ABSTRACT

Title of Dissertation: SULFUR ISOTOPE RECORDS IN **NEOARCHEAN CARBONATES:** IMPLICATIONS FOR THE EARLY PRECAMBRIAN SULFUR CYCLE Iadviga Zhelezinskaia, Doctor of Philosophy, 2018 Dissertation directed by: Dr. James Farquhar, Department of Geology,

University of Maryland Dr. Jay Kaufman, Department of Geology, University of Maryland

Mass-independent fractionation of sulfur isotopes found in Early Precambrian records is the main evidence supporting an oxygen-poor atmosphere before ~2.4 Ga when ancient sulfur cycling was different than today. In previous studies, shale facies formed in deep-water environments have been the main target that were used to constraint the ancient sulfur cycle using sulfur isotopes, even though, among sedimentary Neoarchean strata, carbonate rocks are found to be more abundant. In order to follow previous observations and reveal processes operating in shallow water environments, I conducted a series of systematic studies of Neoarchean carbonate archives. Elemental and isotope measurements of sulfur and carbon in carbonate (and some shale) facies were obtained from multiple cores drilled through ~2.7 to 2.5 Ga successions of South Africa (GKF01, GKP01, and BH1-Sacha), Western Australia (AIDP-2, AIDP-3, BB, PR, RP, and RG) and Brazil (GDR-117). This study demonstrates that carbonate facies preserve distinctive MIF-S

compositions relative to shale facies. Drilled pyrites in carbonate formations mostly preserved negative Δ^{33} S values suggesting that the major sulfur source to shallow environments was atmospheric sulfate that also was isotopically redistributed through microbial sulfate reduction producing $\delta^{34}S > 35\%$ isotope fractionation. Atmospheric sulfate was the main source for seawater sulfate making its concentration in the Neoarchean ocean of less than 10µM/l. At this low concentration, reservoir effects would be pronounced leading to the formation of carbonate associated pyrites with highly positive δ^{34} S compositions ranging to > +30‰. The bulk pyrites in most carbonate formations from South African and Western Australian cores possess small positive Δ^{33} S signals (<+3.0‰) suggesting the incorporation of 20-35% of photolytic elemental sulfur. Photolytic sulfate with $\Delta^{36}S/\Delta^{33}S$ deviations found in macroscopic pyrites with negative $\Delta^{33}S$ from the Carawine Formation provide evidence for changes in atmospheric reactions during periods of an organic hazy atmosphere. My study of $\Delta^{36}S/\Delta^{33}S$ in contemporaneous Jeerinah shale indicates the possible temporal decoupling of the MIF-S signal on a basinal scale implying heterogeneous haze structure. Integration of sulfur and carbon isotopes measured in carbonate facies suggests that sulfur-metabolizing microbes such as sulfur phototrophs and sulfate reducers were actively recycling these elements in shallow marine environments.

SULFUR ISOTOPE RECORDS IN NEOARCHEAN CARBONATES: IMPLICATIONS FOR THE PRECAMBRIAN SULFUR CYCLE

by

Iadviga Zhelezinskaia

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Advisory Committee: Professor Alan Jay Kaufman, Chair Professor James Farquhar Professor Shuhei Ono, Dr. Igor Puchtel Professor Raghuram Murtugudde, Dean's Representative © Copyright by Iadviga Zhelezinskaia 2018

Dedication

Посвящаю маме и академику Феликсу Петровичу Митрофанову

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List of Abbreviations

- ARA Archean Reference Array
- AVS Acid Volatile Sulfur
- CAP Carbonate Associated Pyrite
- CAS Carbonate-Associated Sulfate
- CRS Chromium-Reducible Sulfur
- GC Gas Chromatography
- GMM Gaussian Mixture Model
- GOE Great Oxidation Event
- IRMS Isotope-Ratio Mass Spectrometry
- MC Monte Carlo
- MDF Mass-Dependent Fractionation
- MIF-S Mass-Independent Fractionation of Sulfur Isotopes
- MSR Microbial Sulfate Reduction
- OM Organic Matter
- PAL Present Atmospheric Level
- SDB Sulfur-Disproportionation Bacteria
- SIMS Secondary-Ion Mass Spectrometry
- SRB Sulfate-Reducing Bacteria
- V-CDT Vienna Canyon Diablo Troilite
- V-PDB Vienna Pee Dee Belemnite

Chapter 1: Introduction

1.1. Chapter summaries

This dissertation consists of an introduction (Chapter 1), three chapters with research content, and a conclusion (Chapter 5). Chapters 2, 3, and 4 are presented in the format of manuscripts for publications; the general content of each is provided below.

Chapter 2 is part of a 5-year project funded by the National Science Foundation Frontiers in Earth System Dynamics (FESD) program on The Dynamics of Earth System Oxygenation started in 2013. In this chapter I present data from two Agouron Foundation cores AIDP-2 and AIDP-3 drilled in the Pilbara Craton, Western Australia. This was a team effort with the sulfur and carbon abundance and isotope data produced at the University of Maryland in collaboration with colleagues at Harvard University and the University of Washington, respectively. The elemental sulfur data were provided by colleagues at the University of California, Riverside, and the collections management and initial sample preparations were done at Arizona State University. My analytical efforts resulted in the sulfur, carbon, and oxygen isotope data collection for carbonate facies of the Carawine and Jeerinah formations. The main observations were of large δ^{34} S fractionations, similar to the Batatal study (Zhelezinskaia et al., 2014), and anomalous $\Delta^{36}S/\Delta^{33}S$ in carbonate facies. My work demonstrated a statistical difference in sulfur and carbon cycling between shallow and deep-water Neoarchean settings. Furthermore, a geochemical model of the data reveals the importance of both atmospheric chemistry and of biology on the preserved sulfur isotope abundances of Neoarchean sedimentary pyrite. Finally, the integrated sulfur and carbon data are evaluated in terms of previously reported hypotheses of organic haze fluctuations in the atmosphere (Zerkle et al., 2012; Izon et al., 2015), and of microbial activity in the oceans (Zhelezinskaia et al., 2014).

In Chapter 3, I present data from Neoarchean carbonates from multiple cores drilled from locations in Western Australia and South Africa. The Western Australia materials were provided by collaborator Dr. Bruce Simonson at Oberlin College, while the South African samples were collected from BH1-Sacha core by Dr. Gareth Izon, and the Agouron Foundation GKP and GKF cores stored at the Smithsonian Institution by myself with the help of curator Dr. Douglas Erwin. Sulfur and carbon isotope analyses were conducted in order to test hypotheses derived from my earlier research (Zhelezinskaia et al., 2014). While the same cores were analyzed previously, sulfur isotope researchers have focused mostly on their shale facies (Ono et al., 2003; Ono et al., 2009; Kendall et al., 2010; Zerkle et al., 2012; Izon et al., 2015). My whole rock pyrite analyses in carbonate-rich samples revealed linear relationships of sulfur isotope abundances that define two arrays. One follows the well-known Archean reference array (with Δ^{33} S ~0.9× δ^{34} S) and the second follows a newly defined array with a much shallower slope (Δ^{33} S ~0.1× δ^{34} S). Samples that define each of these arrays also have noticeable carbon isotope differences. In light of these results, I argue for the role of biology in the cycling of photolytic sulfur in shallow marine carbonate settings.

Chapter 4 explores issues involving Neoarchean seawater sulfate concentration and composition. These are important constraints for modeling early Earth's atmospheric oxygen content, as well as for understanding processes related to sulfur sinks and sources in various reservoirs, and to biological sulfur transformations. Recent studies using different techniques and proxies have come to different conclusions regarding these aspects of Archean seawater sulfate (Crowe et al., 2014; Zhelezinskaia et al., 2014; Paris et al., 2014). In this chapter, I explore a wide range of data and hypotheses, and evaluate their relative strengths and weaknesses to further consider the abundance and isotopic composition of ancient seawater sulfate. Based on a new high-resolution collection of the Batatal Formation carbonate preserved in the GDR-117 core, I produced time-series sulfur isotope data from macroscopic pyrite that confirm previous findings of a temporal Δ^{33} S shift in the lower part of the Batatal carbonate strata (Zhelezinskaia et al., 2014). Based on this high resolution data and a revised geochemical model, oceanic seawater concentration and residence time are further constrained.

1.2. Overview of early Earth environments

The focus of my studies are on chemical sediments that precipitated from seawater and accumulated into thick successions along ocean margins billions of years ago. A layman might argue that given the vast distance and time, objective assessments of the ancient environment would not be possible. Nonetheless, significant efforts have been made recently by many geoscientists to explore the early Earth, and to constraint the physical and chemical parameters on its surface. It is now possible to say that we know a lot about the environments of early Earth, but there is still more to learn. It is often thought that relative to today biological processes in the distant past may have been less important than abiotic processes. In contrast, the work of this dissertation, and my scientific vision, follows a quote by one of the founders of biogeochemistry, Prof. Vladimir Ivanovich Vernadsky, who said, "Living matter is the most powerful geological force." He continued to say that it is not only relevant for our today's bluegreen planet, but perhaps for entire Earth's history since time when life was evolved. Research conducted in this dissertation aimed to demonstrate that biology played a significant role in the Neoarchean sulfur cycle.

1.2.1. Atmosphere oxygen evolution

Our Earth >2.5 Ga (billion years ago) was a dramatically different place than it is today. While now we have 21% oxygen in the atmosphere, the Hadean (>3.9 Ga) and the Archean (3.9 - 2.5 Ga) eons (or the first two billion years of the planet history) lacked atmospheric oxygen (Holland, 1962; Lyons et al., 2014). In the Archean, only microbial life existed, appearing perhaps as early as 3.8 Ga (Mojzsis et al., 1996). The rise of atmospheric oxygen at around 2.4 Ga ago, also called the Great Oxidation Event (or GOE; Holland, 1999), required this microbial life to have developed the capability to produce oxygen by photosynthesis and established one of the most profound changes in the Earth's surface environment. The rise of oxygen then allowed for the evolution and diversification of eukaryotes and complex multicellular life (Catling et al., 2005; Raymond and Daniel Segrè, 2006), and much later the evolution of mammals (Falkowski et al., 2005) including *Homo sapiens*. The history and evolution of oxygen on the Earth's surface is not only essential for the history and evolution of life and environments on Earth, but also for searching for life on other planets.

The concept of the early Earth being oxygen-lean compared to today has been in the minds of scientists for more than 90 years (e.g. Oparin, 1924; MacGregor, 1927; Vernadsky, 1934; Poole, 1941; Rubey, 1955). Geological evidence cited to support the absence of free O₂ in the Archean atmosphere include: i.) the presence of detrital uranite and pyrite in sedimentary rocks >2.7 Ga (Ramdohr, 1958, Rasmussen and Buick, 1999), ii.) the absence of bedded sulfate deposits in sedimentary successions between 3.2 and 2.4 Ga (Huston, and Logan, 2004), and iii.) the predominance of ferrous iron in Precambrian chemical sediments (MacGregor, 1927), including the massive banded iron formations that formed between 2.7 and 2.2 Ga (Garrels et al., 1973). In spite of these observations, some scientists have rejected the idea of an oxygen-lean early atmosphere, and argued that Earth's atmospheric oxygen was near the present atmosphere level (PAL) since at least 4 Ga (Dimroth and Kimberley, 1976; Ohmoto and Felder, 1987; Clemmey and Badham 1982; Ohmoto, 1997; Ohmoto et al., 1999).

The strongest geochemical evidence for insignificant levels of oxygen in the early atmosphere has come from the documentation of mass-independent sulfur isotope fractionation (MIF-S), which is observed throughout Archean sedimentary records and disappears abruptly soon after the Archean-Proterozoic boundary (Fig. 1.1, Farquhar et al., 2000a; Bekker et al. 2004; Guo et al., 2009; Luo et al., 2016). According to a photochemical model (Pavlov and Kasting, 2002), MIF-S was linked to atmospheric oxygen and could be produced and preserved in surface environments at O₂ levels < 10^{-5} PAL. Such MIF-S anomalies were first recognized by Farquhar et al. (2000) and have been used to track atmospheric evolution, and importantly the timing of the GOE at ~2.3-2.4 Ga (Bekker et al., 2004; Guo et al., 2009; Luo et al., 2016). The disappearance of MIF-S is thus linked to a rise in oxygen levels above ~ 10^{-5} PAL (or <0.0002%, Pavlov and Kasting, 2002). At this threshold, the pathway to the production

of elemental sulfur aerosols closes, but at this threshold O_2 level, an ozone shield still could not form (Kasting and Donahue, 1980). Thus direct harmful UV radiation would still reach the earth surface and influence microbial habitats (Margulis, 1976).

Several hypotheses for the rise of oxygen $>10^{-5}$ PAL across the GOE have been proposed. These include: i.) the onset of oxygenic photosynthesis (e.g. Vernadsky, 1934; Holland, 1962; Kopp et al., 2005), ii.) hydrogen escape as a result of water dissociation (Poole, 1941; Dole, 1965; Catling et al., 2001; Zahnle et al., 2013) under more intense Archean UV radiation, iii.) a change in mantle redox state (Kasting et al., 1993, Kump et al., 2001), iv.) a collapse in atmospheric methane levels (Zahnle et al., 2006; Konhauser et al., 2009), and v.) a change in the mode of volcanism (Kump and Barley, 2007; Gaillard et al., 2011) from dominantly submarine to subaerial. These processes might have operated simultaneously, ultimately forcing changes of O_2 sources and sinks (Holland, 1962) in a way that resulted in shutoff of MIF-S production and promote the rise of atmospheric O₂ (Catling and Claire, 2005). Even though the Archean atmosphere was almost lacking in oxygen, signs of shallow ocean oxygenation appeared in Neoarchean times (Eigenbrode and Freeman, 2006; Kaufman et al., 2007; Kendall et al., 2010), suggesting that this interval was characterized by the critical transition from dominantly anaerobic to aerobic metabolisms.



Figure 1.1 Plot of Δ^{33} S variations over geological timescale. Compiled data are from Zhelezinskaia et al., 2014 and references therein.

Even at oxygen levels low enough to produce MIF-S signals that could be preserved in marine sediments, other proxies for atmospheric oxygen concentration, including trace element abundances and isotope compositions in both marine sedimentary rocks and terrestrial paleosols, suggest "whiffs of oxygen" in the Neoarchean atmosphere (Anbar et al., 2007; Voegelin et al., 2010; Kendall et al., 2013; Partin et al., 2013; Stueken et al., 2015). Furthermore, evidence exists for some level of oxidative weathering that extends to successions as ancient as 3 Ga (Crowe et al., 2013; Large et al., 2014; Mukhopadhyay et al., 2014). Oxidative weathering does not necessarily require an increase in free atmospheric oxygen above the level that would shut down MIF-S production (Johnson et al., 2016). For example, oxidative processes might have occurred on a small scale in exposed terrestrial soils that would have been "at profound redox disequilibrium with the atmosphere" (Lalonde and Konhauser, 2015). On the other hand, the participation of oxidants other than O₂ in a reducing

atmosphere (e.g. H_2O_2 suggested by Kasting et al., 1985) could be an alternative agent that drove 'oxidative weathering'.

1.2.2. Archean environments under reducing atmosphere

It was proposed that the Archean atmosphere had to be rich in the greenhouse gases NH₃, CO₂, and CH₄ in order to explain the Faint Young Sun Paradox (Owen et al., 1979; Sagan and Chyba, 1997; Pavlov et al., 2000; Wolf and Toon, 2010). However, the prevailing view today is that the atmosphere was only weakly reducing, with the dominance of CO₂, N₂ and H₂O (Rubey 1955, Walker, 1977, Kasting, 1993) and only occasional whiffs of CH₄ (Hayes, 1994; Zerkle et al., 2012). In spite of higher concentration of these gases, geological evidence suggests that surface conditions in the Archean were somewhat similar to the present day: surface temperatures at 3.4 Ga are interpreted to be no more than 40°C (Hren et al., 2009; Blake et al., 2010) and atmospheric pressure at 2.7 Ga (Som et al., 2016) were no more than 1 bar or lower based on the analysis of fossil raindrop impressions. As evidence accumulates, proposals for the Archean atmospheric composition are constantly changing. Based on sulfur and carbon isotope data, it was recently proposed that an organic-rich hazy atmosphere may have alternated with haze-free periods in the interval between about 3.2 and 2.5 Ga (Domagal-Goldman et al., 2008; Izon et al., 2015; Zerkle et al., 2012). These periods of hazy atmosphere (similar to what is observed on Saturn's moon Titan) were geologically brief (<1 Ma, Izon et al., 2017), and plausibly related to episodic biogenic release of CH₄ to the atmosphere.

Higher CO₂ concentration (Kasting, 1993) would lead to higher weathering rates relative to today, which would have delivered nutrients to the ocean faster and

thereby stimulating primary productivity (Fabre et al., 2011). Insofar as the Archean continental crust was more mafic in composition, Archean seawater should have been characterized by higher concentrations of HCO₃⁻, Fe(II), and Mg, as well as higher Mg/Na and a lower Ca/Na and pH than today (Hao et al., 2017). Mobility of Fe²⁺ in oxygen-free world led to the development of iron rich (or ferruginous) oceans (Reinhard et al., 2009). The source of this iron was most likely from hydrothermal fluids and the weathering of continents (Isley and Abbott, 1999). Even if the Archean ocean was more saline than today (Knauth, 2005), sulfate concentration in seawater was nonetheless much lower (Crowe et al., 2014; Zhelezinskaia et al., 2014).

1.2.3. Microbial life in the Archean

The microbial life that drives Modern elemental cycles most-likely played an important role on the Archean Earth (Sumner 1997; Waldbauer et al., 2009). However, at low oxygen levels and absence of protective ozone layer in the stratosphere, organisms on the surface would not have had a sufficient shield to harmful UV radiation (Cockell, 2000). At the same time, evidence of shallow marine stromatolites at 3.5 Ga (Walter et al., 1980) make it clear that even without an ozone shield, other protections or repair mechanism had to have existed. For example, organisms might hide deeper in the ocean (Sagan, 1973) or below a sedimentary veil (Margulis et al., 1976); microbial communities that formed biofilms, which led to stromatolites, might have been protected by trapped sedimentary grains, carbonate cementation, or the presence of Fe²⁺ in the water column (*cf.* Pierson et al., 1993; Phoenix et al., 2001; Gauger et al., 2015). On the other hand, because of high UV exposure, microorganisms probably did not fully occupy the Archean terrestrial environment (Berkner and

Marshall, 1965), although there is emerging evidence for the presence of a terrestrial biota by ~2.7 Ga (Watanabe et al., 2000; Stüeken et al., 2012).

In marine environments, the first signs of microbial life are found in at least 3.5 Ga sedimentary rocks (Schopf, 1993), or perhaps even as far back as 3.8 Ga (Mojzsis et al., 1996), but certainly after the last of the ocean-vaporization bombardment events. Assuming a reducing atmosphere, the first microbes would have evolved anaerobic metabolic strategies, utilizing widespread electron donors such as hydrogen and ferrous iron that emanated from volcanic vents, as well as electron acceptors, including sulfur and nitrogen species that were available in ocean water. By harnessing the available nutrients and redox gradients in the Archean ocean, it is likely that multiple anaerobic ecosystems operated on the early Earth (Canfield et al., 2006; Kharecha et al., 2005).

Stromatolites preserved in 3.5 Ga sedimentary rocks are thought to be signposts for photosynthetic organisms (Des Marais, 2000). Given the requirement of only one photosystem and reaction center, anoxygenic photosynthesis, which dissociates hydrogen sulfide instead of water as a source of electrons, was probably ancestral to oxygenic photosynthesis (Blankenship, 2010). This view is consistent with the absence of biomarkers for oxygenic photosynthesis (e.g., 2α methyl-hopanoids) in Neoarchean sedimentary rocks (French et al., 2015), although some geochemical studies argue for the existence of oxygen-producing cyanobacteria by 3.0 Ga (Crowe et al., 2013; Planavsky et al., 2014).

Phototrophic iron-oxidizing bacteria may have played a key role in the deposition of Archean banded iron formations (Posth et al., 2013). These organisms

directly oxidize ferrous iron via anoxygenic photosynthesis (e.g. Crowe et al., 2008). It is notable that high concentration of ferrous iron in the deep Archean water column and its upwelling to shallow environments could have led to cyanobacterial toxicity (Swanner et al., 2015), and thus would have restricted O₂ production. Fermentative methanogens and methane-consuming methanotrophs also likely played an important role in Neoarchean surface environments (Hayes, 1994; Kharecha et al., 2005; Eigenbrode and Freeman, 2006; Zerkle et al., 2012), and perhaps older environments as well (Ueno et al., 2006).

Sulfur-based metabolisms may have been among the earliest on Earth. It has been proposed that microbial sulfate reduction was active as a carbon cycling strategy as far back as 3.4 Ga (Shen et al. 2001; Ueno et al. 2008; Wacey et al. 2010; 2011a). Sulfate reducers are obligate anaerobes, which as heterotrophs (some are also phototrophs) are responsible for at least 30% of carbon mineralization in modern ocean sediments (Jørgensen, 1977; Bowles et al., 2014). In addition, elemental sulfur disproportionation may have cycled photolytic sulfur (Philippot et al. 2007; Wacey et al. 2010; 2011a; Galić et al., 2017) and phototrophs may have oxidized sulfide by Paleoarchean time (Wacey et al. 2011b). Thus, highly diverse microbial communities driven by sulfur metabolisms were established very early in Earth history.

1.2.4. Sedimentary records in the Archean

Archean sedimentary strata are represented by wide varieties of siliciclastic (conglomerate, sandstone, mudstone, shale, etc.) and chemical (banded iron formation, carbonate, chert, etc.) rocks together with their metamorphic siblings (Pettijohn, 1943).

In this thesis I focus on well-preserved Neoarchean carbonate and shale rocks from low grade environments for detailed geochemical characterization.

1.2.4.1.Shale and carbonate facies

Shale is a laminated (having thin layers and able to fissile) clastic argillaceous (size of particles < 0.004 mm) rock type consisting of mostly clay, quartz and other silicate minerals (Pettijohn, 1957). If shale is dark in color and has high amount of organic matter, it is referred to black or carbonaceous shale. Black shales are also typically rich in iron sulfides (mostly pyrite), but poor in carbonate content (< 6%; (Pettijohn, 1957). In modern environments, laminated black shale is deposited under anaerobic conditions in *deep* enclosed basin (>1500 m depth e.g. in Black Sea), borderland basin zone (>500 m depth e.g. in S. California), continental slopes (>100m depth, e.g., Peru, Namibia) and sometimes in *shallow* stratified basins (e.g. estuaries, fjords) and coastal zones where the laminations are not disturbed by burrowing organisms (e.g., lagoons, tidal flats) (Berry and Wilde, 1978; Arthur and Sageman, 1994). In the Neoarchean, black shale accumulated in marine environments on the deep shelf and slope (Simonson et al., 2000; Schröder et al., 2006). As today, the rate of black shale accumulation was low resulting in condensed strata (Pettijohn, 1957; Altermann and Nelson, 1998).

Carbonates consist predominantly of Ca- and Mg-bearing minerals (dolomite, calcite, aragonite) that precipitate directly from ions dissolved in seawater if carbonate saturation is achieved. Most of the carbonates in modern marine environments are biological in origin, either by template-directed mineralization, by the modification of seawater that promotes the inorganic formation of the minerals. Most modern

carbonates are formed in shallow water (depths <100 m) because the organisms that produce most of the carbonate are photosynthetic (Flügel, 2010). Significant portion of modern carbonate rocks consist of calcite and aragonite (CaCO₃) as bioclasts created by calcareous organisms. In the Archean, fine-grained dolomite (Ca,Mg)(CO₃)₂ is the most common mineral in most carbonate facies (Sumner. 1997).

Today carbonate depositional environments are located along *shallow* warm carbonate platforms and shelves where reef building organisms are active, as well as tidal flats where algal mats and stromatolites are formed. Calcite also accumulates in the *deep* ocean above the carbonate compensation depth (CCD; 3,000 - 5,000 m) as foram and cocolith oozes. In the Archean long before the evolution of calcareous nanoplankton, carbonate minerals were formed directly on the sea floor due to high levels of carbonate saturation, which would have been facilitated by the presence of photosynthetic organisms that drew CO₂ out of the water column (Sumner, 1997, Sumner and Grotzinger, 2004).

Carbonate formation is generally controlled by the flux of siliciclastic material into the depositional basin, which typically inhibits chemical precipitation by sediment masking. Nonetheless, mixed carbonate-bearing strata is common and may be formed by various processes (Mount, 1984). In this work, if rocks have more than 80% of carbonate minerals they are refer to as carbonates. If carbonate content is between 50% and 80%, the rock is called a shaly carbonate if laminated, and a muddy carbonate if massive. If shale has carbonate content between 20 and 50%, it is called a calcareous shale in this dissertation.

The concentration of sulfur in carbonate rocks is typically quite low, and thus is generally unreported. However, in their compilations of carbonate geochemical data Veizer et al. (1989) and Veizer et al. (1990) found sulfur concentration in Archean samples to range between 0.01-0.08 wt.%. In my previous study of the Batatal Formation (Zhelezinskaia et al., 2014), sulfur abundances in carbonates ranged between 0.01 and 0.05 wt.%. In contrast, Neoarchean black shales contain 2.9 ± 2.8 and 0.98 ± 1.41 wt.%, respectively (see Kaufman et al., 2007 and Kendall et al., 2010), which is a hundred times more than in contemporaneous carbonates.

1.2.4.2.Evolution of Archean carbonate platforms

Insofar as this study focuses on carbonate sedimentary rocks, a detailed understanding of Archean carbonate platform evolution and distribution is important. The abundance of bedded carbonates in the geologic record increases dramatically from the Paleoarchean to the Neoarchean eras. Grotzinger (1989) discussed a broad spectrum of Archean carbonates and suggested that the Neoarchean was a time when stable carbonate platforms first dominated the sedimentary record. This is a period that also correlates with the stabilization of continents (Condie, 1998), around which extensive continental shelves were formed.

Carbonates from the Paleoarchean are typically thin, with layer thicknesses of only a few centimeters to a few meters, and are characterized by a restricted and discontinuous spatial distribution. These carbonates are often replaced by chert. It is thought that these carbonates accumulated not on the stable platform, but as part of a sequence in the evolution of greenstone belts. Most of the carbonates from the Warrawoona (Pilbara), Onverwacht and Fig Tree (Barberton) groups were formed after extensive volcanic eruptions and are interpreted to be deposited as shallow-water facies during a pause in tectonic activity (Grotzinger, 1989).

Mesoarchean carbonates from the Steep Rock (Superior Province, Canada) and Nsuze (Pongola Supergroup, South Africa) groups are thought to have accumulated on the first small, but stable, carbonate platforms (Grotzinger, 1989). They formed carbonate layers with the thickness of tens to hundreds of meters, including stromatolitic features that imply shallow water deposition.

In contrast, the Neoarchean Era is characterized by the establishment of widespread and remarkably thick (hundreds to thousands of meters) carbonate platforms on many different cratons (Fig.1.2) including: the Yellowknife Supergroup (Slave Province, Canada), Ngezi Group (Belingwe Greenstone Belt, Zimbabwe), Transvaal Supergroup (South Africa), and Mount Bruce Supergroup (Western Australia). These carbonate successions are characterized by diverse and complex assemblages of carbonate facies, as well as evidence for ramps, rimmed shelves, barrier reefs and isolated carbonate buildups (Grotzinger, 1989).



Figure 1.2 Thickness of preserved carbonate and black shale strata through time (data are from Condie et al., 2001 and Grotzinger, 1989)

1.3.1. Isotopic notations and mass fractionations

Sulfur has four stable isotopes with different natural abundances: 32 S (95.04%), 33 S (0.75%), 34 S (4.20%), and 36 S (0.015%) (Coplen et al., 2002). Variations in isotopic composition are described using the delta notation (δ), which is defined in terms of the reference-normalized ratios of two isotopes (where the denominator is the most abundant isotope). For sulfur isotopic systematics:

$$\delta^{3x}S = \left[\frac{\left(\frac{^{3x}S}{^{32}S}\right)sample}{\left(\frac{^{3x}S}{^{32}S}\right)std} - 1\right] \times 1000$$

where x is 3, 4, or 6 and standard (std) is VCDT (Vienna-Canyon Diablo Troilite) – an iron meteorite from Meteor Crater (Arizona, USA).

Physical and chemical processes fractionate sulfur isotopes because of differences in their properties resulting principally from differences in isotopic masses. Chemical processes leading to mass-dependent fractionation can be reversible (equilibrium isotope effects) or unidirectional (kinetic isotope effects). In addition to Mass-Dependent Fractionations (MDFs), another class of fractionations arise from factors other than isotopic mass differences. These effects are called non-mass-dependent isotope effects (or Mass-Independent Fractionation (MIF)). Fractionations produced by equilibrium processes are related to vibrational frequencies of different isotopes in molecules, which can be theoretically calculated (Urey et al. 1947), and measured empirically. The reference frame for mass-dependent fractionations is defined by an approximation of equilibrium. These reference fractionation arrays are given by the following equations (Farquhar and Wing, 2003):

$$\delta^{33}S \approx {}^{33}\lambda \times \delta^{34}S \qquad \qquad \delta^{36}S \approx {}^{36}\lambda \times \delta^{34}S$$

where the exponents are defined for high temperature processes as:

$${}^{33}\lambda = \frac{\frac{1}{M({}^{32}S)} - \frac{1}{M({}^{33}S)}}{\frac{1}{M({}^{32}S)} - \frac{1}{M({}^{34}S)}} \approx 0.516 \quad ; \quad {}^{36}\lambda = \frac{\frac{1}{M({}^{32}S)} - \frac{1}{M({}^{36}S)}}{\frac{1}{M({}^{32}S)} - \frac{1}{M({}^{34}S)}} \approx 1.89$$

In order to distinguish between non-mass dependent and mass-dependent isotope effects, a capital delta (Δ) notation has been developed. This capital delta notation represents the difference in a measured isotope ratio from that predicted by a mass-dependent reference fractionation array. For processes operated at surface temperature the reference arrays ³³ λ and ³⁶ λ were defined as 0.515 and 1.9 (Hulston and Thode, 1965):

$$\Delta^{33}S = \delta^{33}S - \left[\left(1 + \frac{\delta^{34}S}{1000} \right)^{0.515} - 1 \right] \times 1000 \quad ; \quad \Delta^{36}S = \delta^{36}S - \left[\left(1 + \frac{\delta^{34}S}{1000} \right)^{1.9} - 1 \right] \times 1000$$

1.3.2. Mass-dependent isotope fractionation and biological sulfur cycling

Since the finding of different sulfur isotopic compositions of end-member components, scientists started to think about fractionations that occurred at each steps in the overall process (Tudge and Thode, 1950). The constancy of sulfur isotopic composition in meteorites was suggested to reflect primodial composition, from which terrestrial fractionation processes (the most important being sulfate reduction) continuously redistributed sulfur isotopes between reservoirs, resulting in the spread of sulfur isotopic compositions observed today (Fig. 1.3, MacNamara and Thode, 1950; Ault and Kulp, 1959; Thode et al., 1961). The isotopic compositions of terrestrial reservoirs are represented in Fig. 1.3. Sulfate in the Modern oceans is uniform with a stable concentration of 28 mM and sulfur isotopic composition of δ^{34} S ~ +21 ‰ (Rees et al., 1978). The residence time of seawater sulfate is estimated in the millions of years, which makes sulfate a highly conservative element. Sulfur species entering the atmosphere (usually in the form of SO₂, and to a lesser extent H₂S, SO₃, and COS), have a combined sulfur isotopic composition close to that of meteoritic value ~0‰ (Nielsen et al., 1991). The residence time of atmospheric sulfate aerosols is measured on the scale of days (Charlson et al., 1992). It has been proposed that in the Archean, atmospheric sulfur input from volcanic sources also had an isotopic composition of ~0‰ (Farquhar et al., 2000).

