Organic Geochemistry and Stable Isotope Constraints on Precambrian Biogeochemical Processes

by

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SUBMITTED TO THE DEPARTMENT OF EARTH, ATMOSPHERE AND PLANETARY SCIENCES IN THE PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTERS OF SCIENCE IN GEOCHEMISTRY

AT THE

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

SEPTEMBER 2011

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Organic Geochemistry and Stable Isotope Constraints on Precambrian Biogeochemical Processes:

Examples of the Late Proterozoic Coppercap Formation, NWT Canada
and Archean Gorge Creek Group, Pilbara

by

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Submitted to the Department of Earth, Atmospheric and Planetary Sciences
on July 15, 2011 in Partial Fulfillment of the Requirements for the
Degree of Masters of Science in Earth, Atmospheric and Planetary Sciences

Abstract

Details of the biogeochemical cycles and the dominant mechanisms present in Precambrian remain heavily debated topics. The events of the Late Proterozoic onset to glaciations and what types of early life existed in the Archean are two of the many provoking topics within the Precambrian. We set out to improve the understanding of these geologic intervals by examining stable isotopic signatures and molecular fossils (biomarkers) in Late Proterozoic and Mesaoarchean ages sedimentary rocks in Northwestern Territories, Canada and Pilbara, Western Australia, respectively. This thesis presents sulfur, carbon, oxygen and nitrogen stable isotopic data along with distribution of steranes and hopanes biomarkers. Geochemical data is analyzed in the context of elucidating the key biological and environmental factors involved in the Mesaoarchean marine biosphere and the Late Proterozoic onset of glaciations. Stable isotopic analysis of the Gorge Creek Group in Pilbara, Western Australia reveals organisms capable of microbial sulfur disproportionation were likely the dominant biological players in Mesaoarchean deep-ocean sulfur cycling. Biomarker and isotopic proxies of the Coppercap Formation reveal diverse biological activity directly prior to the Sturtian Glaciation with communities of green and purple sulfur bacteria as well as methanotrophs and cyanobacteria. Possible environmental implications of these communities co-existing are explained in context of changes in ocean chemistry and the diversification of eukaryotic life.

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Acknowledgements

I am eternally grateful for the generous support and encouragement of my extended community of advisors, coworkers, family and friends. The foremost thanks go to Shuhei Ono, my thesis advisor. Professor Ono's assistance in the lab, willingness to discuss material, commentary, and support demonstrate his dedication to his students and their research. A very large thank you goes to Dr. Christian Hallmann for all his help in the preparation of this thesis, guidance, friendship and encouragement throughout the process. I would like to thank Dr. Francis Macdonald for his collaboration, valuable discussions and endless enthusiasm. Finally, I would also like to show my great appreciation to Roger Summons and Tanja Bosak, for their insight, excitement and support that lead me to study geobiology initially, as well as continue my studies.

I would also like to thank Andrew Whitehill, Harry Oduro and Jon Grabenstatter for comments on my thesis work and all the wonderful people of E25 for their discussions, smiles and for providing the most nurturing work environment I can imagine. I would like to recognize M. Jansen, T. Goff, A. LeMessurier, N. Hanselmann, M. Sori, my parents and my housemates for being there for me every step of the way.

This thesis is written in the memory of my great uncle Robert Thomas who passed away June, 2010. I will always remember him for his eloquent letters, his whimsical stories and as being a constant source of inspiration and encouragement to all those around him.
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Chapter 1 Introduction:

Though the Precambrian accounts for nearly 90% of time on Earth, many facts about the evolution of the Earth and biological processes taking place during this time period remain poorly constrained. Knowledge about the Precambrian is limited in part due to poor preservation of outcrops of Precambrian age. Cautious examination of the state of rock samples must be performed as concerns regarding sample alteration due to pressure, heat, weathering, fluid interactions, secondary precipitation and dissolution, increase as samples go back further in the geologic record.

Of the largest changes that took place in the Precambrian were the development and break up of continents, the advent of microbial and eukaryotic life, and the rise of oxygen (e.g. Holland, 2002). A range of marine conditions have been suggested for the Archean and Proterozoic worlds, ranging from iron rich, to sulfide rich waters with a stratified, weakly mixing ocean being one of the key factors affecting marine chemistry (Holland, 2002; Pavlov and Kasting, 2002). As sulfur, carbon, iron, nitrogen and phosphorous are all intimately involved in the metabolic processes of life, biogeochemical cycling, redox conditions and biological communities present have been implied from the study of these elements (Anbar and Knoll, 2002).

Throughout the Archean, evidence of extensive microbial life is evidenced in biostratigraphy (namely stromatolites) and isolated microfossils remains (mostly in silicified beds) (Duck et al., 2007; Brasier, 2002). Significant alterations in biogeochemical cycles are noted with excursions within $^{13}$C isotopes indicating the beginning of biological effects on geochemistry. The discovery of mass independent fractionation of sulfur (Farquhar et al., 2000), redox state changes in chemical signatures (Reinhard et al., 2009), and presence of microscopic life (Schopf, 1993; Duck et al., 2007), indicate environmental and biological changes taking place in the oceans. However, life in the Archean and
the cause of many of these signals is still highly suspect and debated (Brasier, 2002; Farquhar et al., 2001; Kaufman et al., 2007; Ohmoto et al., 2006).

Based on our current understanding, the Archean before the Great Oxidation Event (2450-2320 Ma), the ocean was thought to be iron rich and sulfur poor, reflective of a lack of oxygen to oxidate sulfides and remove Fe$^{2+}$ from the marine reservoir. The questions of what early life looked like and what microbial species where prevalent remains an ongoing discussion. Black shales from continental margin and deep marine environments of the Mesoarchean are analyzed and discussed in Chapter 4 on the Gorge Creek Group (~3.2 Ga) from the Pilbara Craton in Western Australia. Stable isotope composition and elemental content for carbon and nitrogen and multiple sulfur isotope analysis were used to analyze the respective sources of organic matter in shales.

The other section analyzed in this thesis examines a more turbulent time period in Earth's history, the Late Neoproterozoic. During this time period the Earth underwent severe climatic changes that were accompanied by large shifts in the isotopic record. Environmental perturbation during the Cryogenian included tectonic activity, changes within biogeochemical cycling and within marine chemistry. A negative $\delta^{13}$C$_{\text{carb}}$ excursion is witnessed before and during the Strutian, which has been explained by large removal of organic carbon from the system by burial (e.g. Macdonald et al., 2010). Additionally, evidence for a sulfidic ocean have implications on the evolution of metazoans, as many animals would not have been able to survive in anoxic euxinic waters (Kaufman et al., 2007). An anoxic ocean would have allowed for organic material to be buried without being oxidized, gradually increasing the amount of oxygen in the water column and in the atmosphere as more organic matter is buried (Logan et al., 1995).

Chapter 5 examines the changes in the Neoproterozoic by examining the ~730 Ma Coppercap Formation of the MacKenzie Mountains in Northwestern Canada. This section, deposited directly before the Sturtian glaciation, represents a shallow marine depositional environment and record of
history of chemistry and biogeochemical cycling marking the onset of the glaciation. Sulfur and carbon stable isotope analysis is used to interpret geochemical cycles along with lipid biomarker, steranes and hopanes, to deduce environmental and biological changes of the Late Neoproterozoic.

1.1 Thesis Outline

Chapter 2 presents Analytical Background of the isotopic proxies and specific biomarkers analyzed in this thesis to allow for each proxy to be placed in context of previous research and the proxy’s analytical limits. Chapter 3 discusses the various methods that were used in this thesis to obtain the isotopic data and biomarker values. Chapter 4 discusses data from the Mesoarchean Gorge Creek Group in Western Australia and the question of the source of organic rich shales in the Archean. Based on multiple sulfur isotopic data it is most likely that microbial sulfur disproportionators were the dominant source of biomass. Chapter 5 presents data from the Coppercap Formation in the MacKenzie Mountains of Canada. Stable isotopic values correlated with biomarker data determine that the communities and redox conditions of the Coppercap Basin. Changes in isotopic data and theories regarding the onset of the Sturtian Glaciation are discussed in connection with previous published theories and data.
Chapter 2: Analytical Background

Stable isotope geochemistry is a powerful tool used in chemical analysis of the geologic record to gain insight into the environmental conditions and biogeochemical cycles on Earth. The stable isotope analysis of some of the main elemental components of rocks and life, carbon, sulfur, oxygen and nitrogen, in particular, allow for changes in the paleobiology and geology to be recorded over geologic time spans. Changes in stable isotopes can allude to changes within sea level, depositional conditions, redox stability, nutrient flux, marine chemistry, productivity and temperature. These variations can be recorded on the short term in modern environmental samples, as well as extrapolated over long periods of time to show alterations in continental weathering, atmospheric conditions, carbon burial and sedimentary sulfur burial and how these processes are interrelated to advents in biological evolution.

The elements studied in stable isotope geochemistry are common in the Earth’s sediments and atmosphere and are readily incorporated and affected by biology. Additionally, these elements, with two or more stable isotopes, are incorporated at different rates in environmental geochemistry and biology (Canfield et al., 2001). The changing ratio of isotopes can deliver evidence of changes that occur in geological sediments. Conventionally, the record of isotopic ratios is referred to in terms of δ notation where:

$$\delta = \frac{(R_{\text{sample}} - R_{\text{standard}})}{R_{\text{standard}}}$$

and R is defined as the ratio of abundance of the more rare isotope (usually heavier) over the most common isotope. $R_{\text{standard}}$ is different for each element and serves as basis for which samples can be
universely compared to. $R_{\text{standard}}$ and the unique $\delta$ notation for each element will be discussed in detail below.

A variety of factors influence the rate and degree of isotope fractionation. Heavier isotopes, in general, have a greater bond strength than lighter isotopes since vibrational energy changes with respect to the mass of isotopes. Thus heavier isotopes tend to remain in higher oxidation states while lighter isotopes will more readily be incorporated into volatile reduced molecular states. Subsequently, heavier isotopes for this same reason tend to fractionate less than lighter isotopes due to the increasingly smaller ratios of mass differences between light and heavy isotopes as overall molecular mass increases. As reaction rate increases, the rate at which fractionation occurs decreases since bonds are being broken faster and relative differences between isotopic mass are less of a barrier towards chemical reactions taking place. As temperature increases, fractionation between isotopes decreases. Additionally, in systems where overall abundance is limited for a particular element, both isotopes will be utilized in full and fractionation is minimized.

Molecular fossils, or biomarkers, are natural products that can survive in sediments with only slight alteration of the original structure so that one can trace a specific biological origin. Under the appropriate diagenetic conditions, hydrocarbon chains of specific compounds will remain intact, leaving enough biological information to individually correlate with specific taxa (Brocks et al., 2003).

2.1 Sulfur

Sulfur enters the atmosphere through biological processes and volcanic outgassing of $\text{H}_2\text{S}$ and $\text{SO}_2$. The reduced sulfur gas is oxidized to $\text{SO}_2$ or $\text{H}_2\text{SO}_4$ and is removed from the atmosphere within a matter of days. The of sulfur in the atmosphere is fast, on the order or days, as a result of
sulfur related molecules quickly forming cloud condensation nuclei making sulfuric acid, which is lost from the atmosphere in rain and wet deposition (Ono et al., 2003). The ocean reservoir of sulfur consists of dissolved sulfate. This sulfate is a product of sedimentary sulfide weathering and by the outgassing of volcanic gases (Canfield et al., 2004). The isotopic composition of sulfate in the ocean depends on the fluxes of the ocean of weathering and deposition of shales, respectively, and the amount of sulfides being weathered. Sulfur in the lithosphere is stored in the form of sedimentary sulfides and evaporites.

Low temperature sulfur isotope fractionation occurs as a result of evaporation, bacterial sulfate reduction and assimilatory sulfide. The largest fractions occur as a result of anaerobic oxidation of organic matter, with an upper bound $\geq 70\%$. This leads to higher, positive $\delta^{34}S$ values of the ocean. Evaporation yields a minimal isotopic difference between oceanic sulfate and evaporites, which incorporate the heavier $^{34}S$ that is not as readily evaporated. The 1-2\% fractionation that occurs between evaporites and oceanic sulfate has been used in the interpretation of evaporites a proxy for oceanic sulfate isotopic values (McFadden and Kelly, 2011).

