfate potentially substitutes for a carbonate anion during precipitation of calcite (or other carbonate mineral). The position of the sulfate within calcite has implications for the ability of CAS to withstand diagenetic alteration. To analyze the position of sulfate within calcite, modern and ancient calcium-carbonate rich samples, as well as several synthetic calcite samples, were analyzed using Fourier transform infrared spectroscopy. The spectra for all samples show peaks associated with vibrational stretching in the $v_3$ band of sulfate, and are consistent with crystallographic sulfate incorporation into calcite as a substitute for the carbonate anion.

2.2 Introduction

The exact process by which sulfate becomes trapped within carbonate (i.e. calcite, aragonite) during precipitation is not fully known. The sulfate concentration of the depositional environment and growth rate of calcium carbonate has been shown to positively correlate with the amount of sulfate incorporated under laboratory conditions.
(Busenburg and Plummer, 1984) as might be expected. However, sulfate concentration within modern oceanic carbonate can vary considerably (200 – 24000 ppm), which is apparently affected by the biological fraction (biogenic carbonate contains more CAS) and crystal structure of the carbonate mineral (Staudt and Schoonen, 1995; Takano, 1980). Therefore, while the concentration of sulfate within the environment helps determine the final CAS concentration, other factors play a substantial enough role that it is impossible to determine ancient seawater sulfate concentration from CAS concentration.

The position of the sulfate ion within the carbonate mineral structure has been a subject of intense study (see Staudt and Schoonen (1995) for a summary) but remains poorly quantified. A number of techniques have been utilized to identify the location and nature of sulfate including Fourier transform infrared (FTIR) and Raman spectroscopy (Staudt et al., 1994; Takano, 1985; Takano et al., 1980), XAFS (Staudt et al., 1994), and XANES (Pingitore et al., 1995). FTIR and Raman spectroscopy have yielded vibrational spectra in the $v_1$, $v_3$ and $v_4$ bands for the S-O bond that are offset from the single $v_3$ peak associated with sulfate in solution and may be distinctly associated with sulfate in carbonate bearing minerals (Takano et al., 1980).

The S-O bond in sulfate is active for IR under different bonding conditions depending on the symmetry of the sulfur bearing compound. In solution, sulfate produces a triply degenerate stretching vibration for $v_3$ at 1105 cm$^{-1}$ with an IR inactive $v_1$ vibration at 980 cm$^{-1}$ (Hug, 1997). When the symmetry is lowered through bonding, the $v_1$ band becomes active (~970 cm$^{-1}$), and the triply degenerate peak splits into two or three peaks depending on bonding (Hug, 1997). The range from 950 to 1250 cm$^{-1}$ covers
the active $v_1$ and $v_3$ stretching vibrations and is thus the focus of this study. Takano (1980) demonstrated three distinct peaks for $v_3$ vibrational stretching at 1140, 1160, and 1180 cm$^{-1}$ associated with CAS in travertine. The samples Takano (1980) analyzed were acid washed to create fresh surfaces and remove any adsorbed sulfate. The samples were also analyzed for the presence of other sulfate-bearing minerals through x-ray diffraction and none were found (Takano, 1980). The peaks measured by Takano (1980) were also distinct from those associated with S-O vibrations stretching during adsorption (Peck et al., 1999). This led to the assertion that the peaks are associated with sulfate being incorporated into the travertine as part of the carbonate lattice, and not as a separate phase.

Takano (1985) showed that the sulfate peaks within travertine were distinct from those of associated sulfur-bearing organic material establishing that the peaks associated with CAS are from an inorganic source. Pingitore et al. (1995), utilizing x-ray absorption near edge structure (XANES), showed that sulfur within carbonate is present in the $6^+$ oxidation state, also suggesting it is present as sulfate. The presence of sulfate as demonstrated by Pingitore et al. (1995) suggests the sulfate is either incorporated into the carbonate structure or present as a separate sulfate phase. However, XAFS of carbonate, aragonite, and dolomite all provided the same spectra for sulfate and were distinct from one another (Pingitore et al., 1995). This suggests that if the sulfate were a trace phase it is different under different mineralogy, but is the result expected for sulfate substituting under different structures. Staudt et al. (1994) demonstrated that the larger tetrahedral selenate can be incorporated into the calcite lattice under laboratory conditions,
substituting for a carbonate anion. This suggests that the smaller sulfate tetrahedra can occupy a similar position within the carbonate lattice (Staudt et al., 1994).

The possibility remains that sulfate is present within carbonate as a separate phase, such as sodium or calcium sulfate remains. Sodium ions are incorporated into carbonate during crystal growth, as the distortion of the carbonate lattice created by introducing the larger sulfate ion (compared to carbonate) has been suggested to be balanced by the inclusion of the smaller sodium ions (compared to calcium) (Busenberg and Plummer, 1984). However, the ratio of Na/Ca and SO$_4$/Ca in the depositional environment under laboratory conditions can control these ratios in the synthetic carbonate, suggesting that sodium and sulfate would provide a positive correlation without a coupled incorporation mechanism making any coupled mechanism difficult to deconvolve (Staudt et al., 1993). Overall, the current body of evidence shows CAS is present as sulfate substituting for a carbonate anion within calcite or other carbonate mineral.

To examine the S-O vibrational peaks associated with CAS, a set of natural and synthetic calcite samples were analyzed using Fourier transform infrared spectroscopy (FTIR) after the method of Takano et al. (1980). A diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) detector was utilized. This technique has been shown to provide vibrational spectra which are modified by sulfate bonding which affects symmetry. Changes to the symmetry of the sulfate as it is incorporated to the carbonate can provide information as to the nature of the bond and potentially its position within the carbonate matrix. The natural samples included modern calcareous sediments from Fayetteville Green Lake (FGL; Chapter Four) and ancient limestone from the Permian
Meishan section (S. China, Chapter Five). The synthetic samples were provided by Dr. Martin Schoonen (SUNY Stony Brook) and contain known amounts of sodium and sulfate. These samples were chosen because they represent three different conditions where CAS can be analyzed. The ancient limestone samples are known to contain CAS of various isotopic composition (Chapter Five), while the modern carbonaceous mud all contain similar CAS concentrations and isotopic composition (Chapter Four). The synthetic samples provide a comparison of known crystallization conditions and concentrations.

The ability of CAS to withstand diagenetic alteration has also remained a concern when interpreting CAS isotopic values from ancient limestone. If CAS were present as a separate phase within the carbonate mineral, or adsorbed to the surface, it may be more readily exchanged during diagenesis than if CAS is substituted into the calcite lattice. This is especially important for isotopic values of CAS which fall outside of normal seawater isotopic composition, such as those measured prior to the end-Permian mass extinction (Chapter Five, Seven) where diagenetic alteration is a significant concern.

2.3 Method

The limestone and mud samples were dried and powdered prior to analysis. All samples were diluted with the same amount of KBr for analysis using DRIFTS. The CAS concentrations for the Meishan samples are ~4000 ppm for MBPT 34B, ~5000 ppm for MBPT 30H, and ~1700 ppm for MDPT -3. The FGL samples all contained substantially higher CAS concentrations ranging between 15000-20000 ppm. The synthetic calcite samples contained between 2700-4000 ppm. The Meishan and Shangsi samples were analyzed on a Thermo Nicolet Nexux 670 at SUNY Stony Brook. The
FGL samples were analyzed on a Bruker IFS 66/S FTIR at the Penn State Materials Research Institute. All were scanned from 3500 to 600 cm\(^{-1}\) wavelength. Fischer-brand pure calcite was also analyzed under the same conditions. The spectrum for calcite was subtracted from the Meishan sample spectra to remove peaks associated with pure CaCO\(_3\) making the S-O peaks easier to examine. The spectra were analyzed using PeakFit software (ver. 4.12) where an artificial baseline was set at 1250 and 950 cm\(^{-1}\) and residual peaks were determined using a Gaussian-amp distribution.

2.4 Results

Three representative spectra collected from the Meishan section can be seen in Fig. 2.1. Peaks within the active range for S-O vibrational stretching are labeled. Spectra for the FGL samples are shown in Fig 2.2. The FGL spectra provided peaks similar to those measured in the ancient limestone samples (Fig. 2.2). The synthetic calcite samples also provided a similar array of peaks for the 950 to 1250 cm\(^{-1}\) range and are shown in Fig. 2.3. All three sample sets yielded peaks near 1140, 1160, and 1180 cm\(^{-1}\) which are associated with the \(v_3\) band for sulfate. Peaks associated with the \(v_3\) band of sulfate were found in all samples, while only the synthetic samples contained measurable peaks for the \(v_1\) band as well.

2.5 Discussion

Analysis of the ancient limestone, modern calcite rich mud and synthetic calcite provide spectra associated with the \(v_3\) band for sulfate. In all cases, vibrational stretching associated with the \(v_3\) band provides three distinct peaks, as the initial, triply degenerate peak is divided from 1100 cm\(^{-1}\) to 1140, 1160, and 1180 cm\(^{-1}\) (Takano, 1980). This peak
Figure 2.1 Three representative FTIR spectra from Meishan section. The active region for S-O bonding is shown. Main curve is the collected spectra, labeled small peaks are residual peaks from Peakfit. The peaks at 1180, 1160, and 1140 cm⁻¹ are associated with S-O bonding.
Figure 2.2 Spectra from three samples spanning the oxic core at FGL. Note the different horizontal scales between the three panels. Label indicates depth below the sediment water interface. Peaks found the same as Fig. 2.1.
Figure 2.3 FTIR spectra for the synthetic calcite samples. Peaks associated with the $v_3$ band for sulfate are labeled. The peak at 1082 cm$^{-1}$ is from the calcite spectra. Peaks found through the same method as Fig. 2.1.
placement for the \( v_3 \) spectra in all of the sample sets is similar to that of Takano (1980), although several of the peaks from FGL are shifted slightly, which may be due to the less lithified nature of the samples (Fig 2.2). For sulfate incorporated into carbonate, the \( v_1 \) band is shifted to 1016-1018 cm\(^{-1}\) (Takano, 1980). The peak associated with the \( v_1 \) band is not visible in the Meishan or FGL samples, but is present in the synthetic calcite samples (Fig. 2.1, 2.2, 2.3). The missing peak associated with the \( v_1 \) band may be obscured in the natural samples by the large peak at \( \approx 1030 \) cm\(^{-1}\). This would make it impossible to see any smaller peak associated with a trace amount of sulfate. There are two peaks measured in the 950-1250 cm\(^{-1}\) range which are not associated with sulfate. All of the samples from Meishan contain moderate to high clay components and the peaks observed at 1030 and 1112 cm\(^{-1}\) may be due to the clay component of the limestone. The peak at 1030 cm\(^{-1}\) is active for montmorillonite and the peak at 1112 cm\(^{-1}\) is associated with Si-O-Al containing compounds (Mashal et al., 2005; Lee et al., 2003).

### 2.5.1 CAS Incorporation vs. Adsorption

The possibility that the included CAS sulfate is adsorbed onto the surface of the samples must also be considered. Peak et al. (1999) measured adsorption of sulfate onto goethite using a flow-through cell with attenuated total reflectance on FTIR. The peaks determined to be associated with S-O bonds were at 1170, 1133, 1051 cm\(^{-1}\) for \( v_3 \), and 977 cm\(^{-1}\) for \( v_1 \) (Peak et al., 1999). The peak at 1170 cm\(^{-1}\) shifts to 1200 cm\(^{-1}\) when dried for analysis under DRIFTS (Peak et al., 1999). These are distinct from the peaks measured for all of the samples in the present study. This is especially important for the FGL samples, where adsorbed sulfate was most likely to be present, due to the lack of lithification in the samples and the extremely high CAS concentrations. Therefore, the
Figure 2.4 Spectra of thenardite and gypsum compared to a representative limestone from Meishan. Note the different horizontal scales between the panels. The peaks are determined through the same method as Fig 2.1.
absence of peaks normally associated with adsorption in samples suggests that the sulfate being measured here is not adsorbed onto surfaces, but is incorporated into the calcite.

2.5.2 Other Sulfate Bearing Minerals

The possibility of the sulfate being present in a separate mineral phase must also be considered. Spectra from sodium sulfate (thenardite) and calcium sulfate (gypsum) collected at SUNY Stony Brook, were compared to the spectra from the limestone samples (Fig. 2.4). Gypsum is expected to provide three peaks in the $v_3$ range at 1117, 1145, 1167 cm$^{-1}$ (Prasad et al., 2005). The gypsum analyzed for this study provided all three of these peaks (Fig. 2.3). The peaks at 1114 cm$^{-1}$ and 1145 cm$^{-1}$ are similar to the 1112 cm$^{-1}$ and 1140 cm$^{-1}$ peaks measured in the samples at Meishan. This could indicate the presence of some gypsum. However, the lack of an 1167 cm$^{-1}$ peak and that the 1140 cm$^{-1}$ peak is present for CAS and the 1112 cm$^{-1}$ peak is associated with clay mineralogy makes determining the presence of gypsum inconclusive by this method alone. The peaks for the $v_3$ band of sulfate measured in the Meishan and FGL samples do not appear to contain calcium sulfate as a contaminant.

Thenardite produces peaks associated with S-O bonding at 983 ($v_1$), 1120, 1138, and 1153 cm$^{-1}$ (Takano, 1980). The sample measured here produced a peak at 978, 1158, and 1199 cm$^{-1}$, but not at 1138 or 1120 cm$^{-1}$. The $v_1$ peak associated with thenardite does not match any of the carbonate samples, and only one of the peaks for the $v_3$ in the measured sample is similar to that of the carbonate. Overall, comparison of other sulfate bearing minerals to calcite samples from Meishan, FGL, and synthetic calcite provides
distinct peak differences (Fig. 2.4). Therefore, the sulfate is most likely present as a substitute for carbonate anion and not as a separate phase.

2.6 Conclusions

The spectra collected here are in agreement with those of Takano et al. (1980), suggesting the sulfate is present as a substitute for carbonate anion within the limestone. The spectra from FGL are similar to the ancient limestone, with slight differences in peak placement. The synthetic calcite samples provide similar peaks to the natural samples collected. The incorporation of sulfate into the calcite lattice suggests that it is not easily altered during diagenesis without extensive recrystallization, which helps to support the integrity of CAS as an isotopic proxy for ancient seawater sulfate. This is particularly important for the FGL samples which are the least indurated and therefore most likely to be altered during burial. The spectra measured for the natural and artificial samples support the current paradigm that CAS is incorporated into the carbonate mineral as a substitution for carbonate anion.

2.7 Acknowledgements

I would like to thank Martin Schoonen (SUNY Stony Brook) for laboratory access and providing the synthetic carbonate samples and Alex Smirnov (SUNY Stony Brook) for assistance in running the FTIR. I would also like to thank Josh Stapleton at the Penn State Materials Research Institute for analyzing the Fayetteville Green Lake samples. This work was supported by the Penn State Biogeochemical Research Initiative for Education (BRIE) sponsored by NSF (IGERT) grant DGE-9972759.
Chapter 3

A Comparison of Extraction Methodologies for Carbonate Associated Sulfate

3.1 Introduction

The potential for bias between the different carbonate associated sulfate (CAS) extraction methods utilized in various published studies has remained a concern in comparing CAS isotopic values. The various techniques employed to extract CAS all follow a similar methodology but differ in the number and length of cleaning treatments. The purpose of these treatments is to remove any sulfur bearing compounds which could contaminate the final CAS extract. The samples are typically rinsed with some combination of deionized water (DIW), sodium hypochlorite, hydrogen peroxide, and acetone. The deionized water removes any salts which may have precipitated, while the sodium hypochlorite removes any organic sulfur compounds. Hydrogen peroxide can be substituted for sodium hypochlorite in samples which are high in pyrite and acetone is only used when high concentrations of elemental sulfur are suspected (i.e. modern samples).

To test the effect different extraction methodologies may impart, a series of extractions were performed on several late Ordovician samples collected from the Salona formation (near Reedsville, Pennsylvania). Extraction methods from three different laboratories (Penn State (Riccardi et al, 2006), UC Riverside (Tim Lyons, Pers. Comm.) and USC (Pedro Marenco, Pers. Comm.) were performed. The results show that while
there was some scatter between the methods, no single method provided consistently lower or higher CAS isotopic values. Therefore the exact length of the various cleaning procedures does not significantly alter the final results, but remain important in preparing a sample for analysis.