The greatest range of δ^{34} S compositions is observed in sedimentary rocks where pyrite is formed most often by biological processes that strongly fractionate S isotopes. Today, sedimentary pyrite formation mostly occurs in marine coastal environments (Canfield and Des Marais, 1991; Bowles et al., 2014) by microbial sulfate reduction (MSR). Sulfate-reducers are anaerobic heterotrophic (but sometimes autotrophic) microorganisms that are responsible for more than 1/3 of organic carbon mineralization in the shallow oceans (Jorgensen, 1977; Canfield and Des Marais, 1993; Bowles et al., 2014), and they are often linked to the lithification of microbial mats through carbonate ion production (Baumgartner et al., 2006).

The highest sulfate reduction rate is observed in shallow marine sediments (<50 m water depth, Bowles et al., 2014) where most carbonate precipitation occurs. Taking into account that most Neoarchean carbonates preserve stromatolitic features (e.g., continuous BH1-Sacha core, Altermann and Siegfried, 1997), processes

occurring during stromatolite and microbial mats formation in the modern environments may be applicable to our understanding of Archean pyrite formation. According to measurements of Visscher et al. (1998), more than 50% of the total organic carbon in the stromatolitic mats is mineralized through sulfate reduction. Studies of modern marine stromatolites in Highborne Cay and hypersaline Salt Pan mats in the Bahamas demonstrated that SRB plays a prominent role raising alkalinity and driving carbonate precipitation (Visscher et al., 2000; Dupraz et al., 2004). A simplified net reaction of sulfate reduction mediating CaCO₃ precipitation (Visscher et al., 1998) is as follows:

$$SO_4^{2-} + 2[CH_2O] + OH^- + Ca^{2+} \rightarrow CaCO_3 + CO_2 + 2H_2O + HS^-$$

Dissimilatory MSR is one of the dominant mechanisms generating terrestrial sulfur isotope fractionation at low temperature, and can change initial δ^{34} S values by more than 75‰ (Rudnicki et al., 2001; Canfield et al., 2010; Sim et al., 2011). Sulfate-reducers use organic carbon or H₂ gas as electron donors and sulfate as an electron acceptor, and preferentially incorporate the light ³²S isotope (Canfield, 2001a) to form the byproduct hydrogen sulfide, thereby leaving residual sulfate ³⁴S-enriched:

$${}^{32}SO_4{}^{2-} + 2[CH_2O] \rightarrow H_2{}^{32}S + 2HCO_3{}^{-}$$

 ${}^{32}SO_4{}^{2-} + 4H_2 + 2H^+ \rightarrow H_2{}^{32}S + 4H_2O$

Available ferrous iron combines with hydrogen sulfide to form the highly insoluble mineral pyrite, thereby preserving the sulfur isotopic signature of MSR in the rock record. It is thought that positive δ^{34} S composition of seawater today was formed by continuous microbial sulfate reduction through billion years that removed ³²S from seawater sulfate (Canfield 2001). Fractionation of sulfur isotopes by MSR depends on

many factors, including the concentration of sulfate (Habicht et al., 2002), the type of organic substrate (Canfield, 2001b), and temperature (Harrison and Thode, 1958). All these factors can change the rate of MSR, such that the higher the rate of sulfate reduction the lower the fractionation of sulfur isotopes (Harrison and Thode, 1958, Leavitt et al., 213).

Today, most of the sulfide (80-95%, Jørgensen, 1982) produced by sulfate reduction is re-oxidized back to sulfate by sulfide-oxidizing bacteria using oxygen or nitrate as electron donors (Visscher et al., 1998):

 $HS^- + 2O_2 + CaCO_3 \rightarrow HCO_3^- + Ca^{2+} + SO_4^{2-}$

 $5HS^{-} + 8NO_{3}^{-} + 3HCO_{3}^{-} + 3Ca^{2+} \rightarrow 3CaCO_{3} + 4N_{2} + 4H_{2}O + 5SO_{4}^{2-}$

The purple and green sulfur bacteria are the most dominant sulfur oxidizers in anoxic environments. In culture experiments of anoxygenic oxidation of sulfur compounds, fractionations usually do not exceed 5‰ (Toran and Harris, 1989; Zerkle et al., 2009). Abiotic oxidation of sulfide to sulfate during either oxygenic or anoxygenic pathways produce small fractionation <1‰ (Balci et al., 2007). However, oxidation of sulfide is more complicated process than just conversion of sulfide to sulfate, with intermediate reaction steps producing a variety of sulfur compounds of intermediate oxidation states (e.g., Zopfi et al., 2004 for a review). Sulfur intermediate compounds (sulfite (SO₃^{2–}), elemental sulfur (S₀), thiosulfate (S₂O₃^{2–}), dithionate (S₄O₆^{2–}), and tetrathionate (S₄O₆^{2–})) are used by disproportionating bacteria that produce both sulfide and sulfate (Bak and Cypionka, 1987), e.g.:

$$4SO_3^{2-} + H^+ \rightarrow HS^- + 3SO_4^{2-}$$
$$4S_0 + 4H_2O \rightarrow 3HS^- + SO_4^{2-} + 5H^+$$

In modern anoxic sediments, the concentration of these intermediate compounds may be sufficiently high (Jorgensen, 1990; Zopfi et al., 2004) to even exceed sulfate abundance (Jorgensen, 1990). During the Archean, when environments were mostly anoxic, these compounds might have played a far more important role in microbial sulfur cycling (Philippot et al., 2007). Sulfur disproportionators produce large isotopic effect between the two products of the reaction: sulfate and sulfide. With elemental sulfur as a substrate, fractionation may reach about 30‰, with sulfate being ³⁴S-enriched relative to sulfide (Johnston et al., 2005). During sulfite disproportionation fractionation may exceed 55‰ (Johnson et al., 2005). The measured extent of sulfur fractionation by sulfur-respiring bacteria is illustrated in Fig. 1.3.



Figure 1.3. Sulfur isotopic composition of common sulfur reservoirs (blue and red bars, from Hoefs, 2009) and extent of isotopic fractionation by various sulfur-respiring bacteria (green bars, from Canfield, 2001; Canfield et al., 2010; Watanabe et al., 2009; Johnston et al., 2005; Kaplan and Rittenberg, 1964)

On the other hand, the inorganic precipitation of sulfate minerals yield only small magnitudes of fractionation, typically around 2‰ (Raab and Spiro, 1991). Hence, evaporites (e.g. gypsum) or carbonate-associated sulfate (CAS), which is the sulfate incorporated into the carbonate lattice during precipitation, are widely used to estimate the sulfur isotopic composition of seawater at the time of precipitation (Strauss, 2004).

1.3.3. Sources of MIF-S and the Archean sulfur cycle

The observed MIF-S signatures (or non-zero Δ^{33} S and Δ^{36} S values) in Archean sedimentary rocks (Farquhar et al., 2000a) have been explained by photochemical reactions involving SO₂ in the oxygen-free early atmosphere (e.g. Farquhar et al., 2001). Further support for this view comes from detailed experimental work (Farquhar et al., 2001; Masterson et al., 2011; Whitehill and Ono, 2012; Franz et al., 2014; Ono et al., 2013; Whitehill et al., 2014) as well as geochemical modelling (e.g. Pavlov and Kasting, 2002; Zerkle et al., 2012; Halevy, 2013). Sufficient photodissociation of SO₂ gas occurs by absorption of short UV wavelength between 190 and 220 nm (e.g. Farquhar et al., 2001). The reaction is written as $3SO_2 + hv => 2SO_3^* + S$ (* - excited state; Ustinov et al., 1988). The sulfite (SO₃) product of the reaction is thought to have negative Δ^{33} S values and can further react with H₂O forming sulfuric acid (H₂SO₄) (Farquhar et al., 2001). On the other hand, elemental sulfur (S^0) , which exists mostly as a ring structure S₈ at low temperatures (Steudel and Holz, 1988), likely carries positive Δ^{33} S signatures (e.g. Farquhar et al., 2001; Masterson et al., 2011). The low predicted oxygen concentrations in the Archean atmosphere ($<10^{-5}$ of the present atmospheric level (PAL) or < 0.0002%, Pavlov and Kasting, 2002) prevented homogenization of two sulfur channels, so that their unique MIF-S signatures could be transferred to the surface and preserved in the rock record.

The currently accepted model for the Archean sulfur cycle is depicted in Figure 1.4. Initial volcanic SO₂ had mantle sulfur isotopic compositions of δ^{34} S and Δ^{33} S close to 0‰ (Gao and Thiemens, 1993; Farquhar et al., 2000a; Labidi et al., 2013). Volcanic SO₂ under atmospheric reducing conditions was subjected to photochemical reactions resulting in formation of two reaction products (sulfate and elemental sulfur) with distinctive multiple sulfur isotopes. Throughout the Archean the magnitude of Δ^{33} S in reaction products probably changed as indicated by compilation of Archean sulfur records (Fig. 1.1) with peak positive and negative values in the Neoarchean. These Δ^{33} S changes over time were attributed to different chemical reaction pathways (Farquhar et al., 2007), or variability in the oxidation state of volcanic sulfur volatiles (Halevy et al., 2010). Probably, much of the early record preserved MIF-S was recycled through subduction zone and later incorporated in volcanic rocks (Cabral et al., 2013).



Figure 1.4 The Archean sulfur cycle model (modified from Kasting, 2001)
Insofar as the Archean atmosphere was anoxic (Pavlov and Kasting, 2002), it is possible that other sulfur gases such as hydrogen sulfide (H₂S), carbonyl sulfide (OCS), and carbon disulfide (CS₂) might account for MIF-S. Photolysis experiments on H₂S (Farquhar et al., 2000b) and OCS (Hattori et at., 2011) demonstrate small magnitude MIF-S, but experiments on CS₂ (Colman et al., 1996; Zmolek et al., 1999) showed large Δ^{33} S variations. Non-photochemical mechanisms might also take part in the MIF-S formation, but their exploration was only recently introduced and resulting hypotheses need thorough evaluation, including: i.) recombination reactions involving sulfur gases and polysulfur aerosols in the atmosphere (Babikov, 2017; Babikov et al., 2017; Kumar and Francisco, 2017), and ii.) dissociation reactions in electrical discharges of SO₂ gas (Ignatiev et al., 2017).

1.3.4. Biological carbon cycling

Carbon has two stable isotopes: ¹²C and ¹³C with natural abundances of 98.89% and 1.11%, respectively (Coplen et al., 2002), and variations in the carbon isotopic compositions are reported using the delta notation (δ), a ratio of isotopes in sample to the same ratio in the standard material (Vienna Pee Dee Belemnite (V-PDB)):

$$\delta^{13}C = \left[\frac{\binom{13}{C}}{\binom{13}{C}}_{\text{std}}^{2} - 1\right] \times 1000$$

Carbon is an important element in surface processes as an essential constituent in organic molecules, carbonate species in oceans (whose relative abundances largely control oceanic pH), and carbon-bearing gases (e.g., CO₂ and CH₄). The isotopic composition of the main carbon-bearing reservoirs are depicted in Fig. 1.5 together

with transformations of carbon into different forms with subsequent isotope fractionations. Biological processes produce the largest fractionations of carbon isotopes in a way that biomass during metabolic activities is typically ¹²C-enriched (Fig. 1.5). However, methanogens produce CH₄ from either CO₂ or organic material that is highly ¹³C-depleted by <50‰ relative to the initial substrate. Today isotopic composition of biomass is dominated by fractionation produced by Calvin Cycle oxygenic photosynthesis, which is around 25 - 30%. In the Archean, it is likely that more primitive types of autotrophic or fermentative metabolisms such as anoxygenic photosynthesis, methanogenesis, or methanotrophs were responsible for the wide range of $\delta^{13}C_{org}$ compositions in sedimentary rocks (Eigenbrode and Freeman, 2006). Even though organic matter in the sedimentary records represents a mixture of primary and secondary sources, isotopic variations to some extent indicate the dominance of one metabolism over another (e.g. Hayes, 1994). Because carbon isotopes are not the main focus in this study, details on carbon cycling are given in chapter sections significant for each individual study.



Figure 1.5. Carbon isotopic composition of common carbon reservoirs (blue and red bars, from Des Marais, 2001) and extent of isotopic fractionation by various carbon metabolisms (green bars, from Des Marais, 2001; Wong et al., 1975; Coombs et al., 1975; Reibach and Benedict, 1977; Jahnke et al., 1999).

1.4. Goals and motivation

Since the discovery of mass-independent fractionation of sulfur isotopes (MIF-S) in Archean sedimentary rocks (Farquhar et al., 2000a), the majority of sulfur isotope measurements have been conducted on fine-grained siliciclastic rocks, predominantly organic- and pyrite-rich shale, with fewer analyses of chemical sedimentary rocks, including banded-iron formations, barites, and carbonates. My time-series study of ~2.5 Ga Batatal Formation from south-central Brazil, which contains a depositional record of both shale and carbonate facies, revealed that pyrite grains hosted in carbonates preserved large magnitude mass-dependent fractionation of sulfur isotopes together with consistently negative Δ^{33} S values (Zhelezinskaia et al., 2014). This novel observation, which had not been systematically recognized in previous studies, highlights the importance of microbial sulfate reduction in the

Neoarchean carbon cycle. The contrast between Carbonate Associated Pyrite (CAP) and pyrite in shale from the Batatal Formation, along with equivalent analyses of shalerich successions in South Africa and Western Australia (*cf.* Kaufman et al., 2007; Ono et al., 2009; Kendall et al., 2010) suggested that sulfur sinks, fluxes and processes of sulfur cycling were different in carbonate vs. shale depositional environments. The Batatal data were further consistent with earlier suggestions of a negative Δ^{33} S seawater sulfate reservoir (Ono et al. 2003; contra Paris et al., 2014), and a geochemical model of the time-series data resulted in an estimate of Neoarchean seawater sulfate concentrations that were 1000-fold lower than in the Modern ocean.

Following these findings, this dissertation focuses on Neoarchean carbonate facies worldwide to determine if i.) sulfur isotope distributions and fractionations in carbonate facies are similar on a global scale, ii.) sulfur fluxes and transformations in carbonate environments are fundamentally different from those in shale environments, and iii.) the importance of biological processes on the preservation of MIF-S signals in Neoarchean rocks.

Drill core samples used in these subsequent studies came from three locations: South Africa, Western Australia and Brazil. Previously, lithological controls on preservation of MIF-S signals were suggested by some authors (e.g. Eigenbrode and Freeman, 2003; Ono et al., 2003; Ono et al., 2009) based on a small survey of carbonates from those locations. Their conclusions, however, were made based on very few pyrite measurements (e.g., Ono et al., 2003, where only three Carawine Formation samples were used) or SIMS analyses of selected pyrite grains (e.g. Kamber and Whitehouse, 2007). This dissertation greatly expands the number and stratigraphic distribution of carbonate multiple sulfur isotope analyses, and importantly includes the measurement of Δ^{36} S compositions, which were not reported in the earlier studies. In light of recent evidence for anomalous Δ^{36} S values in pyrite from discrete intervals of Neoarchean sedimentary successions (Zerkle et al., 2012), I have used this additional measure in CAP samples to address the potential for episodic changes in atmospheric chemistry associated with the buildup of methane in the Neoarchean atmosphere.

Chapter 2: Environmental controls on the preservation of atmospheric sulfur in Neoarchean marine facies

<u>Abstract</u>

Geochemical investigations of new scientific drill-cores intersecting ~2.7 Ga Neoarchean marine sedimentary facies in Western Australia are used to explore hypotheses related to the cycling of sulfur by photolytic reactions in an anoxic atmosphere. I interpret multiple sulfur isotopic data to reflect atmospheric conditions dominated by an organic haze that were overprinted in shallow environments through microbial sulfur cycling. Multiple sulfur isotope measurements reveal significant differences between shale- and carbonate-dominated facies of the subtidal Jeerinah Formation and of the intertidal to supratidal carbonates of the overlying Carawine Dolomite. Bulk shale samples are characterized by δ^{34} S, Δ^{33} S, and Δ^{36} S relationships that are similar to those established for other shale-dominated successions of broadly equivalent age. I interpret this signal as dominated by photolytic fluxes of elemental sulfur from the atmosphere with minimal biological contribution. In contrast, a large δ^{34} S range (>35‰) and persistently negative Δ^{33} S compositions observed in carbonate associated pyrite, coupled with systematic deviations from expected $\Delta^{33}S/\delta^{34}S$ and Δ^{36} S/ Δ^{33} S reference arrays, suggest that the major sulfur source to this environment was atmospheric sulfate, which was isotopically redistributed through microbial sulfate reduction. These observations support the view that Neoarchean oceanic sulfate had a negative Δ^{33} S signature. Furthermore, geochemical modeling suggests that deviations of data from established reference arrays may result from both changes in atmospheric reactions associated with the shielding effects of an organic haze and in the degree of microbial recycling of organic carbon in the oceans.

2.1. Introduction

Like Titan, Saturn's orange shrouded moon, the anoxic atmosphere enveloping the Archean Earth may have contained enough methane to form an organic haze (Pavlov et al., 2001; Zerkle et al., 2012; Izon et al., 2015). This haze would have attenuated the solar UV flux and thereby protected surface environments from high energy radiation (Wolf and Toon, 2010). Based on recent computer models and laboratory experiments (e.g. Trainer et al., 2004; Domagal-Goldman et al., 2008), a methane haze would form if the CH₄/CO₂ ratio was >0.2 (relative to 0.005 in the modern oxygenated atmosphere). Due to the shielding effect of N₂, any such haze would accumulate above the surface and would be heterogeneously distributed with latitude (Wolf and Toon, 2010). A thinner organic haze (and lower optical depth) would develop in lower latitudes due to vertical atmospheric motion at the equator.

Evidence of an increase in the biological production and utilization of methane in the Neoarchean (ca. 2.7 to 2.5 Ga; Eigenbrode and Freeman, 2006) suggests the possibility that this greenhouse gas would accumulate to sufficient concentrations in the atmosphere to form such a haze, which may then have induced changes in atmospheric sulfur chemistry. It has been suggested that the photolysis of volcanogenic SO₂ and the consequent production of elemental sulfur (S₈) and sulfate (SO₄²⁻) aerosols with mass-independent sulfur isotope signatures in an anoxic atmosphere (Farquhar et al., 2000) – which rained down and were preserved in Earth's surface environments – may have been affected by the presence or absence of an organic haze. For example, haze has been invoked to explain temporal shifts of $\Delta^{36}S/\Delta^{33}S$ data arrays in Mesoarchean successions (Farquhar et al., 2007), and then again for several coupled Neoarchean C/S isotope excursions in Western Australian and South African strata characterized by $\delta^{13}C$ values of organic matter that are < -37‰ and $\Delta^{36}S/\Delta^{33}S$ data arrays of < -1.0 (Zerkle et al., 2012; Izon et al., 2015; Izon et al., 2017).

To further test these observations and models, I targeted two cores drilled into Neoarchean (> 2.6 Ga) successions of Western Australia. The broadly equivalent cores from the Hamersley Basin, which intersect the shale-dominated Jeerinah Formation in both the center of the basin and again stratigraphically below the Carawine Dolomite towards the eastern margin, provide a stratigraphic framework to study the preservation of atmospheric sulfur inputs to both deep water shale and shallow marine carbonate environments (Fig. 2.1). Due to high abundances of pyrite in subtidal shales that accumulated beneath anoxic bottom waters (Poulton and Canfield, 2011), this deep water facies has been a prime target of deep time geochemists interested in reconstructing the Archean sulfur cycle. In contrast, carbonate facies, which are typically lean in organic carbon and pyrite, and likely accumulated beneath a shallower water column, have not been the focus of many sulfur isotope studies.

My previous whole rock and ion probe sulfur isotope study of pyrite in a Neoarchean carbonate platform of Brazil (Zhelezinskaia et al., 2014) revealed large and previously unreported δ^{34} S fractionations (ca. 50‰) associated with microbial sulfate reduction (MSR). This is an important biological process in marginal marine settings that recycles a significant proportion of photosynthetically derived sedimentary organic matter back to CO₂ and alkalinity (Bowles et al., 2014 and references therein). The Brazilian study additionally showed that carbonate associated pyrite (CAP) preserves dominantly negative Δ^{33} S compositions with some strongly negative δ^{34} S signatures when compared to Neoarchean shales, further arguing for long-term stability of seawater sulfate Δ^{33} S composition and low sulfate abundance (Zhelezinskaia et al., 2014) between ~1 and 10 µM relative to 28 mM today. In this study, we present CAP data from the Carawine Dolomite that similarly preserves negative Δ^{33} S values with some samples exhibiting strongly negative δ^{34} S compositions – again indicating the importance of MSR in carbonate environments. My new results also extend those of Izon et al. (2015) confirming that Δ^{36} S/ Δ^{33} S <-0.9 are not seen in Neoarchean strata below the Carawine C/S excursion, in spite of strongly negative δ^{13} Corg compositions of organic matter. Here, I explore the role of biology as a potential agent (after atmospheric chemistry) for generating variable and negative shifts of Δ^{36} S/ Δ^{33} S arrays.

2.2. Geological setting

The two broadly equivalent Neoarchean cores were drilled in 2012 as part of the Agouron Institute Drilling Program (AIDP) on the Pilbara Craton of Western Australia (Fig 2.1). The sedimentary successions in these regions of the Hamersley Basin have experienced only low levels of burial metamorphism (prehnite-pumpellyite facies; Smith et al., 1982, Rasmussen et al., 2005a; but see Peters et al., 2016 for a greenschist facies interpretation from chlorite paleothermometry) at temperatures between 250 to 350°C and pressures between two to seven kilobars (Smith et al., 1982). The AIDP-2 core was taken from the Ripon Hills (S21°16'16.9", E120°48'56.3") on the eastern edge of the Hamersley Basin, and intersected the Carawine Dolomite and the Jeerinah Formation (formerly called the Lewin Shale, Simonson, 1992). This core was drilled near the site of the previously studied RHDH-2a (Richards, 1985) core (Fig. 2.1). The lower part of the pyritic and organic-rich Jeerinah shale contains several volcanoclastic and cherty horizons, while doloarenite and calcarenite occur sporadically in the overlying interval that is capped by an exceptionally thick limestone. This laminated limestone facies, which contains thin shale partings, marks the transition into the massive Carawine Dolomite. In the eastern Hamersley Basin the Carawine is overlain by the Pinjian Chert Breccia, which is a silicified paleokarst of uncertain (Simonson et al., 1993) but likely Paleoproterozoic (Blake et al., 2011) age.

The Carawine Dolomite contains sedimentologic evidence for shallow marine deposition ranging from sub-tidal to evaporitic supra-tidal environments. The unit is characterized by laminites, stromatolites, oncolites, and symmetrical wave ripples, as well as local occurrences of evaporite crystal pseudomorphs and oolitic to pisolitic textures (Murphy and Sumner, 2008). The most diagnostic textures indicative of high degrees of seawater evaporation, are rare cubic halite pseudomorphs and distinct layers of vertically-oriented chevrons that resemble pseudomorphs of syn-genetic gypsum (Simonson, 1993). Near the base of the Carawine Dolomite is a thick dolomite breccia (preserved between ~210 and 240 meters depth in the AIDP-2 core) that contains sand-sized K-feldspar spherules with quenched and devitrified textures; this breccia has been interpreted as a proximal debris flow deposit associated with a bolide impact (Simonson, 1992).

A thin but compositionally and texturally similar impact spherule layer is preserved near the top of the Jeerinah Formation in the AIDP-3 core, which was drilled at Ballyeerina Creek near Thoomina Bore (S21°46'32", E117°34'11") in the center of the Hamersley Basin (Fig. 2.1) some 320 km from the AIDP-2 drill site and closer to the previously studied WRL-1 (Meakins, 1987) core. Here the Jeerinah Formation, which is conformably overlain by the Marra Mamba Iron Formation (IF), is predominantly composed of laminated black shale that is also notably rich in disseminated pyrite, as well as pyrite in bedding parallel lenses, nodules, and mm- to cm-thick laminae. U-Pb zircon ages from volcanic horizons in the Jeerinah Formation in this region constrain its age between $2,629 \pm 5$ Ma and $2,684 \pm 6$ Ma (Arndt et al., 1991; Nelson at al., 1999).

While it has historically been assumed that the Carawine Dolomite is equivalent to thick dolomitic carbonate strata of the Wittenoom Formation within the Hamersley Basin, the equivalence of the impact spherule beds in AIDP-2 and AIDP-3 indicates that the Carawine is older (e.g. Simonson et al., 2009). A recent U-Pb radiometric date (2630 ± 6 Ma) for a volcanic tuff in the Carawine ~30 m beneath the spherule layer (Rasmussen et al, 2005b) supports this refined intra-basinal correlation. Deposition of the Marra Mamba IF and upper Jeerinah shale (~10m) in the deep basin and slope was synchronous with that of carbonate on the shallow water platform (Eigenbrode and Freeman, 2006). An inter-basinal correlation of this impact horizon in Western Australia to a compositionally similar impact spherule bed in the Monteville Formation (Simonson et al., 1999) – a Neoarchean carbonate-rich unit from the Griqualand West Basin of South Africa whose age is constrained between 2642 ± 2 Ma and 2521 ± 3 Ma (Rasmussen et al., 2005b) – is also quite likely.



Figure 2.1. Simplified geological map of the Hamersley Basin, Pilbara Craton (after Simonson, 1993) showing drill core locations (including the previous studied WRL-1 and RHDH-2a cores, Izon et al., 2015) and AIDP cores' stratigraphy. The spherule layer is depicted as a correlation between carbonate breccia in the Carawine Formation and the impact spherule layer at the top (~71 m depth) of the Jeerinah Formation (see text for more details). Ages are in Ga from: 1. Woodhead et al., 1998 (Pb-Pb), 2. Rasmussen et al., 2005b (U-Pb), 3 -Trendall et al., 1998 (U-Pb), 4. Nelson et al., 1999, 5 – Arndt et al., 1991 (U-Pb).



2.3. Methods and materials

Samples were collected at ~1-2 meter intervals through the Jeerinah Formation and the Carawine Dolomite. The selected carbonates and shales included samples containing discrete macroscopic pyrite grains and laminations (Fig. 2.8). Billets of the carbonate samples were cut at Arizona State University (ASU) and shipped to the University of Maryland in College Park (UMD) for preparation and analysis. Shale samples were crushed at ASU and aliquots of the powders were shipped to the University of Washington (UW) for organic carbon abundance and isotope determinations, and to the University of California, Riverside (UCR) for chromiumreducible sulfur (CRS) extraction of disulfides, which were isolated as Ag₂S precipitates (*cf.* Canfield et al., 1986) for subsequent SO-SO₂ analysis at UMD and SF₆ analyses at Harvard University (HU).

Polished billets of carbonates were observed petrographically and microdrilled to produce powders. Carbonate C/O isotopes were measured on these powders by continuous flow-isotope ratio mass-spectrometry in the UMD Paleoclimate CoLaboratory using a refined method for the analysis and correction of carbon (δ^{13} C) and oxygen (δ^{18} O) isotopic composition of 100 µg carbonate samples. Precision for both isotopes is routinely better than 0.1% (1 σ) (Evans et al., 2016). At UMD, bulk carbonate samples were crushed (200 mesh) in a ceramic mortar and pestle that was cleaned between samples with baked quartz sand. Bulk crushed powders were weighed and then repeatedly acidified with 3M HCl to quantitatively remove carbonate. A selection of the Carawine carbonate samples that revealed unusual levels of ¹³C enrichment in organic residues were sent to UW for repeated hot 6 M HCl treatment for comparison with UMD standard technique (see Table 2.1). This comparison revealed that hot 6 HCl treatment is better suited for the quantitative removal of recalcitrant ferrous or manganiferous carbonate minerals. In both cases, the residues, including siliciclastic grains, pyrite, and organic matter, were then washed with 18 M Ω Milli-Q water until solutions reached neutral pH prior to drying in an oven at 80°C overnight. At UW, bulk shale powders were treated three times with 6M HCl at 60°C to quantitatively dissolve the iron-bearing carbonates typical of this facies, and then

washed with deionized water to neutralize the solutions. The samples were then left to dry in a 60°C oven for two days.

At both institutions the dried residues were weighed in order to calculate % carbonate in the bulk samples, and then aliquots of between 0.5 and 5 mg were measured into tin cups for organic carbon determinations. The organic carbon abundance and isotope composition were measured by combustion in either a Eurovector elemental analyzer in-line with a second Eurovector Isoprime IRMS (UMD) or a Costech ECS 4010 elemental analyzer in-line with a Thermo Finnigan 253 (UW). At UMD, two urea standards were measured between each set of 10 samples and uncertainties for each analytical session based on the standard analyses were determined to be better than 1.0% and 0.1%, respectively for abundance and carbon isotope composition. At UW, in-house standards calibrated with USGS 40 and USGS 41 were used to normalize abundance and isotope measurements; based on the reproducibility of a dried salmon standard these uncertainties were 0.7% and 0.06%, respectively. Total organic carbon contents were calculated by quantifying the % carbonate in the bulk samples and their IRMS CO₂ peak areas relative to those from measured amounts of urea standards.

The sulfur abundance and isotope composition of bulk and micro-drilled pyrites, as well as the Ag₂S precipitates produced by CRS extractions at the University of California, Riverside, were initially measured by combustion with a Eurovector elemental analyzer in-line with the continuous flow Isoprime system at the University of Maryland. In these analyses, ~1000 μ g of V₂O₅ was added to the tin cups with the samples and standards as an additional oxidant. Isotopic results are expressed in the

delta notation as per mil (‰) deviations from the Canyon Diablo (V-CDT) standard. Two NBS-127 and two NZ-1 standards were measured between each set of 10 samples, and uncertainties (1σ) for each analytical session based on these standard analyses were better than 1.0% for abundance and 0.3‰ for both δ^{34} S and Δ^{33} S isotope compositions. Minor sulfur isotope abundances of the shale Ag₂S extracts produced at the University of California, Riverside, as well as CRS extracts from acidified residues of some of the bulk and micro-drilled carbonate samples, were determined by SF₆ analysis at Harvard University and the University of Maryland, respectively. At both institutions, Ag₂S samples were fluorinated under a $\sim 10x$ excess of F₂ at 250°C for 8 hours in Ni reaction chambers. The product SF₆ was cleaned via chromatographic and cryogenic techniques, and measured on a Thermo Finnigan MAT 253 gas source massspectrometer. Uncertainties (2σ) on fluorination were determined based on long-term reproducibility of international standards and are 0.3‰, 0.016‰, and 0.30‰ for δ^{34} S, Δ^{33} S, and Δ^{36} S, respectively. IAEA S-1 measured on this scale yields values of -0.30‰, 0.094‰ and -0.68‰, for δ^{34} S, Δ^{33} S, and Δ^{36} S, respectively. IAEA S-2 measured on this scale yields 22.25‰, 0.035‰ and 0.21‰, for δ^{34} S, Δ^{33} S, and Δ^{36} S, respectively. Comparison of δ^{34} S and δ^{33} S compositions of the shale Ag₂S extracts determined by the continuous flow SO-SO₂ method at the University of Maryland and the dual inlet SF₆ method at Harvard University demonstrate a high level of consistency (Fig. 2.9). Slopes of the ³³S and ³⁴S data from both cores are very near unity and are highly correlated. This observation supports the use of the combined data for the interpretation of results, and further supports the use of the SO-SO₂ method for rapid characterization of time-series sulfur isotope variations in Archean sedimentary successions.

