## BIOGEOCHEMISTRY OF NEOPROTEROZOIC BLACK SHALES: RECORD OF THE CO-EVOLUTION OF ATMOSPHERIC OXYGEN AND LIFE

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McGill University Montréal, Québec June, 2016

A thesis submitted to McGill University in partial fulfillment of the requirements of the degree of Doctor of Philosophy

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For Erik and Kirsten - the light at the end of the day.

### Acknowledgments

This thesis represents many years of work in the lab, the field, and in front of my computer. I certainly did not invent something profound like the wheel, but it was nevertheless a huge challenge, and I put a lot of work and enthusiasm into it. It goes without saying that the energy and skills necessary to pursue such a project require contributions from many people. My sincere thanks and gratitude go to Galen Halverson for his guidance over the years and his friendship. His selfless, extremely generous support and trust in his students is something I always keep in mind (and will certainly never forget) when I teach other people. I also thank him for giving me the freedom to succeed and — equally important — to fail on my own. I am lucky to have had him as my advisor. I am very grateful to Boswell Wing for gradually becoming my second advisor. I learned a lot from his deep understanding of isotope geochemistry, and it is from working with him that I came to understand the power of quantifying and modeling geochemical processes. I also thank him for many enthusiastic and productive discussions. I owe a big thanks to Clint Scott for invaluable feedback on my manuscripts. It's a pity that we did not have more time overlap at McGill, but I am very grateful for many quick email responses.

My time at McGill was only very special because I had the privilege to be part of a wellfunctioning research group that always created a special atmosphere. I would like to thank all former and present PROPS members for countless support and discussions; Peter Crockford (We are a great team!), Thi Hao Bui, Malcolm Hodgskiss, André Pellerin, Grant Cox, Sarah Wörndle, Emma Bertran, Kristyn Rodzinyak, Matt Hryciuk, Eric Bellefroid, Pierre Sansjofre, Tim Gibson, Jesse Colangelo-Lillis, Louise-Marie Meunier, Mônica Mendes, and Thomas Maguire. Many many thanks to all of you—I had a great time with you guys!

Many other people provided critical feedback over the years. I am sure I will forget to name some (but you are certainly not forgotten...my apologies). I thank Paul Hoffman for an unforgettable field season in northern Namibia and his continuous interest and support. Tea breaks and discussions with Bjørn Sundby were always a welcome distraction from my computer. His critical thinking, chemistry knowledge, and encouragements were always helpful. I also thank Justin Strauss, Erik Sperling, Noah Planavsky, Bill Minarik, Andrey Bekker, Tim Lyons, David Carozza, Dirk Schumann, Al Mucci, Francis Macdonald, Rob Rainbird, Vivien Cumming, and Vincent van Hinsburg for discussions, feedback, and/or field companionship.

I thank André Poirier, Ranjan Roy, Anna-Katharina Jung, and Isabelle Richer for technical help in the lab. Many thanks to Anne Kosowski, Angela DiNinno, and Kristy Thornton for administrative help.

My friends in Germany and Australia, in particular Tobias Höfig, Gregor Barth, André Duczek, Sascha Duczek, and Martin Griessmann are thanked for their interest in my work. I particularly thank Gregor Barth for many discussions on IAT<sub>E</sub>X. Although I live far away, I will never forget you guys and I always look forward to skyping with you!

I want to thank the Schumann family for their friendship and for regularly inviting us for short vacations. It was always a welcome break from my thesis.

Many thanks to my family, in particular my sister Romy, my mother and Robert, for their continuing support and interest.

My very special thanks to my wonderful wife Kirsten. Her understanding and support made this thesis possible. I deeply apologize to her and our little boy Erik for being away so often (either physically or in my mind when I cannot stop thinking...).

Financial support for the research presented in this thesis was provided by grants issued to Galen Halverson from the National Sciences and Engineering Research Council of Canada, the American Chemical Society, the Yukon Geological Survey, and the Polar Continental Shelf Program. I am thankful for several personal fellowships I received as graduate student at McGill, namely the GREAT and Graduate Mobility Award, the Geotop Student Fellowship (twice), the J.B. Lynch Fellowship (twice), the Robert Wares Fellowship, and the Eric Mountjoy Fellowship.

### Abstract

The Neoproterozoic Era (1000 to 541 million years ago (Ma)) was marked by significant environmental changes, including (but not limited to) an increase in atmospheric oxygen levels, ice sheets reaching tropical latitudes during the 717 Ma Sturtian and 635 Ma Marinoan glaciations, and the emergence of Metazoa. Although these events had profound impact on the habitability of Earth's surface environments and the biogeochemical cycling of bioessential elements, making them popular targets for research, their temporal relationships remain elusive. In this thesis, I investigate the evolution of oceanic redox conditions and atmospheric oxygen levels and their temporal relationship to low-latitude glaciations and the evolution of life in the Neoproterozoic.

I present iron speciation data and redox-sensitive trace element abundances from organicrich shales deposited on a continental shelf in northeastern Svalbard between 835–630 Ma, i.e., spanning the Sturtian and Marinoan glaciations and the time interval when early metazoans likely colonized shelf environments. The data suggest that suboxic to anoxic-ferruginous conditions prevailed during deposition of the entire succession. Taking published paleoredox data sets into consideration, I propose that the Sturtian glaciation was not related to significant changes in atmospheric oxygen levels. This conclusion is consistent with the most recent biomarker evidence and molecular clock estimates for simple metazoans before the Sturtian glaciation, which means that if a rise in oxygen concentration facilitated the emergence of these organisms, it likely occurred before the Sturtian glaciation. Although several lines of evidence suggest an increase in atmospheric oxygen after the Marinoan glaciation, continental shelf environments in Svalbard and elsewhere remained dominantly anoxic, likely due to high organic matter loading. In contrast, oxygen concentrations may have been higher in low-productivity zones further offshore, where downwelling of oxygenated surface waters may have even increased oxygen concentrations in the deep ocean. Multiple sulfur isotope data from pyrites in the samples from Svalbard, along with additional data from Australia, northwestern Canada, Russia, and the United States, suggest onset of a globally operating re-oxidative sulfur cycle in the aftermath of the Marinoan glaciation. This result supports the view of a general increase in atmospheric oxygen concentration in the early Ediacaran Period and further helps to quantify the rise in  $pO_2$ . By using a previous estimate for the oxygen requirements of re-oxidative sulfur cycling, we suggest that atmospheric oxygen levels increased from a maximum of 5% present atmospheric levels (PAL) before the Marinoan glaciation to at least 18% PAL in the aftermath. This rise in oxygen may have facilitated the emergence of larger animals in the Ediacaran Period.

In contrast to models for the evolution of atmospheric oxygen based on our sulfur isotope, iron speciation, and trace metal data sets, the iron isotope composition of Neoproterozoic shales suggest rising environmental oxygen levels after the Sturtian glaciation. Although the presented iron isotope record is still sparse and future data will likely necessitate revision of the conclusions drawn from it, this result highlights the need to better understand the behavior of different redox proxies and their sensitivity to incremental changes in environmental oxygen levels. Inconsistent constrains drawn from different proxies might be reconcilable if we better understand what oxygen thresholds are required to trigger resolvable signals in the individual proxies.

## Résumé

L'ère Néoprotérozoïque (1000–541 Ma) fut marquée par des changements environnementaux significatifs, incluant entre autre une augmentation des niveaux d'oxygène atmosphérique, des calottes glaciaires atteignant des latitudes tropicales pendant les glaciations du Sturtien (717 Ma) et du Marinoen (635 Ma), et l'émergence des métazoaires. Bien que ces changements ont eu un impact majeur sur l'habitabilité des environnements des surfaces terrestres, ainsi que sur les cycles biogéochimiques des éléments bioessentiels - les rendant ainsi des sujets de recherche privilégiés - leurs relations temporelles sont encore peu définies. Dans cette thèse, j'examine l'évolution des conditions redox océaniques et les niveaux d'oxygène atmosphérique, ainsi que leurs relations temporelles avec les glaciations à basse latitude et l'évolution de la vie au Néoprotérozoïque.

Je présente des données sur la spéciation du fer, ainsi que sur l'abondance d'éléments traces sensibles à la réaction redox dans des échantillons composés de dépôts de shales riches en matière organique provenant d'un plateau continental situé dans le nord-est du Svalbard et datant de la période de 835 à 630 Ma. Cette période recouvre les glaciations du Sturtien et du Marinoen, mais aussi l'intervalle de temps qui a très certainement vu la colonisation des environnements de plateaux par les premiers métazoaires. Les données suggèrent que des conditions allant de suboxiques à anoxique-ferrugineuses prévalent durant l'intégralité de la déposition de la succession stratigraphique. En tenant compte de données de paléoredox préexistantes, je propose que la glaciation du Sturtien n'est pas reliée à des changements significatifs des niveaux d'oxygène atmosphérique. Cette conclusion est en accord avec les récentes découvertes (marqueurs biologiques et estimation de l'horloge moléculaire) indiquant la présence de métazoaires simples avant la glaciation du Sturtien. Ceci implique que s'il y a eu une augmentation de la concentration d'oxygène facilitant l'émergence de ces organismes, il est fort probable qu'elle ait eu lieu avant la glaciation du Sturtien. Même si de multiples éléments de preuves suggèrent une augmentation de l'oxygène atmosphérique après la glaciation du Marinoen, les environnements des plateaux continentaux du Svalbard et d'ailleurs restent majoritairement anoxiques, cette anoxie étant trés certainement causée par une forte production de matière organique. A contrario, les concentrations en oxygène ont potentiellement été plus hautes dans les zones de pleine mer à faible productivité, où des plongées d'eaux de surface oxygénées auraient même pu causer une augmentation des concentrations d'oxygène dans l'océan profond.

De multiples données des isotopes du soufre tiréess d'échantillons de pyrite du Svalbard, ainsi que des données provenant d'Australie, du nord-ouest canadien, de Russie, et des États-Unis d'Amérique, suggèrent que les débuts d'un cycle du soufre prenant place sur une échelle globale sont apparus à la suite de la glaciation du Marinoen. Ce cycle est caractérisé par la réduction du sulfate, suivi par l'oxydation de sulfide, et finalement par la disproportion des composés intermédiaires du soufre. Ce résultat soutient l'idée d'une augmentation générale de la concentration d'oxygène atmosphérique pendant la Période Ediacarienne infèrieure, mais aide aussi à quantifier l'augmentation en pO<sub>2</sub>. En utilisant une estimation préexistante des besoins en oxygène du cycle du soufre, nous suggérons que les niveaux d'oxygène atmosphérique ont connu une augmentation de 5% maximum par rapport aux niveaux atmosphériques actuels avant la glaciation du Marinoen, et une augmentation d'au moins 18% par rapport aux niveaux atmosphériques actuels après la glaciation du Marinoen. Cette augmentation de l'oxygène a potentiellement facilité l'émergence d'animaux de taille plus importante durant la période Ediacarienne.

À la différence des modèles basant l'évolution de l'oxygène atmosphérique sur les isotopes du soufre, la spéciation du fer, et les données des métaux traces, la composition isotopique du fer des shales du Néoprotérozoïque suggère une augmentation des niveaux d'oxygène environnemental à la suite de la glaciation du Sturtien. Bien que l'enregistrement connu des isotopes du fer soit encore peu abondant et que des données futures entraineront très certainement des révisions des conclusions tirées ici, ce résultat souligne le besoin de mieux comprendre le comportement des différents proxies des réactions redox, ainsi que leur sensibilité liée aux changements progressifs des niveaux d'oxygène atmosphérique. Des contraintes inconsistantes apportées par différents proxies pourraient potentiellement être conciliées si nous sommes en mesure de mieux comprendre quels sont les seuilséclend'oxygène nécessaire pour déclencher et donc résoudre les signaux des proxies individuels.

## Preface and author contributions

This thesis contains an introduction and four chapters presenting original research findings that are linked by individual prefaces highlighting the scientific links between chapters. The work presented here was carried out between September 2011 and April 2016. However, some of the work I did during this time is not part of this thesis. At the beginning of my time at McGill University I wrote two papers on data sets that were produced during my time as undergraduate and MSc student. These papers were published as:

Kunzmann, M., Gutzmer, J., Beukes, N.J., Halverson, G.P., 2014, Depositional environment and lithostratigraphy of the Paleoproterozoic Mooidraai Formation, Kalahari Manganese Field, South Africa. South African Journal of Geology. 117 (2), 173–192.

Kunzmann, M., Halverson, G.P., Sossi, P.A., Raub, T.D., Payne, J.L., Kirby, J., 2013, Zn isotope evidence for immediate resumption of primary productivity after snowball Earth. Geology, 41 (1), 27–30.

Furthermore, I contributed to other studies as co-author by sharing data I produced, samples I collected, and providing help with analyses and data interpretation. These include:

Mendes, M., Lobato, L., **Kunzmann, M.**, Halverson, G.P., Rosière, C.A., in press, Iron isotope and REE+Y composition of Paleoproterozoic banded iron formation and related iron ores in the Quadrilátero Ferrífero, Mineralium Deposita.

Cox, G. M., Halverson, G.P., Stevenson, R.S., Vokaty, M., Poirier, A., **Kunzmann, M.**, Li, Z.-X., Dudas, F.O., Strauss, J.V., and Macdonald, F.A., 2016, Continental flood basalt weathering as a trigger for Neoproterozoic Snowball Earth, Earth and Planetary Science Letters, 446, 89–99.

Sperling, E.A., Wolock, C.J., Morgan, A.S., Gill, B.C., **Kunzmann, M.**, Halverson, G.P., Macdonald, F.A., Knoll, A.H., Johnston, D.T., 2015, Statistical analysis of iron geochemical data suggests limited Late Proterozoic oxygenation. Nature, 523, 451-454.

Ader, M., Sansjofre, P., Halverson, G.P., Trinidade, R.I.F., Busigny, V., **Kunzmann, M.**, Nogueira, A., 2014, Ocean redox structure across the Late Neoproterozoic Oxygenation Event: A nitrogen isotope perspective. Earth and Planetary Science Letters, 396, 1-13.

Macdonald, F.A., Strauss, J.V, Sperling, E.A., Halverson, G.P., Narbonne, G.M., Johnston, D.T., **Kunzmann, M.**, Schrag, D.P., Higgins, J.A., 2013, The stratigraphic relationship between the Shuram carbon isotope excursion, the oxygenation of Neoproterozoic oceans, and the first appearance of the Ediacara biota and bilaterian trace fossils in northwestern Canada. Chemical Geology, 362, 250-272.

Research chapters in this thesis were published or are currently in review or in preparation for submission. Each paper contains a list of co-authors. Therefore, I am listing the individual author contributions to every chapter below.

**Chapter 2:** Marcus Kunzmann and Galen Halverson conceived the project. Fieldwork was carried out by Marcus Kunzmann, Galen Halverson, Francis Macdonald, Malcolm Hodgskiss, Pierre Sansjofre, and Robert Rainbird. Scanning Electron Microscopy was carried out by Dirk Schumann and Marcus Kunzmann. The paper was written by Marcus Kunzmann with input from all co-authors.

**Chapter 3:** Marcus Kunzmann and Galen Halverson conceived the project. Field work and sampling was carried out by Galen Halverson. Marcus Kunzmann did all analyses, partly with advice from William Minarik. Marcus Kunzmann interpreted the data with help from Clint Scott. The paper was written by Marcus Kunzmann with input from all co-authors.

**Chapter 4:** Marcus Kunzmann and Boswell Wing conceived the project. Galen Halverson and Timothy Lyons did field work and provided samples. Geochemical analyses were carried out by Marcus Kunzmann. Compilation of literature data was done by Marcus Kunzmann and Clint Scott. Geochemical modeling was carried out by Marcus Kunzmann and Thi Hao Bui, with advice from Boswell Wing. Data were interpreted by Marcus Kunzmann, Boswell Wing, and Peter Crockford. The paper was written by Marcus Kunzmann with input from all co-authors.

**Chapter 5:** Marcus Kunzmann and Galen Halverson conceived the project. Field work and sampling was carried out by Galen Halverson, Marcus Kunzmann, and Erik Sperling. Geochemical analyses were performed by Marcus Kunzmann, Timothy Gibson, Galen Halverson, and Malcolm Hodgskiss. André Poirier and Grant Cox provided help with measurements. Geochemical modeling was carried out Marcus Kunzmann, Thi Hao Bui, and David Carozza, with advice from Boswell Wing. Marcus Kunzmann interpreted the data and wrote the paper with input from all co-authors.

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#### 1 Introduction

The origin of oxygenic photosynthesis in the Archean Eon (4.0 to 2.5 billion years ago (Ga)) was the most important step for the accumulation of oxygen in the atmosphere and ocean (Rosing and Frei, 2004; Kopp et al., 2005; Kirschvink and Kopp, 2008; Planavsky et al., 2014a). Following this biological innovation, Earth's surface environments are generally thought to have experienced two major oxygenation steps, one at the beginning and one at the end of the Proterozoic Eon (2.5 to 0.54 Ga). The first step, commonly referred to as the "Great Oxidation Event" (GOE), occurred between 2.47 and 2.32 Ga (Holland, 2002; Bekker et al., 2004; Holland, 2006; Lyons et al., 2014) and is marked by atmospheric oxygen levels exceeding  $10^{-5}$ % present atmospheric levels (PAL) (Pavlov and Kasting, 2002) for the first time in Earth's history. The timing of the GOE is relatively well constrained by the disappearance of detrictal uraninite, siderite, and pyrite (e.g., Holland, 2006), and in particular, by the disappearance of the mass independent fractionation (MIF) of sulfur isotopes (Farquhar et al., 2000; Farquhar and Wing, 2003; Bekker et al., 2004). Considering the much greater abundance of well-preserved Neoproterozoic (1.0 to 0.54 Ga) sedimentary successions, the timing and magnitude of the second Proterozoic oxygenation event are surprisingly poorly understood (for recent review see Och and Shields-Zhou, 2012). Various geochemical proxies suggest a significant increase in atmospheric oxygen levels at this time (e.g., Des Marais et al., 1992; Hurtgen et al., 2005; Fike et al., 2006; Canfield et al., 2007; Scott et al., 2008; Sahoo et al., 2012; Lyons et al., 2014; Pogge von Strandmann et al., 2016; Turner and Bekker, 2016) but current estimates of atmospheric oxygen range from <0.1 to 40%PAL (Sperling et al., 2015). One reason for the poor constraints on Neoproterozoic oxygenation is that environmental oxygen levels in the preceding Mesoproterozoic (1.6 to 1.0 Ga) are poorly understood (Planavsky et al., 2014b; Gilleaudeau et al., 2016; Zhang et al., 2016). Specifically, it is unknown from what baseline concentration oxygen levels in the Neoproterozoic actually increased.

Furthermore, no "straightforward" geochemical tool exists that can unambiguously constrain atmospheric oxygen thresholds, unlike the MIF signal of sulfur isotopes across the GOE. In the absence of a single, smoking-gun proxy like MIF in sulfur isotopes, Neoproterozoic oxygenation must be inferred from a variety of less direct proxies. This approach requires a global redox data set, constructed from geological units of varying age and location. Therefore, careful correlation of geological successions and the analysis of samples spanning the entire Neoproterozoic is essential to building a continuous record from as many basins as possible.

Neoproterozoic oxygenation receives significant attention because its timing and magnitude is crucial for our understanding of major evolutionary steps in this period (Fig. 1.1). Although the oldest fossils of unambiguous eukaryotic microfossils likely date to 1.6–1.8 Ga, major eukaryotic diversification and emergence of multiple known crown groups appears to have been delayed until ca. 800 million years ago (Ma)—i.e., the early Neoproterozoic (Knoll et al., 2006; Knoll, 2014; Cohen and Macdonald, 2015). Furthermore, molecular clock estimates place the origin of animals at ca. 750–800 Ma (Erwin et al., 2011; Erwin, 2015), and this timeframe is supported by molecular fossils indicative of sponges found in rocks up to 750 Ma (Love et al., 2009; Brocks et al., 2015), and putative sponge-like body fossils older than 635 Ma (Maloof et al., 2010). Unambiguous and complex animal fossils occur in the early Ediacaran (635 to 541 Ma) (e.g., Xiao et al., 1998; Yin et al., 2007), and a diversification in marine algae at this time has been interpreted to reflect increasing ecosystem complexity driven by predatory animals (Peterson and Butterfield, 2005). In addition, the middle and late Ediacaran is famous for the appearance of Ediacaran-type macrofossil assemblages, which include the first macroscopic animals capable of widespread preservation. It is widely debated whether an increase in atmospheric oxygen facilitated biological innovation, or if the emergence of large animals itself contributed to an increase in environmental oxygen levels (for discussion see Anbar and Knoll, 2002; Butterfield, 2009; Knoll and Sperling, 2014; Lenton et al., 2014). Nevertheless, the appearance of certain organisms in the geological record provides minimum constrains on oxygen concentrations. Simple sponges in the middle Neoproterozoic suggest that oxygen levels were at least 0.5-4% PAL (Mills et al., 2014), and the appearance of large, metabolically active animals like carnivores in the latter Ediacaran suggest minimum concentrations of 2–7% PAL (Sperling et al., 2013a, 2015).

In addition to increasing oxygen levels and major biological innovations, the Neoproterozoic

also witnessed other significant events in the history of our planet (Fig. 1.1). Ice sheets likely reached tropical latitudes during the ca. 720 to 660 Ma Sturtian and 635 Ma Marinoan glaciations (Harland, 1964; Kirschvink, 1992; Hoffman et al., 1998; Hoffman and Schrag, 2002) and the supercontinent Rodinia assembled and broke-up in the early and late Neoproterozoic, respectively (e.g., Z.-X. Li et al., 2008). These events overlap with the emplacement and weathering of several large igneous provinces (Halverson et al., 2014; Cox et al., 2016), and major perturbations to the carbon cycle (e.g., Halverson et al., 2005).

This dissertation was undertaken to better understand the evolution of atmospheric oxygen in the Neoproterozoic and its relationship to other events in the Neoproterozoic. Specifically, I studied biogeochemical signatures of organic-rich marine shales to shed light on the temporal evolution of atmospheric oxygen levels, oceanic redox conditions, and its relationship to the evolution of life and low-latitude glaciations. Furthermore, I provide a quantitative estimate of the rise in atmospheric oxygen and also investigate the effect of dominantly anoxic conditions and rising oxygen levels on the marine iron cycle.

## 1.1 Oceanic redox conditions in the Neoproterozoic

The chemical composition of the ocean tracks the evolution of atmospheric oxygen. Low oxygen concentration in the Proterozoic likely only permitted an oxic surface mixed layer, whereas the ocean below storm wave base may have remained anoxic (for recent review see Lyons et al., 2014). Increasing atmospheric oxygen levels allowed oxygen to penetrate deeper into the water column, and the latest Neoproterozoic may have experienced oxidation of the deep ocean (Canfield et al., 2007; Lyons et al., 2014). However, rising atmospheric oxygen levels also changed seawater chemistry by increasing continental weathering, which, in turn, increased the riverine supply of sulfate and bioessential trace metals to the ocean. Increasing concentration of trace metals like molybdenum has the potential to stimulate biological evolution (e.g., Anbar and Knoll, 2002), while increasing sulfate levels promotes microbial sulfate reduction, which produces hydrogen sulfide and can therefore drive parts of the ocean euxinic (anoxic and sulfidic) (Canfield, 1998). Widespread euxinia, in turn, has negative effects on biological evolution through the near quantitative removal of certain bioessential trace metals from the water column (Anbar and Knoll,

2002).

In his classical model of Proterozoic ocean chemistry, Holland (1984) argued that the disappearance of banded iron formation from the geological record ca. 1.84 billion years ago indicates oxidation of the deep ocean. Later, Canfield (1998) proposed that the disappearance of banded iron formation could alternatively be explained by a switch to a global euxinic deep ocean, in which dissolved Fe(II) would be removed as pyrite through reaction with dissolved sulfide. Although several subsequent studies reporting evidence for euxinic conditions in the Mesoproterozoic initially appeared to confirm the Canfield hypothesis of global deep ocean euxinia (Shen et al., 2002, 2003; Poulton et al., 2004; Brocks et al., 2005), more recent studies clearly indicate that the ocean below storm wave base was ferruginous with only local euxinia (Poulton et al., 2010; Planavsky et al., 2011; Reinhard et al., 2013; Sperling et al., 2015). Consistent with this hypothesis and based on a large paleoredox data set from numerous basins, Canfield et al. (2008) proposed that the early and middle Neoproterozoic ocean was dominated by anoxic-ferruginous (anoxic with disolved Fe(II)) conditions, with very limited euxinic environments. This view subsequently received support from more detailed studies focusing on individual successions and basin transects (Johnston et al., 2010; C. Li et al., 2012; Sperling et al., 2013b; Tahata et al., 2015), but the spatial and temporal resolution of oceanic redox data remains sparse.

The redox state of the Ediacaran ocean has been studied in more detail but available data sets suggest either dominantly oxic (McFadden et al., 2008; Johnston et al., 2012; Sahoo et al., 2012; Ader et al., 2014; Sansjofre et al., 2014) or anoxic basins (C. Li et al., 2010; Johnston et al., 2013). This discrepancy highlights the temporally and spatially heterogeneous nature of the Ediacaran — and, most likely, Proterozoic ocean in general (Lyons et al., 2012, 2014; Sperling et al., 2014; Kendall et al., 2015) — which hinders a better understanding of the extent and exact timing of the proposed oxygenation of the Ediacaran deep ocean. Whereas some studies propose significant oxygenation (Fike et al., 2006; Canfield et al., 2007; Sahoo et al., 2012), more recent studies suggest that the transition to a mostly oxygenated Phanerozoic ocean was marked by fluctuating redox conditions (Kendall et al., 2015) and that oxygenation in the Ediacaran was less significant than traditionally thought (Sperling et al., 2015; Sahoo et al., 2016).

Several key questions about the evolution of oceanic redox conditions in the Neoproterozoic can be identified:

- Will the early to middle Neoproterozoic record confirm the proposed dominance of ferruginous conditions below storm wave base and that euxinic conditions were only a local phenomenon in the Neoproterozoic? Answering this question will require significantly expanding the oceanic redox data base. Additional data from multiple basins should help to resolve the redox structure of the whole Neoproterozoic ocean and to better understand the significance of redox heterogeneity.
- What is the relationship between oceanic redox conditions (and by inference atmospheric oxygen concentration) and the Sturtian and Marinoan low-latitude glaciations? Specifically, was the long-lived (>50 Ma) Sturtian glaciation related to increasing or decreasing oxygen concentration? Alternatively, could oxygen levels have remained relatively stable across the glaciation? Furthermore, can additional data help to reconcile paleoredox data from different post-Marinoan (Ediacaran) successions and help us to better understand the extent of the proposed oxygenation in the aftermath of the Marinoan glaciation?
- Was early animal evolution linked to changing oceanic redox conditions and atmospheric oxygen levels? In other words, did oxic environments expand between the Sturtian and Marinoan glaciation, the time of putative fossil (Maloof et al., 2010) and biomarker (Love et al., 2009) evidence for sponges? Or did oxic environments expand around 750 Ma, the time of the currently oldest biomarker evidence for sponges (Brocks et al., 2015) and converging molecular clock estimates for the origin of animals (Erwin et al., 2011; Erwin, 2015)?

To start to address these questions, we conducted a paleoredox study (Chapter 3) of the relatively understudied, ca. 835–630 Ma Neoproterozoic succession in Svalbard, which was deposited on a stable continental shelf. This succession is remarkably complete and hosts glacial deposits of the Sturtian and Marinoan glaciation, allowing us to integrate this new data set into global records. We have applied iron speciation and redox-sensitive trace metals (a brief introduction to these proxies will be given in Chapter 3) to reconstruct oceanic redox conditions during deposition of organic-rich shales. Our results confirm the dominance of ferruginous conditions below storm wave base (but also allow intermittently oxic conditions) in the Neoproterozoic and also confirm that euxinic conditions were not a common feature of the ocean at this time. The Sturtian glaciation does not appear to have coincided with significant changes in oceanic redox conditions. Similarly, the Cryogenian interglacial interval, for which biomarker and putative fossils suggest that sponges inhabited shelf environments, did not experience significant oxygenation or expansion of oxic conditions in marine environments. This redox stasis implies that oxygen requirements for simple sponges (0.5–4% PAL, Mills et al., 2014) were already met in the middle Neoproterozoic, i.e. that an increase of oxygen concentration to this threshold had already been met by this time<sup>1</sup>. The data from Svalbard suggest the continuation of anoxic-ferruginous conditions in shelf environments after the Marinoan glaciation, which supports some results from other basins such as northwestern Canada (e.g., Johnston et al., 2013) but is notably inconsistent with conclusions drawn from data from the Doushantuo Formation in South China (Sahoo et al., 2012). In Chapter 3, we reconcile these seemingly contradictory results by suggesting an early Ediacaran redox structure characterized by anoxic shelf environments due to high primary productivity rather than only low overall oxygen concentrations. In contrast, lower rates of primary productivity offshore may have permitted higher oxygen levels at depth.

# 1.2 A global signal of bacterial sulfur disproportionation in the Neoproterozoic

The marine sulfur cycle is intimately linked to atmospheric oxygen concentrations. Oxidative weathering of crustal sulfides consumes oxygen and supplies sulfate to the ocean, while oceanic redox conditions control the burial efficiency of the sedimentary sulfide sink. The burial of sedimentary sulfide minerals, in turn, represents a net source of atmospheric oxygen. Therefore, constraints on the evolution of the marine sulfur cycle, in particular through application of sulfur isotopes, has long been employed to better understand the evolution of atmospheric oxygen (e.g., Canfield, 1998; Canfield and Raiswell, 1999; Canfield, 2005; Johnston et al., 2005b; Fike et al., 2006; Planavsky et al., 2012a; Scott et al., 2014).

Current estimates for Neoproterozoic atmospheric oxygen levels span a broad range of < 0.1

<sup>&</sup>lt;sup>1</sup>Note that the biomarker evidence for sponges around 750 million years ago (Brocks et al., 2015) was not published by the time Chapter 3 was published. Therefore, this data set is not addressed in our study, although it is consistent with the results.

to 40% PAL (Sperling et al., 2015). However, the emergence of large and metabolically active animals in the Ediacaran indicate minimum atmospheric oxygen levels of 2–7% PAL (Sperling et al., 2013a, 2015). This range spans the  $\sim 5\%$  PAL estimate of the minimum oxygen threshold required to initiate local sulfide oxidation by chemolithotrophic sulfide-oxidizing bacteria, and hence the onset of re-oxidation of dissolved sulfide in marine sediments (Canfield and Teske, 1996). Atmospheric oxygen at this level would allow the establishment of a re-oxidative sulfur cycle, marked by disproportionation of sulfur compounds with intermediate redox state, producing sulfate and sulfide. Whereas  $\sim 5\%$  PAL are necessary to initiate local sulfide oxidation,  $\sim 18\%$ PAL may be required for this re-oxidative sulfur cycle to be globally significant and to trigger an evolutionary radiation of chemolithotrophic sulfide-oxidizing bacteria (Canfield and Teske, 1996). These estimates suggest that a rise in Neoproterozoic oxygen levels can be inferred from the behavior of the global sulfur cycle, but can we identify the onset of (globally significant) re-oxidative sulfur cycling in the Neoproterozoic?

To test this prediction, we analyzed the multiple sulfur isotope composition of Proterozoic pyrites (Chapter 4). We focused on Neoproterozoic samples from Svalbard, northwestern Canada, and Australia, but also included data from Mesoproterozoic pyrites from the United States and previously published data from Russia and Canada. To identify a signal of re-oxidative sulfur cycling, we coupled our data to an isotope mass-balance model (Chapter 4). Our results indicate that re-oxidative sulfur cycling was at most a local phenomenon before the 635 Ma Marinoan glaciation, constraining atmospheric oxygen levels to have likely remained below  $\sim 5\%$  PAL until this time. In contrast, isotopic evidence for disproportionation of intermediate sulfur compounds and, thus, a re-oxidative sulfur cycle, in samples from three different basins after the Marinoan glaciation suggests that atmospheric oxygen levels likely exceeded  $\sim 18\%$  PAL in the early Ediacaran Period.

Because this paper (Chapter 4) is formatted for the journal *Geology*, the manuscript does not provide enough space to introduce the basics of re-oxidative sulfur cycling and multiple sulfur isotope geochemistry. Therefore, I provide a brief introduction below.

#### 1.2.1 Re-oxidative sulfur cycling

A large fraction of the organic matter that reaches the sediment water interface in modern continental shelf environments is oxidized by microbial sulfate reduction (MSR; Jørgensen, 1982). The waste product of this metabolism is hydrogen sulfide ( $HS^-$  and  $H_2S$ ), which can be scavenged by reactive iron to form metastable iron monosulfides. These monosulfides then transform to pyrite during early diagenesis (Berner, 1970, 1984). However, at least 90% of the hydrogen sulfide in modern marine sediments is re-oxidized to  $SO_4^{2-}$  (sulfate) or intermediate sulfur compounds like  $S^0$  (elemental sulfur),  $SO_3^{2-}$  (sulfite), and  $S_2O_3^{2-}$  (thiosulfate) (Fig. 1.2; Jørgensen, 1990; Elsgaard and Jørgensen, 1992). Abiological or biological oxidation of HS<sup>-</sup> can occur in oxic or anoxic environments through reaction with O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, or Fe(III) and Mn(IV) compounds (e.g., Howarth, 1984; Aller and Rude, 1988). Biological pathways include phototrophic and chemolithotrophic sulfur oxidation. The most important groups of phototrophic sulfur oxidizers are green and purple sulfur bacteria. Because they require light, these bacteria live either in stratified water columns where sulfidic waters reach into the photic zone or in the upper millimeters of anoxic sediments in shallow settings (e.g., Van Gemerden and Mas, 1995). Sulfide oxidation in marine sediments by reaction with  $O_2$ ,  $NO_3^-$ , Fe(III) and Mn(IV) species is often mediated by chemolithotrophic bacteria (e.g., Kelly et al., 1997).

Intermediate sulfur compounds can be reduced back to hydrogen sulfide, or oxidized to sulfate. However, the majority of intermediate sulfur compounds undergo bacterial sulfur disproportionation (BSD, Fig. 1.2), a chemolithotrophic process in which intermediate sulfur compounds are transformed to sulfide and sulfate, without an external electron donor and acceptor (Bak and Cypionka, 1987; Bak and Pfennig, 1987; Thamdrup et al., 1993). The disproportionation of thiosulfate in oxygen-free environments is an exergonic reaction ( $\Delta G^{0'} = -21.9 \text{ kJ mol}^{-1} \text{ S}_2 \text{ O}_3^{2-}$ ; Bak and Cypionka, 1987) and follows the reaction:

$$S_2 O_3^{2-} + H_2 O \longrightarrow SO_4^{2-} + HS^- + H^+$$

$$\tag{1.1}$$

(Bak and Pfennig, 1987). The disproportionation of sulfite is also exergonic ( $\Delta G^{0'} = -58.9 \text{ kJ}$  mol<sup>-1</sup> S<sub>2</sub>O<sub>3</sub><sup>2-</sup>; Bak and Cypionka, 1987) and follows the reaction:

$$4SO_3^{2-} + H^+ \longrightarrow 3SO_4^{2-} + HS^- \tag{1.2}$$

(Bak and Pfennig, 1987). The disproportionation of elemental sulfur is endergonic and microorganisms can only gain energy from this reaction if the produced sulfide is scavenged by Fe-oxyhydroxides or Fe-carbonate:

$$3S^0 + 2FeOOH \longrightarrow SO_4^{2-} + 2FeS + 2H^+ \tag{1.3}$$

$$4S^0 + 3FeCO_3 + 4H_2O \longrightarrow SO_4^{2-} + 3FeS + 3HCO^- + 5H^+ \tag{1.4}$$

(Thamdrup et al., 1993). The amount of energy released depends on the activity of  $H_2S$  and  $H^+$  (Thamdrup et al., 1993). A more detailed review of bacterial sulfur disproportionation is provided by Finster (2008).