Sulfur isotopic values are measured in reference to the Canyon Diablo Troilite. Sulfur isotopic ratios are represented as:

$$\delta^xS = \left(\frac{^{x}S/^{32}S}_{\text{sample}} / \left(^{x}S/^{32}S\right)_{\text{CDT}} - 1\right) \times 1000$$

where $x$ refers to 33, 34, or 36. The deviations from the mass-dependent isotopic fraction of the less common 33 and 36 isotopes are defined as (Farquhar, 2000):

$$\Delta^{33}S = 1000 \times \ln(1 + \delta^{33}S / 1000) - 0.515 \times 1000 \ln (1 + \delta^{34}S/1000)$$

and

$$\Delta^{36}S = 1000 \times \ln(1 + \delta^{34}S / 1000) - 1.9 \times 1000 \ln (1 + \delta^{34}S/1000).$$
The record of $\Delta^{33}\text{S}$ and $\Delta^{34}\text{S}$ has been studied in depth as a result of the finding that during the Archean sulfates and sulfides had an unconventional relationship between isotopes that violates mass-dependent rules. The isotopic fractionation of sulfur on Earth has changed since the advent of atmospheric oxygen. The record of $\delta^{34}\text{S}$ over time shows variation during the geologic record showing an overall increase of fractionation through time and preference towards positive $\delta^{34}\text{S}$ values (Figure 1).

![Figure 1: $\delta^{34}\text{S}$ over geologic time](image)

**Figure 1:** $\delta^{34}\text{S}$ over geologic time: Modified from Farquhar *et al.* (2000), demonstrates the compiled sulfur isotope studies over geologic time. Larger fractionations became prevalent after the GOE along with more negative values for $\delta^{34}\text{S}$.

Before the Great Oxidation Event, sulfur in the oceans was largely available through fall out of atmospheric aerosol particles. In the absence of oxygen, photolysis of sulfur will fractionate into two distinct anomalous members: elemental sulfur and sulfate, yielding opposite $\Delta^{33}\text{S}$ values. The
MIF signature is most commonly explained by this fractionation of sulfur during photolysis which was experimentally shown to yield a similar fractionation as what is observed in the environment (Farquhar, 2001). As oxygen levels rose, photolysis of sulfur no longer yielded the mass independent signature and it is thought that the input of sulfur from continental sulfide weathering became more prominent (Figure 2).

Figure 2: $\Delta^{33}S$ values over geologic time: Modified from Farquhar et al. (2000). $\Delta^{33}S$ values over geologic time show large values present prior to the Great Oxidation Event with minimal deviance from the mass dependent values observed since the rise of oxygen.
2.2 Carbon

Carbon is ubiquitous on Earth and exists in a variety of stable forms in the hydrosphere, biosphere, atmosphere and lithosphere. Carbon can exist in oxidation states ranging from -IV to IV. This allows carbon to form many of the most common and most necessary parts of biological and environmental systems and metabolic pathways. The more common $^{12}$C is measured against the other stable much less common isotope $^{13}$C. Fractionation mainly occurs in the reduced forms of carbon in organic matter with respect to inorganic carbon (carbon dioxide and dissolve inorganic carbon). Organic carbon is usually found in the form of hydrocarbons bonded with metals or sulfur, nitrogen, phosphorous or oxygen.

In the oceans, carbon exists in dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) reservoirs. DIC in the ocean is related to the exchange between atmosphere and water at the interface. There is a ~8‰ enrichment of $^{8}$C involved in the dissolution of inorganic carbon into water. While the DIC in the modern ocean is defined as 0‰, the DOC pool lies much closer to -20‰ as a result of metabolic pathways. Furthermore, the biosphere reservoir contains marine biota and particulate matter. While the marine biosphere reservoir is currently smaller than the terrestrial biosphere reservoir, until the Permian, the majority of life existed within the sea lending to more marine control of the carbon cycle.

Carbon fixation processes preferentially incorporate lighter isotopes of elements into biomass, thus, biomass is usually depleted in the heavier isotope of carbon, $^{13}$C. Additionally, the isotopic composition of the autotrophic organism consumed will be reflected in the isotopic composition of animals further up the food chain. Carbon in the atmosphere is mainly found in the form of carbon dioxide, though carbon monoxide, methane and other organic gases are also present in the atmosphere. Carbon dioxide in the atmosphere has an average isotopic composition of -6‰, while the much more reduced methane has an average atmospheric composition of -50‰.
Carbon isotopic values are measured in reference to the Vienna PeeDee Belemite (VPDB). Carbon isotopic ratios are represented as:

\[
\delta^{13}C = \left( \frac{^{13}C/^{12}C}_{\text{sample}} / \frac{^{13}C/^{12}C}_{\text{VPDB}} - 1 \right) \times 1000
\]

Additionally, information regarding the carbon cycle is recorded in the amount of organic carbon present in a sample and its carbonate weight percent. These parameters are used to determine what amount of the rock is inorganic carbon and organic carbon. Inorganic carbon amount is determined by dissolving the rock in hydrochloric acid, which will dissolve carbonates, inorganic carbons. The remaining rock sample is analyzed for its content of C, which yields the value for only the total organic carbon.

2.3 Lipid Biomarker Analysis

Diagenetic processes involving chemical conversion or microbial degradation are critical in the preservation of organic matter (Eglinton, 1973). In oxic sedimentary environments, biolipids such as sterols and carotenoids, will be degraded and will be poorly preserved (Didyk *et al.*, 1978). Anoxic sedimentation conditions allow for the preservation of lipids by preventing the bacterial degradation and predation in the water column. Higher values of TOC, above 10%, are therefore often attributed to anoxic conditions of sedimentation (Thiede and Andel, 1977).
2.3.1 Pristane and Phytane

Oceanic chemical conditions can be reconstructed by examining the ratios of specific biomarkers. The pristane to phytane ratio is used to determine the redox state of depositional environment. Pristane (2,6,10,14-tetramethylpentadecane) and phytane (2,6,10,14-tetramethylhexadecane) are natural saturated isoprenoid alkanes (Figure 3) that derive from the alkyl side chain of chlorophyll $\alpha$. During, this hydrocarbon tail (the phytol chain) is cleaved from the molecule to form the alcohol phytol. Phytol is converted to pristane and phytane in different ratios depending on the redox conditions. Pristane is produced through oxidative pathways, while phytane is generated in reductive pathways (Didyk et al., 1978).

![Pristane and Phytane](image)

**Figure 3 Pristane and Phytane:** Pristane (above) and phytane (below). The ratio of pristane and phytane records the redox state of the sediment. Pristane is preferentially produced in oxic conditions, leading to pr/ph values less than unity. In anoxic conditions, phytane is preferentially produced and the pr/ph ratio is greater than unity.

Under anoxic conditions the phytol is degraded to phytane, yielding low pr/ph values. In oxic conditions, on the other hand phytol is degraded to phylenic acid, which then is degraded to
pristane. This leads to higher pr/ ph ratios in oxic sediments. The breakdown of chlorophyll to pristane and phytane is illustrated in Figure 4 below.

**Figure 4 Breakdown of Chlorophyll**: Breakdown of Chlorophyll in to pristane and phytane. The breakdown of Chlorophyll to phytol is shown above. In oxic ocean conditions phytol is broken down into phylenic acid and then pristane. In anoxic ocean conditions phytol is degraded to phytane. The ratio of pristane to phytane, thus, reveals the redox state of the ocean (Hallmann and Summons, 2011)

### 2.3.2 Chromatiaceae and Chlorobiaceae

The specificity of biomarkers allows for very specific environmental reconstruction.

Diagnostic and geologically stable hydrocarbon biomarkers can be found for Chromatiaceae (purple sulfur bacteria) and Chlorobiaceae (green sulfur bacteria). Purple sulfur bacteria and green sulfur bacteria are unique in that they require reduced sulfur species and light (Brocks *et al.*, 2003). Thus, green and purple sulfur bacteria are paleoenvironment indicators for euxinic conditions in the photic...
zone within ancient lacustrine and marine environments. Chromatiaceae and Chlorobiaceae are, thus, representative of two possible conditions in a marine environment:

1) shallow environments where the sediment-water interface is located in the euphotic zone forming bacterial mats

2) photic zone euxinia where H₂S plumes rose into the photic zone.

2.3.3 C₃₀ Steranes

There are several specific biomarkers to differentiate between marine and lacustrine environments. Elevated concentrations of C₃₀ tetracyclicpolyrenoids (Holba et al., 2003) is indicative of lacustrine environments ranging from fresh to brackish waters. Marine waters can be identified by the presence of n-propylcholestane. The presence of n-propylcholestane is uniquely representative of the remains of marine pelagophytes (Heterokont algae). The most commonly studied biomarker of marine environments is 24-n-propylcholestrane, a widely occurring 30-carbon steranes that originate from the catagenetic and diagenetic degradation of 24-n-propylcholesterols that is biochemically synthesized by chrysophyte algae (Moldowan, 1990). The presence of n-propylcholestane will indicate the sediments were of marine nature. 24-n-propylcholesterols are subsequently found in a variety of marine invertebrates; this finding has been attributed to the invertebrate ingestion of the marine algae.
24-n-propylcholestane is a C30 sterane with no alkyl groups on ring A. It exists as (24R + 24S)-24-n-propylcholestane. It is used as a molecular biological fossil as evidence of marine input in the source rock or oil coming from algae in the class Pelagophyceae.

2.3.4 2-Methyl hopanoids and 3-Methyl hopanoids

An additional C on the A-ring of a hopanoid yields 2-Methyl hopanoid or 3-Methyl hopanoid compounds, which can be used to determine the presence of taxon specific compounds. The biological precursor of 2α-Me is diagnostically altered to the more stable 2β-Me; 3β-Me remains stable in the geologic record (Summons et al., 1999). 2α-Me have been associated with cyanobacteria, but have also been found in low concentrations in other organisms. 3β-Me is found in extant aerobic methanotrophs and are specific to Type I (and X) group of the γ-proteobacteria which thrive in low methane high oxygen environments. Their abundance has been correlated with low δ13C values (Eigenbrode et al., 2008). These compounds have been used to infer changes in biological compounds and environmental conditions throughout the geologic record by comparing taxon specific methylhopanoids to the less specific non-methylated counterparts (Eigenbrode et al., 2008). The methyl-hopane index (MeHI) is defined as: MeHI (%) = 100 × C31 methyl-17α (H) 21β(H)-hopane/ (C31 methyl-17α (H) 21β(H)- hopane + C30 methyl-17α (H) 21β(H)- hopane) (Summons and Jahnke, 1990). Previous work by Eigenbrode et al. has shown that there is a correlation with 3β-MeHI and δ13Corg (Eigenbrode et al., 2008).
Chapter 3 Experimental Procedures

3.1 Sampling

Samples from the Coppercap Formation in the Coates Lake Group of the Northwestern Territories, Canada were selected from two drill cores (76Y-4 and 77Y-3). The samples were provided by Dr. Rigel L. Lustwerk, who previously analyzed samples for trace metals and strontium isotopes, from the lower portions of the core at Pennsylvania State University, University Park, Pennsylvania, as part of her dissertation. The 76Y-4 and 77Y-3 cores were drilled as part of a mineral exploration project undertaken by Shell Company. Core samples were stored in heavy duty cotton drill sampling bags for transport and storage.

Samples from the Lower Gorge Creek Group in Pilbara, Australia were selected from the diamond drilled cores SSD-14 and SSD-18. The core samples were provided by the late John Lindsay (Johnson Space Center at the time). The lower portions of the core, containing volcanic massive sulfide mineralization and volcanoclastic sediments encompassing the Upper and Lower Strelley Sequences had previously been analyzed by Dr. Susan Vearncombe, concentrating on the lithology and causes of the VMS section of Sulfur Springs, at the University of Western Australia.

3.2 Sample Preparation

General Procedural notes: Organic free solvents from Omnisolv were used during sample preparation and analysis of sample for molecular biomarker, total organic carbon and carbon isotope analysis. All glassware and aluminum foil were fired for 8 hours at 550°C; silica gel, sand, glass wool and all pipettes were fired for 8 hours at 450°C. De-ionized water from a Milli-Q system used on
the carbon isotope analysis and lipid analysis was additionally cleaned by five liquid-liquid
extractions with dichloromethane before use on samples.