2.4. Results

Results from this sulfur and carbon isotope study are presented in Tables 2.2 and 2.3 and illustrated in Figures 2.2, 2.3, and 2.4. As expected, the stratigraphic plots of geochemical data reveal that shale and carbonate facies differ significantly in the abundance of carbonate (Fig. 2.2A), total organic carbon (Fig. 2.2D), and pyrite sulfur (Fig. 2.2F). Shaly carbonate and shale layers in the Carawine Formation were studied for carbon but not sulfur isotopic compositions (Fig. 2.2). While the carbon isotope compositions of Carawine Dolomite and Jeerinah limestone are similar (Fig. 2.2B), the iron-rich carbonate interbedded with shale lower in the Jeerinah Formation are notably depleted in ¹³C. The carbon isotope composition of organic matter (Fig. 2.2E) in both formations is remarkably ¹³C depleted (down to -50‰), although some of the dolomite samples near the top of the core preserve significantly more ¹³C enriched organic carbon compositions on average by ~5‰.

Based on multiple sulfur isotope trends through the stratigraphic succession, the AIDP-2 core can be separated into three distinct intervals, including: (I) Jeerinah shale and calcarenite, (II) lower Carawine Dolomite below the carbonate impact breccia, and (III) upper Carawine Dolomite. In interval I, δ^{34} S rises in a step-wise fashion from a plateau at ~ 0‰, to a second plateau at about 8‰ and then to a third plateau at +12‰. Δ^{33} S compositions also start at a value of 0‰ and then rise to 8‰ midway through the second δ^{34} S plateau. Above this, Δ^{33} S values range widely between 0 and +12‰, with the highest values preserved in the calcareous facies. At the base of interval II, δ^{34} S values decrease to a stable value of approximately +9‰ and the Δ^{33} S variability ranges between -2 and +8‰. Higher in interval II and just below the carbonate impact breccia the δ^{34} S compositions exhibit greater variability with negative values just below the carbonate impact breccia, while the Δ^{33} S variability decreases to a range between -3 and +2‰. Above the breccia in interval III both bulk and drilled pyrite reveal large, but non-systematic, variations in δ^{34} S and Δ^{33} S compositions, with both bulk and micro-drilled pyrite having predominantly negative Δ^{33} S values and micro-drilled phases revealing the largest magnitude of δ^{34} S fractionation with values as low as -17‰.

Abundances of total organic matter and pyrite sulfur, as well as the δ^{13} C compositions of TOC through the ~125 m thick organic- and pyrite-rich shale intersected in the AIDP-3 core from the Jeerinah Formation in the central part of the Hamersley Basin are similar to those in the AIDP-2 shale samples (Table 2.2 and Figs. 2.3 and 2.4). However, CRS extracted bulk pyrite through this interval reveal only minor changes in δ^{34} S compositions (rising from roughly 0 to +5‰ from the base to the top), and the Δ^{33} S signal is homogenous with values near +5‰ near the base of the shale that becomes more variable moving upward to a range that extends from a low of -1‰ to a high of +7‰ near the top, immediately below the impact spherule horizon.







Figure 2.3. Time-series organic carbon (A-C) and sulfur (D-G) abundance and isotopic data from the AIDP-3 core. Orange line depicts position of spherule layer. For lithology see legend in Fig.1. Error bars are smaller than the data points except for the $\Delta^{36}S / \Delta^{33}S$ values.



Figure 2.4. A. Cross-plot of Δ³³S versus δ³⁴S values for bulk rock/bulk pyrite (circles) and drilled pyrites (py, diamonds) from the AIDP-2 and AIDP-3 cores for different intervals (see text). Slope Δ³³S = δ³⁴S×0.9 is referred to ARA – Archean Reference Array (Ono et al., 2003, Kaufman et al., 2007). Uncertainties are within the size of the points; B. Cross-plot of Δ³³S vs. Δ³⁶S from AIDP-2 and AIDP-3 shales and carbonates. Uncertainties are 2σ. Linear regression (red line) through Carawine data is shown together with equation.

In Figure 2.4A the relationship of δ^{34} S and Δ^{33} S compositions in both of the AIDP cores is illustrated. The shale data form a general field that is consistent with previous studies of Neoarchean shale-dominated successions. In contrast, the Jeerinah limestone samples from AIDP-2 interval I reveal ³⁴S enrichments of up to 5‰ relative to the Archean Reference Array (ARA; Ono et al., 2003), and bulk pyrite in dolomite

samples from interval II reveal similar or even greater δ^{34} S values. The data from interval III in the upper Carawine Dolomite are characterized by broad ranges in δ^{34} S compositions and predominantly near zero to negative Δ^{33} S values. The multiple sulfur isotopic contrast between shale and carbonate facies is further highlighted in a plot of Δ^{33} S vs. Δ^{36} S compositions (Fig. 2.4B). In this illustration, Jeerinah shale data generally fall along the ARA slope of ~ -0.9, while limestone data from the same unit scatter away from the array principally to negative Δ^{36} S values. Carbonates of the Carawine Dolomite with negative Δ^{33} S deviate strongly to positive Δ^{36} S by on average 10 times analytical uncertainty. Three of eight of the Carawine carbonates with positive Δ^{33} S compositions deviate more than 3 σ to negative Δ^{36} S values and one analysis to a positive Δ^{36} S value. The remaining four analyses are within 3 σ of the ARA. Linear regression of the carbonate data does not pass through the origin and yields a slope of approximately -1.3.

2.5. Discussion

My high-resolution isotopic data for the Jeerinah Formation and Carawine Dolomite in the AIDP-2 and AIDP-3 cores are consistent with previous studies of the same units in different cores (Ono et al., 2003; Eigenbrode and Freeman, 2006; Izon et al., 2015). The $\delta^{13}C_{org}$ compositions of shale samples in the Jeerinah and Carawine are depleted in ¹³C, with values < -40‰, while $\delta^{13}C_{org}$ in some dolomite samples are enriched in ¹³C, with a 5‰ average enrichment in the Carawine carbonates relative to the Jeerinah shales. The $\delta^{34}S$ and $\Delta^{33}S$ values of shales from the Jeerinah Formation are mostly positive, correlated, and follow the ARA ($\Delta^{33}S \approx 0.9 \times \delta^{34}S$, Ono et al., 2003) with a $\Delta^{36}S/\Delta^{33}S$ relationships of ~-0.9 (Farquhar et al., 2000; Kaufman et al., 2007). Pyrites from the Carawine Dolomite exhibit more variable $\delta^{34}S$ compositions that also fall away from the ARA and pyrites with negative $\Delta^{33}S$ values yielded anomalous $\Delta^{36}S/\Delta^{33}S < -1.5$.

2.5.1. Sulfur sources for shale and carbonate facies

While the deep water shales of the Jeerinah Formation preserve sulfur isotope compositions that reflect a significant contribution from the positive Δ^{33} S atmospheric endmember, the variable Δ^{33} S compositions of pyrites from the Carawine Dolomite (similar to those of the Neoarchean Batatal Formation; Zhelezinskaia et al., 2014) primarily reflect the negative Δ^{33} S endmember. The identity of these endmembers was first explored by Farquhar et al. (2000) based on sulfur isotope measurements of Archean sedimentary rocks. These authors argued from analyses of Paleoarchean barite that Archean seawater sulfate and its principal source, atmospheric sulfate, had a negative Δ^{33} S (and positive Δ^{36} S) composition. They also argued that its complement was an insoluble reservoir of reduced sulfur species. Subsequent work (Kasting, 2001; Farquhar et al., 2001; Masterson et al., 2011; Whitehill et al., 2012) suggested that the reservoir with positive $\Delta^{33}S$ was connected to elemental sulfur. Sulfur isotopic composition of the Neoarchean seawater sulfate was not only based on experimental data but was empirically defined using limited Carawine pyrite isotope data determined by Ono et al. (2003). My study extends those measurements and demonstrates more variable composition of the Carawine pyrites for both Δ^{33} S and δ^{34} S values. Large δ^{34} S variation in these pyrites indicates that MSR was an active recycling process during formation of the CAP samples. Because these pyrites with large fractionation also preserve negative Δ^{33} S signals, I infer that the atmospheric sulfate flux imparts a negative Δ^{33} S composition on oceanic sulfate in the Neoarchean (but see Paris et al., 2014 for an alternative hypothesis), which appears to dominate the MIF-S signature in the carbonate depositional environment.

Alternatively, the terrestrial oxidation of pyrite (Kendall et al., 2010, Stüeken et al., 2012, Reinhard et al., 2013) might account for different sulfur isotopic signatures in shallow environments compared to deeper ones, assuming the riverine flux was preferentially sequestered in carbonate facies. However, my findings of highly negative Δ^{33} S and Δ^{36} S/ Δ^{33} S compositions (those were not observed in pre-Neoarchean records), as well as the cm- and mm-scale heterogeneity of pyrite in the carbonate facies from this study and my companion study of the Batatal Formation (Zhelezinskaia et al., 2014), suggest that terrestrial oxidation of exposed igneous or sedimentary sulfur minerals, and, thus, the sulfur riverine flux was not a major contributor to shallow environments and the marine sulfur cycle in general.



Figure 2.5. Left. Cross-plots of Δ^{33} S versus δ^{34} S values and Right. Δ^{36} S versus Δ^{33} S values from this study and previously published data for Neoarchean carbonates and shales (Ono et al., 2003, Zerkle et al., 2012, Izon et al., 2015). J – Jeerinah Formation and C – Carawine Dolomite. Two slopes are shown including the ARA with Δ^{33} S/ δ^{34} S = 0.9 (Δ^{36} S/ Δ^{33} S = -0.9) and potential slopes of S₈ compositions (see text for details). Orange fields represent combined results of SO₂ photolysis experiments (Farquhar et al., 2000, Ono et al., 2013, Endo et al., 2016) and green fields are SO₂ photoexcitation experiments (Whitehill et al., 2014, Endo et al., 2016).

The wide range of Δ^{33} S and δ^{34} S compositions in CAPs from the Carawine Dolomite support my view that MSR was an important metabolism in this shallow water facies. The negative pyrite Δ^{33} S compositions in the peritidal Carawine Dolomite contrasts sharply with the positive values recorded in the deeper water shale facies (as well as the subtidal marine limestones from the uppermost Jeerinah Formation). [It is worth noticing that this study does not take into account pyrite nodules and laminae in the Jeerinah Formation that might preserve sulfur isotope signature different from the bulk rock analyses I present here. However, limited number of analyses that have been done on Jeerinah macropyrite from AIDP-3 suggest a predominantly elemental sulfur source (Gregory et al., in preparation)]. It has been suggested that sulfide produced by sulfate reducers will react in the presence of elemental sulfur to form polysulfides, which rapidly equilibrate isotope compositions between the aqueous species (e.g. Kamyshny et al., 2003). Pyrite formed in systems where elemental sulfur is present will therefore yield a composition intermediate between sulfide and elemental sulfur pools that is weighted by the ratio of elemental sulfur to MSR-derived sulfide. The positive δ^{34} S and Δ^{33} S of shales are thus interpreted to reflect the imprint of a significant standing pool of elemental sulfur onto sulfide produced by MSR (Farquhar et al., 2013; Rickard, 2014; again see Paris et al., 2014 for an alternative interpretation). Even if the elemental sulfur flux was the same for both deep and shallow environments, relative higher sedimentation rates on Archean carbonate platforms (up to an order of magnitude greater than shale facies, Altermann and Nelson, 1998) could explain the lower proportion of atmospheric signals from photolytic elemental sulfur in the Carawine Dolomite.

The Carawine Dolomite exhibits variability of sulfur isotopic composition between drilled pyrite and bulk rock samples. Pyrite grains and laminations (Fig. 2.4) mostly preserved the negative Δ^{33} S seawater sulfate signal, whereas the bulk pyrite analyses with more variable Δ^{33} S values reflect mixing between positive and negative Δ^{33} S endmembers. In these dolomites, the primary atmospheric signal was likely obscured by mass-dependent processes, such as MSR, which could produce hydrogen sulfide with variable δ^{34} S compositions (e.g. Canfield, 2001a). Pyrite could have been formed directly from the product hydrogen sulfide (Rickard and Luther, 1997), or indirectly through reactions involving elemental sulfur and polysulfide (Luther et al., 1991). Variable contribution from the elemental sulfur endmember with positive Δ^{33} S and sulfide derived from sulfate with negative Δ^{33} S (and variable δ^{34} S) likely accounts for the triangular shaped field of pyrite compositions that I observe in this study (Fig. 2.5A).

2.5.2. Atmospheric endmembers and slope variations

Linear relationships between Δ^{33} S and δ^{34} S (~ 0.9, Ono et al., 2003) and between Δ^{36} S and Δ^{33} S (~-0.9, Farquhar et al., 2000) observed in Neoarchean successions reflect mixing between two isotopically distinct atmospheric sulfur reservoirs (Ono et al., 2003) with a possible overprint of mass-dependent effects associated with MSR and other sulfur cycling processes (Ono et al., 2006, Kaufman et al., 2007). While the alignment of the Jeerinah shale data along the ARA (Figs. 2.4A and 2.5A) suggests the same pathway of elemental sulfur production as proposed in younger Neoarchean intervals (Kaufman et al., 2007, Ono et al., 2003), some Jeerinah limestone and Carawine pyrite data (also see data reported in Izon et al., 2015, fig. 2.5A) are notably enriched in ³⁴S. These observations suggest a systematic offset from the ~0.9 slope (Fig. 2.5A). In Carawine pyrites the Δ^{36} S/ Δ^{33} S deviation from the -0.9 slope (Fig. 2.4B) records the possible impact of changing atmospheric chemistry (Zerkle et al, 2012; Izon et al., 2015) or of microbial processes (Kaufman et al., 2007), issues that I will later examine in detail.

Photochemical experiments with sulfur dioxide have shown that isotope effects and resulting fractionation of products depend on reaction conditions and on the wavelengths of incident radiation. Recent experiments (Whitehill et al. 2012; Endo et al., 2016) show that shallow positive slopes for $\Delta^{33}S/\delta^{34}S$ (<0.1) are produced with photolysis reactions using wavelengths shorter than ~220 nm, and steeper slopes (>3) are produced when longer wavelengths (240 – 340 nm) cause photoexcitation (Fig. 2.5A). Similarly, photolysis of SO₂ yields steeper negative $\Delta^{36}S/\Delta^{33}S$ (<-2), while photoexcitation reactions yield positive $\Delta^{36}S/\Delta^{33}S$ (Fig. 2.5B, e.g. Whitehill et al., 2012). It has been proposed that the mismatch between experimental results and data from Archean sedimentary rocks reflects mixing between these two photochemical processes (e.g. Endo et al., 2016). Extending this reasoning, shifts to shallower $\Delta^{33}S/\delta^{34}S$ and more negative $\Delta^{36}S/\Delta^{33}S$ would be anticipated with the attenuation of shorter-wavelength UV light resulting in greater proportional photolysis reactions.

Shifts in the UV spectrum that drive photolysis might be associated with shielding of ultraviolet wavelengths by a photochemical haze (e.g. Wolf and Toon, 2010), although quantitative details are lacking. However, the shift to more positive Δ^{36} S/ Δ^{33} S and more positive Δ^{33} S from the ARA when applying modelled organic haze UV blocking capacity (Wolf and Toon, 2010) has not been proposed for hazy intervals

in the Archean, suggesting that other processes may have been active. Indeed, some of the data from my study with $\Delta^{33}S/\delta^{34}S < 0.7$ plot in a $\Delta^{36}S/\Delta^{33}S$ field that defines a slope that is slightly more negative than -0.9. These observations are consistent with previous field-based studies (e.g. Domagal-Goldman et al., 2008; Zerkle et al., 2012) that were suggested to reflect hazy intervals. Empirically defined ARAs in either $\Delta^{33}S/\delta^{34}S$ (Ono et al., 2003) or $\Delta^{36}S/\Delta^{33}S$ (Kaufman et al., 2007) fields are assumed to be formed at non-haze conditions.

The variable Δ^{33} S/ δ^{34} S and Δ^{36} S/ Δ^{33} S relationships seen in my dataset (Fig. 2.5) suggest that the elemental sulfur endmember might change its isotopic composition with time, such that the defined ARA may not be the only relationships describing mass-independently fractionated sulfur isotope compositions. Regarding the Δ^{33} S/ δ^{34} S relationship, some of my data reveal that this ratio is much less than 0.9 – similar to data from Izon et al., (2015) – that could provide several vectors pointing to a different elemental sulfur endmember compositions (Fig. 2.5A). As noted above, this elemental sulfur endmember may result from the existence of a hazy atmosphere above Earth's Archean surface (Zerkle et al., 2012), which likely differed from the presentday haze on Titan. Failure to match observations from photochemical SO₂ experiments with existing Archean data (e.g., Endo et al., 2016) might imply that the photolysis of sulfur dioxide alone may not have been the singular cause of atmospheric MIF-S. Other gases such as H₂S, SO, OCS and CS₂ could have been involved in photochemical reaction networks (e.g. Kasting, 2001). Their variable concentrations and relative abundance might also cause shifts in the isotopic signals (Ono et al., 2003, Halevy et al., 2010).

2.5.3. ³⁶S variations in CAP: organic haze and biological redistribution

Deviations from the Neoarchean ARA defined by the relationship of Δ^{33} S and Δ^{36} S data have been argued to result from the effects of an organic haze on SO₂ photochemistry (Domagal-Goldman, 2008; Zerkle et al., 2012; Izon et al., 2015), and in other cases, biological redistribution of the minor isotopes by sulfate reduction and disproportionation (Kaufman et al., 2007; Ueno et al., 2008; Shen et al., 2009; Zhelezinskaia et al., 2014). I suggest that evidence for both types of processes are present in AIDP-2 data from the Carawine Formation. Variations of $\Delta^{36}S/\Delta^{33}S$ arrays were first noted in Mesoarchean successions (Farguhar et al, 2007) and interpreted to reflect a change in atmospheric chemistry. Domagal-Goldman et al. (2008) argued that the slope changes in $\Delta^{36}S/\Delta^{33}S$ relationships specifically reflect the development of an organic haze. Evidence for other changes in $\Delta^{36}S/\Delta^{33}S$ that are coupled with negative excursions in $\delta^{13}C_{org}$ values have been argued for four, and possibly five events between 2.5 and 2.6 billion years ago (Zerkle et al., 2012; Izon et al., 2015). The oldest of these would be related to a 20 meter interval in the Monteville Formation of South Africa, and the > 100 meter thick Carawine Dolomite studied here, which are likely correlative.

The exact correlation of spherule beds in Jeerinah, Carawine, and Monteville strata impacts the haze hypothesis by suggesting that the $\Delta^{36}S/\Delta^{33}S$ signal could be variably preserved in sections depending on how the haze structure was established. The presence of a standing oceanic sulfate pool that exhibited shifts in $\Delta^{36}S/\Delta^{33}S$ could transfer the haze signal to localities that may have previously been haze free (possibly the CAP of the Monteville Formation microbialites or the Carawine Dolomite). The deposition of elemental S with anomalous $\Delta^{36}S/\Delta^{33}S$ (down to -1.5) could produce a signal such as the one seen in the parts of the Monteville Formation that preserve positive $\Delta^{33}S$, but are largely lacking in contemporaneous parts of the Jeerinah Formation or Carawine Dolomite (Fig. 2.5B). An alternative hypothesis not supported by current photochemical atmospheric models is that the haze could have been a regional phenomenon. If true, it also follows that the observed $\Delta^{36}S/\Delta^{33}S$ would not reflect the full signal of the atmospheric chemical reactions, but instead the relative contributions of atmospheric reactions on a regional scale. A modulated signal might also explain part of the variability that is seen in $\Delta^{36}S/\Delta^{33}S$ values, where some studies have suggested slopes even shallower than -0.9 (e.g. Kaufman et al., 2007), while others have demonstrated arrays that are steeper than -1.5 (e.g. Farquhar et al., 2007).



Figure 2.6. A: Cross-plot of Δ^{33} S vs. Δ^{36} S values from this study together with results from two mixing models (see text for details) explaining Δ^{33} S/ Δ^{36} S excursion in the Carawine carbonates. Triangular fields depict an exchange pathway between SRB products (different models) and elemental sulfur end-member. Grey fields – Rayleigh model, darker area depicts model at f<0.4. Blue circles: 1 –seawater sulfate with Δ^{33} S/ Δ^{36} S = -0.9, 2 - seawater sulfate end-member with Δ^{33} S/ Δ^{36} S = -2. Carawine pyrites with negative Δ^{33} S values demonstrate large 36 S-enrichment explained by sulfate reduction imposed on sulfate with composition 2. Black circle is elemental sulfur end-member with Δ^{33} S/ Δ^{36} S = -0.9. B: Cross-plot of Δ^{33} S versus δ^{34} S evaluating distillation model with changing fractionation. Triangle is a mixing between elemental sulfur end-member with Δ^{33} S/ Δ^{36} S = -0.9 (δ^{34} S=12‰) and sulfide derived from seawater sulfate (Δ^{33} S/ Δ^{36} S = -2) through MSR. Black circle is elemental sulfur end-member.

While it is feasible that an atmospheric haze could shift δ^{34} S compositions by small degrees (Fig. 2.5A), MSR stimulated by the concentrated increase of atmospherically derived sulfate in dolomite facies is implicated by the large δ^{34} S fractionations (Canfield, 2001a). This important microbial process may also explain the ³⁶S enrichments in the Carawine Dolomite (Johnston et al., 2007). Laboratory culture experiments and geochemical models demonstrate ³⁶S enrichment in residual sulfate while product sulfide can be depleted by ~1-2‰ (Ono et al., 2006; Johnston et al., 2007). Due to the production of alkalinity during MSR, carbonate saturation increases in pore fluids and can result in the formation of authigenic carbonate and cementation of the sediments, thereby restricting the diffusion of sulfide back to seawater. Considering this likely environmental scenario, I constructed a Rayleigh distillation model under closed-system condition in order to evaluate Δ^{36} S/ Δ^{33} S changes during MSR.

The possibility that biology could be a factor in controlling the $\Delta^{36}S/\Delta^{33}S$ slope and intercept on plots of $\Delta^{36}S$ vs. $\Delta^{33}S$ was explored using a 0-D incremental batch distillation model with both constant and variable fractionation. When fractionation is held constant and increment size approaches 0, the incremental batch model converges to a value similar to that produced by the Rayleigh equation (${}^{3i}R={}^{3i}R_0$ $f^{(\alpha-1)}$). In this model, the isotopic composition (${}^{3i}R={}^{34, 33, \text{ or } 36}S/{}^{32}S$) of a finite amount of residual reactant changes as the fraction of reactant (*f*) decreases from 1 (100%) to 0 (0%) when acted upon by a process that fractionates following a constant isotopic fractionation factor (α). The incremental batch approach allows the fractionation to decrease as the distillation process proceeds. The composition of the instantaneous product in both models is given by $\alpha^{\bullet^{3i}R}$, and the possible compositions of the product were further expanded by including provisions for exchange with an endmember having positive $\Delta^{33}S$ and $\delta^{34}S$ and negative $\Delta^{36}S$ (elemental sulfur).

The calculations with constant fractionation are presented in Figure 2.6A (grey field) for parameterization with an atmospheric $\Delta^{36}S/\Delta^{33}S$ slope of -0.9 and biological fractionations of 50% following fractionation laws of ${}^{33}\alpha^{1/0.510} = {}^{34}\alpha = {}^{36}\alpha^{1/1.94}$ (see Johnston et al., 2007). The results from this model are beyond the limits that biology can produce (Johnston et al., 2007), but they nonetheless illustrate the process. While the isotopic composition of residual sulfate lies above the -0.9 array and the isotopic composition of sulfide extends below the -0.9 array, the δ^{34} S composition of residual sulfate is also driven to extreme positive values (up to +60%). If the Rayleigh model adjusts to observed δ^{34} S ~30‰, then f is around 0.4 with Δ^{36} S and Δ^{33} S values that do not extend to Carawine pyrite compositions. Thus, this iteration of the model fails to reproduce the observations with reasonable fractionations for all four sulfur isotopes. In contrast, the fit between model and data improves if the atmospheric $\Delta^{36}S/\Delta^{33}S$ slope is made steeper, and if the fractionations are allowed to change as distillation proceeds. In this case, the residual sulfate is not driven to extreme positive δ^{34} S values, and sulfide yields more positive δ^{34} S and Δ^{36} S values, plotting with Δ^{36} S values >2‰ below the imposed atmospheric $\Delta^{36}S/\Delta^{33}S$ array. In this case the fractionations are within the limits that biology can produce. For the sulfate, I set the $\Delta^{36}S/\Delta^{33}S$ slope at -2 and that of the elemental sulfur endmember at -0.9. This shift is sufficient to introduce scatter around the array, but still requires an atmospheric array steeper than -0.9. If I select the results with reasonable ranges of δ^{34} S (from -20 to +30‰), the model produces sulfide with Δ^{36} S values below the mixing trend that reproduce Carawine pyrites compositions with negative Δ^{33} S values (Fig. 2.6A), but notably not those with positive Δ^{33} S compositions.

Mixing between sulfate-derived sulfide (as a result of MSR) and elemental sulfur results in products with variable Δ^{36} S/ Δ^{33} S (Fig. 2.6B). If two endmembers have Δ^{36} S/ Δ^{33} S as selected (-2 for sulfate and -0.9 for elemental sulfur), the model broadly matches most, but not all, of the shale and carbonate data (Fig. 2.6B). In order to explain the mismatch between the data and the model, several possibilities can be considered. For example, the elemental sulfur endmember composition could vary in time (and perhaps spatially), and in some intervals be characterized by Δ^{36} S/ Δ^{33} S < -0.9. During atmospheric photochemical reactions with sulfur dioxide (or other gases) there could also be a third endmember composition, thereby forming a triangular mixing field in Δ^{36} S/ Δ^{33} S space that would encompass all of the pyrite compositions I have measured (Fig. 2.6A). I suggest that the pyrites with Δ^{36} S/ Δ^{33} S < -1.5 from the Carawine Dolomite captured a sulfate signal that was distinct from elemental sulfur in the Jeerinah shales with Δ^{36} S/ Δ^{33} S \approx -0.9.

2.5.4. Causes of temporal and spatial variability of sulfur isotopes

The variability of Δ^{33} S within and between facies (or formations) is interpreted to reflect variable contributions of the two recognized atmospheric sources generated by various exchange processes and reactions occurring in pyrite-forming environments. This variation may also record changes in the magnitude and characteristics of Δ^{33} S produced by atmospheric chemistry. The variability observed in Δ^{33} S values in both the AIDP-2 and AIDP-3 cores increases up section through the Jeerinah Formation. This probably results from changing contributions from the positive Δ^{33} S elemental S endmember, and from MSR-derived sulfide with a negative Δ^{33} S signature. Variations in the average Δ^{33} S composition of samples (e.g. Kaufman et al., 2007) or the relationship between Δ^{36} S and Δ^{33} S compositions (e.g. Zerkle et al., 2012) may also correspond with geographic or temporal changes in the atmospheric reactions that produce sulfur isotope anomalies. Both experimental data and geochemical models suggest that changes in the production and ³³S abundance of photolytic S₈ may be controlled by (i) the rate of volcanic outgassing of SO₂ (Ono et al., 2003, Ono et al, 2013), (ii) the balance of SO₂ and H₂S in the atmosphere (Halevy et al., 2010), and (iii) variations of atmospheric CH₄ that could induce changes in atmospheric chemistry alone (Ono et al., 2003), or by transitions from haze free to haze present states (Domagal-Goldman et al., 2008; Zerkle et al., 2012). These environmental controls on atmospheric reactions may be global or local in scope. The effect of local volcanic activity might influence pSO_2 or the balance of SO₂ to H₂S (or other sulfur gases) in the atmosphere over the basin margin. On the other hand, such changes may also reflect long-term switches from submarine to subaerial volcanism (Halevy et al., 2010; Gaillard et al., 2011). Speculatively, changes in the flux of methane to the atmosphere and the progressive development of an organic haze may explain the two very different Δ^{33} S trends between formations and variations within formations.

A homogeneous organic haze is formed at high altitude (~60 km), but as haze particles settle and grow, its structure becomes stable around 20 km altitude and heterogeneous with latitude (Wolf and Toon, 2010). This heterogeneity expresses as a thinner organic haze (and lower optical depth) in low latitudes due to vertical atmospheric motions (Fig. 4S in Wolf and Toon, 2010). If an organic haze controlled the multiple sulfur isotope signal, the regional production of S₈ could lead to variations in its signal as a function of latitude. For example, elemental sulfur formed and deposited in tropical regions (where organic haze is thin) at the same time would have different isotopic composition then S₈ formed in mid-latitude (where organic haze is thick). On the other hand, if the oceanic sulfate MIF-S signal was well mixed even from multiple local sources, the products from these two endmember atmospheric fluxes could have been decoupled on a basinal scale.



Figure 2.7. Cross plot of Δ^{33} S/ Δ^{36} S vs. δ^{13} C_{org} values for shale and carbonate facies from this study and Zerkle et al., 2012, for comparison. Dashed bold line is the Archean array Δ^{33} S/ Δ^{36} S = - 0.9. Uncertainties shown are 2 σ .

The equivalence of the thin impact spherule bed in AIDP-3 with the thick spherule-bearing carbonate breccia in AIDP-2 (along with available age constraints) implies that the deposition of some portion of Carawine Dolomite in AIDP-2 and RDHD-2 above breccia interval was contemporaneous with the upper ~10 m of the Jeerinah Formation in WRL-1 and AIDP-3. If true, the latter accumulated in distal deep water settings at the same time as the former formed in shallow intertidal to supratidal environments. If the atmospheric organic haze was structured rather than uniform, the

Carawine Dolomite possesses a globally mixed sulfur isotopic signal while the Jeerinah Formation (in AIDP-3) preserves a local signal from thin-haze (or non-haze) portion of the atmosphere. If the deposition of two end-members was controlled by latitude then this would explain the different $\Delta^{36}S/\Delta^{33}S$ preserved by the Carawine Dolomite when compared to the upper Jeerinah Formation in AIDP-3 and WRL-1. (Fig. 2.5). As noted by Izon et al. (2015), even if Jeerinah organic matter is strongly depleted in ¹³C, it lacks a significant shifts in the $\Delta^{36}S/\Delta^{33}S$ slope from -0.9 suggesting non-haze photolytic S₈ signal. Carawine samples with the same degree of ¹³C depletion as observed in Jeerinah shale (Fig. 2.7) notably define a slope $\Delta^{36}S/\Delta^{33}S$ much more negative than -0.9 implying a photolytic signal associated with an organic haze.

2.5.4. Photosynthesis and carbon isotope variations below hazy atmosphere

The presence of an organic haze would have shielded surface environments from harmful UV radiation that would allow ammonia (a strong greenhouse gas) to accumulate in the lower atmosphere, and have shifted upward the peak wavelength of solar radiation reaching the oceans (Wolf and Toon, 2010). Insofar as an organic haze in the Neoarchean atmosphere would scatter and absorb UV and visible wavelengths (Wolf and Toon, 2010), it may have influenced photosynthetic reactions and primary productivity. In this regard, the pigments used during anoxygenic photosynthesis differ from those associated with oxygenic photosynthesis in their molecular details and peak wavelength of light absorbed. Notably the peak absorption wavelength for chlorophylla used by oxygen-producing plants and cyanobacteria is 100-200 nm less than the bacteriochlorophylls used during anoxygenic photosynthesis. The development of a significant haze may thus have shifted primary production of organic matter towards anoxygenic photosynthesis where the electrons necessary to drive the metabolic activity ultimately come from the oxidation of H₂S or Fe(II) (rather than from H₂O in oxygenic photosynthesis). Photoferroautotrophy, which has been suggested as the dominant source of primary production in the Archean (Canfield et al., 2006), may not have been a significant metabolism in environments where the Carawine Dolomite accumulated (Czaja et al., 2010). Insofar as iron-oxidizing bacteria use carotenoids that absorb visible light with wavelengths <600nm (Hegler et al., 2008), the metabolic process would have been diminished in the presence of an organic haze. Instead, autotrophic sulfur-oxidizing bacteria could have been the main primary producers in these settings.