#### 1.2.2 Sulfur isotopes and the identification of bacterial sulfur disproportionation

The element sulfur has four stable isotopes:  ${}^{32}S$ ,  ${}^{33}S$ ,  ${}^{34}S$ , and  ${}^{36}S$  with natural abundances of 94.93%, 0.76%, 4.29%, and 0.02%, respectively (Rosman and Taylor, 1998). Certain biological and chemical reactions can cause slight but systematic and measurable variations in the ratios of S isotopes. Studies of variations in S isotope ratios have traditionally focused on the two major isotopes,  ${}^{32}S$  and  ${}^{34}S$ , and isotope ratio measurements are presented in standard delta ( $\delta$ ) notation:

$$\delta^{34}S = 1000 \times \left[ \frac{({}^{34}S/{}^{32}S)_{sample}}{({}^{34}S/{}^{32}S)_{CDT\text{-std}}} - 1 \right]$$
(1.5)

where CDT-std refers to the Cañon Diablo troilite standard. Results from natural environments, pure cultures, and modeling indicate that MSR is associated with a negative isotope effect  $({}^{34}\varepsilon)$ of up to -70‰ (Canfield et al., 2010; Sim et al., 2011; Wing and Halevy, 2014), approaching the thermodynamic equilibrium between aqueous sulfate and sulfide. In comparison, phototrophic sulfide oxidation only produces small positive fractionations in the range of 0–3‰ (Zerkle et al., 2009, references therein). Abiologic sulfide oxidation with oxygen causes a small negative fractionation between -7.5 to -4.1‰ (Frey et al., 1988) and a similar fractionation has been assumed for oxidation by MnO<sub>2</sub> (Böttcher and Thamdrup, 2001). The oxidation of sulfide by chemolithotrophic bacteria has not been constrained yet, but it seems reasonable to assume equally small fractionations. The disproportionation of elemental sulfur produces H<sub>2</sub>S depleted by up to 8.6‰ and SO<sub>4</sub><sup>2-</sup> enriched by up to 20.2‰ (Canfield and Thamdrup, 1994; Canfield et al., 1998). A  $\delta^{34}$ S signature of BSD could theoretically be identified if sulfide minerals are more depleted than possible by MSR alone (Canfield and Thamdrup, 1994); however, most sulfides in the geological record are less than 70‰ lighter than coeval sulfate, precluding identification of BSD by  $\delta^{34}$ S values alone (Sim et al., 2011).

Advances in analytical techniques now permit precise measurements of ratios of the minor isotopes, i.e.  ${}^{33}S/{}^{32}S$  and  ${}^{36}S/{}^{32}S$ . The first-order mass-dependent fractionation law indicates that, due to mass differences between  ${}^{32}S$ ,  ${}^{33}S$ , and  ${}^{34}S$ , data should plot along the equilibrium mass-dependent fractionation line with a slope of 0.515 in a  $\delta^{33}S-\delta^{34}S$  cross-plot. The slope of this line is denoted as  ${}^{33}\lambda$ . However, different processes can cause deviations from this fractionation line, such that  ${}^{33}\lambda \neq 0.515$ . These deviations are expressed as either positive or negative  $\Delta^{33}S$ values (Fig. 1.3), defined as:

$$\Delta^{33}S = \delta^{33}S - 1000 \times \left[ \left( 1 + \frac{\delta^{34}S}{1000} \right)^{33\lambda - ref} - 1 \right]$$
(1.6)

where  ${}^{33}\lambda$ -ref is 0.515.

One process that generates non-zero  $\Delta^{33}$ S values is mass-independent fractionation of sulfur isotopes, mentioned earlier in the introduction. This unique type of isotopic fractionation occurred commonly in the Archean atmosphere, where vanishingly low atmospheric oxygen concentrations allowed UV photolysis of volcanic SO<sub>2</sub>. This reaction generates  $\Delta^{33}$ S values between -2 and 12‰. Although large  $\Delta^{33}$ S require mass-independent fractionation, mass-dependent fractionation can also generate small but measurable deviations from the equilibrium mass-dependent fractionation line. Specifically, microbial sulfur metabolisms such as MSR and BSD cause fractionations that deviate from the equilibrium mass-dependent fractionation line (Fig. 1.3), resulting in  $\Delta^{33}$ S values one order of magnitude lower than mass-independent fractionations. MSR and BSD produce unique <sup>33</sup> $\lambda$  values, with MSR never exceeding 0.5145, while BSD typically produces <sup>33</sup> $\lambda$  values >0.5145 (Johnston et al., 2005a). Therefore, by identifying  ${}^{33}\lambda$ , it is possible to distinguish the isotope effects of these two metabolisms (Farquhar et al., 2003; Johnston et al., 2005a, 2008; Pellerin et al., 2015). We applied this approach in Chapter 4 to monitor the importance of sulfur disproportionation reactions on the global sulfur cycle spanning the Cryogenian glaciations. A detailed review about multiple sulfur isotopes (including  ${}^{36}S/{}^{32}S$  relationships) is provided by Johnston (2011) and a recent review focusing on the ancient sulfur cycle can be found in Fike et al. (2015).

## 1.3 Iron isotope composition of Neoproterozoic shales

The concentration of dissolved Fe is generally very low in modern aquatic environments. The high concentration of oxygen in Earth's surface environments today causes Fe to occur mainly in its trivalent state (ferric iron, Fe(III)), which is highly insoluble at the circumneutral to alkaline pH conditions of most aquatic environments, causing it to precipitate as ferric Fe-oxyhydroxide minerals (e.g., ferrihydrite, lepidocrocite, goethite). In modern oxygen-deficient aquatic environments, Fe mostly occurs in its reduced, divalent form (ferrous iron, Fe(II)), which is much more soluble at circumneutral and alkaline pH conditions. Therefore, the concentration of dissolved Fe(II) can be significantly higher than the concentration of dissolved Fe(III). However, Fe(II) concentrations in modern, circumneutral anoxic aquatic environments is usually limited by the low solubility of Fe-sulfides. Furthermore, Fe(II) can also be removed from anoxic waters by formation of Fe-carbonates (e.g., siderite, ankerite, ferrous dolomite), Fe-phosphates (e.g., vivianite), or mixed valence oxides (magnetite).

In contrast to modern marine environments, lower oxygen concentration in the Proterozoic resulted in widespread anoxic conditions below the surface mixed layer of the ocean (e.g., Lyons et al., 2014). Furthermore, low marine sulfate levels caused these anoxic water masses to generally contain insignificant concentrations of sulfide, allowing the build-up of high Fe concentrations and hence the establishment of ferruginous conditions. Upwelling of sub-surface ferruginous water masses across the chemocline into the oxic surface ocean resulted in (partial) oxidation of the ferrous seawater iron reservoir, and precipitation of Fe(III)-minerals. The degree of oxidation (non-quantitative or near-quantitative) would have depended on environmental oxygen levels and

might be traceable through the Fe isotope composition of sedimentary rocks because the oxidation of ferrous iron to ferric iron is associated with a large isotope effect (e.g., Schauble et al., 2001; Johnson et al., 2002; Anbar et al., 2005; Polyakov et al., 2007). Near-quantitative oxidation of the ferrous iron pool will result in Fe-oxyhydroxides with a Fe isotope composition similar to the source (dominantly hydrothermal iron in anoxic deep oceans) while non-quantitative oxidation will cause Fe-oxyhydroxides to be significantly heavier (The fundamentals of iron isotope fractionation will be introduced in detail in Chapter 5.). Therefore, Fe isotopes appear to be a potentially powerful redox proxy to constrain redox conditions and atmospheric oxygen levels in deep time, at least at a qualitative level.

The application of Fe isotopes to paleoredox questions, however, depends on our understanding of the fundamental controls on isotopic compositions of sediments and sedimentary rocks. It is still unclear whether water column processes such as the degree of oxidation of a ferrous iron reservoir and the precipitation of Fe-oxyhydroxides control the isotopic composition (Rouxel et al., 2005; Planavsky et al., 2012b; Busigny et al., 2014) or the cycling of iron during diagenesis (Johnson et al., 2008a,b; Heimann et al., 2010) exerts the dominant control on final sedimentary iron isotope compositions. Whereas the first hypothesis would imply that the Fe isotopic composition of bulk sedimentary rocks and Fe-oxyhydroxides can be used as direct proxies for the degree of oxidation, a major role for diagenetic iron cycling involving mineral precipitation (e.g., Fe-sulfides, Fe-carbonates) and transformation (e.g., Fe-oxyhydroxides to magnetite) would complicate the application of Fe isotopes for paleoredox interpretations.

While deciphering the relative importance of water column and diagenetic processes on the isotopic composition of sedimentary rocks is a major question, we can also identify other important questions concerning the application of Fe isotopes to investigating the Neoproterozoic rise of oxygen. First, does Fe isotope compositions of marine sedimentary rocks show secular variation during the Neoproterozoic like many other proxies do? Second, given a more complete understanding of how Fe isotopic compositions can be used to infer paleoredox conditions and enviornmental oxygen levels, how does the Fe isotope trend compare to other proxies in terms of implications for the timing of Neoproterozoic oxygenation?

To address these questions, we analyzed the bulk rock Fe isotope composition of more than 100 marine organic-rich shales from Svalbard, northwestern Canada, and Siberia that cover

the time interval from 1050 to 570 Ma (Chapter 5). We combined these results with Fe/Al ratios and iron speciation data. Furthermore, we created an isotope mass-balance model to better understand the isotopic consequences of iron cycling during diagenesis and to evaluate the relative importance of diagenetic processes for the bulk shale Fe isotope ratio. Our results indicate that water column processes are much more important than diagenetic iron cycling, encouraging us to use Fe isotope ratios as a qualitative redox proxy. The Fe isotope record of the pre-Cryogenian Neoproterozoic (i.e., older than ca. 720 Ma) is characterized by large isotopic variation within individual stratigraphic units, but with values on average significantly heavier than the hydrothermal iron source. These data suggest non-quantitative oxidation of a ferrous seawater iron reservoir, and by inference relatively low environmental oxygen levels. However, the average Fe isotope composition of individual stratigraphic units approaches the composition of the hydrothermal iron source for post-Sturtian units. This shift in average iron isotope ratios suggests an increase in oxygen levels between the Sturtian and Marinoan glaciation, a result that appears inconsistent with our constraints in Chapters 3 and 4. This discrepancy highlights the need to better understand the fundamental controls on different redox proxies and to constrain the minimum oxygen thresholds at which redox proxies show a discernible signal. The records from these different proxies can only be reconciled if their individual minimum thresholds are understood. This will be a challenging task, but essential to quantify the Proterozoic evolution of atmospheric oxygen and relate it to other fundamental changes to Earth's surface environment, namely the evolution of eukaryotes.
# **Figures**



Fig. 1.1 Summary of major events in the Neoproterozoic (modified from Halverson and Shields-Zhou (2011)). The carbon isotope record of marine carbonate rocks indicates generally high  $\delta^{13}$ C values, punctuated by global negative anomalies (data from Halverson and Shields-Zhou, 2011). Eukaryotic organisms underwent significant diversification around 800 million years ago (Knoll et al., 2006; Knoll, 2014; Cohen and Macdonald, 2015). Similarly, molecular clock (mol. clock) estimates date the origin of animals to 800 Ma (Erwin et al., 2011; Erwin, 2015), consistent with the first biomarker evidence of sponges before the 717 Ma Sturtian glaciation (Brocks et al., 2015) and additional biomarker and putative fossil evidence for sponges before the 635 Ma Marinoan glaciation (Love et al., 2009; Maloof et al., 2010). Unambiguous fossil evidence for early animals come from the lower part of the post-Marinoan Doushantuo Formation in South China (e.g., Xiao et al., 1998; Yin et al., 2007). Ediacaran-type macrofossils are found on different cratons in strata younger than the ca. 580 Ma Gaskiers glaciation. The assembly of the supercontinent Rodinia began in the late Mesoproterozoic and continued in the early Neoproterozoic (Z.-X. Li et al., 2008). Rifting and occurred between 850 and 635 Ma and the supercontinent Gondwana started to assembly in the middle Ediacaran (Z.-X. Li et al., 2008). Also shown is the occurrence of large igneous provinces (LIPs) associated with Rodinia break-up (compiled by Cox et al., 2016). PCB = Precambrian-Cambrian boundary.



Fig. 1.2 Schematic portrayal of the re-oxidative sulfur cycle in anoxic marine sediments (modified from Jørgensen (1990)). Numbers refer to the the percent of sulfur (with respect to sulfur reduced by microbial sulfate reduction (MSR)) following the pathway. Numbers in blue were determined for thiosulfate only, ignoring other possible intermediate sulfur compounds. Abbreviations: oxi. = oxidation; red. = reduction; disp. = disproportionation.



Fig. 1.3 A diagram demonstrating multiple sulfur isotope systematics and nomenclature. Mass-dependent fractionation will cause a slope  $(^{33}\lambda)$  of 0.515. However, microbial-driven fractionation can cause deviations from this mass-dependent fractionation line, which produce shallower  $(^{33}\lambda < 0.5145; \text{MSR})$  or steeper  $(^{33}\lambda > 0.5145; \text{BSD})$  slopes. Deviations are expressed as positive or negative  $\Delta^{33}$ S values. Abbreviations: MSR = microbial sulfate reduction; BSD = bacterial sulfur disproportionation.

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#### Preface to Chapter 2

Although this thesis focuses on the biogeochemistry of Neoproterozoic marine black shales, Chapter 2 is a stratigraphic study of the ca. 850 Ma Chandindu Formation. This unit is part of the early Neoproterozoic Fifteenmile Group exposed in northwestern Canada. It is mostly composed of fine-grained siliciclastic rocks and, therefore, provides a good example of the type of rocks that were studied for this thesis. However, samples from the Chandindu Formation were not analyzed and are not part of any biogeochemical data set presented herein.

In this chapter, we officially define the Chandindu Formation as distinctive stratigraphic unit and provide the first description of its sedimentology and lateral variability. A more detailed study focusing on the sequence stratigraphic architecture and sedimentology of the entire Fifteenmile Group (including the Chandindu Formation) will be published independently of this thesis. Chapter 2 was published as part of a series of papers from our research group and collaborators at Harvard University, aiming to formalize the stratigraphic nomenclature and better understand the geological evolution of late Proterozoic strata in northwestern Canada. Our motivation of working on this succession is not only to answer geological questions, but also to extract the rich record of biological and biogeochemical change, like increasing eukaryote diversity, global glaciations, and increasing levels of atmospheric oxygen, that these rocks contain.

I strongly believe that biogeochemical data from ancient sedimentary successions are most meaningful when placed in a detailed sedimentological, geochronological, and stratigraphic context. Therefore, the role of Chapter 2 in this thesis is to demonstrate the field methodology that underpins the research our group carries out in order to understand the geological context of the samples we collect. The first step towards a meaningful biogeochemical data set from ancient rocks is careful field work, including mapping and stratigraphic section logging. I believe that it is essential to consider the depositional setting of the samples, the lateral variability of the sampled unit, and intrabasinal and global correlations. Samples studied in this thesis come from four different regions; Svalbard, northwestern Canada, Siberia, and Australia. I collected only a subset of the samples that I analyzed for this thesis (from northwestern Canada); most samples were collected by Galen Halverson (Svalbard, Siberia, northwestern Canada, Australia), with some others taken by our collaborator Francis Macdonald (northwestern Canada). All these rocks were sampled during mapping and stratigraphic section logging, reflecting our philosophy of how to approach the reconstruction of ancient environmental conditions and evolution of Earth's surface environments.

# 2 | The early Neoproterozoic Chandindu Formation of the Fifteenmile Group in the Ogilvie Mountains<sup>1</sup>

#### Abstract

Studies of biogeochemical and evolutionary change in the Neoproterozoic require a detailed understanding of stratigraphic successions and their intrabasinal correlation to integrate those records into regional and global frameworks. The early Neoproterozoic Fifteenmile Group in the Ogilvie Mountains has previously been shown to archive important information on the evolution of the biosphere, including ocean redox and early evolution of eukaryotes. Here, we formally define the Chandindu Formation, a 150 to 420-m-thick siltstone-dominated mixed carbonate-siliciclastic succession of the lower Fifteenmile Group in the Coal Creek and Hart River inliers. We present ten sections of the Chandindu Formation and propose a type section and formalization to promote the development of a consistent stratigraphic framework for Proterozoic successions in northwest Canada. The Chandindu Formation begins with muddy tidal flat facies, which are succeeded by shale-siltstone-sandstone coarsening-upward cycles deposited in a predominantly subtidal environment. However, carbonate occurrences throughout the entire unit suggest localized carbonate buildups, likely nucleated on fault-bound paleohighs where siliciclastic background sedimentation was low. These paleohighs originated from rift-inherited complex basin topography and syn-depositional faulting during deposition of the upper Chandindu Formation.

<sup>&</sup>lt;sup>1</sup>This chapter was published as: "Kunzmann, M., Halverson, G.P., Macdonald, F.A., Hodgskiss, M., Sansjofre, P.D., Schumann, D., Rainbird, R.H., 2014, The early Neoproterozoic Chandindu Formation of the Fifteenmile Group in the Ogilvie Mountains. In: Yukon Exploration and Geology 2013, K.E. MacFarlane, M.G. Nordling, and P.J. Sack (Eds.), Yukon Geological Survey, p. 93–107."

# 2.1 Introduction

Proterozoic strata in northwest Canada are exposed in erosional windows through Phanerozoic cover (Fig. 2.1A); from west to east, these are the Tatonduk, Coal Creek, and Hart River inliers of the Ogilvie Mountains, the Wernecke inlier in the Wernecke Mountains, and the Mackenzie Mountains. Broad stratigraphic correlation between Neoproterozoic successions in the Mackenzie Mountains and elsewhere in the Amundsen Basin in Arctic Canada is relatively straightforward (e.g. Rainbird et al., 1996), although new radiometric ages and chemostratigraphy (Jones et al., 2010; Macdonald et al., 2010b) motivate refinement of this correlation. Although broad stratigraphic similarities between Proterozoic inliers in northwest Canada were noticed decades ago (e.g. Gabrielse, 1972; Eisbacher, 1978a; Young et al., 1979), refined correlations on the formation scale have remained elusive. The difficulty in correlating between the inliers is due to many factors, including a paucity of radiometric dates, incomplete stratigraphic records, complex tectonostratigraphic evolution, and significant lateral facies changes, even within inliers (Macdonald et al., 2012). Nonetheless, a detailed understanding of regional correlations based on mapping, stratigraphic analysis including the definition and introduction of new formations, geochronology, and geochemistry, is necessary both to reconstruct the tectonic setting and basin evolution, and also to calibrate records of biogeochemical change and biological evolution obtained from these strata. The early Neoproterozic Fifteenmile Group in Yukon was deposited during a time span characterized by globally increasing eukaryotic diversity (e.g. Schopf et al., 1973; Porter and Knoll, 2000; Butterfield, 2004; Knoll et al., 2006) possibly facilitated by a non-sulphidic deep ocean (Canfield et al., 2008; Johnston et al., 2010; Sperling et al., 2013). Recent studies of the Fifteenmile Group identified scale microfossils (Macdonald et al., 2010a; Cohen et al., 2011; Cohen and Knoll, 2012) of which some show the "earliest compelling evidence for biologically controlled eukaryotic biomineralization" (Cohen et al., 2011). A recent study of the Fifteenmile Group by Sperling et al. (2013) concluded that mostly ferruginous deep waters were overlain by oxygenated shelf waters and that the oxygen level in the surface mixed laver should have been high enough to support early metazoa.

In this paper, we describe the sedimentology and lateral variation of the Chandindu Formation of the lower Fifteenmile Group in the Coal Creek and Hart River inliers, and also describe a proposed type section in detail. These data provide constraints on the depositional environment and basin topography, which in turn have implications for basin evolution, regional correlations and biogeochemical data obtained from this succession.

#### 2.2 Fifteenmile Group

The Fifteenmile Group (Fig. 2.1B, Thompson et al., 1987; Roots and Thompson, 1992; Thompson et al., 1994) in the Ogilvie Mountains is part of the early Neoproterozoic "Succession B" of northwestern Laurentia which also comprises the Mackenzie Mountains Supergroup in the Wernecke and Mackenzie mountains, and the Shaler Supergroup on Victoria Island (Young et al., 1979; Eisbacher, 1981; Rainbird et al., 1996; Long et al., 2008). In the central Ogilvie Mountains, the Fifteenmile Group originally included all strata that unconformably rest on the late Paleoproterozoic Wernecke Supergroup (Delaney, 1981; Thorkelson, 2000; Thorkelson et al., 2005) and unconformably underlie the mid-Neoproterozoic Callison Lake dolostone (Abbott, 1997; Macdonald and Roots, 2010) and Mount Harper Group (Mustard and Roots, 1997; Macdonald et al., 2011; Cox et al., 2013) of the Windermere Supergroup. Following initial subdivision of the Fifteenmile Group into five lower (PR1–PR5) and three upper (PF1–PF3) map units (Thompson et al., 1994), Abbott (1993) introduced a fourth upper map unit (PF4) and extended the nomenclature to the Hart River inlier. Subsequently, Abbott (1997) renamed PF4 the "Callison Lake dolostone" and interpreted the entire succession between Wernecke Supergroup and Callison Lake dolostone to represent the Pinguicula Group in the Ogilvie Mountains. The Pinguicula Group is a mixed siliciclastic-carbonate unit and was originally defined in the Wernecke Mountains (Eisbacher, 1978b, 1981), where it was subdivided into five units (A–E). Young et al. (1979) subsequently correlated it with the Mackenzie Mountains and Shaler supergroups. Later, Thorkelson et al. (2005) proposed that only the upper units correlate with the Mackenzie Mountains Supergroup. Following re-mapping, Macdonald et al. (2011) assigned the lower four map units (PR1–PR4) to the Pinguicula Group and the upper map units (PF1–PF3) to the Fifteenmile Group. Correlation of PR1 and PR2 with the Pinguicula Group was also suggested by Medig et al. (2010) based on stratigraphic similarities and contact relationships with the underlying Wernecke Supergroup. Medig et al. (2013) subsequently suggested that the base of

the purported Pinguicula Group in the Coal Creek inlier (PR1, or PA in our mapping) is in fact an older unit. This raises the possibility that the Pinguicula Group does not occur in the Coal Creek inlier.

Recently, new radiometric ages coupled with chemostratigraphy motivated revised regional correlations of the Fifteenmile Group in the central Ogilvie Mountains with strata in other inliers in Yukon, the Mackenzie Mountains, and on Victoria Island (Macdonald et al., 2010a; Macdonald and Roots, 2010; Macdonald et al., 2010b; Halverson et al., 2012; Macdonald et al., 2012). The first direct age constraint on the Fifteenmile Group came from a tuff in the upper half of the succession (Fig. 2.1b) that yielded a U-Pb zircon age of  $811.51 \pm 0.25$  Ma (Macdonald et al., 2010b). A 717.43  $\pm$  0.14 Ma U-Pb zircon age from a rhyolite in the Mount Harper Volcanic Complex, upper Mount Harper Group, places a minimum age on the Fifteenmile Group. Subsequently, Macdonald and Roots (2010) correlated the Fifteenmile Group in the Coal Creek inlier with the Lower Tindir Group of the Tatonduk inlier and refined correlations with strata in the Hart River inlier. As a consequence, Macdonald et al. (2011) recommended abandonment of the term Tindir Group to simplify stratigraphic nomenclature across the inliers. Furthermore, they subdivided the Fifteenmile Group into a "Lower Assemblage" composed of mixed clastic rocks and dolostone, conformably followed by the "Craggy Dolostone" (Macdonald et al., 2011). Most recently, Halverson et al. (2012) subdivided the "Lower Assemblage" into the "Gibben", "Chandindu", and "Reefal Assemblage" formations. They proposed correlation of a basal sandstone in the Gibben formation with map unit PPD1 in the Hart River inlier (Abbott, 1997), correlation of the remaining Gibben formation with PPD2, and correlation of the Chandindu formation with PPD3.

The basal sandstone unit in the Gibben formation unconformably overlies the Pinguicula Group (as mapped), and grades upward into shallow marine ooid and coated-grain packstone and grainstone, with microbial laminite and evidence of subaerial exposure increasing up section (Halverson et al., 2012; Macdonald et al., 2012). In the Hart River inlier, the Gibben formation, as currently defined, includes a basal interval of fine-grained siliciclastic rocks, which is succeeded by a shoaling upward carbonate sequence that is virtually identical to that described in the Coal Creek inlier. Due to syn-depositional extensional tectonics and deposition in fault-bound grabens, the thickness can vary from less than 20 m to 600 m (Halverson et al., 2012; Macdonald et al.,

2012).

The Gibben formation is overlain by a prominent interval of mud-cracked, maroon shale and siltstone which grade into grey shale, and siltstone and sandstone with rare stromatolite bioherms and olistoliths. This mainly clastic unit comprises the up to 400-m-thick Chandindu formation, as informally proposed by Halverson et al. (2012). The top of the Chandindu formation is a prominent flooding interval.

The overlying 500 to 1700-m-thick Reefal Assemblage is mostly composed of thick, grey, stromatolitic boundstone, grainstone, ribbonite, and rhythmite interbedded with prominent black shale intervals representing maximum flooding surfaces (Halverson et al., 2012; Macdonald et al., 2012). The formation is marked by significant lateral facies changes controlled by early Fifteenmile Group syn-depositional, down-to-the-northwest, normal faulting that generated significant basin relief. Lateral facies variation is interpreted to represent NW-prograding reef systems that grade laterally into siliciclastic basinal deposits representing grabens or half-grabens (Halverson et al., 2012; Macdonald et al., 2012).

The following >500-m-thick Craggy Dolostone is mostly composed of light grey, strongly silicified and recrystallized, ridge-forming dolostone, consisting mostly of microbial laminite, ooid and coated-grain packstone and grainstone, tabular clast conglomerate, and gravity flow breccia. Macdonald et al. (2012) concluded that the Craggy Dolostone represents the establishment of a broad stable carbonate platform and infilling of Reefal Assemblage sub-basins. However, more recent observations show significant lateral facies changes and large volumes of gravity flow breccia that imply more complex seafloor topography and may indicate continued extensional tectonism. The top of the Craggy Dolostone is truncated by the sub-Callison Lake Dolostone unconformity.

## 2.3 Chandindu Formation (new)

The proposed type section of the Chandindu Formation is M103, about 15 km northeast of Mount Harper (Fig. 2.2). A northeast-trending ridge provides continuous exposure of the unit, which is typically recessive weathering and slightly more vegetated than the grey-weathering rubble-covered slopes of the over and underlying units (Fig. 2.3). Here the Chandindu Formation is 249-m-thick (Fig. 2.4), with clear lower and upper boundaries. The base of the section

(N64°45′15.4″, W139°32′21.9″) is located on a north-facing slope and repeated by a fault. This fault causes a repetition of about 20 m of the uppermost underlying Gibben formation and the base of the Chandindu Formation (Fig. 2.5A).

The top of the underlying Gibben formation is composed of medium-grey and mediumbedded microbial laminite and minor grainstone indicating deposition in a peritidal environment. Secondary black chert bands up to 5 cm thick cut carbonate bedding in places. A sharp contact with a prominent mud-cracked (Fig. 2.5B), reddish siltstone with grey-brown shale interbeds marks the base of the Chandindu Formation. This distinct and laterally continuous mud-cracked interval makes identifying the base of the Chandindu Formation straightforward. In this section, the mud-cracked interval consists of 17 m of alternating fine-grained, grey-green (black-weathering), mostly thickly laminated to very thinly bedded, well-sorted sandstone with common mudcracks and grey-green siltstone. The mud-cracked interval is succeeded by 232 m of moderately well defined coarsening-upward cycles with no mudcracks. These cycles typically consist of dark grey to black, thinly laminated silty shale and shale between a few decimeters and a few meters thick at the base; a middle interval of tens of meters of grey-green, thickly laminated siltstone; and finegrained, well sorted, very thinly bedded, grey sandstone ranging in thickness from 1 decimeter to 1-2 m at the top (Fig. 2.5C). Coarsening-upward cycles are typical for the Chandindu Formation and are observed in every section (Fig. 2.8). Sandstone beds commonly contain hummocky cross-stratification (e.g. in section MY1301, Fig. 2.8), and locally other indications of a stormdominated environment (Fig. 2.5D). Three beds of ribbonite-facies carbonate (facies types were described by Macdonald and Roots (2010) and Macdonald et al. (2012)) also occur throughout this interval. A prominent feature of the uppermost Chandindu Formation in this section is the occurrence of olistoliths: a 2-m-thick block of stromatolite and a 6-m-thick block of grainstone and stromatolite. Following Halverson et al. (2012), we place the top of the Chandindu Formation at the base of the uppermost maximum flooding surface (that is an abrupt shift to finer grained rocks, typically black shale) which separates the siliciclastic-dominated Chandindu Formation from the overlying carbonate-dominated informal Reefal Assemblage. However, we note that in more siliciclastic-dominated sections, this boundary can be somewhat difficult to identify.

## 2.4 Petrography of Siliciclastic Rocks

To characterize the siliciclastic Chandindu Formation, we applied optical microscopy and scanning electron microscopy (SEM) on specimens of sandstone, siltstone, and shale collected from type section M103. Here, we describe one example from each type. Petrographic thin sections were investigated with a Hitachi S-3000N Variable Pressure-SEM (VP-SEM) equipped with an Oxford INCA microanalytical system (energy dispersive X-ray spectrometry (EDS) detector). The samples were studied in backscattered electron (BSE) SEM mode at an acceleration voltage of 15 kV, an emission current of 64  $\mu$ A, and a vacuum pressure of 20 Pa. Selected areas were analyzed with the SEM-EDS microanalytical system for approximately 15 to 20 minutes to obtain element distribution maps. Descriptions of the carbonate facies types can be found elsewhere (e.g. Macdonald et al., 2012).

Sandstone (M103.1.0): This sample comes from a 3.1 m-thick sandstone interval at the base of M103 (Fig. 2.4). The black-weathering, fine-grained sandstone is reddish-grey on fresh surfaces and breaks into laminae 0.5–1.0 cm thick. Siltstone interbeds, shale partings, mm-scale mud drapes, and mud cracks occur. In thin section, the rock is composed of about 90% quartz and 10% sericite. The mineralogically mature rock is very well sorted with up to 160  $\mu$ m-large monocrystalline quartz crystals that show slight undulose extinction. Roundness and sphericity of quartz grains are difficult to evaluate due to compaction (Fig. 2.6A), which causes straight crystal boundaries and the undulose extinction. However, quartz grains seem to have a high sphericity. Porosity is estimated to be less than 1%. The sericite occurs in mud drapes up to 2 cm long and 2 mm thick and indicates alteration of primary phyllosilicates. Precise identification of minerals would require Transmission Electron Microscopy (TEM) and X-ray powder diffraction (XRD). The mud drapes show an internal parallel and continuous lamination caused by a material difference (Fig. 2.6A) and also include up to 100  $\mu$ m-large, anhedral, round to elliptical opaque phases (Fig. 2.6A). Scanning electron microscopy shows that these phases are often composed of a concentric core of organic matter and an iron oxyhydroxide rim (Fig. 2.6B–D). The rim also contains small quartz and phyllosilicate crystals, which are likely inclusions that could suggest a secondary origin of the iron oxyhydroxide. These inclusions are also visible on element distribution maps (Fig. 2.6E–H). Alternatively, the iron oxyhydroxide could have precipitated early and quickly in association

with the inclusions. These structures could be fragments of microbial mats preserved by the iron oxyhydroxide rim or even represent microfossils, but additional SEM and TEM studies are necessary to distinguish between these possibilities.

Siltstone (M103.143.2): This sample comes from the top of a 21.1-m-thick siltstone interval (Fig. 2.4). The grey to dark grey, partly rusty-weathering siltstone breaks into laminae ~ 0.5 cm thick. The sample was taken at the contact with overlying fine-grained sandstone (Fig. 2.7A, B). The rock is composed of about 50% quartz and 50 % small phyllosilicate crystals, likely sericite resulting from alteration and low-grade metamorphism of clay minerals and mica. Individual quartz grains show undulose extinction and are up to 30  $\mu$ m in diameter (Fig. 2.7C). The phyllosilicate crystals are <10  $\mu$ m across (Fig. 2.7C, D). Organic matter mostly occurs as <50  $\mu$ m-large irregular accumulations and is always mixed with quartz crystals (Fig. 2.7C, E). In contrast to organic matter occurrences in mud drapes of the sandstone sample M103.1.0, organic matter in siltstone does not occur as round structures and is not rimmed by iron oxyhydroxide (Fig. 2.7C, E). Organic matter accumulations in overlying fine-grained sandstone are also irregular but larger (<80  $\mu$ m) and more common (Fig. 7B).

Shale (M103.111.2): The shale sample described here comes from a 1-m-thick interval in the middle of the Chandindu Formation (Fig. 2.4). The rock is dark-grey and contains some sub-millimeter-thick silt laminae. SEM study reveals that the rock consists of about 20% quartz and 80% phyllosilicates (Fig. 2.7F–H). The quartz crystals are less than 15  $\mu$ m in diameter. Phyllosilicate crystals are less than 10  $\mu$ m across (Fig. 2.7F). Element mapping helped to identify calcium-phosphorous-bearing minerals, likely apatite (Fig. 2.7G, H).

#### 2.5 Lateral variability of the Chandindu Formation

Ten sections of the Chandindu Formation were logged in the central and eastern Ogilvie Mountains (Fig. 2.8). Nine were logged in the Coal Creek inlier, about 80 km north of Dawson City, and one section was logged in the Hart River inlier, about 120 km north of Mayo. In the western part of the Coal Creek inlier, near Mount Harper, the Chandindu Formation thickness is between 150 and 250 m. Further to the east, at Fifteenmile River and Mount Gibben, the thickness increases to 400–420 m (Fig 2.8). In the Hart River inlier, the top of the Chandindu Formation is commonly

truncated on a low-angle unconformity beneath the Callison Lake dolostone (Abbott, 1997; Macdonald et al., 2011); however, in our measured section, it is truncated by an unconformity at the base of the early Paleozoic Bouvette Formation, resulting in a partial thickness of the Chandindu Formation of less than 200 m.

The dominant lithology in the Chandindu Formation is siltstone with minor shale and sandstone typically arranged in coarsening-upward cycles (for example in the type section M103 or in MY1301 about 190–260 m above base, Figs. 2.4, 2.5C). However, carbonate rocks representing diverse depositional environments occur in every section.

## 2.6 Discussion

The Chandindu Formation is conformably bound by the older Gibben formation and the younger Reefal Assemblage (Fig. 2.1B). The sharp base of the Chandindu Formation reflects an abrupt change of the depositional environment from a shallow marine carbonate environment dominated by microbial laminite formed on tidal flats and high-energy grainstone bars, to a muddy tidal flat where fine-grained siliciclastic sediments were deposited. The contact with the overlying Reefal Assemblage is marked by a prominent maximum flooding surface indicated by the occurrence of black shale. This flooding interval is usually overlain by the first reef deposits of the Reefal Assemblage. An exception is the section reported by Macdonald and Roots (2010) north of Mount Harper where deposition of black shale continued to dominate until deposition of the upper Reefal Assemblage.

The laterally extensive mud-cracked siliciclastic interval at the base of the Chandindu Formation (Fig. 2.8) suggests deposition on a large, partly exposed, muddy tidal flat. Base level rise upsection is indicated by the transition of this mud-cracked interval to coarsening-upward cycles of shale, siltstone, and sandstone, sporadically capped by carbonate, commonly stromatolitic (Halverson et al., 2012). The coarsening-upward cycles indicate progradation and shallowing of the depositional environment. The occurrence of stromatolites at the top of some cycles points towards decreasing siliciclastic sedimentation rates and presages the eventual proliferation of stromatolite reef facies in the overlying Reefal Assemblage. Hummocky cross-stratification in sandstone of upward-coarsening cycles is evidence of common storm events and suggest deposition

between storm and fair weather wave base (e.g. Dott and Bourgeois, 1982; Duke, 1985; Leckie and Krystinic, 1989; Dumas and Arnott, 2006). Mild lateral thickness and facies variations, in particular in the lower part of the formation (Fig. 2.8), may indicate less extensional tectonic activity compared to the underlying Gibben formation. However, map relationships (Fig. 2.2) and the occurrence of large olistoliths in the upper part of the formation (for example in the type section, Fig. 2.4, see also Macdonald et al. (2012)) indicate syn-depositional faulting. Significant basin relief is also likely the reason why lithostratigraphic correlation of coarsening-upward cycles in the Chandindu Formation is not readily apparent. However, at least one flooding event (indicated by shale intervals) in the middle part of the unit is present in every section west of Mount Gibben.

One of the most striking features of the Chandindu Formation is the occurrence of different carbonate facies types throughout the formation in every section. The carbonate facies range from supratidal intraclast breccia to deep marine debris flow deposits and rhythmite (Fig. 2.8), and often forms laterally discontinuous mounds. Carbonate deposition was therefore not restricted to one depositional environment and the carbonate factory was never completely overwhelmed by the abundant siliciclastic input. What controlled carbonate versus siliciclastic deposition? A possible explanation is that a laterally extensive carbonate depositional environment, parallel to the shoreline, was interrupted by terrigenous input from a delta. Lateral migration of distributary channels could have controlled the spatial distribution of siliciclastic versus carbonate deposition. Another possible explanation is that rift-inherited complex basin topography, further enhanced by syn-depositional faulting, controlled the sedimentation regime. Carbonate deposition established in areas of low siliciclastic background sedimentation, for example, on paleohighs on fault-bound rift blocks. Here, stromatolite bioherms and grainstone bars (the two most common carbonate facies types in the Chandindu Formation) preferentially developed (Fig. 2.8), providing a source for olistoliths in the Chandindu Formation (e.g. M103, Figs. 2.4, 2.8).