For sulfide and carbonate associated sulfur analysis, all samples were processed using de-
ionized water from a Milli-Q purification system. All glassware was rinsed thoroughly with de-
ionized water following normal washing procedures. Glassware for carbonate associated sulfate
studies were additional soaked for 24 hours in a 5% reagent grade hydrochloric acid de-ionized
water solution and rinsed with de-ionized water directly prior to use. Chemical reagents for this
study were purchased from Sigma Aldrich and are high purity reagent grade.

Core samples were cleaned using de-ionized water and rinsed with methanol and
dichloromethane. Each sample was then manually filed to remove the top 2mm on each surface.
Core samples were then ultra-sonicated in methanol and then dichlormethane. Each sample was
individually wrapped in fired aluminum foil and crushed manually. They were ground to a fine
powder using a SPEX Shatterbox fitted with an alumina ceramic puck mill for the 77Y-3 core, and a
steel puck mill for the 76Y-4 core. The puck mills were diligently cleaned between samples with fired
sand (up to five rounds), de-ionized water, methanol and dichloromethane.

3.3 Sulfur Isotope Analysis:

Samples were analyzed for pyrite (FeS₂), which contains inorganic sulfur using the methods
outlined in Canfield et al. (1986). The removal of inorganic sulfur was achieved through a process
using chromium chloride solution, chromic chloride hexachloride and 12N concentrated
hydrochloric acid. Approximately 30mL of chromium chloride and 3g of zinc metal were used per
sample. The zinc metal and chromium chloride solution are placed in a sealed Erlenmeyer flask and
is flushed with nitrogen gas for fifteen minutes then sealed. The zinc metal then reduces the chromium chloride:

\[ 2\text{Cr}^{3+} + \text{Zn} \rightarrow 2\text{Cr}^{2+} + \text{Zn}^{2+} \]

Sample amounts used in sulfide extraction were adjusted depending on the pyrite content of the rock. Rock powder amounts used in this study were adjusted based on calculations to get 2 mg of pyrite in each extraction. Sulfur content was estimated based on Chartrand and Brown (1985) and Lustwerk's (1990) description of lithology and rock composition. Two test samples (136 and 156) were ran to estimate the necessary amount of rock powder for different lithologies. Approximately 2g of rock powder were used for chromium reduction. Then reduced chromium chloride, natured reagent grade ethanol and hydrochloric acid is added to the rock powder and heated to 140°C under nitrogen. The reduced chromium subsequently reduces the pyrite within the sample:

\[ 2\text{Cr}^{2+} + \text{FeS}_2 + 2\text{H}^+ \rightarrow 2\text{Cr}^{3+} + \text{Fe}^{2+} + \text{H}_2\text{S} \]

The hydrogen sulfide gas is then bubbled through a 100 mL water trap and collected in a 50 mL zinc acetate trap, precipitating zinc sulfide:

\[ \text{H}_2\text{S} + \text{Zn}^{2+} \rightarrow \text{ZnS} + 2\text{H}^+ \]

Approximately 5 mL of silver nitrate was added to the zinc acetate solution. The zinc sulfide reacted with silver nitrate to form silver sulfide, which is precipitated out.

Selected samples were analyzed for carbonate associated sulfate (CAS). CAS is presumably structurally substituting carbonate, and is thought to be precipitated and trapped within the carbonate matrix through crystal effects or through substitution with the carbonate ion. Previous studies show that CAS is a good proxy for seawater sulfate (Fike et al., 2007 and Hurtgen et al., 2005). Powdered samples were rinsed in de-ionized water to remove soluble sulfates (e.g. from
sulfide oxidation), and then soaked for 24 hours in a 10% sodium hydroxide and de-ionized water solution while agitated using a VWR Mini-Shaker at 400 rpm to remove water soluble sulfates (e.g. anhydrites). Samples were filtered using a Whatman 440 filter and dissolved in 12N hydrochloric acid for 24 hours at room temperature. Fike (2007) previously reported that there is no $\delta^{34}$S difference between dissolving carbonates under nitrogen gas at 60°C and at room temperature. The sample was once again filtered to remove insoluble residues and an excess of 0.5M barium chloride solution is added to the solute to precipitate out barium sulfate. The barium sulfate is washed in de-ionized water three times and dried.

Following methods outlined by Kiba (1957a,b), a tin (II)-strong phosphoric acid solution is used to extract the sulfate from the precipitated barium sulfate in the form of hydrogen sulfide. The Kiba reagent is made using phosphoric acid, which is dehydrated over two hours by heating at 260°C under vacuum with N$_2$ flow. 30g of tin chloride is added to the dehydrated phosphoric acid (300mL) and again is heated to 260°C with N$_2$ flow until the tin chloride is dissolved into solution. The Kiba reagent is allowed to degas hydrogen chloride during this step into a water trap. 15mL of Kiba solution is added to ~6mg of barium sulfate and is mixed together. The mixture is heated to 260°C and hydrogen sulfide gas is bubbled through to a zinc acetate trap. The zinc acetate reacts with the hydrogen sulfide to form zinc sulfide, which is subsequently precipitated into silver sulfide using 5mL of silver nitrate.

Evaporite samples from the 6Y4 core (Samples 81 and 83) were analyzed using a solution of hydroiodic acid, hypophosphoric acid and hydrochloric acid is mixed together to form Thode reagent. 1g of evaporite was added to a round bottom flask with the 30 mL Thode reagent and heated to 130°C for 2 hours. Hydrogen sulfide gas is bubbled through to a zinc acetate trap, like in the aforementioned procedures and is eventually precipitated into silver sulfide.
The silver sulfide samples were placed in a chemical oven at 60°C overnight to accelerate the precipitation process. The silver sulfide precipitate was rinsed, once in ammonium nitrate, and three times in de-ionized water, and dried. 2 mg of it is weighed into aluminum cups for isotope-ratio mass spectrometric (IRMS) analysis. The Ag₂S was fluorinated at 300 °C to form SF₆. The SF₆ (6 to 8 μmol) was purified by a preparatory gas chromatography system developed and described in Ono et al., (2006), and introduced to an isotope ratio mass-spectrometer using a dual-inlet mode to measure masses 127, 128, 129, and 131. Reproducibility for complete analysis, from fluorination, GC purification, and isotope ratio analysis are 0.1, 0.2 and 0.4 ‰ (1σ) for δ³⁵S, δ³⁴S and δ³⁶S, respectively, and 0.01 and 0.1 ‰ (2σ) for Δ³⁵S and Δ³⁶S, respectively.

Sulfur isotope values are reported as δ values relative to the Vienna Canyon Diablo Troilite Standard (V-CDT) by defining IAEA S-1 to be: δ³⁵S = -0.055 ‰, δ³⁴S = -0.300 ‰ and δ³⁶S = -1.14 ‰ with respect to the V-CDT scale. All values for δ³⁴S_pyrite were calculated from replicate analyses of samples and laboratory standards. One standard is run for every eight samples.

3.4 Carbon Isotope, Total Organic Carbon and Carbonate Weight percent analysis

δ¹³C of carbonate carbon was measured according to the methods described in Ostermann & Curry (2000). Samples were additionally measured and analyzed for their total organic carbon (TOC). To measure TOC, bulk powdered rock samples were acidified in purified 6N hydrochloric acid to remove carbonate minerals. The samples were then rinsed to neutrality in pre-cleaned de-ionized water, filtered, and dried. Approximately 2 mg of dried samples was loaded into tin cups for isotopic analysis. The samples were then flash combusted in a Carlo Erba NA1500 Elemental Analyzer fitted with an AS200 auto sampler at 1060°C and a reduction furnace at 650°C. The CO₂
generated during this combustion process was then analyzed by a Delta plus XP Isotope Ratio Mass Spectrometer operated with Isodat 2.0 Software. Analysis of samples in triplicate allowed for the calculation of standard deviation for each sample. Carbon isotope values will be reported here as δ values relative to the V-PDB standard where δ^{13}C is defined as:

\[
\delta^{13}C = \frac{\frac{^{13}C}{^{12}C}_{\text{sample}} - \frac{^{13}C}{^{12}C}_{\text{standard}}}{\frac{^{13}C}{^{12}C}_{\text{standard}}} 
\]

(Equation 3.4)

All δ^{13}C_{org} values were corrected by calibration against the in-house standards “Acetanilde” and “Arndt Acetanilde”, as well as against international standards, “IAEA-CH-6 sucrose” and “NBS-22”. Standards are run interspersed within the sample analysis.

3.5 Molecular Biological Material Analysis

Bitumen was extracted from rock powder with dichloromethane (DCM)/ methanol (MeOH) (9:1) using a Dionex Accelerated Solvent Extraction (ASE) device. Activated copper was used to remove elemental sulfur, solvent removed under a mild stream of nitrogen, and concentrated bitumen fractionated into saturated hydrocarbons, aromatic hydrocarbons, and polar non-hydrocarbon compounds using small- scale open column liquid chromatography; protocol was modified after Bastow et al (Bastow et al “Rapid small-scale separation of saturate, aromatic and polar compounds in petroleum”, 2007). Samples were re-suspended in dichloromethane and activated copper was added to remove elemental sulfur from the samples. Copper beads were activated using a weak HCl solution and then rinsed with de-ionized water until the pH neutralized. Activated copper was added to the total lipid extract (TLE) and left for 30 minutes. The elemental sulfur
reacted with the activated copper forming black copper sulfide. This process was repeated until there was no change in the color of the copper.

The bitumen samples were subsequently transferred to the top of an open silica gel-packed Pasteur pipette column. When the TLE sample had dried, another rinsing was added on top of the column. This process was repeated 4 times. Using Three-Fraction Column Chromatography the saturates, aromatics and polar fractions are extracted in sequence. The extraction was done by adding solvents, in series, to the column (eluting the column). Saturates and unsaturates are extracted first by eluting with hexane. Aromatics are collected using a 1:1 ratio of hexane and DCM. The samples are collected in 4ml vials and allowed to dry in the atmosphere, the aliquots were transferred to 2ml vials with adapters for gas chromatography mass spectrometry (GC-MS) analysis.

Following the extraction of bitumen, approximately 40g of the residual rock powders were decalcified with 6N HCl; this process was done for samples from the 7Y-3 core of the Coppercap Formation. Upon cessation of the reaction, the samples were rinsed with DI water to neutrality, dried and again extracted with hexane to recover bitumen that was previous inaccessible due to occlusion within the minerals (bitumen-2). The samples were extracted three times by ultra-sonication and the solvent extracts were transferred to 60 mL vials. The bitumen-2 total lipid extracts (TLE) were evaporated under constant N₂ flow in a Turbovap device and treated like described earlier for the first bitumen extraction.

Aliquots of 1 μL of the saturated and aromatic, respectively, hydrocarbon fractions were analyzed by an Agilent 5971 mass-selective detector (MSD) coupled to an Agilent 5975C gas chromatograph (GC). The GC was equipped with a DB-1 MS column (60m, 0.25mm, 0.25μm) for the analysis of saturated hydrocarbons and with a DB-5 MS column (60m, 0.25mm, 0.25μm) for the analysis of aromatic hydrocarbons. Saturates and aromatic hydrocarbons were analyzed in single ion
monitoring (SIM) modes and quantified in relation to internal standards. No corrections were made for different response factors.

For the analysis of steranes, aliquots of 1 μL of the saturated hydrocarbon fraction were analyzed by the Autospec Ultima magnetic sector MS, coupled to a gas chromatograph that was fitted with a DB-1 MS column (60m, 0.25mm, 0.25 μm). The MS was operated in a metastable reaction monitoring (MRM), scanning the transitions: 372-217, 386-217, 400-217, 414-217, 414-231, 404-221. Target compounds were quantified by comparison to internal standards assuming a uniform response.
Chapter 4 Gorge Creek:

Abstract

Geochemical analysis of sedimentary rocks provides evidence of the evolution of environmental changes in atmospheric, oceanic, volcanic, and biological systems. Stable isotope analysis of Archean sedimentary rocks can help place constraints redox conditions in the atmosphere and ocean as well as yield information regarding the antiquity of different metabolic processes. In this study, we report high-precision quadruple sulfur isotope analyses ($^{32}\text{S}/^{34}\text{S}/^{36}\text{S}$) of sulfides in the organic rich black shale turbidite section of the 3.2 Ga Gorge Creek Group in Western Australia. Based on the quadruple sulfur isotope systematics ($\delta^{34}\text{S}-\Delta^{33}\text{S}-\Delta^{36}\text{S}$), our results suggest that isotopic variation in the Mesoarchean deep ocean are mainly controlled by a combination of non-mass dependent sulfur aerosol inputs and bacterial sulfur disproportionators. All samples yield distinct non-mass-dependent signatures with a $\Delta^{34}\text{S}/\Delta^{33}\text{S}$ slope of $\sim0.96$. Gorge Creek samples have $+\Delta^{33}\text{S}$ with $\delta^{34}\text{S}$ ranging from $-6\%$ to $8\%$, representing different communities utilizing aerosol elemental sulfur and its byproducts from other metabolisms. This supports the evidence of active microbial sulfur disproportionation in the Mesoarchean and alludes to the existence of different sulfur utilizing communities in the coastal slopes and in the deeper ocean.