In light of differences of $\delta^{13}C_{org}$ compositions in the Jeerinah and Carawine formations (Fig. 2.8), it is interesting to speculate on the dominant metabolic processes in the shale and carbonate environments, respectively. Previously, Eigenbrode and Freeman (2006) interpreted the significant ¹³C depletion (with δ^{13} C values as low as ca. -50‰) of organic matter in Jeerinah shales (along with relative ¹³C enrichment in Carawine carbonates) as a function of chemosynthetic relative to photosynthetic inputs. The former metabolic pathway would dominate in anoxic deep-water environments where methane was produced by fermentative processes, while the latter would be promoted in oxidized habitats where aerobic ecosystems proliferated. My study of the AIDP-2 and AIDP-3 cores confirms these empirical results and further documents the greatest degree of ¹³C enrichment in carbonate-bound organic carbon in interval III above the Carawine impact breccia and upper part of interval II (Figs. 2.2). However, if a methane haze dominated the Neoarchean atmosphere and promoted anoxygenic photosynthesis, the carbon isotope contrast between shale and carbonate lithofacies may have otherwise been dependent on the dominant anaerobic microbial community.



Figure 2.8. Carbon isotopic compositions of samples from the Jeerinah and Carawine formations. Boxes represent 99% confidence interval. Grey circles are $\delta^{13}C_{org}$ of samples. Yellow lines indicate mean values.

The two major groups of anoxygenic photosynthesizers are the purple (PSB) and green (GSB) sulfur bacteria. Like plants and cyanobacteria that produce O₂, the PSB fix CO₂ using Rubisco in the Calvin Cycle. In contrast, the GSB utilize HCO₃⁻ to fix carbon into organic matter in the reverse TCA cycle. The carbon isotope compositions of dissolved CO₂ and HCO₃⁻ differ by 8-10‰ at equilibrium, so that organic matter produced by GSB should be similarly enriched in ¹³C (see empirical results presented in Zyakun et al., 2009). This observation provides an alternative explanation for the ¹³C enrichment of organic matter in the Carawine Dolomite. If correct, a significant fraction of the preserved organic matter in these Neoarchean successions may have formed through anoxygenic photosynthesis.

2.6. Conclusions

The correlation of impact spherule layers in the AIDP-2 and AIDP-3 cores provides a unique timeline to compare the sedimentary geochemistry of shallow and
deep water lithofacies that accumulated across the Hamersley Basin shelf. The correlation indicates the equivalence of deep water shale and intertidal to supratidal carbonate lithologies, which have contrasting multiple sulfur and carbon isotope compositions. These appear to reflect the differential preservation of the two proposed fluxes of MIF-S from an anoxic atmosphere (i.e. elemental sulfur with positive Δ^{33} S and sulfate with negative Δ^{33} S) in the two environments. Large magnitude δ^{34} S fractionation and ³⁶S enrichments in CAP from samples of the Carawine Dolomite relative to the Jeerinah Formation shale and limestone data suggest a role for the biological redistribution of multiple sulfur isotope compositions via MSR. Furthermore, deviations of the Carawine sulfur isotope data away from arrays $(\Delta^{33}S/\delta^{34}S \text{ and } \Delta^{36}S/\Delta^{33}S)$ that typically define Neoarchean successions support the likelihood of an organic haze-dominated atmosphere, which may have been episodic or continuous, resulting in either regional or global effects. Furthermore, hazy atmosphere could influence photosynthetic community and led to flourishing of anoxygenic photosynthesizers (e.g. sulfur-oxidizing bacteria).

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2.7. Supplementary materials

AIDP-2 2cm 146.82-146.84m 177.90-177.92m 179.19-179.21m 180.87-180.89m 202.52-202.54m 200.87-200.89m 194.40-194-42m 195.40-195.42m 205.33-205.35m 247.31-247.33m 206.32-206.34m 245.29-245.31m 256.14-256.16m 255.21-255.23m 275.77-275.79m 293.63-293.65m AIDP-3 180.35-180.37m 168.44-168.46m 75.86-75.88m 139.74-139.76m

Figure 2.9. Billets of some carbonate and shale samples where pyrite microscopic grains and laminations were drilled for sulfur isotopic analyses (places of drilling are shown by red circles)

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Figure 2.10. Comparison of SO-SO₂ (UMD) and SF₆ (Harvard) measurements for rare sulfur isotopes from AIDP-2 and AIDP-3 cores. Uncertainties of SO-SO₂ technique are shown as 2σ while for SF₆ method they are within sizes of the data points.

	$\delta^{13}C_{org}$	$\delta^{13}C_{org}$	Difference
Sample	hot 6M HCl	3M HCl	
127.47	-39.5	-33.25	6.25
130.52	-38.7	-35.73	2.97
134.76	-32.9	-30.28	2.62
136.24	-33.3	-15.85	17.45
138.86	-33.6	-27.74	5.86
151.82	-33.0	-32.26	0.74
153.15	-32.8	-29.59	3.21
156.45	-32.4	-28.1	4.3
158.11	-31.6	-27.03	4.57
160.35	-31.9	-32.13	-0.23
164.34	-29.5	-29.43	0.07
170.57	-32.6	-30.05	2.55
173.59	-38.9	-36.52	2.38
175.11	-32.6	-32.25	0.35
181.9	-34.0	-33.05	0.95
183.91	-30.0	-19.69	10.31
188.03	-34.3	-26.73	7.57
189.41	-33.5	-24.54	8.96
192.26	-34.7	-31.96	2.74
242.65	-34.4	-33.89	0.51
251.41	-34.5	-34.31	0.19
251.91	-33.7	-31.46	2.24
265.51	-34.2	-34.09	0.11
283.63	-34.8	-33.64	1.16

Table 2.1. Comparison of organic matter carbon isotopic composition in some samples fromcarbonate facies of the AIDP-2 core treated by 3M HCl at UMD and hot 6M HCl at UW.Technique using hot 6M HCl acid removes carbonates minerals better than 3M HCl.

Core	Litholog y	TIC (wt.%)	TOC (wt.%)	$\delta^{13}C_{org}$	S (wt.%)	$\delta^{13}C_{carb}$	δ ¹⁸ Ocarb
	Jeerinah Shale	4.6 – 98.8 (av. 15.49, n=124)	5.16±2.75 (n=124)	-42.15±1.59 (n=124)	2.06±1.68 (n=25)	- 9.73±6.29 (n=7)	-12.61±2.30 (n=7)
AIDP-2	Jeerinah Limeston e	87.07±15.43 (n=13)	0.15±0.17 (n=13)	-38.38±4.73 (n=13)	0.15±0.18 (n=10)	- 0.35±1.11 (n=7)	-9.87±1.19 (n=7)
	Carawine Dolomite (carb)	94.1±7.2 (n=60)	0.2±0.27 (n=60)	-38.84±4.98 (n=60)	0.60±1.17 (av. 0.60, n=47)	0.26±0.37 (n=7)	-6.35±0.87 (n=7)
AIDP-3	Jeerinah Shale	14.00±9.90 (n=128)	4.87±2.40 (n=128)	-42.15±1.59 (n=128)	2.27±2.65 (n=95)		

 Table 2.2. Average geochemical parameters for different lithological units in the AIDP-2 and AIDP-3 cores

AIDF	2-2																	
Depth	Formation	TIC, wt.%	TOC, wt.%	$\delta^{13}C_{org}$	δ ¹³ C _{carb} ‰	δ ¹⁸ O _{carb} ‰	Type of sulfur	S, wt. %	δ ³⁴ S, ‰ (SO-SO ₂)	Δ ³³ S, ‰ (SO-SO ₂)	δ ³⁴ S, ‰ (SF ₆)	2σ	Δ ³³ S, ‰ (SF6)	2σ	Δ ³⁶ S, ‰ (SF6)	2σ	Δ ³⁶ S/Δ ³³ S	2σ
124.29	Carawine	98.0	0.11	-39.16	0.02	-6.05	bulk	0.22	8.494	0.600								
124.29	Carawine						py		16.759	0.739								
127.47	Carawine	98.1	0.15	-39.46	-0.60	-6.38	bulk	0.07	21.635	1.789								
129.23	Carawine	89.6		-38.45	-0.45	-5.66	bulk	0.24	18.330	1.234	18.78	0.30	1.00	0.016	-0.83	0.30	-0.84	0.45
130.52	Carawine	97.4	0.11	-38.74	-0.32	-5.95	bulk	0.06	19.071	1.983								
132.82	Carawine				-0.10	-6.15												
134.76	Carawine	98.5	0.02	-32.88	0.13	-7.88	bulk	0.28	5.768	0.263								
136.24	Carawine	95.7	0.02	-33.34	0.17	-5.63	bulk	0.01	868.8	0.886								
138.86	Carawine	100.0	0.00	-33.65														
140.58	Carawine	92.6	0.47	-41.68	0.01	-6.09	bulk	0.24	12.760	3.816	12.17	0.30	4.41	0.016	-4.86	0.30	-1.10	0.22
141.53	Carawine	51.4	4.2	-43.4														
143.25	Carawine	44.9	4.9	-43.6														
146.83	Carawine	95.1	0.21	-38.06	-0.48	-6.73	bulk	0.27	8.825	0.031								
146.83	Carawine						py		-5.847	-0.563	-2.99	0.30	0.25	0.016	-0.41	0.30	-1.66	1.64
148.37	Carawine			-41.71	-0.28	-5.92												
149.36	Carawine	47.6	3.9	-43.1														
151.82	Carawine	98.9	0.07	-32.95	0.55	-6.42												
153.15	Carawine	99.2	0.04	-32.83	0.53	-6.51												
156.45	Carawine	99.7	0.03	-32.43	0.59	-6.96	bulk	0.00	19.001	-3.424								
158.11	Carawine	100.0	0.00	-31.59	0.62	-5.98												
160.35	Carawine	99.7	0.02	-31.90	0.60	-6.15	bulk	0.00	21.160	-0.866								
162.23	Carawine	95.7	0.33	-42.47	0.27	-6.09	bulk	0.11	12.920	5.146								
164.34	Carawine	100.0	0.00	-29.47	0.46	-6.17												
165.79	Carawine	90.8	0.04	-43.12	0.21	-5.78	bulk	0.28	2.586	0.715								
168.22	Carawine	93.7	0.08	-43.45	-0.38	-6.39	bulk	2.15	13.068	5.035								
170.57	Carawine	98.8	0.02	-32.62	-0.12	-5.73	bulk	0.02	1.966	-0.173								
173.59	Carawine	91.8	0.18	-38.86	0.20	-6.32	bulk											
175.11	Carawine	99.5	0.04	-32.57	0.34	-6.70	bulk	0.01	-4.076	1.560								
177.91	Carawine	90.1	0.47	-45.94	-0.10	-6.45	bulk	1.07	6.683	2.002	6.37	0.30	1.84	0.016	-2.25	0.30	-1.22	0.30
177.91	Carawine						py		1.479	-0.799								
179.2	Carawine	89.7	0.38	-47.25	-0.13	-5.91	bulk	0.81	1.697	-2.024	2.11	0.30	-1.53	0.016	2.44	0.30	-1.60	0.33
179.2	Carawine						py		-3.615	-1.285	-3.56	0.30	-1.59	0.016	2.42	0.30	-1.52	0.32

Table 2.3 Elemental / isotopic carbon\oxygen and sulfur data from the AIDP cores.

180.88	Carawine			-43.99	-0.08	-5.87	py		-16.399	-1.340	-14.57	0.30	-1.62	0.016	2.54	0.30	-1.57	0.32
180.88	Carawine						py		-11.525	-1.583	-9.71	0.30	-1.41	0.018	2.56	0.30	-1.81	0.35
181.9	Carawine	9.99	0.01	-34.02	0.31	-7.09	bulk	0.01	14.803	0.281								
183.63	Carawine				0.04	-9.02												
183.91	Carawine	99.2	0.00	-29.98	0.29	-6.58	bulk	0.00	12.021	0.587								
185.21	Carawine			-33.97	0.56	-7.86	bulk	0.00	12.951	-0.506								
188.03	Carawine	97.9	0.02	-34.26	0.43	-7.13	bulk	0.04	14.690	0.600								
189.41	Carawine	99.4	0.01	-33.55	0.62	-7.27	bulk	0.00	12.392	-1.002								
192.26	Carawine	100.0	0.00	-34.72	0.46	-8.12	bulk	0.00	14.308	-0.271								
194.41	Carawine	90.6	0.19	-41.56	0.26	-5.41	bulk	0.35	-2.941	-1.771	-1.73	0.30	-1.71	0.016	2.60	0.30	-1.52	0.31
194.41	Carawine						py				-5.32	0.30	-2.28	0.016	3.17	0.30	-1.39	0.27
195.41	Carawine	76.7	0.71	-44.09	-0.19	-6.19	bulk	0.55	0.204	-1.191	3.35	0.30	-0.64	0.016	1.57	0.30	-2.47	0.66
195.41	Carawine						py		-4.990	-2.480	-4.74	0.30	-2.11	0.016	3.32	0.30	-1.58	0.28
197.6	Carawine	89.9	0.33	-43.11	-0.04	-6.54	bulk	0.14	7.496	0.705								
198.52	Carawine	54.3	6.7	-51.0														
198.63	Carawine	52.8	6.9	-51.0														
198.7	Carawine	48.9	6.8	-51.0														
198.76	Carawine	48.7	7.1	-50.9														
200.88	Carawine	64.2	1.31	-44.20			bulk	5.66	9.464	-2.090	9.61	0.30	-2.33	0.016	4.07	0.30	-1.75	0.26
200.88	Carawine						py		4.050	-2.742	4.04	0.30	-2 .33	0.016	3.60	0.30	-1.54	0.26
202.07	Carawine	99.1																
202.53	Carawine	95.9	0.25	-44.59	0.01	-6.71	bulk	0.15	8.217	0.323								
202.53	Carawine						py		12.896	-1.341								
202.53	Carawine						py		9.491	-1.385	10.17	0.30	-2.21	0.016	4.10	0.30	-1.86	0.27
203.07	Carawine	34.6	5.6	-52.0														
204.26	Carawine	96.8	0.09	-39.14	0.31	-6.30												
205.34	Carawine				0.11	-6.20	py		0.539	-1.991	1.09	0.30	-1.52	0.016	2.58	0.30	-1.70	0.33
205.34	Carawine						py		9.656	-1.989	9.68	0.30	-1.59	0.016	3.25	0.30	-2.05	0.32
205.62	Carawine	93.4	6.0	-46.6														
205.79	Carawine	92.8	0.47	-44.95	0.00	-6.42	bulk	0.18	7.208	1.212	7.18	0.30	1.14	0.016	-1.37	0.30	-1.20	0.40
205.79	Carawine						py		6.516	0.578	6.89	0.30	0.81	0.016	-0.96	0.30	-1.19	0.53
206.33	Carawine	89.0	0.64	-45.26	0.37	-5.05	py		-0.543	-1.811	0.27	0.30	-1.48	0.016	2.66	0.30	-1.79	0.34
242.04	Carawine				0.74	-5.33												
242.65	Carawine	99.8	0.00	-34.43	0.86	-5.67	bulk	0.02	20.772	0.715								
243.5	Carawine	99.3																
244.36	Carawine	98.8																

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245.3	Carawine	88.7	0.24	-44.90	0.46	-5.48	bulk	1.81	4.209	-1.824	5.03	0.30	-1.93	0.016	3.98	0.30	-2.06	0.29
245.3	Carawine						py				2.98	0.30	-2.19	0.016	4.67	0.30	-2.13	0.27
245.3	Carawine						py				5.95	0.30	-2.33	0.016	4.79	0.30	-2.06	0.26
245.95	Carawine	16.3	3.6	-49.4														
246.22	Carawine	24.0	3.6	-49.4														
246.3	Carawine						py		4.489	-2.328								
247.32	Carawine	97.2	0.16	-42.64	0.44	-5.06	bulk	0.63	8.792	-0.905	9.19	0.30	-1.22	0.016	3.28	0.30	-2.69	0.39
247.32	Carawine						py		7.483	-0.784								
247.32	Carawine						py		8.911	-1.100	9.02	0.30	-1.00	0.016	2.80	0.30	-2.80	0.45
249.04	Carawine	97.1	0.06	-38.85			bulk	0.04	2.880	0.322								
251.41	Carawine			-34.47	0.48	-5.80	bulk	2.35	7.736	0.693								
251.91	Carawine	9.66	0.01	-33.74	0.73	-4.98	bulk	0.01	-1.811	-0.267								
254.26	Carawine	6.4	2.6	-50.9														
255.22	Carawine	95.9	0.15	-46.47	0.13	-5.44	bulk	0.09	7.827	1.958								
256.15	Carawine	70.3	1.04	-41.75	0.12	-5.59	bulk	4.51	8.604	0.119	8.94	0.30	0.19	0.016	1.41	0.30	7.25	2.15
256.15	Carawine						py		8.630	-1.700	8.83	0.30	-1.91	0.016	4.14	0.30	-2.17	0.29
260.61	Carawine	82.7	0.44	-38.41	-0.07	-6.47	bulk	2.77	7.363	2.730	7.99	0.30	2.98	0.016	-2.55	0.30	-0.85	0.24
260.61	Carawine						py		9.932	6.281	10.70	0.30	5.78	0.016	-5.04	0.30	-0.87	0.21
263.67	Carawine	97.6	0.06	-38.78	0.64	-5.45	bulk	0.13	7.488	1.997								
265.51	Carawine	98.4		-34.18	0.45	-6.26	bulk	0.14	8.510	4.945								
266.68	Carawine	94.0	0.17	-39.57	0.58	-5.84	bulk	0.11	6.108	3.445								
268.49	Carawine	91.9	0.22	-38.95	0.51	-6.24	bulk	0.16	7.995	2.547								
270.48	Carawine	98.2	0.06	-38.96	0.66	-5.43	bulk	0.13	7.968	3.036	8.00	0.30	2.68	0.016	-2.23	0.30	-0.83	0.25
270.6	Carawine	96.9	3.4	-40.2														
270.98	Carawine	96.1	3.3	-40.2														
272.22	Carawine	93.8	0.24	-39.74	0.58	-6.32	bulk	0.14	8.769	3.842								
273.76	Carawine	91.1	0.34	-39.55	0.34	-6.48	bulk	0.09	6.985	2.534								
275.78	Carawine	91.9	0.29	-48.88	0.71	-8.18	bulk	0.73	13.159	3.271	13.18	0.30	2.98	0.016	-3.51	0.30	-1.18	0.24
275.78	Carawine						py		9.260	-0.525	9.87	0.30	-1.35	0.016	3.03	0.30	-2.24	0.36
275.78	Carawine						py		9.867	-0.663	10.13	0.30	-1.27	0.022	2.78	0.30	-2.19	0.37
276.85	Carawine	93.4	0.09	-43.03	0.76	-8.34	bulk	1.55	12.629	0.725	12.51	0.30	-0.16	0.016	1.66	0.30	-10.27	2.68
276.85	Carawine				1.08	-8.08	py				12.99	0.30	-0.35	0.016	1.66	0.30	-4.78	1.19

AIDP	-2																	
Depth	Formation	TIC, %	TOC, %	$\delta^{13}C_{org}$	$\delta^{13}C_{carb}$	$\delta^{18}O_{\rm carb}$	Type of sulfur	S, wt. %	δ ³⁴ S, ‰ (SO-SO ₂)	Δ ³³ S, ‰ (SO-SO ₂)	δ ³⁴ S, ‰ (CRS, SF ₆)	2σ ,	Δ ³³ S, ‰ (CRS, SF ₆)	2σ (Δ ³⁶ S, ‰ CRS, SF ₆)	2σ	Δ ³⁶ S/Δ ³³ S	2σ
278.05	Jeerinah	94.8	0.02	-46.0	0.23	-10.318												
278.61	Jeerinah	97.6	0.16	-36.6	1.24	-8.5822	bulk	0.04	11.97	9.90								
278.75	Jeerinah		5.7	-37.1														
279.04	Jeerinah	96.4	3.9	-35.7														
280.48	Jeerinah	95.7	2.5	-35.6														
280.59	Jeerinah	95.9	0.10	-33.6	1.08	-8.9233	bulk	0.03	10.12	8.58	10.98	0.30	9.68	0.016	-8.97	0.30	-0.93	0.20
282.33	Jeerinah	85.4	0.06	-34.2	0.48	-9.1217												
283.63	Jeerinah	97.8	0.05	-34.8			bulk	0.02	9.74	6.78								
286.08	Jeerinah	93.9	0.12	-40.9	0.27	-9.3258	bulk	0.05	18.61	10.69								
287.61	Jeerinah	78.5	0.67	-45.6	-1.72	-10.29	bulk	0.28	12.74	5.27	11.56	0.30	5.84	0.016	-5.89	0.30	-1.01	0.21
292.57	Jeerinah	89.0	0.13	-39.1	-1.79	-10.008	bulk	0.06	13.53	6.15								
293.64	Jeerinah	81.4	0.25	-40.4	-1.36	-10.926	bulk	0.59	14.31	10.82	14.65	0.30	10.83	0.016	-9.39	0.30	-0.87	0.20
293.64	Jeerinah	50.5	0.13	-28.6	-1.50	-11.123	bulk		12.37	7.87	13.73	0.30	9.77	0.016	-8.12	0.30	-0.83	0.20
293.64	Jeerinah	50.5					py		13.75	10.79	14.83	0.30	10.68	0.016	-8.82	0.30	-0.83	0.20
294.85	Jeerinah	96.5	0.08	-43.5	-0.06	-10.98	bulk	0.16	10.22	4.27								
296.01	Jeerinah	93.3	0.06	-39.8	-1.31	-11.341	bulk	0.09	9.90	4.15	9.89	0.30	5.29	0.016	-6.08	0.30	-1.15	0.21
296.99	Jeerinah	96.0	0.16	-42.6	0.25	-7.5078	bulk	0.16	8.85	3.30								
299.24	Jeerinah		3.1	-43.4														
300.43	Jeerinah	12.5	1.8	-42.4														
301.07	Jeerinah	15.4	3.2	-42.5														
302.11	Jeerinah	15.9	5.1	-42.8														
302.65	Jeerinah	10.1	7.6	-42.2														
303.28	Jeerinah	12.8	6.1	-42.6														
304.25	Jeerinah	18.4	2.2	-40.3			CRS	1.30	6.86	7.89	6.86	0.30	8.09	0.016	-7.06	0.30	-0.87	0.45
305.05	Jeerinah	15.6	4.9	-42.9														
306.05	Jeerinah	10.6	4.8	-42.8														
307.17	Jeerinah	10.5	3.5	-43.0														
307.64	Jeerinah	8.8	6.8	-44.1														
309.12	Jeerinah	8.1	8.3	-43.9			CRS	0.95	4.57	5.75	4.57	0.30	5.87	0.016	-4.99	0.30	-0.85	0.45
309.8	Jeerinah	10.3	6.4	-44.2														
310.51	Jeerinah	10.1	5.8	-44.7														
311.15	Jeerinah	10.9	3.1	-46.3														
312.03	Jeerinah	8.0	4.9	-46.7														

Minimum Minimum <t< th=""><th>Matrix Matrix Matrix<</th><th>Jeerinah</th><th>9.5</th><th>4.38</th><th>-45.6</th><th></th><th>bulk</th><th>0.64</th><th>8.16</th><th>6.11 2.20</th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th></t<>	Matrix Matrix<	Jeerinah	9.5	4.38	-45.6		bulk	0.64	8.16	6.11 2.20								
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ait 55 90 450 ait 35 90 454 724 530 547 0016 434 030 679 ait 35 450	1 5 90 450 - 450 - 431 0016 - 434 030 - 630 10 3.3 4.0 3.0 5.4 0.016 -4.34 0.30 -4.34 0.30 -4.34 0.30 -4.34 0.30 -0.34 0.30 -0.34 0.30 -0.34 0.30 -0.34 0.30 -0.34 0.30 -0.34 0.30 -0.34 0.30 -0.34 0.30 -0.34 0.30 -0.34 -0.30 -0.34 0.30 -0.34 0.30 -0.34 -0.30 -0.34 -0.30 -0.34 -0.30 -0.34 -0.30 -0.34 -0.30 -0.34	nah	7.2	8.0	-46.0													
1 5 8 9 454 CRS 142 7.24 5.30 5.47 0.016 -4.34 0.30 -0.30 11 11 4 13 4.0 CRS 0.87 4.81 3.39 4.81 0.30 5.45 0.30 0	10 58 80 454 -108 1.42 7.31 7.34 6.010 4.34 0.00 4.34 0.00 4.34 0.00 4.34 0.00 4.34 0.00 0.35 11 12 4.3 4.31 2.35 0.016 3.36 0.016 3.36 0.016 3.36 0.016 3.36 0.016 3.06 0.30 0.35 11 12 4.3 13 2.4 0.36 0.36 0.016 3.06 0.30 0.35 11 13 3.6 4.14 0.30 6.57 0.30 6.57 0.30 0.35 0.30 0.35 11 14 4.31 0.31 4.34 0.30 5.57 0.30 0.35 0.30 0.35 0.35 0.30 0.35 0.30 0.35 0.30 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35 0.35	nah	5.5	9.0	-45.0													
and 3.5 4.60 and 1.9 4.0 4.0 and 1.9 4.0 4.0 and 1.3 4.13 3.3 6.41 0.30 3.58 0.016 -3.06 0.30 -0.86 and 1.21 3.2 43.0 7.8 1.45 6.47 6.33 6.47 0.30 5.56 0.30 -0.87 and 1.23 3.6 41.0 7.2 6.47 0.30 6.55 0.016 -3.06 0.30 -0.87 and 1.22 3.4 4.10 7 6.47 0.30 6.55 0.016 -3.06 0.30 0.30 0.87 and 1.17 0.4 4.11 7 <td>11 32 45 460 11 40 403 11 41 403 11 41 403 11 41 413 11 41 647 948 359 356 414 11 12 41 7 41 030 553 306 916 506 030 987 087 11 13 36 414 54 647 030 655 030 537 030 087 11 10 431 441 547 647 030 655 030 630 030 030 11 10 431 441 485 547 030 557 030 050 030 11 10 43 445 647 030 655 030 557 030 031 11 10 24 248 144 485 <td< td=""><td>nah</td><td>5.8</td><td>8.9</td><td>-45.4</td><td></td><td>CRS</td><td>1.42</td><td>7.24</td><td>5.30</td><td>7.24</td><td>0.30</td><td>5.47</td><td>0.016</td><td>-4.34</td><td>0.30</td><td>-0.79</td><td>0.45</td></td<></td>	11 32 45 460 11 40 403 11 41 403 11 41 403 11 41 413 11 41 647 948 359 356 414 11 12 41 7 41 030 553 306 916 506 030 987 087 11 13 36 414 54 647 030 655 030 537 030 087 11 10 431 441 547 647 030 655 030 630 030 030 11 10 431 441 485 547 030 557 030 050 030 11 10 43 445 647 030 655 030 557 030 031 11 10 24 248 144 485 <td< td=""><td>nah</td><td>5.8</td><td>8.9</td><td>-45.4</td><td></td><td>CRS</td><td>1.42</td><td>7.24</td><td>5.30</td><td>7.24</td><td>0.30</td><td>5.47</td><td>0.016</td><td>-4.34</td><td>0.30</td><td>-0.79</td><td>0.45</td></td<>	nah	5.8	8.9	-45.4		CRS	1.42	7.24	5.30	7.24	0.30	5.47	0.016	-4.34	0.30	-0.79	0.45
null 110 40 400 null 13 42 413 50 536 530	110 40 400	nah	8.2	3.5	-45.0													
		nah	11.9	4.0	-40.9													
		nah	7.3	4.2	-41.3		CRS	0.87	4.81	3.39	4.81	0.30	3.58	0.016	-3.06	0.30	-0.86	0.45
ind 12 49 416 CR8 145 6.47 6.38 6.47 0.30 6.55 0.016 5.72 0.30 0.30 ind 133 3.6 414 431 431 431 431 431 431 431 431 431 431 431 431 431 431 431 431 431 432 337 0.016 5.72 0.30 0.35 null 15.2 2.4 410 4.85 3.46 4.85 0.30 3.57 0.016 5.72 0.30 0.35 null 15.2 2.4 4.10 4.85 3.46 4.85 0.30 3.57 0.016 5.72 0.30 0.35 null 15.4 4.85 0.45 0.35 0.35 0.35 0.30 0.35 0.35		inah	15.1	3.2	-43.6													
		inah	12.2	4.9	-41.6		CRS	1.45	6.47	6.38	6.47	0.30	6.55	0.016	-5.72	0.30	-0.87	0.45
		inah	13.3	3.6	-41.4													
		nah	15.9	5.3	-43.0													
		nah	11.7	0.4	-43.1													
	null 216 28 42.3 42.3 0.3 <th< td=""><td>nah</td><td>18.3</td><td>2.1</td><td>-43.1</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></th<>	nah	18.3	2.1	-43.1													
		nah	21.6	2.8	-42.3													
	nal 9.8 2.9 4.2.1 nal 86.3 0.5 40.8 nal 84.9 0.12 -37.4 16.86 -10.507 nal 16.6 2.5 -42.8 11.431 9.95 8.48 9.95 0.30 8.45 0.016 -7.29 0.30 -0.36 nal 16.6 2.5 -42.8 11.431 9.01 9.38 7.80 9.45 0.016 -7.29 0.30 -0.36 nal 17.1 3.4 -43.0 11.431 9.14 9.38 7.80 9.45 0.016 -7.29 0.30 -0.36 nal 17.1 3.4 -43.0 1.41 9.38 7.80 1.41 </td <td>nah</td> <td>15.2</td> <td>2.4</td> <td>-41.0</td> <td></td> <td>CRS</td> <td>1.01</td> <td>4.85</td> <td>3.46</td> <td>4.85</td> <td>0.30</td> <td>3.57</td> <td>0.016</td> <td>-3.09</td> <td>0.30</td> <td>-0.87</td> <td>0.45</td>	nah	15.2	2.4	-41.0		CRS	1.01	4.85	3.46	4.85	0.30	3.57	0.016	-3.09	0.30	-0.87	0.45
	nal 86.3 0.5 -40.8 nal 84.9 0.12 -37.4 -16.86 -10.507 0.30 8.45 0.016 -7.29 0.30 0.30 nal 16.6 25 -42.8 114.3 9.95 8.48 9.95 0.30 8.45 0.016 -7.29 0.30 -0.86 nal 15.5 2.4 -33.0 114.31 bulk 0.81 9.38 7.80 9.95 0.30 8.45 0.016 -7.29 0.30 -0.86 nal 16.5 2.4 -43.0 114.31 bulk 0.81 9.38 7.80 1.8	nah	19.8	2.9	-42.1													
	inal 849 0.12 -37.4 -16.86 -10.507 inal 16.6 2.5 -42.8 -10.507 inal 16.6 2.5 -42.8 -11.431 inal 16.5 2.4 -43.0 ould -14.36 -11.431 inul 16.5 2.4 -43.0 ould -14.36 -11.431 inul 17.1 3.4 -43.0 ould -14.36 -11.431 inul 18.5 6.9 -43.9 ould -14.36 -11.431 inul 27.5 6.9 -43.9 ould -14.36 -11.431 inul 17.1 3.4 -43.0 ould -14.36 -11.431 inul 18.5 6.9 -43.9 ould -14.36 -11.431 inul 28.5 6.9 -43.9 ould -14.36 ould -14.36 ould -14.36 ould -14.38 ould -14.	inah	86.3	0.5	-40.8													
inal 16.6 2.5 4.2.8 0.31 8.45 0.016 -7.29 0.30 -0.36 inal 54.2 0.67 -39.6 -14.36 -11.431 bulk 0.81 9.38 7.80 -9.95 0.30 8.45 0.016 -7.29 0.30 -0.86 inal 16.5 2.4 -43.0 -11.431 bulk 0.81 9.38 7.80 -7.29 0.30 -7.29 0.30 -0.86 inal 16.5 2.4 -43.0 -11.431 bulk 0.81 9.38 7.80 -14.3	Ind 16.6 2.5 4.2.8 1.14 9.95 8.48 9.95 0.30 8.45 0.016 -7.29 0.30 0.30 0.30 inah 54.2 0.67 -39.6 -14.36 -11.431 bulk 0.81 9.38 7.80 9.95 0.30 8.45 0.016 -7.29 0.30 -0.86 inah 16.5 2.4 -43.0 - - - - - - 0.30 8.45 0.016 -7.29 0.30 -0.86 inah 16.5 2.4 -43.0 - - - - - - - - - - - 0.30 - - 0.30 - - - - - - - - - - - - - - 0.30 - 0.30 - - - - - - - - - - <td< td=""><td>inah</td><td>84.9</td><td>0.12</td><td>-37.4</td><td>-16.86 -10.507</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></td<>	inah	84.9	0.12	-37.4	-16.86 -10.507												
inal 54.2 0.67 -39.6 -14.36 -11.431 bulk 0.81 9.38 7.80 inal 16.5 2.4 -43.0 inal 17.1 3.4 -43.3 inal 10.5 6.9 -43.9 inal 8.5 5.7 -44.3 inal 8.7 8.8 -42.7 inal 14.3 5.2 -43.3 inal 14.3 5.2 -43.3	inal 54.2 0.67 -39.6 -14.36 -11.431 bulk 0.81 9.38 7.80 inal 16.5 2.4 -43.0 inal 17.1 3.4 -43.3 inal 8.5 6.9 -43.9 inal 8.5 7.7 -44.3 inal 8.7 8.8 -42.7 inal 8.7 8.3 6.15 5.78 6.15 0.30 5.87 0.016 -4.93 0.30 -0.84 inal 14.3 5.2 -43.3	inah	16.6	2.5	-42.8		CRS	1.14	9.95	8.48	9.95	0.30	8.45	0.016	-7.29	0.30	-0.86	0.45
inal 16.5 2.4 -43.0 inal 17.1 3.4 -43.3 inal 10.5 6.9 -43.9 inal 8.5 5.7 -44.3 inal 8.7 8.8 -42.7 inal 14.3 5.2 -43.3 inal 14.3 5.2 -43.3	inal 16.5 2.4 -43.0 inal 17.1 3.4 -43.3 inal 8.5 6.9 -43.9 inal 8.5 5.7 -44.3 inal 8.7 8.8 -42.7 CRS 3.33 6.15 5.78 6.15 0.30 5.87 0.016 -4.93 0.30 -0.84 inal 8.7 8.8 -42.7 CRS 3.33 6.15 5.78 6.15 0.30 5.87 0.016 -4.93 0.30 -0.84 inal 8.13 5.2 -43.3 6.15 5.78 6.15 0.30 5.87 0.016 -4.93 0.30 -0.84	nah	54.2	0.67	-39.6	-14.36 -11.431	bulk	0.81	9.38	7.80								
Inal 17.1 3.4 -43.3 Inal 10.5 6.9 -43.9 Inal 8.5 5.7 -44.3 Inal 8.7 8.8 -42.7 Inal 14.3 5.2 -43.3 Inal 14.3 5.2 -43.3	Inah 17.1 3.4 -43.3 Inah 10.5 6.9 -43.9 Inah 8.5 5.7 -44.3 Inah 8.7 8.8 -42.7 Inah 8.7 8.8 -42.7 Inah 8.7 8.8 -42.7 Inah 8.7 8.8 -43.3 Inah 8.7 8.7 0.016 -4.3 CRS 3.33 6.15 5.78 Inah 14.3 5.2 -43.3	inah	16.5	2.4	-43.0													
nah 10.5 6.9 -43.9 nah 8.5 5.7 -44.3 nah 8.7 8.8 -42.7 CRS 3.33 6.15 5.78 6.15 0.30 5.87 0.016 -4.93 0.30 -0.84 nah 14.3 5.2 -43.3	nah 10.5 6.9 -43.9 nah 8.5 5.7 -44.3 nah 8.7 8.8 -42.7 CRS 3.33 6.15 5.78 6.15 0.30 5.87 0.016 -4.93 0.30 -0.84 nah 14.3 5.2 -43.3	nah	17.1	3.4	-43.3													
nah 8.5 5.7 -44.3 nah 8.7 8.8 -42.7 CRS 3.33 6.15 5.78 6.15 0.30 5.87 0.016 -4.93 0.30 -0.84 nah 14.3 5.2 -43.3	nah 8.5 5.7 -44.3 nah 8.7 8.8 -42.7 CRS 3.33 6.15 5.78 6.15 0.30 5.87 0.016 -4.93 0.30 -0.84 nah 14.3 5.2 -43.3	nah	10.5	6.9	-43.9													
nah 8.7 8.8 -42.7 CRS 3.33 6.15 5.78 6.15 0.30 5.87 0.016 -4.93 0.30 -0.84 nah 14.3 5.2 -43.3	nah 8.7 8.8 -42.7 CRS 3.33 6.15 5.78 6.15 0.30 5.87 0.016 -4.93 0.30 -0.84 nah 14.3 5.2 -43.3	nah	8.5	5.7	-44.3													
inah 14.3 5.2 -43.3	inah 14.3 5.2 -43.3	inah	8.7	8.8	-42.7		CRS	3.33	6.15	5.78	6.15	0.30	5.87	0.016	-4.93	0.30	-0.84	0.45
		nah	14.3	5.2	-43.3													