### 3.2 Methods

For all methods samples were cut and powdered before the cleaning procedures. Each sample for all the methods was also analyzed for pyrite concentrations on a CE 2500 elemental analyzer. The results are presented in wt % relative to the initial dry mass.

#### 3.2.1 Penn State Method

Following the method of Riccardi et al. (2006), samples were immersed in 300-400 mL of sodium hypochlorite (6%), stirred for 1h, and left covered for 12h. The solution was then filtered and rinsed three times with DIW to remove any remaining bleach or contaminants which may have been oxidized during this step. The samples were then dissolved and filtered as described for the Demirtas samples. The remaining solution had 25 mL of a 250 g/L BaCl$_2$ solution added and was heated for 1h. The solution was allowed to precipitate for 12h, before the barite was filtered and prepared for isotopic analysis. Subsets of the barite (0.4-0.5 mg) were combined with 4-5 times by weight V$_2$O$_5$ to stabilize oxygen isotope ratios after (Yanagisawa and Sakai, 1983) and sent to the Stable Isotope Laboratory at Indiana University, Bloomington for analysis. All isotopic values are reported in standard per mille notation ($\‰$) relative to VCDT.
3.2.2 UC Riverside Method: Bleach

Following the method provided by Tim Lyons (Pers. comm.) samples were covered with ~1L DIW and left for 24h to remove soluble sulfate salts. After this, the DIW was decanted and this step was repeated. The samples were then immersed in 300-400 mL of a sodium hypochlorite (6%) solution for 48h. Following this, the samples were filtered and rinsed with DIW to remove oxidized sulfide or other contaminates and reacted with the 25% HCl solution and filtered as described above. The dissolved limestone had 125 mL of concentrated BaCl₂ solution added to it and left to precipitate overnight. Samples were collected on 0.45 µm filters and dried before being weighed and prepared for isotopic analysis.

3.2.3 UC Riverside Method: Hydrogen Peroxide

The samples were prepared identically to above, except a 30% hydrogen peroxide solution was substituted for the 6% sodium hypochlorite solution for 48h.

3.2.4 USC Method

Following the method provided by Pedro Marenco (Pers. comm.) powdered samples were immersed in ~1L DIW for 8h. The samples were then filtered, and a second 8h DIW rinse was performed. The samples were filtered again and treated with a sodium hypochlorite solution containing 52.5 mL 6% NaOCl in 947.5mL DIW for 8h. The samples were filtered and rinsed multiple times with DIW and dissolved in HCl and filtered as described above in the previous methods. The original USC method used exact stoichiometric ratios of HCl for each sample. This was because of worry that excess HCl would oxidize pyrite. This was changed since the end result of complete
dissolution is the same, and there is currently no evidence that pyrite oxidizes this readily. The dissolved limestone then had 50 mL of the BaCl\(_2\) solution added to it and was left to precipitate for 3 days before the barite was collected and prepared as described above.

### 3.2.5 Hybrid Method

The samples were immersed in 1L deionized water (DIW) for 24h, and decanted before 300-400 mL of a 6\% sodium hypochlorite solution was added and left for 18h. The sodium hypochlorite solution was decanted off and samples were filtered and rinsed three times in DIW. The samples were then reacted with a 25\% HCl solution until no visible reaction remained and left on a stir plate for 1h, before a small quantity of acid was added to ensure the reaction had run to completion. The samples were filtered using Whatman 40 filter paper to remove insoluble residue. The solution was then filtered through 0.45 \(\mu\)m membrane filters, 50 mL of a saturated (250g/L) BaCl\(_2\) was solution added, and the mixture was heated for 30 min and left to precipitate for 12-18h. The precipitated barite was filtered using 0.45 \(\mu\)m membrane filters, dried, weighed and prepared for isotopic analysis as above.

### 3.3 Results

The isotopic values for each sample under the various methods are shown in Fig. 3.1. The variation between the methods was small (average standard deviation of 1.65\%) with no individual method trending towards lighter or heavier values throughout. The concentration of CAS from each method varied somewhat more than the isotopic composition with standard deviations ranging from 40 to 140 ppm (Fig. 3.2). Again, no individual method provided consistently higher or lower values, and the differences in
concentration did not correlate with the changes to isotopic composition. Pyrite concentration for all samples was very low (Table 3.1).

**Table 3.1** Data from the comparison of different CAS extraction methods. The $\delta^{34}$S is for CAS and relative to VCDT. Spy = pyrite sulfur; [CAS] = CAS concentration in ppm SO$_4$.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Penn State [CAS]</th>
<th>UC: Bleach $\delta^{34}$S</th>
<th>UC: Peroxide [CAS]</th>
<th>USC [CAS]</th>
<th>Hybrid [CAS]</th>
<th>$\delta^{34}$S (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>143</td>
<td>16.44</td>
<td>167</td>
<td>101</td>
<td>127</td>
<td>16.71</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>-</td>
<td>91</td>
<td>139</td>
<td>80</td>
<td>24.85</td>
</tr>
<tr>
<td>3</td>
<td>218</td>
<td>15.56</td>
<td>139</td>
<td>257</td>
<td>164</td>
<td>18.08</td>
</tr>
<tr>
<td>4</td>
<td>496</td>
<td>19.60</td>
<td>199</td>
<td>204</td>
<td>174</td>
<td>22.49</td>
</tr>
</tbody>
</table>

**Figure 3.1** Changes in the isotopic composition of CAS for the test samples under various extraction methods.
3.4 Discussion

The various methodologies for CAS extraction did not provide evidence for bias from any single method. However, the range of variation in the results for a given sample merits some concern. While the standard deviation between the methods when compared to the average is low (~1.5‰) the overall scatter is larger (~5‰). The largest scatter was measured in the sample processed with hydrogen peroxide. Hydrogen peroxide is typically used in samples containing high concentrations of pyrite and oxidizes some of the pyrite which is then removed with DIW rinses. However hydrogen peroxide only oxidizes ~30% of the pyrite at most and leaves the majority untouched (Borah et al., 2005). The easily oxidized pyrite which would be most likely to contaminate the final CAS extract is therefore removed. All of the samples measured in this study contained low concentrations of pyrite sulfur (0 to 0.1%), however, leaving the
contribution of pyrite oxidation during sample analysis a concern. The differences in CAS concentration between the methods suggest that extreme care must be taken during extraction, as slight changes during sample collection can result in different concentrations. Overall, the lack of bias imparted by any given extraction procedure suggests that all are providing similar results and are all valid methods for extracting CAS.

3.5 Conclusion

The low standard deviation between the methods shows that data sets from various laboratories can be compared with little difference however, since these variations are much smaller than those measured in actual sections (Newton et al., 2005; Chapters Five, Seven). Therefore, while the cleaning and pre-rinsing steps are important during sample preparation, slight variations do not impart a particular bias to the final result. Overall, the exact methodology should be designed specifically for the sample set in question. The pyrite concentration, presence of sulfur bearing salts, and other sulfur compounds should be examined to determine which rinse steps are necessary to ensure that the final extract contains only CAS sulfur and not sulfur from any other source.

3.7 Acknowledgements

I would like to thank Pedro Marenco (USC) and Ben Gill (UC Riverside) for providing their laboratory methodologies for use in this comparison and for helpful discussion along the way. I would also like to thank William Rouse for his help during sample preparation. This work was funded by the Penn State Biogeochemical Research Initiative for Education (BRIE) sponsored by NSF (IGERT) grant DGE-9972759.
Chapter 4

Evaluation of Carbonate Associated Sulfate as an Isotopic Proxy under Euxinic Conditions

4.1 Abstract

Carbonate associated sulfate (CAS) is an important proxy in determining changes in global sulfur cycling over geologic time. However, there have been few studies examining the stability of CAS as an isotopic proxy in modern environmental settings, particularly under euxinic conditions. To examine possible changes to CAS initially incorporated in surface waters and deposited under euxinic vs. oxic water conditions, lake water and sediment core were collected from meromictic Fayetteville Green Lake. The sediments and lake water were analyzed for sulfate and sulfide concentration and isotopic composition. The isotopic values for CAS remained constant at both sections despite large quantities of sulfate reduction within the pore water. The CAS isotopic values remained the same as those found in the mixolimnion, showing that CAS can be resistant to diagenetic effects during the early stages of burial under both oxic and euxinic conditions.

4.2 Introduction

Variations in the isotopic composition of oceanic sulfate provide information about past environmental conditions. Carbonate associated sulfate (CAS) is an important proxy for determining isotopic composition and, perhaps, concentration of ancient seawater sulfate. For example during the Neoproterozoic extremely small CAS
concentrations, combined with high positive excursions in $\delta^{34}S_{\text{CAS}}$ have been hypothesized to indicate an isolated, anoxic ocean experiencing almost total sulfate reduction created during snowball Earth conditions (Hurtgen et al., 2002). Prior to the development of CAS as an isotopic proxy, the majority of sulfur isotopic data was obtained from evaporites (which are relatively rare in the stratigraphic record) and pyrite (the seawater component of which can be difficult to deconvolve). CAS, being deposited in open ocean environments has no such bias, and limestone is ubiquitous in the rock record allowing for a more complete examination of changes to sulfate isotopic values through time. Burdett et al. (1989) showed that CAS accurately records the $\delta^{34}S$ of oceanic sulfate with insignificant fractionation during burial in modern to Neogene marine carbonates. Burdett et al. (1989) showed that CAS can be effectively used as a proxy for paleo-seawater sulfate isotopic composition.

However, the exact position of sulfate within carbonate minerals remains a subject of intense study. Several studies have indicated that sulfate is most likely incorporated into carbonate, substituting for a carbonate ion. The sulfate is known to be present in the $6^+$ oxidation state, suggesting it is present as sulfate (Pingitore et al., 1995). Fourier transform infrared spectroscopy (FTIR) has been utilized to show that the sulfate in calcite is not present as an organic compound (Takano, 1985) and that the alterations in peak positions associated with the S-O bond suggest the sulfate is bonded within the carbonate (Takano et al., 1980). The tetrahedral selenate ion has been shown to substitute for the carbonate ion in synthetic calcite under laboratory conditions, suggesting that the smaller sulfate ion can be incorporated through a similar process (Staudt et al., 1994). These studies along with the work presented in Chapter Two
suggest sulfate is present in carbonate as a substitution for a carbonate ion, and not present as a separate phase.

Previous work (Lyons et al., 2004) has shown that CAS is resistant to isotopic overprinting during early diagenesis, even in the presence of significant post-depositional sulfate reduction. The Florida bay site chosen for the Lyons et al. (2004) study is extremely iron poor limiting mineralization of sulfide, and therefore may not fully assuage concern over the ability of CAS to withstand alteration in active pyrite forming environments. The Florida bay site also is overlain by oxic water and the effect of euxinic conditions on the preservation of CAS has not been extensively studied in modern environments. To investigate this possibility we have chosen Fayetteville Green Lake (FGL) as a study site to examine changes to CAS concentration and isotopic composition during burial under euxinic and non-euxinic conditions in a meromictic lake. FGL (Fig. 4.1) is a small (surface area: 0.258 km$^2$), deep (~52 m) stratified lake, with oxygenated surface waters and euxinic deep waters separated by a chemocline, typically at 18 to 20 m depth (Brunskill and Ludlam, 1969). The sulfate concentration in the lake is approximately half that of modern seawater, and is derived from groundwater input to the monimolimnion from a watershed replete with Silurian gypsum-bearing evaporites (Takahashi et al., 1968).

Several studies have documented the isotopic composition and concentration of sulfate and sulfide within the water column at FGL. The isotopic composition of sulfate in the water column has remained consistent through time in all studies, values of $\delta^{34}\text{S}$ for lake water studies are within 1‰ of those measured in this study (Brunskill and Ludlam,
Figure 4.1 Fayetteville Green Lake, sample sites are marked (1) Oxic core; (2) Euxinic core. Inset shown location near Syracuse, NY. Modified after Brunskill and Ludlam (1969) and Thompson et al. (1990). DMP = Dead Man’s Point.
1969; Deevey et al., 1963; Fry, 1986). Water column dissolved sulfide $\delta^{34}\text{S}$ may have varied by up to 5‰ at any given depth between all studies. There is little pyrite formation within the lake water (15% of total pyrite), with the majority formed in the top 10 cm of the sediment (Suits and Wilkin, 1998). The sediments from the euxinic portion of the lake are varved, unlike those from the oxic portion. Suits and Wilkin (1998) found remarkable similarity in pyrite concentration, organic carbon concentration, and degree of pyritization between sediments deposited under oxic conditions and those deposited under euxinic conditions. A difference in the isotopic composition of chromium reducible sulfide between the oxic and euxinic sediments of approximately 10‰ was measured over the top 20 cm of the core samples by a previous study (Suits and Wilkin, 1998). Sulfate within the sediments and pore water has not previously been examined.

Two sediment cores (Fig 4.1) were collected, in Fall, 2006, along with water samples spanning the depth of the lake. The lake water and pore water samples were analyzed for sulfide and sulfate concentrations and isotopic compositions, and CAS and Fe-sulfide was extracted from the sediment to determine sulfur concentration and isotopic composition. Isotopic analysis confirms that CAS retains a faithful record of overlying water isotopic composition despite the presence of iron sulfide formation, and sulfate reduction.

### 4.3 Method

#### 4.3.1 Lake Water

Samples from FGL were collected in November of 2006. Lake water was collected from a single location at the deepest part of the lake (Fig 4.1). The lake water
was pumped from depth, filtered through a 0.45 µm inline filtration system, and added to 250 mL beakers containing 15-20 mL of either a saturated (250 g/L) BaCl$_2$ solution or a 20% ZnAc solution, precipitating sulfate or sulfide respectively. The containers were filled to the top leaving no headspace, sealed, and kept chilled for transport back to the lab. The precipitate was filtered (24-48 h later), dried and weighed before being prepared for isotopic analysis.

4.3.2 Core Samples: Pore Water

Core samples were taken at two locations (Fig 4.1) using a 45 cm long gravity core. The oxic core samples were taken from the shallow neck of the lake at ~17 m depth (above the chemocline) and the euxinic core samples near the middle of the round part of the lake at 52 m depth. The core from shallow depth is termed “oxic” and the deep core “euxinic” based on the overlying water chemistries. The coring device contained plastic liners, which were immediately sealed upon core retrieval for transportation to the shore. The core samples were separated into 3 cm$^3$ intervals in a N$_2$ glovebox, sealed in centrifuge tubes and kept on ice for transport back to Penn State. In the lab, the tubes were centrifuged at 3500 rpm for 7 minutes and the pore waters decanted and filtered at 0.2 µm in an anoxic glove box. ZnS was precipitated through the addition of 1 mL of ZnAc to each sample. The remaining sediment was frozen for later analysis. The ZnS precipitate was removed by filtration, and 1 mL of a concentrated BaCl$_2$ solution added to the remaining lake water to precipitate sulfate. Exact concentrations of pore water sulfide at FGL were not measured due to co-precipitation of zinc carbonate with zinc sulfide.
4.3.3 Core Samples: Sediment

Sediment from the core samples were soaked in 1 L deionized water (DIW) for 24 h. The DI was then decanted off and the samples were soaked in acetone for 24 h to remove any elemental sulfur. The acetone was filtered and the remaining solid samples rinsed in DIW. This was followed by a 24 h rinse in a 6% sodium hypochlorite solution before being filtered and rinsed in DIW again. The samples were then dissolved in a 25% HCl solution and the insoluble residue was filtered using Whatman 40 filter paper, followed by 0.45 µm membrane filters. The remaining solution had 50 mL of saturated barium chloride solution added to it and was allowed to sit for 24 h to precipitate. The filtrate was collected and prepared for isotopic analysis. The insoluble residue from this procedure was dried and approximately 1 g was added to a reaction vessel for extraction of acid volatile sulfide and chromium reducible sulfide (AVS+CRS) following the procedure of Canfield et al. (1986).

4.3.4 Carbon

Sediment from the core samples was dried, and decarbonated using 25% HCl, before being filtered through 0.45 µm membrane filters. The insoluble residue was combusted on a CE 2500 (C, N, S) elemental analyzer. The results are presented at weight % relative to initial dry mass.

4.3.5 Isotopic Analysis

Sample preparation for isotopic analysis was the same for all samples, following the method of Yanagisawa and Sakai (1983). Barite samples were weighed into 0.4-0.5 mg increments and mixed with 4-5 times by weight V_2O_5. For sulfide samples, 0.2-0.3
mg of samples were weighed and again mixed with 4-5X V₂O₅ before being loaded into tin capsules and sent to Indiana University, Bloomington for analysis. All isotopic values are reported in standard per mille notation (‰) and are relative to VCDT.