4.1 Introduction:

In the Archean before the Great Oxidation Event (2450-2320 Ma), the ocean was thought to be iron rich and sulfur poor, reflective of a lack of oxygen to oxidate sulfides and remove $\text{Fe}^{2+}$ from the marine reservoir (Canfield et al., 2004). Mass independent fractionation of multiple sulfur isotopes occurs when the oxygen levels are below $10^{-5}$ PAL (present atmospheric level) (Farquhar et al., 2000). Production and preservation of a MIF signal in an oxygenated environment is difficult as ozone shields UV photolysis and would oxidize distinct sulfur species. While the origin of non-mass- dependent fractionation of sulfur is still debated (Farquhar et al., 2001; Ohmoto et al., 2006), laboratory experiments of $\text{SO}_2$ photolysis (Farquhar et al., 2001) have been correlated with observed trends on minor sulfur isotopes in pre- 2.4 Ga sedimentary rocks. This suggests that $\text{SO}_2$ photodisassociation, at oxygen concentrations less $10^{-5}$ PAL, breaking into elemental sulfur and sulfate yielding a $+\Delta^{33}\text{S}$ and a $-\Delta^{33}\text{S}$, respectively, is likely the source of the Archean MIF signal (e.g. Ono et
These values along with $\delta^{34}S_{pyrite}$ can help explain what metabolic processes were taking place and from what substrate they originated. In this study core samples from the black shale turbidite section of Gorge Creek Group, Pilbara, Western Australia (~3.2Ga) (Buick et al., 2002), are analyzed to determine the main contributors to organic matter in the beginning of the Mesoarchean.

### 4.2 Gorge Creek Geologic Background:

Samples used in this study are from the SSD-14 and SSD-18 cores taken from the Sulfur Springs area of the Kelly Greenstone Belt within the Archean Pilbara craton in Western Australia. Pilbara is home to some of the oldest and best preserved samples for the mid-Archean and late Archean. The Gorge Creek Group of Eastern Pilbara is underlain by the Warrawoona Group. The Warrawoona Group is comprised dominantly of greenschist volcanic rocks, but also contains smaller stratigraphic areas of mafic, felsic, sedimentary and intrusive rocks (Van Kranendonk et al., 2002).

The Sulfur Springs Group, directly underlying the Gorge Creek Group, consists of the oldest known volcanic massive sulfide (VMS)-type base metal deposits, volcanoclastic rocks and mudstone. VMS-type felsic mineralization of the Six Mile Creek Group is overlain by the Strelley Granite. This is then followed by sections of wacke and then the felsic volcanic rocks of the Kangaroo Caves Formation. Geochemical and structural analysis of the Sulfur Springs Strelley Granite and Kangaroo Caves demonstrate that they are a cogenic suite (Vearncombe et al., 1996). The Strelley Granite led to hydrothermal circulation which caused the deposition of Cu-Zn-type volcanic massive sulfide deposits in the Kangaroo Caves Formation (Vearncombe et al., 1996). This hydrothermal circulation, however, preceded the deposition of the sedimentary section of the Gorge Creek Group and is not thought to have altered the primary geochemical signals.
Figure 6: Gorge Creek Group Stratigraphy: Image modified from Buick (2002) showing the geological background behind the Gorge Creek Group. Gorge Creek Group is magnified with the section representing the mudrock layers cores SSD-14 and SSD-18 that were analyzed in this study.

Samples analyzed in this study come from the lower section of the Gorge Creek Group in the Soanesville Subgroup. Samples are located within the Corboy Formation of the Gorge Creek Group that is composed of sandstone, grey wacke, pebble and pebble conglomerate with shale deposited in local areas. East of the Strelley granite, the Corboy sequence is composed of meters thick sandy turbidite beds with a conglomerate base. The layers are downwards oriented into the marker chert of the lower Sulfur Springs Group. Above the Corboy sequence lays the Paddy Market Formation which is composed of shales and mudstones that have undergone silicification to chert. Eriksson et al. (1981) examined the Corboy and Paddy Markey Formation concluding that the
sedimentology of these sequences represent a platform (alluvial) to trough (turbidite) facies relationship with no evidence of a shallow marine shelf facies (Vearncombe et al, 1996).

4.3 Results

Samples from The Gorge Creek Group from the SSD-14 and SSD-18 diamond drilled cores were analyzed for organic carbon isotopes, organic nitrogen isotopes, total organic carbon and multiple sulfur isotopes. Samples within the SSD-14 core and the SSD-18 core were selected for organic rich black shales of the Soanesville Subgroup, overlaying a sandstone clastic conglomerate and underlying the granite of the Honeyleater and Coenia Basalts.

Core samples from the SSD-14 Core were found to be anywhere from 15 to 58% carbonate by weight, averaging around 32%. The SSD-18 core ranged from 25% to 49% carbonate by weight, averaging at about 33%. The middle samples of each core section were the most carbonate poor while the upper layers of both cores were substantially more carbonate rich.

Approximately 15mg of hydrochloric acid digested rock powder were analyzed in the Elemental Analyzer for carbon and nitrogen. Total organic carbon (TOC) was found to be relatively high in both core samples, with values between 0.75% to 2.07% for the SSD-14 Core and 1.5% to 2.1% for the SSD-18 core, averaging 1.4% and 2.0% respectively. Organic Carbon $\delta^{13}C$ isotopic values were measures have minimal variation and lie around -30‰. The more organic rich middle section was found to have slightly more depleted values encompasses a 3‰ difference from the lowest samples of the section analyzed.

Organic nitrogen values were found to be high compared to other Archean samples, ranging from 0.047% to .103% in the SSD-14 core and from 0.030% to 0.079% in the SSD-18 core. The
\( \delta^{15}N \) nitrogen isotopic values for both cores averaged at 2\% with values nominally changing throughout the analyzed samples. Enrichments of 2\% were seen in the middle of the section where more depleted \( \delta^{13}C \) values were observed. The ratio of Carbon to Nitrogen (C/N) ranged from 10.6 to 31.85 in SSD-14 core and 20.2 to 48\% in the SSD-18 core.

Sulfur isotope values based on ~2g powdered rock for \( \delta^{34}S \) V-CDT yielded values mostly within \( \pm 1\% \). Error in sample processing by fluorination is +/-0.2\%. The middle samples that were less carbonate rich and had more depleted \( \delta^{13}C_{\text{org}} \) and enriched \( \delta^{15}N_{\text{org}} \) values have enriched \( \delta^{34}S_{\text{py}} \) values of up to 3.79\% in the SSD-14 core and 9.33\% in the SSD-18 core. \( \Delta^{33}S \) values demonstrate Mass Independent Fractionation (MIF) and are all positive (> 0) values. \( \Delta^{33}S \) values go up to +1.32\% in the SSD-14 core and +2.37\% in the SSD-14 core. Values for \( \Delta^{36}S \) are all negative (< 0) and have a minimum value of -1.29\% in the SSD-14 core and -1.22\% in the SSD-18 core.

\( \Delta^{34}S \) values when plotted against the \( \Delta^{36}S \) values for the SSD-14 core yield a slope of \( y = -0.9197 - 0.112 \) for the SSD-14 core (\( R^2 = .9824 \)). \( \Delta^{33}S \) versus \( \Delta^{36}S \) for the SSD-18 yields a slope of \( y = -0.8915x - 0.1169 \) (with \( R^2 = 0.981 \)).
Figure 7: Data Table: Gorge Creek, Pilbara, Western Australia  Core SSD-14

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38
Figure 8. Data Table: Gorge Creek, Pilbara, Western Australia Core SSD-18

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<tr>
<td>218.6</td>
<td>15.21</td>
<td>2.7</td>
<td>-31.9</td>
<td>26.1%</td>
<td>0.079</td>
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<td>33.7</td>
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<tr>
<td>229.1</td>
<td>17.94</td>
<td>1.8</td>
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<td>42.0%</td>
<td>0.063</td>
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<tr>
<td>237</td>
<td>12.93</td>
<td>2.0</td>
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<td>25.5%</td>
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<td>3.1</td>
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<tr>
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<td>18.59</td>
<td>1.9</td>
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<td>27.1%</td>
<td>0.039</td>
<td>2.4</td>
<td>48.3</td>
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</table>
Figure 9: Stratigraphic section for SSD-14 along with measured values.
Figure 10: Stratigraphic section of SSD-18 core with measured values.

41
Figure 11: $\Delta^{33}S / \Delta^{34}S$ plot for SSD-14 centered at 0 showing a slope of -1.06

Figure 12: $\Delta^{33}S / \Delta^{34}S$ plot for SSD-18 centered at 0 showing a slope of -1.0
4.4 Discussion:

4.4.1 Diagenetic concerns:

The area of the Soanesville Belt (previously referred to as the Soaneville syncline and the Strelly Belt) have been studied in depth for its mineralogical content, volcanic sediments with concentration especially focused on the Sulfur Springs and Kangaroo Caves VMS (volcanic massive sulfide) deposit, the oldest known VMS deposit dates at 3.2Ga (Veamecombe et al., 1995; Buick et al., 2002). With the hydrothermal deposits below and igneous intrusions throughout the Soanesville, whether the primary geochemical signals were or were not influenced by thermal or fluid alteration was considered.

While the uppermost rocks of the Sulfur Springs Group show distinct characteristics of hydrothermal alteration, the uncomfortably deposited basal rocks of the Gorge Creek Group have no evidence of alteration (Buick et al., 2002; Morant, 1995; Morant, 1998). In the Sulfur Springs Group, block-faults radiate from the upper surface of the Strelley Grainite (Veamecombe et al., 1998); these block-faults, however die out before reaching the Gorge Creek Group. Additionally, samples from Gorge Creek and Sulfur Springs Group, analyzed by Duck et al. (2007) showed preserved organic matter (hydrothermal microbial remains) within the chert layer. The oil reflectance index of these organic matter bundles and of the samples indicate that temperatures never exceeded 90°C-100°C.
4.4.2 Deep Marine environment:

The nature of the Archean deep sea and the biogeochemical cycling of the deep ocean remain a mystery (Canfield et al., 2004). Most Precambrian preserved rock samples record coastal shelf environments above the fair weather wave base, allowing for interpretation of only samples within shallower waters or basin environments.

A kerogen rich shale matrix is present within these brecciated samples. The boundary between the Sulfur Springs Group and the Gorge Creek Group was subsequently scoured and eroded, showing a hiatus in the depositional sequence (Brauhart et al., 1999; Buick et al., 2002). This marker chert has been interpreted as a change in sedimentation from volcanoclastic to epiclastic sediments (Morant, 1995; Morant, 1998).

Sulfur Springs Group and Gorge Creek Group have both been interpreted as being deposited in deep marine environments (Vearncombe et al., 1995; Morant, 1995; Buick et al., 2002). This has been evidenced by pillow andesites and basalts and unbrecciated volcanic rocks (due to underwater pressure). Additionally, Gorge Creek Group has been classified as showing turbidite lithologies. The turbidite demonstrates laterally interfingered relationships. The lowermost turbidite, which is analyzed in this study, is composed of sandstone and siltstone lithofacies that shows characteristic cyclicity in the turbidite divisions of Bourma divisions A, B, minor C, D and E(t) (Vearncombe et al., 1999). Due to differing stratigraphic depths in different drill sites and representations in the lithology, official divisions between the Sulfur Springs Group and the Gorge Creek Group differ (Van Kranendonk and Morant, 1997; 1998, Buick, 2002). The divisions marked in Van Kranendonk and Morant (1998) as adopted by Buick et al. (2002) and lithological descriptions are used in this study.
4.4.3 Nitrogen Weight Percent and N/C

Organic nitrogen by weight percent was found to be between 0.06% to 0.1%. These values are common within Precambrian sediments, and represent an overall decreased amount of biomass present in the sediments. When compared to overall carbon content values, N/C closely resemble those estimated by Beaumont and Robert (1999) with values averaging 0.0075.