The Chandindu Formation in the Hart River inlier contains a significantly higher ratio of sandstone to siltstone, which is consistent with the occurrence of a deltaic system to the east (in present coordinates) and at least partial correlation of the Chandindu Formation with the Katherine Group. In the Wernecke and Mackenzie mountains, the Katherine Group is a thick succession of fluvial-deltaic quartz arenite and marine siltstone and sandstone (Eisbacher, 1978b, 1981; Thorkelson, 2000; Thorkelson et al., 2005; Turner, 2011; Long and Turner, 2012) that likely represents the proximal facies of a delta. Rainbird et al. (1997) previously postulated that the Katherine delta was fed by continent-scale, northwesterly migrating river systems that originated from the Grenvillian orogeny based on the predominance of ca. 1 Ga detrital zircons in the Katherine sands. The high degree of maturity of the sandstones in the Chandindu Formation (see petrographic description) is consistent with an interpretation of distal equivalent of parts of the Katherine Group, although documentation of Grenvillian-aged tectonothermal activity in the northern Cordillera (Thorkelson et al., 2005; Milidragovic et al., 2011) allows that the ca. 1 Ga zircons may have been more locally sourced. Correlation of the lower Fifteenmile Group in the Coal Creek and Hart River inliers with parts of the Katherine and Hematite Creek groups in the Wernecke Mountains (Turner, 2011; Macdonald et al., 2012) is still poorly understood and needs to be tested in future studies.

#### 2.7 Conclusion

We describe the type section of the early Neoproterozoic Chandindu Formation. This overall deepening-upward unit represents diverse depositional regimes ranging from supra and intertidal to subtidal environments dominated by siliciclastic sedimentation. Deposition of carbonate most likely occurred on rift-related paleohighs where the site of deposition was protected from siliciclastic input. Parts of the fluvial-deltaic Katherine Group further to the east (present coordinates) are a possible source of the terrigenous material.

### Acknowledgments

We are grateful for financial support from the Yukon Geological Survey, NSERC, American Chemical Society Petroleum Research Fund, and the Polar Continental Shelf Program. MK acknowledges support by a GEOTOP scholarship and a J.B. Lynch Fellowship. Justin Strauss, Emily Smith, Eric Bellefroid, Thomas Maguire, Lyle Nelson, and Danielle Thomson helped in the field. Hojatollah Vali is thanked for access to the Facility for Electron Microscopy Research (FEMR) at McGill and Tanja Bosak for discussions. We sincerely thank Charlie Roots and his family for their hospitality and help with logistics. Charlie Roots is also thanked for a constructive and detailed review that improved the paper. We acknowledge logistical support by Don Francis. Finally, we thank Fireweed Helicopters for safe transportation.

# **Figures**



Fig. 2.1 Simplified geology and stratigraphy of the study area. A) Distribution of Proterozoic strata in inliers in Yukon and the Northwest Territories. Black box of the Coal Creek inlier indicates the area shown in Fig. 2. Modified from Macdonald et al. (2011). B) Lithostratigraphy of Tonian and Cryogenian strata in the Ogilvie Mountains. Modified from Macdonald et al. (2012).



#### The early Neoproterozoic Chandindu Formation



Fig. 2.3 View northwestward of Fifteenmile Group including the well exposed and proposed type section of the Chandindu Formation. Field of view is about 3 km.



Fig. 2.4 Lithostratigraphy of M103, the type section of the Chandindu Formation. See Figs. 2.2 and 2.3 for location.



**Fig. 2.5** Outcrop photos of the Chandindu Formation. A) Base of the Chandindu Formation in section M103 (yellow arrow) looking westward. The Gibben-Chandindu contact is repeated by a fault. Person (yellow ellipse) for scale. B) Mudcracks of the basal Chandindu Formation in section M103. Coin for scale is 2.65 cm across. C) Shale-siltstone-sandstone cycles in section MY1301 between 190 and 260 m above base. Person (yellow ellipse) for scale. D) Cross-section of sand-filled gutter cast in the lower Chandindu Formation in section MY1301. Pencil length is 15 cm.



Fig. 2.6 Thin section and SEM-BSE images of the sandstone sample M103.1.0. A) Sericitized mud drape (red arrow, brown interval) floats in well-sorted quartz arenite (green arrow). The mud drape shows an internal parallel lamination (white arrow) and about 100  $\mu$ m-large opaque phases (orange arrow). Cross-polarized light. B) SEM imaging reveals that many opaque phases consist of a core of organic matter. The object shown in C) is indicated by the orange arrow. C) Higher magnification shows that <5  $\mu$ m-large quartz crystals occur as inclusion in the rim. (orange arrow). Note small crystal size (<10  $\mu$ m, red arrow) of sericite. D) Close-up of organic matter in C) that forms the core. E)–H) Element distribution maps of the area shown in C) clearly distinguishes the carbon-rich core, iron-rich rim and aluminium- and silica-rich phyllosilicates (sericite) of the surrounding material. Scale shown in E) also applies to maps (F–H) of other elements.


Fig. 2.7 Thin section and SEM-BSE images of the silstone sample M103.143.2 (A–E) and shale sample M103.111.2 (F–H). A) Thin section photograph of the contact (orange arrow) between siltstone (below) and fine-grained sandstone (above). B) SEM backscatter image of the siltstone-sandstone contact (orange arrow). Note significant larger size of quartz crystals (red arrows) above the contact and larger accumulations of organic matter (white arrows). C) Higher magnification of the siltstone part shows up to 30  $\mu$ m-large quartz crystals (orange arrows), less than 10  $\mu$ m-large phyllosilicates (red arrows), and an irregular accumulation of organic matter (white arrow, black clots). D) Aluminium distribution map shows dominance of phyllosilicates and occurrence of larger quartz crystals (lack of aluminium, dark areas). E) Carbon distribution map helps to identify the concentration of organic matter in the upper right corner of photo (C). See (D) for scale. F) SEM-BSE image of shale sample M103.111.2. Note occurrence of quartz crystals (orange arrows), phyllosilicates (red arrows), and apatite (white arrow). G) and H) Distribution maps of calcium and phosphorous show correlation in some areas (for example orange arrow) indicating occurrence of apatite. Scale in G) also applies to H).



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### Preface to Chapter 3

In the following chapter we present biogeochemical data from a nearly complete continental shelf succession in northeastern Svalbard, which spans more than 200 million years of Neoproterozoic Earth history. These rocks were deposited between ca. 835 and 630 Ma and span the ca. 717 Ma Sturtian and ca. 635 Ma Marinoan low-latitude glaciations. Therefore, our data set allows us to contribute to an increasing number of paleoredox studies that try to better characterize the temporal and spatial evolution of ocean chemistry in the Neoproterozoic. The ultimate goal of these studies is to better understand the link between oceanic redox conditions, atmospheric oxygen concentration, global glaciation, and the emergence of complex life.

Recent biomarker (Love et al., 2009) and putative body fossil evidence (Maloof et al., 2010) suggests that sponges emerged before the Marinoan, and possibly even before the Sturtian glaciation (Brocks et al., 2015)<sup>2</sup>. Furthermore, recent molecular clock studies date the origin of Metazoa to ca. 800–750 Ma (Erwin et al., 2011; Erwin, 2015). It is debated whether an increase of atmospheric oxygen concentration stimulated biological evolution (e.g., Butterfield, 2009; Knoll and Sperling, 2014; Lenton et al., 2014), but if true, we expect evidence for increasing oxygen levels before or after the Sturtian glaciation. Alternatively, emergence of early Metazoa without a measurable increase in oxygen levels suggests that its concentration was at least high enough to support their simple body plans, currently estimated to be in the range of 0.5–4.0% present atmospheric levels (Mills et al., 2014).

The nearly complete Neoproterozoic succession in Svalbard provides an outstanding opportunity to test whether the Sturtian and Marinoan glaciations were associated with changes in environmental oxygen levels. We used iron speciation and redox-sensitive trace element concentrations to evaluate paleoredox conditions of shelf environments at the time of early animal evolution.

 $<sup>^{2}</sup>$ This paper was not published before Chapter 3 was published. Therefore, we do not consider its conclusions in Chapter 3.

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Mills, D. B., Ward, L. M., Jones, C. A., Sweeten, B., Forth, M., Treutsch, A. H., and Canfield, D. E., 2014. Oxygen requirements of the earliest animals. *Proceedings of the National Academy* of Sciences of the USA 111, 4168–4172. 3 Geochemistry of Neoproterozoic black shales from Svalbard: Implications for oceanic redox conditions spanning Cryogenian glaciations<sup>1</sup>

### Abstract

We present paleoredox data from black shales from the ca. 835–630 Ma Akademikerbreen and Polarisbreen groups, northeastern Svalbard. These iron speciation, trace metal, and organic carbon data include the first record of ocean redox conditions leading up to the Sturtian glaciation and contribute to the emerging narrative of protracted Neoproterozoic oxygenation. Sampled shales were deposited under dominantly suboxic to anoxic-ferruginous conditions on a stable continental shelf. Together with data from other basins, these data show no evidence of dramatic increases in environmental oxygen levels prior to or following the Sturtian glaciation. Proposed global oxygenation in the aftermath of the Marinoan glaciation did not lead to long-term oxygenation of shelf environments in Svalbard or northwestern Canada. We suggest that this reflects sufficient organic matter loading to maintain suboxic to anoxic water columns on continental margins. In contrast, oxygen concentrations may have been higher in low-productivity zones further offshore, where downwelling of oxygenated surface waters may have even increased oxygen concentrations in the deep ocean.

<sup>&</sup>lt;sup>1</sup>This chapter was published as: "Kunzmann, M., Halverson, G.P., Scott, C., Minarik, W.G., Wing, B. A., 2015, Geochemistry of Neoproterozoic black shales from Svalbard: Implications for oceanic redox conditions spanning Cryogenian glaciations. Chemical Geology 417, 382–393."

## 3.1 Introduction

The Neoproterozoic Era was marked by extreme environmental changes including low-latitude glaciations (e.g. Kirschvink, 1992; Hoffman et al., 1998; Hoffman and Schrag, 2002), emplacement of several continental flood basalts (e.g. Halverson et al., 2014), diversification of microscopic eukaryotes (Knoll et al., 2006; Cohen and Macdonald, 2015), emergence of metazoa (Love et al., 2009; Maloof et al., 2010), and oxygenation of Earth's surface environments (e.g. Fike et al., 2006; Canfield et al., 2007; Sahoo et al., 2012). Causal relationships are commonly evoked among these features. For example, the diversification of multicellular eukaryotes, including early animals, is widely inferred to be tied intimately to the oxygenation of Neoproterozoic surface environments (e.g. Anbar and Knoll, 2002), although the nature of this connection is controversial (Butterfield, 2009; Lenton et al., 2014). Hence, understanding the redox properties of the ancient ocean and its temporal evolution is central to understanding the latest Precambrian emergence of a complex biosphere.

Previous chemostratigraphic studies have shown that the water column below storm wave base in the Neoproterozic was dominated by anoxic-ferruginous conditions (Canfield et al., 2008; Johnston et al., 2010; Sperling et al., 2013, 2015b) and that euxinic conditions in Meso- to Neoproterozoic oceans developed only locally and were presumably restricted to continental margins (Logan et al., 1995; C. Li et al., 2010; Poulton et al., 2010; Planavsky et al., 2011; Reinhard et al., 2013). Multiple data sets point to an Ediacaran (635–541 Ma) rise in oxygen concentrations (e.g. Hurtgen et al., 2005; Fike et al., 2006; Canfield et al., 2007; Sahoo et al., 2012) that broadly coincides with the first appearance of fossils interpreted as bilaterian embryos (e.g. Xiao et al., 1998). However, redox studies from individual Ediacaran basins have revealed ambiguous results, variably indicating anoxic (C. Li et al., 2010; Johnston et al., 2013) or oxic (McFadden et al., 2008; Johnston et al., 2012; Ader et al., 2014; Kendall et al., 2015) water columns below the surface mixed layer. Although spatially and temporally heterogeneous ocean chemistry may help account for these seemingly contradictory results (Lyons et al., 2012, 2014; Sperling et al., 2014; Kendall et al., 2015), additional data from sedimentary basins worldwide are required to paint a more detailed picture of the spatial and temporal variability of Neoproterozoic oceanic redox conditions.

The emerging evidence that sponges may have inhabited the Cryogenian interglacial ocean (Love et al., 2009; Maloof et al., 2010), along with molecular clock evidence for key early metazoan branching points well before the Ediacaran Period (Erwin et al., 2011) raises the question of whether environmental oxygen levels may have increased before or during the Cryogenian (ca. 717–635 Ma) period. If so, what was the relationship between Cryogenian global glaciations and oxygenation? To begin to answer these questions, we conducted a paleoredox study of the ca. 835–630 Ma Akademikerbreen and Polarisbreen groups in northeastern Svalbard (Fig. 3.1). The unusually complete succession spans the global Sturtian and Marinoan glaciations and includes black shales deposited on a stable continental margin prior to, during, and after the Cryogenian period. We measured iron speciation and redox-sensitive trace metal abundances in these black shales. Interpreted within the context of other Neoproterozoic datasets, these data suggest no abrupt changes in environmental oxygen levels until after the Marinoan glaciation, when high productivity and efficient organic carbon burial increased oxygen concentrations and stimulated accumulation of Mo in seawater and authigenic enrichment in euxinic sediments.

## 3.2 Geological setting

The Neoproterozoic succession in Svalbard is presently exposed in a N–S striking, 160-km-long fold-and-thrust belt on the islands of Spitsbergen and Nordaustlanded (Fig. 3.1a). The succession represents one of the most complete records of early to middle Neoproterozoic Earth history (Fig. 3.1b) and hosts glacial deposits of the  $\sim$ 717 Ma Sturtian and  $\sim$ 635 Ma Marinoan glaciations (Halverson et al., 2004; Halverson, 2011). The stratigraphy is nearly identical to the coeval succession in East Greenland, prompting the widely accepted view that both were deposited in a single, continuous basin (e.g. Fairchild and Hambrey, 1995; Hoffman et al., 2012).

The Veteranen Group at the base of the succession (Fig. 3.1b) is younger than  $\sim 950$  Ma (Gee et al., 1995; Johansson et al., 2000) and has been interpreted to record an initial rift-phase of basin development (Maloof et al., 2006). In contrast, the overlying Akademikerbreen and Polarisbreen groups (Fig. 3.1b) were deposited on a stable, thermally subsiding continental shelf. Studied shale samples come from all three groups, however, most samples are from the Polarisbreen Group because the Veteranen and Akademikerbreen groups are dominated by coarse siliciclastic and

carbonate rocks, respectively (e.g. Wilson, 1958, 1961; Knoll et al., 1986; Maloof et al., 2006; Halverson et al., 2007). The sampled shales represent the deepest facies preserved and were deposited at or below storm wave base (see Supplementary Information for details).

The Akademikerbreen Group shows broad evolution from a storm- dominated carbonate ramp (Grusdievbreen Formation) to a rimmed carbonate platform with abundant stromatolites and shallow carbonate facies (Svanbergfjellet and Draken formations) (e.g. Wilson, 1961; Knoll and Swett, 1990; Halverson et al., 2007). Shale samples come from rare muddy intervals that reflect maximum flooding surfaces. The upper Grusdievbreen and lower Svanbergfjellet formations contain the globally synchronous Bitter Springs negative carbon isotope anomaly (Maloof et al., 2006; Halverson et al., 2007) constrained to have started after  $\sim 811$  Ma and ended before  $\sim 789$ Ma (Macdonald et al., 2010; Swanson-Hysell et al., 2015). The upper Akademikerbreen Group records a shift to a mixed carbonate-siliciclastic ramp (Backlundtoppen Formation). Black limestone rhythmites and shales (Russøya Member) form the base of the Polarisbreen Group (Figs. 3.1b, 3.2). Glaciomarine deposits of the Petrovbreen Member (Fairchild and Hambrey, 1984) unconformably overlie the Russøya Member and are correlative with  $\sim 717$  Ma Sturtian deposits globally (Macdonald et al., 2010; Halverson, 2011). Importantly, the sub-Petrovbreen unconformity truncates the Russøya Member to the top of the Islay negative carbon isotope excursion (Hoffman et al., 2012). New geochronological age constraints from NW Canada suggest that the Islay anomaly predates the Sturtian glaciation by  $\sim 15$  Ma (Strauss et al., 2014). Thus, assuming that the Islay excursion is a globally synchronous event, a hiatus of  $\sim 15$  Ma could be present in the Neoproterozoic succession in Svalbard. Shales from the overlying post-glacial MacDonaldryggen Member in Svalbard and correlative Arena Formation in East Greenland were deposited below storm wave base, followed by shoaling and deposition of shallow-water carbonates of the Slangen Member in Svalbard.

The unconformably overlying terrestrial Wilsonbreen Formation (Fairchild and Hambrey, 1984) is correlative to  $\sim 635$  Ma Marinoan glacial deposits elsewhere (Hoffmann et al., 2004; Condon et al., 2005; Halverson, 2011; Rooney et al., 2015). The pre-glacial Trezona negative carbon isotope excursion (e.g. McKirdy et al., 2001; Halverson et al., 2002) is absent from strata in Svalbard (Hoffman et al., 2012), suggesting a significant hiatus, difficult to constrain, beneath the Wilsonbreen glacials. The Wilsonbreen Formation is overlain by a typical post-Marinoan cap

dolostone of the lower Dracoisen Formation that deepens-upward into outer shelf black shales (Halverson et al., 2004). The Neoproterozoic succession is truncated by an unconformity beneath the Cambrian Oslobreen Group and likely has a minimum age of  $\sim$ 575 Ma (Bowring et al., 2003) based on the absence of Ediacaran fossil assemblages (Knoll and Swett, 1987).

### 3.3 Materials, methods, and basic interpretive concepts

### 3.3.1 Samples

Seventy-five dark grey to black shales were sampled routinely during mapping and stratigraphic logging over the course of multiple field seasons. With the exception of seven samples from the Arena Formation in East Greenland (equivalent to the MacDonaldryggen Member in Svalbard), all samples come from outcrops in northeastern Svalbard. Fresh samples were targeted, and all samples were cut and cleaned to remove any weathered surface prior to crushing and grinding in a chrome-steel ring mill. Detailed information on individual stratigraphic sections can be found in the Supplementary Information.

#### 3.3.2 Iron speciation

Total iron concentration and iron speciation results were previously reported in Sperling et al. (2015b) as part of a large iron speciation compilation but are discussed here in a detailed stratigraphic and geological framework for the first time. Sequential iron extraction followed the methods outlined in Poulton and Canfield (2005). The leachates were analyzed on a PerkinElmer AAnalyst 100 Flame atomic absorption spectrometer (AAS). We also tested whether the choice of instrument for iron concentration measurements influences the results. Replicate solutions were analyzed on a Thermo Scientific iCAP 6000 series ICP-OES and a Thermo Scientific Genesys 10s UV-VIS Spectrophotometer. All methods yielded comparable concentrations, standard deviations, and standard errors of the mean (see Supplementary Information for details; Tab. 3.6). In summary, the spectrophotometer and the ICP-OES usually had a slightly smaller standard deviation and standard error of the mean compared to the AAS. Based on duplicate analyses, the precision of sequentially extracted Fe was better than 5% (see Supplementary Information). The pyrite iron (FePy) content was determined gravimetrically (assuming FeS<sub>2</sub> stoichiometry) after trapping the sulfide liberated during chromium reduction as  $Ag_2S$  (Canfield et al., 1986).

#### 3.3.3 Major and trace elements

Powdered samples were combusted at 550°C for 5h to oxidize the organic matter (Dean, 1974). Samples were then subjected to a two-step digestion method starting with a mixture of HCl-HF-HNO<sub>3</sub> followed by aqua regia. Digestion was performed in a clean lab with double-distilled acids. Trace metal concentrations were measured on a Thermo Finnigan iCAP Q ICP-MS and major element concentrations on a Thermo Scientific iCAP 6000 series ICP-OES. Accuracy and precision were monitored by analyzing duplicates as well as the certified reference materials BHVO-2 (basalt), SCo-1 (black shale) and SCHS-1 (black shale). Reproducibility was better than  $\pm 5\%$ .

#### 3.3.4 Carbon and sulfur abundances

Total carbon, total organic carbon (TOC) and sulfur concentrations were measured on an Eltra CS 800 carbon and sulfur analyzer. For TOC measurements, shale samples were first leached twice in 2 M HCl for 12 hours to dissolve carbonate minerals. Accuracy and reproducibility were monitored through analyses of duplicates and the certified reference material Slg-1 (black shale). Reproducibility was better than  $\pm 8\%$ . Total sulfur abundances measured on the C/S analyzer compare well with S extracted by the CRS-method suggesting that most sulfur in the samples occurs as sulfide (Fig. 4.1). However, generally slightly higher total sulfur values suggest contribution from a minor organic-bound sulfur pool. See Supplemental Information for a more detailed description of methods.

#### 3.3.5 Interpretive framework for paleoredox data

#### Iron speciation

Iron speciation is an extraction method for operationally defined iron pools (Poulton and Canfield, 2005, 2011). The sum of Fe in carbonates (Fe<sub>carb</sub>; mainly ankerite, siderite, ferrous dolomite), Fe(III) minerals (Fe<sub>ox</sub>; mainly goethite, hematite, ferrihydrate, lepidocrocite), mixed valence Fe minerals (Fe<sub>mag</sub>; mostly magnetite), and Fe in sulfides (FePy; mostly pyrite) is referred

to as highly reactive iron (FeHR) because it is available for reductive dissolution processes (FeHR=Fe<sub>carb</sub>+ Fe<sub>ox</sub>+Fe<sub>mag</sub>+FePy). Total iron content (FeT) also includes an unreactive silicate iron pool (FeU), derived from the detrital flux. If FeHR/FeT ratios >0.38 anoxic conditions are inferred (Raiswell and Canfield, 1998; Poulton and Canfield, 2011; Farrel et al., 2013) and if these sediments additionally have FePy/FeHR ratios >0.7 (Poulton and Canfield, 2011), the water column is interpreted as euxinic (i.e. anoxic and sulfidic). However, a FeHR/FeT ratio of 0.38 is a maximum value for oxic shales, and Phanerozoic and modern sediments deposited under oxic conditions have average FeHR/FeT ratios of  $0.14\pm0.08$  and  $0.26\pm0.09$ , respectively (Raiswell and Canfield, 1998; Poulton and Raiswell, 2002; Anderson and Raiswell, 2004; Poulton and Canfield, 2011). Thus, anoxic sediments (FeHR/FeT > 0.38) can typically be distinguished from oxic sediments (FeHR/FeT < 0.22). However, intermediate ratios (0.22 < FeHR/FeT < 0.38) may represent deposition under oxic or anoxic conditions because mass balance requirements dictate that not all anoxic sediments can be enriched in FeHR (Poulton and Canfield, 2011). Rapid sedimentation rates (e.g., deposition from turbidity currents) can result in low FeHR/FeT ratios, despite deposition under anoxic conditions, but no lithologic units deposited under these conditions were included in this study. Anoxic enrichments in highly-reactive iron are generally also manifested in elevated FeT/Al ratios exceeding typical values for the upper continental crust (UCC  $\approx 0.4-0.5$ ; Lyons and Severmann, 2006). During burial and metamorphism, FeHR can be transferred into the unreactive silicate pool, thus lowering FeHR/FeT. Considering FeT/Al ratios along with Fe speciation data is therefore a useful approach, as FeT/Al ratios are not affected by burial and metamorphism (Lyons and Severmann, 2006).

#### Trace metals

The concentration of Mo, U and V in organic-rich fine-grained siliciclastic sediments is primarily controlled by the redox chemistry of the overlying water column (e.g. Emerson and Huested, 1991; Tribovillard et al., 2006). The primary source of these elements to the ocean is riverine delivery following oxidative continental weathering. Mass balance requires a significant dissolved seawater trace metal reservoir to generate a marked authigenic enrichment (Algeo, 2004; Scott et al., 2008; Partin et al., 2013). Under oxic conditions, Mo behaves conservatively in seawater and is mainly present as molybdate ( $MoO_4^{2-}$ ) (Broecker and Peng, 1982). However, when sulfide concentration exceeds ~10  $\mu$ M, molybdate is converted into the particle-reactive oxythiomolybdate anion  $(MoO_x S_{4-x}^{2-})$  and scavenged by organic matter and sulfide minerals (Helz et al., 1996; Erickson and Helz, 2000). Significant authigenic enrichments of Mo require both an oxidative source of molybdate and persistently euxinic local conditions (Scott and Lyons, 2012), which can deplete the local and even global seawater Mo reservoir (e.g. Algeo, 2004; Scott et al., 2008).

U(VI) mainly occurs as the uranyl carbonate anion  $(UO_2(CO_3)_3^{4-})$  under oxic conditions. It is reduced to U(IV) and precipitates as UO<sub>2</sub>, U<sub>3</sub>O<sub>7</sub>, or U<sub>3</sub>O<sub>8</sub> under mildly anoxic conditions (e.g. Klinkhammer and Palmer, 1991; Tribovillard et al., 2006). In contrast to Mo, authigenic U enrichment is decoupled from the abundance of ambient sulfide (e.g. Klinkhammer and Palmer, 1991; McManus et al., 2005; Tribovillard et al., 2006). Transport of U from the water column to the sediment is likely accelerated by the formation of organometallic complexes (Klinkhammer and Palmer, 1991; Zheng et al., 2002; McManus et al., 2005).

In an oxic water column, vanadium occurs as V(V) in vanadate oxyanions  $HVO_4^{2-}$  and  $H_2VO_4^{-}$ . Under anoxic conditions V(V) is reduced by dissolved organic compounds or hydrogen sulfide to V(IV), forming  $VO^{2-}$ ,  $VO(OH)_3^{-}$ , or  $VO(OH)_2$ , and becomes enriched in sediments (Lewan and Maynard, 1982; Breit and Wanty, 1991). Stronger enrichment occurs under euxinic conditions, when V(IV) is further reduced to V(III), which can be incorporated in porphyrins, precipitated as  $V_2O_3$ , or incorporated into clay minerals (Breit and Wanty, 1991; Wanty and Goldhaber, 1992).

#### 3.3.6 Interpretive framework for provenance data

#### Major and trace elements

Major and trace element systematics in shales from Svalbard were also investigated to better understand the provenance and its potential effect on paleoredox proxies. A potential signature of continental flood basalt (CFB) weathering was accessed by major and trace element ratios (namely K, Ti, Al, Th, Sc, La, and Co). During most igneous differentiation processes, La, Th, and K behave as incompatible elements and typically become more enriched in felsic magmas than the more compatible elements Sc and Co (Taylor and McLennon, 1985). Therefore, felsic rocks generally have higher Th/Sc, Th/Co, La/Sc, and K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratios than mafic rocks. In contrast, they have lower Ti/Al ratios because Ti behaves as more compatible element during magmatic differentiation processes. These different behaviors permit using these elemental ratios to evaluate the source region, for example whether it has a composition similar to upper continental crust (UCC) or if a significant mafic component is required to explain the measured shale composition. These results were linked to the Chemical Index of Alteration (CIA) to test if provenance signatures can be explained by different degrees of weathering in the source region or if a different composition of the source region is required. The CIA tracks the preferential loss of Ca, Na, and K cations during silicate weathering:  $CIA = [Al_2O_3/(Al_2O_3+CaO^*+Na_2O+K_2O)]^*$  100 (e.g. Nesbitt and Young, 1982, 1984; Fedo et al., 1995), where CaO\* refers to the siliciclastic CaO content only.

### 3.4 Results

TOC and S contents in the studied shales reach up to 3.3 wt.% (mean 0.6 wt.%, 1SE=0.07, Fig. 3.3b) and 2.0 wt.% (mean=0.51 wt.%, 1SE=0.06), respectively (Tab. 3.1). FeHR/FeT ratios vary between anoxic and equivocal, with only few samples falling below the oxic threshold (mean=0.43, 1SE=0.03; Figs. 3.2b, 3.3a). FePy/FeHR values are below the euxinic threshold for the entire succession (mean=0.18, 1SE=0.02; Figs. 3.2c, 3.3a). However, whereas the pre-Sturtian units have very low FePy/FeHR (Tab. 3.3), FePy/FeHR ratios in the Cryogenian MacDonaldryggen Member and Arena Formation, as well as in the post-Marinoan Dracoisen Formation are significantly higher (Fig. 3.2c). FeT/Al ratios have a mean of 0.59 (1SE=0.04), suggesting a minor enrichment of iron when compared to UCC, consistent with an overall enrichment in highly reactive iron. However, FeT/Al ratios show significant variation from 0.10 to 1.37, i.e. from depleted values relative to UCC to strongly enriched (Fig. 3.2d). These results are similar to findings from other Neoproterozoic basins (C. Li et al., 2012; Sperling et al., 2013, 2015a) but are not yet fully understood (cf. Sperling et al., 2013). Bulk Mo (<5.1 mg/kg, mean=0.6mg/kg, 1SE=0.01 mg/kg), U (<4.5 mg/kg, mean=2.2 mg/kg, 1SE=0.1 mg/kg), and V (<194 mg/kg, mean=86 mg/kg, 1SE=6.9 mg/kg) concentrations and calculated authigenic fractions are low in the pre-Sturtian and Cryogenian samples (Figs. 3.2e-g, 3.3c-e), with the exception of elevated V concentrations (up to 194 mg/kg) and authigenic enrichments (up to 100 mg/kg) in the Cryogenian units. Here, a systematic up-section trend of decreasing V concentrations is apparent

(Fig. 3.2g) and correlates with FeT/Al ratios (R<sup>2</sup>=0.89 for bulk V and FeT/Al). FeHR/FeT ratios show an opposite trend in the same samples (Fig.3.2b). In contrast to the pre-Marinoan units, Mo (<17 mg/kg, mean=2.8 mg/kg, 1SE=1.0 mg/kg), U (<9.6 mg/kg, mean=4.7 mg/kg, 1SE=0.5 mg/kg), and V (<638 mg/kg, mean=170 mg/kg, 1SE=41 mg/kg) show minor authigenic enrichments and elevated trace metal/TOC ratios in the post-Marinoan Dracoisen Formation (Fig. 3.2e-g, Tab. 3.2).

CIA values (49–83) in all units are typical for slightly to moderately weathered source regions (Fig. 3.4a). Trace and major element geochemistry demonstrate that the Cryogenian MacDonaldryggen and Arena units have elevated Ti/Al ratios and low Th/Sc, Th/Co, La/Sc, and  $K_2O/Al_2O_3$  ratios, indicative for a significant mafic contribution to the detrital fraction (Fig. 3.5).

### 3.5 Discussion

#### 3.5.1 Provenance variability and its effect on paleoredox proxies

We used the CIA and major and trace element characteristics to assess source area heterogeneity and to constrain to what degree paleoredox proxies may be a function of different source compositions. CIA values indicate slightly to moderately weathered source regions for all sampled units (Fig. 3.4a). Most samples show evidence of secondary K-enrichment (Fedo et al., 1995), which pulls data points towards the K apex in the C-N-K ternary plot. This is a common phenomenon (e.g. Tosca et al., 2010; Johnston et al., 2013) and a correction typically only increases CIA values by 5 units (Fig. 3.4a). Since the source areas were not strongly weathered (CIA<90), the ratios of biogeochemically inactive elements like Ti, Al, Th, Sc, and La in shales reflect those of the source region (Taylor and McLennon, 1985; Young and Nesbitt, 1998). Furthermore, since these elements have different compatabilities in felsic and mafic rocks, they can be used to infer the composition of the detrital input.

With the exception of the interglacial rocks, all samples have Ti/Al ratios comparable, though slightly higher, than UCC and equal to Post-Archean Average Shale (PAAS; Fig. 3.5a). Many samples have lower Ti and Al concentrations than UCC (McLennon, 2001) due to varying degrees of dilution by organic carbon and carbonate. The interglacial Arena Formation in East Greenland has significantly higher Ti/Al ratios and plots exactly on a mixing line between UCC and the Franklin CFB (Fig. 3.5a). The Franklin CFB erupted in northern Laurentia just before and partially overlapping with the Sturtian glaciation  $\sim$ 723–712 Ma ago (Denyszyn et al., 2009; Cox et al., 2015), and Franklin dikes are also present in Greenland. The Franklin CFB covered an area of  $2.2 \times 10^6$  km<sup>2</sup> (Ernst et al., 2008), thus representing a large source area of matic material. Samples from the MacDonaldrygen Member in Svalbard do not plot exactly on a mixing line but are also characterized by elevated Ti/Al ratios (Fig. 3.5a). This may be explained by greater distance to the source area and possible contribution from a far-flung occurrence of the Franklin CFB with slightly different Ti/Al ratios than the center of the Franklin CFB (Cox et al., 2015). The mafic detrital component in Cryogenian shales is also manifested in Fe and Mg addition, pulling samples towards the FeO+MgO apex in Fig. 3.4b. Th-Sc, Th/Co-La/Sc, and La/Sc-K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> relationships (Fig. 3.5b-d) also indicate a significant matic component in Cryogenian shales. Cobalt concentrations in shales are partly controlled by redox conditions (Tribovillard et al., 2006; Swanner et al., 2014). However, because of the absence of euxinic conditions in shelf environments in Svalbard and very slow kinetics that limit the incorporation of CoS in iron sulfides (Huerta-Diaz and Morse, 1992), redox conditions did not likely influence the Co concentrations in our shales. The estimated fraction of the mafic component in the Arena Formation varies depending on which elements are considered (Fig. 3.5a-d) but provides a rough estimate of  $\sim$  30–50% when UCC and Franklin CFB are considered as end members. The discrepancy can be explained by a different offset between our samples and UCC, used here as the end member composition of non-CFB continental crust.

Mafic rocks have higher Fe and V concentrations than felsic rocks, which raises the question to what degree a significantly elevated mafic component in the provenance of the Cryogenian units biased Fe- and V- based paleoredox proxies. The observed parallel trends in FeT/Al and V concentrations and the opposite trend shown by FeHR/FeT (Fig. 3.2) suggest that weathering of CFB can account for the elevated FeT/Al and V values in shales deposited right after the Sturtian glaciation. This inference is supported by positive correlation between FeT/Al and Ti/Al ratios in the MacDonaldryggen Member (Fig. 4.2). However, lack of a correlation despite elevated Ti/Al ratios in the Arena Formation indicates that high FeT/Al ratios must partly be due to Fe enrichment from an anoxic water column. An upsection decrease likely reflects the gradually decreasing mafic detrital flux. Whereas FeT/Al ratios are significantly elevated (up to 1.1, Fig. 3.2d), V concentrations are only slightly higher than UCC (Fig. 3.2g). Considering that this is the case for samples from East Greenland despite closer proximity to Franklin dikes, it is clear that flood basalt weathering has only limited spatial influence on the V concentration in shales. Furthermore, the stratigraphic range (<100 m) of the influence of flood basalts on bulk shale geochemistry is also limited (Fig. 3.2). In conclusion, it is unlikely that flood basalt weathering results in erroneous redox interpretations because its influence is strongly limited in space and time and only strongly influences FeT/Al ratios. Nevertheless, because we do have other redox data available, we do not consider FeT/Al and V data in our evaluation of Cryogenian redox conditions.

#### 3.5.2 Redox chemistry

Svalbard shales generally have low TOC and only minor enrichments of the redox-sensitive trace metals Mo, V, and U. These characteristics are consistent with minimal sulfide production in the sediments and pore waters and the absence of  $H_2S$  in the bottom waters. Iron speciation data cluster between equivocal and clearly anoxic, supporting an interpretation that Neoproterozoic outer and middle shelf environments in Svalbard were predominantly anoxic-ferruginous, but allowing for intermittently oxic conditions. Importantly, our data suggest no significant long-term change in water column redox conditions on the Svalbard continental shelf (Fig. 3.2).

High Cryogenian FePy/FeHR ratios approaching the euxinic threshold, coupled to high amounts of total sulfur (up to 2 wt.% — the highest values in our data set) may suggest that these shales were deposited under anoxic conditions, despite equivocal FeHR/FeT ratios. Comparable FePy/FeHR ratios also exist in the post-Marinoan Dracoisen Formation (Fig. 3.2c) and likely suggest that pyrites formed close to the sediment-water interface (SWI). However, Mo is not authigenically enriched in the Cryogenian interglacial shales (Fig. 3.2e). It is unlikely that a severely depleted seawater Mo reservoir is responsible for the complete lack of Mo enrichments because euxinic shales from early Neoproterozoic and coeval basins show Mo concentrations up to tens of ppm (Scott et al., 2008; C. Li et al., 2012; Sperling et al., 2013; Thomson et al., 2015). Hence the lack of authigenic Mo enrichment more likely indicates that pore water H<sub>2</sub>S concentrations never reached the ~10  $\mu$ M threshold required for formation of particle-reactive thiomolybdates (e.g. Erickson and Helz, 2000). The lack of Mo enrichment, despite the preservation of appreciable pyrite, suggests that  $H_2S$  produced during bacterial sulfate reduction was rapidly consumed by reaction with FeHR, preventing the buildup of significant  $H_2S$  concentrations in pore waters.

The concentration of V in Svalbard shales is similar to that of modern suboxic sediments (e.g. Nameroff et al., 2002). Because  $H_2S$  is not required for the reduction of V(V) to particulate-reactive V(IV) species, the enrichment of V is not inconsistent with the absence of authigenic Mo. Rather, these two trace metals together imply a system where bottom waters were likely suboxic to anoxic, and thus promoting the burial of small amounts of organic matter, but where low  $H_2S$  production allowed for rapid titration by reactive Fe.