4.4 Results

4.4.1 Lake Water

The results from the lake water analyses are shown in Fig. 4.2 (A, B). Sulfate concentration in the lake increases from ~11 mmol/L near the surface to ~16 mmol/L just below the chemocline before slightly decreasing towards the bottom of the lake (Fig. 4.2A). The sulfide concentration remains zero until the chemocline where it rises abruptly to 0.3 mmol/L and then increases to ~1.1 mmol/L at depth (Fig. 4.2A). Total sulfur (sulfate + sulfide) concentrations increase throughout the mixolimnion reaching a maximum at the chemocline (Fig. 4.2A). The isotopic values for the sulfate (Fig. 4.2B) remain ~24‰ for the mixolimnion, and steadily increases below the chemocline to ~29‰ at depth. The sulfide isotopic values decrease from the chemocline to 30 m depth before increasing through the monimolimnion (Fig. 4.2B). These changes create Δ³⁴S values of around 50‰ for the monimolimnion with a peak at 30 m (Fig. 4.2B). Results from isotopic analyses on lake water collected and analyzed in November 2002 are shown for comparison (Fig. 4.2B).
4.4.2 Oxic Core

Pore water sulfate concentrations decrease from 7 mmol/L near the sediment water interface to 1 mmol/L at the bottom of the core (Fig 4A). The pore water sulfate concentration at the top of both cores is ~7 mmol/L lower than that of the overlying surface water which is most likely due to a loss of the sediment-water interface during coring. The $\delta^{34}S$ of pore water increases from 30-60‰ along this same range (Fig 4.3B). The CAS isotopic composition remains constant (~24‰) for the entire length of the core (Fig 4.3C), with CAS concentration remaining between 15000-20000 ppm $SO_4$ (Fig 4.3D). The $CaCO_3$ component of the sediment remains between 80-90% for the majority of the core, with one sample containing only ~60% (Fig. 4.3E). The sulfide concentration in the sediment (in the form of AVS +CRS) decreases from 3 to 12 cm and
remains low until 30cm when it increases to its highest values at the bottom of the core (Fig 4.3F). The isotopic composition of the AVS+CRS remains near -21‰ for the majority of the core, before trending towards much heavier values below 30cm (Fig 4.3G); data from Suits and Wilkin (1998) are shown for comparison. This produces a fairly constant $\Delta^{34}S$ (for core sediments, $\Delta^{34}S=\delta^{34}S_{\text{CAS}} - \delta^{34}S_{\text{AVS+CRS}}$) for the core of ~45‰ (Fig. 4.3H) with the exception of the deepest sample. Organic carbon concentrations within the sediment increase slightly with depth from 1.5 to 2.5 wt%, with a peak of 3.5 wt. % at 20 cm (Fig 4.3I).

4.4.3 Euxinic Core

In contrast to the oxic core, the euxinic core displays a lesser signature of early diagenesis in its pore water concentrations and isotopic values. The pore water sulfate concentrations decrease slightly with depth (with one exception) from ~9 to ~5 mmol/L (Fig 4.4A). The pore water sulfate isotopic values increase with depth from ~35 to 45‰ (Fig 4.4B) while the CAS isotopic values (Fig 4.4C) remain constant at ~25‰ (with one exception). CAS values remain between 15000-20000 ppm (Fig 4.4D), although one sample contained ~55000 ppm. The sample with unusually high pore water sulfate concentration also had heavier CAS isotopic composition but not unusually high CAS concentration. The percent CaCO$_3$ in the euxinic core also remains high (80-100%) with one sample containing only ~75%. AVS+CRS concentration in the sediment decreased slightly with depth (Fig 4.4F) while the isotopic values remained fairly constant (Fig 4.4G) producing a $\Delta^{34}S$ around 50‰ (Fig 4.4H). Organic carbon concentrations increased from 1 to 2.0 wt% at 13 cm depth before decreasing to 0.60% to the bottom of the core (Fig 4.4I).
Figure 4.3 Data from the oxic core (site 1). (A) Porewater sulfate concentration; (B) Porewater sulfate isotopic composition; (C) CAS isotopic composition; (D) CAS concentration; (E) AVS+CRS concentration in sediment; (F) AVS+CRS isotopic composition; (G) $\Delta^{34}S$ ($\delta^{34}S_{CAS}-\delta^{34}S_{AVS+CRS}$); (H) Organic carbon concentration.
Figure 4.4 Data from the euxinic core (site 2), note different vertical scale from oxic core. (A) Porewater sulfate concentration; (B) Porewater sulfate isotopic composition; (C) CAS isotopic composition; (D) CAS concentration; (E) AVS+CRS concentration in sediment; (F) AVS+CRS isotopic composition; (G) $\Delta^{34}S$ ($\delta^{34}S_{\text{CAS}}-\delta^{34}S_{\text{AVS+CRS}}$); (H) Organic carbon concentration.
4.5 Discussion

4.5.1 Lake Water

Sulfur concentrations in the lake reach a maximum just below the chemocline, and remain relatively constant throughout the monimolimnion (Fig. 4.2B). This is consistent with sulfur input to the lake from sulfate-rich groundwater. The constant total sulfur throughout the monimolimnion suggests ongoing sulfate reduction, as sulfate concentrations decrease, while sulfide concentrations increase with depth (Fig. 4.2A). This is supported by $\Delta^{34}$S values ~50‰ for the monimolimnion, which are typically associated with disproportionation reactions (Canfield and Thamdrup, 1994). Continued disproportionation (through the production of thiosulfate and elemental sulfur) within the monimolimnion would explain these higher fractionations. An isotopic mass balance of the sulfate and sulfide for the monimolimnion shows that the isotopic depletion of the sulfide matches the enrichment of the sulfate until 30m depth. A secondary chemocline associated with additional groundwater input and therefore an influx of sulfur has been previously suggested for 30m depth (Torgersen et al., 1981). While total sulfur appears to remain constant (Fig. 4.2B) the lack of detailed sampling around this region does not preclude this possibility. Below 30m the $^{34}$S depletion in sulfide is not sufficient to match the $^{34}$S enrichment of sulfate. Additional sulfide formation (approximately ~1.6 mmol/L) would balance, suggesting additional sulfur species may be present. Regardless, disproportionation reactions appear to play a large role in the sulfur cycle of the lake below 30m depth.
4.5.2 Pore Water

Alteration of the CAS isotopic signal during early diagenesis does not appear to have substantially altered the oxic or euxinic core samples. CAS from both the oxic and euxinic cores at FGL show remarkable consistency with depth, despite changes to the surrounding pore water sulfate concentration and isotopic composition (Fig 4.3C, 4.4C). The isotopic composition of the pore water sulfate in the oxic core increases by almost 30‰ over the 42cm depth, driven by sulfate reduction as the pore water sulfate concentration decreases (Fig 4.3A, B). A similar pattern is observed in the euxinic core, where pore water sulfate concentrations also drop but don’t reach the low values of the oxic core, leading to a smaller increase in pore water sulfate isotopic compositions (Fig 4.4A, B).

The decrease in pore water sulfate concentration is controlled by two processes, diffusion of sulfate from the overlying lake water and sulfate reduction within the pore water. To evaluate the relative importance of these two processes, a simple box model of the system was created using Stella (v. 8.1.4, ISEE systems). Twelve layers, each 7cm, were created to cover a greater area than the oxic core length. The model was constructed over a greater depth than was sampled to avoid influence of the lower boundary condition (zero) on the results. The upper boundary condition was set to 13 mmol/L, the concentration of sulfate in the water overlying the oxic core. Diffusion between the layers was calculated according to Fick’s law, with a diffusion coefficient for sulfate of 316 cm²/yr (Aller, 1980). The data are best fit to the model (using sulfate reduction rate as the tuning parameter) with high sulfate reduction rates in the topmost layer (~25 mM/yr), a drop to ~4 mM/yr in the second layer, and then 1 mM/yr for the remainder of
calculated depth (Fig. 4.6). The oxic core data are set to slightly (3.5 cm) deeper values to crudely account for the unknown amount of sediment was lost off the top of the core, due to the loss of the sediment water interface while coring. These rates compare favorably with those measured in euxinic sediments of the Mariager Fjord, who measured a similar trend in sulfate reduction rates within their sediments (Sorensen and Canfield, 2004).

This decrease in pore water sulfate with an accompanying increase in isotopic composition is similar to measurements of Black Sea sediment (Jorgensen et al., 2004). In the Black Sea sediments, a corresponding increase in H$_2$S concentration within the pore water was measured as pore water sulfate decreased (Jorgensen et al., 2004). The difference between H$_2$S and SO$_4$ isotopic compositions in the Black Sea pore waters remained high (~60‰) which Jorgensen et al. (2004) suggested was created by continued disproportionation reactions within the sediment through redox reactions with an iron-rich layer. While no data on the H$_2$S concentrations for Green Lake was available, the similarities in the sulfate concentration and isotopic composition, as well as the high $\Delta^{34}$S values measured in the lake water also favor continued disproportionation reactions within the lake below the chemocline.

4.5.3 Sulfide

Sulfide is measured in the sediment as AVS+CRS, and provides similar isotopic composition to that of the overlying surface waters for all but the lower sediments of the oxic core. The isotopic composition of the sulfide within the oxic core sediments differs from that of Suits and Wilkin (1998) where a 12‰ shift from the top of the core to
approximately 15 cm depth was measured (Fig 4.3G). The deeper euxinic core of Suits and Wilkin (1998) is similar to that of this study where the isotopic value remained constant but at slightly heavier (~-22‰) values vs. those observed here (Fig 4.4F).

The possibility of the iron sulfide precipitation being controlled by precipitation in the water column is unlikely given previous estimates of framboidal pyrite sources in both the oxic and euxinic sediments have shown only 15% of the pyrite is formed in the water column (Suits and Wilkin, 1998). The oxic core is above the chemocline and thus, its iron sulfide must be forming in the sediment. The iron sulfide formation has been measured to occur mostly in the upper 10 cm of the sediment (Suits and Wilkin, 1998) column much of which was presumably lost during the coring. The similarities of the $\Delta^{34}$S and $\delta^{34}$S$_{AVS+CRS}$ values with those of the overlying water combined with higher iron

**Figure 4.5** Stella model results compared to measured data from the oxic core. Oxic core data are offset by 3.5cm to account for sediment loss during coring.
concentrations in the surface sediments than below (Hilfinger et al., 2001), suggest that much of the pyrite is forming near the sediment water interface. This pyrite therefore, can be forming from either sulfide from above or sulfide diffusing upward from below. The stability of the sulfide isotopic composition with depth until 30 cm would suggest that much of the iron sulfide is forming at the sediment water interface from locally available sulfide and not dominated by upwardly diffusing H₂S. This is also consistent with the higher calculated sulfate reduction rates at the top of the oxic core.

The increase in both AVS+CRS concentration and isotopic composition at the bottom of the oxic core is similar to the pattern obtained at the Black Sea with larger increases in the isotopic values of AVS+CRS at depth (Jorgensen et al., 2004). This suggests the formation of iron sulfide at depth, where the isotopically heavy pore water sulfate is being used as the source, supplementing the AVS+CRS formed at the sediment water interface.

The concentration of organic carbon vs. AVS+CRS sulfur within the sediments provides no apparent correlation for either core (Fig. 4.7). For both Green Lake cores the values fall below the normal marine line (Berner, 1970), with lower values for sulfide than would be expected for the organic carbon concentrations. This is similar to the Black sea sediments from Unit II, which showed a similar pattern with higher concentrations (Wilkin and Arthur, 2001). This is the same sediment bed which displays the higher AVS+CRS concentrations and isotopic values (Jorgensen et al., 2004) similar to what has been measured here.
4.5.4 Carbonate Associated Sulfate

The changes in pore water sulfur concentration and isotopic value and are not associated with changes in the values measured for CAS. The CAS concentration of the oxic core remains constant aside from one sample (36-39 cm) for which the concentration was a factor of two higher. Despite this increase in concentration, the isotopic value remains unchanged. A similar increase in CAS concentration occurs in one euxinic core sample (18-21 cm) but again with no change to the isotopic value. These samples both contain significantly lower CaCO$_3$ than the surrounding samples while producing a similar amount of CAS creating the higher concentrations. The only variation in CAS isotopic value occurs in one euxinic core sample (9-12 cm), which also has a higher pore water sulfate concentration.

![Figure 4.6](image.png)

Figure 4.6 Iron sulfide (AVS+CRS) concentration vs. organic carbon concentration for both the oxic and euxinic cores in this study. The normal marine value of C/S =2.8 is shown as the black line (Berner, 1970).
While the similarity between the $\delta^{34}$S$_{\text{CAS}}$ and pore water sulfate $\delta^{34}$S could reflect contamination, the repeated rinse steps employed during sample processing should have removed any such contamination. All of the sediment samples were characterized by unusually high CAS concentrations compared to marine carbonate and most closely resembled concentrations measured in shallow water marine corals (Staudt and Schoonen, 1995). The high concentration of CAS may be related to the environment of formation of the calcite. The calcite in FGL is biologically precipitated by \textit{Synechococcus}, which is also known to precipitate gypsum in the lake water of FGL (Thompson and Ferris, 1990). The repeated rinse steps for the samples should have removed any gypsum preventing it from changing the final concentrations.

\textbf{4.6 Conclusions}

The isotopic values of CAS from both cores are similar to that of the mixolimnion, not the monimolimnion. This suggests that the majority of the CAS is incorporated into carbonate formed higher in the water column, and that the CAS is not significantly altered during settling and burial. The results from FGL suggest that CAS is a robust proxy for overlying water isotopic composition, and retains its initial isotopic composition in the presence of iron sulfide formation and significant post-depositional sulfate reduction. This result supports the integrity of CAS as an isotopic proxy showing that it is not easily altered and continues to accurately record the sulfate isotopic value of the water in which it was precipitated.
4.7 Acknowledgements

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Chapter 5
Sulfur Isotopic Evidence for Chemocline Upward Excursions During the End-Permian Mass Extinction

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5.1 Abstract

The latest Permian was a time of major change in ocean chemistry, accompanying the greatest mass extinction of the Phanerozoic. To examine the nature of these changes, samples from two well-studied marine sections that span the Permian-Triassic boundary have been analyzed: the Meishan and Shangsi sections located in Southern China. Isotopic analysis of the carbonate-associated sulfate in these samples provides a detailed record of several isotopic shifts in $\delta^{34}S_{CAS}$ approaching and across the PTB, ranging from +30‰ to -15‰ (VCDT), with repeated asynchronous fluctuations at the two locations. We interpret the patterns of isotopic shifts, in conjunction with other data, to indicate a shallow unstable chemocline overlying euxinic deep water which periodically upwelled into the photic zone. These chemocline upward excursion events introduced sulfide to the photic zone stimulating a bloom of phototrophic sulfur oxidizing bacteria. We hypothesize that elemental sulfur globules produced by these organisms and $^{34}$S-depleted pyrite produced in the euxinic water column were deposited in the sediment; later oxidation led to incorporation as CAS. This created the large changes to the $\delta^{34}S_{CAS}$ observed in the latest Permian at these locations.
5.2 Introduction

The end-Permian interval leading up to the Permian-Triassic boundary (PTB) represents a period of great change in the chemistry of the oceans, as well as the evolution of life on the planet (Benton, 2003). During this interval approximately 50% of marine families and 70% of marine genera went extinct (Erwin, 1993). Additional evidence for terrestrial extinctions across the Permian-Triassic Boundary (PTB) implies a change to Earth’s entire biosphere (Huey and Ward, 2005). The main pulse of extinction and the initiation of the isotopic shifts occur below the Permian-Triassic boundary (which is defined as the first occurrence of the conodont *Hindeodus parvus*) and the main extinction horizon is often defined as the “event horizon” (Erwin, 1993).