4.4.4 $\delta^{13}C_{org}$ and TOC

Throughout the two sections $\delta^{13}C_{org}$ and TOC vary moderately. The relatively stable $^4$C isotopic composition in both the SSD-14 and SSD-18 cores show that there was little change in the prominent biogenic processes during the deposition of the section. The isotopic values for $\delta^{13}C_{org}$ range from -35‰ to -25‰ with a mean value of -30‰. While values of -25‰ are representative of TCA reverse biogenic fractionation, the slightly more depleted values seen in the Gorge Creek samples could be representative other organisms such as produced by methanotrophs (Hayes et al., 2001). Duck et al. (2007) and Buick (personal communication) analyzed samples from upper Sulfur Springs and the lower section of Gorge Creek Group and found values to be within the same range. Values in Sulfur Springs Group near the VMS, however, yielded enriched values near -25‰ indicating thermal alteration of the section as a result of hydrothermal fluids. Additionally, the range of values for $\delta^{13}C_{org}$ found in this study are consistent with previously published values for Archean organic rich sediments (Schidlowski et al., 2001).

In the SSD-14 core, $\delta^{13}C_{org}$ results show an overall trend towards more enriched values (from -35‰ to -30‰) while $\delta^{13}C_{org}$ values in the SSD-18 core remains constant (variations of less than 1.5‰). The 5‰ enrichment can be representative of many different factors; it could represent thermal alteration, changes in biogenic processes or a change in lithology. Thermal alteration is an unlikely cause of change since thermal alteration usually occurs closer to chert interbedding, while
the gradual trend towards heavier values in this section is the opposite of the trend observed by Duck et al. (2007). Likely, this shift would be in part a result of changing lithologies in the Bourma sequence leading to input from more proximal facies along the continental slope (Vearncombe, 1999).

Values for TOC are consistent with values for organic rich sediments. Slight variation in TOC occurs through the sections, but have no correlation to $\delta^{13}$C$_{org}$. TOC values averaging at 2% indicate a source of reduced organic matter and the possibility of finding trapped hydrocarbons.

4.4.5 Sulfur Concentrations and Multiple Sulfur Isotopes

$\delta^{34}$S$_{pyrite}$ values are centered around 0‰ with a trend of enrichment for half the section. This is followed by a depletion of $\delta^{34}$S$_{pyrite}$ values up to 9‰ (in SSD-18) over the height of less than 10m, and then another enrichment cycle. These cycles could indicate a sudden change in biological activity or depositional environment taking place over a short stratigraphic section.

Based on lithological constraints of the Gorge Creek Group and observed trends in the stable isotopes, the variations in $\delta^{34}$S$_{pyrite}$ can be explained by the deposition of a new unit of the Bourma sequence that contains sulfide that resulted from the deposition of elemental sulfur aerosols through chemical or biological reduction of sulfur (Ono et al., 2003; Farquhar et al., 2001) coupled with microbial sulfate reduction of new sulfate (Ueno et al., 2008). The variation within $\delta^{34}$S$_{pyrite}$ and positive $\Delta^{33}$S indicate a more complex system of the Meso-Archean sulfur cycling system with co-occurring deposition of microbial sulfate reduction and microbial sulfur disproportionation (Canfield and Thamdurp, 1994).
Anomalous sulfur fractionations of the minor sulfur isotopes, $^{33}$S and $^{34}$S, have been shown in sedimentary rocks prior to 2.4Ga (Farquhar et al., 2000). Photolysis of SO$_2$ in low oxygen conditions ($O_2$ levels less than $10^{-5}$ that of present atmospheric levels) yields two anomalous reservoirs of sulfur aerosols, elemental sulfur and sulfate particles (Farquhar et al., 2000). While elemental sulfur bears a positive $\Delta^{33}$S value, sulfate will possess a negative $\Delta^{33}$S signal. This division allows for tracking of sulfur microorganism metabolic processes as both signatures $\Delta^{33}$S are maintained even after secondary microorganism metabolism. Additionally, Pavlov and Kasting (2002) demonstrated that under atmospheric conditions where oxygen < $10^{-5}$ that the independent
sulfur reservoirs will not undergo oxygenation or homogenization during fall out and are able to be deposited in the ocean and in sediments maintaining their primary photolysis signature.

Investigations into the isotopic effects of these two sulfur end members has lead to an increasingly more clear image of the metabolic processing of organisms and their resultant isotopic compositions. Non- mass dependent elemental sulfur will contain $+\Delta^{33}\text{S}$ values representative of the elemental sulfur input, and $+\delta^{34}\text{S}$, while non-mass dependent sulfate will yield $-\Delta^{33}\text{S}$ and $-\delta^{34}\text{S}$. The mixing of these two reservoirs accounts for the variation found within $\Delta^{33}\text{S}$ of the samples (Farquhar et al., 2000). Microbial sulfate reduction, utilizing the sulfate aerosols, will lead to the formation of pyrite with $-\Delta^{33}\text{S}$ and $-\delta^{34}\text{S}$; however, under a restricted sulfate pool undergoing Rayleigh distillation, $\delta^{34}\text{S}$ will become enriched leading to $+\delta^{34}\text{S}$ values. Microbial sulfur disproportionation will use $+\Delta^{33}\text{S}$ elemental sulfur and will yield pyrite with values of $-\delta^{34}\text{S}$. Subsequent microbial sulfate reduction of sulfate, however, can lead to $+\delta^{34}\text{S}$ values (Ueno et al., 2008).

Effects from samples mixing with sulfur from a mass dependently fractionized reservoir have been ruled out as a cause for the changes seen within $\Delta^{33}\text{S}$ and $\delta^{34}\text{S}$. $\Delta^{36}\text{S} / \Delta^{33}\text{S}$ shows the typical Archean slope of $\sim 0.9$ (Ono et al., 2003; Ueno et al., 2008; Ono et al., 2009). This slope likely represents the mixing line between elemental sulfur and sulfate reservoirs produced by the atmospheric photolysis reactions of SO$_2$ (e.g. Ono et al., 2003). While exact mechanisms are still not fully understood, this slope has been noted in Archean samples in different cratons and distinctly differs from the $\Delta^{36}\text{S} / \Delta^{33}\text{S}$ slope of post 2.4 Ga samples. Both cores were found to have an $R^2$ value of .95 or more.

The signatures present in Gorge Creek have $+\Delta^{33}\text{S}$ values ranging from 2.37‰ (SSD18-208.4m) and 0.03‰ (SSD18-239.5m). This variation between $\Delta^{33}\text{S}$ values in the core suggests a dominance of microbial sulfur disproportionation within the marine shelf environment. Large
amount of sediment could be deposited over very short periods of time, burying microbial communities in the sediment (Vearncombe et al., 1999). Under this scenario, sudden enrichments in $\delta^{34}$S (SSD18-229.1m) sudden jumps in isotopic composition would be possible as a new unit of turbidite flow is deposited. In this case, small concentrations of sulfate undergoing microbial sulfate reduction in the sediment could lead to the $+\delta^{34}$S that are observed over the sections. In the SSD-14 core which lies at a slightly higher level than the SSD-18 core, $\delta^{34}$S is mostly negative with sample SSD-14 147.5m lying having a value of 3.8‰. The $\sim$4‰ difference from samples lying $\pm$10m in the section indicates a sudden change in microbial activity or due to changes in sulfate concentrations. A small concentration of sulfate can lead to varied large fractionations of $\delta^{34}$S (Canfield et al., 2010) which is observed in Gorge Creek. Wacey et al. (2010), analyzed individual pyrite grains for sulfur isotopes from the 3.4 Ga Strelley Pool Formation and found evidence of both microbial sulfur disproportionation and sulfate reduction. The interpretation of both metabolic processes being present in the deeper depositional environment of Gorge Creek suggests that the open marine sedimentary hosted ecosystems had variable populations of sulfate reducers and sulfur disproportionators with a stronger prevalence for disproportionators in a sulfate limited ocean (Kah et al., 2004; Canfield et al., 2010).

Samples from Gorge Creek fill in a previously empty place in the Mesoarchean for multiple sulfur isotopes. These values for Gorge Creek are consistent with values present in the earlier Mesoarchean and 2.9Ga sections.
Conclusion

The Gorge Creek Group of Pilbara Western Australia yields $+\Delta^{34}S$ with varying values for $\delta^{34}S_{\text{pyrite}}$. These values suggest that microbial sulfur disproportionation was the main active sulfur metabolizing process taking place in the deep marine waters. Variations within the $\delta^{34}S_{\text{pyrite}}$ can be explained by small amounts of sulfate undergoing microbial sulfate reduction, though due to sulfate limitations, this process was not as active in the deep marine environment. Small concentrations of sulfate and turbidite influx of new sediment explains variations in isotopic data through the two cores.
Chapter 5: Coppercap Formation

Abstract:

The mechanisms that lead to the onset of the Late Proterozoic global glaciations remain unresolved, but can be correlated through globally observed chemostratigraphical changes. Here we present a geochemical record of paired carbonate associated sulfate ($\delta^{34}$S$_{CAS}$) and pyrite ($\delta^{34}$S$_{pyr}$), organic carbon ($\delta^{13}$C$_{org}$) and carbonate ($\delta^{13}$C$_{carb}$) along with lipid biomarker analysis of the Coppercap Formation in the Northwest Territories, Canada, which was deposited just prior to the onset of the Sturtian glaciation.

Trimethylarylisoprenoids carotenoid-derived lipids indicative of purple and green sulfur bacteria were found throughout the section and indicate persistent euxinia in the shallow sediments deposited in a syn-rift basin. We observe an average $\Delta^{34}$S$_{CAS-pyr}$ of $\sim$ 25‰ which is typical for Neoproterozoic deposits. Increased burial of organic carbon and sedimentary sulfide is implicated from an isotopic shift in $\delta^{13}$C$_{carb}$ and $\delta^{34}$S$_{CAS}$. Severe euxinic conditions mid-section is evidenced from increased concentrations of aryl-isoprenoids and which coincides with a $\sim$15‰ increase in $\delta^{34}$S$_{CAS}$, showing an interplay between more restricted conditions and marine ingressions. The implications of these geochemical signals and biomarker distributions are placed into a context of the onset of the Late Proterozoic glaciations.
5.1 Introduction

During the Neoproterozoic time period the Earth underwent severe climatic changes that were accompanied by large shifts in the isotopic record. Environmental perturbation during the Cryogenian included tectonic activity, changes of biogeochemical cycling and within marine chemistry (Hayes et al., 1994; Rothman et al., 2003). A large $\delta^{13}C_{\text{carb}}$ excursion is witnessed during the Prestrutian, which has been explained by large removal of organic carbon from the system by burial (e.g. Macdonald et al., 2010). Additionally, evidence for a sulfidic ocean has implications on the evolution of metazoans, as many animals would not have been able to survive in anoxic euxinic waters (Kaufman et al., 2007). An anoxic ocean could have allowed for organic material to be buried without being oxidized. Organic matter pellets and increased organic carbon burial has been used as the mechanism for accumulation of oxygen in the water column buried (Logan et al., 1995). Chapter 5 examines the changes in the Neoproterozoic by examining the $\sim$730 Ma Coppercap Formation of the MacKenzie Mountains in Northwestern Canada. This section, deposited directly before the Sturtian glaciations, represents a shallow marine depositional environment and records the biogeochemical cycling at the onset of the glaciation. Sulfur and carbon stable isotope analysis is used to interpret geochemical cycles along with lipid biomarker (steranes and hopanes) to deduce environmental and biological changes of the Late Neoproterozoic.

5.2 Geologic Setting

The MacKenzie Mountains encompass a sedimentary rock sequence deposited before and during the break-up of the supercontinent Rodinia and the subsequent opening of the proto-Pacific Ocean. The Windermere Supergroup in the MacKenzie Mountains records the rifting, subsidence...
and evolution of a passive margin in the low latitudes. The sedimentary succession documents shallow shelf to continental slope deposits with shallower sediments in the northeast and deeper successions in the southwest orientation (Narbonne and Aikten, 1995). The Coppercap Formation lies directly above the Redstone River Formation and below the Sayunei Formation in the Rapitan Group, separated by a few meters of siltstone.