344.18	Jeerinah	8.7	7.3	-43.9														
344.99	Jeerinah	6.5	8.4	-42.6														
346.03	Jeerinah		12.0	-41.2														
347.00	Jeerinah		9.2	-42.2			CRS	1.72	9.39	6.94	9.39	0.30	7.03	0.016	-5.84	0.30	-0.83	0.45
347.83	Jeerinah	7.2	12.3	-45.0														
348.55	Jeerinah	5.9	10.0	-44.3														
349.14	Jeerinah	59.3	1.81	-44.6	-6.14	-12.667	bulk	0.57	9.73	5.79								
349.31	Jeerinah	6.1	9.0	-46.3			CRS	2.61	9.95	5.66	9.95	0.30	5.80	0.016	-4.85	0.30	-0.84	0.45
350.44	Jeerinah	6.6	7.4	-48.1														
351.16	Jeerinah	98.8	7.7	40.4														
352.5	Jeerinah				-4.18	-17.302												
352.56	Jeerinah	9.2	11.3	-40.0			CRS	3.67	7.73	7.19	7.73	0.30	7.21	0.016	-6.14	0.30	-0.85	0.45
352.82	Jeerinah	8.4	9.3	-41.2														
353.66	Jeerinah	8.7	8.9	-41.0														
354.66	Jeerinah	9.1	7.3	-40.6			CRS	3.85	7.10	6.68	7.10	0.30	6.82	0.016	-5.87	0.30	-0.86	0.45
355.54	Jeerinah	8.0	8.0	-40.9														
356.19	Jeerinah	8.3	7.0	-41.0														
357.13	Jeerinah	82.9	0.57	-40.7	-4.91	-12.819	bulk	0.85	5.94	5.87								
357.37	Jeerinah	7.0	11.1	-44.7														
358.09	Jeerinah	6.8	10.2	-42.7			CRS	5.31	7.57	5.24	7.57	0.30	5.19	0.016	-4.13	0.30	-0.80	0.45
358.58	Jeerinah	7.8	9.1	-42.7														
359.39	Jeerinah	6.8	12.5	-44.9			CRS	4.54	5.88	3.81	5.88	0.30	3.80	0.016	-3.15	0.30	-0.83	0.45
360.39	Jeerinah	6.5	10.7	-44.3														
360.88	Jeerinah	84.5	0.55	-41.8	-3.91	-12.909	bulk	5.90	5.28	4.28								
360.88	Jeerinah						py		7.75	5.94								
361.42	Jeerinah	5.5	8.9	-43.1														
362.08	Jeerinah	6.3	9.6	-43.5			CRS	5.47	7.02	5.29	7.02	0.30	5.22	0.016	-4.19	0.30	-0.80	0.45
363.04	Jeerinah	8.5	8.0	-42.6														
364.26	Jeerinah	7.6	4.7	-42.2														
365.73	Jeerinah		5.0	-41.2			CRS	2.39	2.44	4.51	2.44	0.30	4.69	0.016	-4.26	0.30	-0.91	0.45
366.34	Jeerinah	13.1	3.6	-41.0														
367.38	Jeerinah	12.3	4.9	-41.5														
368.14	Jeerinah	13.5	4.2	-41.0														
369.05	Jeerinah	12.8	4.3	-41.2														
369.72	Jeerinah	11.3	6.4	-42.2														
370.34	Jeerinah	11.6	6.0	-42.9														

							q	continue	le 2.3. c	Tabl						
0.45	-0.30	0.30	0.15	0.016	-0.49	0.30	1.47	-0.52	1.47	0.33	CRS	-42.4	2.6	13.1	Jeerinah	419.59
												-40.9	2.5	15.5	Jeerinah	417.26
												-41.1	2.2	15.4	Jeerinah	416.85
												-41.3	2.1	14.8	Jeerinah	416.69
												-41.2	1.6	14.4	Jeerinah	416.44
												-42.2	3.3	15.2	Jeerinah	416.03
0.45	-1.35	0:30	-1.58	0.016	1.17	0.30	0.55	1.02	0.55	0.27	CRS	-41.3	3.2	17.7	Jeerinah	415.6
												-41.5	2.9	17.8	Jeerinah	415.45
												-41.1	2.9	17.3	Jeerinah	415.33
												-36.2	0.1	32.9	Jeerinah	407.15
												-41.8	2.2	14.4	Jeerinah	397.88
												-42.0	2.6	13.6	Jeerinah	394.57
												-41.7	2.8	13.7	Jeerinah	393.54
												-41.7	2.5	14.6	Jeerinah	392.79
0.45	-1.18	0.30	-2.00	0.016	1.69	0.30	0.02	1.61	0.02	0.48	CRS	-41.9	3.0	14.9	Jeerinah	392.33
												-43.0	3.6	16.3	Jeerinah	390.56
												-40.2	1.6	12.1	Jeerinah	389.03
												-41.8	2.0	10.6	Jeerinah	388.52
												-41.6	2.8	23.9	Jeerinah	386.82
0.45	-0.98	0.30	-3.50	0.016	3.56	0.30	3.24	3.31	3.24	0.30	CRS	-42.4	2.9	22.6	Jeerinah	386.28
												-42.0	2.7	33.2	Jeerinah	384.66
												-42.1	3.4	18.9	Jeerinah	382.76
												-41.8	3.2	14.1	Jeerinah	382.34
												-41.3	3.4	12.3	Jeerinah	381.43
0.45	-0.95	0.30	-4.56	0.016	4.80	0.30	5.77	4.71	5.77	0.78	CRS	-41.9	3.9	11.7	Jeerinah	380.37
												-45.2	5.4	12.6	Jeerinah	377.89
												-45.7	6.0	10.4	Jeerinah	377.05
												-45.5	5.5	12.4	Jeerinah	375.94
0.45	-0.86	0.30	-5.17	0.016	6.00	0.30	5.03	5.84	5.03	4.45	CRS	-45.7	5.7	13.5	Jeerinah	374.67
												-44.3	5.7	12.1	Jeerinah	374.04
												-44.1	5.2	10.5	Jeerinah	372.86
												-44.3	6.6	11.4	Jeerinah	371.8
0.45	-0.94	0.30	-4.48	0.016	4.78	0.30	0.24	4.81	0.24	2.53	CRS	-43.2	5.7	11.6	Jeerinah	371.54
												-43.0	5.9	10.9	Jeerinah	371.07
												-44.1	5.5	11.1	Jeerinah	370.98
												-43.2	5.2	11.4	Jeerinah	370.69

				0.45									
				-1.33									
				0.30									
				-1.74									
				0.016									
				1.31									:
				0.30									i
				1.79									
													:
				1.12									
				1.79									
				0.31									i
				CRS									
-44.9	-43.7	-44.3	-42.7	-43.2	-43.3	-43.2	-43.4	-43.3	-43.5				
3.5	3.1	3.2	3.1	3.0	3.3	3.3	3.8	3.5	3.6				
14.1	15.5	13.0	15.3	15.2	14.9	15.1	14.4	15.8	15.4	15.8	15.7	15.3	
Jeerinah	:												
420.41	420.58	422.11	422.34	426.62	427	427.6	427.91	428.06	428.16	430.1	430.19	430.38	

Data in bold were received from Buick's group (WU, &¹²Corg and TIC), Tim Lyons' group (University of California, Riverside, S, wt. %)

and David Johnston (Harvard, CRS SF6 measurements) Other data are from University of Maryland, College Park

Jepth I	Formation	TIC %	TOC %	δ ¹³ C _{org} %0	Spy, wt. %	δ ³⁴ S, ‰ (CRS, SO- SO ₂)	Δ ³³ S, ‰ (CRS, SO- SO ₂)	δ ³⁴ S, ‰ (CRS, SF ₆)	2σ	Δ ³³ S, ‰ (CRS, SF ₆)	2σ	Δ^{36} S, ‰ (CRS, SF ₆)	2σ	$\Delta^{36} {\rm S}/\Delta^{33} {\rm S}$	2σ
66.03	Jeerinah	13.1	3.7	-40.8	1.81	1.18	0.52	0.74	0.30	0.45	0.016	-0.54	0.30	-1.19	1.07
66.71	Jeerinah	95.5	4.1	-47.5											
67.17	Jeerinah	8.4	4.4	-41.0	4.80	-1.80	-0.20	-2.48	0.30	-0.50	0.016	0.34	0.30	-0.69	0.59
68.22	Jeerinah	8.2	3.7	-41.2	7.99	2.87	-0.35	2.15	0:30	-0.59	0.016	0.64	0:30	-1.09	0.76
68.59	Jeerinah	9.4	5.0	-40.6	1.43			-0.32	0.30	-0.44	0.016	0.34	0:30	-0.77	0.72
68.92	Jeerinah	12.5	5.4	-40.5	1.60	1.11	-0.33	0.65	0.30	-0.59	0.016	0.41	0.30	-0.69	0.51
70.55	Jeerinah	9.1	6.8	-43.1	2.86			7.84	0:30	5.16	0.016	-4.69	0:30	-0.91	0.21
70.62	Jeerinah	11.3	6.3	-42.0	3.13	8.63	6.21	8.37	0.30	6.05	0.016	-5.50	0:30	-0.91	0.21
70.69	Jeerinah				2.11			1.67	0:30	-0.39	0.016	0.33	0.30	-0.85	0.90
70.82	Jeerinah	10.1	5.1	-42.3	2.26	8.19	6.30	8.01	0.30	5.99	0.016	-5.50	0:30	-0.92	0.21
71.05	Jeerinah	6.0	8.1	-41.2	1.39	1.65	-0.29	1.43	0.30	-0.49	0.016	0.47	0.30	-0.96	0.81
71.12	Jeerinah	5.0	7.3	-41.9	2.13	2.98	1.29	2.65	0:30	1.08	0.016	-0.96	0:30	-0.89	0.38
71.22	Jeerinah	6.0	8.2	-41.5	1.53	2.65	-0.08	2.16	0:30	-0.21	0.016	0.01	0:30	-0.06	0.24
71.44	Jeerinah	6.9	7.4	-42.1	2.60	4.32	1.87	4.21	0.30	1.50	0.016	-1.42	0.30	-0.95	0.32
71.94	Jeerinah	6.2	5.9	-41.9	0.59										
72.44	Jeerinah	6.1	6.5	-42.7	0.84	7.81	4.20								
74.11	Jeerinah	10.9	6.8	-42.6	0.67										
76.99	Jeerinah	5.0	4.9	-42.1	1.44	5.59	4.59								
77.52	Jeerinah	9.1	4.5	-41.5	0.44	7.26	3.30	2.56	0.30	0.47	0.016	-0.41	0.30	-0.89	0.79
78.56	Jeerinah	8.9	4.0	-40.4	1.67	5.44	4.44	5.09	0.30	2.02	0.016	-1.61	0.30	-0.80	0.25
79.36	Jeerinah	4.6	7.3	-41.8	4.35	2.55	-0.20	4.36	0.30	1.16	0.016	-0.54	0.30	-0.46	0.26
79.78	Jeerinah	5.7	8.2	-41.7	4.35	4.98	1.13								
80.78	Jeerinah	1.1	9.9	-43.3	4.72	4.34	0.74	4.53	0.30	3.00	0.016	-2.21	0.30	-0.74	0.22
82.19	Jeerinah	4.8	8.4	-43.6	17.60	9.29	7.88	4.44	0.30	3.08	0.016	-2.35	0.30	-0.76	0.22
83.23	Jeerinah	4.3	8.6	-43.6	8.13	4.38	2.42	96.0	0.30	0.13	0.016	0.31	0.30	2.31	
83.93	Jeerinah	4.9	9.5	-43.7	10.08	4.44	2.64	3.23	0.30	1.91	0.016	-1.47	0.30	-0.77	0.26
84.56	Jeerinah	4.5	9.9	-43.7	8.94	1.00	-0.26	3.11	0.30	-0.08	0.016	0.17	0.30	-2.16	
85.4	Jeerinah	5.8	9.2	-44.4	4.87	3.20	1.46	1.71	0.30	-0.66	0.016	0.78	0.30	-1.19	0.75
86.54	Jeerinah	5.3	7.9	-42.5	7.17	3.16	-0.55	3.61	0.30	-0.70	0.016	0.86	0.30	-1.22	0.72
87.7	Jeerinah	4.3	6.4	-43.5	8.86	1.47	-1.27	5.84	0.30	3.29	0.016	-2.46	0.30	-0.75	0.22
22 77	Tooningh		0	111											

88.78	Jeerinah	3.2	8.4	-42.6	2.14	5.88	2.83	4.34	0.30	0.01	0.016	0.46	0:30	44.31	
89.93	Jeerinah	3.8	11.6	-43.1	2.53	6.71	2.85	4.13	0.30	0.50	0.016	-0.26	0.30	-0.51	0.46
91.67	Jeerinah	5.0	10.2	-43.4	3.46	4.33	-0.43	5.96	0.30	2.18	0.016	-1.63	0.30	-0.75	0.24
92.83	Jeerinah	5.6	11.4	-42.2	3.44	4.00	0.21	7.91	0.30	6.26	0.016	-5.05	0.30	-0.81	0.21
93.89	Jeerinah	6.5	8.4	-41.0	5.07	5.79	1.61	6.05	0:30	3.38	0.016	-2.76	0.30	-0.82	0.22
95.49	Jeerinah	6.4	5.8	-41.8	3.65	7.87	5.97	4.29	0:30	0.19	0.016	-0.06	0:30	-0.34	0.76
95.92	Jeerinah	6.3	7.3	-42.0	3.76	6.01	3.04	6.02	0.30	4.11	0.016	-3.34	0.30	-0.81	0.22
97.13	Jeerinah	6.5	9.0	-41.8	3.12	4.35	-0.30	4.72	0.30	1.99	0.016	-1.70	0.30	-0.85	0.26
97.55	Jeerinah	6.4	5.3	-42.1	2.77	6.04	3.71	3.74	0:30	3.32	0.016	-3.02	0.30	-0.91	0.23
101.77	Jeerinah	9.6	4.4	-42.8	6.14	4.49	1.83	1.63	0:30	0.52	0.016	-0.55	0.30	-1.07	0.84
104.5	Jeerinah	22.1	3.9	-41.6	0.39	3.79	3.07	4.46	0:30	4.59	0.016	-3.87	0.30	-0.84	0.21
104.92	Jeerinah	13.9	8.3	-41.4	2.38	1.57	0.67	2.25	0.30	1.64	0.016	-1.52	0.30	-0.93	0.30
105.4	Jeerinah	12.3	4.8	-42.6	0.55	4.47	4.53	2.99	0.30	3.26	0.016	-3.08	0.30	-0.95	0.23
106.82	Jeerinah	14.3	4.8	-41.0	1.16	2.27	1.56								
107.18	Jeerinah	14.1	5.1	-41.0	1.04	3.11	3.62	96.0	0.30	1.70	0.016	-1.74	0.30	-1.02	0.31
108.39	Jeerinah	16.0	5.5	-40.9	0.34	3.09	3.39	96.0	0.30	1.37	0.016	-1.48	0.30	-1.08	0.37
109.06	Jeerinah	16.8	5.0	-40.9	0.35	1.00	1.89	1.87	0.30	2.74	0.016	-2.54	0.30	-0.93	0.24
109.9	Jeerinah	23.2	3.7	-40.5	0.47	1.17	1.55	2.00	0.30	3.10	0.016	-2.95	0.30	-0.95	0.23
111.48	Jeerinah	23.8	4.1	-40.9	0.25	1.94	3.32	0.27	0.30	1.95	0.016	-2.09	0.30	-1.08	0.30
111.6	Jeerinah	28.2	3.5	-40.5	0.26	1.92	3.02	3.66	0.30	5.28	0.016	-5.04	0.30	-0.95	0.21
112.36	Jeerinah	35.0	0.5	-38.2											
113.35	Jeerinah	28.7	0.6	-38.6											
114.59	Jeerinah	16.6	3.2	-40.8	0.14	0.39	2.16	3.77	0.30	4.85	0.016	-4.42	0.30	-0.91	0.21
115.35	Jeerinah	21.6	4.0	-40.3	1.10	3.60	5.51				0.016				
115.82	Jeerinah	16.8	4.1	-41.0	0.60	3.79	5.01	4.38	0.30	3.42	0.016	-3.52	0.30	-1.03	0.23
116.39	Jeerinah	19.6	4.4	-40.9	0.49	2.49	4.21	4.55	0:30	4.22	0.016	-4.03	0.30	-0.96	0.22
117.74	Jeerinah	52.8	0.2	-37.7											
118.32	Jeerinah	15.2	4.3	-40.4	0.76	4.34	2.43	1.86	0.30	3.23	0.016	-3.27	0.30	-1.01	0.24
119.05	Jeerinah	14.7	4.7	-40.6	1.35	4.63	4.61	-0.36	0.30	1.13	0.016	-1.34	0.30	-1.19	0.46
120.4	Jeerinah	14.9	4.6	-41.1	0.77	1.90	3.07	-1.10	0.30	0.81	0.016	-1.17	0.30	-1.44	0.74
121.08	Jeerinah	12.9	4.2	-41.4											
121.47	Jeerinah	11.8	3.5	-39.4	0.31	-0.37	1.49	-0.37	0:30	2.11	0.016	-2.33	0.30	-1.10	0.29
123.01	Jeerinah	20.5	3.5	-39.6	1.12	-1.22	0.06	1.58	0.30	3.29	0.016	-3.30	0.30	-1.01	0.23
123.22	Jeerinah	17.8	4.7	-40.5	1.09	-0.44	0.73	3.24	0:30	3.23	0.016	-3.30	0.30	-1.02	0.24
124.08	Jeerinah				0.73	1.53	3.17	2.33	0.30	2.96	0.016	-3.03	0.30	-1.02	0.24
124.52	Jeerinah	13.5	4.5	-41.3	0.85	3.26	3.41	2.41	0.30	2.67	0.016	-2.93	0.30	-1.10	0.26

ıtinued	
2.3. con	
Table 2	

125 54	Jeerinah.	13.0	47	-41.9	0.78	233	3 08	1 66	030	1 48	0.016	-1 82	030	-1 23	0.39
125.8	Jeerinah	12.9	5.2	42.4	1.71	2.44	2.81		0		010:0		0.00		
127.17	Jeerinah	24.0	4.6	-43.5	1.84	1.65	1.68	0.42	0.30	3.33	0.016	-3.19	0.30	-0.96	0.23
127.83	Jeerinah	13.3	3.4	-41.5	0.42	-0.05	3.37								
128.7	Jeerinah	12.8	5.7	-43.0	0.71	0.34	3.59	1.31	0.30	2.83	0.016	-2.64	0.30	-0.93	0.24
129.65	Jeerinah	11.0	5.0	-42.2	0.51	-0.17	3.16	1.21	0.30	3.54	0.016	-3.45	0.30	-0.97	0.23
130.17	Jeerinah	13.2	4.6	-41.6	1.00	1.31	2.82	2.33	0.30	1.05	0.016	-1.20	0.30	-1.14	0.48
131.31	Jeerinah	13.6	4.1	-41.7	0.89	1.27	3.42	-0.84	0.30	0.84	0.016	-1.09	0.30	-1.29	0.64
131.98	Jeerinah	12.1	4.7	-41.8	2.07	2.37	1.07	-0.39	0.30	1.05	0.016	-1.19	0.30	-1.13	0.47
132.78	Jeerinah	14.1	5.6	-42.0	2.95	-0.55	0.98	-0.86	0.30	1.65	0.016	-1.66	0.30	-1.01	0.32
133.32	Jeerinah	14.7	3.7	-41.2											
134.13	Jeerinah	12.3	4.7	-41.9	0.78	-0.23	1.07	-0.50	0.30	2.44	0.016	-2.44	0.30	-1.00	0.26
134.82	Jeerinah	13.6	5.1	-41.6	0.58										
135.86	Jeerinah	11.4	4.5	-42.2											
137.54	Jeerinah	13.5	4.1	-40.9	0.50			-0.17	0.30	2.98	0.016	-3.11	0.30	-1.04	0.24
138.53	Jeerinah	13.4	4.6	-40.2	0.56	-0.73	1.54	0.57	0.30	3.07	0.016	-3.10	0.30	-1.01	0.24
138.99	Jeerinah	13.7	4.2	-40.5	0.56	-0.44	2.74								
139.55	Jeerinah	13.4	4.6	-40.7	0.68	0.73	3.12	-0.12	0.30	3.46	0.016	-3.29	0.30	-0.95	0.23
140.36	Jeerinah	13.8	5.5	-41.4	1.00	-0.14	2.95	-0.25	0.30	3.38	0.016	-3.38	0.30	-1.00	0.23
141.28	Jeerinah	13.0	5.0	-41.4	1.16	0.62	2.61								
141.75	Jeerinah	13.0	4.3	-40.7	1.06	-0.03	2.80	0.18	0.30	3.69	0.016	-3.48	0.30	-0.94	0.22
142.04	Jeerinah	13.7	3.9	-40.5	0.51	-0.03	3.37								
142.11	Jeerinah	15.0	4.3	-40.4	1.01	-0.21	2.89	1.10	0.30	3.61	0.016	-3.21	0.30	-0.89	0.22
142.31	Jeerinah	19.6	4.7	-40.7	0.87	-0.20	2.50	0.69	0.30	2.35	0.016	-2.69	0.30	-1.14	0.28
142.53	Jeerinah	20.2	4.9	-40.7	1.14	0.24	3.40								
142.72	Jeerinah	20.1	4.6	-40.1	1.08	0.66	3.23								
142.99	Jeerinah	18.4	4.9	-40.5											
144.72	Jeerinah	19.1	5.5	-41.4	1.09	1.23	3.18	1.56	0.30	3.84	0.016	-3.56	0.30	-0.93	0.22
145.77	Jeerinah	16.8	7.0	-42.6	2.61	0.56	1.88	0.42	0.30	3.68	0.016	-3.59	0.30	-0.97	0.23
146.29	Jeerinah	18.1	5.2	-41.9	1.28	1.06	2.59	0.63	0.30	4.38	0.016	-4.16	0.30	-0.95	0.22
149	Jeerinah	18.4	5.1	-42.8	2.41	2.27	3.60	-0.70	0.30	4.24	0.016	-4.16	0.30	-0.98	0.22
150.06	Jeerinah	13.7	5.3	-43.6											
151.23	Jeerinah	12.2	4.6	-43.7											
151.96	Jeerinah	12.9	5.2	-43.9											
152.84	Jeerinah	11.4	5.3	-43.3	0.65	1.32	3.89	3.03	0.30	3.03	0.016	-2.69	0.30	-0.89	0.23
153.81	Jeerinah	16.3	3.8	-42.6											

Data in bold were received from Roger Buick's group (WU, δ^{13} Corg, TOC and TIC), Tim Lyons' group (University of California, Riverside, S, wt. %) and David Johnston's group (Harvard, CRS SF6 measurements)

Other data are from University of Maryland, College Park

-45.0

1.0 0.3 0.5 0.7

14.8 20.0 15.5

45.1

204.37

43.5

1.6 0.9 2.4 0.7 0.8 0.9

19.3 20.6 16.6 12.2 15.4

Jeerinah

Jeerinah Jeerinah Jeerinah

Jeerinah Jeerinah Jeerinah Jeerinah

15.1 15.2 17.0

-45.4 -44.5 -44.6 44.6 -43.3

3.06

2.67

1.31

-43.0

Jeerinah

Jeerinah Jeerinah

-43.1 -43.3

-44.4

Jeerinah

Jeerinah

Jeerinah Jeerinah Jeerinah

44.4 -43.3 -43.2 -45.1

4.52

-1.41

1.15

-43.8

-44.8 -42.8 -45.7

3.5 3.5 3.2 3.2 5.2 5.3 5.3 5.2 5.2 2.9 0.7 0.7 1.7 1.7

Jeerinah

Jeerinah

43.3

Jeerinah

Jeerinah Jeerinah

4.41

0.22

3.73

-45.2

3.63

-0.50

1.84

42.0

Jeerinah Jeerinah Jeerinah Jeerinah Jeerinah

154.9

155.75 156.89 158.26 159.96 160.33 160.88 161.62 164.12 165 165.74 169.62 171.56 173.76 174.11 174.77 181.23 181.53 183.36 185.71 189.55 193.27 194.39 198.32 200.58

Jeerinah

154.46

42.4 -42.4 -44.4

-41.6

Chapter 3: Microbial-mediated sulfur cycling in shallow marine Neoarchean carbonate environments

<u>Abstract</u>

The Neoarchean period (2.8-2.5 Ga) is characterized by large MIF-S signals and evidence for periods of organic haze inferred from sulfur and carbon isotope anomalies observed in deep marine platform shale facies. In this study, multiple sulfur and carbon isotope measurements of $\sim 2.7-2.5$ Ga carbonate facies from several cores drilled in Western Australia and South Africa were conducted in order to understand isotopic deviations from the Archean Reference Array (ARA), which has been primarily defined on the basis of pyrite measurements in shales. Using a statistical Gaussian mixture model to analyze the multiple sulfur isotope data, I identify two subpopulations: one that shares characteristics with the previously defined ARA $(\Delta^{33}$ S~0.9× δ^{34} S) and is attributed a photolytic origin, and a second one that follows the empirical relationship Δ^{33} S~0.1 δ^{34} S, defined by a narrow range of positive Δ^{33} S values but a remarkably wide range of δ^{34} S compositions up to +32‰. Notably, no significant changes in $\Delta^{36}S/\Delta^{33}S$ are observed in the same data set, indicating stable atmospheric sulfur chemistry. The second subpopulation likely resulted from biological and environmental controls on δ^{34} S and Δ^{36} S in marine system under low sulfate conditions. Model results suggest that the sulfur isotopic compositions of ³⁴S-enriched pyrites were controlled by a reservoir effect associated with intensive microbial sulfate reduction that controlled the isotopic composition of water column and/or pore sulfate. The small positive Δ^{33} S signals preserved in these pyrites also suggest that they incorporated up to 20-35% photolytic elemental sulfur. The shallow sulfur isotope array, which is notably associated with samples that are ¹³C-enriched in organic matter, suggests a tight linkage between microbial transformations of photolytic sulfur species in shallow environments and carbon cycling driven by sulfur phototrophs and microbial sulfate reduction.

3.1. Introduction

Mass-independent fractionation of sulfur isotopes (MIF-S) found in Archean sedimentary rocks is one of the key geochemical observations supporting an oxygenpoor Archean atmosphere (Farquhar et al. 2000a). Such an atmosphere would lack a defined ozone layer (Pavlov and Kasting, 2002), which would have impacted surface biota with harmful UV radiation, and could have profoundly altered the Archean sulfur cycle. Under Archean conditions, the main sulfur source was volcanic. Once in the atmosphere, sulfur-bearing gases underwent photolytic reactions, with their products acquiring MIF-S that were ultimately preserved in the Archean sedimentary records (e.g. Kasting, 2001). According to both models and experiments, these reactions produced distinct MIF-S signals for sulfate, which had negative Δ^{33} S and δ^{34} S¹ compositions (with positive Δ^{36} S¹ values), while elemental sulfur had positive Δ^{33} S and δ^{34} S (but negative Δ^{36} S values) (Farquhar et al., 2001; Masterson et al., 2011).