The search for a cause of the end-Permian extinction has long been of intense interest, leading to the generation of numerous hypotheses which invoke both internal and external mechanisms. Hypotheses for internal extinction mechanisms include widespread ocean anoxia (Isozaki, 1997; Knoll et al., 1996; Wignall and Twitchett, 1996), low atmospheric oxygen (Berner, 2005; Huey and Ward, 2005), the development of euxinia in the oceans (Grice et al., 2005; Kump et al., 2005; Nielsen and Shen, 2004), the destabilization of methane clathrates in the oceans (Heydari and Hassanzadeh, 2003; Krull and Retallack, 2000; Krull et al., 2000), and Siberian trap volcanism (Renne and Basu, 1991), among others. External forces have also been invoked as extinction mechanisms, mainly in the form of a bolide impact to the ocean (Becker and Poreda, 2001; Becker et al., 2004; Kaiho et al., 2001), but the evidence for this remains controversial (Koeberl et al., 2004; Renne et al., 2004; Wignall et al., 2004).
Siberian trap volcanism may have been the ultimate trigger for warming-induced anoxia, but low atmospheric oxygen levels may have predisposed the ocean to this state (Berner, 2005). Studies involving numerical models of differing complexity have continued to debate the possibility of ocean-wide anoxia. Some models (Winguth and Maier-Reimer, 2005; Zhang et al., 2001) suggest that the oceans were vigorously circulating during the end-Permian leading to a well oxygenated Panthalassic ocean. Other studies (Hotinski et al., 2001; Kiehl and Shields, 2005) emphasize that prolonged anoxia or euxinia was primarily the result of warmer deep water source regions and elevated oceanic phosphate concentrations, rather than a change in the thermohaline overturning rate. The warming of high-latitude surface waters at the end of the Permian would have led to a decrease in the oxygen concentration of deep water formed in these regions. The more poorly oxygenated waters would then have become rapidly anoxic due to the consumption of oxygen during the oxidation of organic matter sinking from the productive surface waters (Hotinski et al., 2001). Deepening of anoxia led to euxinia and a buildup of dissolved gases (i.e. \( \text{H}_2\text{S} \), \( \text{CO}_2 \)), in deep water masses which then resulted in massive upwelling of \( \text{H}_2\text{S} \) and \( \text{CO}_2 \) (Knoll et al., 1996; Kump et al., 2005).

Sedimentological evidence in support of widespread ocean anoxia has been found at a number of marine sections spanning the late Permian through early Triassic both in the paleo-Tethys and Panthalassa; see Wignall and Twitchett (2002) for a review. Panthalassic sections from Japan exposed in accreted terranes contain evidence for anoxia from the late-Permian through early Triassic (Isozaki, 1997), while Tethyan sections are characterized by brief intervals of anoxia in shallow-water to deep-water carbonate-rich sections. Some sedimentologic evidence exists for euxinic conditions
during the late-Permian for a deep-water Panthalassic section (Nielsen and Shen, 2004) from the late Wujapingian, and a shallow-water Tethyan section (Wignall et al., 2005) spanning the Permian-Triassic boundary. Pyrite sulfur isotopic data from the deep sea Tanba terrane in Japan (Kajiwara et al., 1994) have been interpreted as representing intensification of euxinia in the Panthalassic Ocean, and shifts in the isotopic composition of carbonate associated sulfate (CAS) from the Siusi section in Italy (Newton et al., 2004), as well as green sulfur bacteria biomarker evidence from both Meishan in S. China and the Hovea-3 core from W. Australia (Grice et al., 2005) suggest widespread euxinia in the Tethys Ocean during the latest Permian.

The occurrence of large carbon isotope variations during the early Triassic and their relationship to changes in the marine biota as well as sedimentologic evidence (Pruss et al., 2005) shows a prolonged recovery time for the ocean ecosystem after the PTB event, which may mean that the environmental stress which led to the extinction continued well into the Triassic (Payne et al., 2004). The extinction mechanism therefore could have created conditions which prevented the expansion and diversification of many surviving taxa.

The isotopic composition of seawater sulfate, measured from evaporites reached a Phanerozoic low in the latest Permian (~10‰) and increased to ~30‰ during the earliest Triassic (Strauss, 1997). However, a more recent study reveals that the δ³⁴S of the oceans may have varied rapidly in the time leading up to the extinction event, suggesting a greater change to the sulfur cycle than had previously been proposed (Newton et al., 2004).
To evaluate this possibility we have analyzed the CAS and pyrite sulfur isotopic compositions from the Meishan and Shangsi sections of south China (Figure 5.1). CAS is sulfate which was trapped within the crystal lattice of biogenic and inorganic calcite when it is precipitated and has been shown to record the isotopic composition of seawater sulfate (Burdett et al., 1989; Strauss, 1999). The Meishan and Shangsi sections are both deep-shelf, carbonate-rich sections that span the Permian-Triassic boundary and were located on the Northeast corner of the paleo-Tethys ocean during the latest Permian (Baud et al., 1989; Wignall et al., 1995). We find large uncorrelated fluctuations in CAS $\delta^{34}$S that require substantial additions of low $\delta^{34}$S sulfate either to the basinal waters or diagenetic pore fluids. These patterns indicate that intermittent euxinic conditions were present in the photic zone during the latest Permian and early Triassic in the S. China region, in support of the Kump et al. (2005) hypothesis.

Figure 5.1 (A) Modern locations for Meishan and Shangsi sections and (B) Approximate paleoogeographic location of both sections (255 Ma) marked X. World map modified after Scotese (2001), modern location modified after Wignall et al. (1995).
5.3 Method

5.3.1 Bulk Chemical Analyses

An oriented slab from each sample was cut from the main sample and saved for petrographic and geochemical analysis. Acetate peels were prepared after the method of Ali (1968) and petrographically examined for evidence of textural alteration. Bulk chemical analyses were performed on the carbonate fraction of the samples utilizing a Leeman Labs PS3000UV ICP-AES at the Materials Characterization Laboratory at Penn State University with an average analytical uncertainty of ±10 wt% for the calcium and ±5 wt% for trace elements. The material was powdered and dissolved in a 5% hydrochloric acid solution. The solution was filtered to remove any insoluble residue and submitted for analysis of Fe, Mn, Sr, and Ca concentrations. CAS and total inorganic carbon concentrations were determined through mass balance during the extraction process. Powdered samples were decarbonated in 25% HCl. Organic carbon and pyrite S concentrations were measured through combustion in a CE Instruments NC2500 elemental analyzer.

5.3.2 Carbon and Oxygen Isotopes

Carbonate powders were dissolved individually in an automated common-acid-bath system at 90°C and analyzed on a Finnigan 252 Mass Spectrometer in the Penn State Stable Isotope Biogeochemistry laboratory. A laboratory standard was run every seven samples and National Bureau of Standards (NBS) 19 was analyzed at the beginning and end of each run. The variation between replicate analyses was ~0.02‰ and the samples are reported in standard delta notation relative to V-PDB.
We did not perform analyses of the $\delta^{18}O_{\text{CAS}}$. However, changes to the $\delta^{18}O_{\text{CAS}}$ would be expected to show values similar to those from bacterial sulfide oxidation during a CUE event, and would be indistinguishable from sulfide oxidation occurring later in the sediments making this an unsuitable proxy for determining diagenetic effects in this case.

5.3.3 Sulfur

CAS was extracted using modified methods from Burdett et al. (1989) and Hurtgen (2002). The limestone samples (50-60g) were powdered and rinsed with a sodium hypochlorite solution (4-6%) for ~12 hours to remove any metastable or organic sulfur compounds. The powder was rinsed multiple times with deionized water (DI) and then dissolved in a 25% HCl solution. The insoluble residue from this dissolution step was rinsed three times with DI and preserved. Saturated barium chloride solution was added to the dissolved fraction to precipitate barite. This solution furnished Ba in excess of that required to precipitate the maximum anticipated sulfate. The solution was heated for approximately 1 hour and set aside for ~12 hours. The precipitate (barite) was collected (filtered) the following day. The residue was added to an extraction vessel containing CrCl$_2$ and concentrated HCl and heated to ~120°C for one hour. The vessel was purged with nitrogen gas prior to the extraction, and the sulfur was released as H$_2$S, which flowed through a condenser into a zinc-acetate solution where it precipitated as ZnS (Canfield et al., 1986). A small portion of the barite (~0.30mg) or zinc sulfide (~0.20mg) was mixed with 5-times its weight in V$_2$O$_5$ and loaded into 5x7mm tin capsules. The V$_2$O$_5$ was added in this ratio because it has been shown to produce consistent $^{18}$O/$^{16}$O isotope ratios (Yanagisawa and Sakai, 1983). The $^{34}$S/$^{32}$S ratio is affected by the overlapping ion currents produced by $^{32}$S$^{16}$O$^{18}$O$^+$ and $^{34}$S$^{16}$O$^{16}$O$^+$, and
through keeping the $^{18}\text{O}/^{16}\text{O}$ ratio constant, a single correction factor can be applied among all the samples analyzed (Hurtgen et al., 2002). The samples were calibrated against known amounts of NBS-127 barite and internal laboratory standards. The samples were sent to the Stable Isotope Research Facility at Indiana University, Bloomington, IL for analysis on a VG Optima series II mass spectrometer with the variation between replicate analyses being 0.12‰.

5.4 Results

The results for the $\delta^{34}$S$_{\text{CAS}}$ of the samples for the Meishan section along with the $\delta^{34}$S$_{\text{py}}$ (pyrite), $\Delta^{34}$S ($\delta^{34}$S$_{\text{CAS}}$-$\delta^{34}$S$_{\text{py}}$) and the concentration of CAS and pyrite within the samples can be seen in Figure 5.2. The results for these analyses from the Shangsi section are shown in Figure 5.3. The concentration and isotopic composition of CAS for both sections varies considerably in the upper Permian and to a lesser extent in the early Triassic. Several values for $\delta^{34}$S$_{\text{CAS}}$ are extremely low (~ -20‰) relative to normal seawater values. The changes in $\delta^{34}$S$_{\text{CAS}}$ around the event horizon and PTB at Meishan are similar to those reported in a previous study (Kaiho et al., 2001), but the new data have been collected at higher temporal resolution. CAS $\delta^{34}$S oscillates between -20 to -20‰ at Meishan with no obvious trend until the event horizon when values plunge to –
**Figure 5.2** Isotopic composition and concentration of the carbonate associated sulfate and pyrite for the Meishan section. Radiometric dates marked with * from Bowring et al. (1998), ** from Mundil et al. (2001). The shaded box shows dates from both sources for the event horizon.
Figure 5.3 Isotopic composition and concentration of the carbonate associated sulfate and pyrite for the Meishan section. Radiometric dates marked with * from Bowring et al. (1998), ** from Mundil et al. (2001). The shaded box shows dates from both sources for the event horizon.
15‰. The δ^{34}S of CAS at Shangsi is lower overall for the Permian than at the Meishan section. Changxingian values fluctuate but trend toward less negative values, varying from -10‰ to 25‰ up-section toward the PTB.

The pyrite sulfur isotopic composition at Meishan is relatively constant before the boundary interval, which is marked by fluctuations. The pyrite sulfur at Shangsi becomes more ^{34}S-enriched approaching the boundary, then drops to values around -40‰ before rapidly returning to -20‰ higher in the section (Figure 5.3). The Δ^{34}S at Shangsi tracks changes in δ^{34}S_{cas} throughout the late Permian (Figure 5.3); the relationship is not as clear in Meishan where fewer pyrite samples were analyzed (Figure 5.2). The Δ^{34}S at Meishan is relatively stable below the boundary at values of about 20-30‰ and increases to 40-50‰ during the extinction event (Figure 5.2). The Δ^{34}S at Shangsi increases approaching the event from values around 20‰ and also reaches values between 40-50‰, at the event horizon, but then remains relatively high into the early Triassic diminishing somewhat toward the top of the measured section. The CAS concentrations at both sections average around 1000-1500ppm, but a few samples contain significantly higher or lower concentrations of sulfate (Figures 5.2 & 5.3). These samples are of concern because of their anomalous geochemical characteristics: we discuss the possibility of diagenetic alteration below.

The results of the chemical analysis for iron, manganese and strontium in the acid soluble fraction are shown in Figure 5.5. The iron concentration in the samples from both sections increases sharply around the relatively clay-rich beds, but returns to lower values in more carbonate rich beds above at both sections. Mn/Sr ratios are characterized
Figure 5.4 Stratigraphic profile of the Fe concentration and Mn/Sr, Fe/Ca, Fe/Mn, and Sr/Ca weight ratios for the Meishan and Shangsi sections. Sr/Ca ratios have been multiplied by 1000.
by a few extremely high values at Meishan in the lower Triassic, but no corresponding change is seen at Shangsi. The Fe/Ca ratios for both sections rise across the event horizon and PTB (Figure 5.4). Mn/Ca weight ratios for the majority of the samples at both Meishan and Shangsi (Figure 5.4) provide slightly different trends as well. At Shangsi, the Mn/Ca ratio in carbonates increases before the event horizon and then returns to pre-Extinction values through the lower Triassic. The samples from higher in the section at Shangsi return to the pre-extinction values. The Mn/Ca values at Meishan remain low up to the event horizon and then increase through the PTB. The Mn/Ca ratios decline higher in the section trending toward pre-extinction values. The Sr/Ca weight ratios for the Meishan section have values ranging from 0.5 to 8 with some values near zero (Figure 5.4). For the Shangsi section the Sr/Ca values are as high as 14 with a few smaller values in the lower Triassic (Figure 5.4).

The lithostratigraphy, micrite texture abundance (based on petrographic analysis of acetate peels), and amount of dolomitization (on the basis of Mg/Ca ratios) are shown in Figure 5.5 for both sections. The sections are both composed mainly of limestone, with clay-rich layers near the extinction horizon at both sections. The majority of the samples in the Permian are micritic, and vary between bioturbated and finely laminated with primarily bioturbated intervals present throughout the Permian and close to the PTB. The samples are notably darker in color in the Permian because of somewhat higher total organic carbon contents (TOC) (Figure 5.5). Both sections are dominantly micritic in the upper Permian but there is almost no micrite in the lower Triassic with some recrystallization. The lithostratigraphy shown in Figure 5.2 for Meishan is from Kexin et al. (1997), and Figure 5.3 for Shangsi is from Wignall et al. (1995).
Figure 5.5 Stratigraphic profile for the Meishan and Shangsi sections, with calcium carbonate (%), organic carbon (wt. %) per sample. The % micrite was estimated from acetate peel analysis, and the Mg/Ca ratios are shown as a proxy for dolomitization. Note the different horizontal scales between the two sections.
5.5 Discussion

5.5.1 Integrity of Isotopic Compositions

Below we argue that the large asynchronous variations in $\delta^{34}S_{\text{CAS}}$ measured at both sections (including large negative values) are the result of very early diagenetic processes driven by fluctuating overlying water-column chemical conditions. In this regard they are not primary signatures, but they have paleoenvironmental significance nonetheless. However, we must rule out other possibilities, including artifacts from sample treatments and significant meteoric and diagenetic influences.

5.5.1.1 Oxidation during Sample Digestion

The possibility of pyrite oxidation during sample treatment and digestion remains despite our precautions. However, high pyrite concentrations do not correspond with low values of $\delta^{34}S_{\text{CAS}}$ (Figure 5.6). Furthermore, the hydrochloric acid used during dissolution has been shown by others (Goldberg et al., 2005) to have no oxidizing effect on pyrite and therefore pyrite oxidation does not contribute to CAS isotopic composition during sample extraction. Neither high apparent Fe concentration (Figure 5.7) nor high CAS concentrations (Figures 5.8B & 5.9B) correspond to $\delta^{34}S_{\text{CAS}}$ as might be expected if pyrite oxidation during sample pretreatment had occurred. Thus, while we cannot rule out pyrite
Figure 5.6 Pyrite sulfur concentrations plotted against $\delta^{34}S_{CAS}$ for Meishan and Shangsi.

Figure 5.7 Iron concentration plotted against $\delta^{34}S_{CAS}$ for Meishan and Shangsi.
oxidation, we find it unlikely. We are currently performing a comprehensive comparison of various CAS extraction methodologies and will be making a recommendation for standardization of sample processing soon.

The Fe/Ca and Mn/Ca ratios for the carbonate fraction of the samples increase approaching (Shangsi) or through (Meishan) the event horizon (Figure 5.4). This could reflect a primary trend, the onset of water-column anoxia leading to an increase in the amount of reduced Fe and Mn present during carbonate precipitation. However, the Meishan samples which display the highest Fe/Ca and Mn/Ca ratios also contain higher non-carbonate fractions (Figures 5.4 & 5.5). Thus, the higher Fe and Mn concentrations may be due to Fe and Mn leaching from the clay fraction during hydrochloric acid dissolution. One might expect higher Fe concentrations if pyrite oxidation had taken place, but there is no correspondence between pyrite (sulfur) concentration and HCl-extractable Fe in samples.