**Figure 14: Map of the Coppercap Formation.** The Coppercap Formation is located in the MacKenzie Mountains near the border of the Northwest Territories and Yukon (Image: Google Earth).
Figure 15: Stratigraphy of the Coppercap Formation. Underlying the Coppercap Formation is the Redstone River. The area of CP1 consists of a transitory section between the Redstone River and the Coppercap including sandstone siltstone facies with copper and bornite mineralization. Evaporites from this lower section were analyzed biomarkers and sulfur isotopes in the 76Y-4 core. Samples in the 77Y-3 core begin at CP2.
Figure 16: James et al (2001) diagram of the Windermere Supergroup, showing the subsiding basin that the Coates Lake Group was deposited.

Figure 17. Photograph of the transition from the MacKenzie Mountain Supergroup to the Windermere Supergroup in Northwest Territories, Canada, showing the Coates Lake Group. (Image modified from Northwest Territories Geoscience, www.nwtgeoscience.ca)
Deposition of the Coates Lake Group occurred during active crustal extension (Jefferson and Ruelle, 1986). The Coates Lake Group is not continuous in some places and has extremely variable thicknesses forming in many areas wedges bound by unconformities. Isopach maps of the Mackenzie mountains indicates thickening towards the southwest (Aitken and Long, 1978) along with parallelism between the isopachs and fold axes leading to only a slight distortion from predeformational configurations. Despite this tectonic deformation, the organic matter in the Coppercap samples were found to be immature and extremely well preserved (Aitken and Long, 1978). Additionally, bornite minerals have been identified in the lower section of the Coppercap Formation. Bornite has an upper thermal stability of 125°C indicating that temperatures during diagenesis of the Coppercap Formation did not exceed 125 °C.

The lithology of the Coppercap Formation changes between grainstone and organic carbon rich limestone rhythmite/ micrite. At the top, there is a thin evaporite layer between two layers of grainstone. The section is capped with a layer of diamictite (though the samples in this study do not go into the diamictite layer). Ages attributed to the Coates Lake Group range from 780 Ma to 735 Ma. The Sturtian and Marinoan in age with the Coppercap Formation dating to the ~733Ma (Rooney, 2011) based on Re-Os dating.
5.3 Results

Samples from the Coppercap Formation from the 76Y-4 and 77Y-3 diamond drilled cores were analyzed for carbonate carbon isotopes, oxygen isotopes, organic carbon isotopes, total organic carbon, multiple sulfur isotopes, as well as for taxa specific hydrocarbon biomarkers. Samples within the 77Y-3 core were analyzed for carbonate and organic carbon, oxygen and multiple sulfur isotopes as well as biomarkers. Samples within the 76Y-4 core were analyzed for carbonate and organic carbon, oxygen isotopes and biomarkers. Samples were selected from each core to span the height of a ~400 meter section while leaving out samples from the copper mineralization at the base. For that reason, the analyzed sections begin at ~80m from the base of the Coppercap Formation.

Carbonate content was found to be varied in the section. The lower CP2-3 units yielded a low carbonate content compared to CP4 and CP5. The carbonate content rises in with the mass flow turbidity limestone layer in CP5 having the largest carbonate composition at ~97%. CP6 values drop sharply to a 30% carbonate composition within the grainstone and breccias units (Figure 29).

For the 77Y-3 core, the $\delta^{18}$O$_{carb}$ varies between values of -10.8‰ to 0.4‰ with values averaging at -4.69‰ (Figure 29). There is a slight depletion $\delta^{18}$O$_{carb}$ towards the top of the section in CP6. $\delta^{13}$C$_{carb}$ values vary from -5.7‰ to 7.4‰. The values steadily increase through 300m from the base, reaching the maximum positive values in the area of CP5-CP6 boundary between the layer of limestone and the layer of grainstone, and then decrease in the last 50m down to 1.86‰. In a $\delta^{13}$C$_{carb}$ against $\delta^{18}$O$_{carb}$ plot (Figure 29), there is a general "shotgun" scattered pattern observed located on the negative $\delta^{18}$O$_{carb}$ side (as only one value for $\delta^{18}$O$_{carb}$>0). The $\delta^{13}$C$_{carb}$ are divided in the plot, with negative values in CP2-3 and positive values in CP4 and higher. The 15‰ difference in $\delta^{13}$C$_{carb}$
accounts for all variation in the $\delta^{18}O_{\text{carb}}$ and $\delta^{13}C_{\text{carb}}$. No clear correlation was observed between $\delta^{18}O_{\text{carb}}$ and $\delta^{13}C_{\text{carb}}$.

Total organic carbon (TOC) values averaged at 0.24% throughout the section with little variation (Figure 29). The TOC values were highest in the limestone rhythmite sections averaging 0.3%. 77Y-3 sample 156 had the highest TOC value at 0.42% lying in a thin layer of limestone between two layers of grainstone. This depth is also correlated with a decrease in $\delta^{34}S_{\text{pyrite}}$ and a sudden increase in the value of $\delta^{13}C_{\text{carbonate}}$. The areas with the lowest TOC were the CP6 area, with breccias and evaporites, with values averaging at 0.15%.

$\delta^{13}C_{\text{org}}$ values range from -34.0% to -16.5% and co-vary with the $\delta^{13}C_{\text{carb}}$ values. At the base of the formation, $\delta^{13}C_{\text{org}}$ are more variable, possibly associated with lower TOC values. $\delta^{13}C_{\text{org}}$ fluctuate less in the CP4 range and begin to steadily increase with small variations until CP6, decreasing to the minimum value at the boundary of CP6. The values then diverge from the $\delta^{13}C_{\text{carb}}$ and are slightly enriched in the breccias layer.

The difference between $\delta^{13}C_{\text{org}}$ and $\delta^{13}C_{\text{carb}}$ vary slightly with lithology, but remains fairly constant throughout the section, averaging at 26% difference (Figure 29). The largest differences in values are found in the TOC rich limestone rhythmite layers.

$\delta^{34}S_{\text{pyrite}}$ range between -26.2% and 11.6% with error for $\delta^{34}S$ at +/- 0.2%. The more depleted values are found in the base of the limestone section of CP2-3 (Figure 28). Values generally become more enriched, close to a value of 0%, until the base of the limestone section in CP4. Between the first grainstone unit and the limestone unit the maximum enriched value of 11.57% is observed. In the second grainstone unit, the values become depleted again to the near 0% values. In CP5 and CP6 $\delta^{34}S_{\text{pyrite}}$ values become further depleted, with values in the brecciated unit at -22.82%. The depletion in the top unit coincides with the changes in $\delta^{13}C_{\text{org}}$ and $\delta^{13}C_{\text{carb}}$ values. There is a strong positive correlation between the carbonate composition and the $\delta^{34}S_{\text{pyrite}}$ (%) where
increasing carbonate content is related to positive excursions in the $\delta^{34}S_{\text{pyrite}}$ values. The $\delta^{34}S_{\text{pyrite}}$ values become higher within the limestone rhythmite sections and lower within the grainstone layers. $\delta^{34}S_{\text{pyrite}}$ increase slightly within the evaporite layer and decrease again in the grainstone top layer. There is a 20% difference from the most enriched $\delta^{34}S_{\text{pyrite}}$ value, in the grainstone layer of CP4, and the most depleted $\delta^{34}S_{\text{pyrite}}$ values, in the brecciated unit of CP6 (Figure 28).

$\Delta^{34}S$ values for the $S_{\text{pyrite}}$ extraction range from 0.2% to -0.08%. Small positive values are observed at the base of the section and varying slightly positive and slightly negative values continue into the base of the first grainstone unit in CP4. Values higher in the section are negative through the grainstone and limestone units of CP6. The $\Delta^{34}S$ values become positive and increase to the maximum value in the brecciated layers on top. $\Delta^{34}S$ values for $S_{\text{pyrite}}$ extraction range from -1.79% to 0.57% following the same trends in change as $\Delta^{34}S_{\text{pyrite}}$. When $\Delta^{34}S$ is plotted against $\Delta^{34}S$, it yields a line with a slope of $y = -6.74x$.

$S_{\text{CAS}}$ was ran on samples in the middle of the section, CP3, CP4 and CP5, which have a lower pyrite weight percent and higher carbonate content. These samples were selected to minimize the effects of pyrite oxidation. $\delta^{34}S_{\text{CAS}}$ values range from -0.9% to 41.0% (Figure 26). In CP3 enriched samples are observed while in CP4 slightly less enriched values are present. In CP5 $\delta^{34}S_{\text{CAS}}$ remain enriched, with a decrease at the boundary between CP5 and CP6 between the limestone and grainstone units. Values decrease through CP6, but are higher in the brecciated layer near the exposure surface. When compared to $\delta^{34}S_{\text{pyrite}}$, there is a 24% offset on average between the two values, with the largest difference being 36.9% and the smallest being 9.79%. The largest differences are observed at the base of CP4 between the limestone layer of CP3 and the grainstone layer of CP4. The smallest difference between $\delta^{34}S_{\text{CAS}}$ and $\delta^{34}S_{\text{pyrite}}$ is observed at the boundary of the breccias in CP6. These location coincide with changes in $\delta^{34}S_{\text{pyrite}}$, $\delta^{13}C_{\text{org}}$ and $\delta^{13}C_{\text{carb}}$. The analysis of
sterane biomarkers yields an inverse relationship between pristane to phytane ratio to $\delta^{29}$S$_{prist}$. Lower pristine/ phytane ratios were observed in the middle of section.

The sum of 2,3,4-substituted and 2,3,6- substituted aryl- isoprenoids ($\Sigma 2,3,4$ and $\Sigma 2,3,6$) indicates the relative prominence of purple sulfur bacteria and green sulfur bacteria in all samples in the Coppercap Formation. In the studied samples the two cores, both series of aryl-isoprenoids are present in significant amounts. Since green and purple sulfur bacteria are require hydrogen sulfide and light, this suggests the presence of reduced sulfur species in the shallow photic zone.

![MRM 9 Channel El+ 134.109>134.109](image)

**Figure 18 2,3,4-substituted and 2,3,6- substituted aryl- isoprenoids** for sample 77Y-3 136 ($\Sigma 2,3,4$ and $\Sigma 2,3,6$): Presence of green and purple sulfur bacteria were found in all samples within the 77Y-3 and 76Y-4 cores. Green and purple sulfur bacteria require hydrogen sulfide and light.

High concentrations of 2α-methylhopane and 3β-methylhopane were found to be present in all samples. 2α-methylhopane index values were found to be as high as 6, while 3β-methylhopane index values were as high at 7.5 (Figure 30).
Figure 19: 2α-methylhopane and 3β-methylhopane for sample 77Y-3 136. All samples contained high values for both hopanoid structures.

The chromatogram for (C_{27}) and (C_{30}) steranes for sample 77Y-3 136 are displayed below with the relevant peaks labeled. The first four peaks (Figure 20) are: βα 20S, βα 20R, αβ 20R, αβ 20S (Figure 21). These peaks are representative of diasteranes, which are sterols that are converted during diagenesis. It is assumed that this conversion takes place when acidic sites on clay catalyze the sterols. This saturates a double bond in the sterols during catagenesis leads results in diasteranes. The second set of peaks (Figure 21) are: αα S, αββ R, αββ S and αα R, respectively. These peaks are representative of steranes.

Diasterane to sterane ratios are examined to the degree of catagenesis and temperature degradation that has occurred to the steranes. The low diasterane/sterane ratios are commonly associated with carbonate source rock. There is better preservation in environments with lower diasterane/sterane ratios since it is representative of a higher pH, anoxic environment. The high diasterane/sterane ratios are commonly associated with abundant clays and organic lean carbonates.
There is poor preservation in environments with high diasterane/sterane ratios since it is representative of a lower pH, oxic environment.

Figure 20. C27 chromatograph for Coppercap Sample 132 with labeled peaks. Diasterane peaks and sterane peaks come out clearly for all samples and for all ranges evaluated in MRM mode analysis.