Despite evidence for reducing bottom waters, we find only minor enrichments of U in Svalbard shales (authigenic fraction of up to 7 mg/kg). However, while U(VI) is converted to U(IV) under mildly reducing conditions, its enrichment in sediments has been associated with organometallic complexes (Klinkhammer and Palmer, 1991; Zheng et al., 2002; McManus et al., 2005) and thus linked to the supply of TOC. Partin et al. (2013) used the concentration of U in anoxic black shales to argue for a depleted U seawater reservoir in the Proterozoic. Our results are consistent with this argument. However, it is possible that U was reduced in Svalbard bottom waters and pore waters but that there was insufficient supply of organic matter to act as a host in the sediments. For example, McManus et al. (2005) reported relatively high (2–8 mg/kg) U contents in modern sediments deposited under oxic bottom waters with high organic carbon delivery rates, highlighting the importance of organic matter in addition to seawater U concentrations. Thus, while the minor enrichments of U in Svalbard shales (up to 10 mg/kg) is consistent with our interpretation of reducing bottom waters, they do not necessarily speak to the size of the seawater U reservoir in general.

The post-Marinoan Dracoisen Formation, in particular the uppermost sampled shales (Fig. 3.2), show minor enrichments in Mo, U, and V (authigenic fractions of up to 15.7 mg/kg, 7.1 mg/kg, and 544 mg/kg). Bulk Mo concentrations up to 17 mg/kg suggest that H<sub>2</sub>S concentrations were sufficiently high to form thiomolybdate species. However, the low degree of trace metal enrichment compared to coeval black shales in South China (Sahoo et al., 2012) suggests that H<sub>2</sub>S was restricted to pore waters (Scott and Lyons, 2012), consistent with iron speciation data.

### 3.5.3 Data from Svalbard in a global context

Since Canfield et al. (2008) first proposed that deep waters in the middle Neoproterozoic were mostly ferruginous, multiple independent studies on individual basins have yielded data that support this hypothesis. Sperling et al. (2013) investigated the ca. 850–800 Ma Fifteenmile Group, northwestern Canada, and demonstrated that environments below storm wave base were mostly ferruginous. Similarly, the  $\sim$ 742 Ma Chuar Group, Grand Canyon (United States), was mostly deposited under ferruginous conditions with limited euxinia (Johnston et al., 2010). Data from the Russøya Member presented here provides the first record of oceanic redox conditions leading up to the  $\sim$ 717 Ma Sturtian glaciation and demonstrate the continuation of anoxic-ferruginous to suboxic conditions. These results are consistent with an emerging picture of dominantly ferruginous conditions and a statistically significant lower abundance of euxinic water masses in the early and middle Neoproterozoic (Guilbaud et al., 2015; Sperling et al., 2015b).

The stratigraphic record between the Sturtian and ca. 635 Ma Marinoan glaciations has only been sparsely investigated in terms of oceanic redox conditions. Data from the Datangpo Formation in the restricted Nanhua basin (South China), indicate persistent deepwater anoxia with varying euxinic and ferruginous conditions (C. Li et al., 2012), whereas data from the interglacial Twitya and Keele formations in northwestern Canada indicate predominantly ferruginous to mildly oxic conditions (Sperling et al., 2015a). Our data from Cryogenian interglacial strata in Svalbard and East Greenland confirm dominantly ferruginous conditions. In contrast to iron speciation data, the authigenic enrichment of redox-sensitive trace metals in shales deposited under euxinic conditions allow global inferences because a significant size of the dissolved trace metal reservoir, controlled by oxidative continental weathering and the redox state of the global ocean, is a prerequisite. Euxinic samples from South China (C. Li et al., 2012) show only limited Mo enrichment and no evidence for significant Cryogenian growth of the marine trace metal reservoir similar to that which followed the Marinoan glaciation (Scott et al., 2008; Sahoo et al., 2012). Samples from middle and outer shelf environments in Svalbard and Greenland (MacDonaldryggen Member and Arena Formation) also show no evidence for higher oxygen levels compared to pre-Sturtian samples from the same succession (Russøya Member). Taken together, available data are inconsistent with significant oxygenation of the biosphere during the

Cryogenian interglacial interval. Thus, potential biomarker and body fossil evidence for animals in the Cryogenian rock record (Love et al., 2009; Maloof et al., 2010) does not correspond to increasing oxygen levels, at least not to a degree that can be resolved with iron speciation and redox-sensitive trace metal data. This conclusion implies that atmospheric oxygen levels must have already been in the range of  $\sim 0.4-5\%$  present atmospheric levels (PAL), the minimum estimate for oxygen requirements of early animals based on modeling and observations from modern oxygen minimum zones (Sperling et al., 2013; Mills et al., 2014). Future application of novel redox proxies, such as Cr isotopes (e.g. Frei et al., 2009; Planavsky et al., 2014), that allow better quantification of oxygen levels, may help elucidate oceanic redox conditions during this critical period.

Significant authigenic Mo enrichment in shales immediately overlying Marinoan glacial deposits in South China (Sahoo et al., 2012) suggest growth of the global oceanic Mo reservoir, and by inference oxygenation of Earth's surface environments. However, post-Marinoan strata from northwestern Canada and Svalbard (this study) do not testify to an oxygenation event. Strata from northwestern Canada show consistently ferruginous conditions (Johnston et al., 2013) and the shales from Svalbard (this study), deposited in a shelf setting, also show suboxic to anoxic-ferruginous conditions, comparable to pre-Marinoan samples from the same succession. Importantly, the study by Sahoo et al. (2012) focused on the lowermost  $\sim 10$  m of shales immediately overlying the post-glacial cap dolostone, whereas in this study and Johnston et al. (2013), samples span hundreds of meters of strata following the glaciation, and inferentially, represent a much longer timescale, complicating a direct comparison. However, even if a global oxygenation event in the early Ediacaran is not apparent in the data from Svalbard and northwestern Canada due to lower sampling density and a focus on longer timescales, it is nevertheless clear that such an event did not result in complete oxygenation of shelf environments in other basins that can be resolved by iron speciation data. Therefore, it is unclear to what degree the Marinoan glaciation is related to increasing oxygen levels in Earth's surface environments, and in particular, what the redox structure of the Ediacaran ocean was. If data from the Doushantuo Formation reflect a global oxygenation event, why did anoxic (ferruginous) conditions persist in shelf environments of other basins at this time?

The concentration of dissolved oxygen in seawater is controlled by the interplay between

atmospheric  $pO_2$ , seawater temperature, and local organic carbon loading (Canfield, 1998). A post-Marinoan oxygenation event, as implied by the results of Sahoo et al. (2012), is thus expected to lead to higher dissolved  $O_2$  concentrations in the water column. However, increasing seawater temperatures, as expected in the post-Marinoan super-greenhouse climate that prevailed during deposition of the Dracoisen cap dolostone (and cap dolostones worldwide, e.g. Hoffman and Schrag, 2002; Higgins and Schrag, 2003), likely caused an increase of seawater temperature, thus lowering dissolved oxygen concentrations (Sarmiento and Gruber, 2006). However, the post-glacial supergreenhouse climate only lasted up to a few million years until climate rebounded to normal conditions (Le Hir et al., 2009). Since sampled shales from Svalbard and northwestern Canada (Johnston et al., 2013) were deposited well above the cap dolostone, it is unlikely that high temperatures accounted for long-lived anoxic conditions in many basins at this time. In the absence of another explanation, significant local organic matter loading and aerobic respiration in the water column is required to balance increasing post-Marinoan oxygen levels inferred by Sahoo et al. (2012) and may be the reason for persistently anoxic oceanic conditions in shelf environments during deposition of the Sheepbed Formation (NW Canada) and the Dracoisen Formation (Svalbard). This hypothesis is consistent with a model of immediate recovery of primary productivity after the Marinoan glaciation (Elie et al., 2007; Kunzmann et al., 2013). This bloom in primary productivity is a predictable response to intense surface runoff and nutrient supply during post-glacial weathering (Kirschvink et al., 2000) and would result in heavy organic matter loading on continental margins globally. The deposition of organic-rich black shales would have triggered rising oxygen levels in the early and middle Ediacaran. Shales from this time interval are not notably enriched in TOC, but this is not surprising given that buried organic matter would have been diluted by the large volume of continental shelf sediments deposited following Rodinia break-up (Z.-X. Li et al., 2013).

Persistent anoxic conditions in Ediacaran shelf environments as recorded in NW Canada (Johnston et al., 2013) and Svalbard (this study) is not inconsistent with evidence for increasing oxygen concentrations in Earth's surface environment (Sahoo et al., 2012). Taken together, these results suggest that higher oxygen concentrations may have existed in surface waters of the open ocean and that oxygen may have even been delivered to the deep ocean via downwelling. As a consequence, the redox structure of the early Ediacaran ocean would have begun to resemble

that of the Phanerozoic ocean, characterized by an oxygen minimum zone beneath the surface layer. The key difference is that under the still lower atmospheric oxygen levels (compared to the Phanerozoic), the high rates of organic matter loading maintained anoxic conditions below the surface mixed layer on continental margins. Importantly, the anoxic shelf waters in the early Ediacaran were not euxinic, probably due to low oceanic sulfate levels (Crockford et al., 2016). These conditions allowed the build-up of a large seawater Mo reservoir (Sahoo et al., 2012) but apparently depleted the seawater U reservoir, judging from the low U concentrations in organic-rich euxinic black shales in South China (Sahoo et al., 2012).

### 3.6 Conclusion

Geochemical analysis of black shales from the  $\sim 835-630$  Ma old succession in northeastern Svalbard extends the evolving global database of oceanic redox conditions in the late Proterozoic. The shelf succession was dominantly deposited under suboxic to anoxic-ferruginous conditions. These results are consistent with recent findings from other basins (Canfield et al., 2008; Johnston et al., 2010; Sperling et al., 2013, 2015b), and demonstrate that this glaciation was not related to changes in oceanic redox conditions. Similarly, oxygen levels in outer to middle shelf environments appear to have remained largely unchanged across the Cryogenian period, which suggests that oxygen levels were probably already high enough to accommodate simple animals that may have inhabited Cryogenian oceans (Love et al., 2009; Maloof et al., 2010). This conclusion suggests that atmospheric oxygen levels were at least in the range of  $\sim 0.4-5\%$  PAL, a lower estimate for oxygen requirements of early animals (Sperling et al., 2013; Mills et al., 2014). Post-Marinoan oxygenation as recorded in strata from South China (Sahoo et al., 2012) did not lead to long-term oxygenation of Ediacaran shelf environments in other basins, likely due to heavy organic matter loading. We envision an Ediacaran redox structure with anoxic shelf environments and possible higher oxygen concentrations in the open ocean where primary productivity rates were lower. Downwelling of oxygenated surface waters in the open ocean may have also increased oxygen levels in the deep ocean.

# Acknowledgments

We thank Ranjan Roy, Isabelle Richer, and Anna-Katharina Jung for help with the analyses. We acknowledge discussions with Grant Cox, Peter Crockford, Timothy Gibson, and Sarah Wörndle-Quëx; and the editorial handling by Michael E. Böttcher as well as thoughtful reviews by Andrey Bekker and Erik Sperling. The Stable Isotope Laboratory at McGill is supported by the FQRNT through the GEOTOP research center. BAW acknowledges support from an NSERC Discovery grant (RGPIN-2014-06626). CS was supported at McGill by a postdoctoral fellowship from the Canadian Astrobiology Training Program (funded by an NSERC CREATE grant to BAW). GPH received financial support from NSERC and the American Chemical Society Petroleum Research Fund. MK acknowledges financial support through fellowships from the Department of Earth & Planetary Sciences, McGill University and Geotop.

# **Figures**



**Fig. 3.1** Locality map and generalized stratigraphy of the studied Neoproterzoic succession in Svalbard. a) Bedrock geology of the glaciated Caledonian fold-and-thrust belt on the islands of Spitsbergen (Spitsb.) and Nordaustlanded (Norda.) showing the location of measured sections (modified from Hoffman et al. (2012)). ESZ=Eolusletta Shear Zone, LFZ= Lomfjorden Fault Zone b) Generalized lithostratigraphy (modified from Halverson et al. (2007).



Fig. 3.2 Litho- and chemostratigraphy of the Neoproterozoic succession in northeast Svalbard. a) TOC content. b) Ratio of highly reactive iron to total iron (FeHR/FeT). Vertical dashed line is the average of Phanerozoic oxic shales (Poulton and Raiswell, 2002) and the shaded area (0.22–0.38) marks equivocal results where shales were either deposited under oxic or anoxic conditions (Poulton and Canfield, 2011). Samples with FeHR/FeT > 0.38 are interpreted to reflect anoxic conditions (Raiswell and Canfield, 1998). c) Ratio of Fe bound in pyrite to highly reactive iron (FePy/FeHR). Samples with ratios > 0.7 likely reflect euxinic conditions (März et al., 2008). d) Ratio of FeT/Al. Shaded area shows composition of upper continental crust (UCC) (McLennon, 2001). e)–g) Bulk Mo, U, and V contents and calculated authigenic enrichments. Authigenic fractions were calculated by substracting the detrital fraction from the bulk concentration. The detrital fraction is calculated as: detrital trace metal=(trace metal/Al)<sub>UCC</sub> x Al<sub>sample</sub>.



Fig. 3.3 Fe speciation, Mo, U, V and total organic carbon (TOC) relationships. a) The ratios of FeHR/FeT plotted against the ratios of FePy/FeHR. Vertical line represents average Phanerozoic oxic shales (Poulton and Raiswell, 2002) and the grey shaded area represents equivocal ratios. Horizontal line represents the cut-off between anoxic-ferruginous and anoxic-euxinic shales (März et al., 2008). Note that only samples from the post-Sturtian Arena, MacDonaldryggen, and Dracoisen units have elevated FePy/FeHR ratios and that only few samples plot below the oxic threshold. b) Positive relationship between TOC content and enrichment in FeHR because anoxic conditions favor both high TOC and FeHR contents. c)–e) Relationship between Mo, U, V and TOC. Only limited trace metal enrichment is observed, indicating suboxic to ferruginous conditions during deposition.



**Fig. 3.4** Major element systematics. a) Classical ternary  $Al_2O_3$ -CaO<sup>\*</sup> +Na<sub>2</sub>O-K<sub>2</sub>O diagram to evaluate the degree of weathering (Nesbitt and Young, 1982, 1984; Fedo et al., 1995). CaO<sup>\*</sup> refers to CaO in silicate minerals only. Samples show characteristics of a slightly to moderately weathered source area. Most samples experienced post-depositional K-addition, that pulls data points away from the predicted weathering trend (black arrow) and towards the K apex. However, a correction (grey arrow; Fedo et al., 1995) generally only increases CIA values by about 5 units. The Arena Formation plots on the weathering trajectory of UCC. However, assuming that the samples contain a significant Franklin detrital component, their weathering trajectory should be further to the left, originating between Franklin and UCC composition. Thus, Arena samples may have experienced K-addition as well. b) Contribution of Fe and Mg by flood basalt weathering pull samples from the MacDonaldryggen and Arena units toward the FeO+MgO apex. However, loss of CaO<sup>\*</sup>, Na<sub>2</sub>O, and K<sub>2</sub>O during weathering explains why these samples do not plot on a mixing line with the Franklin CFB. Samples from the Russøya Member plot on a mixing line between illite and and the FeO+MgO apex. PAAS and UCC composition from Taylor and McLennon (1985); Franklin CFB composition from Dostal et al. (1986) and Shellnut et al. (2004).



Fig. 3.5 Provenance plots. a) Ti/Al ratios are comparable to PAAS and UCC with the exception of the interglacial Arena Formation (Greenland) and MacDonaldryggen Member. Both units have elevated Ti/Al ratios and samples from the Arena Formation plot on a mixing line between UCC and the Franklin CFB. b) and c) A significant mafic signal in the MacDonaldryggen Member and Arena Formation is also observed in Th-Sc and Th/Co-La/Sc cross-plots. Non-Cryogenian samples have slightly higher Th contents and Th/Co ratios than average UCC, suggesting that the source area was slightly more differentiated. d) La/Sc - K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> systematics also show that samples from the Arena Formation are influenced by weathering of the Franklin CFB. Different degrees of weathering led to secondary modification of K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratios, explaining data scattering. Higher degree of weathering also explains low K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratios of the Russøya Member (see Fig. 3.4a).
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# 3.7 Supplementary Information

The supplementary information lists all results and provides details about sample location and analytical methods. Furthermore, I present an analytical test of the iron speciation technique.

### 3.7.1 Additional materials, methods, and data

### Sampling, cleaning, crushing

Organic-rich shale samples were collected during mapping and stratigraphic logging. Fresh samples without obvious weathered surfaces were targeted. Following washing with water and a hand brush, samples were cut with a diamond saw to remove weathered edges. Remaining weathered parts were removed with sand paper. Dried samples were crushed and grinded in a chrome steel shatter box which was cleaned with ethanol and pre-contaminated with sample material between samples. Grinding of samples in a chrome steel ring mill may contaminate samples with Fe, which could be a concern because iron-based paleoredox proxies are used in this study. Hickson and Juras (1986) systematically studied contamination by different grinding tools to the Ottawa sand standard and demonstrated that the use of a chrome steel shatter box leads to significant contribution of Fe, Cr, and Mn. However, Hickson and Juras (1986) also state that this contamination is very small for soft samples (like shales studied here) that are only crushed for a short time. This was also confirmed by a test presented in the Supplementary Information of Sperling et al. (2013).

#### Major and trace element abundances

Approximately 1 g of powdered sample was combusted at 550 °C for 5 hours to oxidize organic complexes and determine loss on ignition (cf. Dean, 1974).

The following steps were performed in a clean lab at Geotop, Montreal. All acids were double distilled. About 40 mg of combusted sample material was weighed out into Savillex<sup>TM</sup> teflon beaker and digested in a mixture of 2 ml 6 M HCl : 1 ml 50% HF :  $0.5 \text{ ml } 7 \text{ M } \text{HNO}_3$  at ~80 °C for 48 h. Samples were then dried down, however,  $0.5 \text{ ml } 6 \text{ M } \text{HNO}_3$  were added before complete drying to prevent the formation of apatite group minerals. The samples were taken up in a

mixture of 2 ml 6 M HCl :  $0.65 \text{ ml 7 M HNO}_3$  and put back on the hot plate at ~80 °C for 24-48 h. After the samples were dried down again, they were taken up in 2 ml of 6 M HCl, and aliquots were taken for other analyses. The samples were then dried down, taken up again in 0.5 ml 7 M HNO<sub>3</sub>, and subsequently dried down again. This step was performed to ensure the removal of chlorine to avoid mass interferences during ICP-measurements. Samples were finally taken up in 7 M HNO<sub>3</sub> and aliquots were taken for ICP-OES (major elements) and ICP-MS (trace elements) analyses.

Dilutions for elemental analyses were prepared with 2% HNO<sub>3</sub>. Trace element abundances were measured on a Thermo Finnigan iCAP Q ICP-MS and major element abundances on a Thermo Scientific iCAP 6000 series ICP-OES, both housed in the Department of Earth & Planetary Sciences, McGill University. Blanks, duplicates and the certified reference materials BHVO-2, SCo-1, and SCHS-1 were routinely digested and measured to monitor accuracy and reproducibility, which were  $\pm 5\%$  for all measured elements. Some samples were previously analyzed on an Agilent 7500cs ICP-MS at the University of Adelaide, Australia, and were not available for additional measurements. Therefore, we were not able to measure every element concentration on every sample (Tab.3.1, 3.2). Element concentrations of all analyzed samples are listed in Tab. 3.1 and Tab. 3.2.

## Carbon and sulfur abundances

Total carbon (TC), total sulfur (TS) and total organic carbon (TOC) were analyzed on an Eltra CS 800 Carbon Sulphur Determinator. Every sample was analyzed twice. The accuracy and reproducibility of measurements was additionally monitored by analyzing the black shale standard SLg-1. Analytical reproducibility was  $\pm 8\%$ . For TOC measurements, all samples were de-carbonated before the analyses. About 1–1.5 g of sample material was weighed into 15 ml centrifuge tubes and 10 ml of 2 M HCl were added. The samples were agitated and left under a fume hood for 12 h, centrifuged and the acid was decanted. The dissolution step was repeated to ensure total removal of carbonate. Few samples had higher carbonate contents therefore a third dissolution step was necessary. The sample tubes were then filled with 15 ml distilled water, agitated, centrifuged, and the water was decanted. This step was repeated at least three times to increase the pH to ~5. The samples were then dried overnight at ~60 °C. Finally the samples

were run on the carbon sulfur analyzer and the measured TOC content was related to the initial mass. The reference material SLg-1 was also prepared for every batch of 12 samples. The amount of total inorganic carbon (TIC) was calculated by subtracting TOC from TC. Results are listed in Tab. 3.1.

#### Fe speciation

**Sequential extraction** Operationally defined iron pools (carbonate-bound iron – Fe<sub>carb</sub>, ferric oxide-bound iron – Fe<sub>ox</sub>, and magnetite-bound iron – Fe<sub>mag</sub>) were sequentially extracted following the protocol developed by Poulton and Canfield (2005). Results are listed in Tab. 3.3. About 150 mg of powdered shale was weighed into 15 ml centrifuge tubes. Iron associated with carbonate minerals, like ankerite, siderite, and ferrous dolomite, was extracted with 1 M sodium acetate solution buffered with acetic acid to a pH of 4.5. This extraction step was performed on a shaking table for 48 h at 50 °C. Iron bound to (oxy)hydroxides, like goethite, hematite, and lepidocricite, was quantified with 50 g/l sodium dithionite solution buffered with 0.35 M acetic acid and 0.2 Msodium citrate to pH 4.8 for 2 h on a shaking table at room temperature. Iron associated with mixed-valence phases like magnetite was extracted with  $0.2 \,\mathrm{M}$  ammonium oxalate —  $0.17 \,\mathrm{M}$  oxalic acid solution buffered with ammonium hydroxide to pH 3.2 for 6 hours on a shaking table at room temperature. After the first and second extraction, the samples were centrifuged, an aliquot was taken for analyses, and the remaining solution was completely removed with care taken not to disturb the sample powder. All three extraction steps were performed on the same powders. Sequential extractions were run in batches of 48 samples including five internal replicates from different Neoproterozoic units from Svalbard (four replicates) and NW Canada (one replicate). Diluted solutions were prepared with 2% HNO<sub>3</sub> (preparation with MQ-H<sub>2</sub>O gave comparable results) and analyzed on a Perkin Elmer AAnalyst 100 Flame atomic absorption spectrometer (AAS).

Certified reference materials do not exist for Fe speciation measurements. Therefore, the reproducibility of the sequential extractions at McGill University was evaluated by running six replicate samples reported in Sperling et al. (2013) and analyzed in the Johnston Lab at Harvard University. Each replicate sample was processed and analyzed twice. The extractions were analyzed on a Thermo Scientifc Genesys 10s UV-VIS spectrophotometer (the same instrument used in the Harvard University analyses). A summary of the results from Sperling et al. (2013) is shown in Tab. 3.4, and results from extractions performed at McGill University are shown in Tab. 3.5. Replicate samples processed at McGill University had on average 18% more extractable iron (ranging from 13 to 27%, median of 15%). Slightly more iron was generally extracted from every iron pool, with the exception of samples with very low amounts of ammonium oxlate extractable iron (Tab. 3.5). It is unclear what the source of the discrepancy between the two labs is, but importantly, the end results (ratios) from both labs are in good agreement and would yield similar interpretations. Furthermore, more recent analyses of the replicate samples at Harvard yielded higher Fe concentrations than originally (Sperling, pers. comm.).

Labs that routinely produce Fe speciation data use different instruments to analyze the iron concentration in leachates. Instruments commonly used include Atomic Absorption Spectrometers (AAS), Spectrophotometers, Inductively Coupled Plasma-Mass Spectrometers (ICP-MS) and Inductively Coupled Plasma-Optical Emmission Spectrometers (ICP-OES). The application of different instruments, in particular the use of Spectrophotometers (using the ferrozine technique after Stookey (1970)), generated discussion about reliability and comparability of results. To evaluate reliability, we prepared all internal replicates ten times and measured the iron concentrations on the Spectrophotometer, AAS and ICP-OES. Exactly the same solution was analyzed on the AAS and ICP-OES, while a different solution (prepared with ferrozine; Stookey (1970)) was analyzed on the Spectrophotometer. Results are listed in Tab. 3.6.

In general, all instruments yielded similar results, standard deviations, and standard errors of the mean (Tab. 3.6). In detail, the Spectrophotometer and the ICP-OES usually had a smaller standard deviation and standard error of the mean than the AAS. Iron concentrations of individual leachates only vary more noticabley when the concentration is very low (for example sample G155.83.6) because the ratio of error to measured iron concentration becomes significant. Lower detection limits of the OES and AAS allow precise determination of concentration while the Spectrophotometer yields zero iron for solutions with very low concentrations (mostly the ammonium oxalate fraction). Lower dilution factor may help labs that use the spectrophotometer to overcome this issue. The Fe concentration in sodium acetate measured on the AAS is often slightly elevated (for example G435.45) resulting in overall slightly higher extractable iron. However this is a minor effect and we conclude that the final FeHR/FeT ratio is not significantly influenced.

For the AAS results (as the actual samples for this study were analyzed by AAS), the precision was better than 5%, which is comparably to trace element measurements routinely performed on ICP-MS and indicates the reliability of the iron speciation technique. One exception is sample G306.150, which has large sodium acatete- and sodium dithionite-extractable iron pools (Tab. 3.6). Standard deviations are about 0.160 wt.% (for 1.5 wt.% Fe) and standard errors of the mean of about 0.05. This may be explained with Fe concentrations at the high end of the calibrated concentration range and further dilution in the future will likely improve the precision.

**Pyrite extraction** The amount of Fe associated with pyrite was quantified by the chromiumreducible sulfur (CRS) method developed by Canfield et al. (1986). Depending on the TS content, 0.1-5 g of sample powder was weighed into reaction vessels, which were flushed with N<sub>2</sub> gas to ensure anoxic conditions. 15 ml of 6 M HCl was added to the reaction vessel, followed by 15 ml of 1 M chromic chloride acidified to 0.5 M HCl. The reaction vessels were heated to near-boiling and the reaction was performed for 2h. Pyrite-sulfur (plus elemental sulfur and acid-volatile monosulfides; (Canfield et al., 1986)) is further reduced to  $H_2S$  and trapped in a 4% (w/w) zinc acetate solution following passage through a MQ-H<sub>2</sub>O-water trap. The resulting zinc sulfide was converted to silver sulfide (Ag<sub>2</sub>S) by adding 1 ml of 0.1 M silver nitrate (AgNO<sub>3</sub>). The Ag<sub>2</sub>S was vacuum-filtered on to a pre-weighed  $0.45\,\mu\mathrm{m}$  cellulose filter attached to a 15 ml chimney, washed with two volume-equivalents MQ-H<sub>2</sub>O, one volume-equivalent ammonium hydroxide  $(NH_4OH)$ , and finally at least three volume-equivalents MQ-H<sub>2</sub>O. The filters were dried overnight at 80 °C and again weighed to gain the mass of Ag<sub>2</sub>S. The amount of Fe in pyrite was calculated stochiometrically assuming all CRS-extracted sulfur was pyrite. Abundant elemental or acidvolatile sulfur (AVS) would bias the results towards higher FePy contents. However, the existence of AVS was periodically tested with hot 6 M HCl and AVS was never found as is typical for ancient shales (cf. Sperling et al., 2013).

Tab. 3.7 lists the results of replicate CRS extraction of two samples with different pyrite concentrations. Standard deviations are 0.002 and 0.097 for samples with ca. 0.065 and 0.883 wt.% FePy, respectively. Standard errors of the mean are significantly smaller than average pyrite concentrations (0.001 and 0.032, respectively), demonstrating the reliability of the CRS

extraction.

Fig. 4.1 shows a cross-plot of total sulfur measured on the C/S analyzer and S extracted with the CRS-method. In general, the amount of chromium-reducible sulfur was less than total sulfur, which is likely due to organic-bound sulfur, a pool that cannot be extracted with the CRS-method (Canfield et al., 1986). The data show a positive correlation and demonstrate that most sulfur in the rock is in the form of pyrite. Besides organic-bound S as additional sulfur pool, some difference between the two methods may also be explained with the standard error on the C/S analyzer and the fact that some of the zinc sulfide produced by the CRS-method will always stick to the apparatus and be quantitatively removed.

#### Chemical Index of Alteration

The Chemical Index of Alteration (CIA) is a method for quantifying the degree of weathering by determining the ratio of predominantly immobile  $Al_2O_3$  and the mobile oxides  $Na_2O$ ,  $K_2O$  and CaO (Nesbitt and Young, 1982, 1984; Fedo et al., 1995). The CIA is defined as

$$CIA = \frac{Al_2O_3}{Al_2O_3 + Na_2O + K_2O + CaO^*} \cdot 100$$
(3.1)

where the major oxides are given as molecular proportions.  $\text{CaO}^*$  represents the CaO content in silicate minerals (Fedo et al., 1995). This means that the CaO content in carbonate minerals and phosphate minerals (mostly apatite) is subtracted from bulk rock CaO abundance based on TIC and P<sub>2</sub>O<sub>5</sub> concentrations. However, Bahlburg and Dobrzinski (2011) point out that CaO in phosphates may not be considered because CIA values will not change by more than ca. 1 unit. Following this approach, a correction for phosphate minerals was not done because P concentrations were not available for all samples. However, CIA values generally change by less than 1 unit when a phosphate correction is applied to samples were P concentrations are available, consistent with Bahlburg and Dobrzinski (2011).

The CIA represents the ratio of primary and secondary minerals, such as clay minerals. It is a dimensionless number that ranges from 50, for fresh rocks, to 100, for completely weathered rocks (only composed of secondary minerals like kaolinite and gibbsite). The CIA values for average shales fall between 70 and 75. A CIA value above 90 represents a strongly weathered source

region.

CIA values for the investigated samples from Svalbard are listed in Tab. 4.1 and shown in Fig. 3.4a. Most samples are slightly to moderately weathered with CIA values between 60 and 80. Some samples from the MacDonaldryggen Member and Dracoisen Formation have CIA vales below 60, indicating a very small degree of weathering. The samples generally follow the predicted weathering trend from upper continental crust (UCC) to illite. However, most samples, in particular from the MacDonaldryggen Member and Dracoisen Formation show post-depositional K addition, pulling the samples slightly towards the K apex. This is a common phenomenon in siliciclastic sediments (e.g. Condie, 1993; Tosca et al., 2010) and lowers the calculated CIA values. However, a correction can be made by drawing a line through the UCC composition parallel to the A-CN contour (black arrow in Fig. 3.4a) (Fedo et al., 1995). Measured samples that experienced K addition then need to be moved towards this line (grey arrow in Fig. 3.4a) and the corrected CIA value can be determined. A correction for K addition could be useful for samples from the MacDonaldryggen Member and Dracoisen Formation (Fig. 3.4a) but will only elevate the CIA value by approximately 5 units, thus not changing the overall estimate of the degree of weathering (Fig. 3.4a). Samples from the Arena Formation likely experienced some K addition as well because their predicted weathering trend should not go through UCC, i.e. should not follow the black arrow in Fig. 3.4a due to influence of the Franklin CFB.

## FeT/AI ratios in Cryogenian shales

Major and trace element data in shales from the Cryogenian MacDonaldryggen Member and Arena Formation suggest significant contribution of weathering of mafic rocks to the detrital flux. Since mafic rocks have higher Fe concentrations, this raises the question whether a higher detrital flux of Fe can elevate FeT/Al ratios in marine shales, similar to values that are traditionally interpreted to reflect Fe-enrichment from an anoxic water column. The MacDonaldryggen Member and Arena Formation both have FeT/Al ratios higher than upper continental crust. We test whether these elevated ratios are controlled by the detrital flux or not by plotting FeT/Al against Ti/Al ratios, a proxy only controlled by provenance (Fig. 4.2). A positive correlation in shales from the MacDonaldryggen Member suggest that elevated FeT/Al ratios in these samples can indeed be explained by a higher Fe/Al ratio of the detrital flux. The MacDonaldryggen Member also plots on a mixing line between UCC and Franklin CFB. In contrast, samples from the Arena Formation do not show a correlation despite plotting on a mixing line as well. This suggests contribution of Fe from weathering of the mafic Franklin CFB but also that a significant part of the elevated FeT/Al ratio is due to Fe-enrichment from an anoxic water column.

## 3.7.2 Description of stratigraphic sections

The following information are re-produced from the Supplementary Information provided by Sperling et al. (2015) because the same samples were used for both studies. The iron speciation data presented in this study (with the exception of data from sections G517, P5014, G519) are also part of the compiled Precambrian to Phanerozoic iron speciation data set ( $n\approx4700$ ; including 832 previously unpublished data, which include the data presented here) presented by Sperling et al. (2015). In the present study, this data set is integrated into the regional stratigraphic framework from Svalbard (and East Greenland - section GR12), tied to previously unpublished major and trace element data, and interpreted independently and in detail.

#### G426

Locality: These samples were collected from an exposure of the Raudstupet-Sälodden Formation of the upper Veteranen Group to the southeast of Eltonbreen glacier on the north coast of Wahlenbergfjorden, Nordaustlandet at N79°48.2′, E18°34.6′. The samples are from a black pencil shale located 25 m below a quartzite in the upper Veteranen (exact stratigraphic height unknown). **Depositional environment:** This shale is inferred to have been deposited below storm wave base on a siliciclastic margin near the time of the rift-drift transition. **Age:** The Veteranen Group is constrainted to be younger than about 940 Ma and older than 811 Ma (based on correlation of the Bitter Springs anomaly in the overlying Grusdievebreen Formation) with the Fifteenmile Group in the Yukon Territory, Canada (Macdonald et al., 2012). Thermal subsidence modeling suggests an age ca. 835 Ma for the upper Veteranen Group.

### G155

**Locality:** The base of this section is at N79°58.0′, E18°37.7′, on the Krystalfjellet Peninsula in eastern Murchisonfjord, Nordaustlandet. This section is within an east-dipping panel of the

Svanbergfjellet Formation and the collected samples are from the maximum flooding interval within a 13 m-thick shoaling upward sequence that marks the carbon isotope recovery from the Bitter Spring anomaly at the base of the informally defined lower limestone member (Svanberfjellet member 2). Here, 0.4m of black shale grade upwards into green, then tan and green shale, which is then overlain by 6.8 m of Conophyton stromatolites. This sequence overlies a succession of dominantly ribbon-bedded carbonates with minor grainstone. **Depositional environment:** The black shales were deposited at or just below storm-wave base on a carbonate ramp during a transgression that followed subaerial exposure. **Age:** Based on correlation of the Bitter Springs anomaly in Svalbard with what is inferred to be the same anomaly in the Fifteenmile Group, Ogilvie Mountains, Yukon and an age model developed for that succession (Macdonald et al., 2012), these samples are estimated to be ca. 802 Ma.

## G471

Locality: The base of this section is at N80°09.1′, E18°20.1′ on the northern Storstein peninsula in northeastern Nordaustlandet. The section spans the sequence boundary that marks the end of the Bitter Springs negative carbon isotope anomaly, as in section G155. The black shale samples are from the lowermost part of a shoaling upward sequence that is 19.6 m thick and overlies an exposure surface. The black shales sit above 3.3 m of silty green shale and mark the maximum flooding interval of the sequence. **Depositional environment:** The black shales were deposited at or just below storm-wave base on a carbonate ramp during a transgression following subaerial exposure. **Age:** Based on correlation of the Bitter Springs carbon isotope excursion in Svalbard with what is inferred to be the same anomaly in the Fifteenmile Group, Ogilvie Mountains, Yukon (Macdonald et al., 2012) and an age model developed for that succession, these samples are estimated to be ca. 802 Ma.

#### G512

**Locality:** The base of this section is on a steep slope of shallowly dipping Svanberfjellet Formation on the western edge of Klofjellet nunatak in Olav V Land, Spitsbergen, at N78°50′44.5″, E18°06′24.2″. This section is entirely within Svanbergfjellet member 3 (Upper Algal dolomite) and the base of the section is at the top of a prominent stromatolite biostrome. The black shales grade

vertically into limestone rhythmites and dolomite ribbonites. **Depositional environment:** Here the black shale occurs within the lower parts of poorly developed shale-to-carbonate parasequences, the lower part of which appears to have been deposited below storm wave base during a rare muddy interval in the otherwise carbonate-dominated Akademikerbreen Group. **Age:** Based on an age model developed for Svalbard, the upper Svanbergfjellet member 3 is ca. 795 Ma.

## G517

**Locality:** This sample was collected at N78°43.6′, E18°8.7′ from the transitional contact between the Draken Formation below and the Backlundtoppen Formation on the Klofjellet nunatak in Olav V Land, Spitsbergen. It was likely deposited in a lagoonal environment during a gradual transgression. **Age:** Based on an age model developed for Svalbard, this contact is ca. 780 Ma.