Archean sedimentary records preserve a diverse range of lithological facies. The most studied for sulfur isotopes being black shale, which in the Neoarchean are

 $^{1}\Delta^{33}S = \delta^{33}S - 1000((1 + \delta^{34}S/1000)^{0.515} - 1)$ and $\Delta^{36}S = \delta^{36}S - 1000((1 + \delta^{34}S/1000)^{1.90} - 1)$ characterize mass-independent fractionation of sulfur isotopes (MIF-S) at non-zero values.

$$\delta^{3x} S = \left[\frac{({}^{3x} S/{}^{32} S)_{\text{sample}}}{({}^{3x} S/{}^{32} S)_{\text{std}}} - 1 \right] \times 1000, \text{ where } x \text{ -} 3, 4, \text{ or } 6$$

characterized by positive Δ^{33} S and a well-defined positive correlation between δ^{34} S and Δ^{33} S values (Ono et al., 2003; Kaufman et al., 2007). The empirically defined slope of this array is Δ^{33} S / δ^{34} S ≈ 0.9 is referred to as the Archean Reference Array (ARA, Ono et al., 2009), which is interpreted as a mixing line between two end-members ultimately derived from photolytic atmospheric reactions (Ono et al., 2003). Overprinting of the atmospheric signal would have been mediated by mass-dependent effects associated with microbial sulfate reduction (MSR) and other sulfur cycling processes (Ono et al., 2006; Kaufman et al., 2007). Some authors have argued that the preservation of this array indicates that MSR did not play a significant role in Archean sulfur cycling (e.g. Johnston et al., 2011). However, multiple sulfur isotope evidence from Neoarchean carbonate facies of the Batatal Formation in Brazil argue for overprinting by MSR in shallow environments as evidenced from ³⁴S fractionations exceeding 50‰, even under very low marine sulfate concentration (Zhelezinskaia et al., 2014).

The ratio of Δ^{36} S to Δ^{33} S in Archean sedimentary pyrite has been observed to be relatively stable across most stratigraphic intervals (Kaufman et al., 2007; Farquhar et al., 2013), with a mean value of -0.9. This relationship has been interpreted similarly to the ARA, and is attributed to mixing between the two products of a relatively stable atmospheric sulfur photochemistry. In some cases, however, variations from this linear array have been observed (Farquhar et al., 2007; Zerkle et al., 2012; Izon et al., 2015) and interpreted to reflect shifts in atmospheric composition. Zerkle et al. (2012) and later Izon et al. (2015) argued that for some Neoarchean shale facies, Δ^{36} S/ Δ^{33} S variations (in concert with negative stratigraphic deviations in δ^{13} Corg) reflect the establishment of an atmospheric organic haze. The periods of hazy atmosphere are inferred to have been short of ~1 million years and driven by episodic fluxes of biogenic CH₄ from surface environments (Izon et al., 2017).

Fewer studies have focused on multiple sulfur isotope compositions in Neoarchean carbonates. Given that carbonates are widely distributed throughout Neoarchean successions (Grotzinger and James, 2000), further study of pyrite in these facies is warranted. This study, therefore, focuses on Neoarchean carbonate platforms from multiple locations deposited on the oceanic margins of the Kaapvaal (South Africa) and Pilbara (Western Australia) cratons. Here, sulfur and carbon isotopic compositions from carbonate facies are reported and used to shed light on processes operating in the Neoarchean ocean where shallow carbonate platforms were deposited. These data are compared to the extensive existing shale data to determine how sulfur cycling in shallower platform environments differed from those of deep-water settings.

3.2. Materials

Samples for this study came from cores drilled in the Kaapvaal Craton (South Africa) and the Pilbara Craton (Western Australia). In November 2013 African samples were collected from the Agouron Institute GKF01 (n=9) and GKP01 (n=10) cores (Fig. 3.10) drilled approximately 24 km apart and currently archived at the Smithsonian Institution. Samples included carbonate facies from the Klein Naute, Nauga, Reivilo, and Boomplaas formations. The GKF01 core represents a proximal position on the platform slope, while the GKP01 core indicates more distal position on the slope (Schröeder et al., 2006). In addition to carbonates from these two cores, carbonate powder samples (n=53) from another core (Kathu or BH1-Sacha, Fig. 3.10) drilled in 1988 (Altermann and Siegfried, 1997) were provided by Dr. Gareth Izon. These

samples extend and complement shale samples from the same core (Ghaap Plateau facies) that have been previously reported (Izon et al., 2015). The BH1-Sacha core captures shallow water platform environments and represents much shallower facies than the two Agouron Institute cores (Fischer et al., 2009). Samples studied here were collected from the Vryburg, Monteville, Reivilo, Gamohaan, Boomplaas, Klipfontein Heuwel, Papkuil, Klippan, and Kogelbeen formations. The age of the Campbellrand Subgroup is constrained by the age of the overlying Kuruman Iron Formation (2521±3 Ma; Sumner and Bowring, 1996) and the underlying Vendersdorp Supergroup (2714±8 Ma; Armstrong et al., 1991).

Samples from Western Australia were donated by Dr. Bruce Simonson at Oberlin College in Ohio, from his collection of samples from the Billygoat (BB), Pearana (PR), Ripon Hills (RP), and Range Gorge (RG) cores (Fig 3.11). These ~2.6-2.45 Ga sedimentary formations are part of the Mount Bruce Supergroup preserved within the Hamersley Province on the Pilbara Craton. Five samples from the RG core represent the Wittenoom Formation, whereas samples from the BB (n=7), PR (n=13), and RP (n=4) cores are from the Carawine Formation. Sedimentary textures in Wittenoom carbonate rocks (thin lamination, turbidites, roll-up structures) were interpreted as deposited in deeper water environments, including the carbonate slope and basin floor at several hundred meters depth (Simonson et al., 1993). The Carawine Dolomite outcrops in the northeastern part of the Hamersley Group along the Oakover Syncline (Simonson et al., 1993); it rests over either the Marra Mamba Iron Formation or the Jeerinah Formation. The Carawine Dolomite consists of dolomite, some argillite in the form of thin interbeds, and cherty nodules. Rare ferroan carbonate minerals have been observed, but no limestones are known for this strata. According to a detailed sedimentological study, the Carawine Dolomite formed in intertidal to subtidal environments (down to the lower limit of the photic zone or ~100m) as evidenced by the presence of stromatolites, oncolites, wave ripples, pseudomorphs after gypsum, and pisolitic textures (Simonson et al., 1993; Simonson and Jarvis, 1993). The Carawine Dolomite, once believed to be equivalent to the Wittenoom Formation (2561±8 Ma, Trendall et al., 1998), is now known to be older. This assessment is based on U-Pb zircon analyses indicating that a tuff layer within the Carawine Dolomite is 2630±6 Ma (Rasmussen et a., 2005). Given this age constraint, the Carawine is most likely correlative with upper portion of the Jeerinah Formation from the eastern part of the Hamersley Basin (previously known as the Lewan Shale).

3.3. Methods

Carbonate samples were crushed with a ceramic pestle and mortar. On average 15 to 20 grams of powder were acidified with 3M HCl in a 300 mL pyrex beaker. After effervescence ceased, the solutions with residues were transferred to 50 mL centrifuge tubes, centrifuged and decanted; then a new aliquot of acid was added to assure that all carbonates have quantitatively reacted. Milli-Q-H₂O was then used repeatedly to wash the residues of acid. After centrifugation, the solutions were decanted and residues dried in an oven at \sim 50°C overnight. The difference between initial mass of powder and the acidified residue was determined to calculate the initial percentage of carbonate.

After acidification, residues were used for chrome-reducible sulfur (CRS) extractions. For whole rocks, the method is described in Canfield et al. (1986) where hot 5M HCl is used to liberate acid volatile sulfur (AVS). A Cr(II) reduction solution

is subsequently used to extract sulfur from pyrite and other disulfides. This process takes about 3.5 hours during which hydrogen sulfide gas is released and trapped in a 0.3M AgNO₃ solution by the formation of Ag₂S. Precipitates were aged for one week in the dark to allow silver metal and silver hydroxide contaminants to be dissolved into the nitrate solution. Then the Ag₂S samples were filtered, washed with 1M NH₄OH and ultrapure Milli-Q-H₂O, and dried at 50°C overnight. Sulfur contents of samples were determined by weighing Ag₂S residues and recalculating sulfur concentration for the bulk rock based on the percent of carbonate content.

Silver sulfide samples (2-3 mg) were weighed and sealed in aluminum capsules for fluorination analyses. Silver sulfide precipitates were loaded into Ni reaction vessels with fluorine gas and heated up to 250°C overnight to produce SF₆. The SF₆ gas was purified through several steps of cryogenic separation, passivation, and gas-chromatographic separation. Purified SF₆ was loaded into the bellows of the ThermoFinnigan MAT 253 mass-spectrometer in the Stable Isotope Laboratory at the University of Maryland, College Park. The isotopic ratios were determined by the intensity of SF₅⁺ ion beams at masses 127, 128, 129, and 131. The uncertainties were estimated to be 0.14, 0.008, and 0.2‰ for δ^{34} S, Δ^{33} S, and Δ^{36} S, respectively, based on long-term analyses of standard materials.

Isotope measurements of organic carbon were done using a Eurovector elemental analyzer and Elementar Isoprime continuous flow isotope ratio mass spectrometer in the UMD Paleoclimate CoLaboratory. For CO₂ measurements acidified residues were weighed together with a urea standard ($100\pm10 \mu g$). The tin cups were sequentially dropped with a pulsed O₂ purge of 12 ml into a catalytic

combustion reactor of a Eurovector elemental analyzer furnace operating at 1040°C. The reaction column was packed with chromium oxide and silvered cobaltous/cobaltic oxide and heated to 1040°C and the analyte also flows through a second column at 650°C packed with high purity reduced copper wire for O₂ resorption. The CO₂ was separated from other gases with a 3-m stainless steel GC column packed with Porapak-Q heated to 60°C. Timed pulses of CO₂ reference gas (Airgas 99.999% purity, ~6 nA) were introduced at the beginning of the run using an injector connected to the IRMS with a fixed open ratio split. The isotope ratios of reference and sample peaks were determined by monitoring ion beam intensities relative to background values. The cycle time for these analyses was 430 s with reference gas injection as two a 30-s pulse beginning at 15 and 60 s. Sample CO₂ peaks begin at 200 s and return to baseline around 240 s. Carbon isotope ratios were determined by comparing integrated peak areas of m/z 45 and 44 for the reference and sample CO₂ pulses, relative to the baseline that is approximately 2×10^{-11} A. The background height was established from the left limit of the sample CO_2 peak. Isotopic results are expressed in the delta notation as per mil (‰) deviations from the Vienna Pee Dee Belemnite (V-PDB) standard. Two urea standards were measured between each set of 10 samples and uncertainties for each analytical session based on these standard analyses were determined to be better than 0.1‰ (1σ).

3.4. Results

Results from this sulfur and carbon isotope study are presented in Table 3.2 and illustrated in Figure 3.1. The carbonate content of samples from the Western Australian cores RG, BB and RP and half of the samples from the RP core are greater than 95%. Similarly, all samples from the South African cores, except those from the Klein Naute, Vryburg, and Boomplaas formations, have more than 90% of carbonate. Sulfur contents vary between formations and cores, with carbonates of the Hamersley Group (Carawine = 218 ± 174 ppm and Wittenoom = 302 ± 193 ppm) having less sulfur than those from the Ghaap Group (<2000 ppm with extreme abundances in the Gamohaan and Reivilo formations from the BH1-Sacha core) (Table 3.2)

The isotopic signatures of carbonate-associated pyrite (CAP) from both the South African and Western Australian successions have similar trends, although some differences are apparent. The isotopic composition of CAP from the Hamersley Group ranges between -7.2 to +20.7‰ for δ^{34} S and from -4.0 to +4.6‰ for Δ^{33} S. Only two samples from the Carawine Formation (PR core) have both negative δ^{34} S and negative Δ^{33} S signatures (Fig. 3.1). Sample PR-13, which was analyzed twice, revealed the most negative Δ^{33} S value known for bulk Archean rock at ~-4.0‰. Pyrites from the Ghaap Group exhibit a greater range of δ^{34} S values, from -7.9 to +31.7‰, yet only three samples have negative δ^{34} S values (Fig. 3.1); in contrast, Δ^{33} S values are positive ranging from +0.4 to +9.4‰.



Figure 3.1. Cross-plot of Δ³³S versus δ³⁴S and Δ³³S versus Δ³⁶S values for bulk rock from this study together with published data for comparison from South Africa (GKF01 core data from Ono et al., 2009 and Zerkle et al., 2012, and Sacha-H1B from Izon et al., 2015) and Western Australia (Izon et al., 2015: from WRL1 (Wittenoom Fm.) and RHDH2a (Carawine Fm.) cores). This study revealed pyrite compositions with small positive Δ³³S and wide range of positive δ³⁴S up to 21 and 32‰ for Western Australia and South Africa, respectively.

More than half of African samples (in the Boomplaas, Nauga, Monteville, Vryburg, Reivilo (for BH1-Sacha core), and Gamohaan formations) and Wittenoom pyrites follow a Δ^{33} S- δ^{34} S relationship similar to that defined by the ARA (Kaufman et al., 2007; Ono et al., 2009; Zerkle et al., 2012) (Fig. 3.1). With the exception of a few samples from the PR core, sulfur isotopic compositions of carbonates like those

reported for the Carawine and Wittenoom formations with negative Δ^{33} S values (Ono et al., 2003; Partridge et al., 2008) were not seen in the new collection of samples (see Fig. 3.1). Most of the pyrites from the Carawine Formation do not follow ARA, but rather have small positive Δ^{33} S values (average ~+1‰) and positive δ^{34} S values, ranging from +3 to +21‰. The same trend is observed in African pyrites from the Reivilo Formation (GKF01 core) and from the Monteville, Papkuil, Kogelbeen, and Klippan formations (BH1-Sacha). Here pyrites demonstrate slightly positive Δ^{33} S (average ~1‰) and wide range of δ^{34} S values ranging from -5 to +32‰.

For comparison, very large positive δ^{34} S values and small Δ^{33} S signatures were published from CAS (carbonate-associated sulfate) from Archean carbonates (Domagal-Goldman et al., 2008). Recently, Gregory et al. (2015) reported data from microanalyses of CAP measured by SHRIMP techniques with positive δ^{34} S values (up to +16‰) for the Paraburdoo Member of the Wittenoom Formation, but most of the Δ^{33} S measurements were slightly negative with an average value of ~ -1‰. Meyer et al. (2017) using a SIMS technique conducted measurements of pyrites from the Lokammona Formation with δ^{34} S signal up to +27‰ and slightly negative Δ^{33} S compositions.

3.5. Cluster analysis

I was intrigued by the possible existence of two discrete $\Delta^{33}S-\delta^{34}S$ arrays defined by the African and Australian pyrite isotopic compositions (Fig. 3.1): one array following the ARA where $\Delta^{33}S \approx 0.9 \times \delta^{34}S$ and another following a more shallow trend defined approximately by $\Delta^{33}S \approx 0.1 \times \delta^{34}S$. In order to evaluate the likelihood that these define two different populations, I applied Gaussian mixture models (GMM, Fraley

and Raftery, 1998) using MatLab code (MATLAB, 2015) to the data. In these models, both diagonal or full covariance matrices, and shared or unshared covariance matrices, were tested (Fig. 3.12). According to these analyses, the best GMM fit was realized if the model included two components and a fullunshared covariance matrix structure (Fig. 3.13). Full covariance matrices allow for

Formation	cluster 1	cluster2
Boomplaas	8	
Gamohaan	9	
Klein Naute	1	1
Klipfontein	1	
Klippan		2
Kogelbeen		4
Monteville	6	4
Nauga	4	1
Papkuil	2	8
Reivilo_Sacha	10	
Reivilo_GKF01	1	5
Vryburg	4	
Wittenoom_	4	1
Carawine_BB	4	3
Carawine_RP	2	2
Carawine_PR	3	10
	Formation Boomplaas Gamohaan Klein Naute Klipfontein Klippan Kogelbeen Monteville Nauga Papkuil Reivilo_Sacha Reivilo_Sacha Reivilo_GKF01 Vryburg Wittenoom_ Carawine_BB Carawine_PR	Formationcluster 1Boomplaas8Gamohaan9Klein Naute1Klipfontein1Klipfontein1Klippan1Kogelbeen6Monteville6Nauga4Papkuil2Reivilo_Sacha10Reivilo_GKF011Vryburg4Wittenoom_4Carawine_BB4Carawine_RP2Carawine_PR3

Table 3.1. Number of samples in formationsthat were assigned to each cluster by theGaussian mixture model

correlated predictors and unshared covariance matrices indicate that all components have their own covariance matrix.

Results highlighting the separation of data into two clusters are presented in Fig. 3.2 and Table 3.1. The first cluster (I) refers to the data that follows the ARA, and the second cluster (II) scatters around the shallow trend with a wide range of δ^{34} S values and a narrow range in Δ^{33} S. Table 3.1 reveals the formation level division of the data into either cluster I or II. While the overlap of some samples makes the cluster analysis

somewhat arbitrary (Fig. 3.14), I further evaluate the likelihood that these represent different environmental conditions by performing a statistical analysis on the data sets identified by the GMM.



Figure 3.2. Cross-plot of Δ^{33} S vs. δ^{34} S (left) and Δ^{36} S vs. Δ^{33} S (right) values of all data from this study divided using cluster analysis (see text). Cluster I (blue circles) is a set of data approximately scattered around ARA and Cluster II (red circles) represents the set of analyses that define the significantly shallower trend.

Plotting data for Δ^{36} S against that for Δ^{33} S, yielded no statistically-resolvable differences between cluster I and cluster II (Fig. 3.2). However, close inspection of the position of points relative to the ARA, reveals that almost all cluster II data plot slightly above the Archean array, while cluster I points scatter around it. The few samples that strongly deviate from the ARA are from the Carawine Formation (see Chapter 2). Below I focus on providing possible environmental and biological explanations for the difference between the two clusters.

Considering other geochemical parameters that were measured on these same samples, there is support for an environmental control on the sulfur isotope differences between clusters. Cluster I samples contained less carbonate (average ~88%) and more negative $\delta^{13}C_{org}$ values (average ~-32‰) than samples from cluster II (with average

values of ~ 95% and ~-29‰, respectively). Similarly, the concentration of pyrite sulfur in cluster I (2800 ppm) is ~6x higher than for cluster II (400 ppm) (Fig. 3.3), and samples with higher sulfur abundances typically carry more positive Δ^{33} S signals (Fig. 3.3).



Figure 3.3. Cross-plots of the concentration of pyrite sulfur vs. Δ^{33} S compositions (left) and carbonate content vs. $\delta^{13}C_{org}$ values (right) for all data from this study separated using cluster analysis (see text) with average calculated values (diamonds) for each cluster shown.

3.6. Discussion

A first step in seeking to understand the origin and geological significance of clusters I and II is to ask whether the subpopulation of data in cluster I conforms with the already known ARA (Ono et al., 2003; Kaufman et al., 2007) or not. Given the similar isotopic characteristics and common Archean ages, the principle of parsimony would dictate that the two are related. Therefore, it is reasonable to suggest that the origin of the isotopic variability in cluster I arises from the mixing of two products of sulfur chemistry formed in the anoxic Neoarchean atmosphere. The generation of cluster II, however, would likely involve a different type of atmospheric photochemistry, or additional mass-dependent and environmentally-driven processes

that overprints the former and thereby spreads the sulfur isotopic population in a heretofore unknown region.

3.6.1. A non-photochemical origin for the new shallow array

Photochemical experiments with SO₂ demonstrate that sulfur isotopic relationships for Δ^{33} S- δ^{34} S and Δ^{36} S- Δ^{33} S depend on the wavelengths of incident radiation (Masterson et al., 2011; Whitehill et al., 2014; Ono et al., 2013). These studies demonstrated that photolysis reactions, which occur at wavelengths in the 190-220 nm range yield Δ^{33} S/ δ^{34} S ~ 3 and Δ^{36} S/ Δ^{33} S < -2. At wavelength between 300 and 350 nm during SO₂ photoexcitation, products were shown to have compositions with Δ^{33} S ~ $0.1 \times \delta^{34}$ S and Δ^{36} S/ Δ^{33} S> 1 (Fig. 3.4: Ono et al., 2013, Whitehill et al., 2012). The combination of these effects, with the additional involvement of mass-dependent fractionation processes, has been invoked as a possible source for the range of MIF-S compositions along the Archean ARA (Endo et al., 2016). Similarly, the observation of variations in the Δ^{36} S/ Δ^{33} S of sample sets from some Archean successions have been used to argue for changes in the atmospheric chemistry (Farquhar et al., 2007; Zerkle et al., 2012; Izon et al. 2015). Significant variations in Δ^{36} S/ Δ^{33} S and small MIF-S in the Archean were observed in the period between 3.2 to 2.7 Ga, when sedimentary sulfur preserved isotopic signatures Δ^{33} S values no greater than +2‰ also exhibits Δ^{36} S/ Δ^{33} S \neq -0.9 (Farquhar et al., 2007). This was interpreted by Domagal-Goldman et al. (2008) to reflect a possible methane haze. Likewise, Zerkle et al. (2012) present Neoarchean shale data with a correlation between more negative carbon isotopic data (compared to background $\delta^{13}C_{org}$ values) and deviations of $\Delta^{36}S/\Delta^{33}S$ to < -0.9 (see Fig. 3.1), which were proposed to reflect episodes of organic haze in the Neoarchean

atmosphere caused by elevated methane concentrations. There are no significant changes in Δ^{36} S/ Δ^{33} S (Figs. 3.1, 3.2, and 3.4) between cluster I and cluster II, however, so it is more straightforward to explain the shallow Δ^{33} S - δ^{34} S trend by the contribution of a process that is neither atmospheric, nor mass-independent.



Figure 3.4. Cross-plots of Δ³³S vs. δ³⁴S and Δ³⁶S vs. Δ³³S values of all data from this study separated using cluster analysis. Orange fields represent combined results of SO₂ photolysis experiments (Farquhar et al., 2000, Ono et al., 2013, Endo et al., 2016) while the green fields are SO₂ photoexcitation experiments (Whitehill et al., 2014, Endo et al., 2016)

3.6.2. A mass-dependent origin for the new shallow array

3.6.2.1. Microbial sulfur cycling by microbial sulfate reduction

Large variations in δ^{34} S values >40‰ in my data for cluster II could equally reflect mass-dependent processes, such as microbial sulfate reduction. MSR requires sulfate that for the Archean should have had a negative Δ^{33} S composition (Ono et al., 2003, Zhelezinskaia et al., 2014); however, I noted that pyrites of cluster II from my data have a positive Δ^{33} S signature. This might result from the biological reduction of seawater sulfate that possessed positive Δ^{33} S, as was proposed from CAS analyses by an ICP-MS technique in another locality (Paris et al., 2014), but this view is problematic. In particular, recent fine-scale (mm to µm) studies of pyrites from the Carawine (Chapter 2) and Wittenoom dolomites (Gregory et al., 2015) along with those from Neoarchean carbonates in South African successions (Farquhar et al., 2013; Fischer et al., 2014; Meyer et al., 2017) reveal small scale heterogeneity in pyrite multiple sulfur isotope compositions. This observation suggests that pyrite formed from two sulfur reservoirs, one with negative Δ^{33} S attributed to photolytic sulfate and another with positive Δ^{33} S attributed to elemental sulfur. The small positive Δ^{33} S of these samples is thus interpreted to reflect mixing of sulfur derived from seawater sulfate (with negative Δ^{33} S) by microbial processes with another elemental sulfur endmember (with positive Δ^{33} S).

Microbial sulfate reduction yields sulfide that is incorporated into pyrite that is ³⁴S-depleted. Thus depending on the dominance of the reaction and the size of the reservoir, residual sulfate would be shifted to ³⁴S-enriched compositions. Assuming a starting sulfate composition with δ^{34} S of ~+10‰ (Ono et al., 2003; Meyer et al., 2017) and negative Δ^{33} S values, MSR would yield a range of sulfide compositions that should occupy the negative δ^{34} S and Δ^{33} S fields (Fig. 3.5), but these compositions were not observed in this study. Furthermore, biological and abiotic sulfide or elemental sulfur oxidation processes alone produce only small fractionations (<5‰) in product sulfate (Fry et al., 1988; Zerkle et al., 2009), and thus cannot account for the observed δ^{34} S variations in cluster II. The observed ranges of positive δ^{34} S and Δ^{33} S signatures therefore call for another mechanism(s). One possibility is for some combination of: i.) intermediate steps prior to pyrite formation, such as isotope exchange between sulfur species, ii.) MSR operating under closed system conditions, iii.) involvement of microbial metabolisms other than MSR, and iv.) a reservoir effect at low oceanic sulfate concentration.



Figure 3.5. Schematic model the Archean sulfur cycling and biological transformations with constraints on δ^{34} S fractionations in different sulfur metabolisms (see text for references)

It has been suggested that if sulfide is present in combination with elemental sulfur, then both compounds will rapidly equilibrate their isotopic compositions (Kamyshny et al., 2003; Amrani et al., 2006). It has also been suggested for Archean environments where elemental sulfur is constantly formed by atmospheric photochemical reactions and sulfide is formed by MSR, that pyrite would accumulate with an isotopic composition intermediate between that of the sulfide and elemental sulfur pools. Because most of pyrites from cluster II have positive δ^{34} S values, one could infer that both the sulfide and the elemental sulfur had positive δ^{34} S values. Moreover, since the sulfide produced by MSR is typically fractionated to lower, often negative δ^{34} S values, it either means that MSR expressed only small fractionations in these settings, which can happen when sulfate concentrations are low and/or when sulfate reduction rates are high (Habicht et al., 2002; Leavitt et al., 2013), or that sulfide

production occurred in pore waters that were somehow closed to isotopic exchange with external sulfate. Observation of δ^{34} S values higher than 10‰ (some pyrites in cluster II have δ^{34} S>20‰) indicate that the isotopic composition of this sulfate was similarly enriched. The slight positive Δ^{33} S combined with strongly positive and variable δ^{34} S values of pyrite in this unique isotope array is thus attributed to mixing of sulfur from sulfide and elemental sulfur in a way that pyrite sulfur acquired both positive δ^{34} S and Δ^{33} S signatures (Fig. 3.5).

3.6.2.2. Sulfur disproportionation

Sulfur metabolisms, such as disproportionation of sulfur compounds (elemental sulfur, sulfite, etc.) produce highly fractionated metabolic products (Canfield et al. 1998; Haicht et al., 1998; Böttcher et al. 2001; Johnston et al., 2005). Given the likely flux from atmospheric reactions, elemental sulfur disproportionation was probably the most important among other disproportionation mechanisms as the substrate was plentiful in Archean ocean water. In carbonate sediments, elemental sulfur could be disproportionated to ³⁴S-enriched sulfate and ³⁴S-depleted hydrogen sulfide (Fig. 3.5). Culture experiments showed that sulfate gains isotopic compositions of up to 35% relative to the elemental sulfur reactant (Bottcher et al., 2005). Correspondingly, the hydrogen sulfide becomes depleted in ³⁴S by up to 9‰ (Canfield et al., 1994). MSR might further reduce ³⁴S enriched sulfate (in a closed system) so that product hydrogen sulfide will be imparted with highly positive δ^{34} S values (>30‰) similar to those observed in the Reivilo Formation (Fig. 3.1). Hydrogen sulfide derived from disproportionation reactions could form ³⁴S-depleted pyrites if available iron in the pore water system becomes oxidized by the metabolic activities of phototrophic
bacteria, or simply escapes to seawater. In the pore water environment, sulfate concentrations would increase through oxidation reactions, which would further stimulate MSR. If correct, both the residual sulfate and resulting sulfide could become ³⁴S enriched, and, if incorporated into pyrite, could preserve super-heavy (>20‰) compositions.

Involvement of microbial disproportionation could thus be capable of yielding the highly positive δ^{34} S values, as recorded in Cluster II data (Fig. 3.5). However, for this mechanism to work, the primary elemental sulfur substrate for SDB must only have carried a small positive Δ^{33} S composition. This conclusion, however, contrast with inferences from experiments, models, and observations (Endo et al., 2016 and references therein). It is thus considered improbable that SDB account for the array of pyrites in cluster II (Figs. 3.2 and 3.5).

3.6.2.3. Reservoir effect

Low sulfate concentration in the Archean ocean (Habicht et al., 2002; Zhelezinskaia et al., 2014; Crowe et al., 2014) could lead to a phenomenon known as the "reservoir effect". This effect is usually observed where sulfate is a limiting factor (Crowe et al., 2014; Canfield et al., 2010; Gomes and Hurtgen, 2013), including some restricted basin and fjords (Sælen et al., 1993). As demonstrated in geochemical models at low oceanic sulfate levels, a reservoir effect may have a greater impact than direct biological controls – even though concentrations were indirectly controlled by microbial activities (Gomes and Hurtgen, 2015). This geochemical model suggests that due to i.) low sulfate abundance, ii.) rapid water column MSR (suggesting anoxia), and iii.) the water column precipitation of pyrite, both sulfate and sulfide near the watersediment interface would become ³⁴S-enriched relative to shallow more ventilated conditions. Dissolved sulfide that accumulated near the basin floor would be converted to pyrite as long as iron was available, with sulfur isotopic composition close to that of the initial sulfate (Gomes and Hurtgen, 2013).

In Archean environments, a reservoir effect was probably responsible for formation of sulfide at the sediment-water interface through MSR with negative Δ^{33} S and positive δ^{34} S close to surface oceanic sulfate ~+10‰ (Ono et al., 2003; Meyer et al., 2017). At the same time, sulfate at the sediment-water interface would gain extreme positive δ^{34} S compared to contemporaneous free water column sulfate and to product sulfide by a value of δ^{34} S fractionation (Fig. 3.5). In modern low sulfate systems, pore water sulfate approaches isotopic compositions more than 30‰ enriched compared to free water column sulfate (Gomes and Hurtgen, 2013). Assuming that the sulfur isotope fractionation expressed by MSR in the Archean ocean was more than 30‰ (Crowe et al., 2014; Zhelezinskaia et al., 2014), bottom water sulfate might then have acquired δ^{34} S of > +40‰ composition.

3.6.2.4. Rayleigh distillation

The formation of super heavy pyrites has similarly been used as an indicator of low Ediacaran Period sulfate levels (e.g., Ries et al., 2009). In this model, pore water sulfide produced by MSR might reach or exceed the ³⁴S isotopic composition of sulfate due to a Rayleigh distillation process (e.g., Ono et al., 2009). Culture experiments have shown that MSR typically yields sulfide that is ³⁶S-depleted by > 1‰ (Johnston et al., 2007; Ono et al., 2006; Zhelezinskaia et al., 2014), which is notably not observed in cluster II data (Fig. 3.2). For a Rayleigh process that distills S isotopes like that envisioned for the sulfate pool, the ³⁶S will become enriched in the sulfate which may explain the small ³⁶S enrichment in cluster II data (Fig. 3.6).