<table>
<thead>
<tr>
<th>Peak Label</th>
<th>Compound Name</th>
<th>Compound Class</th>
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<tbody>
<tr>
<td>A</td>
<td>βα 20S</td>
<td>Diasterane</td>
</tr>
<tr>
<td>B</td>
<td>βα 20R</td>
<td>Diasterane</td>
</tr>
<tr>
<td>C</td>
<td>αβ 20R</td>
<td>Diasterane</td>
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<tr>
<td>D</td>
<td>αβ 20S</td>
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<td>E</td>
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</tr>
<tr>
<td>H</td>
<td>αα R</td>
<td>Sterane</td>
</tr>
</tbody>
</table>

Figure 21: Compound names and classes for diasterane and sterane peaks in MRM chromatographs. Each represents a broken down part of the hydrocarbon chain.
For all samples, very clear individual peaks for diasteranes and steranes were observed. This shows that the samples have not been heavily biodegraded. The C₃₀ plot (Figure 20) is specific interest since C₃₀ n-propyl cholestane steranes are thought to be representative of marine pelagophytes (Moldowan, 1990).

![C₃₀ Chromatogram](image.png)

**Figure 22:** C₃₀ chromatogram for sample 77Y-3 136 showing individual peaks for diasterane and sterane peaks indicating minimal biodegradation and presence of marine pelagophytes.

In all samples C₃₀ peaks were found to be present with unique sterane peaks. This is indicative of marine pelagophytes being present throughout the Coppercap Formation indicating marine influence for all samples.

Isopropyl C₃₀ steranes are representative of demosponges, however, no evidence of isopropyl C₃₀ steranes were found in samples from either core.
Figure 23: Data Table: Coppercap Formation: 77Y-3 Sulfur from Pyrite
Coppercap Formation: 77Y-3 S pyrite:

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Figure 24: Data Table: Coppercap Formation: 77Y-3 Sulfur from CAS
Figure 25: Data Table: Coppercap Formation: 77Y-3 Carbon

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**Figure 26: Data Table: Coppercap Formation: 77Y-3 TOC, Oxygen and Carbonate %**

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Figure 27: Data Table: Coppercap Formation: 77Y-3 Molecular Biomarkers

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Figure 28: Coppercap Formation: 77Y-3 Stratigraphic Section with Sulfur Data
Figure 29: Coppercap Formation: 77Y-3 Stratigraphic Section with Carbon and Oxygen Data
Figure 30: Coppercap Formation: 77Y-3 Stratigraphic Section with Molecular Biomarker Data
Figure 31: Coppercap Formation: 77Y-3 Stratigraphic Section with Key Trends in Data

- Diamictite and Shale of Rapitan
  - No samples from this section

- Depletion of $\delta^{34}$S, $\delta^{34}$CAS, $\delta^{13}$Corg, $\delta^{13}$carb at CPS CP6 boundary

- Enrichment of $\delta^{34}$S, $\delta^{34}$CAS, $\delta^{13}$Corg, $\delta^{13}$carb at CP2-3 CP4 boundary

- Samples from CP2 and higher. Depleted $\delta^{34}$S, $\delta^{34}$CAS, $\delta^{13}$Corg, $\delta^{13}$carb values

- Base of Coppercap Formation
5.4 Discussion:

5.4.1 Diagenetic Considerations:

The stable isotope compositions and lipid biomarker preservations can be affected by a number of processes that can simultaneously alter the primary geochemical composition of carbonates. These processes include metamorphisms, fluid-rock interactions, early diagenesis, and dissolution of primary carbonate with secondary reprecipitation. The geochemical alteration of carbonates is thus necessary to examine the geochemical alteration of carbonates to distinguish primary signals from those arising from post-depositional alteration.

The stable oxygen and carbon isotope composition of limestones and dolostones have been analyzed to determine the post-depositional processes on carbonate lithologies (Kaufman et al., 1997). Depleted $\delta^{18}O_{\text{carb}}$ values are indicative of post-depositional isotopic exchange occurring between meteoric and hydrothermal fluids and the rock as a result of dissolution and reprecipitation carbonate cements. Positive correlations between $\delta^{18}O_{\text{carb}}$ and $\delta^{13}C_{\text{carb}}$ suggest that meteoric diagenesis potentially could have altered geochemical compositions. However, in the Coppercap Formation, we see no clear correlation between $\delta^{18}O_{\text{carb}}$ and $\delta^{13}C_{\text{carb}}$ (Figure 30).
Figure 32: Coppercap Formation $\delta^{18}O$ vs. $\delta^{13}C_{\text{carb}}$. Samples are marked in black with image modified from McFadden and Kelly (2011). Samples from the Coppercap Formation do not show significant evidence of diagenetic fluid alteration in the $\delta^{18}O$ vs. $\delta^{13}C_{\text{carb}}$ plot.

Data from the 77Y-3 and 76Y-4 cores are plotted in Figure 30 along with typical trends for diagenetic alterations. Our samples demonstrate variable $\delta^{13}C_{\text{carb}}$ values within the bounds that do not indicate secondary alteration. A large excursion is noted in the $\delta^{13}C_{\text{carb}}$, however no correlation between $\delta^{18}O_{\text{carb}}$ is apparent. The lower half of the stratigraphic section yields negative $\delta^{13}C_{\text{carb}}$ values, while the top half of the section yields positive $\delta^{18}O_{\text{carb}}$ values. The excursion in $\delta^{13}C_{\text{carb}}$ has been noted in the same 700-750 Ma time span in stratigraphic sections in Svalbard, Namibia and the Yukon (Macdonald et al., 2010). Correlations of the $\delta^{13}C_{\text{carb}}$ excursion with other sections prior to the Sturtian glaciation is here interpreted as a global trend being represented in $\delta^{13}C_{\text{carb}}$. Section CP6, however, may have been subjected to some sub-ice fluid flow, as samples show negative $\delta^{18}O_{\text{carb}}$ values (Corsetti and Kaufman, 2005). This leads us to be cautious of interpretations in CP6 as it is likely demonstrating both the signal of onset of glaciations and the isotopic trends and changes in environment leading up to greater glacial structures and that of the glaciations itself. It is
important to note that such alteration could be affecting the decrease in the $\delta^{13}$C$_{\text{carb}}$ isotopic values as well. However, the correlated changes in $\delta^{13}$C$_{\text{carb}}$ and $\delta^{18}$O$_{\text{carb}}$ have been present in various other Neoproterozoic sections (e.g. Macdonald, 2010; Hayes, 2001; Des Marias, 2001; Corsetti and Kaufman, 2005). In the Rainstorm Member of the Johnnie Formation in Death Valley, for example, samples of well preserved rocks yielded $\delta^{18}$O$_{\text{carb}}$ values of -6 to -11‰ (Hurtgen et al. 2005; Kaufman et al., 2007). Our values for the Coppercap Formation falling within this range suggest only minor resetting of the $\delta^{18}$O$_{\text{carb}}$ values. Since this maybe a signal of glacial alteration of samples directly below the Rapitan diamictite, CP6 $\delta^{13}$C$_{\text{carb}}$ and $\delta^{18}$O$_{\text{carb}}$ values are therefore considered in this study to provide insight to the first signs of onsetting glaciation.

An additional point can be raise based on the presence of copper and bornite mineralization in the Redstone River unit that underlies the Coppercap Formation. These minerals exclude a significant rise in temperature as the sulfidic bornite, deposited along the copper mineralizations is unstable above $\sim$125 °C during diagenesis. This temperature regime is below the stability threshold of most lipid biomarkers.

Biomarkers for hopanes and steranes were analyzed for 7 different thermal maturity parameters. These thermal maturity parameters are a ratio of a more thermally altered state of a molecule to the total sum of the altered and unaltered form. These samples were subsequently found to be very immature in the earliest stages of oil generation.
Figure 33: Thermal Maturity Parameters show that the Coppercap samples are relatively immature in the Early Oil Generation stage.

5.4.2 $\delta^{13}$C$_{\text{carb}}$ and $\delta^{13}$C$_{\text{org}}$

Prior to the onset of glaciations (850-500 Ma), minimal deviation is observed within the $\delta^{13}$C$_{\text{carb}}$ values with isotopic compositions lying between -1‰ and +4‰ (Kah et al., 1999). However, the time period between 850 Ma and 500 Ma is marked by globally sensed positive $\delta^{13}$C$_{\text{carb}}$ excursions that are individually interspersed with large negative excursions (between -2 and -6‰). These negative excursions have been correlated to the ice ages of the Late Neoproterozoic (Kaufman et al., 1997; Knoll et al., 1986).

In the Redstone River Formation, which grades conformably into the Coppercap Formation, Lustwerk (1990) observed positive $\delta^{13}$C$_{\text{carb}}$ values in the base of the Upper Redstone River Formation that became depleted to values of -3‰ near the top of the section. The ~-3‰ depleted
values from the top of the Redstone River Formation correlate with the values obtained in this study for the base of the Coppercap Formation. This negative excursion has been marked in several other sections during the Cryogenian, including sections further east in the MacKenzie Mountains in the Yukon, within Namibia and Svalbard (e.g. Macdonald, 2010). Within the CP2-3 section we see the last of the negative excursion with a recovery of values consistent to those observed prior to the excursion and then a further increase of $\delta^{13}$C$_{\text{org}}$ into more positive values.

![Image modified from Macdonald (2010) with Coppercap data in black. Red dots indicate samples from Svalbard, blue dots indicate samples from Namibia, and green dots indicate samples from the Yukon. Dates are from the top Franklin large igneous province in the Yukon, and are correlated with known U-Pb dates from Svalbard and Namibia. The Coppercap Formation is C-isotope correlated with previously published data to show comparable sizes of negative excursion going into the Sturtian Glaciation. Organic rich limestone from the Coppercap Formation has been dated to 733 ± 4 Ma (Rooney, 2011) matching the dated time spans of Yukon, Svalbard and Namibia sections. Subsequently, the $\delta^{13}$C$_{\text{org}}$ values in CP5 and CP6 signaling the initiation of changing climate as the values decrease by 6% over the course of ~30m of stratigraphic section. Positive values.]

Figure 34. Neoproterozoic $\delta^{13}$C$_{\text{org}}$: Image modified from Macdonald (2010) with Coppercap data in black. Red dots indicate samples from Svalbard, blue dots indicate samples from Namibia, and green dots indicate samples from the Yukon. Dates are from the top Franklin large igneous province in the Yukon, and are correlated with known U-Pb dates from Svalbard and Namibia. The Coppercap Formation is C-isotope correlated with previously published data to show comparable sizes of negative excursion going into the Sturtian Glaciation. Organic rich limestone from the Coppercap Formation has been dated to 733 ± 4 Ma (Rooney, 2011) matching the dated time spans of Yukon, Svalbard and Namibia sections.
\( \delta^{13}\text{C}_{\text{carb}} \) values suggest increased biological productivity and organic burial which leads to the drawdown of pCO\(_2\).