5.5.1.2 Meteoric Diagenesis

Oxidation of reduced sulfur compounds and subsequent reincorporation in diagenetic calcite as CAS during early and late diagenesis is another possibility. Although textural evidence mitigates against significant alteration of this type, geochemical evidence can also be brought to bear in the analysis. A crossplot of the $\delta^{13}C_{\text{carb}}$ and $\delta^{18}O_{\text{carb}}$ exhibiting a positive correlation is commonly interpreted as a sign of meteoric diagenesis (Gross and Tracey, 1966; Meyers and Lohmann, 1985), and a plot of $\delta^{18}O_{\text{carb}}$ vs. $\delta^{34}S_{\text{cas}}$ yielding a positive correlation would suggest meteoric diagenesis influenced both the carbonate oxygen isotopes and sulfate incorporated in carbonate
Figure 5.8 Elemental and stable isotope analysis from Meishan for analysis of diagenetic alteration. No significant trends are visible in any given panel.
Figure 5.9 Elemental and stable isotope analysis from Shangsi section for analysis of diagenetic alteration.
(Hurtgen et al., 2004) assuming that meteoric waters were much more $^{18}$O depleted than the original seawater. No correlation between the $\delta^{18}$O$_{carb}$ and $\delta^{34}$S$_{cas}$ for both the Meishan and Shangsi sections is observed (Figures 5.8A & 5.9A). In addition no relationship is found between $\delta^{18}$O$_{carb}$ and the CAS concentration for either section (Figures 5.8C & 5.9C).

Some $\delta^{18}$O values for carbonate at Meishan are extremely low (-10 to -12‰) whereas the $\delta^{18}$O at Shangsi remains between -5 and -8‰. The $\delta^{18}$O trend in apparently reasonable preserved Phanerozoic marine carbonates, while increasing since the Precambrian, exhibits lower values around the PTB with a lowest value of $\sim$ -10‰ and a mean value of -7‰ (Veizer et al., 1999). The overall trend suggests that most of the $\delta^{18}$O values reported here are within the average for this time period. The only samples which lie far outside this range are two values at Meishan which do not occur in samples with low $\delta^{34}$S$_{CAS}$ values. Crossplots of the isotopic composition of carbonate-carbon and carbonate-oxygen are shown in Figure 5.10. As with the other plots, no discernable trend is visible.

As an additional test of alteration the $\delta^{18}$O$_{carb}$, $\delta^{34}$S$_{cas}$, and CAS concentration were plotted against Mn/Sr ratios for all samples (Hurtgen et al., 2004). Strontium is often removed during diagenesis while Mn is enriched resulting in higher Mn/Sr ratios and low Sr/Ca ratios (Hurtgen et al. 2004). The crossplots against the Mn/Sr ratios for both Meishan (Figure 5.8 D,E,F) and Shangsi (Figure 5.9 D,E,F) provide no correlation to suggest meteoric influence. From the partition coefficient and today’s seawater Sr/Ca ratio (Bathurst, 1971) calcite is expected to have Sr/Ca equal to 1.2 mmol/mol. The majority of the samples are above this value, with some exceptions near the PTB (Figure
5.4), suggesting that the Meishan and Shangsi samples as a whole were only moderately
diagenetically altered. That is, that the samples experiences compaction and cementation
but not wholesale dissolution, reprecipitation, or major pore filling cementation. Those
samples with low Sr/Ca values also do not have extremely low values for $\delta^{34}\text{S}_{\text{CAS}}$.

![Graph](Image)

**Figure 5.10** $\delta^{13}\text{C}_{\text{carbonate}}$ vs. $\delta^{18}\text{O}_{\text{carbonate}}$, no diagenetic trend is observed in the samples.

5.5.1.3 Early Marine Diagenesis

The low values of $\delta^{34}\text{S}_{\text{CAS}}$ in some samples and the significant fluctuations of $\delta^{34}\text{S}$
at both sampled locations are most likely not the result of meteoric diagenesis (exposure,
freshwater circulation, and/or deep meteoric events). They are also not likely to represent
variations in the global oceanic value, most simply because they do not correlate between
the two sections. However, diagenesis that reflects changes in primary environmental
conditions may play an important role. Local addition of $^{34}\text{S}$-depleted sulfur to the
sediment, either immediately upon deposition or somewhat later as an early seafloor
diagenetic overprint may have played an important role. Petrographic examination of acetate peels exhibited evidence for recrystallization although the samples were dominantly micritic. However, CAS in lime-mud has been shown to be remarkably resistant to alteration during early diagenesis, even in the presence of large quantities of organic matter and sulfate-reducing bacteria in pore water (Lyons et al., 2004). It is important to note that the Lyons et al. (2004) study was conducted in Florida Bay, which is well oxygenated. In contrast, the Meishan and Shangsi seafloors are interpreted to have been episodically overlain by euxinic water-masses. If so, reduced sulfur minerals precipitated in the water column, with low values of $\delta^{34}$S, could have been episodically deposited in the sediments. If the overlying waters became oxygenated during the intervals between euxinia, oxygen could have diffused into the sediment, oxidizing the reduced sulfur minerals and releasing $^{34}$S-depleted sulfate into the pore water. The product sulfate could have later become incorporated into the limestone as CAS, if the carbonate sediments were able to buffer the acidity created by the oxidation of pyrite.

The pyrite sulfur concentration in samples throughout each section remains fairly consistent and does not correlate with changes to $\delta^{34}$S$_{\text{CAS}}$ (Figure 5.6). The samples with the most depleted $\delta^{34}$S values also contain some of the lowest iron concentrations suggesting that an alternative source for the addition of $^{34}$S depleted sulfur must be considered to fully explain the changes to $\delta^{34}$S$_{\text{CAS}}$.

5.5.1.4 Summary of Diagenesis

From the above petrographic, chemical, and isotopic analyses, we conclude that early diagenetic alteration may have played a primary role in creating the rapid shifts observed in $\delta^{34}$S$_{\text{CAS}}$ at both sections. However, this proposed early diagenetic alteration
is considered to be a direct result of rapid environmental variations (oxic-anoxic cycles). The extremely light values for the CAS sulfur isotopes and the recrystallization textures petrographically observed in many samples are consistent with early marine diagenesis. Geochemical evidence suggests that later diagenesis and meteoric diagenesis is unlikely to explain the observed changes and pyrite alone as the source of this $^{34}\text{S}$-depleted sulfate is not the sole source of additional sulfur because rapid changes in $\delta^{34}\text{S}_{\text{CAS}}$ occur despite relatively constant pyrite sulfur concentrations. While not necessarily representing the original surface-water $\delta^{34}\text{S}$ values, the $\delta^{34}\text{S}_{\text{CAS}}$ indicate a change to the sulfur input to the sediments during the end-Permian and early Triassic that may provide a clue to the environmental changes occurring at this time.

5.5.2 Euxinia

Numerical modeling has shown that the deep water of the ocean could have become euxinic during periods of prolonged anoxia such as the end Permian (Hotinski et al., 2001), and that the chemocline between the oxygenated surface waters and the sulfide rich deep water could become unstable with $\text{H}_2\text{S}$ concentrations higher than 1 mmol/kg (Kump et al., 2005). This would have led to chemocline upward excursion (CUE) events where sulfidic deep water would be transferred to the shelf environment and hydrogen sulfide would be released to the atmosphere (Kump et al., 2005).

5.5.2.1 CUE Events and Sulfur Isotopes

Sulfide in the euxinic deep-water would have been $^{34}\text{S}$-depleted, being derived from bacterial sulfate reducers thriving in anoxic waters. Newton et al. (2004) suggested that a reduction of 30% of oceanic sulfate to sulfide and storage of this sulfide in euxinic
deep-waters would be enough to produce the shifts between 11.5‰ and 27‰ they observe in δ\(^{34}\)S\(_{\text{CAS}}\). The problem with this mechanism is that isotopically light sulfide upwelling into the photic zone, would be accompanied by isotopically heavy sulfate resulting from Rayleigh distillation isotope effects during water-column sulfate reduction. Upon oxidation the two would mix creating a parcel of water that had the original (undistilled) seawater value. Thus, we must find other mechanisms for preservation of the light sulfur isotope values. In other words, we must identify mechanisms for sequestering the isotopically light sulfur before it oxidizes and mixes with the accompanying isotopically heavy deep-water sulfate.

5.5.2.2 The Effect of CUE events on Sediment Chemistry

One method for sequestering the sulfide is for bacteria or inorganic geochemical reactions to immediately convert it into a relatively insoluble phase (elemental sulfur or pyrite) under euxinic conditions. The episodic excursions of euxinic water in the photic zone proposed by Kump et al. (2005) would have led to conditions favorable for blooms of phototrophic purple and green sulfur bacteria. Elemental sulfur derived from this bacterial source would have been isotopically depleted in \(^{34}\)S, being derived from an isotopically light source and potentially subjected to subsequent disproportionation during oxidation. Disproportionation reactions (cycling sulfur between sulfide and elemental sulfur) could have occurred in a shallow chemocline creating \(^{34}\)S-depleted sulfides and the large Δ\(^{34}\)S values (Figures 5.2 & 5.3; Canfield and Thamdrup, 1994). The elemental sulfur produced in the water column would have fallen to the ocean floor and become incorporated into the surface sediments. Sulfur globules have been shown to form in the surface waters off the coast of Namibia during build up and release of H\(_2\)S.
from the sediments (Weeks et al., 2004). These elemental sulfur globules have been mapped in satellite images being transported along the coast for later deposition (Weeks et al., 2004), similar to the mechanism being suggested here for the end-Permian. In the presence of ferrous iron, some of the upwelling sulfur might have also been sequestered as FeS or FeS$_2$ and deposited in the sediments, to later become oxidized. However, due to the lack of a correlation between Fe and $\delta^{34}$S$_{CAS}$ and other limitations on pyrite as the source of sulfur discussed above, we favor elemental S as the primary shuttle of low $\delta^{34}$S sulfur to the sediments.

The values for $\delta^{34}$S$_{cas}$ at Meishan and Shangsi reach a maximum just before the event horizon, coinciding with the with both the biomarker evidence for green sulfur bacteria Grice et al. (2005) and with the highest values for $\Delta^{34}$S at both sections, and then fall to extremely low values across the extinction horizon (Figures 5.2 & 5.3). Evaporite sulfur $\delta^{34}$S$_{CAS}$ values representing open oceanic sulfate reach a minimum in the late Permian (~12‰) and trend towards heavier values through the latest Permian and into the Triassic where they reach a high of ~25‰ (Kampschulte and Strauss, 2004). The values measured at both Meishan and Shangsi (Figures 5.2 & 5.3) trend toward the extrapolated evaporite curve while repeatedly deviating to more $^{34}$S-depleted values throughout the latest Permian, which we hypothesize to indicate repeated CUE events in this region.

At the end of the CUE events, the sediment-water-interface (SWI) would have become oxic, leading to the oxidation of the elemental sulfur and some of the pyrite (possibly as Fe monosulfide) creating pore waters with low pH. These low pH waters would have driven recrystallization, by dissolving portions of the lime mud sediments until the carbonate system was able to buffer the acidity and allow for precipitation of
secondary (diagenetic) carbonate incorporating $^{34}$S-depleted sulfate as CAS. Assuming that 1 wt% of the sediments was elemental sulfur formed within the water column, approximately 20,000 ppm of $^{34}$S-depleted sulfate could have been generated. With the average CAS concentration within the primary micrite being ~1000 ppm (Figure 5.2, 5.3) the sulfate within the sediments would have been overwhelmed, thereby creating the isotopically light signals observed. While this is technically a “diagenetic” effect, it is driven by the input of sulfur from the CUE events providing evidence of photic zone euxinia.

A small decrease in the $\delta^{34}$S$_{\text{CAS}}$ also occurs at the PTB, which is the second location at Meishan where green sulfur bacteria biomarkers were detected indicating a second major bloom of phototrophic sulfur bacteria as the result of euxinia in the photic zone (Grice et al., 2005). These results are consistent with those of Pruss et al. (2005) and Payne et al. (2004) which indicate that anoxia and, now, perhaps euxinia continued well into the early Triassic and impeded the biotic recovery from the end-Permian mass extinction.

5.6 Conclusions

The large amplitude, apparently rapid variations in $\delta^{34}$S$_{\text{CAS}}$ measured in this study indicated that multiple chemocline upward excursion (CUE) events occurred in S. China and likely elsewhere during the end-Permian mass extinction. Repeated changes in the oxidation state of the uppermost sediments due to the incursion and retreat of euxinic waters onto the continental shelf led to the generation of considerable quantities of reduced sulfur minerals (elemental and pyrite S). These reduced sulfur minerals were deposited in surface sediments during CUE events and then oxidized as euxinic waters
retreated to the deep sea. As a result the sulfur isotopic composition of the sulfate trapped in carbonate minerals underwent large, local fluctuations. The inferred changes to the sulfur cycle during the end-Permian strongly suggest that an internal mechanism was the trigger for the extinction and that the perturbations began before the main pulse of extinction and continued well into the Triassic.

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Chapter 6
Carbon Isotopic Evidence for Chemocline Upward Excursions during the End-Permian Event

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6.1 Abstract

A negative shift in marine inorganic carbon isotope composition ($\delta^{13}C_{\text{carb}}$) during the end-Permian mass extinction has been used as evidence for several different extinction mechanisms. Changes to the $\delta^{13}C$ of organic matter and the difference between it and $\delta^{13}C_{\text{carb}}$ ($\Delta^{13}C = \delta^{13}C_{\text{carb}} - \delta^{13}C_{\text{org}}$) have been examined at few locations, with conflicting interpretations. We examine the changes to both organic and inorganic carbon isotopes across the Permian-Triassic boundary at two marine sections from South China (Meishan and Shangsi) and compare these to data from other previously published sections. Through these analyses, we demonstrate that a decrease in $\Delta^{13}C$ occurred during the extinction event throughout the Paleo-Tethys ocean. The extent and intensity of the decrease varies by location averaging a negative shift of $\sim 5\%e$. Several possibilities as to the cause of this shift exist, including Siberian trap volcanism, a change in the terrestrial/marine organic carbon input to the system, or a change in the dominant marine biota brought about through environmental changes (such as widespread ocean anoxia/euxinia). The decrease in $\Delta^{13}C$ observed at many of these sections across the
event horizon, is here interpreted to represent a shift from algae/cyanobacteria to less fractionating phototrophic sulfur bacteria in marine shelf environments resulting from upward excursions of the chemocline. These chemocline upward excursions would release euxinic water to the photic zone allowing phototrophic sulfur bacteria to thrive. The limited available biomarker data are consistent with this interpretation.

6.2 Introduction

The end-Permian mass extinction was the greatest mass extinction of the Phanerozoic, with an estimated loss of 90% of marine species (Erwin, 1993). The cause of the end-Permian extinction remains a subject of intense debate, with mechanisms internal and external to the biosphere being invoked. Many internal mechanisms focus on widespread ocean anoxia (Wignall and Twitchett, 1996; Isozaki, 1997), possibly creating euxinic oceans leading to a buildup, and catastrophic outgassing of, $H_2S$ (Kump et al., 2005), or rapid global warming either through the destabilization of methane clathrates (Krull and Retallack, 2000) or from Siberian Trap volcanism (Renne and Basu, 1991). External mechanisms focus on a bolide impact to the ocean (Becker and Poreda, 2001; Kaiho et al., 2001; Becker et al., 2004), but the evidence for this remains highly controversial (Kerr, 2004; Koeberl et al., 2004). The main phase of the extinction appears to be coincident with the eruption of the Siberian Traps (Mundil et al., 2004).

The above mechanisms have all been invoked to explain the worldwide decrease in the $\delta^{13}C$ of marine carbonate ($\delta^{13}C_{\text{carb}}$) seen at the event horizon of the mass extinction. The event horizon is the bed where the largest number of species became extinct and is distinct from the Permian-Triassic boundary which is defined as the first occurrence of the conodont Hindeodus parvus (Yin, 1996). While many studies focus separately on the
changes to the inorganic and organic carbon isotope records, few (e.g., Magaritz et al. 1992) examine the changes to $\Delta^{13}$C ($\delta^{13}$C_{carb}-$\delta^{13}$C_{org}). The change in $\Delta^{13}$C during the end-Permian seems to vary geographically with some locations (South China: Cao et al., 2002; Slovenia: Schwab and Spangenberg, 2004) showing a decrease in $\Delta^{13}$C at the event horizon and others (Carnic Alps: Magaritz et al., 1992; Japan: Musashi, 2001) showing parallel excursions in both organic and inorganic carbon and thus no change in $\Delta^{13}$C.