To explore how biology controls the Δ^{36} S/ Δ^{33} S slope, a 0-D incremental batch distillation model was used with δ^{34} S fractionation of 50‰ (from Zhelezinskaia et al., 2014) following fractionation laws of ${}^{33}\alpha^{1/0.510} = {}^{34}\alpha = {}^{36}\alpha^{1/1.94}$ (see Johnston et al., 2007). The calculations with constant fractionation are presented in Fig. 3.6 for parameterization with an atmospheric Δ^{36} S/ Δ^{33} S slope of -0.9. While the isotopic composition of residual sulfate lies above the -0.9 array and the isotopic composition of sulfide extends below the -0.9 array, the δ^{34} S composition of residual sulfate is also driven to extreme positive values (up to +60‰). If the Rayleigh model adjusts to expected δ^{34} S ~40‰ from the Cluster II data, then *f* is around 0.4. In this case modelled sulfate compositions might explain isotopic compositions of pyrites from Cluster II that are slightly ³⁶S-enriched compared to pyrites from Cluster I (Fig. 3.6).

In the Rayleigh distillation model I describe, sulfide that formed at the beginning of the process, which was ³⁴S- and ³⁶S-depleted, would need to be removed from the system in order to preserve the enriched ³⁶S-enriched signal in pyrite formed by later MSR. Conceptually this is possible if the first formed sulfide diffused out of the pore water system through unconsolidated sediments, while the later sulfide was trapped by progressive cementation of the sediments as MSR increase carbonate saturation.



Figure 3.6. Cross-plot of Δ³³S vs. Δ³⁶S values from two clusters together with results from mixing model explaining Δ³⁶S/Δ³³S ratios in the Cluster II. Triangular fields depict an exchange pathway between SRB products and elemental sulfur end-member. Grey fields – Rayleigh model, darker area depicts model at *f*<0.4. Insertion is a histogram of Δ³⁶S/Δ³³S_{dev} (=-1×(-0.9×Δ³³S – Δ³⁶S)), a deviation from the ARA, for two clusters; positive values mean above ARA and accordingly Cluster I pyrites are less ³⁶S-enriched then pyrites from Cluster II.

3.6.2.5. Pyrite formation pathways and mixing compositions

Observation of two clusters of pyrites with distinctive Δ^{33} S/ δ^{34} S relationships indicate that the formation of FeS₂ in each cluster occurred via different pathways. Pyrites of cluster I have positive Δ^{33} S compositions, follow the ARA, and carry a strong signature of photolytic elemental sulfur. This sulfur was deposited in the Archean in the form of orthorhombic S₈ rings – the most stable form of elemental sulfur at ambient pressure and temperature (Roy and Trudinger, 1970). However, elemental sulfur is not generally reactive unless it is activated by reaction with HS⁻ to form polysulfides and other S chains (Steudel, 2003). The polysulfide combining with Fe²⁺ forms pyrite with an sulfur isotopic composition predominantly from polysulfide (derived from elemental sulfur) even in the presence of FeS derived from sulfide (Butler et al., 2004). Pyrites formed through this pathway assumed to populate the cluster I data (Fig. 3.2). If hydrogen sulfide is present, pyrite gains an intermediate isotopic composition between S from FeS and H₂S (Butler et al., 2004). In environments where pyrites of cluster II were formed, the H₂S pyrite-forming mechanism was dominant due to MSR as suggested by the large range of δ^{34} S values. Even though in my samples I observed only few bulk pyrite sulfur with negative Δ^{33} S signals, many microscale studies of the same formations reveal that such pyrites exist, supporting the H₂S-directed pyriteforming mechanism (Farquhar et al., 2013, Fischer et al., 2014; and see Chapter 2).

The relatively constant and small positive Δ^{33} S signals in bulk pyrites of cluster II indicate that H₂S played a larger role in pyrite formation than for those in cluster I. However, this does not mean that sulfate reducers were forming more H₂S, but that in those particular environments where cluster II pyrites were formed, the proportion of S₈ to H₂S (SO₄-derived) was much lower than for environments where cluster I pyrites precipitated. The gap between two clusters in my data set (Fig. 3.2) and absence of intermediate compositions between two arrays suggest that these environments were more or less exclusive to each other (but see below). This is also suggested by difference in the sulfur concentrations of samples in these two clusters (Fig. 3.3).

For a low sulfate ocean (Crowe et al., 2014; Zhelezinskaia et al., 2014), sulfate will be a conservative species with respect to its concentration only if its residence time significantly exceeded that of the mixing time of the oceans. Under this scenario, the oceans would also have a homogeneous sulfate sulfur isotopic composition. If sulfate concentrations are not conservative, isotopic variations will occur if there are fractionations associated with either its sinks or sources. Moreover, since ³⁴S abundances are significantly fractionated by MSR, but Δ^{33} S values are not, the homogeneity (and response times) of these two tracers can be decoupled. One would expect low and relatively stable flux of sulfur (carrying negative Δ^{33} S signal) to sediments and thus a homogeneous pool (on global scale). I observe this from cluster II data with a low average S concentration of ~400 ppm.

The second pool of sulfur – elemental sulfur –did not homogenize on a global scale, and rained out as it was formed in the atmosphere from a volcanic SO₂ plume. In this case, the flux of elemental sulfur (and its Δ^{33} S signal) would be variable in time and also in space. In other words, the concentration of elemental sulfur in sediments would vary based on location, size of the volcanic plume, and the rate of volcanic SO₂ release to the atmosphere.

Carbonates of cluster II were thus conceivably deposited during intervals of volcanic quiescence, when elemental sulfur formation was diminished. Cluster I carbonates were formed during active volcanism when the SO₂ flux was higher leading to more positive Δ^{33} S compositions in product S₈, and large flux of elemental sulfur to surface environments as well (Ono et al., 2013). During intense intervals of volcanic activity, the formation of photolytic sulfate was also elevated, but homogenizing this flux with the global oceanic pool would not significantly change either the concentration or isotopic composition of seawater sulfate. However, locally such

changes might be preserved as seen in the Batatal dolomite interval (Zhelezinskaia et al., 2014, Chapter 4).



Figure 3.7. Cross-plot of Δ^{33} S vs. δ^{34} S of the data from the Reivilo Formation received from this study and previous literature (see text for more details).

The samples that demonstrated the greatest variability in δ^{34} S values in my CAP data are from the Reivilo or Lower Nauga formations. If the new carbonate pyrite data from these units are combined with previous published measurements from shale facies from cores GKF01 (Ono et al., 2009; Zerkle et al., 2012; Farquhar et al., 2013), GKP01 (Ono et al., 2009), and Sacha (Izon et al., 2015), a triangular region of compositions forms (Fig. 3.7). Because the sediments from these correlated formations accumulated at different depth, the analyses represent a wide spectra of deposition environments. The triangular field of data from the South African cores is similar to the field of data from the Carawine Formation in Western Australia (Chapter 2). This spread of compositions is consistent with the mixing of photolytic elemental sulfur and hydrogen sulfide produced by SRB.

For the Revillo and Lower Nauga samples, a mixing model could be constructed to account for the proportional abundance of the two atmospheric endmembers in the cluster II pyrites. For example, my model assumes that seawater had sulfate with Δ^{33} S of -2‰ (an assumption based on systematic studies of CAS from the Carawine and Batatal formations: Chapters 2 and 4), hydrogen sulfide with a δ^{34} S range from -20 to 40‰, and an elemental sulfur end-member Δ^{33} S of 10‰ and δ^{34} S of ~11‰. With these constraints in mind, the sulfur isotopic composition of pyrites from cluster II would be the record of a 20-35% fraction of elemental sulfur and a 65 to 80% fraction of hydrogen sulfide (Fig. 3.8). Of course the proportions of these two end-members could vary considerably, thereby forming a continuous spectrum of compositions, similar to the spread seen in of values in the Revillo Formation (Fig. 3.7).



Figure 3.8. Mixing model for the highly positive δ^{34} S compositions in Cluster II pyrites

My mixing model includes all data from my carbonate measurements and implies that SRB were active in water column and/or in sediments during carbonate formation. Pyrites with more positive δ^{34} S compositions were probably formed where

distillation processes were most pronounced. On the other hand, the formation of pyrites with more negative δ^{34} S that was controlled by MSR produced the largest fractionation in sediments. If my mixing model for Δ^{33} S and δ^{34} S is correct, then it could explain the non-zero positive intercept in Δ^{33} S- δ^{34} S space observed in other formations (Gallagher et al., 2017).

3.6.3. Coupling of carbon and sulfur isotope data

The two modeled clusters that are defined by the sulfur isotopic compositions of CAP samples were also evaluated with regard to their organic carbon isotope abundances. Fig. 3.9 documents my statistical analysis of carbon measurements from the two sulfur isotope clusters. Organic matter in Cluster I with pyrite compositions following the ARA is more ¹³C-depleted, with an average composition of -31.9‰. Cluster II preserves relatively ¹³C-enriched organic matter, with an average δ^{13} C of -28.2‰. Even though the difference is only 3.7‰, the 99% confidence intervals in two data sets show that these two clusters are distinct in terms of their ¹³C abundances (Fig. 3.8). Such differences in both isotope systems suggest a link between carbon and sulfur cycling in shallow Neoarchean environments.



Figure 3.9. Carbon isotopic compositions of samples from two clusters. Boxes represent 99% confidence interval. Black circles are outliers. Green lines are mean values.

The organic carbon isotopic composition of sedimentary rocks is a mixture of primary and secondary OM and isotopic effects associated with OM production, assimilation, degradation, and burial (Hayes, 1993). If I assume that carbonates from the two clusters were affected by the same post-depositional processes, then the OM isotopic compositions can be viewed as related to specific biological metabolisms active during carbonate accumulation. Primary production today is mostly the result of oxygenic photosynthesis (Field et al., 1998). While photosynthetic reactions likely drove the biosphere as far back as 3.4 Ga (Tice and Lowe, 2004), the timing of the onset of oxygenic photosynthesis is a matter of current debate. A recent biomarker study by French et al. (2015) demonstrated that the biomarker evidence for 2.7 Ga oxygenic photosynthesis (Brocks et al., 1999) was the result of the introduction of younger biomolecules into older sediments. Insofar as the sulfur and carbon cycles are linked, changes in OM isotopic composition by primary producers (autotrophs) or secondary consumers (heterotrophs) that use sulfur species should be considered.

According to experiments on SRB, the biomass acquired during heterotrophic sulfate reduction via the TCA cycle becomes ¹³C-enriched by up to 10‰ (Londry et al., 2004; Goevert et al. 2008). Autotrophs that use sulfur as the electron acceptor are known from the purple and green sulfur bacteria. The oxidative photosynthesis that is responsible for most primary production today produces fractionation around 30‰ (Raven, 2009). Eigenbrode and Freeman 2006 proposed that more ¹³C-enriched organic matter in Neoarchean carbonates is a sign for proliferation of oxygenic photosynthesis. However, anoxygenic photosynthesis may also be able to produce similar magnitudes of fractionations, including the autotrophic purple sulfur bacteria that fix CO₂ using the

Calvin cycle and produce carbon isotope fractionations of up to 35‰ (Whelan, 1973; Wong et al., 1975). On the other hand, green sulfur bacteria use PEP carboxylase and HCO_3^- as a substrate, and thus results in carbon isotope fractionation of <20‰ (Coombs et al., 1975; Reibach and Benedict, 1977).

I suggest that organic matter in the Cluster II compared to Cluster I samples was derived by activity of sulfate reducers, as well as the green sulfur bacteria that utilized the sulfide produced by MSR, resulting in the accumulated biomass being relatively more enriched in ¹³C. While other authors have proposed that the primary producers in the anoxic Archean oceans were predominantly iron-reducing bacteria (Kharecha, 2005; Canfield, 2006) (given the plentitude of Fe²⁺ in the deep ocean), it seems equally possible that primary production in the more ventilated carbonate environments was associated with S-based autotrophic reactions.

3.7. Conclusions

Measurements of bulk pyrites from multiple South African and Australian formations reveal two notable trends in Δ^{33} S - δ^{34} S scatter plots. One of these follows the well-known ARA and is attributed the mixing of two photolytic end-members that rained onto Earth's surface. The other trend includes samples with small positive Δ^{33} S compositions and a >30‰ range of positive δ^{34} S values. This shallow array was not apparently formed by atmospheric reactions, and has Δ^{36} S/ Δ^{33} S values that deviate from the ARA. I infer that pyrites from the shallow array were formed by microbial sulfate reduction in a low sulfate ocean. These are associated with a reservoir effect similar to that observed in modern low sulfate water column and/or in carbonate sediments, where progressive closed-system conditions are possible due to sediment sealing through cementation. A mixing model suggests that elemental sulfur was incorporated in these pyrites in a fraction of 20-35% of total sulfur. Such low input would be possible during stable periods of volcanic activity. Carbon isotope analyses of these two sets of samples suggest that carbon and sulfur cycles were connected in carbonate environments. Environments where pyrites with a shallow δ^{34} S- Δ^{33} S trend were formed were dominated by processes such as S phototrophy and MSR, and they controlled cycling of organic carbon, in contrast to other Neoarchean settings.

ransvaal basin 26°S North tought Here BH1--Sac 28 100 km Bushveld Complex Kuruman Iron Formation Penge Iron Formation GKF01 Campbellrand Platform Malmani Platform GKP01 Schmidtsdrif Group Wolkberg Group rieska o borehole 30% 24ºE NE Prieska facies / Ghaap Plateau SW BH1-Sacha 50km Kuruman Formation Klein Naute / Gamohaan GKF01 Kogelbeen Klippan Papkuil Klipfonteir Upper Nauga / GKPO Fairfield Reivilo Kamder Lower Nauga / Reivilo Monteville Formation Lokammona Formation **Boomplaas Formation** Vryburg Formation K Ventersdorp Formation

3.8. Supplementary materials

Figure 3.10. <u>Upper</u> - schematic geological map of the Transvaal Supergroup preserved on the Kaapvaal Craton in South Africa. Modified after Fischer et al., 2009. <u>Lower</u> - A schematic southwest to northeast cross-section of the Transvaal Supergroup stratigraphy within Griqualand West Basin. Formations are divided on Prieska and Ghaap Plateau facies for GKF01/GKP01 and BH1-Sacha cores, respectively. After Fischer et al., 2009



Figure 3.11. <u>Upper</u> - Geologic map of Pilbara Craton, Western Australia and core drilling localities used in this paper. Cores shown are: RG - Range Gorge, BB –Billygoat Borehole, PR – Pearana, and RP - Ripon Hills. After Jahn and Simonson, 1995. <u>Lower</u> - Stratigraphy of Mount Bruce Supergroup. Ages are in million years; from Trendall et al., 1998, Nelson et al., 1999, Woodhead et al., 1998. Modified after Simonson, 1993



Figure 3.12. Results of clustering sulfur isotope data using Gaussian Mixture Models with different covariance matrices parameters in the Δ^{33} S- δ^{34} S space. "Diagonal covariance matrices indicate that the predictors are uncorrelated, while full covariance matrices allow for correlated predictors. Shared covariance matrices indicate that all components have the same covariance matrix, while unshared covariance matrices indicate that all components have their own covariance matrix." (MATLAB, 2015) Each combination of specifications determines the shape and orientation (major and minor axes) of the ellipsoids that visually represent cluster 1 and 2. Crosses are mean Δ^{33} S and δ^{34} S values for each cluster.



Figure 3.13. Plots of information criteria: Akaike's Information Criterion (AIC) and the Bayesian Information Criterion (BIC) for number of components, k, and appropriate covariance structure, Σ . "These criteria take the optimized, negative log likelihood, and then penalize it with the number of parameters in the model (i.e., the model complexity). The BIC penalizes for complexity more severely than AIC. Therefore, the AIC tends to choose more complex models that might overfit, and BIC tends to choose simpler models that might underfit" (MATLAB, 2015). The lower AIC or BIC values the better fitting models. According to BIC that favors the simpler model, a two-component system with full and ushared covariance matrices (yellow) provide the best fit for sulfur isotope data collected in this study.



Figure 3.14. Plot of Δ^{33} S- δ^{34} S field and data using soft clustering (MATLAB, 2015), an alternative clustering method that allows to determine data points that belong to multiple clusters. Points in circles are ones that could be in either cluster with cluster membership posterior probabilities in the interval [0.3,0.7].

	Formation	Depth	CaCO ₃	δ ¹³ C, ‰	Spy, ppm	δ ³⁴ S, ‰	1σ	∆ ³³ S, ‰	1σ	∆ ³⁶ S, ‰	1σ	Cluster
WESTER	IN AUSTRALI	A										
Billygoat bo	rehole											
BB-18B	Carawine	374.45	95.3	-32.1	24	12.47	0.03	4.62	0.02	-5.09	0.04	1
BB-1B	Carawine	83.1	7.00	-32.9	2	3.76	0.01	0.04	0.00	0.05	0.04	2
BB-32	Carawine	314.4	97.5	-50.4	294	6.37	0.01	2.38	0.01	-2.19	0.05	1
BB-35	Carawine	308.4	99.3	-33.3	14	4.34	0.00	4.35	0.01	-4.22	0.03	1
BB-7	Carawine	205.1	100.0	-30.4	2	8.35	0.02	0.00	0.01	0.70	0.05	2
BB-3A	Carawine	155.3	99.2	-34.5	8	7.49	0.00	3.46	0.01	-3.68	0.06	1
BB-1A	Carawine	83.1	8.66	-31.4	2	2.63	0.00	0.18	0.01	0.27	0.04	2
Pearana c	ore											
PR-1	Carawine	496.3	98.4	-37.2	493	16.90	0.00	1.43	0.01	-0.53	0.03	2
PR-10	Carawine	212.7	84.0	-30.0	269	8.22	0.00	0.09	0.01	0.59	0.07	2
PR-11	Carawine	152.5	36.6	-23.0	448	-1.69	0.00	-2.50	0.01	2.94	0.07	1
PR-12A	Carawine	143.8	9.66	-29.2	38	12.54	0.00	3.71	0.00	-0.19	0.01	1
PR13	Carawine	139.2	86.3	-30.0	376	-5.68	0.00	-4.01	0.01	4.24	0.06	1
PR-2	Carawine	479.7	92.1	-30.7	348	14.84	0.00	0.96	0.02	-0.20	0.01	2
PR-3	Carawine	309.7	99.2	-30.0	371	20.67	0.00	0.88	0.00	-0.29	0.03	2
PR-5	Carawine	299.5	57.1	-17.3	19	9.85	0.00	-0.02	0.01	0.83	0.02	2
PR-6	Carawine	289.3	79.1	-27.7	190	15.19	0.00	0.21	0.01	0.22	0.09	2
PR-8	Carawine	288.2	98.6	-28.6	285	11.95	0.00	0.56	0.00	0.12	0.02	2
PR-9A	Carawine	281.8	91.0	-28.3	301	14.98	0.00	0.14	0.00	0.34	0.05	2
PR-7	Carawine	288.6	96.5	-23.9	n.a.	4.53	0.01	0.20	0.00	0.65	0.19	2
PR-4	Carawine	302.5	98.2	-32.0	n.a.	17.75	0.00	2.48	0.00	-1.50	0.08	2
Ripon Hills												
RP-29	Carawine	203.1	99.4	-36.5		12.08	0.00	1.52	0.01	-1.03	0.10	2
RP-3	Carawine	189.2	98.3	-39.0		2.38	0.00	-1.29	0.01	2.53	0.05	1
RP-10A	Carawine	172.7	99.4	-39.6	313	6.20	0.00	0.63	0.00	3.23	0.03	2
RP-15	Carawine	129.72	9.66	-30.3		-0.30	0.00	0.17	0.00	-0.44	0.03	1
Range Gorge												
SIM-92978B	Wittenoom		97.6	-30.2	510	-1.29	0.01	2.66	0.02	-2.54	0.07	1

Table 3.2. Sulfur and carbon data for Neoarchean W.Australian and S.African samples

SIM_92994	Wittenoom		98.6	-29.3	215	-1.84	0.02	2.21	0.03	-2.52	0.30	1
SIM-92966	Wittenoom		98.9	-29.9	248	2.84	0.01	0.53	0.02	-0.14	0.10	2
SIM 92992	Wittenoom		99.4	-30.8	484	6.40	0.01	3.86	0.01	-3.65	0.10	1
SIM92967	Wittenoom		98.9	-28.6	52	1.42	0.02	1.27	0.04	-1.20	0.22	1
	Form	ation	Depth	CaCO ₃	δ ¹³ C,‰	Spy, ppm	δ ³⁴ S, %0	1σ	Δ ³³ S, ‰	1σ	Δ^{36} S, ‰	1σ
SOUTH AFRICA												
GKF01 core												
GKF-100-1	Klein Naute	301	33.1	-35.2	19332	1.50	0.01	1.82	0.02	-1.69	0.08	1
GKF-296-1	Nauga	857	98.5		37	6.38	0.31	1.40	0.03	-1.13	0.17	2
GKF-441-3	Reivilo	1269	9.66	-30.1	542	31.74	0.02	1.14	0.03	-0.67	0.21	2
GKF-443-1	Reivilo	1246	98.6	-33.7	8504	6.38	0.02	4.46	0.01	-3.31	0.16	1
GKF-441-1	Reivilo	1267	99.5	-31.6	2044	22.03	0.00	2.12	0.02	-1.67	0.11	2
GKF-441-2	Reivilo	1268	99.8	-28.3	170	18.87	0.03	2.05	0.04	-1.68	0.08	2
GKF-442-1	Reivilo	1270	98.7	-30.3	1947	17.47	0.01	1.05	0.03	-0.54	0.11	2
GKF-447-1	Reivilo	1284	99.8	-30.0	317	23.90	0.02	2.86	0.01	-2.43	0.09	2
GKP01 core												
GKP-93-1	Klein Naute	286.00	18.6	-26.22	2153	-7.94	0.01	0.70	0.02	-1.24	0.28	2
GKP-295-1	Nauga	866.00	97.8	-34.4	4511	4.23	0.01	7.00	0.02	-7.13	0.05	1
GKP-292-1	Nauga	856.50	99.1	-29.2	1387	6.76	0.01	2.34	0.02	-2.30	0.01	1
GKP-293-1	Nauga	860.00	97.8	-30.8	2672	5.01	0.02	5.54	0.03	-5.62	0.20	1
GKP-294-1	Nauga	863.00	98.8	-34.3	1213	6.49	0.01	7.05	0.02	-7.15	0.10	1
GKP-382-1	Boomplaas	1117.00	81.8	-29.9	6551	8.05	0.02	6.96	0.04	-6.64	0.06	1
GKP-382-3	Boomplaas	1117.50	97.3	-28.6	804	3.70	0.01	3.17	0.02	-3.12	0.07	1
GKP-384-1	Boomplaas	1123.40	79.0	-32.5	2698	4.32	0.01	2.72	0.02	-3.10	0.10	1
GKP-384-2	Boomplaas	1123.50	93.0	-32.3	3204	6.00	0.01	4.10	0.01	-4.23	0.21	1
GKP-385-1	Boomplaas	1125.40	96.8	-29.4	586	4.56	0.01	4.23	0.01	-3.56	0.13	1
BH1-Sacha core												
Sacha 330	Gamohaan	330.00	91.5	-35.2	5928	6.41	0.01	5.43	0.01	-4.79	0.11	1
Sacha 337	Gamohaan	337.00	93.0	-33.6	5506	6.90	0.01	4.26	0.02	-3.91	0.10	1

Table 3.2. Continued

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Contin	
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Table	

a 338.20 87.8 -30.5 6578 5.62	87.8 -30.5 6578 5.62 21.0 21.0 000 2.42	-30.5 6578 5.62	6578 5.62 201	5.62		0.01	2.71	0.02	-2.31	0.15	
n 340.00 96.2 -31.9 928 n 341.90 92.9 -34.8 7292	90.2 -31.9 928 92.9 -34.8 7292	-31.9 928 -34.8 7292	7292		2.34 6.10	0.01	5.87	0.02	-4.83	0.04	- -
n 343.30 96.8 -31.9 518	96.8 -31.9 518	-31.9 518	518		6.79	0.03	5.32	0.01	-4.28	0.09	1
n 344.00 98.0 -32.0 7169	98.0 -32.0 7169	-32.0 7169	7169		18.24	0.04	6.32	0.02	-4.62	0.53	1
n 345.70 95.7 -35.5 3682	95.7 -35.5 3682	-35.5 3682	3682		6.69	0.02	6.08	0.00	-4.92	0.05	1
n 347.50 96.7 -33.8 5415	96.7 -33.8 5415	-33.8 5415	5415		9.74	0.04	8.27	0.03	-7.59	0.13	1
n 417.00 99.6 -28.2 10760	99.6 -28.2 10760	-28.2 10760	10760		8.14	0.02	1.51	0.01	-0.33	0.01	2
n 435.00 96.2 -24.7 56	96.2 -24.7 56	-24.7 56	56		8.93	0.05	1.99	0.03	-0.84	0.09	2
n 725.70 98.9 -27.1 1675	98.9 -27.1 1675	-27.1 1675	1675		9.19	0.01	1.20	0.02	-0.73	0.05	2
n 748.60 94.8 -27.6 51	94.8 -27.6 51	-27.6 51	51		15.44	0.07	1.92	0.02	-1.08	0.18	2
1222.95 98.2 -26.2 82	98.2 -26.2 82	-26.2 82	82		13.22	0.00	0.80	0.00	-0.46	0.05	2
1227.00 97.7 -22.4 322	97.7 -22.4 322	-22.4 322	322		12.36	0.01	2.16	0.02	-1.43	0.08	2
1247.90 96.6 -25.5 92	96.6 -25.5 92	-25.5 92	92		-4.92	0.03	0.48	0.03	-0.11	0.07	2
1257.90 91.0 -27.5 141	91.0 -27.5 141	-27.5 141	141		15.50	0.01	1.06	0.02	-0.27	0.07	2
1266.70 98.9 -26.9 27	98.9 -26.9 27	-26.9 27	27		13.13	0.07	0.42	0.03	0.77	0.04	2
1275.55 96.9 -26.2 624	96.9 -26.2 624	-26.2 624	624		2.18	0.02	0.93	0.04	0.52	0.09	1
1284.90 96.7 -24.2 203	96.7 -24.2 203	-24.2 203	203		12.42	0.02	1.36	0.03	-0.63	0.04	2
1311.10 99.6 -26.9 582	99.6 -26.9 582	-26.9 582	582		24.31	0.00	0.80	0.02	-0.42	0.08	2
1329.25 95.2 -26.1 55	95.2 -26.1 55	-26.1 55	55		14.21	0.01	0.74	0.03	-0.22	0.07	2
1330.45 99.2 -27.9 159	99.2 -27.9 159	-27.9 159	159		8.10	0.02	1.13	0.00	0.07	0.09	2
1340.45 98.2 -27.4 242	98.2 -27.4 242	-27.4 242	242		5.02	0.02	1.06	0.01	-0.01	0.11	2
1400.00 97.9 -29.7 1345	97.9 -29.7 1345	-29.7 1345	1345		3.40	0.00	1.85	0.02	-1.00	0.07	1
n 1514.00 98.1 -31.8 497	98.1 -31.8 497	-31.8 497	497		0.74	0.01	0.51	0.02	0.15	0.12	1
1790.00 96.0 -31.3 1060	96.0 -31.3 1060	-31.3 1060	1060		2.18	0.00	1.94	0.00	-2.93	0.02	1
1917.00 90.0 -29.7 4356	90.0 -29.7 4356	-29.7 4356	4356		0.73	0.01	4.03	0.01	-3.32	0.03	1
1969.70 98.9 -31.2 78	98.9 -31.2 78	-31.2 78	78		6.87	00'0	7.67	0.01	-6.77	0.07	1
1990.20 98.7 -28.9 2400	98.7 -28.9 2400	-28.9 2400	2400		2.88	0.01	4.62	0.01	-3.86	0.05	1
2020.00 99.2 -30.1 175	99.2 -30.1 175	-30.1 175	175		10.95	0.01	5.19	0.01	-4.56	0.05	1
2038.30 99.2 -31.3 821	99.2 -31.3 821	-31.3 821	821		4.36	0.00	3.60	0.01	-3.08	0.06	1
2057.10 99.0 2729	99.0 2729	2729	2729		7.71	00'0	7.85	0.00	-7.17	0.03	1
				1							Ī

1	1	1	1	1	1	1	1	2	2	2	2	1	1	1	1	1	1	1	1
0.03	0.02	0.06	0.07	0.16	0.11	0.14	0.08	0.01	0.63	0.09	0.03	0.04	0.19	0.21	0.12	0.09	0.11	0.26	0.02
-5.28	-3.19	-7.15	-7.19	-8.67	-6.97	-5.44	-6.52	-0.33	3.59	3.13	-0.60	-4.42	-2.21	- 4.04	-3.49	-1.15	-1.17	-1.14	-5.37
0.01	0.00	0.00	0.00	0.02	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.00	0.01	0.01	0.03	0.03	0.02	0.03	0.03
5.65	3.31	7.19	7.70	9.36	7.76	6.94	7.00	0.88	0.83	0.86	0.96	4.38	2.45	4.60	4.57	0.77	0.76	1.02	6.14
0.00	0.01	0.02	0.00	0.01	0.01	0.01	0.02	0.02	0.00	0.01	0.02	0.00	0.02	0.02	0.02	0.00	0.02	0.00	0.01
5.88	5.95	10.48	7.94	10.49	9.37	12.97	6.25	6.44	8.66	8.31	9.76	8.63	1.50	5.26	3.11	1.15	-0.68	2.61	5.95
3691	1300	15373	7556	1199	895	560	866	368	573	573	156	992	193	1258	483	681	1293	7579	206
	-34.0		-32.7	-31.2	-29.8	-28.2	-31.2	-30.0	-35.5		-30.0	-31.5	-28.5	-31.1	-33.3	-37.2	-36.6	-37.1	-35.9
98.1	0.06	90.6	90.9	98.9	98.6	98.1	96.4	98.9	9.66	9.66	7.00	97.6	57.3	54.9	86.6	21.0	24.8	33.1	96.3
2076.00	2491.00	2514.00	2696.15	2703.90	2721.50	2732.10	2740.00	2745.30	2765.40	2765.40	2812.00	2827.90	3230.00	3245.00	3306.30	3401.40	3420.00	3435.00	3457.00
Reivilo	Reivilo	Reivilo	Monteville	Boomplaas	Boomplaas	Boomplaas	Vryburg	Vryburg	Vryburg	Vryburg									
SA188	SACHA2491	KM44	SA55	SA61	SA43	SA29	SA12	SA8	SA117_2	$SA117_1$	SA89	Sa81	KM78-7280	Sacha 3245	Sacha 3306.3	SACHA 3401.4	Sacha_3420	Sacha_3435	KM82_3457

Table 3.2. Continued

Chapter 4: Neoarchean seawater sulfate: insights from CAP in the Batatal Formation of Brazil

Abstract

Knowledge of the isotopic composition and concentration of seawater sulfate in the Archean ocean is important when considering the evolution of the sulfur and oxygen cycles prior to the Great Oxidation Event, and are thus the subject of active debate. To move this debate forward, I present new high-resolution sulfur isotope measurements of the carbonate interval in the 2.5 Ga Batatal Formation that I previously modelled in order to constrain the abundance of Neoarchean seawater sulfate. These measurements coupled with a refined geochemical model are consistent with earlier findings that seawater sulfate concentration ranged between 2 and 8 μ mol/L. If correct, this estimate suggests a residence time of ~15,000 to 50,000 years, and given a modern mixing time of the oceans, conservative behavior of the sulfate ion. The significance of observed sulfur isotopic compositions and variations of the Batatal carbonate-associated pyrites is further discussed in the context of recent proposals that provide alternatives to the standard model of the Archean sulfur cycle.

4.1. Introduction

The Archean sulfur cycle differed from the modern (Kasting, 2001) due to the insignificant levels of oxygen in the atmosphere and hydrosphere (e.g. Lyons et al., 2014). Atmospheric anoxia would have diminished fluxes of sulfate to the oceans through oxidative weathering, leading to low seawater sulfate concentrations and limited sulfate evaporite precipitation (Huston and Logan, 2004). Thus the main source 116

of sulfur to the Archean oceans came from the atmosphere, ultimately derived from volcanic sulfur gases that were transformed by photochemical reactions to aerosol form. This view is supported by the observation of mass-independent fractionation of sulfur isotopes (MIF-S) preserved in Archean sedimentary archives (Farquhar et al., 2000; Johnston et al., 2011). Nonetheless, debate persists about the specific mechanisms of MIF-S formation, the isotopic and molecular composition of atmospheric sulfur channels to surface environments (e.g. Ueno et al., 2009; Halevy et al., 2010; Claire et al., 2014; Babikov et al., 2017), and the Archean seawater sulfate isotopic composition (Ono et al., 2003; Domagal-Goldman et al., 2008; Zhelezinskaia et al., 2014; Paris et al., 2014).