## G521

Location: This section was measured on the southwestern edge of the Backlundtoppen nunatak in Olav V Land, Spitsbergen at N78°42′48.3″, E18°12′43.7″. The section is of the lower-middle Russøya Member, where it overlies a karstified surface of the underlying 'Dartboard Dolomite', which forms the top of the Akademikerbreen Group. The lowermost Russøya member here a thick-bedded grey limestone, which transitions upward to marly dolomitic shale, then black shale. The datum of the section is the top of the limestone. The black shale transitions upward into brown dolomitic silty shales. **Depositional Environment:** The lower-middle Russøya black shales occur within the maximum flooding interval within a single,  $\leq 150$  m-thick parasequence that marks the transition from the Akademikerbreen to Polarisbreen groups. The shale is inferred to have been deposited on a mixed carbonate-siliciclastic ramp below storm wave base. **Age:** Based on an age model developed for the Polarisbreen and Akademikerbeen using correlated ages, this part of the Russøya member is estimated to be ca. 743–740 Ma.

## G406, P5014

**Location:** The base of this section is at N79°56.2′, E18°19.7′, east of Sveanor on the south coast of Murchisonfjord in Nordaustlandet. This section is from the the Russøya member, which comprises the basal Elbobreen Formation of the Polarisbreen Group, corresponding to measured

section 7 in Halverson et al. (2004) and MS7 in Hoffman et al. (2012). The collected black shale samples are from an 85 m-thick interval of black limestone ribbonites with molar tooth structure and interbedded rhythmite and black shale within the middle of a 145 m-thick shoaling upward sequence. Sample heights are in meters above the 79 m level. This sequence occurs beneath the Sturtian-equivalent Petrovbreen Member glacial deposits. **Depositional environment:** The black shale in this sequence was deposited at or just above storm wave base on a carbonate ramp. **Age:** These rocks are inferred to be 740 Ma based on a thermal subsidence model calibrated with correlated ages.

## G407

Location: The base of this section is at N79°53.5′, E18°29.3′, southeast of Backaberget on the south side of Murchisonfjord in Nordaustlandet. It lies within a nearly complete west-dipping panel of Akademikerbreen-Polarisbreen strata. The samples are from the lower-middle Macdonaldryggen Formation, whose base is at 188 m in the section. Samples are black shale samples within an overall dark grey muddy siltstone. **Depositional environment:** The shales were deposited at or below storm wave base on a broad mud-dominated platform. **Age:** Based on correlations of glacial successions, the age of the Cryogenian interglacial Macdonaldryggen Member is estimated to be ca. 660 to 645 Ma. These samples are estimated to be about 655 Ma.

### GR12

Location: This section was measured on the northern part of Ella Island in the East Greenland Fjordland, at N72°52′46″, W25°07′56″. The section is of the interglacial Arena Formation, which is equivalent to the Macdonaldryggen Formation in Svalbard. Here, the Arena Formation is mostly covered, but exposed section includes fine sandstone, siltstone, and grey to black shale. The base of the section (0 m) is the base of the Arena Formation. The analyzed black shale samples are from the lower part of the formation, which contains minor calcite cement and grades upward into fine, green sand with mud chips. Depositional environment: The lower Arena Formation was deposited below storm wave base on a broad, thermally subsiding platform. The uppermost analyzed samples come from an interval with interbedded ripple cross-laminated silts, suggesting deposition near or slightly above storm wave base. Age: Similar to the

Macdonaldryggen Member in Svalbard, the lower Arena Formation is estimated at ca. 660-655 Ma.

## G435

Location: The top of this section is at N79°48.8′, E18°36.2′, 1.5 km south of the Forsiusbreen glacier near Gimleoden in western Nordaustlandet. It lies on the east side of a syncline cored by the Dracoisen Formation. Samples are from the middle-upper Macdonaldryggen Member, with the 0 m datum marking the base of the overlying Slangen Member and the section measured downward from that datum. This section is mixed black silty shale and grey siltstone. Depositional environment: The middle-upper Macdonaldryggen Member in this location was deposited below storm wave base on a thermally subsiding siliciclastic platform. Age: The samples are estimated to be ca. 650–645 Ma based on the occurrence just below the Slangen Member, which lies beneath the Marinoan Wilsonbreen Formation, but is presumably separated by a disconformity.

### G419

Location: The base of this section is at N79°56.46′, E18°17.73′ near the south Murchisonfjord coastline at Sveanor. Samples are from the uppermost Macdonaldryggen Member, with the 0 m datum marking the base of the overlying Slangen Member and the section measured downward from that datum. This section is mixed black silty shale and grey siltstone. It grades upwards into muddy limestone ribbons. **Depositional environment:** The upper Macdonaldryggen Member in this location was deposited above storm wave base on a thermally subsiding platform during a transition from a dominantly siliciclastic to carbonate environment. **Age:** The samples are estimated to be ca. 645 Ma based on the fact that they occur just below the Slangen Member, which lies beneath the Marinoan Wilsonbreen Formation, but is presumably separated by a disconformity.

## G411

**Location:** The base of this section is at N79°53.5′, E18°29.3′, approximately 0.5 km to the northwest of section G407, southeast of Backaberget on the south side of Murchisonfjord in Nordaustlandet. The samples are from the lower Dracoisen Formation, whose base is 0 m in the section. The Dracoisen Formation includes the cap carbonate sequence, which overlies the Marinoan Wilsonbreen Formation. The Dracoisen cap dolostone in this section is 6 m-thick. Sam-

ples are black shale from Member 2 of the Dracoisen Formation. **Depositional environment:** These shale samples were deposited at or below storm wave base on a broad mud-dominated platform, following the post-glacial transgression and maximum flooding. **Age:** Assuming the Dracoisen Formation includes the basal Ediacaran cap carbonate, then the base of the Dracoisen is approximately 635 Ma. Dracoisen member 2 is interpreted to be between 635–630 Ma.

## G436

Location: The base of this section is at N79°48.6′, E18°34.6′, 1.5 km south of the Forsiusbreen glacier near Gimleoden in western Nordaustlandet and 1 km west of section G435. Samples are from the lower Dracoisen member 2, with the 0 m datum marking the base Dracoisen Formation. The samples are from the an interval of black shale grading up to silty black shale. Depositional environment: These shale samples were deposited at or below storm wave base on a broad mud-dominated platform, following the post-glacial transgression and maximum flooding. Age: Assuming the Dracoisen Formation includes the basal Ediacaran cap carbonate, then the base of the Dracoisen is approximately 635 Ma. Dracoisen member 2 is interpreted to be between 635–630 Ma.

## G306

**Location:** The base of this section is at N79°05.0′, E18°26.6′, on the Dracoisen nunatak in Ny Friesland. It corresponds to section 4 in Halverson et al. (2004). The section begins on a north-facing slope at the base of the Dracoisen Formation. All samples analyzed here are from Member 2 of the Dracoisen Formation, which comprises a shoaling-upward shale-silt sequence above the basal Dracoisen cap dolostone and is capped by an exposure surface. **Depositional environment:** Analyzed samples are from an interval of black to dark grey shales deposited below storm-weather wave base on what is interpreted to be a broad, thermally subsiding continental platform. **Age:** Assuming the Dracoisen Formation includes the basal Ediacaran cap carbonate, then the base of the Dracoisen is approximately 635 Ma. Dracoisen Member 2 is interpreted to be between 635–630 Ma.

## **Figures and Tables**



Fig. 3.6 Cross-plot of total sulfur measured on the C/S Analyzer and sulfur extracted with the CRS-method (Canfield et al., 1986).



Fig. 3.7 Cross-plot of FeT/Al versus Ti/Al. The MacDonaldryggen Member is the only unit with a positive correlation, suggesting that FeT/Al ratios are controlled by weathering of mafic rocks with high Fe contents in the source area. The equivalent Arena Formation also plots on a mixing line between UCC and Franklin CFB, suggesting an important influence of weathering of the mafic Franklin CFB on FeT/Al ratios. However, lack of correlation is interpreted that FeT/Al ratios are also elevated compared to UCC due to Fe enrichment from an anoxic water column. All other units show now correlation between FeT/Al and Ti/Al, suggesting that the provenance did not control Fe enrichments.

Sample		Unit	TC	TIC	TOC	LS	Fe	Al	Fe/Al	Li	Ca	K	Mg	Na	Ь	CIA
section	height		wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	
G306	159.0	Dra	3.30	0.0	с. С	1.16	1.43	6.78	0.21	0.40						
G306	150.0	Dra.					4.93	4.40	1.12	0.25						
G306a	143.0	$\mathrm{Dra.}$	5.14	4.11	1.03	1.44	2.63	7.12	0.37	0.43						
G306	131.0	Dra.	1.23	0.00	1.23	1.12	3.53	6.92	0.51	0.39	0.83	3.02	1.71	1.25	0.04	00
G436	138.0	Dra.	2.67	2.49	0.18	0.04	2.63	7.12	0.37	0.43	5.39	3.50	3.34	1.21		56
G436	120.0	Dra.	0.59	0.46	0.13	0.04	4.26	8.33	0.51	0.46	1.09	3.21	2.28	1.10		68
G436	105.0	Dra.	1.28	0.76	0.52	1.24	5.19	7.34	0.71	0.43	1.74	2.86	1.76	1.38		63
G436	101.5	Dra.	0.88	0.27	0.61	0.60	3.31	7.92	0.42	0.46	0.70	3.27	1.70	1.37		65
G436	95.5	Dra.	0.74	0.48	0.27	0.33	3.82	8.42	0.45	0.48	0.54	3.54	1.77	1.05		02
G436	88.0	Dra.	0.28	0.11	0.17	0.01	3.61	8.66	0.42	0.48	0.63	3.70	1.77	1.19		66
G436	64.0	$\mathrm{Dra.}$	1.25	0.40	0.84	0.88	3.46	7.96	0.44	0.47	1.68	3.14	1.97	1.56		09
G436	42.0	Dra.	1.89	1.62	0.27	0.06	3.04	7.53	0.40	0.46	4.10	3.42	2.47	1.40		56
G436	10.5	Dra.	0.95	0.39	0.56	1.15	3.71	7.60	0.49	0.44	1.20	3.03	1.88	1.36		63
G411	72.0	Dra.	1.74	1.64	0.10	0.09	3.81	6.80	0.56	0.32	5.20	2.12	1.51	2.04	0.04	49
G411	67.0	Dra.	0.18	0.04	0.14	0.00	4.32	8.22	0.53	0.44	0.34	3.52	1.98	1.02	0.05	67
G411	45.0	Dra.	4.73	4.56	0.17	0.05	3.38	4.88	0.69	0.18						
G411	41.0	Dra.	5.63	5.48	0.14	0.38	4.37	3.81	1.15	0.11						
G411	37.0	Dra.	2.40	2.11	0.30	0.04	4.42	6.71	0.66	0.39	4.97	2.78	2.64	1.18	0.06	56
G419	2.6	Mac.	5.56	4.92	0.64	0.68	1.63	4.19	0.39	0.23	9.03	2.21	5.29	0.98	0.06	53
G419	6.7	Mac.	4.19	3.64	0.55	0.97	2.23	4.41	0.51	0.24						
G419	12.3	Mac.	2.95	2.25	0.71	0.89	2.41	5.52	0.44	0.32	4.19	2.98	3.31	1.28	0.07	57
G435	18.0	Mac.	1.28	1.06	0.22	0.06	2.19	6.96	0.32	0.48	2.24	3.37	2.12	1.68		59
G435	25.0	Mac.	2.47	2.23	0.24	0.25	2.48	5.83	0.43	0.35	4.23	3.00	2.98	1.17		58
G435	35.0	Mac.	2.11	1.31	0.80	0.79	3.37	7.08	0.48	0.50	3.33	3.54	2.79	1.04		58
G435	45.0	Mac.	1.69	0.86	0.83	0.95	4.18	7.56	0.55	0.54	2.14	3.67	2.34	0.89		63
G435	56.0	Mac.	1.64	1.05	0.59	0.95	4.44	7.69	0.58	0.54	2.33	3.60	2.42	0.91		64

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61	61	59	63	66	63	57		64	68	64	63	64		80	68	64	61		78	62	83	81	83	78	83	83	62	78	78	80	77	66
			0.05	0.05	0.05	0.05	0.06	0.17	0.05	0.07	0.05	0.06		0.08	0.15	0.24	0.52	0.06														0.02
0.93	0.90	0.97	0.65	0.58	0.67	0.65	1.40	2.43	1.45	1.40	1.36	1.84		0.00	0.43	0.26	0.13	0.00	0.57	0.48	0.40	0.49	0.37	0.53	0.46	0.45	0.44	0.48	0.45	0.12	0.23	0.10
2.21	2.88	2.68	3.68	4.10	3.59	4.14	2.88	2.69	2.99	2.86	3.05	3.02		1.39	5.35	0.37	1.33	0.21	0.87	0.89	1.50	0.99	1.33	0.58	1.22	1.08	0.69	0.41	0.45	0.88	0.83	0.47
3.56	3.13	3.16	3.29	2.95	2.80	2.63	1.81	1.07	1.51	1.77	1.77	1.62		2.61	1.54	1.34	2.23	0.03	2.00	1.98	1.35	1.57	1.26	1.64	1.18	1.41	1.48	1.53	1.71	2.31	2.15	3.11
1.93	3.67	4.11	3.34	4.25	4.97	6.05	2.14	1.14	0.79	0.99	1.69	1.13		0.25	1.92	0.49	1.31	37.79	0.18	0.17	0.15	0.03	0.10	0.18	0.07	0.14	0.16	0.12	0.18	0.29	0.41	0.14
0.55	0.50	0.51	0.53	0.56	0.53	0.54	0.74	0.54	0.74	0.69	0.74	0.77	0.17	0.54	0.34	0.17	0.23	0.01	0.49	0.49	0.46	0.42	0.47	0.48	0.49	0.48	0.48	0.44	0.37	0.53	0.53	0.18
0.57	0.62	0.61	0.65	0.72	0.72	0.72	0.93	0.99	1.09	1.03	0.99	0.95		0.48	0.57	0.20	0.38	0.83	0.37	0.55	0.97	0.59	1.16	0.27	0.84	0.66	0.45	0.19	0.22	0.24	0.34	0.15
7.55	6.89	6.95	6.77	6.42	6.31	6.15	7.70	7.37	7.51	7.48	7.41	7.07	1.51	8.69	4.97	3.29	5.11	0.12	7.93	7.98	7.67	7.11	7.24	7.07	7.03	7.60	6.77	6.31	6.86	8.69	7.88	4.71
4.32	4.24	4.22	4.41	4.60	4.56	4.40	7.15	7.26	8.17	7.70	7.34	6.69		4.20	2.84	0.67	1.92	0.10	2.95	4.40	7.42	4.16	8.40	1.92	5.89	5.02	3.05	1.19	1.54	2.09	2.66	0.71
1.08	1.28	0.94	0.00	0.00	0.02	0.00	0.08	0.97	0.97	1.03	1.33	2.03	0.63	0.00	0.00	0.17	0.18		0.02	0.06	0.04	0.92	0.02	0.02	0.07	0.03	0.11	0.08	0.20	0.01	0.02	0.05
0.89	0.68	0.52	0.19	0.20	0.23	0.24	0.28	0.20	0.22	0.22	0.24	0.38	0.78	0.29	0.31	1.42	1.69		0.31	0.59	0.29	0.60	0.52	0.59	0.38	0.71	0.92	1.44	1.77	1.06	0.80	0.69
0.60	1.69	1.82	1.56	2.29	2.55	2.68		0.47	0.13	0.00	0.35	0.35	0.00	0.00	0.79	0.00	0.06		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.00	0.01	0.00	0.00	0.00
1.49	2.37	2.34	1.75	2.49	2.78	2.92		0.66	0.36	0.22	0.59	0.73	0.78	0.29	1.11	1.42	1.75		0.31	0.59	0.29	0.60	0.52	0.59	0.38	0.77	0.92	1.44	1.78	1.06	0.80	0.69
Mac.	Mac.	Mac.	Mac.	Mac.	Mac.	Mac.	Are.	Rus.	Rus.	Rus.	Rus.	Rus.	Rus.	Rus.	Rus.	Rus.	Rus.	Rus.	Rus.	Rus.	Rus.	Rus.	Rus.	Rus.	Rus.	Bac.						
66.0	76.0	79.5	278.0	261.0	245.0	233.0	78.0	71.0	64.5	15.9	10.5	8.5	3.3	а	q	42.0	35.0	0.0	46.0	44.4	40.5	36.0	33.0	30.0	26.4	23.4	19.6	18.9	13.2	6.2	3.7	I
G435	G435a	G435	G407	G407	G407	G407	GR12	G519	G519	G406	G406	G406	G521	G517																		

78	2		73	81			70	69	73				73	73
							0.02	0.05	0.10		0.01		0.03	0.03
0.06	00.0		0.36	0.08			0.00	0.00	0.00		0.00		1.07	0.71
<i>6</i> 2 U	1	0.95	0.68	0.49			1.80	1.75	4.07		0.20		1.56	1.31
9 01	7.01	3.14	2.52	1.92			5.84	5.76	2.22		0.05		0.95	3.63
66 0	1		0.18	0.09			0.24	0.28	0.39		2.67		0.39	0.11
0.40	0.50	0.62	0.40		0.62	0.45	0.38	0.48	0.32		0.48		0.36	0.51
036	0000	0.28	0.10	0.11			0.35	0.32	0.66	1.37		0.78	1.34	0.58
617	11.0	11.92	6.45	6.45			10.15	9.84	5.54	0.74		0.24	6.51	9.54
766	H 7 7	3.36	0.61	0.72			3.52	3.16	3.67	1.01	0.39	0.19	8.74	5.57
0.02	0.03	0.00	0.07	0.51	0.02	1.55	0.00	0.03	0.02	0.19	0.04	0.05	0.00	0.09
$\begin{array}{c} 0.63 \\ 1.38 \end{array}$	0.69	0.19	0.73	2.38	1.73	0.81	0.30	0.35	0.09	1.72	0.25	0.28	0.21	0.15
00.0	0.14	0.00	0.00	0.00	0.16	0.00	0.01	0.00	0.00	7.58		5.56	0.00	0.00
1 38	0.83	0.19	0.73	2.38	1.89	0.81	0.30	0.35	0.09	9.30		5.84	0.21	0.15
Sva	Sva.	Sva.	Sva.	Sva.	Sva.	Sva.	Sva.	Sva.	Sva.	Sva.	Sva.	Sva.	Vet.	Vet.
60.5 55 0	47.9	40.6	35.2	26.2	24.1	21.2	8.3	6.1	149.3	149.1	133.5	83.6	ı	ı
G512 G512	G512	G512	G512	G512	G512	G512	G471	G471	G155	G155	G155	G155	G426a	G426b

approximatio	n of the so	urce area												
Sample		Mo	Mo/TOC	Mo (a.)	D	U/TOC	U (a.)		V/TOC	V (a.)	La	$^{\mathrm{Th}}$	$S_{\rm C}$	Co
section	height													
G306	159.0	16.98	5.15	15.71	6.46	1.96	4.10	170.81	51.81	80.60	38.64	12.35	9.88	2.70
G306	150.0	5.80		4.98	3.60		2.07	120.05		61.51	30.36	8.48	9.42	28.91
G306a	143.0	0.37	0.36	0.00	9.55	9.30	7.07	638.29	621.31	543.55	43.60	8.26	8.40	22.32
G306	131.0	5.05	4.11	3.76	5.42	4.41	3.01	184.46	149.99	92.34	43.17	14.29	12.61	34.74
G436	138.0	0.37	2.07	0.00	9.55	53.18	7.07	638.29	3554.05	543.55	43.60	19.77	15.10	20.32
G436	120.0	0.35	2.62	0.00	3.72	28.08	0.82	99.14	748.28	0.00	43.74	22.05	16.39	16.27
G436	105.0	8.49	16.30	7.12	4.74	9.09	2.18	146.04	280.30	48.33	41.09	19.31	14.71	32.49
G436	101.5	2.44	4.03	0.97	5.55	9.15	2.79	152.68	251.88	47.28	41.82	21.29	16.08	21.98
G436	95.5	0.38	1.41	0.00	5.05	18.80	2.12	113.40	422.24	1.31	39.61	20.56	16.30	37.20
G436	88.0	0.71	4.31	0.00	5.25	31.79	2.23	108.23	655.65	0.00	43.22	21.77	16.97	19.50
G436	64.0	1.17	1.39	0.00	4.92	5.85	2.15	114.79	136.54	8.90	41.32	22.22	15.39	19.40
G436	42.0	0.36	1.32	0.00	8.36	30.61	5.74	622.47	2278.43	522.27	45.75	23.30	16.60	22.32
G436	10.5	2.27	4.08	0.85	4.92	8.86	2.27	127.99	230.55	26.85	40.14	18.53	14.65	17.14
G411	72.0	0.23	2.32	0.00	2.11	21.19	0.00	66.41	665.42	0.00	39.81	12.87	12.73	27.58
G411	67.0	0.25	1.79	0.00	2.84	20.46	0.00	97.51	701.57	0.00	49.21	16.60	13.75	15.72
G411	45.0	0.09	0.51	0.00	1.96	11.45	0.26	45.84	267.38	0.00	26.59	7.17	11.21	9.52
G411	41.0	0.43	2.98	0.00	1.72	11.93	0.39	31.68	220.39	0.00	19.63	3.55	7.61	9.25
G411	37.0	0.16	0.55	0.00	3.02	10.23	0.68	84.71	286.84	0.00	44.13	15.45	14.00	22.25
G419	2.6	0.55	0.87	0.00	2.17	3.40	0.71	38.70	60.57	0.00	21.61	6.78	6.99	4.57
G419	6.7	1.03	1.88	0.21	2.28	4.15	0.74	52.02	94.81	0.00	24.62	8.31	7.68	5.84
G419	12.3	1.58	2.23	0.55	2.06	2.90	0.13	72.74	102.77	0.00	31.08	9.46	8.62	7.59
G435	18.0	0.19	0.88	0.00	2.85	13.25	0.43	75.59	350.99	0.00	36.96	17.03	12.79	8.47
G435	25.0	0.68	2.82	0.00	2.29	9.52	0.26	61.83	256.85	0.00	28.10	10.29	10.26	13.02
G435	35.0	0.39	0.49	0.00	2.99	3.76	0.53	90.71	113.95	0.00	21.82	16.49	14.86	16.62
G435	45.0	0.54	0.65	0.00	2.79	3.35	0.16	107.43	128.85	6.83	35.96	14.67	16.68	21.57

26.95	21.33	26.70	24.22	15.53	14.92	16.47	13.66	12.64	40.38	46.86	41.23	36.57	30.51	7.31	15.42	7.66	0.56	1.48	0.65	6.28	55.61	7.83	10.59	68.87	5.28	4.39	5.30	4.85	11.14	4.79	9.28	13.43
18.17	17.16	15.85	16.38	15.83	17.12	16.79	15.80	25.88	19.83	26.05	23.65	24.77	23.87	5.28	13.68	9.34	4.21	7.78	0.83	16.84	15.97	14.27	14.56	18.63	15.15	11.52	13.46	13.31	20.93	11.84	16.35	13.30
16.12	15.45	13.97	14.02	9.53	8.90	9.35	7.87	8.14	6.49	7.88	7.70	7.81	8.47	1.72	12.89	7.84	5.05	8.57	0.26	18.12	18.55	17.07	16.15	16.14	15.89	16.80	17.27	13.11	23.21	9.66	19.37	18.19
36.07	36.86	35.52	32.42	34.37	32.15	30.91	29.55	30.92	30.24	24.84	32.17	27.76	30.70	15.65	53.74	29.11	31.46	22.03	4.27	41.24		36.46	35.98	39.23	40.39	40.50	37.48	39.10	36.79	30.28	45.51	54.42
9.53	7.09	8.50	14.32	41.31	55.58	56.91	46.51	73.27	59.41	93.65	73.80	84.28	100.20	30.84	0.00	79.60	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
189.26	121.08	147.05	205.77	695.24	694.20	625.73	538.96	635.95	793.25	875.10	792.12	768.27	512.34	65.00	331.49	463.07	15.95	23.92		191.02	107.82	202.23	92.05	121.12	96.27	143.86	78.05	66.54	50.24	32.75	75.61	78.95
111.92	107.57	100.22	106.83	131.46	141.00	140.88	128.30	175.71	157.47	193.54	173.34	182.90	194.34	50.87	94.79	145.70	22.62	40.45	1.49	59.50	63.37	57.89	55.12	63.40	57.07	54.07	55.45	61.03	72.43	57.92	79.78	63.33
0.40	0.33	0.17	0.20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.28	0.00	0.21	0.54	0.13	0.00	0.00	0.00	0.00	0.00	0.37	0.00	0.00	1.65	0.00	0.45	0.00
5.22	3.33	3.77	5.05	11.13	9.54	8.96	7.26	6.21	7.51	8.01	8.82	7.92	5.33	0.65	7.84	6.38	0.78	1.18		9.27	4.06	8.33	3.93	3.89	3.76	7.51	3.43	2.27	2.67	1.29	3.30	3.09
3.08	2.96	2.57	2.62	2.11	1.94	2.02	1.73	1.72	1.49	1.77	1.93	1.89	2.02	0.51	2.24	2.01	1.10	1.99	0.59	2.89	2.38	2.38	2.35	2.04	2.23	2.82	2.44	2.08	3.85	2.28	3.48	2.48
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.79	0.00	0.00	0.00	0.07	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.89	0.60	0.68	0.71	0.65	1.10	0.63	0.79	0.90	1.17	3.64	1.06	1.64	2.09	6.48	0.89	0.49	0.27	0.61		1.25	0.78	0.84	0.80	0.64	1.14	3.02	0.60	0.45	0.16	0.48	0.33	0.58
0.53	0.54	0.46	0.37	0.12	0.22	0.14	0.19	0.25	0.23	0.81	0.23	0.39	0.79	5.07	0.25	0.15	0.39	1.02	0.15	0.39	0.46	0.24	0.48	0.34	0.68	1.13	0.43	0.42	0.23	0.85	0.35	0.46
56.0	66.0	76.0	79.5	278.0	261.0	245.0	233.0	78.0	71.0	64.5	15.9	10.5	8.5	3.3	ı	I	42.0	35.0	0.0	46.0	44.4	40.5	36.0	33.0	30.0	26.4	23.4	19.6	18.9	13.2	6.2	3.7
G435	G435	G435a	G435	G407	G407	G407	G407	GR12	GR12	GR12	GR12	GR12	GR12	GR12	G519a	G519b	G406	G406	G406	G521	G521	G521	G521	G521	G521	G521	G521	G521	G521	G521	G521	G521

1.22	1.23	0.79	0.60		5.31		29.40	5.06	4.05			10.71	6.58	6.05	1.16	0.43	0.68	19.33	12.92
1.21	1.16	0.80	4.88		12.58		22.15	12.91	10.62			17.79	17.53	9.76	1.39	0.07	0.88	11.96	17.85
0.52	0.62	0.31	4.90		11.21		30.18	17.56	15.49			14.61	14.60	10.10	4.79	0.16	0.72	12.27	18.78
			17.21		34.71		9.72	60.51	37.28			48.91	45.15	27.18	42.26	0.39	1.46	37.38	69.18
			0.00		0.00		0.00	0.00	0.00			0.00	36.53	76.41	57.93	7.27	83.37	0.00	5.44
			62.63		37.26		633.18	69.31	20.91			443.66	480.40	1677.34	39.43	36.93	307.21	355.29	889.89
4.43	2.67	1.29	43.39		51.47		119.25	50.75	49.87			131.53	167.49	150.16	67.76	9.20	86.62	72.86	132.42
			0.00		0.38		0.34	0.25	0.36			0.00	0.00	0.00	1.88	0.37	0.63	0.38	0.87
			1.56		1.83		23.85	3.41	1.09			10.26	5.94	14.66	1.25	1.70	2.55	12.91	28.17
0.61	0.69	0.51	1.08		2.53		4.49	2.49	2.60			3.04	2.07	1.31	2.14	0.42	0.72	2.65	4.19
			0.00		0.42		0.00	0.52	0.00			0.00	0.00	0.00	1.04	0.60	0.47	0.00	0.00
			0.65		1.14		3.66	2.35	0.44			1.61	1.62	2.67	0.69	2.53	1.81	1.16	1.19
0.13	0.18	0.12	0.45		1.57		0.69	1.72	1.05			0.48	0.57	0.24	1.18	0.63	0.51	0.24	0.18
52.0	43.5	30.5		60.5	55.0	47.9	40.6	35.2	26.2	24.1	21.2	8.3	6.1	149.3	149.1	133.5	83.6	ı	ı
P5014	P5014	P5014	G517	G512	G512	G512	G512	G512	G512	G512	G512	G471	G471	G155	G155	G155	G155	G426a	G426b

Sample		Unit	FeT	Fecarb	Feox	Femag	FePy	FeHR/FeT	FePy/FeHR
section	height		wt.&	wt.%	wt.%	wt.%	wt.%		
G306	159.0	Dracoisen	1.43	0.21	0.58	0.03	0.35	0.82	0.30
G306a	143.0	Dracoisen	3.96	1.15	0.63	0.06	0.98	0.71	0.35
G306	131.0	Dracoisen	3.53	0.24	0.85	0.07	0.69	0.52	0.37
G436	138.0	Dracoisen	2.63	0.73	0.12	0.06	0.04	0.36	0.04
G436	120.0	Dracoisen	4.26	0.38	0.13	0.19	0.02	0.17	0.03
G436	105.0	Dracoisen	5.19	0.37	0.13	0.13	0.55	0.23	0.47
G436	101.5	Dracoisen	3.31	0.34	0.15	0.11	0.72	0.40	0.54
G436	95.5	Dracoisen	3.82	0.31	0.14	0.19	0.18	0.21	0.22
G436	88.0	Dracoisen	3.61	0.18	0.10	0.11	0.06	0.13	0.14
G436	64.0	Dracoisen	3.46	0.56	0.24	0.11	0.66	0.45	0.42
G436	42.0	Dracoisen	3.04	0.23	0.64	0.11	0.28	0.41	0.22
G436	10.5	Dracoisen	3.71	0.38	0.13	0.11	0.05	0.18	0.08
G411	72.0	Dracoisen	3.81	0.25	0.53	0.19	0.06	0.27	0.06
G411	67.0	Dracoisen	4.32	0.13	0.62	0.20	0.00	0.22	0.00
G411	45.0	Dracoisen	3.38	1.30	0.66	0.08	0.02	0.61	0.01
G411	41.0	Dracoisen	4.37	1.71	0.71	0.07	0.27	0.63	0.10
G411	37.0	Dracoisen	4.42	0.54	0.77	0.19	0.04	0.35	0.02
G419	2.6	Macdonaldryggen	1.63	0.61	0.17	0.01	0.47	0.78	0.37
G419	6.7	Macdonaldryggen	2.23	0.72	0.17	0.03	0.72	0.74	0.44
G419	12.3	Macdonaldryggen	2.41	0.48	0.12	0.03	0.68	0.54	0.52
G435	25.0	Macdonaldryggen	2.48	0.55	0.47	0.05	0.29	0.55	0.21
G435	35.0	Macdonaldryggen	3.37	0.30	0.65	0.05	0.57	0.47	0.36
G435	45.0	Macdonaldryggen	4.18	0.50	0.49	0.14	0.65	0.42	0.37
G435	56.0	Macdonaldryggen	4.44	0.51	0.17	0.14	0.94	0.39	0.54
G435	66.0	Macdonaldryggen	4.32	0.68	0.33	0.17	1.05	0.52	0.47
G435a	76.0	Macdonaldryggen	4.24	0.61	0.23	0.11	0.83	0.42	0.46
G435	79.5	Macdonaldryggen	4.22	0.66	0.12	0.16	0.73	0.40	0.44
G407	278.0	Macdonaldryggen	4.41	0.51	0.35	0.18	0.02	0.24	0.02

G407	261.0	Macdonaldryggen	4.60	0.56	0.47	0.24	0.01	0.28	0.01
G407	245.0	Macdonaldryggen	4.56	0.49	0.60	0.20	0.03	0.29	0.02
G407	233.0	Macdonaldryggen	4.40	0.47	0.56	0.20	0.01	0.28	0.01
GR12	78.0	Arena	7.15	0.46	0.19	0.32	0.14	0.16	0.13
GR12	71.0	Arena	7.26	0.46	0.35	0.39	0.72	0.27	0.38
GR12	64.5	Arena	8.17	0.57	0.20	0.45	0.61	0.22	0.33
GR12	15.9	Arena	7.70	0.55	0.27	0.47	0.83	0.27	0.39
GR12	10.5	Arena	7.34	0.50	0.17	0.30	1.10	0.28	0.53
GR12	8.5	Arena	6.69	0.46	0.19	0.21	1.57	0.36	0.65
GR12	3.3	Arena	3.39	1.93	0.17	0.06	0.43	0.76	0.17
G519a	I	${ m Russ}$ øya	4.20	0.12	1.02	0.34	0.00	0.35	0.00
G519b	I	${ m Russ}$ øya	2.84	0.23	0.17	0.09	0.01	0.18	0.02
G406	42.0	${ m Russøya}$	0.67	0.20	0.31	0.04	0.07	0.92	0.11
G406	35.0	${ m Russøya}$	1.92	0.18	1.17	0.05	0.10	0.78	0.07
G521	46.0	${ m Russ}$ øya	2.95	0.22	0.69	0.21	0.01	0.38	0.01
G521	44.4	${ m Russ}$ øya	4.40	0.18	1.97	0.25	0.02	0.55	0.01
G521	40.5	${ m Russ}$ øya	7.42	0.18	1.06	0.32	0.02	0.21	0.01
G521	36.0	${ m Russøya}$	4.16	0.23	0.35	0.18	0.29	0.25	0.28
G521	33.0	${ m Russøya}$	8.40	0.23	1.52	0.40	0.02	0.26	0.01
G521	30.0	${ m Russøya}$	1.92	0.20	0.51	0.20	0.00	0.48	0.00
G521	26.4	${ m Russ}$ øya	5.89	0.20	2.19	0.47	0.01	0.49	0.00
G521	23.4	${ m Russ}$ øya	5.02	0.27	0.39	0.22	0.00	0.18	0.00
G521	19.6	${ m Russ}$ øya	3.05	0.27	0.57	0.13	0.01	0.32	0.01
G521	18.9	${ m Russ}$ øya	1.19	0.05	1.14	0.08	0.05	1.11	0.03
G521	13.2	${ m Russøya}$	1.54	0.12	0.47	0.04	0.00	0.41	0.00
G521	6.2	${ m Russøya}$	2.09	0.14	0.61	0.23	0.00	0.47	0.00
G517	I	Backlundtoppen	0.71	0.06	0.18	0.04	0.02	0.44	0.08
G512	55.0	Svanbergfjellet	2.24	0.34	0.93	0.18	0.03	0.66	0.02
G512	40.6	Svanbergfjellet	3.36	0.11	0.87	0.29	0.00	0.38	0.00
G512	35.2	Svanbergfjellet	0.61	0.15	0.43	0.03	0.03	1.05	0.05
G471	6.1	Svanbergfjellet	3.16	0.08	0.57	0.16	0.00	0.26	0.00
G155	149.3	Svanbergfjellet	3.67	0.23	0.49	0.16	0.01	0.24	0.01
G155	149.1	Svanbergfjellet	1.01	0.17	0.59	0.03	0.13	0.91	0.14

0.23	0.01	0.00	
0.96	0.13	0.17	
0.04	0.01	0.00	
0.01	0.49	0.45	
0.07	0.33	0.21	
0.06	0.27	0.27	
0.19	8.74	5.57	
Svanbergfjellet	Veteranen	Veteranen	
83.6	ı	I	
G155	G426a	G426b	

	Acetate (wt.%)	Dithionite (wt.%)	Oxalate (wt.%)	Total (wt.%)
G0130.286	0.077	1.405	0.034	1.516
Std. Dev.	0.002	0.037	0.008	0.029
MP.69.5	0.694	0.138	0.018	0.85
Std. Dev.	0.017	0.013	0.029	0.035
MP67.5	0.429	0.13	0.005	0.564
Std. Dev.	0.015	0.012	0.003	0.023
F1018.54.5-1	0.037	0.419	0.094	0.55
Std. Dev.	0.012	0.051	0.021	0.057
F849.112-1	0.747	0.689	0.026	1.462
Std. Dev.	0.013	0.053	0.009	0.042
F849.225-1	0.105	1.14	0.12	1.365
Std. Dev.	0.024	0.045	0.058	0.075