Here we provide new carbonate and organic carbon isotopic data from the well-studied Meishan and Shangsi geologic sections from South China (Fig. 6.1) and compare these to data from sections in Iran (Korte et al., 2004), Slovenia (Dolenec et al., 2004; Schwab and Spangenberg, 2004), Japan (Musashi et al., 2001), Austria (Magaritz et al., 1992; Wolbach et al., 1994), and two other south China sections; Heping and Taiping (Krull et al., 2004) (Fig. 6.1). We evaluate various hypotheses in light of these observations, and conclude that the data are most consistent with a shift in the dominant mode of photosynthesis at these locations to that carried out by non-oxygenic phototrophic green sulfur bacteria.

### 6.3. Materials and Methods

A total of 105 samples were obtained from the Meishan and Shangsi sections located in southern China (Fig. 6.1). The samples were powdered and the inorganic carbonate was dissolved individually in an automated common acid bath system at 90°C and analyzed on a Finnigan 252 Mass Spectrometer in the Penn State Stable Isotope Biogeochemistry laboratory. A laboratory standard was run every seven samples and the calcite standard NBS-19 was also analyzed at the beginning and end of each sample set. Subsets of the carbonate samples were decarbonated using hydrochloric acid, and the
residue was combusted on a CE Instruments NC2500 elemental analyzer. The CO₂ produced was flame sealed in glass vials and transferred to a Finnigan 252 Mass Spectrometer fitted with a special attachment for transferring the gas. The organic carbon isotopic ratio was determined relative to calibrated internal laboratory standards and referenced to V-PDB. The variation between replicate analyses was \( \text{~0.02‰} \) for carbonate and organic carbon, with all data presented in standard per mille (‰) notation relative to V-PDB.

Figure 6.1 Modern (A) and paleogeographic (B) locations for all measured sections shown above. 1: South China (insert modified from Wignall et al. (1995); 2: W. Slovenia; 3: Abadeh (Iran); 4: Gartnerkofel-1 (Austria); 5 Kamura and Taho (Japan). Modified after Scotese (2002).
6.4 Results

For the Meishan section a negative excursion in $\delta^{13}$C$_{org}$ (bed 24) precedes the decrease in $\delta^{13}$C$_{carb}$ (bed 25) (Fig. 6.2), generating a substantial increase in $\Delta^{13}$C just below the event horizon (uppermost bed 24). The $\delta^{13}$C$_{org}$ then increases while the $\delta^{13}$C$_{carb}$ decreases across the event horizon (main extinction interval), creating a marked decrease in $\Delta^{13}$C (Fig. 6.3A). Our data for the Meishan section differ slightly from those previously published (Cao et al., 2002) for the interval below the boundary, but overlap exactly during the period leading up to the extinction interval and through the recovery. For the Shangsi section, $\delta^{13}$C$_{org}$ remains relatively constant until the latest Permian where it rapidly decreases then increases before falling across the event horizon, while $\delta^{13}$C$_{carb}$ increases (Fig. 6.2) leading up to the extinction event (bed 27), again creating an increase in $\Delta^{13}$C. Then both decrease, but with a temporal offset that creates a decline in $\Delta^{13}$C mirroring the one at Meishan (Fig. 6.3B).

Although other sections from the Tethyan Ocean do not show the pre-event rise in $\Delta^{13}$C unambiguously, they do exhibit a decrease in $\Delta^{13}$C across the extinction interval (Fig. 6.3). The simultaneity of these decreases at widely separated sites argues against diagenetic alteration as the cause of the shift. Data from the Wordie Creek formation in Greenland (Stemmerik et al., 2001) suggest a decrease in $\delta^{13}$C$_{org}$ before the drop in $\delta^{13}$C$_{carb}$ but the data are insufficient to determine a change to $\Delta^{13}$C across the boundary, and because of this, are not used in this study. Other higher latitude sections were also not considered due to the lack of both inorganic and organic carbon isotopic data across the PTB. The Western Slovenian section also displays a sharp decrease in $\Delta^{13}$C of
Figure 6.2 Carbonate (closed squares) and organic carbon (open squares) isotopic data for the Meishan and Shangsi sections, southern China. Note that vertical scales differ.
Figure 6.3 Changes to $\Delta^{13}$C across the PTB, with the y-axis zero at the Permian-Triassic boundary. The biostratigraphy and isotope values for each section were modified after the published data (see text for references). The Meishan and Shangsi data are from this study. The light grey boxes are inferred times where cyanobacterial photosynthesis dominated, while the dark grey boxes are periods where euxinic conditions may have existed.
around 5‰ but values remain around the new lower value for the rest of the measured section (Fig. 6.3C). The lack of suitable paleontologic specimens for more precise dating makes it difficult to determine how much of the early Triassic is exposed in this section. The Abadeh (Iran) section also displays a decrease across the boundary after a slowly increasing trend and recovers to pre-extinction values during the early Triassic (Fig. 6.3D). The other S. China sections (Heping and Taiping) both exhibit a decrease across the event horizon (Fig. 6.3 E, F). The Heping section displays a slight increase before the boundary similar to Meishan and Shangsi but this is not as evident at Taiping. The Gartnerkofel (Austria) core (Magaritz et al., 1992; Wolbach et al., 1994) displays a small $\Delta^{13}C$ change with a short-lived negative excursion that begins well before the PTB (Fig. 6.3G). The $\Delta^{13}C$ values reach a peak just before this decrease similar to the change at Meishan, but more spread out due to the higher rate of sedimentation. Interestingly, the shallow-water sections Kamura and Taho from Japan (Musashi et al., 2001), deposited in the open Panthalassic ocean, produce a constant and intermediate value for $\Delta^{13}C$ across the boundary (Fig. 6.3 H).

6.5 Discussion

Changes in the organic and inorganic carbon isotope composition of marine sediments need not be coincident because of additional factors controlling $\delta^{13}C_{org}$ (see below; Kump and Arthur, 1999). Indeed, the negative shift in $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ are not coincident at many of the sections. The use of $\delta^{13}C_{org}$ is therefore unsuitable for determining the location of the event horizon at sections where the paleontology is ambiguous or where $\delta^{13}C_{carb}$ cannot be measured.
The variations in $\Delta^{13}C$ reflect perturbations to the carbon cycle, including changes in one or more of the following factors: atmospheric $pCO_2$ (which influences photosynthetic isotope discrimination) (Bidigare et al., 1997), and/or the dominant source of marine sedimentary organic matter (e.g., dominance by different marine biota or terrestrial organic input) (Sackett and Thompson, 1962). We now evaluate existing hypotheses for end-Permian extinction in terms of these factors and the available data.

### 6.5.1 Siberian Trap Volcanism and Atmospheric $pCO_2$

Because photosynthetic isotope discrimination decreases as $CO_2$ availability falls (Bidigare et al., 1997), the decrease in $\Delta^{13}C$ could have resulted from the removal of $CO_2$ from the atmosphere due to enhanced silicate weathering on the continents, following Siberian Trap eruption as the large amount of basaltic material formed by the trap volcanism was eroded and weathered (Holser and Magaritz, 1987). A trend towards increasing $^{87}Sr/^{86}Sr$ in marine sediment can be interpreted as evidence for increased continental weathering across the event horizon, and the Siberian Traps would have weathered relatively quickly (Grard, 2005). However a dominance of non-radiogenic basaltic weathering would not generate such a trend (Korte et al., 2003). Moreover, a preceding increase in $\Delta^{13}C$ that would have been associated with increasing atmospheric $pCO_2$ during massive Siberian trap eruption is not unambiguously and universally evident in the data.

### 6.5.2 Terrestrial Organic Matter Input

A second possibility to explain the $\Delta^{13}C$ patterns is a change in the ratio of the terrestrial to marine components of organic carbon delivered to sediments during the
extinction period, as a result of the extinctions or accompanying environmental change. The terrestrial organic matter at this time would have been enriched in $^{13}\text{C}$ relative to marine organic matter, as opposed to the situation in modern sediments (Arthur et al., 1985), if atmospheric pCO$_2$ were highly elevated over modern values as predicted by climate models (Kiehl and Shields, 2005). Terrestrial $\delta^{13}\text{C}_{\text{org}}$ values from are indeed less negative than contemporaneous marine $\delta^{13}\text{C}_{\text{org}}$, with an average between -24‰ and -22‰ (Krull, 1999; Ward et al., 2005). A decrease in $\Delta^{13}\text{C}$ would thus demand that the input of terrestrial organic matter to marine environments would have to have increased across the main pulse of extinction.

In fact, slightly higher contents of terrestrial organic matter during the PTB and in the lowermost Triassic have been inferred in two western Slovenian sections, based on compound-specific isotope measurements, sequences that are otherwise dominated by marine organic matter (Dolenec et al., 2004; Schwab and Spangenberg, 2004). However, the increase in terrestrial organic matter concentration in both Slovenian sections does not occur until after the initiation of the main decrease in $\Delta^{13}\text{C}$. In the Abadeh (Iran) section the organic material is entirely marine in origin with no increased terrestrial component across the P/Tr interval based on organic geochemical analyses, but the decline in $\Delta^{13}\text{C}$ is clearly displayed (Korte et al., 2004). Recent evidence for a more widespread change in the terrestrial/marine organic matter input ratio has been suggested through a potential land plant biomarker (Sephton et al., 2005). The negative shift in $\Delta^{13}\text{C}$ measured at Val Badia (Italy) is not as large (~2‰) as the one seen in the majority of sections presented here, and the short-duration pulse of terrestrial matter described by Sephton et al. (2005) would have produced a less pronounced change than the longer term shift in $\Delta^{13}\text{C}$ being
discussed here. An oscillation between marine and terrestrial inputs following the extinction in China has been suggested based on a repeated series of rapid shifts in $\delta^{13}C_{org}$ (Cao et al., 2002). However, this occurs after the measured decrease in $\Delta^{13}C$ and the extinction. Sea-level rise has been documented at these sections during the latest Permian (Wignall and Hallam, 1993; Hallam and Wignall, 1999), which is difficult to reconcile with increased terrestrial input given the increased distance to the source. On balance, the evidence for a terrestrial/marine organic matter shift during the widespread drop in $\Delta^{13}C$ across the event horizon is weak.

6.5.3 Euxinia

A third possibility to explain the $\Delta^{13}C$ decline is a shift from dominantly algal or cyanobacterial productivity prior to the event to a bloom of phototrophic green sulfur bacteria around the boundary. Green sulfur bacteria utilize the reverse TCA cycle during incorporation of carbon, which results in a smaller carbon isotope fractionation than that associated with the more common Calvin cycle (van Breugel et al., 2005). Increasing contribution of green sulfur bacterial biomass to the carbon flux would decrease $\Delta^{13}C$ across the event horizon and up to the PTB. If the apparent fractionation between CO$_2$ and organic carbon for the green sulfur bacteria were -12.5‰, which is the less negative end of the range for potential discrimination (van Breugel et al., 2005), the input of green sulfur bacterial biomass would have to have been approximately 30% of the total organic matter to create the $\Delta^{13}C$ drop from 30 to 25‰. The increase of $\Delta^{13}C$ to pre-extinction values in the early Triassic may have been caused by a return to oxygenic photoautotrophy, due to the re-oxygenation as the chemocline returned to depth.
Green sulfur bacteria may have become prevalent in the photic zone through the formation late Permian, especially during chemocline upward excursion (CUE) episodes (Kump et al., 2005), when euxinic water would have been present in the photic zone (Fig. 6.4). The instability of the chemocline separating the deep euxinic water from oxygenated surface water (Kump et al., 2005) would have generated spatially and temporally variable CUE events. This variability may have created the differences in duration and severity of the decrease in $\Delta^{13}$C between the various measured sections. Some regions, perhaps represented by the Panthalassic Japanese sections (Musashi et al., 2001), might not exhibit a shift in $\Delta^{13}$C, if they were in stable oceanic regions. The shift in $\Delta^{13}$C would therefore not have been a uniform global phenomenon, and would only be observed where photic zone euxinia was present for an extended period of time.

![Figure 6.4 Depiction of a CUE event, compared to changes in $\Delta^{13}$C at Shangsi.](image)

This hypothesis makes a strong prediction, that isorenieratane, a biomarker for green sulfur bacteria, should be found at all sites that exhibit a decreasing $\Delta^{13}$C trend, providing that favorable conditions for preservation existed. Isorenieratane has been
found at the event horizon of Meishan and in the Hoeva-3 core off the coast of Australia (Grice et al., 2005). The continued search for this biomarker at other PTB sections will help to determine the extent of CUE events. Sedimentologic evidence for euxinia in the form of frambiodal pyrite grain distributions exists for the middle to late Permian in Greenland (Nielsen and Shen, 2004), and in the earliest Triassic (Wignall and Twitchett, 2002) and the PTB in India (Wignall et al., 2005). At the Heping and Taiping sections, lithologies change from fossiliferous limestone to calcimicrobial framestone around the event horizon coincident with a decline in species abundance (Krull, 2004). The western Slovenian section shows a change from limestone to a black algal packstone and higher concentrations of extractable sulfur which has been suggested to indicate deposition under euxinic conditions (Schwab and Spangenberg, 2004). The Abadeh section changes to stromatolitic facies in the latest Permian coincident with the decrease in $\Delta^{13}C$ while the sediments grade from red to gray (Korte et al., 2004). These changes in sedimentary facies coincide with the decrease in $\Delta^{13}C$ and during the proposed euxinic interval in Fig. 6.3. Pyrite isotopic composition from a low-sulfur siliceous Japanese section also suggests deep water anoxia/euxinia (Kajiwara et al., 1994) as do changes to the isotopic composition of carbonate-associated sulfate from the Suisi section in Italy (Newton et al., 2004).

6.6 Conclusion

The shift in inorganic carbon isotopes during the end-Permian extinction has been shown here to be accompanied by a non-parallel change in organic carbon isotopes, documenting a change in the fractionation factor between organic and inorganic carbon for the Paleo-Tethys ocean. CUE events provide a potential trigger for the extinction
event through the release of hydrogen sulfide to the surface waters and atmosphere (Kump et al., 2005). The asynchronous duration and onset of the shift in $\Delta^{13}C$ would have easily been created by CUE events in different parts of the Paleo-Tethys ocean during the latest Permian. Widespread photic zone euxinia, (substantiated by biomarker (Grice et al., 2005) and sedimentary (Wignall and Twitchett, 2002; Nielsen and Shen, 2004) evidence, would have led to a significant change in the dominant marine biota, enough to alter the mean fractionation between inorganic and organic carbon at many but not all locations during the end-Permian extinction.

6.7 Acknowledgments

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Chapter 7

Sulfur and Carbon Isotopic Changes Associated with the Permian-Triassic Boundary, Demirtas, Turkey

7.1 Abstract

Rapid variations in the sulfur isotopic composition of carbonate associated sulfate (CAS) during the latest Permian have been interpreted to represent upwelling of euxinic water by means of a fluctuating chemocline during the largest of Phanerozoic mass extinctions. Geochemical studies of a carbonate platform section located in Turkey have again yielded rapid variations in the sulfur isotopic composition of sulfate, with some values well below the expected range of seawater isotopic composition at this time. Both inorganic and organic carbon isotopes were also examined, and the expected decrease in inorganic carbon isotopes coinciding with the extinction was observed, accompanied by a decrease in the carbon isotopic values of organic carbon. Unlike the case at many other locations, no shift in $\Delta^{13}C\left(\delta^{13}C_{\text{carb}}-\delta^{13}C_{\text{org}}\right)$ presumed to reflect a shift to S phototrophy, was observed in connection with the boundary at Demirtas. This suggests intermittent euxinic conditions may have existed in the surface waters of the late Permian creating the changes in CAS isotopic composition, but did not persist long enough to change the dominant marine biota.