This increase in geochemical evidence for biological activity happens in the areas corresponding to CP4 and CP5 where biomarker abundances, especially that of total aryl-isoprenoids are especially high (See Figure 28 above). This trend is also recorded in the form of \( \delta^{13}\text{C}_{\text{org}} \) which largely covaries with \( \delta^{13}\text{C}_{\text{carb}} \). As the isotopic composition of \( \delta^{13}\text{C}_{\text{carb}} \) rise to more positive values, \( \delta^{13}\text{C}_{\text{org}} \) follows. In the CP4 and CP5 section with biological activity increasing and total aryl-isoprenoid concentrations increasing, the D\(^{13}\text{C} \) value (or difference between \( \delta^{13}\text{C}_{\text{carb}} \) and \( \delta^{13}\text{C}_{\text{org}} \)) decreases to a slightly lower value. This change could mark changes on the global scale as overall biological activity is decreasing across the earth as carbon dioxide levels decrease and temperatures drop. Alternately, it could be representative of a change from a domination of cyanobacteria biomass to an increased proportion of green sulfur bacteria and purple sulfur bacteria as isotopic fractionation begins to correlate with that produced by reverse TCA metabolic cycles (Hayes, 2001). However, this change is D\(^{13}\text{C} \) is not a unique trend as a decrease of up to 10% in D\(^{13}\text{C} \) has been recorded in age correlated stratigraphy across the 740-700Ma time span, in agreement with the timing of the Coppercap Formation’s deposition. Correlation with complimentary sections from the same time interval show identical trends in \( \delta^{13}\text{C}_{\text{carb}}, \delta^{13}\text{C}_{\text{org}} \) and D\(^{13}\text{C} \). This shows that the Coppercap Formation is yielding a similar trend to previously published values for \( \delta^{13}\text{C}_{\text{carb}} \) and \( \delta^{13}\text{C}_{\text{org}} \) and is showing global carbon cycling signal.
5.4.3 $\delta^{34}S_{CAS}$, $\delta^{34}S_{pyrite}$, $\Delta_{34}S$ and $\Delta^{34}S$

At the boundary of CP3 and throughout CP4 and the bottom of CP5 there are indications of diminished microbial reduction of sulfate as $\delta^{34}S_{pyrite}$ values become higher. A renewed source of sulfate and nutrients would lead to less complete fractionation of the total sulfate reservoir. From the change in $\delta^{34}S_{pyrite}$ and changes in lithology as well as rise in carbonate weight percent (indicating higher carbonate precipitation taking place), the transition from CP3 to CP4 is interpreted as a connectivity to open marine waters flooding the basin. This connection to marine waters is also evidenced by strontium isotopic ratios in the CP3-CP5 section that mirror that of seawater. This influx of marine water would have provided the large influx of sulfate which would then lead to the isotopic shift in $\delta^{34}S_{pyrite}$, which begins at the top of CP3 and continues into CP4. The large influx of sulfate would provide enriched $\delta^{34}S_{sw}$ (seawater) values that then would gradually be reduced by the purple and green sulfur bacteria in the water column. The influx of new seawater continues into CP5 with relatively constant fractionation of sulfate to sulfide being recorded in the pyrite deposits ($\sim$0%).
Figure 35: $\delta^{34}$S$_{pyrite}$ and $\delta^{34}$S$_{CAS}$ with changing water levels is illustrated to explain the changing trends in the Coppercap Formation. As water level decreased, the basin will become restricted enriching sulfate isotopic values.

After the initial influx of water, the $\delta^{34}$S$_{pyrite}$ and $\delta^{34}$S$_{CAS}$ values remain largely constant into the bottom section of CP5. At this point a renewed restriction has been interpreted based on lithology changes (brecciated units and exposure surfaces) and shifts in $\delta^{34}$S$_{pyrite}$ and $\delta^{13}$C$_{org}$.

Additionally, $\delta^{34}$S$_{pyrite}$ values begin to decrease, as do $\delta^{34}$S$_{CAS}$ values. The restriction of the basin from further oceanic influx is further supported by the deposition of evaporites in CP6. Along with the subsidence of the basin, a large regression would be necessary to trigger such a dramatic and sudden complete isolation of the basin. From the $\delta^{13}$C$_{carb}$ and $\delta^{13}$C$_{org}$ the area of CP5 and CP6 demonstrate the changing climate and likely development of ice leading to the decrease in sea level over this interval.

From the Redstone River Formation into CP2-CP3, depleted $\delta^{34}$S values are observed ranging from -23‰ to -3‰. These depleted values are representative of active bacterial sulfate reduction in this section, which also correlates with the high sulfur yields and high amounts of
biomarkers for purple sulfur bacteria and green sulfur bacteria. However, over the course of CP2-CP3, there is an enrichment of $\delta^{34}S$ values to a maximum value at the boundary between CP3 and CP4. The enrichment of $\delta^{34}S$ values during the Proterozoic is attributed to a smaller sulfate pool (Kah et al., 2004; Hurtgen et al., 2005). As sulfate concentrations decrease, a complete or near complete consumption of the sulfate reservoir will take place, leading to a subsequent overall enrichment of the pyrite values. As previously discussed, at this boundary of CP3 and CP4, there is an influx of marine seawater into the basin, leading to an increase in sulfate concentration in the basin. The $\delta^{34}S$ values become depleted again in the more open marine stage. As the basin became more restricted again, in the top of section CP5 and CP6 values became to become more depleted again, which could be a result of a return to bacterial sulfate reduction due to an influx of nutrients and sulfate, or due to a change in the isotopic composition of the marine waters themselves.

Microbial reduction of sulfate to hydrogen sulfide leads to the formation of sedimentary pyrite which serves as the primary sink of reduced sulfur in the ocean. In the process of reducing sulfate, organic matter and, to a lesser degree, hydrogen becomes oxidized. The reduction process of sulfate requires anaerobic biological mediation, which continues to dominant as the main mechanism for organic degradation in oxygen minimum zones areas, such as the Black Sea. The hydrogen sulfide waste product of this reaction subsequently reacts with iron oxides, delivered to the ocean along with detrital grains, to form pyrite. Since most of the reduced organic matter that becomes oxidized comes predominantly from oxygen producing photosynthesis, the formation and burial of pyrite is a source of atmospheric oxygen along with the burial of reduced organic carbon.

CAS, carbonate associated sulfate, is the sulfate that is captured and preserved within the lattice of the carbonate structure itself. Samples in the Coppercap Formation were extracted for pyrite and CAS to yield the estimated isotopic offset between oceanic sulfate and the bacterial sulfate reduction (Fike et al., 2006). The offset between CAS and sulfide from a single water column sample,
however, can be offset by sulfur disproportionation activities, and thus may not give a completely accurate assessment of the bacterial reduction taking place. Samples for the less pyrite rich section were analyzed for CAS to minimize the effects of pyrite oxidation on the CAS values. After the initial influx of seawater at the boundary of CP3 and CP4, $\delta^{34}$S$_{CAS}$ begins to become more depleted. The offset between $\delta^{34}$S$_{CAS}$ and $\delta^{34}$S$_{pyrite}$ remains relatively constant throughout the upper section, averaging at around 20-25%. This offset has also been observed by other researchers in Late Proterozoic samples (Fike et al., 2006, Kaufman et al., 2007, Hurtgen et al., 2005; Farquhar et al., 2000; Johnston et al., 2005). There is a slight decrease in the difference between $\delta^{34}$S$_{CAS}$ and $\delta^{34}$S$_{pyrite}$ within CP5 and CP6 that can be attributed to a depleted sulfate pool leading to less fractionation between sulfate and hydrogen sulfide, as well as decreasing populations of purple sulfur bacteria and green sulfur bacteria in this section.

![Graph](https://via.placeholder.com/150)

**Figure 36: CAS and evaporite samples from the Neoproterozoic:** $\delta^{34}$S values during the Neoproterozoic from CAS and evaporite samples. CAS yields more reliable values that have been shown to be only 1–2% offset from the seawater sulfate composition, while evaporites have a slightly larger isotopic offset during deposition. Compiled data from Farquhar et al. (2000) 700Ma, Johnston et al. (2005) Evaporites 750Ma, Kaufman et al. (2007) and Hurtgen et al. (2007). Coppercap samples are represented in the light grey squares at 733Ma.
While the sulfate concentrations most likely decreased during the glacial time spans of the Late Proterozoic, since continental pyrite weathering would have been low or non-existent, it remains unclear to what extent the euxinia persisted within the oceans. Many of the sections analyzed that were deposited during this time period, including the Coppercap Formation, represent subsiding basins on the continental margin that are of shallow depths. Therefore, determining whether samples are yielding regional or global trends is of great importance. While shallow basins may have had low sulfate concentration concentrations, it is unclear whether at the deeper depths the ocean remained more iron rich (Canfield et al., 2008; Li et al., 2010). Due to the limited representation of continental margins during the Proterozoic and efficient pyrite burial, the possibility of the deep ocean remaining anoxic and iron rich over this time period remains a quite likely possibility (Canfield et al., 2004).

5.4.5 Molecular Biomarkers

Samples throughout the entire section contain high concentrations of aryl isoprenoids, 2-methylhopanes and 3-methylhopanes. These compounds are indicative of green and purple sulfur bacteria, cyanobacteria, and methanotrophs, respectively. The concentrations noted in this section are comparable or larger than that of the MacArthur Basin studies (Summons et al., 1988; Brocks et al., 2005).

The pristane to phytane ratio represents the redox state of the depositional environment. Values above 1 represent slightly oxic conditions in which pristane is preferentially produced from the phytol tail of chlorophyll a. Values below 1 indicate the presence of a more reducing environment. A transition from reducing chemistry to slightly more oxidative conditions is observed in the first section of limestone. More reducing oceanic chemistry is noted in throughout the first grainstone into the second layer of limestone.
Total aryl-isoprenoids, when standardized to TOC and the standard, show an increase at the layer of marine influx. This pattern reflects an overall increase in the total lipid extract for aryl-isoprenoids in the CP5, CP6 section. This could indicate larger populations of purple and green sulfur bacteria present in the time period directly preceding the Sturtian Glaciation. A change in water level could have led to a different depositional environment more suitable for green and purple sulfur bacteria (Figure 23).

Figure 37: TOC and total aryl-isoprenoids normalized to TOC. At the likely marine influx at CP4a large increase in aryl-isoprenoids is noted alluding to greater communities of green and purple sulfur bacteria.

Furthermore, the high concentrations of 3β-methylhopanes, derived from Type 1 methanotrophs, demonstrates that there was overall low oxygen concentrations in the lower waters. 2α-methylhopanes have a relatively high concentration throughout the section, showing that there
was a moderate oxic top layer. The 2Me-HI (methylhopane index) and 3Me-HI yield values averaging at 15 and 3, respectively. These high methylhopane index values suggest active communities of both cyanobacteria and methanotrophs were present in the Coppercap Formation.

Figure 38: 2Me-HI and 3Me-HI values for the Coppercap Formation were found to be high compared to other sections such as the MacArthur Basin.

This leads a model of a stratified depositional environment of the Coppercap basin, as both the presence of cyanobacteria and microaerophilic organisms indicate oxygen rich top waters and anoxic bottom waters. This stratified ocean, Black Sea type model, is further evidenced by the biomarker gammacerane, which is considered a biomarker for stratified and hypersaline conditions. Gammacerane is present in low quantities throughout the 76Y-4 core with higher values in CP5 and CP6; in the 77Y-3 core it is present only in CP5 and CP6.
5.4.6 Environmental Reconstruction and Implications

From stable isotopic analysis and biomarker analysis of the Coppercap Formation we generate an image of an environment prior to the Sturtian Glaciation. While, bulk carbon analysis shows a coupled excursion representative of the global signature recorded in other sections, sulfur isotopes likely represent more regional changes in the base of the section, and more global changes in the top of the section.

The depositional environment of the Coppercap basin could have manifested itself in two fashions. In a deeper depositional environment within the basin, the green and purple sulfur bacteria could have been planktonic, with a cyanobacteria layer in the top most surface waters. Sulfur reducing bacteria and methanotrophs would have thrived near the sediment water interface. In this model of the basin, persistent green and purple sulfur bacteria in the open marine section of the formation would suggest photic zone euxinia in the shelf environments. Hydrogen sulfide rich waters in the shelf, thought to be present in the Mesoproterozoic oceans, would have prevented many oxygen requiring eukaryotic life forms to diversify prior to the Snowball Earth episodes. Continued euxinia in shallow waters would help lend to an explanation of the late onset of eukaryotic radiation in the Neoproterozoic.
Another possible model for the Coppercap Formation would have benthic cyanobacteria and green sulfur bacteria forming mats at the sediment water interface. Cyanobacteria would exist in a top most oxic layer, while suspended purple sulfur bacteria would be in a lower depth in sulfide rich waters, and a cyanobacteria, purple and green sulfur bacteria mats would be in the sediment water interface. This would be representative of a water column less than 20m in depth (as purple sulfur bacteria needs to be within 20m of the water surface to utilize sunlight). While this model has implications of what a successful bacterial community of the Neoproterozoic would look like, it does not have implications that could be extrapolated to the global trends before the Sturtian Glaciation. While some lamination does exist in the limestone layers, lithology alone does not provide ample insight into the distinct depositional environment of the Coppercap Formation.
The Coppercap Formation represents a shallow marine basin with intermittent restriction. Directly before the Sturtian Glaciation, organic carbon and sedimentary sulfide burial was likely a sink for carbon dioxide leading the onset of glaciations. Euxinic shallow waters are suggested by the presence of biomarkers by green and purple sulfur bacteria, though the extent of euxinia is unknown. High concentrations of methanotrophs and cyanobacteria biomarkers suggest that the water column was stratified. Anoxic, sulfide rich waters in the shelf environments could have played a part in preventing the earlier diversification of eukaryotic life in the Neoproterozoic.
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