**Tab. 3.4** Summary of the sequential extraction results for six replicate samples analyzed by Erik A. Sperling at Harvard University. See Sperling et al. (2013) for details. Compare with results in Tab. 3.5.
G0130.286-1         0.063         1.639         0.052         1.755           0.061         1.646         0.037         1.744           Average         0.062         1.643         0.045         1.749           Std. Dev.         0.001         0.005         0.011         0.007           MP.69.5-1         0.795         0.168         0.036         1.000           Average         0.780         0.158         0.000         0.938           Average         0.787         0.163         0.018         0.969           Std. Dev.         0.011         0.007         0.026         0.044           MP67.5-1         0.492         0.144         0.000         0.636           Average         0.487         0.153         0.000         0.638           Std. Dev.         0.003         0.007         0.000         0.638           Std. Dev.         0.003         0.007         0.000         0.003           F1018.54.5-1         0.042         0.495         0.163         0.699           0.043         0.477         0.173         0.692           Std. Dev.         0.001         0.025         0.015         0.010           F849.112-1		Acetate (wt.%)	Dithionite (wt.%)	Oxalate (wt.%)	Total (wt.%)
0.061 $1.646$ $0.037$ $1.744$ Average $0.062$ $1.643$ $0.045$ $1.749$ Std. Dev. $0.001$ $0.005$ $0.011$ $0.007$ MP.69.5-1 $0.795$ $0.168$ $0.036$ $1.000$ MP.69.5-1 $0.787$ $0.163$ $0.018$ $0.969$ Std. Dev. $0.011$ $0.007$ $0.026$ $0.044$ MP67.5-1 $0.492$ $0.144$ $0.000$ $0.636$ Average $0.487$ $0.153$ $0.000$ $0.638$ Std. Dev. $0.003$ $0.007$ $0.000$ $0.638$ Std. Dev. $0.042$ $0.495$ $0.163$ $0.699$ Std. Dev. $0.043$ $0.477$ $0.173$ $0.692$ Std. Dev. $0.001$ $0.025$ $0.015$ $0.010$ F1018.54.5-1 $0.685$ $0.788$ $0.031$ $1.684$ Average $0.043$ $0.477$ $0.173$ $0.692$ Std. Dev. $0.001$ $0.025$ $0.015$ $0.010$ F849.112-1 $0.879$ $0.753$ $0.024$ $1.656$ $0.865$ $0.788$ $0.031$ $1.684$ Average $0.872$ $0.770$ $0.028$ $1.670$ Std. Dev. $0.016$ $0.072$ $0.015$ $0.010$	G0130.286-1	0.063	1.639	0.052	1.755
Average Std. Dev.0.062 0.0011.643 0.0050.045 0.0111.749 0.007MP.69.5-10.795 0.7800.168 0.1580.036 0.0001.000 0.938Average Std. Dev.0.787 0.0110.163 0.0070.018 0.0260.944MP67.5-10.492 0.4870.144 0.1530.000 0.0000.636 0.640Average Std. Dev.0.489 0.0030.149 0.0070.000 0.0000.638 0.643F1018.54.5-10.042 0.0430.495 0.4590.163 0.1840.699 0.685Average Std. Dev.0.043 0.0010.477 0.0250.173 0.0150.692 0.015F849.112-10.879 0.8650.753 0.7780.024 0.0241.656 0.028Average Std. Dev.0.156 0.0101.335 0.0250.321 0.0051.813 0.020F849.225-10.156 0.1341.284 0.3010.311 1.740		0.061	1.646	0.037	1.744
Average Std. Dev. $0.062$ $1.643$ $0.045$ $1.749$ MP.69.5-1 $0.795$ $0.168$ $0.036$ $1.000$ MP.69.5-1 $0.780$ $0.158$ $0.000$ $0.938$ Average $0.780$ $0.163$ $0.018$ $0.969$ Std. Dev. $0.011$ $0.007$ $0.026$ $0.044$ MP67.5-1 $0.492$ $0.144$ $0.000$ $0.636$ Average $0.487$ $0.153$ $0.000$ $0.638$ Std. Dev. $0.003$ $0.007$ $0.000$ $0.638$ Std. Dev. $0.003$ $0.007$ $0.000$ $0.638$ Std. Dev. $0.042$ $0.495$ $0.163$ $0.699$ $0.433$ $0.477$ $0.173$ $0.692$ Std. Dev. $0.001$ $0.025$ $0.015$ $0.010$ F849.112-1 $0.879$ $0.753$ $0.024$ $1.656$ $0.788$ $0.311$ $1.670$ $0.025$ $0.005$ $0.020$ F849.225-1 $0.156$ $1.335$ $0.321$ $1.813$ $0.145$ $1.284$ $0.311$ $1.740$ Std. Dev. $0.016$ $0.072$ $0.015$ $0.102$					
Std. Dev. $0.001$ $0.005$ $0.011$ $0.007$ MP.69.5-1 $0.795$ $0.168$ $0.036$ $1.000$ $0.780$ $0.158$ $0.000$ $0.938$ Average $0.787$ $0.163$ $0.018$ $0.969$ Std. Dev. $0.011$ $0.007$ $0.026$ $0.044$ MP67.5-1 $0.492$ $0.144$ $0.000$ $0.636$ Average $0.487$ $0.153$ $0.000$ $0.638$ Std. Dev. $0.003$ $0.007$ $0.000$ $0.638$ Std. Dev. $0.003$ $0.007$ $0.000$ $0.003$ F1018.54.5-1 $0.042$ $0.495$ $0.163$ $0.699$ $0.043$ $0.477$ $0.173$ $0.692$ Std. Dev. $0.001$ $0.025$ $0.015$ $0.010$ F849.112-1 $0.879$ $0.753$ $0.024$ $1.656$ $0.788$ $0.311$ $1.684$ $Average$ $0.872$ $0.770$ $0.028$ $1.670$ Std. Dev. $0.010$ $0.025$ $0.005$ $0.020$ $0.020$ $0.025$ $0.005$ $0.020$ F849.225-1 $0.156$ $1.335$ $0.321$ $1.813$ $1.668$ Average $0.145$ $1.284$ $0.311$ $1.740$ Std. Dev. $0.016$ $0.072$ $0.015$ $0.102$	Average	0.062	1.643	0.045	1.749
MP.69.5-10.795 0.7800.168 0.1580.036 0.0001.000 0.938Average Std. Dev.0.787 0.0110.163 0.0070.018 0.0260.969 0.044MP67.5-10.492 0.4870.144 0.1530.000 0.0000.636 0.640Average Std. Dev.0.489 0.0030.149 0.0070.000 0.0000.638 0.643F1018.54.5-10.042 0.0430.495 0.4590.163 0.1840.699 0.685Average Std. Dev.0.043 0.0010.477 0.0250.173 0.0150.692 0.010F849.112-10.879 0.8650.753 0.7880.024 0.0311.656 1.636Average Std. Dev.0.156 0.0100.753 0.0250.028 0.0051.670 0.020F849.225-10.156 0.1341.335 1.2340.3311 0.3011.740 0.012	Std. Dev.	0.001	0.005	0.011	0.007
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$					
0.780         0.158         0.000         0.938           Average         0.787         0.163         0.018         0.969           Std. Dev.         0.011         0.007         0.026         0.044           MP67.5-1         0.492         0.144         0.000         0.636           Average         0.487         0.153         0.000         0.6486           Average         0.487         0.149         0.000         0.638           Std. Dev.         0.003         0.007         0.000         0.638           Std. Dev.         0.003         0.007         0.000         0.638           Std. Dev.         0.042         0.495         0.163         0.699           0.043         0.459         0.184         0.685           Average         0.043         0.477         0.173         0.692           Std. Dev.         0.001         0.025         0.015         0.010           F849.112-1         0.879         0.753         0.024         1.656           0.865         0.788         0.031         1.684           Average         0.872         0.770         0.028         1.670           Std. Dev.         0.015	MP.69.5-1	0.795	0.168	0.036	1.000
Average Std. Dev.0.787 0.0110.163 0.0070.018 0.0260.969 0.044MP67.5-10.492 0.4870.144 0.1530.000 0.0000.636 0.640Average Std. Dev.0.489 0.0030.149 0.0070.000 0.0000.638 0.633F1018.54.5-10.042 0.0430.495 0.4590.163 0.1840.699 0.685Average Std. Dev.0.043 0.0010.477 0.0250.173 0.0150.692 0.010F849.112-10.879 0.8650.753 0.7880.024 0.0311.656 1.684Average Std. Dev.0.872 0.0100.770 0.0250.028 0.0051.670 0.020F849.225-10.156 0.1341.335 1.2340.321 0.3111.813 1.668Average Std. Dev.0.145 0.0161.284 0.0150.311 0.0151.740 0.102		0.780	0.158	0.000	0.938
Average $0.787$ $0.163$ $0.018$ $0.969$ Std. Dev. $0.011$ $0.007$ $0.026$ $0.044$ MP67.5-1 $0.492$ $0.144$ $0.000$ $0.636$ $0.487$ $0.153$ $0.000$ $0.640$ Average $0.487$ $0.153$ $0.000$ $0.640$ Average $0.487$ $0.153$ $0.000$ $0.638$ Std. Dev. $0.003$ $0.007$ $0.000$ $0.003$ F1018.54.5-1 $0.042$ $0.495$ $0.163$ $0.699$ $0.043$ $0.459$ $0.184$ $0.685$ Average $0.043$ $0.477$ $0.173$ $0.692$ Std. Dev. $0.001$ $0.025$ $0.015$ $0.010$ F849.112-1 $0.879$ $0.753$ $0.024$ $1.656$ $0.865$ $0.788$ $0.031$ $1.684$ Average $0.872$ $0.770$ $0.028$ $1.670$ Std. Dev. $0.016$ $1.335$ $0.321$ $1.813$ $0.134$ $1.234$ $0.301$ $1.668$					
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MP67.5-10.492 0.4870.144 0.1530.000 0.0000.636 0.640Average Std. Dev.0.489 0.0030.149 0.0070.000 0.0000.638 0.003F1018.54.5-10.042 0.0430.495 0.4590.163 0.1840.699 0.685Average Std. Dev.0.043 0.0010.477 0.0250.173 0.0150.692 0.015F849.112-10.879 0.8650.753 0.7880.024 0.0311.656 1.684Average Std. Dev.0.872 0.0100.770 0.0250.028 0.0051.670 0.020F849.225-10.156 0.1341.335 1.2340.321 0.3111.813 1.668Average Std. Dev.0.145 0.1341.284 0.0310.311 1.740	Std. Dev.	0.011	0.007	0.026	0.044
MP67.5-1 $0.492$ $0.487$ $0.144$ $0.153$ $0.000$ $0.000$ $0.636$ $0.640$ Average $0.487$ $0.153$ $0.000$ $0.640$ Average $0.489$ $0.003$ $0.007$ $0.000$ $0.638$ $0.000$ Std. Dev. $0.003$ $0.007$ $0.000$ $0.638$ $0.000$ F1018.54.5-1 $0.042$ $0.043$ $0.495$ $0.459$ $0.163$ $0.184$ $0.685$ Average $0.043$ $0.001$ $0.477$ $0.025$ $0.173$ $0.015$ $0.692$ $0.015$ Std. Dev. $0.001$ $0.025$ $0.788$ $0.024$ $0.031$ $1.656$ $0.020$ F849.112-1 $0.879$ $0.865$ $0.770$ $0.028$ $1.670$ $0.020$ Std. Dev. $0.010$ $0.025$ $0.005$ $0.020$ F849.225-1 $0.156$ $0.134$ $1.335$ $1.234$ $0.301$ Average $0.145$ $0.145$ $1.284$ $0.311$ $1.740$ Std. Dev. $0.016$ $0.072$ $0.015$ $0.102$					
Average $0.487$ $0.153$ $0.000$ $0.640$ Average $0.489$ $0.149$ $0.000$ $0.638$ Std. Dev. $0.003$ $0.007$ $0.000$ $0.003$ F1018.54.5-1 $0.042$ $0.495$ $0.163$ $0.699$ $0.043$ $0.459$ $0.184$ $0.685$ Average $0.043$ $0.477$ $0.173$ $0.692$ Std. Dev. $0.001$ $0.025$ $0.015$ $0.010$ F849.112-1 $0.879$ $0.753$ $0.024$ $1.656$ $0.865$ $0.788$ $0.031$ $1.684$ Average $0.872$ $0.770$ $0.028$ $1.670$ Std. Dev. $0.010$ $0.025$ $0.005$ $0.020$ F849.225-1 $0.156$ $1.335$ $0.321$ $1.813$ Average $0.145$ $1.284$ $0.311$ $1.740$ Std. Dev. $0.016$ $0.072$ $0.015$ $0.102$	MP67.5-1	0.492	0.144	0.000	0.636
Average Std. Dev. $0.489$ $0.003$ $0.149$ $0.007$ $0.000$ $0.000$ $0.638$ $0.003$ F1018.54.5-1 $0.042$ $0.043$ $0.495$ $0.459$ $0.163$ $0.184$ $0.699$ $0.685$ Average Std. Dev. $0.043$ $0.001$ $0.477$ $0.025$ $0.173$ $0.015$ $0.692$ $0.015$ F849.112-1 $0.879$ $0.865$ $0.753$ $0.788$ $0.024$ $0.031$ $1.656$ $1.684$ Average Std. Dev. $0.872$ $0.010$ $0.770$ $0.025$ $0.028$ $0.005$ $1.670$ $0.020$ F849.225-1 $0.156$ $0.134$ $1.335$ $1.234$ $0.321$ $0.301$ $1.813$ $1.668$ Average Std. Dev. $0.145$ $0.016$ $1.284$ $0.072$ $0.311$ $0.015$ $1.740$ $0.102$		0.487	0.153	0.000	0.640
Average $0.489$ $0.149$ $0.000$ $0.638$ Std. Dev. $0.003$ $0.007$ $0.000$ $0.003$ F1018.54.5-1 $0.042$ $0.495$ $0.163$ $0.699$ $0.043$ $0.459$ $0.184$ $0.685$ Average $0.001$ $0.025$ $0.015$ $0.010$ F849.112-1 $0.879$ $0.753$ $0.024$ $1.656$ $0.865$ $0.788$ $0.031$ $1.684$ Average $0.872$ $0.770$ $0.028$ $1.670$ Std. Dev. $0.010$ $0.025$ $0.005$ $0.020$ F849.225-1 $0.156$ $1.335$ $0.321$ $1.813$ Average $0.145$ $1.284$ $0.311$ $1.740$ Std. Dev. $0.016$ $0.072$ $0.015$ $0.102$		0.400	0.4.40		0.000
Std. Dev. $0.003$ $0.007$ $0.000$ $0.003$ F1018.54.5-1 $0.042$ $0.495$ $0.163$ $0.699$ $0.043$ $0.459$ $0.184$ $0.685$ Average $0.043$ $0.477$ $0.173$ $0.692$ Std. Dev. $0.001$ $0.025$ $0.015$ $0.010$ F849.112-1 $0.879$ $0.753$ $0.024$ $1.656$ $0.865$ $0.788$ $0.031$ $1.684$ Average $0.872$ $0.770$ $0.028$ $1.670$ Std. Dev. $0.010$ $0.025$ $0.005$ $0.020$ F849.225-1 $0.156$ $1.335$ $0.321$ $1.813$ Average $0.145$ $1.284$ $0.311$ $1.740$ Std. Dev. $0.016$ $0.072$ $0.015$ $0.102$	Average	0.489	0.149	0.000	0.638
F1018.54.5-1 $0.042$ $0.043$ $0.495$ $0.459$ $0.163$ $0.184$ $0.699$ $0.685$ Average Std. Dev. $0.043$ $0.001$ $0.477$ $0.025$ $0.173$ $0.015$ $0.692$ $0.010$ F849.112-1 $0.879$ $0.865$ $0.753$ $0.788$ $0.024$ $0.031$ $1.656$ $1.684$ Average Std. Dev. $0.872$ $0.010$ $0.770$ $0.025$ $0.028$ $0.005$ $1.670$ $0.020$ F849.225-1 $0.156$ $0.134$ $1.335$ $1.234$ $0.321$ $0.301$ $1.813$ $1.668$ Average Std. Dev. $0.145$ $0.016$ $1.284$ $0.072$ $0.311$ $0.015$ $1.740$ $0.102$	Std. Dev.	0.003	0.007	0.000	0.003
F1018.54.5-1 $0.042$ $0.495$ $0.163$ $0.699$ $0.043$ $0.459$ $0.184$ $0.685$ Average $0.043$ $0.477$ $0.173$ $0.692$ Std. Dev. $0.001$ $0.025$ $0.015$ $0.010$ F849.112-1 $0.879$ $0.753$ $0.024$ $1.656$ $0.865$ $0.788$ $0.031$ $1.684$ Average $0.872$ $0.770$ $0.028$ $1.670$ Std. Dev. $0.010$ $0.025$ $0.005$ $0.020$ F849.225-1 $0.156$ $1.335$ $0.321$ $1.813$ $0.134$ $1.234$ $0.301$ $1.668$ Average $0.145$ $1.284$ $0.311$ $1.740$ Std. Dev. $0.016$ $0.072$ $0.015$ $0.102$		0.040	0.405	0.169	0.000
Average $0.043$ $0.459$ $0.184$ $0.685$ Average $0.043$ $0.477$ $0.173$ $0.692$ Std. Dev. $0.001$ $0.025$ $0.015$ $0.010$ F849.112-1 $0.879$ $0.753$ $0.024$ $1.656$ $0.865$ $0.788$ $0.031$ $1.684$ Average $0.872$ $0.770$ $0.028$ $1.670$ Std. Dev. $0.010$ $0.025$ $0.005$ $0.020$ F849.225-1 $0.156$ $1.335$ $0.321$ $1.813$ $0.134$ $1.234$ $0.301$ $1.668$ Average $0.145$ $1.284$ $0.311$ $1.740$ Std. Dev. $0.016$ $0.072$ $0.015$ $0.102$	F1018.54.5-1	0.042	0.495	0.163	0.699
Average Std. Dev. $0.043$ $0.001$ $0.477$ $0.025$ $0.173$ $0.015$ $0.692$ $0.010$ F849.112-1 $0.879$ $0.865$ $0.753$ $0.788$ $0.024$ $0.031$ $1.656$ $1.684$ Average Std. Dev. $0.872$ $0.010$ $0.770$ $0.025$ $0.028$ $0.005$ $1.670$ $0.020$ F849.225-1 $0.156$ $0.134$ $1.335$ $1.234$ $0.321$ $0.301$ $1.813$ $1.668$ Average Std. Dev. $0.145$ $0.016$ $1.284$ $0.072$ $0.311$ $0.015$ $1.740$ $0.102$		0.043	0.459	0.184	0.685
Average $0.043$ $0.477$ $0.173$ $0.092$ Std. Dev. $0.001$ $0.025$ $0.015$ $0.010$ F849.112-1 $0.879$ $0.753$ $0.024$ $1.656$ $0.865$ $0.788$ $0.031$ $1.684$ Average $0.872$ $0.770$ $0.028$ $1.670$ Std. Dev. $0.010$ $0.025$ $0.005$ $0.020$ F849.225-1 $0.156$ $1.335$ $0.321$ $1.813$ $0.134$ $1.234$ $0.301$ $1.668$ Average $0.145$ $1.284$ $0.311$ $1.740$ Std. Dev. $0.016$ $0.072$ $0.015$ $0.102$	A	0.049	0.477	0 179	0 609
Std. Dev. $0.001$ $0.023$ $0.013$ $0.010$ F849.112-1 $0.879$ $0.865$ $0.753$ $0.788$ $0.024$ $0.031$ $1.656$ $1.684$ Average Std. Dev. $0.872$ $0.010$ $0.770$ $0.025$ $0.028$ $0.005$ $1.670$ $0.020$ F849.225-1 $0.156$ $0.134$ $1.335$ $1.234$ $0.321$ $0.301$ $1.813$ $1.668$ Average Std. Dev. $0.145$ $0.016$ $1.284$ $0.072$ $0.311$ $0.155$ $0.102$	Average	0.043	0.477	0.173	0.692
F849.112-1 $0.879$ $0.865$ $0.753$ $0.788$ $0.024$ $0.031$ $1.656$ $1.684$ Average Std. Dev. $0.872$ $0.010$ $0.770$ $0.025$ $0.028$ $0.005$ $1.670$ $0.020$ F849.225-1 $0.156$ $0.134$ $1.335$ $1.234$ $0.321$ $0.301$ $1.813$ $1.668$ Average Std. Dev. $0.145$ $0.016$ $1.284$ $0.072$ $0.311$ $0.015$ $1.740$ $0.102$	Std. Dev.	0.001	0.025	0.015	0.010
1349.112-1 $0.379$ $0.733$ $0.024$ $1.030$ $0.865$ $0.788$ $0.031$ $1.684$ Average $0.872$ $0.770$ $0.028$ $1.670$ Std. Dev. $0.010$ $0.025$ $0.005$ $0.020$ F849.225-1 $0.156$ $1.335$ $0.321$ $1.813$ $0.134$ $1.234$ $0.301$ $1.668$ Average $0.145$ $1.284$ $0.311$ $1.740$ Std. Dev. $0.016$ $0.072$ $0.015$ $0.102$	F840 119 1	0.870	0.753	0.094	1 656
Average       0.872       0.770       0.028       1.670         Std. Dev.       0.010       0.025       0.005       0.020         F849.225-1       0.156       1.335       0.321       1.813         0.134       1.234       0.301       1.668         Average       0.145       1.284       0.311       1.740         Std. Dev.       0.016       0.072       0.015       0.102	1'049.112-1	0.879	0.753 0.788	0.024 0.021	1.050
Average Std. Dev. $0.872$ $0.010$ $0.770$ $0.025$ $0.028$ $0.005$ $1.670$ $0.020$ F849.225-1 $0.156$ $0.134$ $1.335$ $1.234$ $0.321$ $0.301$ $1.813$ 		0.005	0.700	0.031	1.004
Average       0.145       1.284       0.311       1.740         Std. Dev.       0.010       0.025       0.005       0.020	Average	0.872	0.770	0.028	1 670
F849.225-1     0.156     1.335     0.321     1.813       Average     0.145     1.284     0.311     1.740       Std. Dev.     0.016     0.072     0.015     0.102	Std Dev	0.012	0.110	0.028	0.020
F849.225-1       0.156       1.335       0.321       1.813         0.134       1.234       0.301       1.668         Average       0.145       1.284       0.311       1.740         Std. Dev.       0.016       0.072       0.015       0.102	Did. Dev.	0.010	0.020	0.000	0.020
Average       0.145       1.284       0.301       1.668         Average       0.145       1.284       0.311       1.740         Std. Dev.       0.016       0.072       0.015       0.102	F849.225-1	0.156	1 335	0.321	1 813
Average0.1451.2840.3111.740Std. Dev.0.0160.0720.0150.102	1010.2201	0.134	1.330	0.301	1.668
Average0.1451.2840.3111.740Std. Dev.0.0160.0720.0150.102		0.101	1.201	0.001	1.000
Std. Dev. 0.016 0.072 0.015 0.102	Average	0.145	1.284	0.311	1.740
	Std. Dev.	0.016	0.072	0.015	0.102

 ${\bf Tab. \ 3.5} \ {\rm Results} \ {\rm of} \ {\rm sequential} \ {\rm extraction} \ {\rm of} \ {\rm Harvard} \ {\rm Replicates} \ {\rm at} \ {\rm McGill} \ {\rm University}. \ {\rm Diluted} \ {\rm solutions} \ {\rm were} \ {\rm analyzed} \ {\rm on} \ {\rm a} \ {\rm Specrophotometer}.$ 

determined on dil	ted solutio	ns on the AAS,	the OES, a	nd the Sp	ectrophoton	neter (Sp.).	ndme sam	a was				DIDM CT
	AAS				OES				Sp.			
	Acetate	Dithionite	Oxalate	Total	Acetate	Dithionite	Oxalate	Total	Acetate	Dithionite	Oxalate	$\operatorname{Total}$
G306.150	1.454	1.207	0.042	2.702	1.419	1.207	0.045	2.670	1.456	1.222	0.039	2.716
	1.447	1.264	0.044	2.755	1.363	1.264	0.048	2.675	1.401	1.284	0.042	2.728
	1.422	1.239	0.046	2.707	1.394	1.239	0.047	2.680	1.423	1.243	0.040	2.706
	1.469	1.234	0.026	2.728	1.389	1.234	0.046	2.669	1.444	1.245	0.039	2.728
	1.334	1.380	0.046	2.760	1.252	1.380	0.047	2.679	1.297	1.385	0.054	2.735
	1.763	0.946	0.042	2.751	1.747	0.946	0.043	2.736	1.613	0.951	0.037	2.602
	1.210	1.010	0.040	2.260	1.645	1.010	0.044	2.699	1.669	1.026	0.038	2.734
	1.711	0.946	0.033	2.691	1.697	0.946	0.044	2.687	1.679	0.953	0.039	2.671
	1.538	1.184	0.037	2.759	1.442	1.184	0.047	2.673	1.505	1.205	0.040	2.750
	1.340	1.344	0.044	2.729	1.247	1.344	0.050	2.641	1.292	1.358	0.044	2.695
		1 7 7				(     						
Average	1.469	1.175	0.040	2.684	1.460	1.175	0.046	2.681	1.478	1.187	0.041	2.706
Std. Dev.	0.168	0.156	0.006	0.151	0.177	0.156	0.002	0.024	0.139	0.157	0.005	0.043
Std err. mean	0.056	0.052	0.002	0.050	0.059	0.052	0.001	0.008	0.046	0.052	0.002	0.014
				0110	100					0000		
G100.83.0	020.0	0.082	0.003	0.110	0.011	0.082	0.000	0.099	0.008	0.008	0.000	0.077
	0.024	0.083	0.004	0.110	0.010	0.083	0.006	0.099	0.008	0.068	0.000	0.076
	0.024	0.082	0.005	0.110	0.011	0.082	0.006	0.099	0.009	0.068	0.000	0.077
	0.026	0.083	0.003	0.113	0.011	0.083	0.006	0.101	0.009	0.067	0.000	0.077
	0.023	0.081	0.000	0.104	0.012	0.081	0.006	0.099	0.016	0.067	0.000	0.083
	0.023	0.081	0.002	0.106	0.009	0.081	0.006	0.097	0.009	0.070	0.000	0.078
	0.026	0.088	0.003	0.116	0.010	0.088	0.006	0.104	0.009	0.069	0.000	0.078
	0.026	0.101	0.003	0.130	0.011	0.101	0.006	0.118	0.008	0.066	0.000	0.074
	0.031	0.100	0.004	0.135	0.011	0.100	0.006	0.117	0.012	0.068	0.000	0.080
	0.019	0.086	0.004	0.109	0.011	0.086	0.006	0.103	0.009	0.067	0.000	0.076
Average	0.025	0.087	0.003	0.114	0.011	0.087	0.006	0.103	0.010	0.068	0.000	0.077

0 0
.114 1.047 0.39
1.120  1.046  0.3
.114  1.046  0.5
1.105 1.004 0.3
.114  1.006  0.
0.099 1.042 0.
.115 1.054 0.
1.108 1.028 0.
0.105  1.042  0.3
.117 1.017 0.5
.111 1.033 0.5
0.07 0.018 0.0
.002 0.006 0.0
.144 0.738 0.5
0.142  0.704  0.3
0.135  0.714  0.135
0.153  0.720  0.153
0.151 0.738 0.3
0.145  0.740  0.33
0.115  0.703  0.6
0.163  0.753  0.53
0.166  0.752  0.3
.175 0.758 0.3
.149  0.732  0.3
0.017 0.020 0.0
0.006 0.007 0.0

0.176	0.181	0.178	0.182	0.178	0.177	0.177	0.179	0.180	0.170	0.178	0.003	0.001
0.004	0.004	0.004	0.005	0.004	0.005	0.003	0.005	0.006	0.003	0.004	0.001	0.000
0.125	0.128	0.127	0.130	0.126	0.126	0.125	0.126	0.125	0.122	0.126	0.002	0.001
0.047	0.049	0.047	0.047	0.049	0.045	0.049	0.047	0.049	0.046	0.048	0.001	0.000
0.210	0.214	0.203	0.211	0.209	0.206	0.206	0.206	0.210	0.208	0.208	0.003	0.001
0.011	0.012	0.011	0.012	0.012	0.012	0.011	0.012	0.012	0.012	0.012	0.000	0.000
0.150	0.150	0.144	0.152	0.147	0.148	0.144	0.147	0.150	0.149	0.148	0.003	0.001
0.049	0.051	0.048	0.047	0.050	0.046	0.050	0.048	0.049	0.048	0.049	0.001	0.000
0.246	0.248	0.237	0.249	0.240	0.245	0.243	0.244	0.249	0.248	0.245	0.004	0.001
0.013	0.009	0.013	0.014	0.009	0.010	0.009	0.012	0.009	0.009	0.011	0.002	0.001
0.150	0.150	0.144	0.152	0.147	0.148	0.144	0.147	0.150	0.149	0.148	0.003	0.001
0.083	0.088	0.081	0.083	0.084	0.087	0.090	0.086	0.090	0.090	0.086	0.003	0.001
G14										Average	Std. Dev.	Std err. mean

	FePy (wt.%)		FePy (wt.%)
P1405.45.1	0.063	MB1401.96.7	0.911
	0.068		0.955
	0.066		0.894
	0.063		0.989
	0.065		0.919
	0.066		0.840
	0.064		0.691
	0.068		0.852
	0.067		0.779
	0.064		1.005
Average	0.065		0.883
Std. Dev.	0.002		0.097
Std. error of mean	0.001		0.032

 ${\bf Tab. \ 3.7 \ Results \ of \ replicate \ CRS \ extraction.}$ 

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### Preface to Chapter 4

In Chapter 3 we used iron speciation and redox-sensitive trace metal concentrations to evaluate oceanic redox conditions during deposition of the ca. 835 Ma to 630 Ma continental shelf succession in Svalbard. By combining our results with results from other studies, we concluded that the ca. 717 Ma Sturtian glaciation was not associated with a significant increase in atmospheric oxygen concentration. Therefore, oxygen levels must have already been high enough to support the simple body plans of early Metazoa (0.5–4% present atmospheric levels; Mills et al., 2014). In contrast, an increase in oxygen levels likely occurred in the aftermath of the ca. 635 Ma Marinoan glaciation. However, a longstanding challenge in the study of Proterozoic redox conditions is the difficulty in quantifying atmospheric oxygen levels. Consequently, the geochemical tools that we applied in Chapter 3, while providing important qualitative constraints on Neoproterozoic redox conditions, only permitted inferential conclusions about the evolution of atmospheric and seawater oxygen levels spanning the Cryogenian glaciations.

The emergence of larger, diverse, and ecologically important animals like carnivores that appeared in the Ediacaran, require higher atmospheric oxygen levels than the simple animals that likely inhibited early and middle Neoproterozoic oceans. Sperling et al. (2013, 2015) estimated that ca. 2–7% present atmospheric levels of oxygen are required to accommodate the macrofaunal organisms and ecosystems that appeared in the Ediacaran Period (635–541 Ma). This range is similar to the estimate of 5% present atmospheric levels that is required to induce an evolutionary radiation of sulfide-oxidizing bacteria (Canfield and Teske, 1996). Through the oxidation of sulfide, these bacteria produce intermediate sulfur compounds like S<sup>0</sup>, SO<sub>3</sub><sup>2-</sup>, and S<sub>2</sub>O<sub>3</sub>, which can be disproportionated to sulfate and sulfide by other bacteria, creating a re-oxidative sulfur cycle. Canfield and Teske (1996) estimated that 18% present atmospheric levels of oxygen is required for a re-oxidative sulfur cycle to operate on a global scale.

The metabolisms of sulfate-reduction and sulfur-disproportionation fractionate sulfur isotopes differently. In particular, these metabolisms produce small, but unique, differences in the mass-dependent fractionation of the minor isotope <sup>33</sup>S (Farquhar et al., 2003; Johnston et al., 2005a,b, 2007; Pellerin et al., 2015). By analyzing the multiple sulfur isotope composition of geological samples, it is possible to identify the effects of disproportionation.

To test the prediction of onset of a re-oxidative sulfur cycle — and thus quantify atmospheric oxygen levels — in the Neoproterozoic, we measured the multiple sulfur isotope composition of pyrites in the same samples that were analyzed for iron speciation and trace elements in Chapter 3. To identify the isotope effect associated with disproportionation, we present a model for the sulfur isotope composition and evolution of pyrites forming in diagenetic environments. The assumption that pyrites in our sample set formed in the sediments (and not in the water column) is based on the paleoredox constraints we present in Chapter 3. To support and test conclusions drawn from the sulfur isotope composition of samples from Svalbard, we also analyzed samples from Australia, the United States, and northwestern Canada. Furthermore, we also consider available literature data from Russia and Canada.

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## 4 Bacterial sulfur disproportionation constrains timing of Neoproterozoic oxygenation<sup>1</sup>

## Abstract

Large and diverse animals, including carnivores, first appeared in the Ediacaran (635–541 Ma). As body size and metabolic rate have a strong control on oxygen demand, their emergence is often linked to increasing atmospheric oxygen levels, broadly consistent with geochemical records from this time indicating oxygenation of Earth's surface environments. Seawater sulfate levels rose at this time too, which has been hypothesized to reflect increased sulfide oxidation in marine sediments caused by sediment mixing of the newly evolved macrofauna. However, the exact timing and degree of oxygenation are not yet understood and recent evidence suggests that physical mixing of sediments did not become important until the late Silurian. Here we report isotopic evidence for onset of globally significant bacterial sulfur disproportionation and re-oxidative sulfur cycling after the 635 Ma Marinoan glaciation. Widespread sulfide oxidation helps to explain the observed first-order increase in seawater sulfate concentrations from the earliest Ediacaran to the Precambrian-Cambrian boundary by reducing the amount of sulfur buried as pyrite. Applying existing estimates of required oxygen levels for re-oxidative sulfur cycling may indicate that  $pO_2$  did not exceed 5% present atmospheric levels (PAL) before the Ediacaran but likely exceeded 18% PAL in the aftermath of the Marinoan glaciation. Thus, our data provide evidence that atmospheric oxygen levels surpassed the critical threshold ( $\sim 2-7\%$ PAL) necessary for the emergence of diverse and ecologically important animals for the first time in Earth's history in the early Ediacaran.

<sup>&</sup>lt;sup>1</sup>This chapter is under review in Geology as: "Kunzmann, M., Bui, T. H., Crockford, P. W., Halverson, G.P., Scott, C., Lyons, T. W., Wing, B. A., Bacterial sulfur disproportionation constrains timing of Neoproterozoic oxygenation."

## 4.1 Introduction

Oxygen demand for the large and active animals that appeared in the Ediacaran Period (635–541 Ma) must have been greater than that of simple animals that existed before them (Sperling et al., 2013). This shift in metabolic demands suggests that Ediacaran atmospheric oxygen levels were higher than those in the preceding Proterozoic. Oxygen levels in the late Paleoproterozoic to early Neoproterozoic are poorly constrained, with recent estimates ranging from <0.1% to >4% PAL (Planavsky et al., 2014; Zhang et al., 2016). Various lines of evidence indicate an increase in  $pO_2$  after the 635 Ma Marinoan glaciation (e.g., Canfield et al., 2007; Sahoo et al., 2012), but geochemical records from different basins are often contradictory (e.g., Kunzmann et al., 2015). Furthermore, it is notoriously difficult to quantify atmospheric oxygen levels and to relate them quantitatively to marine oxygenation (Sperling et al., 2015).

Marine sulfur cycling is closely linked to atmospheric oxygen levels. Oxidative weathering of crustal sulfides provides sulfate to the ocean, whereas the redox state of the ocean controls the burial efficiency of sedimentary sulfides. The burial of sedimentary sulfides, in turn, represents a net source of atmospheric O<sub>2</sub>. In modern marine sediments, the H<sub>2</sub>S produced by microbial sulfate reduction (MSR) is mostly oxidized to intermediate sulfur species like S<sup>0</sup>, SO<sub>3</sub><sup>2-</sup>, and S<sub>2</sub>O<sub>3</sub><sup>2-</sup> by reaction with O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, Fe(III) and Mn(IV) compounds (Elsgaard and Jørgensen, 1992), often mediated by chemolithotrophic sulfide-oxidizing bacteria (Aller and Rude, 1988; Canfield and Teske, 1996). Bacterial sulfur disproportionation (BSD) subsequently ferments the intermediate sulfur species directly to H<sub>2</sub>S and SO<sub>4</sub><sup>2-</sup> (Jørgensen, 1990; Thamdrup et al., 1993). This step completes the re-oxidative sulfur cycle, defined as the progression from sulfate reduction to sulfide oxidation and finally to disproportionation of intermediate sulfur compounds. Because re-oxidative sulfur cycling involves the oxidation of sulfide, it has a minimum oxygen requirement. Thus, evidence for expansion of BSD is tantamount to evidence for increasing pO2.

The demand for oxygen (or any other electron acceptor) in marine sediments is controlled by the organic carbon oxidation rate, with consumption balanced by diffusion from the water column. Based on a compilation of organic carbon oxidation rates and assuming that non-photosynthetic sulfide-oxidizing bacteria produce the intermediate compounds for disproportionation, Canfield and Teske (1996) estimated that 5% PAL is required to initiate local re-oxidative sulfur cycling and  $pO_2$  greater than 18% PAL is needed for a globally significant re-oxidative sulfur cycle. These estimates are within the broad range (0.5–40% PAL) postulated for the late Neoproterozoic (Sperling et al., 2015), suggesting that the Ediacaran may record the global onset of the re-oxidative branch of Earth's surface sulfur cycle.