7.2 Introduction

Change in the oceanic sulfur cycle over time has the potential to provide evidence for environmental conditions during times of biotic stress, such as mass extinction events.
The end-Permian extinction is the largest mass extinction of the Phanerozoic, with a loss of ~90% of marine species accompanied by extensive extinction in the terrestrial realm (Erwin, 1993). The cause of the extinction remains a subject of intense scientific debate with multiple hypotheses for the trigger and kill mechanisms: intense Siberian trap volcanism (Renne and Basu, 1991), oceanic anoxia/euxinia (Kump et al., 2005; Wignall and Twitchett, 2002), catastrophic global warming due to methane release from the oceans (Krull and Retallack, 2000), and bolide impact to the ocean/land (Becker et al., 2004). While the possibility of an external trigger to the extinction has recently become more prominent with the discovery of a possible impact crater (Becker et al., 2004), the crater itself and purported geochemical indicators for impact have been challenged (Kerr, 2004; Koeberl et al., 2004). The evidence for changes to the environment preceding the extinction indicates that changes in ocean chemistry related to the development of widespread oceanic anoxia may have been directly responsible for the extinctions.

Sedimentologic and geochemical evidence for oceanic anoxia (Isozaki, 1997; Wignall and Twitchett, 2002) has been found at several marine sections from both the Paleo-Tethys and Panthalassa. Widespread deposition of black shale (Isozaki, 1997; Wignall and Twitchett, 1996) provides evidence for anoxia and pyrite framboid distribution (Wignall et al., 2005) suggests a euxinic water column over at least part of the oceans as well. Geochemical indicators such as changes in oceanic sulfur isotopic composition in the latest Permian (Newton et al., 2004; Riccardi et al., 2006), and alterations in pelagic chert geochemistry (Kato et al., 2002) also suggest a shift to anoxic/euxinic conditions. Deep ocean anoxia is hypothesized to begin in the late Permian and continue through the mid-Dienerian (Early Triassic), peaking during the
Griesbachian (Wignall and Twitchett, 2002). Kump et al. (2005) demonstrated, through numerical modeling, that the long-term anoxia proposed for the end-Permian could lead to euxinic conditions in the deep ocean. The chemocline separating the deep euxinic water and the overlying oxygenated surface water would have been unstable, leading to chemocline upward excursion (CUE) events where the euxinic deep water impinges on shelf environments (Kump et al., 2005). Hydrogen sulfide from the deep ocean could have been released to the atmosphere as well, triggering the extinction in the terrestrial as well as the marine realm (Kump et al., 2005).

The extinction event is coeval with a worldwide negative shift in inorganic carbonate and the fluctuations in the carbon isotopic composition of carbonates continue well into the Triassic (Payne et al., 2004, Baud, 1989). These fluctuations also correspond to a period characterized by diminutive fauna, and stabilize at the same time the fauna begins to increase in size (Payne et al., 2004) suggesting the environmental disturbances continued after the extinction event. The unusual seafloor depositional environments found through the early Triassic (Pruss and Bottjer, 2004; Pruss et al., 2005) also suggest continued environmental disturbance after the extinction.

Widespread oceanic anoxia/euxinia remains one of the most intensely studied extinction mechanisms, and is the focus of this study. The CUE events proposed by Kump et al. (2005) would have altered the sulfur cycle during the latest Permian and this can be detected in the sedimentary record through studies of carbonate associated sulfate (CAS). CAS has been demonstrated to accurately record the overlying surface water isotopic composition (Burdett et al., 1989) in modern and Neogene strata. Rapid variations in CAS have been reported both in Italy (Newton et al., 2004) and south China
(Riccardi et al., 2006) and, despite differences in mechanism, both studies suggest euxinic deep-water upwelling to the shelf environment.

The end-Permian and early Triassic was a time of great environmental disturbance with large fluctuations in carbon and sulfur isotopic composition of the ocean. The isotopic composition of oceanic sulfate reaches its Phanerozoic low immediately preceding the extinction and its Phanerozoic high during the Early Triassic (Kampschulte and Strauss, 2004). These geochemical changes, combined with the sedimentologic evidence for environmental fluctuations suggest long-term perturbations, creating this environmental stress. The potential for euxinic conditions during this time, with upwelling of \( \text{H}_2\text{S} \) to the surface environment provides additional support for the global disruptions. To further examine the extent of euxinic conditions in the surface water samples were collected from a carbonate platform section deposited in the Paleo-Tethys (Demirtas) located in Turkey (Fig 7.1). This section has not been extensively studied, and no geochemistry has been published previously, but sedimentologic and paleontologic analyses have been performed (Groves et al., 2005). The section exhibits stromatolites and oolites in the earliest Triassic, similar to the facies described elsewhere but not as extreme (Baud et al., 2007). These samples were analyzed for changes to CAS isotopic composition and showed rapid variations in \( \delta^{34}\text{S} \) during the late Permian, similar to those seen in south China and Italy.
Figure 7.1 (A) Map of the modern location of Demirtas, Turkey, modified after Groves et al. (2005); (B) The paleogeographic location of Demirtas during the end-Permian modified from Scotese (2002)
7.3 Methods

7.3.1 Sulfur

The limestone samples (~50g) were cut and powdered prior to extraction using a method modified from Riccardi et al. (2006). Samples were soaked in 1 L deionized water (DIW) for 24h, decanted and 300-400 mL of a 6% sodium hypochlorite solution was added and left to soak for 18h. The sodium hypochlorite solution was decanted off and samples were filtered and rinsed three times with DIW. The samples were then reacted with a 25% HCl solution until there was no visible reaction, left on a stir plate for 1h, and a small quantity of acid was added to ensure the reaction had run to completion. The samples were filtered using Whatman 40 filter paper to remove insoluble residue. The insoluble residue was analyzed on a CE 2500 elemental analyzer for pyrite sulfur concentration. The solution was then filtered through 0.45 µm membrane filters, 50 mL of a saturated (250 g/L) BaCl₂ solution added, and the mixture was heated for 30 min and left to precipitate for 12-18h. The precipitated barite was filtered using 0.45 µm membrane filters, dried, weighed and prepared for isotopic analysis after the method of Yanagisawa and Sakai (1983) and sent to the Stable Isotope facility at Indiana University, Bloomington for analysis.

7.3.2 Carbon

Subsets of the powdered limestone were reacted in 90°C phosphoric acid, individually in an automated common acid bath system connected to a Finnigan 252 mass spectrometer in the Penn State stable isotope biogeochemistry laboratory. Laboratory standards were run every seven samples, with NBS-19 run at the start and each of each sample set. The insoluble residue from above was analyzed for organic carbon isotopic
values on a Thermo Delta XP mass spectrometer. Laboratory standard (Peru Mud) was run every 12 samples, as well as NIST ANU-sucrose every 18 samples for comparison. Replicate analyses were within 0.1‰. All samples are reported in standard per mille (‰) notation relative to VPDB.

7.4 Results

The Permian-Triassic boundary is defined lithologically at Demirtas, based on the first occurrence of stromatolitic facies associated with the early Triassic, and paleontologic studies on this section (Groves et al., 2005). The event horizon (point of the carbon isotopic shift and greatest extinction rate) is the same as the lithologic boundary at Demirtas, while the actual start of the Triassic may be higher in the section but this cannot be determined without conodont stratigraphy. The Permian samples are Changxingian, and the Triassic samples extend into the Scythian (Groves et al., 2005). CAS concentrations and isotopic compositions for the carbonate samples are shown in Fig 7.2. CAS concentrations remain low throughout the section (200-600ppm) with one value reaching ~1500ppm, and concentrations between 900 to 1200 ppm at the top of the measured section. The isotopic composition of the CAS trends overall towards more $^{34}$S enriched values from the Permian into the Triassic, with rapid variations (~ -5 to 20‰) in the Permian (Fig. 7.2). The Triassic samples exhibit a linear increase from values near 13‰ to near 30‰ at the top of the measured section with little variation. Pyrite sulfur concentration also remains low for the entire section (Fig 7.2). Carbon isotopic values for both inorganic, organic, and $\Delta^{13}$C ($\delta^{13}$C$_{\text{carb}}$-$\delta^{13}$C$_{\text{org}}$) are shown in Fig 7.3, along with organic carbon concentration. The organic carbon concentrations remain low throughout the entire section, but are higher in the Permian (Fig. 7.3). The inorganic carbon isotopic
Figure 7.2 CAS concentration, isotopic composition, and pyrite concentration for the Demirtas section plotted in distance in meters from the event horizon.
Figure 7.3 Changes in organic, inorganic carbon isotopic composition and oxygen isotope composition for Demirtas.
composition remains around 4‰ (with some deviations) until the latest Permian, where it drops at the Permian-Triassic boundary to values averaging 1‰ and remains for the rest of the section (Fig. 7.3). The organic carbon isotopic composition remains around -25‰ for the Permian. The values begin to decrease just before the boundary and reach a minimum in the early Triassic of ~ -31‰ (Fig 7.3). This produces a $\Delta^{13}$C that trends from 25 to 30‰ through the entire section but with no definitive shift associated with the boundary. The $\delta^{18}$O_carbonate shows a distinct trend towards $^{18}$O depleted values from the Permian to the Triassic.

7.5 Discussion

The changes to the $\delta^{34}$S_CAS if primary, suggest large changes to the oceanic sulfur cycle, but potential diagenetic alteration must first be taken into account. Alteration during early diagenesis, meteoric diagenesis, hydrothermal alteration, or contamination through laboratory extractions needs to be examined.

7.5.1 Early Diagenesis

Diagenetic alteration remains a concern because some unusually light $\delta^{34}$S_CAS values were obtained in the Permian sequence at this section. Oxidation of pyrite is the most likely source of isotopically light sulfate; however all of the samples were very low in pyrite sulfur concentration (Fig. 7.2). A crossplot of pyrite sulfur concentration with $\delta^{34}$S_CAS shows no correlation, and the highest pyrite-containing samples plotted within the range for normal seawater sulfate isotopic values during this time (Fig. 7.4E). CAS concentration also does not correlate with $\delta^{34}$S_CAS, and again the highest CAS samples
Figure 7.4 Crossplots of carbonate carbon and oxygen isotopes and sulfur isotopes and concentrations to analyze for diagenetic alteration.
provide values similar to the global average for seawater sulfate at this time (Fig. 7.4D). This combined with the overall low concentrations for pyrite sulfur argue that no significant artifact due to pyrite oxidation occurred within these samples. The isotopically light values for CAS observed here are outside what could be expected for the global seawater value, suggesting an additional source of isotopically light sulfur to the sediments in this region during the end-Permian. Elemental sulfur created during episodes of euxinia through sulfur oxidizing bacteria could provide the additional sulfur and will be discussed below.

7.5.2 Meteoric Diagenesis

Diagenetic alteration through meteoric fluids can alter the isotopic values of CAS through the dissolution and re-precipitation of carbonate. Through this process sulfate contained within meteoric fluids could become incorporated into the newly precipitated carbonate. Crossplots of $\delta^{18}$O$_{\text{carbonate}}$ vs. $\delta^{13}$C$_{\text{carbonate}}$ have been used to determine potential diagenetic alteration of carbonates. If a positive correlation exists between the carbon and oxygen isotopic compositions, it is possible that both were altered by meteoric fluids (Hurtgen et al., 2004).

This approach has been extended by others (Hurtgen et al., 2004; Riccardi et al., 2006) to check for alteration of CAS isotopic composition. Meteoric waters have low sulfate concentrations allowing the sulfate to be buffered by the CAS similar to carbon in carbonate (Hurtgen et al., 2004). Meteoric fluids are expected to be depleted in $^{18}$O and $^{34}$S (Hurtgen et al., 2004). Meteoric fluids would be depleted in $^{34}$S similar to the $\delta^{34}$S of riverine sulfate (Hurtgen et al., 2004). Cross plots of $\delta^{18}$O$_{\text{carbonate}}$ vs. $\delta^{34}$S$_{\text{CAS}}$, CAS concentration, and $\delta^{13}$C$_{\text{carbonate}}$ are shown to evaluate this possibility (Fig. 7.4). The
%13C_{carbonate} vs. δ^{18}O_{carbonate} shows a slight positive correlation for the entire section, which is most pronounced in the Triassic samples (Fig 7.4A). This could indicate some alteration of the carbonate through meteoric conditions during the Triassic, particularly in samples above 13m. However, the decrease in δ^{18}O_{carbonate} measured at this section also may indicate a warming trend, which intensifies during the early Triassic. The end-Permian through early Triassic is suggested to be a time of overall warming (Chumakov and Zharkov, 2003) would have been enhanced by Siberian trap volcanism at the PTB (Renne and Basu, 1991). The carbon values for the Permian and through the PTB mirror the changes seen at virtually all marine limestone sections for the end-Permian (Baud et al., 1989) suggesting these values are also unaltered.

The plot of δ^{18}O_{carbonate} vs. CAS concentration does not provide any correlation to suggest an input or removal of sulfate with changes to δ^{18}O. A comparison of δ^{18}O_{carbonate} vs. δ^{34}S_{CAS} provides a negative correlation for the entire section (Fig. 7.4C). This is due to the Triassic samples, and the topmost samples in particular (Fig. 7.4C). If the source of the alteration were meteoric fluids, as the depleted δ^{18}O values would suggest, depleted δ^{34}S_{CAS} values would also be expected. This is created by the oxidation of isotopically light sulfide by the meteoric waters creating an isotopically light source of sulfate. The opposite of this trend is observed here making overprints to δ^{34}S_{CAS} from meteoric diagenesis unlikely.

### 7.5.3 Late Diagenesis – Hydrothermal Fluids

Carbonate hosted ore deposits are common throughout the Tauride mountains making the possibility of hydrothermal overprinting significant (KOPTAGEL et al., 2007).
The Demirtas section is located close to a number of suture zones, which cover most of southern Turkey and the Alanya platform was thrust north onto the mainland during the Eocene (Groves et al., 2005).

Diagenetic fluids associated with orogenic events typically have light $\delta^{18}O$ values (Chen et al., 2001), while the source of the sulfate for the hydrothermal fluid substantially alters the resulting $\delta^{34}S_{\text{sulfate}}$ (Cazafias et al., 2003; Koptagel et al., 2007). However, these values are similar to seawater values during the early Triassic, which is suggested to be a time of warming making a correlation between heavy $\delta^{34}S_{\text{CAS}}$ and light $\delta^{18}O_{\text{carbonate}}$ likely. Therefore, there is no evidence at outcrop for hydrothermal alteration and given the environmental changes associated with the Permian-Triassic boundary hydrothermal alteration of the samples is unlikely.

7.5.4 Contamination during Laboratory Analysis

The possibility of alteration during the extraction of CAS from samples through oxidation of iron sulfides has been a concern given the extremely light values obtained for CAS. Previous studies have tested the possibility of pyrite oxidation, by adding a strong HCl solution to ground pyrite, and analyzing the solute for CAS (Goldberg et al., 2005). The result showed no measurable pyrite oxidation, suggesting that pyrite remains unaltered during extraction with HCl (Goldberg et al., 2005) making contamination during laboratory analysis unlikely.

7.5.5 Summary of Diagenesis

Hydrothermal and meteoric diagenesis do not fully explain the trends to $\delta^{34}S_{\text{CAS}}$ or $\delta^{18}O_{\text{carbonate}}$ observed here. While the overall trend in $\delta^{18}O_{\text{carbonate}}$ correlates with
increasingly heavy sulfate, this mirrors the expected trend for oceanic sulfate at this time combined with a steadily warming Earth. The addition of isotopically light sulfate to the Permian samples, to create the isotopically light values measured does not appear to have come from pyrite, either during burial diagenesis or laboratory contamination. Overall, the samples do not appear to have been diagenetically altered through meteoric or hydrothermal influence, but several late Permian samples may have had an addition of isotopically light sulfate during burial.

7.5.6 CUE Events

The changes to the isotopic composition of CAS during the late Permian could suggest a change to the sulfur cycle of the ocean associated with euxinic deep water. The rapid variations in $\delta^{34}S_{\text{CAS}}$, if primary would indicate a lower sulfate concentration in the ocean. However, measurements of sulfate concentration derived from fluid inclusions studies of late Permian brines, suggest that oceanic sulfate was ~23 mM, only slightly less than modern value of 27 mM (Lowenstein et al., 2001). The global average for sulfate isotopic composition in the ocean is ~13‰ in the late Permian and ~30‰ in the early Triassic (Kampschulte and Strauss, 2004). The $\delta^{34}S_{\text{CAS}}$ for this section from the PTB through the top of the measured section follows this global trend arguing against diagenetic alteration.