The conventional model of the Archean sulfur cycle suggests two channels of atmospheric sulfur exited the atmosphere, each with distinctive isotopic composition (Farquhar et al., 2001). The first channel yielded insoluble elemental sulfur enriched in ³³S and ³⁴S and depleted in ³⁶S relative to initial sulfur gases; and the second yielded soluble sulfate aerosols depleted in ³³S and ³⁴S but enriched in ³⁶S. Due to the different solubilities of these sulfur-bearing substances, they have distinctive transformation pathways in the oceanic environments. This characteristic leads to the formation of pyrites with variable ³³S, ³⁴S, and ³⁶S, and the preservation of sedimentary rocks with varying sulfur isotope compositions (Farquhar et al., 2013). Mixing of these two sulfur sources in pyrite-forming environments produced a continuum of compositions, some of which fall along the Archean Reference Array (ARA, Ono et al., 2003; Kaufman et al., 2007). The standard model posits that sulfate aerosols with negative Δ^{36} S rained to the surface and were converted by MSR to sulfide (and later

pyrite) with Δ^{33} S and Δ^{36} S composition inherited from photolytic SO₄. Exchange reactions between elemental sulfur (when abundant) and MSR produced sulfide in sediments likely smeared the range of measured multiple sulfur isotope compositions. The expression of these signals in ancient rocks thus depends on the concentrations of various sulfur species in different oceanic sedimentary settings (see Chapter 3).

My recent study of Neoarchean carbonates in the Batatal Formation, Brazil suggests that carbonate-associated pyrites (CAP) may be used as a proxy for seawater sulfate composition (Zhelezinskaia et al., 2014). The Batatal CAPs are characterized by constant negative Δ^{33} S values and large magnitude ³⁴S fractionations. These observations support the view that sulfate reduction was a dominant microbial process of carbon recycling in the carbonate environment, and suggests that primary seawater sulfate carried a negative Δ^{33} S composition of around -2‰. The relatively constant Δ^{33} S signal throughout the ~70m thick carbonate layer suggest that flux of atmosphere sulfate with negative Δ^{33} S was uniform over million year intervals. In the lower part of the Batatal carbonate interval, I observed a stratigraphic fluctuation in Δ^{33} S values that I modelled in order to estimate the concentration and residence time of Neoarchean seawater sulfate (Zhelezinskaia et al., 2014). My model estimate of between 1 to 10 mM/L of SO4 for the Neoarchean ocean agrees broadly with that made by Crowe et al. (2014).

In the present study, I have completed analyses on 19 new samples in lower carbonate interval of the Batatal Formation between 1290 and 1320 meters in the GRD-117 core, insofar as the Δ^{33} S excursion through this interval was previously defined by only six samples.

4.2. Material and methods

New samples were collected at ~1-3 meter intervals in the GDR-117 core by Prof. Alan Jay Kaufman during 2015 field work in Brazil through the 2.5 Ga Batatal Formation (Zhelezinskaia et al., 2014). The Batatal Formation is part of the upper Caraça Group of the Minas Supergroup in Brazil. The minimum age of the Batatal Formation is currently constrained by a U-Pb detrital zircon age of 2.58 Ga in the underlying but conformable Moeda Formation (Hartmann et al., 2006) and a Pb-Pb carbonate age of 2.42 Ga of the overlying Gandarela Formation (Babinski et al., 1995).

Batatal strata, consisting of three distinct members – including lower shale, a middle siliceous carbonate, and an upper interval of mixed shale, carbonate, and chert – were intersected by the GDR-117 core at depths between 1210 and 1390 meters. The grey silicified stromatolitic and laminated dolomite member is 67 m thick and is brecciated, heavily silicified, and karstified at its top (Zhelezinskaia et al., 2014). Samples for this project were chosen between 1320 and 1290 meters of shallow marine carbonate interval based on the presence of visible pyrite grains. Samples were cut and polished to better observe and drill macroscopic pyrite grains. In all, nineteen new pyrite powders were produced from visible pyrite grains or laminations >1mm in thickness for sulfur isotope analyses.

Sulfur isotope compositions of drilled pyrites were measured by combustion with a Eurovector elemental analyzer in-line with the continuous flow Isoprime system at the University of Maryland, College Park. Around 100 mg of pyrite powders were weighed in tin cups together with NBS-127 and NZ-1 standards of 200 \pm 20 mg. In these analyses, ~1000 mg of V₂O₅ was added to the tin cups with the samples and standards as an additional oxidant. The tin cups were sequentially dropped with a pulsed O₂ purge of 12 ml into a catalytic combustion of a Eurovector elemental analyzer furnace operating at 1030°C. The frosted quartz reaction tube was packed with high purity reduced copper wire for quantitative oxidation and O₂ resorption. Water was removed from the combustion products with a 10-cm magnesium perchlorate column, and the SO₂ was separated from other gases with a 0.8-m PTFE GC column packed with Porapak 50–80 mesh heated to 115°C. The effluent from the elemental analysis (EA) was introduced in a flow of He (80–120 mL/min) to the Elementar Isoprime IRMS through a SGE splitter valve that controls the variable open split. Timed pulses of SO₂ reference gas (Air Products 99.9% purity, ~3 nA) were introduced at the beginning of the run using an injector connected to the IRMS with a fixed open ratio split.

		NBS-127	7	N	JZ-1 (S-1)	
1	δ^{33} S	$\delta^{34}S$	Δ^{33} S	$\delta^{33}S$	$\delta^{34}S$	Δ^{33} S
2	10.83	21.12	0.01	-0.04	-0.39	0.16
3	10.92	21.10	0.11	0.01	-0.40	0.22
4	10.99	21.07	0.19	0.04	-0.37	0.23
5	10.93	21.17	0.08	-0.22	-0.21	-0.11
6	10.77	21.11	-0.05	-0.12	-0.28	0.02
7	10.80	21.19	-0.05	-0.03	-0.14	0.04
8	10.72	20.99	-0.04			
average	10.85	21.11	0.04	-0.06	-0.30	0.09
1σ	±0.10	±0.07	±0.09	±0.10	±0.11	±0.13

 Table 4.1. Sulfur isotopic measurements (in ‰) of standards between sample sessions after drift correction and correction based on true standard isotopic compositions.

The isotope ratios of reference and sample peaks were determined by monitoring ion beam intensities relative to background values. The cycle time for these analyses was 210 seconds with reference gas injection as a 30-second pulse beginning at 20 seconds. Sample SO₂ pulses begin at 110 seconds and return to baseline values between 150 and 180 seconds, depending on sample size and column conditions. Sulfur isotope ratios were determined by comparing integrated peak areas of m/z 66 and 64 for the reference and sample SO₂ pulses, relative to the baseline that is approximately 1×10^{-11} A. The background height was established from the left limit of the sample SO₂ peak. Isotopic results are expressed in the delta notation as per mil (‰) deviations from the Vienna Canyon Diablo Troilite (V-CDT) standard. Drift correction was performed based on isotopic compositions of standards. Two NBS-127 and two NZ-1 standards were measured between each set of 10 samples, and uncertainties (1σ) for each analytical session based on these standard analyses were determined to be better than 0.15‰ for δ^{34} S, δ^{33} S and Δ^{33} S isotope compositions (Table 4.1). Uncertainties (2σ) for sample measurements were assigned based on maximum uncertainties of standards: 0.2‰ for δ^{33} S, 0.22‰ for δ^{34} S, and 0.26‰ for Δ^{33} S.

4.3. Results and discussion

4.3.1. Mechanisms responsible for Δ^{33} S variations

My new study of Batatal Formation CAP confirms the presence of a Δ^{33} S excursion in the lower part of the carbonate interval (Zhelezinskaia et al., 2014), and the higher resolution sampling places additional constraints on variations of the Δ^{33} S signal in the interval between 1290 and 1320 meter depths in the GDR-117 core (Table 4.2). In Fig. 4.1 I plot new data together with previous measurements of bulk and drilled pyrite grains in the interval between 1320 and 1280 meters in the core (Zhelezinskaia et al., 2014). In this plot the -2‰ baseline is highlighted as a stippled line, and note a peak in Δ^{33} S values (up to -1.1% for a single bulk sample, but averaging around -1.5‰

for all measurements) around 1315 meters and a valley (down to -2.8‰ on average) in the interval between 1305 and 1310 meters, before returning to the baseline composition at around 1295 meters. In the following, I first discuss possible mechanisms of temporal Δ^{33} S variations in the Batatal carbonate interval, and then use this information to constrain the concentration of contemporaneous seawater sulfate.

The standard model of the Archean sulfur cycle (Farquhar et al., 2000; Farquhar et al., 2001; Endo et al., 2016) suggest that negative Δ^{33} S signal was carried by photolytic sulfate aerosols that rained down to the oceans providing the main flux to the Archean seawater sulfate reservoir. Insofar as pyrites from the Batatal carbonate have consistently negative Δ^{33} S signals and large magnitude ³⁴S fractionations, it is clear that they were sourced from seawater sulfate that was reduced to sulfide (and preserved as pyrite) by MSR (Fig. 4.2, Zhelezinskaia et al., 2014).



Figure 4.1. Profile of newly analyzed and published Δ^{33} S in pyrites from the GDR-113 core over depth. Uncertainties are 2σ .

Following this logic, variability of Δ^{33} S in pyrite sulfur through depth of the GDR-117 core records variability in the isotopic composition of seawater sulfate through time. While Zhelezinskaia et al. (2014) suggested that the negative shift in Δ^{33} S values was due to a secular change in the isotopic composition of oceanic sulfate, some details were missing in the original discussion that are clarified here.

Because biological processes produce insignificant Δ^{33} S variations (<0.2‰ in pure culture experiments; Johnston et al., 2007), the temporal variability within the Batatal Formation carbonate might be interpreted to reflect variable contributions of the two recognized mass-independent atmospheric sources generated by various exchange processes, overlain by mass-dependent reactions occurring in pyrite-forming environments. However, the negative and wide ranging δ^{34} S and narrowly ranged Δ^{33} S compositions of these grains (Fig. 4.2) suggest that elemental sulfur of an atmospheric source was at most a minor contributor to the pyrite minerals.

Depth	δ ³³ S	2σ	δ ³⁴ S	2σ	$\Delta^{33}S$	2σ
1299.13	-10.20	±0.20	-15.24	±0.22	-2.32	±0.26
1302.51	-9.82	±0.20	-14.87	±0.22	-2.13	±0.26
1303.31	-9.52	±0.20	-13.53	±0.22	-2.52	±0.26
1304.1	-10.45	±0.20	-15.70	±0.22	-2.33	±0.26
1305.13	-9.92	±0.20	-13.81	±0.22	-2.78	±0.26
1305.95	-10.41	±0.20	-14.69	±0.22	-2.82	±0.26
1306.4	-9.58	±0.20	-13.22	±0.22	-2.75	±0.26
1306.91	-9.09	±0.20	-12.36	±0.22	-2.70	±0.26
1307.25	-10.24	±0.20	-14.72	±0.22	-2.63	±0.26
1308.31	-10.34	±0.20	-14.59	±0.22	-2.80	±0.26
1308.88	-10.86	±0.20	-16.73	±0.22	-2.21	±0.26
1309.1	-6.20	±0.20	-6.51	±0.22	-2.84	±0.26
1309.63	-12.53	±0.20	-19.67	±0.22	-2.34	±0.26
1310.9	-7.31	±0.20	-11.52	±0.22	-1.36	±0.26
1311.84	-7.11	± 0.20	-10.60	±0.22	-1.64	±0.26
1313.4	-7.16	±0.20	-10.96	±0.22	-1.50	±0.26
1314.12	-7.96	±0.20	-12.21	±0.22	-1.65	±0.26
1316.68	-2.18	±0.20	0.32	±0.22	-2.34	±0.26
1317.39	-5.52	±0.20	-6.27	±0.22	-2.28	±0.26

 Table 4.2. Sulfur isotopic measurements of drilled pyrites from the lower carbonate interval of the Batatal Formation.

Temporal Δ^{33} S variations may also record changes in the magnitude and characteristics of Δ^{33} S produced by atmospheric chemistry. Both experimental data and geochemical models suggest that changes in the production and ³³S abundance of

photolytic H₂SO₄ may be controlled by (i) the rate of volcanic outgassing of SO₂ (Ono et al., 2003, Claire et al., 2014), (ii) the balance of pCO₂ in the atmosphere (Domagal-Goldman et al., 2008; Halevy et al., 2010), and (iii) variations of atmospheric CH₄ that could induce changes in atmospheric chemistry alone (Halevy et al., 2010; Zerkle et al., 2012). Given the short temporal window in which this Δ^{33} S excursion occurs and the absence of any variation in $\delta^{13}C_{org}$ values (Zhelezinskaia et al., 2014), it is reasonable to assume that changes in the ³³S abundance of atmospheric sulfate were caused by fluctuation in the SO₂ outgassing rate (Claire et al., 2014; Ono et al., 2013; Endo et al., 2016).



Figure 4.2. Cross-plot of Δ^{33} S vs. δ^{34} S values of carbonate associated pyrites of the Batatal Formation from this study and from Zhelezinskaia et al., 2014. ARA – Archean Reference Array; positions of two end-member sulfur species on the ARA are depicted by blue circles. Paleoarchean barite compositions are from Roerdink et al. (2012) and references therein.

Thus, shift of Δ^{33} S from ~ -1.5 to -3‰ between 1314 and 1302 m of the GDR-

117 core could be a temporal increase in the rate of SO_2 degassing over a few tens of thousands of years. This increase, however, need not be global in scope. It could result from local volcanism with the fractionated products of photochemical reactions leaving

the plume and being deposited locally within the depositional basin (Muller et al., 2016).

Alternatively, the Δ^{33} S temporal shift toward more negative values might result from a brief geological interval of intense chemical weathering. This seems possible, however, only if Paleoarchean sulfates with strongly negative Δ^{33} S compositions were exposed on the terrestrial surface (Roerdink et al., 2012 and references therein). Whatever the process involved in the sulfur isotope perturbation, the very low concentration of seawater sulfate made it possible for the sulfur isotope event to be preserved in the Batatal sedimentary archive (Zhelezinskaia et al., 2014).

4.3.2. Concentration of seawater sulfate in the Neoarchean

Because the Modern concentration of seawater sulfate today is high (the second most abundant anion at 28mM), its residence time of more than 10 million years far outstrips the mixing time of the ocean (Paytan et al., 2004). Therefore, the concentration and isotopic composition of seawater sulfate today is homogeneous throughout the ocean masses. In contrast, the Neoarchean, seawater sulfate concentration is estimated to be <0.1% of the current day ocean (Crowe et al., 2014; Zhelezinskaia et al., 2014). This difference can be understood in terms of sulfate sources and sinks. Today, sulfate sources to the oceans are dominated by oxidative weathering, while ancient sources were dominated by atmospheric rainout. Sinks in both intervals include the formation of pyrite, which may have been more extensive in the Neoarchean due to widespread water column anoxia and the great abundance of ferrous iron in the oceans. In contrast, there was little to no removal of sulfate from the Neoarchean oceans through the precipitation of gypsum or anhydrite as is common on

evaporitic platforms today. To understand whether or not sulfate was a conservative element in the Neoarchean ocean, I must first estimate the residence time for this critical anion.

Zhelezinskaia et al. (2014) performed calculations using a first-order rate law equation to evaluate the residence time of Neoarchean sulfate by modeling the sulfur isotope excursion preserved in the lower Batatal carbonate. This model, however, was based on only six data points from bulk rock pyrite measurements. My new collection through this interval provided an additional 19 analyses of macroscopic pyrite, which are combined with the earlier data in a new time-series model (Fig. 4.1). Using the observed magnitude of sulfur isotope shifts, I constructed a first-order kinetic model to calculate the sulfate concentration of seawater. Carbonate accumulation rates were considered to be within the range of 40-150 m/10⁶ yr based on estimation of Neoarchean carbonate deposition rates elsewhere in the world (Altermann and Nelson, 1998). The sulfur isotope concentration in ocean at time t was then calculated using equation:

$$A_{xS}^{(t)} = F_{vol}/k - (F_{vol}/k - A_{xS}^{(0)}) \times e^{-kt}$$

Where $\mathbf{A_{xS}}^{(t)}$ is a concentration of a sulfur isotope (I used ratios of ${}^{32}\mathbf{S}/{}^{34}\mathbf{S}$ and ${}^{33}\mathbf{S}/{}^{34}\mathbf{S}$) at time t, $\mathbf{F_{vol}}$ is the flux of sulfur emitted from volcanoes that ends up in sediments (estimated at 2× 10¹¹ mol/yr by Canfield, 2004), **k** is a rate constant equal to 1/t_{res} (the residence time) that was adjusted to match observed $\Delta^{33}\mathbf{S}$ shifts (Fig. 4.1), and $\mathbf{A_{xS}}^{(0)}$ is the initial concentration of a sulfur isotope in the oceanic reservoir. The initial composition of sulfate seawater $\Delta^{33}\mathbf{S}$ was set at -2.0‰ with temporal adjustments based on stratigraphic variations (Fig. 4.3).



Figure 4.3. Time vs. Δ^{33} S plot of data and first-order best fitted box models with maximum and minimum assumed sedimentation rates.

With the combined data sets, two computer models were run using different sedimentation rates: one assumed a sedimentation rate of 40m/my (model 1) and the other assumed 150m/m (model 2). Using these constraints, the stratigraphic interval of interest occupied either 18,750 (model 1) or 5,000 (model 2) years. Model results, which were adjusted using a minimum sum of squared residuals, were also compared against changes in Δ^{33} S composition of influx sulfate, which was varied between -4 and 0‰. The solutions to the models are presented as best fit lines (Fig. 4.3). To assess the uncertainty of the residence time estimates, I used a Monte Carlo simulation with 1000 generated synthetic sets of data with a given standard deviation for each measurement.

The best fit for the residence time of Neoarchean seawater sulfate was ~52,000 and ~14,000 years for models 1 and 2, respectively, where the mean deviation from the data was $0.073\pm0.072\%$ and absolute deviation was $3.9\pm4.2\%$ (Fig. 4.3). Monte Carlo simulations indicated 54,300±26,200 years for model 1 and 14,300±5,200 years for model 2, which are consistent with the best fit models (Fig. 4.4). These simulations produce close to normal distribution. I can then use the residence time equation:

$$\tau = V/F$$
,

to estimate the concentration of sulfate in the Neoarchean ocean, where τ is the residence time, V is the size of reservoir, and F is the flux into the system. Assuming steady state conditions and a flux of $(2 \times 10^{11} \text{ mol/yr})$, the calculated size of the oceanic sulfate reservoir ranges between 2.7 and 10.3×10^{15} moles. Assuming the ancient ocean had the same mass as today $(1.37 \cdot 10^{21} \text{ kg})$, the sulfate concentration in the Neoarchean ocean would be between 2.0 and 7.5 µmol/L. These estimates are similar to independent model calculations based on a modern low sulfate reservoir as an Archean analog (Crowe et al., 2014). Sulfate concentration in my model scales with sedimentation rate and volcanic sulfur flux into the Archean ocean. If the volcanic outgassing rate was much higher – as suggested by Holland (2009) at 1×10^{12} mol/yr – then the oceanic sulfate concentration would increase by a factor of five. Likewise, if sedimentation rates for Batatal carbonates were higher (e.g. 270 m/my is observed in some modern carbonate environments; Moore et al., 2004), seawater sulfate would be $< 1 \mu mol/L$ with a residence time on the order of thousands of years (Crowe et al., 2014). Under this condition sulfate would be a non-conservative ion in the ocean (Gallagher et al.,



2017) and thus would not result in the temporal variation implied by the observational data.

Figure 4.4. Results of simulations for residence time and concentration of seawater sulfate using 1D kinetic box model. Yellow dot represents best fit model, and blue bars are histogram for 1000 iterations using the Monte Carlo (MC) approach. Averages of MC simulations and 2σ uncertainties are included.

4.3.3. Isotopic composition of seawater sulfate in the Archean

The model described above is based on the assumption that sulfate exiting the atmosphere and dissolved in Archean oceans carried a negative Δ^{33} S signature. This assumption is based on experimental observations that attempt to match measured Archean samples (Farquhar et al., 2000; Farquhar et al., 2001; Endo et al., 2016). Direct measures of Archean seawater sulfate are possible only if the few barites that are preserved formed directly from seawater or precipitated from hydrothermal vents that had a seawater source. Paleoarchean barites have Δ^{33} S values around -1.5 ‰ and δ^{34} S of ~+5‰ (Roerdink et al., 2012) providing a first order constraint on seawater

composition; sulfate deposits are otherwise unknown from the Archean record. Given the absence of bedded sulfates, attempts have been made to measure the abundance and sulfur isotope composition of carbonate-associate sulfate (CAS) in Archean carbonates (Domagal-Goldman et al., 2008; Paris et al., 2014). While micro-sampling of wellcharacterized carbonate textures could minimize diagenetic overprints, it remains untested whether the CAS in these samples was formed from primary seawater SO₄, or by the oxidation of pre-existing pyrite with positive Δ^{33} S from an initial elemental S source.

Batatal Formation CAP samples preserve relatively constant negative Δ^{33} S values (Fig. 4.2), with the exception of the temporal shift in the lower part of the carbonate succession. As mentioned above, this excursion was probably due to atmospheric perturbations during the production of sulfate aerosols. Furthermore, the wide range of negative δ^{34} S values in the same CAP samples (Fig. 4.2) suggest that MSR was active in the sediments. Based on these large magnitude ³⁴S fractionations (Zhelezinskaia et al., 2014) together with negative Δ^{33} S signal, I suggest that seawater sulfate carried a negative Δ^{33} S composition inherited from sulfate aerosols formed by photochemical reactions in the low O₂ atmosphere (Farquhar et al., 2000). This coupled geochemical evidence challenges recent empirical measurements of Neoarchean seawater sulfate isotope composition (Paris et al., 2014) and some models of the Archean sulfur cycle (Claire et al., 2014; Babikov, 2017).

The question remains: is the consistency of negative Δ^{33} S in the Batatal CAPs is a depositional or diagenetic artifact? Zhelezinskaia et al. (2014) stated that the negative Δ^{33} S values in Batatal pyrites throughout the ~70m carbonate interval were due to "greater contributions of sulfate sourced from the atmosphere (with negative Δ^{33} S)" and "this sulfate dominated over the source of elemental sulfur, and that sources of sulfate from the oxidation of sedimentary sulfides with positive Δ^{33} S were negligible". Below I further explore this critical issue.

In the standard model, shale pyrite primarily preserves the mixed contributions of two atmospheric end-members (Ono et al., 2003; Zhelezinskaia et al., 2014). The same is true for pyrite in some carbonate–dominated formations from Western Australia and South Africa (Chapter 3). Other formations, however, like the Carawine in Western Australia (see Chapter 2) have CAP sulfur isotope values similar to those in the Batatal Formation that do not appear to be the product of mixing of atmospheric channels. In these carbonate examples the elemental sulfur component appears to be missing, and I seek to understand why.

Based on sedimentological indicators, the Batatal carbonates were deposited in a proximal shallow marine environment. The proximity of the carbonate platform to continental sources of sulfate might explain the Batatal and Carawine data if this flux carried a negative Δ^{33} S signal, as suggested by measurements of Archean soil sulfate (Maynard et al., 2013). Insofar as oxidative weathering was attenuated at the time of Batatal carbonate accumulation, the riverine flux would primarily transport this soluble atmospheric sulfate to the oceans. The atmospheric elemental sulfur flux with a positive Δ^{33} S signature, however, should have been deposited from the atmosphere to both the deep and shallow oceans, as well as to the exposed continents. Why might this largely insoluble end-member composition show up in some Neoarchean CAPs and not others? One ad hoc explanation might relate to the tendency for this sulfur-bearing particulate
to attach to fine-grained siliciclastics. Samples from the Batatal and Carawine are almost pure carbonate with little to no siliciclastic fraction (see Table 2.2 for Carawine data), whereas other carbonates that I have studied have greater abundances of finegrained siliciclastics. If correct, the isotopic differences might reflect the mineralogical makeup of pure chemical precipitates relative to those with mixed carbonate/silicate mineralogies.

If the Δ^{33} S of seawater sulfate in the Neoarchean is unambiguous, the δ^{34} S composition is less certain. Primary sulfate formed by photochemical reactions has sulfur isotopic composition that lies on ARA (Fig. 4.2), which encompasses a wide range of δ^{34} S values. After atmospheric sulfate rains out on land or in the ocean, MSR and pyrite burial sequesters the ³²S isotope, which leaves oceanic or pore water sulfate enriched in ³⁴S. Such enrichments are recorded in Modern oceanic sulfate (with δ^{34} S ~21‰) and Paleoarchean barites (Roerdink et al., 2012). Following this logic, Ono et al. (2003) based their estimate of the δ^{34} S composition of Neoarchean seawater sulfate on eight pyrites measurements (three samples) from the Carawine Formation, which range between +3 and +16‰. My measurements of the Carawine (Chapters 2 and 3) extend this range to include compositions between -16 to +22‰, indicating the presence of a mass-dependent overprint of reactant sulfate compositions through MSR, so that the samples fall off of the ARA and complicate my analysis.

To provide some constraints, I consider that the minimum limit on seawater sulfate $\delta^{34}S$ composition would equal that of atmospheric sulfate plotted on ARA (for example, if $\Delta^{33}S = -2\%$ then $\delta^{34}S \sim -3\%$; see Fig. 4.2). For the Paleoarchean barite data (Roerdink et al., 2012) the minimum $\delta^{34}S$ would then be +5‰. The maximum limit for

this end-member composition is unconstrained, but was probably less than the Modern δ^{34} S value of ~+21‰ (Tostevin et al., 2014). When calculating average δ^{34} S values in Carawine CAP samples, I obtained a value of ~+10‰, which is close to the estimate for Neoarchean seawater sulfate composition proposed earlier (Ono et al., 2003; Meyer et al. 2017).

Seawater sulfate in the Archean could vary in isotopic composition of both Δ^{33} S and δ^{34} S signal through time because of its low concentration (Crowe et al., 2014; Zhelezinskaia et al., 2014). Its composition depends on the flux and isotopic composition of atmospheric sources, the magnitude of fractionation produced by MSR (or other microbial processes), and the pyrite burial rate. Measurements of the Batatal and Carawine carbonates suggest that the negative Δ^{33} S sulfate oceanic pool existed for over millions of years.

4.4. Conclusions

The currently accepted model of the Archean sulfur cycle is constantly evolving as new data emerge and as new conceptual models are considered. My timeseries measurements of pyrite from the Batatal carbonate interval confirm a previously recognized Δ^{33} S excursion through a ~20 meter interval of the GDR-117 core. These isotopic shifts are interpreted as the result of fluctuations in the isotopic composition of seawater sulfate responding to coincident changes in atmospheric chemistry. The most-likely cause for these changes was an increase in atmospheric sulfur gases pressure due to a period of intense volcanic eruptions. In this study, I refined my earlier one-box model, improved fitted parameters to the model based on framework constraints, and estimated uncertainties on the fits. My first-order kinetic model shows that observed variations of seawater sulfate Δ^{33} S was possible if its concentration was between ~2 and ~8 µmol/L with short residence time of tens of thousands of years. Multiple sulfur isotope data (Δ^{33} S and δ^{34} S) of CAPs in the Batatal Formation further confirm the view that Neoarchean sulfate had a negative Δ^{33} S composition, which is consistent with the currently established model for the Archean sulfur cycle. My observation is important in light of recently proposed photolytic mechanisms for the formation and fractionation of sulfur in species other than sulfate in the Neoarchean atmosphere that could nonetheless carry a negative Δ^{33} S signal to surface environments (Babikov et al., 2017, Babikov, 2017).

Chapter 5: Conclusions

This manuscript presents results of three studies related to the sulfur cycle that operated in Neoarchean marine environments. All are being prepared for publication. Measurements of multiple sulfur isotopes in 2.7 - 2.5 Ga that targeted mostly carbonate and some shale facies from Kaapvaal (Western Australia), Pilbara (South Africa), and São Francisco (Brazil) cratons, have been performed to improve our understanding of sulfur transformations under a reducing atmosphere and widespread anoxia in the oceans. Here I provide a summary of my findings.

The model of the Archean sulfur cycle that has emerged over the past 15 years draws on a comparison of experimental studies (that provided information about processes responsible for MIF-S formation) and empirical observations that are primarily based on shale measurements. Carbonates, however, dominate the Archean sedimentary archive, and may provide new insights to the workings of the ancient sulfur cycle in shallow marine environments. My interrogation of carbonate facies reveal new insights into the Archean sulfur cycle that have not been previously recognized from shale facies alone. This approach highlights the need to explore diverse rock types and analytical methodologies in order to open a wider window into early Earth processes.

This systematic dissertation thus focused on the sulfur isotope measurements of bulk carbonates collected from scientific cores from multiple Neoarchean locations worldwide. In these studies, I discovered that carbonate facies record atmospheric signals with different ³³S, ³⁴S, and ³⁶S distributions than in shale facies. While shales typically preserve a mixture of purely mass-independent atmospheric signals, 135

carbonates are more likely to record significant mass-dependent biological overprint of the atmospheric sulfate signal. Preservation of the isotopic signals of biological sulfur transformations in carbonates appears possible due to a lower proportion of elemental sulfur incorporated into shallow environments, which may be due to the reactivity of these insoluble particles on fine-grained siliciclatic grains that are swept out to sea and rain out in deeper environments. My calculations based on bulk sulfur analyses suggest <35% of an S⁰ fraction in bulk carbonate facies.

Focusing on macroscopic pyrite in the Kapvaal, Pilbara, and São Francisco Neoarchean carbonates, I found that the Δ^{33} S compositions were consistently negative (with an average of -2‰) and the ³⁴S abundances highly fractionated through MSR. The sulfide produced by this microbial metabolism and incorporated into the macroscopic pyrite grains was apparently mixed with elemental sulfur endmember forming triangular shape of CAP sulfur isotope compositions in the Δ^{33} S- δ^{34} S field. Differences between macroscopic and microscopic pyrite in these samples suggest temporal and/or spatial differences between growth phases; an avenue that requires future research.

In two separate but related studies of the Batatal Formation, ultra-low seawater sulfate concentrations (<10 μ mol/L) were modelled based on published and measurements of a significant Δ^{33} S excursion. Furthermore, based on a systematic comparison of contemporaneous carbonate and shale facies, there appears to be a decoupling of isotopic signals preserved during periods of atmospheric haze. This decoupling most-likely reflects local controls on the expression of the elemental sulfur isotopic signal, rather than a global control on photolytic sulfate inputs to the ocean. All three studies emphasize that pyrite formed in shallow environments provides indirect evidence that Neoarchean seawater sulfate carried a negative Δ^{33} S signal inherited from atmospheric sulfate aerosols. This conclusion supports the current model of the Archean sulfur cycle, which is important in light of alternative views that are emerging from: i.) measurements of CAS in Neoarchean carbonates (Paris et al., 2014) that suggest a positive Δ^{33} S composition for seawater sulfate, ii.) theoretical models of photochemical reactions suggesting positive Δ^{33} S signal carried by sulfate (Ueno et al., 2009, Claire et al., 2014), iii.) non-photochemical mechanisms for MIF-S formation including recombination reactions of sulfur allotropes that may carry negative Δ^{33} S compositions (Babikov et al., 2017, Babikov, 2017).

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