Bacterial sulfur disproportionation produces a negative sulfur isotope fractionation of -6 to -8‰ (Canfield et al., 1998) such that repeated cycles of sulfide oxidation and disproportionation may produce sedimentary sulfides that are isotopically lighter than those produced by MSR alone. However, recent results from natural environments, pure cultures, and modeling suggest that MSR can cause maximum sulfur isotope fractionations between sulfide and sulfate of up to ~ -70% (Canfield et al., 2010; Sim et al., 2011; Wing and Halevy, 2014). Since the sulfur isotope composition of pyrite in the geological record is typically less than 70% lighter than coeval seawater sulfate, it is difficult to identify BSD in ancient environments and thus a fingerprint of re-oxidative sulfur cycling based on  $\delta^{34}$ S values alone. However, MSR and BSD can be distinguished by measuring  ${}^{33}S$  in addition to  ${}^{32}S$  and  ${}^{34}S$  because each metabolism produces a distinctive  $\delta^{33}$ S and  $\delta^{34}$ S relationship (Farquhar et al., 2003; Johnston et al., 2005a; Pellerin et al., 2015). Comparative physiological studies have shown that BSD can produce  ${}^{33}S-{}^{32}S$ fractionations between sulfate and sulfide that are slightly greater than those for MSR, when normalized to the same degree of <sup>34</sup>S-<sup>32</sup>S fractionation (Johnston et al., 2005a). Small <sup>33</sup>S enrichments in Mesoproterozoic carbonate-associated sulfate have been interpreted as a signal of active BSD as a result (Johnston et al., 2005b). However, the large fractionations of <sup>34</sup>S, <sup>33</sup>S, and  $^{32}$ S during MSR at low cell-specific sulfate reduction rates can mimic the effects of BSD in the sulfate reservoir (Sim et al., 2011), necessitating an alternative approach to identify the imprint of BSD in ancient sedimentary rocks. Here we focus on stratigraphic variation in the isotopic composition of Neoproterozoic pyrites viewed through a steady-state isotope model that allows us to investigate how intrinsic microbial fractionations are translated into pyrite S isotopes.

We measured  $\delta^{34}$ S and  $\Delta^{33}$ S in sedimentary pyrites within organic-rich shale intervals deposited at storm-wave base from a ca. 835–630 Ma old Neoproterozoic sedimentary succession in Svalbard (Fig. 4.1a;  $\Delta^{33}$ S =  $\delta^{33}$ S – 1000 × [(1+( $\delta^{34}$ S/1000))<sup>33 $\lambda$ -ref-1]; <sup>33</sup> $\lambda$ -ref is equal to 0.515 and approximates low-temperature equilibrium mass-dependent fractionation). Our data are further bolstered by new data from the post-Marinoan of Australia and Canada, the ca. 1460 Ma</sup> Belt Supergroup of the USA and published data from Palaeo- and Mesoproterozoic sedimentary pyrites from Russia and Canada (Fig. 4.1d).

## 4.2 Results and discussion

Measured  $\delta^{34}$ S and  $\Delta^{33}$ S values in pyrite from the Neoproterozoic succession in Svalbard span large ranges, from -33.0 to +40.0% and -0.175 to +0.232%, respectively (Fig. 4.1a). Samples older than the 635 Ma old Marinoan glaciation generally show a trend of decreasing  $\Delta^{33}$ S with increasing  $\delta^{34}$ S, which is characteristic of fractionations dominated by MSR (Farquhar et al., 2003). In contrast, samples from the post-Marinoan Dracoisen Formation, deposited between 635 and 630 Ma, show a trend of increasing  $\Delta^{33}$ S with increasing  $\delta^{34}$ S (Fig. 4.1a). This is a stratigraphic upsection trend with remarkable little scatter (Fig. 4.4).

We use a steady-state, isotope mass-balance model to distinguish the isotopic influences of MSR and BSD on the sulfur isotope compositions of pyrites (Supplementary Information). In our first model runs, we set  ${}^{33}\lambda_{net}$  to 0.513 and  ${}^{34}\alpha_{net}$  to 0.95; these net fractionation factors for pyrite production are both reasonable values for a population of sulfate reducing microbes (Johnston et al., 2005a). With these fractionations, our model reproduces more than 90% of pre-Marinoan Neoproterozoic pyrite data when the sulfate in the overlying seawater varies between -0.1 and -0.2‰ for  $\Delta^{33}$ S and 10 to 40‰ for  $\delta^{34}$ S (Fig. 4.1b). Such  $\delta^{34}$ S variation is consistent with the strong fluctuations that have been inferred for the Neoproterozoic seawater sulfate reservoir (Halverson and Shields-Zhou, 2011). The variation in  $\Delta^{33}$ S in our model is consistent with the negative  $\Delta^{33}$ S values that have been estimated for early Proterozoic seawater sulfate (Johnston et al., 2008; Scott et al., 2014). Thus, we conclude that re-oxidative sulfur cycling was at most a local phenomenon before the Marinoan glaciation.

Even with a large variation in seawater sulfate isotope values, however, the model cannot reproduce the trend of steeply increasing  $\Delta^{33}$ S values with increasing  $\delta^{34}$ S values in sedimentary pyrites from the post-Marinoan Dracoisen Formation (Fig. 4.7). This trend can only be reproduced by increasing  $^{33}\lambda_{net}$  to 0.516 (Fig. 4.1c). A  $^{33}\lambda_{net}$  value of this magnitude is well above the limit for MSR (Farquhar et al., 2003; Johnston et al., 2005a; Sim et al., 2011) and requires significant disproportionation of intermediate sulfur compounds in concert with relatively intense microbial sulfate reduction (Pellerin et al., 2015). Therefore, our results suggest significant re-oxidative sulfur cycling in the aftermath of the ca. 635 Ma Marinoan glaciation.

In order to test the hypothesis that a globally significant re-oxidative S cycle did not operate before the earliest Ediacaran, we compiled  $\delta^{34}$ S and  $\Delta^{33}$ S data from early Proterozoic pyrites in shales deposited under oxic or anoxic-ferruginous conditions (i.e., the same redox environments as our Svalbard samples; Fig. 4.5). Together with our new measurements from the ca. 1460 Ma Belt Supergroup (USA), this compilation demonstrates that sulfur isotopes in Paleo- and Mesoproterozoic pyrites do not require BSD (Fig. 4.1d).

To test the potential global nature of Ediacaran re-oxidative sulfur cycling, we measured pyrite sulfur isotopes from post-Marinoan shales of the lower part of the early Ediacaran Sheepbed Formation (<635 Ma) in NW Canada and from the latest Cryogenian-earliest Ediacaran upper Black River Dolomite in Tasmania (640.7 $\pm$ 5.7 Ma; Kendall et al., 2009; Rooney et al., 2014). These data fall in the field of disproportionation (Fig. 4.1d). Thus, it seems that the significant re-oxidative sulfur cycling seen in the early Ediacaran of Svalbard was global in nature, starting immediately after the Marinoan glacial interval and lasting for at least the duration over which our samples were deposited (~5 Myr). Sedimentary rocks from the ca. 580 Ma Buah Formation in Oman are independently interpreted to reflect BSD (Wu et al., 2015), indicating that re-oxidative S cycling remained an important part of the Ediacaran sulfur cycle. However, this does not preclude transient fluctuations in oxygen levels or a mostly anoxic Ediacaran deep ocean (Sperling et al., 2015; Sahoo et al., 2016).

Sulfate levels in the immediate aftermath of the Marinoan glaciation may have been as low as  $<300 \ \mu\text{M}$  (Crockford et al., 2016) and perhaps rose to near modern levels (>17 mM; Horita et al., 2002) at the Precambrian-Cambrian boundary. An Ediacaran onset for global re-oxidative sulfur cycling in shelf sediments would help to explain this first-order increase in seawater sulfate levels. Although Ediacaran onset of bioturbation has been proposed as a driver for this rise (Canfield and Farquhar, 2009), sedimentary fabrics indicate that animals did not begin to thoroughly mix sediments until the late Silurian (Tarhan et al., 2015). Enhanced microbial sulfide oxidation followed by BSD at or near the sediment-seawater interface (Canfield and Teske, 1996), however, will inevitably increase seawater sulfate levels by reducing the amount of sulfur buried as pyrite. Relative oxidative sulfur fluxes as inferred from the Svalbard samples (>80% of all sulfide produced)

by MSR oxidized; Supplementary Information) can sustain marine sulfate concentrations that are at least 5 and perhaps 100 times greater than they would be without re-oxidative S cycling (Supplementary Information), providing a plausible mechanism for elevated seawater sulfate in the absence of bioturbation. The first-order increase of the Ediacaran sulfate reservoir may have ultimately ushered in a Phanerozoic-style sulfur cycle.

The emergence of a global re-oxidative sulfur cycle in the aftermath of the Marinoan glaciation indicates an increase in  $pO_2$ . Constraining this oxygenation is not straightforward. However, insofar as the estimate provided by Canfield and Teske (1996) is correct, our data suggest that pre-Ediacaran  $pO_2$  did not exceed 5% PAL (Fig. 4.2), the minimum required to sustain re-oxidative sulfur cycling in a local patch of coastal sediments. In contrast, oxygen levels in the aftermath of the Marinoan glaciation may have exceeded 18% PAL (Fig. 4.2), the estimated  $O_2$  requirement for ~50% of coastal sediments to be oxygenated (Canfield and Teske, 1996). Although revised estimates will likely differ in detail, they are unlikely to differ significantly in magnitude. Thus, our results imply that oxygen levels passed the critical ecological threshold for macrofaunal communities, including diverse carnivores (~2–7% PAL; Sperling et al., 2015), for the first time in Earth's history in the earliest Ediacaran.

## Acknowledgments

We thank Itay Halevy, Ulrich Wortmann, and André Pellerin for discussions. GPH acknowledges funding by NSF and the American Chemical Society. Funding was provided to BAW by NSERC and FQRNT. TWL acknowledges funding by the NASA Astrobiology Institute and the NSF ELT Program.

## **Figures**



Fig. 4.1 Measured, modeled and compiled  $\delta^{34}S$  and  $\Delta^{33}S$  data. a, Measured Neoproterozoic  $\delta^{34}S$  and  $\Delta^{33}S$  data. b, With exception of the Dracoisen Formation and few samples from the Russøya Member and Svanbergfjellet Formation, all samples fall in the field modeled for pore water pyrites formed by MSR only. Each individual curve represents the modeled isotopic composition of pyrites formed from a sulfate reservoir with a composition at the right end of this curve. With on-going sulfate consumption, pyrites will evolve along curves from left to right. c, Increasing  $^{33}\lambda_{net}$  to 0.516, a value requiring disproportionation, can reproduce all other data. d, Compilation of literature data and additional analysis. Published data from Scott et al. (2014) (Zaonega) and Johnston et al. (2006) (Animikie). The reproducibility (1 $\sigma$ ) of analyses (replicate samples) is estimated to be better than 0.1% for  $\delta^{34}S$  and 0.015% for  $\Delta^{33}S$ .



Fig. 4.2 Model for atmospheric oxygen concentrations in the Neoproterozoic and early Paleozoic modified from Sperling et al. (2015). (1) A lack of isotopic evidence for significant re-oxidative sulfur cycling before the Marinoan glacial interval suggests that oxygen levels were likely less than 5% PAL (Canfield and Teske, 1996). (2) A globally significant re-oxidative sulfur cycle after the Marinoan glacial interval requires oxygen levels to have exceeded 18% PAL (Canfield and Teske, 1996) a concentration higher than estimates for the ecological threshold ( $\sim$ 2–7% PAL Sperling et al., 2015) of macrofaunal communities. See Sperling et al. (2015) for Phanerozoic oxygen constraints.

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## 4.3 Supplementary Information

#### 4.3.1 Geological setting

#### Svalbard

The Neoproterozoic succession in Svalbard represents one of the most complete sedimentary records of the middle to late Neoproterozoic and spans the ~717–662 Ma Sturtian and ~635 Ma Marinoan glaciations. Whereas the Veteranen Group at the base of the succession records an initial rift phase of basin development, the overlying Akademikerbreen and Polarisbreen groups were deposited on a stable continental shelf (Maloof et al., 2006). All sampled shales represent comparable depositional environments and were deposited at or just below storm wave base. Most samples come from the mixed siliciclastic-carbonate Polarisbreen Group because the Veteranen and Akademikerbreen groups are dominated by coarse siliciclastic and carbonate rocks, respectively. Cryogenian non-glacial samples were also sampled in East Greenland, where the Cryogenian interglacial Arena Formation represents the lateral equivalent of the MacDonaldryggen Member in Svalbard. Both units were deposited in a single and continuous basin (Fairchild and Hambrey, 1995).

#### Belt Supergroup

The Belt Supergroup of the northwestern United States and Canada was likely deposited in a restricted marine setting (Lyons et al., 2000). The age of the lower part of the succession has been constrained to be between 1470 and 1440 Ma (Anderson and Davis, 1995; Aleinikoff et al., 1996; Sears et al., 1998; Luepke and Lyons, 2001). Samples included in this study come from the Newland Formation, a unit in the lower part of the Belt Supergroup. The samples come from the Helena Embayment, the easternmost extension of the Belt Supergroup where no evidence for metamorphism is observable (Harrison, 1972; Schieber, 1989). The samples studied here were previously described in Lyons et al. (2000). They are microlaminated, organic-rich black shales that are interbedded with cm-scale, muddy turbidites, and represent deep-water deposition. More detailed information on the Belt Supergroup can be found in Winston (1986, 1990) and Winston and Link (1993).

#### Black Canyon River Dolomite, Australia

We analyzed three organic-rich shale samples from the Julius River Member of the Black River Dolomite in Tasmania. All samples are from drill core Forest 1. The Julius River Member represents a diamictite succession with an intercalated carbonate unit within the Black River Dolomite. Re-Os dating of black shales overlying the diamictite succession provides an age of  $640\pm4.7$  Ma for the upper Black River Dolomite (Kendall et al., 2009). The Black River Dolomite is overlain by the Croles Hill diamictite, which was previously correlated with Marinoan glacials in King Island (Cottons breccia) and South Australia (Elatina Formation), suggesting that the Julius River diamictite is Sturtian in age (Kendall et al., 2009). However, a recent U-Pb age of  $636.41\pm0.45$  Ma for the Cottons Breccia in Tasmania indicates its Marinoan age (Calver et al., 2013). This suggests that the Re-Os age from the Black River Dolomite correlates with the global 635 Ma Marinoan glaciation (Rooney et al., 2014). As our samples are interbedded with the diamictite, we suggest that they were deposited during the early stages of deglaciation from the Marinoan glaciation.

#### Sheepbed Formation, NW Canada

Ediacaran strata in NW Canada are exposed in the Ogilvie Mountains, the Wernecke Mountains, and the Mackenzie Mountains. The succession has traditionally been envisioned to have been deposited along an open, continental margin that developed in response to rifting of Rodinia about 780 to 700 Ma ago (e.g., Eisbacher, 1981; Jefferson and Parrish, 1989). However, recent studies suggest a more complex tectonostratigraphic evolution based on major facies changes (Aitken and Narbonne, 1989; Narbonne and Aitken, 1995), large overlapping unconformities (MacNaughton et al., 2000), and late Ediacaran syn-rift volcanics in the southeastern Canadian Cordillera (Colpron et al., 2002). The Sheepbed samples studied here come from a ca. 450-m-thick section (section M106 in Macdonald et al., 2013) at NE Profeit, Wernecke Mountains. Here, the Sheepbed Formation conformably overlies the post-Marinoan Raventhroat cap dolostone (Macdonald et al., 2013). The Sheepbed Formation comprises hundreds of meters of fissile black shale. Samples included in this study come from the lower ~100 m of the unit and are estimated to have been deposited between 635 and 630 Ma. Siltstone and carbonate beds are missing from the sampled interval and no evidence for deposition at or above storm wave base is present. A more detailed description of the Sheepbed Formation and the Ediacaran succession in NW Canada can be found in Macdonald et al. (2013).

#### A global signal of bacterial sulfur disproportionation

In order to evaluate the global importance of bacterial sulfur disproportionation, we measured the sulfur isotopic composition of post-Marinoan samples from three different basins. The basins are spread across Rodinia (Fig. 4.3). All three sample sets show evidence of bacterial disproportionation of intermediate sulfur compounds.

#### 4.3.2 Sulfur isotope analyses

Reduced inorganic sulfur in crushed shale samples was extracted by chromium reduction (Canfield et al., 1986). Depending on sulfur content, 0.2-15 g of sample powder was weighed into reaction vessels that were subsequently flushed with N<sub>2</sub>. 15 ml of 6 M HCl was added to the reaction vessel, followed by 15 ml of 1 M chromic chloride solution prepared with 0.5 M HCl. The reaction vessels were heated to near-boiling and the reaction was performed for 2 h. Pyrite-sulfur, elemental sulfur, and acid-volatile monosulfides (AVS) are reduced to H<sub>2</sub>S. Regular tests by adding only 6 M HCl assured that AVS did not occur in our samples (as common in ancient shales; Sperling et al., 2013). The N<sub>2</sub> carries the H<sub>2</sub>S through a water trap (to remove acid contaminants) and finally through a zinc acetate solution (4% w/w). H<sub>2</sub>S was quantitatively precipitated as ZnS. 1 ml 0.1 M AgNO<sub>3</sub> was added to the zinc acetate solution to convert the ZnS to Ag<sub>2</sub>S. This reaction was carried out overnight in the dark. The Ag<sub>2</sub>S was separated from solution by filtration on a 0.45 µm cellulose filter, attached to a 15 ml chimney, washed with one volume equivalent MQ-H<sub>2</sub>O. The Ag<sub>2</sub>S was dried overnight at 80°C.

About 3 mg of Ag<sub>2</sub>S were reacted in a nickel vessel overnight at about 250°C in the presence of excess F<sub>2</sub>. The SF<sub>6</sub> generated was first purified by cryo-separation at -120°C. A second purification step was carried out by passing the SF<sub>6</sub> through two gas chromatography columns ( $\sim 2 \text{ m}$  Haysep Q and  $\sim 2 \text{ m}$  Molsieve 5A) with ultrapure He as carrier gas at a rate of 20 ml/min. The SF<sub>6</sub> peak was isolated from contaminants and the carrier gas by trapping it on a cold finger at -192°C.

The isotopic composition was measured on a ThermoFinniganMAT 253 dual-inlet gas-source isotope-ratio-mass-spectrometer. Sulfur isotope ratios were determined by measuring the ion beam intensities of  ${}^{32}\text{SF}_5^+$ ,  ${}^{33}\text{SF}_5^+$ ,  ${}^{34}\text{SF}_5^+$ , and  ${}^{36}\text{SF}_5^+$  at mass to charge ratios (m/z) of 127, 128, 129, and 131.

All results are reported using delta notation relative to the Vienna-Cañon Diablo Troilite (V-CDT) international reference scale. On V-CDT scale, the  $\delta^{34}$ S and  $\Delta^{33}$ S values of the Ag<sub>2</sub>S reference material, IAEA-S-1, are defined as -0.3‰ and 0.094‰, respectively (Ding et al., 2001). The reproducibility (1 $\sigma$ ) of analyses (replicate samples) is estimated to be better than 0.1‰ and 0.015‰ for  $\delta^{34}$ S and  $\Delta^{33}$ S, respectively.

Results from the Neoproterozoic succession in Svalbard are shown in Tab. 4.1. Results from the Belt Supergroup (USA), the Black River Dolomite (Tasmania), Sheepbed Formation (Canada), and literature data from the Zaonega Formation (Russia) and Animikie Group (Canada) are shown in Tab. 4.2.

#### 4.3.3 Chemostratigraphy of the Neoproterozoic succession in Svalbard

Total organic carbon (TOC) and S concentration throughout the succession reach 3.3 wt.% (average 0.6 wt.%) and 2.0 wt.% (average 0.4 wt.%), respectively (Fig. 4.4).  $\delta^{34}$ S values show a gradual increase from -25.7‰ in the uppermost Veteranen Group to 40.0‰ in the post-Sturtian Arena Formation (Fig. 4.4). Following this maximum,  $\delta^{34}$ S values gradually decrease to -17.6‰ just below the Marinoan Wilsonbreen diamictite. The post-Marinoan  $\delta^{34}$ S record shows an overall increase from -26.9 to 22.3‰ with second-order variability.  $\Delta^{33}$ S values show some scatter in the pre-Sturtian units, without a systematic relationship to  $\delta^{34}$ S values (Fig. 4.4), and reach their most negative value of -0.175‰ in the post-Sturtian Arena Formation. Importantly,  $\Delta^{33}$ S values gradually increase during the Cryogenian period, mirroring  $\delta^{34}$ S, which is characteristic of fractionations dominated by microbial sulfate reduction (MSR) (Farquhar et al., 2003). In contrast, an upsection trend to a maximum  $\Delta^{33}$ S value of 0.232‰ parallels increasing  $\delta^{34}$ S values in the post-Marinoan Dracoisen Formation with remarkably little scatter (Figs. 4.4, 4.1a). Following the maximum,  $\Delta^{33}$ S values gradually decrease at the top of the section.

#### 4.3.4 Redox conditions during deposition of samples

All analyzed samples were deposited in oxic to anoxic-ferruginous environments. Therefore, we assume that pyrite formation predominately took place in pore waters with excess iron. We compiled published data from samples that were also deposited under oxic to anoxic-ferruginous conditions. Iron speciation, redox-sensitive trace metal concentration or, if available, both types of data were used to constrain redox conditions during deposition. Redox data are listed in Tab. 4.3 and iron speciation data are also presented in Fig. 4.5. We do not show redox data from samples of the Animikie Group (Johnston et al., 2006) because all samples are iron formation (IF), suggesting that pyrites were formed in pore waters with excess iron.

#### 4.3.5 Sulfur isotope model

All analyzed and compiled multiple sulfur isotope data are from samples deposited in non-euxinic environments (Fig. 4.5, Tab. 4.3). Therefore, we assume that pyrites were predominantly formed in pore waters in the presence of excess iron. Thus, we assume rapid and irreversible pyrite formation, and, if present, rapid bacterial sulfur disproportionation (BSD). We model the isotopic composition of pyrites based on a model for sulfate concentration in pore waters (Berner, 1964). This model assumes steady state conditions and that the initial concentration of sulfate in pore waters at a specific depth mostly reflects the sum of three processes: diffusion, deposition plus compaction, and microbial sulfate reduction (MSR) (Berner, 1964):

$$SO4_z = (SO4_0 - SO4_\infty)exp\left[-\frac{k}{\omega}\right] + SO4_\infty$$
(4.1)

where

 $SO4_z$ =concentration of sulfate at any given depth

 $SO4_0$ =initial sulfate concentration

 $SO4_{\infty}$ =concentration of sulfate at infinitive depth, i.e. sulfate left after MSR

k=sulfate reduction rate constant

 $\omega$ =rate of sediment deposition

Because  $SO4_z$  (total) =  ${}^{32}SO4_z + {}^{33}SO4_z + {}^{34}SO4_z + {}^{36}SO4_z$ , equation (4.1) can be re-written for the isotope of interest, ignoring  ${}^{36}S$  due to its low abundance of only 0.02% (Rosman and Taylor, 1998), and the isotopic composition of sulfate at any given depth is

$$\delta^{3i} \mathbf{S}_{SO4} = \left[ \frac{\left(\frac{3^{i} \mathbf{SO4}}{3^{2} \mathbf{SO4}}\right)}{\left(\frac{3^{i} \mathbf{S}}{3^{2} \mathbf{S}}\right)} - 1 \right] \cdot 1000 \tag{4.2}$$

here i equals 3, or 4.

# The sulfur isotope composition of pore water sulfate and the sulfur isotope fractionation factor

The  $\delta^{3i}$ S of pore water sulfate is a function of  $\delta^{3i}$ S composition of seawater at the seafloor, sulfate reduction rate constant (k), sedimentation rate ( $\omega$ ) and S isotope fractionation factor ( $\alpha$ ) produced by sulfate reducing bacteria. This fractionation factor is defined as the ratio of sulfate reduction rate (SRR) of less abundant isotopes (<sup>33</sup>S or <sup>34</sup>S) over the abundant isotope <sup>32</sup>S normalized with corresponding isotope concentration

$${}^{3i}\alpha = \frac{\left(\frac{3i_{SRR}}{3i_{S}}\right)}{\left(\frac{32_{SRR}}{32_{S}}\right)}.$$
(4.3)

The  $\Delta^{33}$ S of pore water sulfate is calculated based on  $\delta^{33}$ S,  $\delta^{34}$ S and the slope  $\lambda$  of the terrestrial mass fractionation line

$$\Delta^{33} S_{SO4} = \delta^{33} S_{SO4} - 1000 \cdot \left[ \left( 1 + \frac{\delta^{34} S_{SO4}}{1000} \right)^{\lambda} - 1 \right].$$
(4.4)

#### The sulfur isotopic composition of pore water sulfide and pyrite

The S isotopic composition of instantaneous  $H_2S$  produced by sulfate reducing bacteria is calculated using ratios of sulfate reduction rates at corresponding depth

$$\delta^{3i} \mathbf{H}_2 S = \left[ \frac{\left(\frac{3i_{\mathrm{SRR}}}{32_{\mathrm{SRR}}}\right)}{\left(\frac{3i_{\mathrm{S}}}{32_{\mathrm{S}}}\right)} - 1 \right] \cdot 1000.$$

$$(4.5)$$

Pyrites preserve the isotope signature of accumulated H<sub>2</sub>S, which varies from instantaneous

H<sub>2</sub>S composition to seawater sulfate composition (when all sulfate is reduced to sulfide).

#### Model parameters, model runs, results

We can account for the isotopic consequences of a re-oxidative sulfur cycle, i.e. bacterial disproportionation of intermediate sulfur compounds. A contribution of a re-oxidative sulfur cycle to the final composition of pyrite would result in  ${}^{33}\lambda_{net}$  (representing the combined effects of MSR and BSD) values >0.5145 (Farquhar et al., 2003; Johnston et al., 2005; Sim et al., 2011a). Tab. 4.4 summarizes the used parameters in our numerical model and Fig. 4.6 shows a graphical representation of the model.

In our first model runs, we only used the  $\delta^{34}$ S and  $\Delta^{33}$ S composition of the starting sulfate as free parameters (Tab. 4.4). We varied the  $\delta^{34}$ S composition between 10 and 40%, consistent with strong fluctuations inferred for seawater sulfate in the Neoproterozoic (e.g. Halverson and Shields-Zhou, 2011). We varied the  $\Delta^{33}$ S composition from -0.2 to 0.1%, comparable to previous constraints from studies of Proterozoic rocks (e.g. Johnston et al., 2008; Scott et al., 2014; Luo et al., 2015; Wu et al., 2015). We fix  $k/\omega$  to 0.1/cm, comparable to Berner (1964) and Pellerin et al. (2015),  ${}^{34}\alpha_{net}$  to 0.95, and  ${}^{33}\lambda_{net}$  to 0.513. Using these parameters, our model can reproduce >90% (45 out of 49) of our pre-Marinoan pyrite sulfur isotope data from Svalbard. However, it cannot re-produce the sulfur isotope trend of steeply increasing  $\Delta^{33}$ S values with decreasing  $\delta^{34}$ S values in the post-Marinoan data set. Even by setting the starting composition to positive  $\delta^{34}$ S and  $\Delta^{33}$ S, a possible composition for the post-Marinoan seawater sulfate reservoir (Crockford et al., 2016), the model cannot re-produce the post-Marinoan sulfur isotope data set (Fig. 4.7).

In our second model run, we additionally changed  ${}^{33}\lambda_{net}$  (Tab. 4.4). With a  ${}^{33}\lambda_{net}$  of 0.516, our model can reproduce most data points of the post-Marinoan pyrite sulfur isotope trend by setting  $\delta^{34}$ S to ~20‰, while leaving  $\Delta^{33}$ S at ~0.05‰ (Fig. 4.1c).

#### 4.3.6 Estimating sulfide re-oxidation rate

We estimate the mininum sulfide oxidation rate with a recent model of re-oxidative sulfur cycling in sediments of Mangrove Lake, Bermuda (Fig. ?? Pellerin et al., 2015). A graphical application of this model suggest a minimum sulfide re-oxidation of 80% (Fig. 4.8). The model presented in Fig. 4.8 also quantifies the proportion of the reaction solely caused by MSR ( $^{34}\varepsilon_{msr}$ ) to ca. 38‰, a value consistent with the most recent culture experiments (Leavitt et al., 2013).

#### 4.3.7 Rising Ediacaran seawater sulfate levels

We estimate the magnitude of rising Ediacaran seawater sulfate levels with a simple model developed by Canfield and Farquhar (2009). The model assumes steady state, i.e. that the flux of sulfur into the ocean equals the flux out:

$$Flux_{\rm in} = Flux_{\rm out}$$
 (4.6)

Sulfur leaves the ocean either as evaporite deposits (sulfate) or as pyrite (sulfide). Pyrite burial depends on the production of sulfide through microbial sulfate reduction (MSR) and the proportion of this sulfide that becomes buried in the geological record, described by the factor x. This means:

$$Flux_{\rm out} = xMSR + evap \tag{4.7}$$

where *evap* stands for the sulfur removed as evaporite deposits. MSR rate depends on the availability of reactive organic matter as electron donor and the concentration of sulfate. This gives:

$$MSR = aOC[SO_4]^y \tag{4.8}$$

where OC represents reactive organic carbon, a is a constant of proportionality, and y is an exponential factor. Equation 6–8 can be combined and as result a simple equation for seawater sulfate is generated:

$$[SO_4] = \left[\frac{[flux_{\rm in} - evap]}{axOC}\right]^{1/y}$$
(4.9)

Canfield and Farquhar (Canfield and Farquhar, 2009) argue that the availability of reactive organic carbon unlikely changed much over the Precambrian, thus they ignore OC in equation 9. If the flux of sulfur into the ocean does not change, and the formation of evaporites is ignored, sulfate levels are controlled by the factors x and y. Considering the onset of a re-oxidative sulfur

cycle at one point in time, the equation can be modified to:

$$\frac{[SO_4]_{\rm i}}{[SO_4]_{\rm j}} = \left(\frac{x_{\rm j}}{x_{\rm i}}\right)^{1/y} \tag{4.10}$$

where subscripts *i* and *j* denote *after* and *before* onset of a re-oxidative sulfur cycle, respectively. The size of the seawater sulfate reservoir, as well as the flux into the ocean, do not significantly change the magnitude of the increase in seawater sulfate concentration, they only change the response time to the onset of re-oxidative sulfur cycling (Canfield and Farquhar, 2009). Canfield and Farquhar (2009) point out that a reduction of *x*, i.e. lowering the proportion of sulfide buried, will inevitable lead to higher seawater sulfate levels. We assume a value of  $x_j$  of 1 before re-oxidative sulfur cycling, i.e. all sulfide produced by MSR is buried as pyrite. Although it is difficult to constrain Neoproterozoic values for *x*, Canfield and Farquhar (2009) suggest a value around 0.2, based on their model. Therefore, we use this value for  $x_i$ . Varying the exponential factor *y* between 1 and 0.3 suggests an increase in seawater sulfate concentration by a factor of 5 and ~200.

#### Figures and tables



**Fig. 4.3** A palaeogeographic reconstruction at ca. 635 Ma showing the location of measured post-Marinoan samples. A, Amazonia; Ae, Avalonia (east); Aw, Avalonia (west); B, Baltica; C, Congo; EA, East Antarctica; ES, East Svalbard; G, Greenland; I, India; K, Kalahari; L, Laurentia; NA, Northern Australia, NC, Northern China; S, Sahara; SA, South Australia; SC, South China; Sf, Sao Francisco; Si, Siberia; T, Tarim; WA, West Africa. Modified from Li et al. (2013).



**Fig. 4.4** Chemostratigraphy of the Neoproterozoic succession in Svalbard. Analytical error for sulfur isotope data is smaller than symbols. V, Veteranen Group; O, Oxfordbreen Formation; Svanberg., Svanbergfjellet Formation; B, Backlundtoppen Formation; Slan., Slangen Member.



Fig. 4.5 Iron speciation data from samples analyzed in this study and compiled data (Planavsky et al., 2011; Scott et al., 2014; Kunzmann et al., 2015). Samples with an FeHR/FeT ratio between 0.18 and 0.38 were either deposited in anoxic or oxic environments. Mass balance requirements dictate that not all anoxic samples can be enriched in highly reactive iron. Enrichments can also be muted by rapid sedimenation(Poulton and Canfield, 2011).


Fig. 4.6 Conceptual model of our pore water sulfur isotope model. The four boxes correspond to the sulfate, hydrogen sulfide, intermediate sulfur compound, and pyrite pools. Black arrows represent sulfur fluxes. The grey arrow indicates the net fractionation factor  $({}^{34}\alpha_{net})$  that includes the combined fractionations during MSR and BSD.



Fig. 4.7 The model fails to re-produce the post-Marinoan sulfur isotope data set when the starting composition of sulfate is set to positive  $\delta^{34}$ S and  $\Delta^{33}$ S values, and  $^{33}\lambda_{net}$  is 0.513, i.e. to low for disproportionation.



Fig. 4.8 Model for the re-oxidative sulfur cycle including disproportionation of sulfite (a) and elemental sulfur (b) (Pellerin et al., 2015). The grey field represents isotopic fractionations by pure cultures of sulfate reducers (Johnston et al., 2005; Sim et al., 2011a,b; Leavitt et al., 2013). Arrows indicate the direction of increasing fractionation by microbial sulfate reduction  ${}^{34}\varepsilon_{msr}$  and fraction of sulfide re-oxidation ( $\phi_{reox}$ ). The x-axis shows the net fractionation ( ${}^{34}\varepsilon_{net}$ ), including sulfate reduction and sulfur disproportionation. The bold lines of the grid indicate the fractionation associated with microbial sulfate reduction alone, where the fraction of re-oxidation is zero. The other set of lines traces the flux of sulfide that is re-oxidized. We identify the fraction of re-oxidized sulfide by moving the grid to maximum  ${}^{33}\lambda_{net}$  values observed for microbial sulfate reduction. The model indicates sulfide re-oxidation of >80%.

**Tab. 4.1** Total carbon (TC), total inorganic carbon (TIC), total organic carbon (TOC), S (all element data from ref. (Kunzmann et al., 2015)), and sulfur isotope data from Neoproterozoic shales in Svalbard. To avoid rounding errors, we report carbon data with two digits.