The Triassic samples from this study are Scythian in age although it is unclear exactly how far into the Scythian the samples extend. Samples for conodont stratigraphy have been collected and are being analyzed by others, but the data is not yet available. The timing of the increase in $\delta^{34}S_{\text{CAS}}$ values measured here is consistent with the global average for oceanic $\delta^{34}S_{\text{CAS}}$ in both magnitude and timing (Kampschulte and Strauss,
Globally, there is a sharp increase to extremely positive $\delta^{34}\text{S}$ for oceanic sulfate during the early Triassic reaching a maximum towards the end of the Scythian. This increase in seawater sulfate $\delta^{34}\text{S}$ may have been created through long term anoxia enriching the isotopic composition of oceanic sulfate, which was subsequently flooded onto the shelf environment (Kampschulte and Strauss, 2004; Holser, 1977). This mechanism requires sequestration of isotopically light sulfide through enhanced pyrite burial under a brine layer in a stratified ocean (Holser, 1977). Numerical modeling (Berner, 2005) suggests that pyrite burial did increase during the Early Triassic coincident with this positive excursion in $\delta^{34}\text{S}$. The positive excursion in oceanic sulfate $\delta^{34}\text{S}$ is coincident with the end of the extreme global deepwater anoxia proposed by Isozaki (1997) and the large scale carbon isotope fluctuations in marine carbonate measured by Payne et al. (2004). The environmental changes from long term anoxia to oxygenated marine conditions shows that the early Triassic was indeed a time of environmental stress which contributed to the delayed recovery from the mass extinction event.

7.5.6.1 Sulfur

The rapid variations in $\delta^{34}\text{S}_{\text{CAS}}$ during the Permian may indicate CUE events occurring similar to those measured at the Meishan and Shangsi sections from south China (Riccardi et al., 2006). The euxinic deep water hypothesized to exist during the late Permian, would have created an unstable chemocline at sulfide concentrations $\sim1\text{mmol/L}$ (Kump et al., 2005). This instability would have led to euxinic water being released to the surface environment. Through the mechanism proposed by Riccardi et al. (2006), the release of this sulfidic deep water into the photic zone would have led to a
bloom in phototrophic sulfur oxidizing bacteria. These bacteria would have oxidized the isotopically light sulfide to both sulfate and elemental sulfur, which would have been deposited in the sediment (Canfield and Thamdrup, 1994). The elemental sulfur could have later been oxidized in the shallow sediment upon the return to oxic bottom-water conditions. The Demirtas section in the Permian oscillates between black limestone and gray limestone. The black limestone tends to correlate with $\delta^{34}S_{\text{CAS}}$ having oceanic seawater values, while the gray limestone tends to contain more $^{34}S$ depleted CAS. This is consistent with the sulfur from a CUE event becoming oxidized and incorporated during oxic marine conditions. This would have created large quantities of isotopically light sulfate within the pore waters, as well as some acidity leading to recrystallization of the carbonate mud with the new isotopically light sulfate incorporated as CAS.

Simply upwelling euxinic deep water does not change the isotopic value of surface water sulfate because the creation of isotopically light sulfide in the deep water would drive the residual sulfate toward heavier values. Upwelling and resultant mixing of these two sulfur reservoirs would remove any fractionation signal created in the deep; therefore a system to isolate the isotopically light sulfide is required. This upwelling of euxinic water and sequestration of isotopically light sulfide could explain the rapid variations in $\delta^{34}S_{\text{CAS}}$ measured for the late Permian at Demirtas and at other sections throughout the Tethys ocean.

7.5.6.2 Carbon

A decrease in $\Delta^{13}C$ coincident with the event horizon of the extinction has been observed at a number of Tethyan marine sections (Chapter Six). A geologically persistent bloom of phototrophic green sulfur oxidizing bacteria could have created a
decrease in $\Delta^{13}C$, since these bacteria discriminate less against $^{13}C$ than the dominant marine biota (i.e Cyanobacteria/Algae) (Van Der Meer et al., 1998). This does not appear to be the case at Demirtas, however, since no significant decrease in $\Delta^{13}C$ was observed. This does not rule out the possibility of a CUE event, but may indicate either a short lived CUE events or a mix of purple and green phototrophic sulfur bacteria. Purple phototrophic sulfur bacteria would not produce a negative shift in $\Delta^{13}C$, since they fractionate carbon to a greater extent than green sulfur bacteria (Van der Meer et al., 1998). The Demirtas section may have been deposited in relatively shallow water, compared to Meishan, (Groves et al., 2005) favoring purple phototrophic sulfur bacteria which tend to live in shallower water than the phototrophic green sulfur bacteria. This is because green phototrophic bacteria can survive in lower light environments and the purple sulfur bacteria are more oxygen tolerant (Pringault et al., 1999).

The steady increase in $\Delta^{13}C$ at Demirtas during the latest Permian and into the Triassic (Fig. 7.3) may be associated with increased $pCO_2$ resulting from carbon input from Siberian trap volcanism. Increasing $pCO_2$ can increase $\Delta^{13}C$ up to values between 30 to 35%, at which point the $\Delta^{13}C$ value becomes less sensitive to changes in $pCO_2$ (Kump and Arthur, 1999). The $\Delta^{13}C$ at Demirtas appears to reach a maximum around these values and remain for the Early Triassic mirroring what would be expected from volcanism during this time.

7.5.6.3 CUE Events – Summary

Overall, the section at Demirtas may reflect the global changes to carbon and sulfur cycles across the Permian Triassic boundary. The increase in $\Delta^{13}C$ during the
latest Permian and reaching maximum values at the event horizon suggests influence from Siberian Trap volcanism through the increase in atmospheric $p\text{CO}_2$. The decrease in $\delta^{18}\text{O}_{\text{carbonate}}$ suggests a period of warming during this time, which continues into the Triassic. This warming would have helped create the anoxic conditions in the deep ocean proposed by others (Wignall, 2002;Isozaki, 1997) and created an environment favorable for euxinia. Global warming would have lowered the oxygen content of ocean water leading to a lower oxygen concentration of oceanic bottom water. These bottom waters would have been more easily stripped of their oxygen during respiration allowing anoxia to form faster than under cooler environmental conditions.

The oscillations in $\delta^{34}\text{S}_{\text{CAS}}$ measured at Demirtas during the Permian suggest that this area did experience CUE events similar to those hypothesized for south China (Chapter Five). The rapid shifts in $\delta^{34}\text{S}_{\text{CAS}}$ are smaller than those measured in south China (Chapter Five), suggesting that this area experienced less severe euxinia during the latest Permian and thus, may more accurately reflect global isotope trends. The overall trend in $\delta^{34}\text{S}_{\text{CAS}}$ is similar to the global average during this time (Kampschulte and Strauss, 2004). Therefore, the Demirtas section may provide a more accurate record of global changes to carbon and sulfur isotopic values during the latest Permian and early Triassic without the overprinting from CUE events as is observed at other marine sections.

### 7.6 Conclusion

The fluctuations in $\delta^{34}\text{S}_{\text{CAS}}$ observed at Demirtas during the late Permian are not as extreme as those measured in south China (Riccardi et al., 2006), but are similar to the variability reported for Italy (Newton et al., 2004). Apparently, the persistence or
frequency of photic-zone euxinia (CUE events) was lower in this region of western Tethys than in the east. The smaller fluctuations in $\delta^{34}$S$_{CAS}$ combined with the mirroring of the global trend for oceanic sulfate in the Triassic indicate that the photic zone euxinia at Demirtas was not as severe as that measured in south China. Short duration CUE events may also explain the lack of a shift in $\Delta^{13}$C associated with a bloom of phototrophic sulfur bacteria observed at many other sections (Riccardi et al., 2007). The overall increase in $\Delta^{13}$C at Demirtas may be created through CO$_2$ input from the Siberian Traps again suggesting that Demirtas provides record of the global trend for $\Delta^{13}$C without as severe an overprint from photic zone euxinia as has been observed in south China. Overall, the changes to $\delta^{34}$S$_{CAS}$ at Demirtas provide further confirmation of widespread euxinia and episodic CUE events during the latest Permian, strengthening the hypothesis that these unstable biogeochemical conditions played an important role in end-Permian mass extinction.

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Chapter 8

Conclusion

The overall aim of this thesis has been to examine the ability of CAS to withstand diagenetic alteration under oxic and euxinic conditions in modern samples and to determine if changes in the isotopic composition of CAS during the end-Permian mass extinction are the result of a euxinic ocean. Through examinations at Fayetteville Green Lake (FGL) CAS has been shown to resist alteration under both euxinic and oxic conditions and retain the sulfate isotopic composition of the overlying water. Samples from the Permian-Triassic boundary have shown evidence for alteration through the incorporation of extremely $^{34}\text{S}$ depleted sulfur, created through upwelling of sulfidic deep water. The rapid variations in CAS measured at the three geographically distinct sections support this interpretation but raises questions regarding CAS preservation. Overall, CAS has been shown to be a fairly robust proxy for seawater sulfate isotopic composition.

8.1 Fayetteville Green Lake

Examinations at Fayetteville Green Lake (Chapter Four) have shown CAS retains the isotopic composition of the sulfate in the water in which it was formed. This is despite ongoing sulfate reduction and iron sulfide formation within the pore water. The ability of CAS to withstand alteration under normal burial conditions is consistent with previous work performed in the oxic, iron poor waters of Florida bay (Lyons et al., 2004). The isotopic composition of CAS retains the signal from the mixolimnion where carbonate is being biogenically produced (Thompson et al., 1997). CAS was shown to be
stable under both oxic and euxinic depositional conditions with no difference in isotopic composition. Therefore, CAS is a robust proxy for overlying water isotopic composition during burial under both oxic and euxinic conditions.

**8.2 The Permian-Triassic Mass Extinction**

CAS has been utilized to provide information about global sulfur cycling during periods of environmental stress (Chapter Five, Seven). Through analysis of marine limestone samples spanning the Permian-Triassic boundary, rapid changes occur in the isotopic composition of CAS were measured (Fig. 8.1). Three marine sections (Meishan & Shangsi, S. China; Demirtas, Turkey) were analyzed here, and the changes to $\delta^{34}S_{\text{CAS}}$ present different patterns of change for each section. These rapid variations in CAS have also been measured in Italy (Newton et al., 2004). Geochemical tests for diagenetic alteration did not reveal evidence for massive alteration at any of the sections from pyrite oxidation, meteoric fluids, or hydrothermal fluids. However, the CAS isotopic values for the Permian samples at all three locations are believed to have been altered by changes to the depositional environment associated with chemocline upward excursion (CUE) events. Euxinic conditions hypothesized (Kump et al., 2005) to be present during the late Permian, would have created the means to introduce large quantities of isotopically light sulfur to the sediments, in the form of elemental sulfur. This sulfur was oxidized after the return to oxic conditions and incorporated as CAS. Thus creating both the extremely negative values and the rapid shifts measured.
Figure 8.1 Changes to the sulfur isotopic composition of carbonate associated sulfate for all three marine sections. (A) Meishan; (B) Shangsi; (C) Demirtas. All are distances from the event horizon.

A decrease in $\Delta^{13}C$ ($\delta^{13}C_{\text{carb}} - \delta^{13}C_{\text{org}}$) was measured at the point of greatest extinction in south China and documented in the literature at a number of other sections (Chapter Six) suggesting a shift in the dominant marine biota. However, this decrease was not observed at Demirtas (Chapter Seven). The negative shift in $\Delta^{13}C$ has been hypothesized to be created through a change from cyanobacteria/algae to photosynthetic green sulfur bacteria which utilize the reverse TCA cycle. The reverse TCA cycle discriminates less against $^{13}C$ during uptake resulting in a smaller $\Delta^{13}C$ (Van Breugel et al., 2005). Upwelled euxinic deep water to the photic zone during CUE events would...
have created favorable environmental conditions for a bloom in phototrophic sulfur bacteria. The lack of a shift to $\Delta^{13}C$ at Demirtas may indicate that this section did not experience the same severity of upwelled euxinic water or possibly the biota did not consist of green sulfur bacteria, but more purple sulfur bacteria which do not utilize the reverse TCA cycle (Van der Meer et al., 1998). The increase in $\Delta^{13}C$ during the latest Permian reaching a max at the event horizon may result from increased $pCO_2$ due to Siberian Trap volcanism. Therefore the Demirtas section, with smaller shifts in $\delta^{34}S_{CAS}$ and no decrease in $\Delta^{13}C$ may have experienced less upwelling of euxinic water when compared to south China and my more accurately reflect global isotopic values at this time. The changes to carbon and sulfur together suggest changes to the global sulfur cycle in the time approaching the end-Permian mass extinction, most likely created through a euxinic deep ocean in support of the Kump et al. (2005) hypothesis.

### 8.3 Significance and Future Work

Overall, CAS has been shown to be a robust proxy for seawater sulfate isotopic composition. The ability of CAS to withstand diagenetic alteration in the presence of sulfate reduction and pyrite formation suggests it can be used to reliably determine paleo-seawater isotopic values. However, tests for diagenetic alteration should be conducted routinely and researchers should recognize the absence of diagenetic indicators does not necessarily indicate that CAS retains its original isotopic signature.

The ability of CAS to withstand diagenetic alteration still requires further study as the work performed at FGL has just begun to test how CAS is preserved during early diagenesis. Deeper core samples from both the euxinic and oxic portion of FGL should be collected and a more complete diagenetic study undertaken. It would also be
interesting to determining if CAS concentration decreases with depth, because modern samples often have higher concentrations than ancient limestone. Examinations of CAS in other modern euxinic environments (Black Sea, Mariager Fjord (Denmark, etc.) would also be beneficial towards determining the stability of CAS during early burial. A systematic sampling of sediments and overlying water from these locations would provide a large data set from which to analyze CAS. A more complete study of the sulfur system of these locations would also be beneficial. The study presented here provided sulfate, and sulfide (in the form of AVS+CRS) isotopic values. Separating acid volatile sulfide from chromium reducible sulfide, as well as analyzing changes to elemental sulfur concentrations and isotopic compositions would provide more information as to the changes in the sulfur cycle during the early stages of burial. Through these studies it would be possible to more thoroughly evaluate changes to CAS under different environmental conditions in the modern environment to better analyze changes measured in ancient samples.

This work has added to our understanding of changes to the oceanic sulfur cycle in the time surrounding the Permian-Triassic mass extinction event. The possibility of a euxinic ocean (Kump et al., 2005), first presented through numerical modeling has been further supported through the isotopic evidence from CAS at all three sections measured here. The samples presented here cover two distinct portions of the paleo-Tethys, but more marine sections from both the Tethys and Panthalassa would further our knowledge as to the extent of euxinia and CUE events during this time. Towards this effort, samples from a second marine section in Turkey (Tashkent) were collected. These sample span the late Permian through the Triassic in a greatly expanded (~1 km) limestone section. A
subset of these samples has already been extracted for CAS but has not yet been analyzed for their isotopic compositions. This could provide a detailed record of change in oceanic sulfate $\delta^{34}$S for this time period. Biomarker evidence for intermittent euxinia has been found at two sections so far, but the presence of isorenieratane at more sections would also further the evidence for photic zone euxinia (Grice et al., 2005). The changes to the global sulfur cycle during the end-Permian must be taken into account when considering other extinction mechanisms proposed as well. This has implications for other times in Earth history where oceanic anoxia is may have been widespread, and the possibility of euxinia should be examined.

Overall, the stability and usefulness of CAS as a proxy for paleo-seawater sulfate isotopic values requires further study. Examinations as to the effect of pyrite formation on CAS should be undertaken in an environment where high pyrite concentrations are known. This would be useful both in determining any burial diagenetic effects, as well as potential contamination during extraction. The samples chosen for the extraction methods presented in Chapter Three were all fairly low in pyrite sulfur concentration and the effect of higher pyrite remains a concern. The ability of CAS concentration to be used as a proxy for ancient seawater sulfate concentrations also remains in question. The results presented here (Chapters Four – Seven) do no provide any correlation suggesting this is the case, but laboratory experiments have shown CAS concentration is dependent on the environmental sulfate concentration among other factors (Busenberg and Plummer, 1984). A systematic study of CAS concentration from limestone sections during times when the sulfate concentration of the ocean is known from other proxies could help to establish the relationship (if one exists) between CAS concentration and
oceanic sulfate concentration. Modern limestone samples should be taken as well, since CAS concentration varies considerably in the modern (Staudt and Schoonen, 1995) when the concentration is known. The source of the CAS (biogeneic, i.e. shells vs. inorganic) must be examined since this has been shown to affect the overall CAS concentration. The ability to utilize CAS as a proxy for seawater sulfate concentration would greatly expand our understanding of the changes to the oceanic sulfur cycle with time.
References


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