Section	Height	Unit	IC	TIC	TOC	S	$\delta^{33}S$	$\delta^{34}S$	$\delta^{36}S$	$\Delta^{33}S$	$\Delta^{36}\mathrm{S}$
	)		wt. $\%$	wt.%	wt. $\%$	wt. $\%$	$\%_0$	$\%_0$	$\%_0$	$\%_0$	$\%_0$
G306	159.0	Dracoisen	3.30	0.00	3.30	1.2	11.50	22.31	41.92	0.070	-0.892
G306	150.0	Dracoisen					3.17	6.17	11.73	-0.001	-0.037
G306a	143.0	Dracoisen	5.14	4.11	1.03	1.4	1.83	3.23	5.05	0.174	-1.091
G306	131.0	Dracoisen	1.23	0.00	1.23	1.1	2.36	4.14	7.54	0.232	-0.349
G436	138.0	Dracoisen	2.67	2.49	0.18	$<\!0.1$	-16.01	-30.95	-57.59	0.049	0.400
G436	120.0	Dracoisen	0.59	0.46	0.13	$<\!0.1$	-4.71	-9.56	-18.87	0.219	-0.786
G436	105.0	Dracoisen	1.28	0.76	0.52	1.2	-1.96	-4.10	-7.95	0.157	-0.163
G436	101.5	Dracoisen	0.88	0.27	0.61	0.6	-2.47	-5.16	-10.98	0.189	-1.188
G436	95.5	Dracoisen	0.74	0.48	0.27	0.3	1.61	2.80	3.98	0.170	-1.343
G436	88.0	Dracoisen	0.28	0.11	0.17	$<\!0.1$	2.41	4.33	6.97	0.180	-1.272
G436	64.0	Dracoisen	1.25	0.40	0.84	0.9	-10.78	-21.05	-40.55	0.119	-0.932
G436	42.0	Dracoisen	1.89	1.62	0.27	0.1	-17.04	-33.01	-61.53	0.099	0.262
G436	10.5	Dracoisen	0.95	0.39	0.56	1.1	-2.19	-4.56	-8.55	0.156	0.091
G411	72.0	Dracoisen	1.74	1.64	0.10	0.1	-0.01	-0.22	-1.16	0.103	-0.752
G411	67.0	$\operatorname{Dracoisen}$	0.18	0.04	0.14	0.0					
G411	45.0	Dracoisen	4.73	4.56	0.17	0.1	-7.83	-15.26	-29.16	0.057	-0.360
G411	41.0	Dracoisen	5.63	5.48	0.14	0.4	-13.65	-26.43	-49.83	0.049	-0.213
G411	37.0	Dracoisen	2.40	2.11	0.30	$<\!0.1$	-13.88	-26.91	-51.22	0.068	-0.708
G419	2.6	Macdonald.	5.56	4.92	0.64	0.7	5.15	9.97	19.04	0.026	0.020
G419	6.7	Macdonald.	4.19	3.64	0.55	1.0	-1.91	-3.83	-6.80	0.059	0.455
G419	12.3	Macdonald.	2.95	2.25	0.71	0.9	4.11	8.00	15.07	-0.003	-0.195
G435	18.0	Macdonald.	1.28	1.06	0.22	0.1	-9.03	-17.55	-33.36	0.050	-0.274
G435	25.0	Macdonald.	2.47	2.23	0.24	0.3	-4.48	-8.71	-16.06	0.017	0.422
G435	35.0	Macdonald.	2.11	1.31	0.80	0.8	6.27	12.20	23.01	0.003	-0.306
G435	45.0	Macdonald.	1.69	0.86	0.83	0.9	12.74	24.92	48.10	-0.015	0.223
G435	56.0	Macdonald.	1.64	1.05	0.59	0.9	15.49	30.32	58.38	-0.016	-0.013
G435	66.0	Macdonald.	1.49	0.60	0.89	1.1	11.00	21.52	41.10	-0.024	-0.188
G435a	76.0	Macdonald.	2.37	1.69	0.68	1.3	13.71	26.84	51.57	-0.027	-0.047

Bacterial sulfur disproportionation constrains timing of Neoproterozoic oxygenation

G435	79.5	Macdonald.	2.34	1.82	0.52	0.9	17.46	34.22	65.88	-0.018	-0.133
G407	278.0	Macdonald.	1.75	1.56	0.19	0.0	2.16	4.20	7.69	0.000	-0.310
G407	261.0	Macdonald.	2.49	2.29	0.20	0.0	5.34	10.59	20.45	-0.100	0.227
G407	245.0	Macdonald.	2.78	2.55	0.23	$<\!0.1$	7.29	14.28	27.77	-0.041	0.472
G407	233.0	Macdonald.	2.92	2.68	0.24	0.0	6.25	12.38	24.11	-0.109	0.444
GR12	78.0	$\operatorname{Arena}$			0.28	0.1					
GR12	71.0	$\operatorname{Arena}$	0.66	0.47	0.20	1.0	17.26	33.95	65.88	-0.082	0.394
GR12	64.5	$\operatorname{Arena}$	0.36	0.13	0.22	1.0	20.24	40.00	79.01	-0.163	1.646
GR12	15.9	Arena	0.22	0.00	0.22	1.0	15.07	29.63	57.14	-0.084	0.091
GR12	10.5	Arena	0.59	0.35	0.24	1.3	18.34	36.14	70.74	-0.112	0.963
GR12	8.5	Arena	0.73	0.35	0.38	2.0	17.95	35.49	69.13	-0.175	0.619
GR12	3.3	Arena	0.78	0.00	0.78	0.6	17.41	34.30	66.56	-0.109	0.390
G519	в	${ m Russ} { m \emptysetya}$	0.29	0.00	0.29	0.0					
G519	р	${ m Russ} { m \emptysetya}$	1.11	0.79	0.31	$<\!0.1$	3.66	7.16	13.33	-0.020	-0.313
G406	42.0	${ m Russ} { m \emptysetya}$	1.42	0.00	1.42	0.2	-0.72	-1.45	-2.93	0.022	-0.177
G406	35.0	${ m Russ} { m \emptysetya}$	1.75	0.06	1.69	0.2	0.15	0.21	-0.12	0.039	-0.514
G406	0.0	${ m Russ} { m \emptysetya}$					16.77	32.94	63.49	-0.061	-0.017
G521	46.0	${ m Russ} { m \emptysetya}$	0.31	0.00	0.31	$<\!0.1$	-4.10	-8.01	-15.34	0.027	-0.186
G521	44.4	${ m Russ} { m \emptysetya}$	0.59	0.00	0.59	0.1	-4.74	-9.38	-18.27	0.096	-0.532
G521	40.5	${ m Russ} { m \emptysetya}$	0.29	0.00	0.29	$<\!0.1$	-7.31	-14.19	-25.88	0.029	0.914
G521	36.0	${ m Russ} { m \emptysetya}$	0.60	0.00	0.60	0.9	11.41	22.29	42.41	-0.006	-0.367
G521	33.0	${ m Russ} { m \emptysetya}$	0.52	0.00	0.52	$<\!0.1$	2.83	5.55	11.15	-0.023	0.591
G521	30.0	${ m Russ} { m \emptysetya}$	0.59	0.00	0.59	$<\!0.1$	15.12	29.35	56.47	0.107	-0.038
G521	26.4	${ m Russ} { m \emptysetya}$	0.38	0.00	0.38	0.1	7.03	13.56	25.48	0.071	-0.432
G521	23.4	${ m Russ} { m \emptysetya}$	0.77	0.05	0.71	$<\!0.1$	12.20	23.72	45.31	0.052	-0.243
G521	19.6	${ m Russ} { m \emptysetya}$	0.92	0.00	0.92	0.1	5.22	10.11	20.66	0.025	1.367
G521	18.9	${ m Russ} { m \emptysetya}$	1.44	0.00	1.44	0.1	3.97	7.63	13.97	0.053	-0.568
G521	13.2	${ m Russ} { m \emptysetya}$	1.78	0.01	1.77	0.2					
G521	6.2	${ m Russ} { m \emptysetya}$	1.06	0.00	1.06	0.0					
G521	3.7	${ m Russ} { m \emptysetya}$	0.80	0.00	0.80	0.0					
P5014	52.0	${ m Russ} { m \emptysetya}$					-3.61	-6.96	-12.93	-0.015	0.256
P5014	43.5	${ m Russ} { m \emptysetya}$					-0.70	-1.45	-2.26	0.042	0.489
P5014	30.5	${ m Russ}$ øya					6.92	13.60	25.99	-0.067	-0.019

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Sample	Unit	Lithology	Age	$\delta^{33}S$	$\delta^{34}S$	$\delta^{36}S$	$\Delta^{33}S$	$\Delta^{36}\mathrm{S}$	Reference
				$\%_{00}$	$\%_{00}$	$\%_{00}$	$\%_{00}$	$\%_{00}$	
C-5190-16	Upper Zaonega U1	shale	2.1-2.0  Ga		17.42		-0.05		Scott et al. $(2014)$
C-5190-83	Upper Zaonega U1	$\operatorname{shale}$	2.1-2.0  Ga		15.41		-0.02		Scott et al. $(2014)$
C-5190-86.9	Upper Zaonega U1	$\operatorname{shale}$	2.1-2.0  Ga		13.26		-0.04		Scott et al. $(2014)$
C-5190-92.5	Upper Zaonega U1	$\operatorname{shale}$	2.1-2.0  Ga		15.87		-0.03		Scott et al. $(2014)$
C-5190-96	Upper Zaonega U1	$\operatorname{shale}$	2.1-2.0  Ga		15.19		-0.03		Scott et al. $(2014)$
C-5190-100	Upper Zaonega U1	$\operatorname{shale}$	2.1-2.0 Ga		15.92		-0.02		Scott et al. $(2014)$
C-5190-136.5	Upper Zaonega U1	$\operatorname{shale}$	2.1-2.0  Ga		14.87		-0.05		Scott et al. $(2014)$
C-5190-146.6	Upper Zaonega U1	$\mathbf{shale}$	2.1-2.0  Ga		13.86		0.00		Scott et al. $(2014)$
C-5190-156	Upper Zaonega U1	$\mathbf{shale}$	2.1-2.0  Ga		5.72		0.00		Scott et al. $(2014)$
C-5190-184	Upper Zaonega U1	$\operatorname{shale}$	2.1-2.0  Ga		16.42		-0.05		Scott et al. $(2014)$
C-5190-199	Upper Zaonega U1	$\operatorname{shale}$	2.1-2.0  Ga		-3.93		0.01		Scott et al. $(2014)$
C-5190-230	Upper Zaonega U2	$\operatorname{shale}$	2.1-2.0 Ga		-18.13		0.03		Scott et al. $(2014)$
C-5190-234.5	Upper Zaonega U2	$\operatorname{shale}$	2.1-2.0 Ga		-19.10		0.04		Scott et al. $(2014)$
C-5190-238.5	Upper Zaonega U2	$\operatorname{shale}$	2.1-2.0 Ga		-19.11		0.07		Scott et al. $(2014)$
C-5190-245	Upper Zaonega U2	$\operatorname{shale}$	2.1-2.0 Ga		-17.94		0.04		Scott et al. $(2014)$
C-5190-248	Upper Zaonega U2	$\operatorname{shale}$	2.1-2.0  Ga		-15.27		0.01		Scott et al. $(2014)$
C-5190-287.5	Upper Zaonega U2	$\operatorname{shale}$	2.1-2.0 Ga		-18.18		0.01		Scott et al. $(2014)$
C-5190-292.5	Upper Zaonega U2	$\operatorname{shale}$	2.1-2.0 Ga		-19.15		0.02		Scott et al. $(2014)$
C-5190-293.2	Upper Zaonega U2	$\operatorname{shale}$	2.1-2.0 Ga		-19.19		0.03		Scott et al. $(2014)$
C-5190-295.6	Upper Zaonega U2	$\operatorname{shale}$	2.1-2.0 Ga		-19.45		0.03		Scott et al. $(2014)$
C-175-36.9	Upper Zaonega U2	$\operatorname{shale}$	2.1-2.0 Ga		22.19		-0.05		Scott et al. $(2014)$
T19	Gunflint	BIF	1.87 Ga		10.20		-0.034	0.51	Johnston et al. $(2006)$
m R2	Gunflint	BIF	1.87 Ga		10.22		-0.009	0.57	Johnston et al. $(2006)$
T13	Gunflint	BIF	1.87 Ga		13.33		-0.046	0.76	Johnston et al. $(2006)$
S22	Gunflint	BIF	1.87 Ga		-0.50		-0.028	0.45	Johnston et al. $(2006)$
S21	Gunflint	BIF	1.87 Ga		-0.43		-0.003	0.26	Johnston et al. $(2006)$
$\mathbf{S1}$	Gunflint	BIF	$1.87 \mathrm{Ga}$		4.07		-0.008	0.32	Johnston et al. $(2006)$

**Tab. 4.2** Multiple sulfur isotope data from non-euxinic samples from the Zaonega Formation (Russia; Scott et al. (2014)), Newland Formation of the Belt Supergroup (USA; new data), the Animicki Group (Gunflint, Biwabik,Trommald, Mahnomen) in Canada (Johnston et al., 2006), the Julius River Member (Black River Dolomite) in Tasmania (new data), and the Sheenbed Formation (Canada: new data)

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B44	Biwabik	BIF	1.87 Ga		6.97		-0.032	0.19	Johnston et al.
B26	Biwabik	BIF	1.87  Ga		9.83		-0.056	0.44	Johnston et al.
B3	Biwabik	BIF	1.87  Ga		3.26		0.003	0.27	Johnston et al.
M13	Trommald	BIF	1.87  Ga		12.24		-0.051	0.49	Johnston et al.
M16	Trommald	$\operatorname{BIF}$	1.87  Ga		15.53		-0.073	0.70	Johnston et al.
M24	Trommald	BIF	1.87  Ga		7.73		-0.048	0.54	Johnston et al.
M25	Trommald	BIF	1.87  Ga		8.05		-0.027	0.73	Johnston et al.
M27	Trommald	BIF	1.87  Ga		8.65		-0.051	0.70	Johnston et al.
M30	Mahnomen	BIF/Chert	1.87  Ga		9.71		-0.062	0.51	Johnston et al.
M31	Mahnomen	BIF/Chert	1.87  Ga		9.59		-0.052	1.03	Johnston et al.
M37	Mahnomen	BIF/Chert	1.87  Ga		13.58		-0.051	0.76	Johnston et al.
M-16-204.8	Newland	$\operatorname{shale}$	1.47  Ga	1.07	1.96	3.13	0.056	-0.603	this study
M-16-204.85	Newland	$\operatorname{shale}$	1.47  Ga	1.04	1.92	3.36	0.051	-0.283	this study
M-16-232.8	Newland	$\operatorname{shale}$	1.47  Ga	2.19	4.17	7.23	0.045	-0.706	this study
M-16-285	Newland	$\operatorname{shale}$	1.47  Ga	2.85	5.55	10.05	-0.002	-0.527	this study
M-16-286.5	Newland	$\operatorname{shale}$	1.47  Ga	-0.15	-0.37	-0.99	0.040	-0.293	this study
M-16-313.6	Newland	$\operatorname{shale}$	1.47  Ga	2.68	5.13	9.40	0.047	-0.360	this study
M-16-371.5	Newland	$\operatorname{shale}$	1.47  Ga	2.72	5.22	9.52	0.037	-0.418	this study
M-16-372.5	Newland	$\operatorname{shale}$	1.47  Ga	2.79	5.32	9.71	0.048	-0.425	this study
M-16-372.55	Newland	$\operatorname{shale}$	1.47  Ga	2.83	5.41	9.84	0.050	-0.465	this study
M-16-495	Newland	$\operatorname{shale}$	1.47  Ga	1.39	2.60	4.64	0.049	-0.301	this study
M-16-495.05	Newland	$\operatorname{shale}$	1.47  Ga	1.36	2.58	4.68	0.031	-0.229	this study
M-16-495.11	Newland	$\operatorname{shale}$	1.47  Ga	1.31	2.44	4.32	0.053	-0.316	this study
M-16-494.15	Newland	$\operatorname{shale}$	1.47  Ga	1.29	2.44	4.19	0.038	-0.445	this study
SC-93-538.6	Newland	$\operatorname{shale}$	1.47  Ga	16.86	33.07	63.49	-0.041	-0.280	this study
SC-93-521.2	Newland	$\operatorname{shale}$	1.47  Ga	13.85	27.08	51.79	-0.009	-0.286	this study
SC-93-526.8	Newland	$\operatorname{shale}$	1.47  Ga	9.77	19.14	36.64	-0.044	-0.037	this study
SC-93-527	Newland	$\operatorname{shale}$	1.47  Ga	9.56	18.66	35.20	-0.010	-0.552	this study
Forest I-894.9	Julius River	$\operatorname{shale}$	$0.64 \mathrm{Ga}$	-5.69	-11.58	-23.51	0.286	-1.626	this study
Forest I-914.9	Julius River	$\operatorname{shale}$	$0.64 \mathrm{Ga}$	-11.47	-22.43	-43.06	0.145	-0.883	this study
Forest I-926.8	Julius River	$\operatorname{shale}$	$0.64 \mathrm{Ga}$	-16.27	-31.63	-59.77	0.154	-0.525	this study
M106-82.5	$\mathbf{Sheepbed}$	$\operatorname{shale}$	$0.64 \mathrm{Ga}$	-6.45	-12.69	-24.91	0.110	-0.927	this study
M106-84.5	Sheepbed	$\operatorname{shale}$	$0.64 \mathrm{Ga}$	-3.01	-6.01	-12.42	0.096	-1.019	this study

125 -1.165 this study	117 -1.210 this study	143 -1.300 this study	158 -1.452 this study	150 -1.254 this study	086 -0.904 this study	137 -1.232 this study	165 -1.494 this study
-19.94 0.	-9.44 0.	-15.28 0.	-13.39 0.	-5.00 0.	14.82 0.	4.22 0.	5.88  0.
-9.93	-4.34	-7.38	-6.30	-1.97	8.25	2.87	3.87
-5.00	-2.12	-3.67	-3.09	-0.87	4.32	1.61	2.16
$0.64~{ m Ga}$	$0.64 { m Ga}$	$0.64 { m Ga}$	$0.64 { m Ga}$	$0.64 { m Ga}$	$0.64 { m Ga}$	$0.64 { m Ga}$	$0.64 \mathrm{~Ga}$
$\operatorname{shale}$	shale						
$\mathbf{Sheepbed}$	$\mathbf{Sheepbed}$	$\mathbf{Sheepbed}$	$\mathbf{Sheepbed}$	$\mathbf{Sheepbed}$	$\mathbf{Sheepbed}$	$\mathbf{Sheepbed}$	Sheepbed
M106-90.5	M106-94.5	M106-96.5	M106-98.5	M106-110	M106-117	M106-123	M106-133

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Sample	Unit	FeHR/FeT	FePy/FeHR	Mo	D	Λ	Reference
				ppm	mqq	mqq	
G306-159	Dracoisen	0.82	0.30	17.0	6.5	170.8	Kunzmann et al. $(2015)$
G306-150.0	Dracoisen			5.8	3.6	120.1	Kunzmann et al. (2015)
G306a-143.0	Dracoisen	0.71	0.35	5.5	5.7	142.1	Kunzmann et al. (2015)
G306-131	Dracoisen	0.52	0.37	5.1	5.4	184.5	Kunzmann et al. (2015)
G436-138	Dracoisen	0.36	0.04	0.4	9.6	638.3	Kunzmann et al. (2015)
G436-120	Dracoisen	0.17	0.03	0.3	3.7	99.1	Kunzmann et al. (2015)
G436-105.0	Dracoisen	0.23	0.47	8.5	4.7	146.0	Kunzmann et al. (2015)
G436-101.5	Dracoisen	0.40	0.54	2.4	5.5	152.7	Kunzmann et al. (2015)
G436-95.5	Dracoisen	0.21	0.22	0.4	5.0	113.4	Kunzmann et al. (2015)
G436-88.0	Dracoisen	0.13	0.14	0.7	5.2	108.2	Kunzmann et al. (2015)
G436-64.0	Dracoisen	0.45	0.42	1.2	4.9	114.8	Kunzmann et al. (2015)
G436-42.0	Dracoisen	0.41	0.22	0.4	8.4	622.5	Kunzmann et al. (2015)
G436-10.5	Dracoisen	0.18	0.08	2.3	4.9	128.0	Kunzmann et al. (2015)
G411-72.0	Dracoisen	0.27	0.06	0.2	2.1	66.4	Kunzmann et al. $(2015)$
G411-67.0	Dracoisen	0.22	0.00	0.2	2.8	97.5	Kunzmann et al. (2015)
G411-45.0	Dracoisen	0.61	0.01	0.1	2.0	45.8	Kunzmann et al. (2015)
G411-42.0	Dracoisen	0.63	0.10	0.4	1.7	31.7	Kunzmann et al. (2015)
G411-37.0	Dracoisen	0.35	0.02	0.2	3.0	84.7	Kunzmann et al. (2015)
G419-2.6	Macdonald.	0.78	0.37	0.6	2.2	38.7	Kunzmann et al. (2015)
G419-6.7	Macdonald.	0.74	0.44	1.0	2.3	52.0	Kunzmann et al. (2015)
G419-12.3	Macdonald.	0.54	0.52	1.6	2.1	72.7	Kunzmann et al. (2015)
G435-18.0	Macdonald.			0.2	2.9	75.6	Kunzmann et al. $(2015)$
G435-25.0	Macdonald.	0.55	0.21	0.7	2.3	61.8	Kunzmann et al. $(2015)$
G435-35.0	Macdonald.	0.47	0.36	0.4	3.0	90.7	Kunzmann et al. (2015)
G435-45.0	Macdonald.	0.42	0.37	0.5	2.8	107.4	Kunzmann et al. (2015)
G435-56.0	Macdonald.	0.39	0.54	0.5	3.1	111.9	Kunzmann et al. (2015)
G435-66.0	Macdonald.	0.52	0.47	0.5	3.0	107.6	Kunzmann et al. (2015)

(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)	(2015)
Kunzmann et al.	Kunzmann et al.	Kunzmann et al.	Kunzmann et al.	Kunzmann et al.	Kunzmann et al.	Kunzmann et al.	Kunzmann et al.	Kunzmann et al.																								
100.2	106.8	131.5	141.0	140.9	128.3	175.7	157.5	193.5	173.3	182.9	194.3	50.9	94.8	145.7	22.6	40.4	1.5	59.5	63.4	57.9	55.1	63.4	57.1	54.1	55.5	61.0	72.4	57.9	79.8	63.3	4.4	2.7
2.6	2.6	2.1	1.9	2.0	1.7	1.7	1.5	1.8	1.9	1.9	2.0	0.5	2.2	2.0	1.1	2.0	0.6	2.9	2.4	2.4	2.4	2.0	2.2	2.8	2.4	2.1	3.9	2.3	3.5	2.5	0.6	0.7
0.5	0.4	0.1	0.2	0.1	0.2	0.2	0.2	0.8	0.2	0.4	0.8	5.1	0.3	0.2	0.4	1.0	0.1	0.4	0.5	0.2	0.5	0.3	0.7	1.1	0.4	0.4	0.2	0.9	0.4	0.5	0.1	0.2
0.46	0.44	0.02	0.01	0.02	0.01	0.13	0.38	0.33	0.39	0.53	0.65	0.17	0.00	0.02	0.11	0.07		0.01	0.01	0.01	0.28	0.01	0.00	0.00	0.00	0.01	0.03	0.00	0.00			
0.42	0.40	0.24	0.28	0.29	0.28	0.16	0.27	0.22	0.27	0.28	0.36	0.76	0.35	0.18	0.92	0.78		0.38	0.55	0.21	0.25	0.26	0.48	0.49	0.18	0.32	1.11	0.41	0.47			
Macdonald.	Macdonald.	Macdonald.	Macdonald.	Macdonald.	Macdonald.	Arena	${ m Russ}$ øya	${ m Russ} { m \&ya}$	${ m Russ} { m \&ya}$	${ m Russ}$ øya	${ m Russ} { m \&ya}$																					
G435a-76.0	G435-79.5	G407-278.0	G407-261.0	G407-245.0	G407-233.0	GR12-78.0	GR12-71.0	GR12-64.5	GR12-15.9	GR12-10.5	GR12-8.5	GR12-3.3	G519a	G519b	G406-42.0	G406-35.0	G406-0.0	G521-46.0	G521-44.4	G521-40.5	G521-36.0	G521-33.0	G521-30.0	G521-26.4	G521-23.4	G521-19.6	G521-18.9	G521-13.2	G521-6.2	G521-3.7	P5014-52.0	P5014-43.5

<sup>5014-30.5</sup>	Russøya			0.1	0.5	1.3	Kunzmann et al. $(2015)$
517	Backlund.	0.44	0.08	0.5	1.1	43.4	Kunzmann et al. (2015)
512-55.0	Svanberg.	0.66	0.02	1.6	2.5	51.5	Kunzmann et al. $(2015)$
512-40.6	Svanberg.	0.38	0.00	0.7	4.5	119.2	Kunzmann et al. (2015)
512-35.2	Svanberg.	1.05	0.05	1.7	2.5	50.7	Kunzmann et al. $(2015)$
512 - 26.2	Svanberg.			1.0	2.6	49.9	Kunzmann et al. (2015)
471-8.3	Svanberg.			0.5	3.0	131.5	Kunzmann et al. $(2015)$
471-6.1	Svanberg.	0.26	0.00	0.6	2.1	167.5	Kunzmann et al. $(2015)$
155 - 149.3	Svanberg.	0.24	0.01	0.2	1.3	150.2	Kunzmann et al. $(2015)$
155 - 149.1	Svanberg.	0.91	0.14	1.2	2.1	67.8	Kunzmann et al. (2015)
155 - 133.5	Svanberg.	0.96	0.23	0.6	0.4	9.2	Kunzmann et al. (2015)
155-83.6	Svanberg.			0.5	0.7	86.6	Kunzmann et al. (2015)
426a	Veteranen	0.13	0.01	0.2	2.6	72.9	Kunzmann et al. (2015)
426b	Veteranen	0.17	0.00	0.2	4.2	132.4	Kunzmann et al. (2015)
-5190-16	Upper Zaonega U1	0.17	0.27				Scott et al. $(2014)$
-5190-83	Upper Zaonega U1	0.70	0.51				Scott et al. $(2014)$
-5190-86.9	Upper Zaonega U1	1.02	0.57				Scott et al. $(2014)$
-5190-92.5	Upper Zaonega U1	0.51	0.13				Scott et al. $(2014)$
-5190-96	Upper Zaonega U1	0.34	0.40				Scott et al. $(2014)$
-5190-100	Upper Zaonega U1	0.43	0.46				Scott et al. $(2014)$
-5190-136.5	Upper Zaonega U1	0.22	0.07				Scott et al. $(2014)$
-5190-146.6	Upper Zaonega U1	0.38	0.54				Scott et al. $(2014)$
-5190-156	Upper Zaonega U1	0.35	0.54				Scott et al. $(2014)$
-5190-184	Upper Zaonega U1	0.24	0.41				Scott et al. $(2014)$
-5190-199	Upper Zaonega U1	0.58	0.59				Scott et al. $(2014)$
-5190-230	Upper Zaonega U2	0.48	0.37				Scott et al. $(2014)$
-5190-234.5	Upper Zaonega U2	0.25	0.33				Scott et al. $(2014)$
-5190-238.5	Upper Zaonega U2	0.12	0.08				Scott et al. $(2014)$
-5190-245	Upper Zaonega U2	0.40	0.48				Scott et al. $(2014)$
-5190-248	Upper Zaonega U2	0.13	0.18				Scott et al. $(2014)$
-5190-287.5	Upper Zaonega U2	0.19	0.44				Scott et al. $(2014)$
-5190-292.5	Upper Zaonega U2	0.29	0.44				Scott et al. $(2014)$
-5190-293.2	Upper Zaonega U2	0.66	0.55				Scott et al. $(2014)$

Scott et al. $(2014)$	Scott et al. $(2014)$	Planavsky et al. (2011)	this study	this study	this study	this study	this study	this study	this study	this study	this study	this study	this study	this study	this study								
											96	180	149										
											1.9	3.4	12.4										
											9	4	10										
0.14	0.59	0.60	0.50	0.40	0.60	0.4	0.5	0.2	0.2	0.2				0.04	0.03	0.13	0.05	0.11	0.11	0.11	0.00	0.04	0.14
0.20	1.04	0.50	0.50	0.40	0.50	0.8	0.6	0.3	0.4	0.5				0.39	0.40	0.34	0.45	0.33	0.44	0.53	0.67	0.64	0.58
Upper Zaonega U2	Upper Zaonega U2	Newland	Julius River	Julius River	Julius River	Sheepbed																	
C-5190-295.6	C-175-36.9	M-16-204.8	M-16-204.85	M-16-232.8	M-16-313.6	M-16-495	M-16-495.05	SC-93-521.2	SC-93-526.8	SC-93-527	Forest I-894.9	Forest I-914.9	Forest I-926.8	M106-82.5	M106-84.5	M106-90.5	M106-94.5	M106-96.5	M106-98.5	M106-110	M106-117	M106-123	M106-133

**Tab. 4.4** Summary of the parameters used in the model.  ${}^{33}\alpha_{net}$  represents the combined effects of MSR and potential BSD.  ${}^{33}\lambda_{net}$  was only treated as free parameter in the second model runs. In the first model runs, it was set to 0.513.

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Fixed parameters	Value	Free parameters	Value
$egin{aligned} & lpha_{net} \ & k/\omega \ & \mathrm{SO4}(0) \end{aligned}$	$0.95 \\ 0.1/{ m cm} \\ 28{ m mM}$	$\delta^{34}{ m S} \Delta^{33}{ m S} {}^{33}{ m \lambda}_{net}$	$10-40\%_0$ -0.2-0.1\%_0 0.511-0.518

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# Preface to Chapter 5

In Chapter 3 we provided a qualitative model for the evolution of atmospheric oxygen in the Neoproterozoic by reconstructing oceanic redox conditions through time. We expanded upon this narrative in Chapter 4 through the application of multiple sulfur isotope ratios and provided a quantitative estimate of oxygen concentrations. Taking these two chapters together, we infer that the water column was mostly suboxic to anoxic ferruginous in shelf environments from ca. 835 to 630 Ma (and likely continued to be anoxic in shelf environments after 630 Ma; Johnston et al., 2013). However, the post-Marinoan ocean was likely characterized by overall higher oxygen concentration and its redox structure may have even started to resemble that of the modern ocean, with a distinct oxygen minimum zone. Our sulfur isotope data indicate that this change in oceanic redox conditions was likely accompanied by an increase in atmospheric oxygen concentration from less than 5% PAL before the 635 Ma Marinoan glaciation to more than 18% PAL afterwards. In Chapter 5, we further explore Neoproterozoic oxygenation through the Fe isotope composition of marine shales. Specifically, after evaluating the importance of different processes that contribute to the Fe isotope composition of ancient sedimentary rocks, we compare the Fe isotope record to models of oxygenation proposed in Chapters 3 and 4.

Iron isotopes are now routinely applied to the ancient rock record to better understand paleoredox conditions and the evolution of atmospheric oxygen (e.g., Rouxel et al., 2005; Planavsky et al., 2012; Fan et al., 2014; Tahata et al., 2015; Zhang et al., 2015). The application of this proxy is based upon the large isotopic fractionation associated with transformations between ferrous and ferric iron (e.g., Schauble et al., 2001; Johnson et al., 2002; Anbar et al., 2005; Polyakov et al., 2007). Although the growing Fe isotope data set from ancient rocks is accompanied by careful studies of Fe isotope fractionation in modern aquatic environments (e.g., Severmann et al., 2006, 2008, 2010; Busigny et al., 2014; Scholz et al., 2014), it remains unclear and debated in the

literature whether water column processes or diagenetic iron cycling are the major control on the Fe isotope composition of sedimentary rocks. Identifying the major control on fractionation is necessary to provide a useful interpretation of the emerging secular Fe isotope trend. If the degree of oxidation of a ferrous seawater iron reservoir in the ancient ocean, which is controlled by environmental oxygen levels, is the major influence on the Fe isotope composition of sedimentary rocks, an interpretation in terms of redox conditions and oxygen levels is relatively straightforward. On the other hand, if diagenetic iron cycling and mineral transformations are more important, interpretations within the context of evolving redox conditions would be much more complicated, even though diagenetic processes are inextricably linked to water column conditions.

To evaluate the importance of water column versus diagenetic processes, we analyzed the bulk rock Fe isotope composition of 124 organic-rich marine shales from Svalbard, northwestern Canada, and Siberia that together cover the time interval from 1050 to 570 Ma. We combine our results with an isotope mass-balance model for diagenetic iron cycling, as well as Fe/Al ratios and iron speciation data. In addition to assessing the controlling mechanism on Fe isotope composition, our data set is also the first step towards a more detailed bulk shale Fe isotope record for the Neoproterozoic, which provides valuable qualitative information about the evolution of oceanic redox conditions and atmospheric oxygen concentrations.

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# 5 | Iron isotope biogeochemistry of Neoproterozoic marine shales<sup>1</sup>

# Abstract

Iron isotopes are widely applied to investigate the redox evolution of Earth's surface environments. However, it is still unclear whether iron cycling in the water column or during diagenesis represent the major control on the iron isotope composition of sediments and sedimentary rocks. Interpretation of isotopic data in terms of oceanic redox conditions is possible if water column processes dominate the isotopic composition, while redox interpretations are less straightforward if diagenetic iron cycling controls the isotopic composition. In the latter scenario, iron isotope data would be more informative about microbial processes such as dissimilatory iron reduction. Here, we present bulk rock iron isotope data from late Proterozoic marine shales from Svalbard, northwestern Canada, and Siberia. Bulk shales span a  $\delta^{56}$ Fe range from -0.45 to +1.04‰. Although  $\delta^{56}$ Fe values show significant variation within individual stratigraphic units, their mean value approaches that of hydrothermal iron in samples post-dating the ca. 717–660 Ma Sturtian glaciation. A correction for the highly reactive iron content in our samples based on iron speciation data suggest that the  $\delta^{56}$ Fe composition of highly reactive iron ranges from -0.84 to +7.41% but more than 90% of our data do not exceed +3%. An isotope mass-balance model indicates that diagenetic iron cycling can only change the isotopic composition of highly reactive iron by <1%, suggesting that water column processes control the isotopic composition of highly reactive iron. Therefore, we interpret our secular  $\delta^{56}$ Fe record to mostly reflect the redox evolution of Earth's surface environments.  $\delta^{56}$ Fe values significantly heavier than hydrothermal

<sup>&</sup>lt;sup>1</sup>This chapter is in preparation for Geochimica et Cosmochimica Acta as: "Kunzmann, M., Gibson, T. M., Halverson, G.P., Hodgskiss, M.S.W., Bui, T.H., Sperling, E.A., Poirier, A., Cox, G.M., Carozza, D.A., Wing, B.A., Iron isotope biogeochemistry of Neoproterozoic marine shales."

iron imply partial oxidation of a ferrous seawater reservoir. In contrast,  $\delta^{56}$ Fe values close to that of hydrothermal iron in post-Sturtian shales reflects near complete oxidation of the ferrous seawater iron reservoir, and by inference, higher environmental oxygen levels. Although consistent with recent constrains from iron isotope data from South China, this conclusion is inconsistent with models of Neoproterozoic oxygenation based on other redox proxies. This inconsistency highlights the need to better understand the sensitivity of different redox proxies to incremental changes in oxygen levels.

# 5.1 Introduction

The distribution of iron isotopes in sediments and sedimentary rocks is a powerful tool in understanding the biogeochemical cycle of Fe in the modern and ancient ocean. By far the largest fractionation of Fe isotopes is associated with redox transformation between ferrous and ferric iron (e.g., Schauble et al., 2001; Johnson et al., 2002; Welch et al., 2003; Anbar et al., 2005; Polyakov et al., 2007; Johnson et al., 2008b), and hence Fe isotope ratios have been applied to tracking the evolution of the seawater iron reservoir in response to increasing atmospheric oxygen levels throughout Earth's history (e.g., Rouxel et al., 2005; Planavsky et al., 2012; Fan et al., 2014; Tahata et al., 2015; Zhang et al., 2015). However, the interpretation of Fe isotope data from ancient sediments is not straightforward because of different isotopic compositions of iron sources to the ocean and the complex cycling of iron in the water column and during early diagenesis. Nevertheless, distinct features in the iron isotope record appear to broadly mirror the evolution of atmospheric O<sub>2</sub>. The Neoarchean to early Paleoproterozoic record shows highly variable but typically negative sedimentary pyrite isotope values ( $\sim -3.5$  to +1.2%) (Rouxel et al., 2005; Archer and Vance, 2006). Younger Proterozoic pyrites are generally less negative but span a broad range from  $\sim -2.0$  to +4.0% (Tahata et al., 2015), while Phanerozoic and modern sedimentary pyrites are also less negative but additionally span a narrower range from  $\sim -1.6$  to +1.2% (e.g., Rouxel et al., 2005; Severmann et al., 2006; Fehr et al., 2008; Severmann et al., 2008; Fehr et al., 2010). The Fe isotope record of banded iron formation and other Fe oxyhydroxide-rich rocks also shows a systematic secular trend. Archean and early Paleoproterozoic iron formation show a large variation in  $\delta^{56}$ Fe values from -2.4 to +1.8% with most samples having heavy isotope ratios (see

compilations in Planavsky et al., 2012; Busigny et al., 2014). Younger Fe oxyhydroxide-rich rocks span a narrower range from -0.9 to +1.2% with most samples falling between -0.5 and +0.5% (Planavsky et al., 2012; Busigny et al., 2014).

Two broad and contrasting approaches have been taken in interpreting the record of iron isotopes in the Precambrian. One group of workers has stressed the importance of ferrous iron oxidation across the chemocline in an anoxic Precambrian ocean as a controlling mechanism for the Fe isotopic composition of sedimentary rocks and minerals. Whereas quantitative oxidation mutes isotope fractionations and produces ferric oxyhydroxides with Fe isotope ratios comparable to the seawater ferrous iron reservoir, non-quantitative oxidation leads to a significant positive isotope effect upon precipitation of Fe-oxyhydroxides with concomitant depletion of the ferrous iron reservoir (Rouxel et al., 2005; Planavsky et al., 2012; Busigny et al., 2014; Mendes et al., in press). By extension, lower oxygen concentration in the Neoarchean and early Paleoproterozoic led to incomplete oxidation of the ferrous seawater iron inventory, producing isotopically heavy Fe-oxyhydroxides (precipitated as banded iron formation with heavy  $\delta^{56}$ Fe) and leaving behind a depleted ferrous reservoir from which pyrites formed (Rouxel et al., 2005; Planavsky et al., 2012). In contrast, higher oxygen levels later in Earth's history allowed for more complete oxidation of ferrous iron, resulting in a narrower range in iron isotope ratios and heavier pyrites. This hypothesis has been challenged because the inferred large negative seawater isotope shift requires that a significant proportion of the dissolved iron inventory precipitates as Fe-oxyhydroxides (50–90%; Yamaguchi and Ohmoto, 2006; Johnson et al., 2008a).

A second approach emphasizes the importance of diagenetic and microbial processes such that the iron isotopic composition of banded iron formation and pyrite reflects significant dissimilatory iron reduction, which produces large amounts of isotopically light iron (Johnson et al., 2008a,b; Heimann et al., 2010; Li et al., 2015). In this case, the secular trend in Fe isotopes in the Precambrian is thought to reflect the evolution of heterotrophic organisms, whereas the link to Earth's evolving redox state is ambiguous. This interpretation easily accounts for strongly negative values seen in some samples; however, while diagenetic processes can explain iron isotope partitioning among different mineral phases, shifts in the bulk rock composition require physical separation of distinct iron isotope pools. Thus, diagenetic processes alone cannot explain the large variation in Precambrian iron formation and bulk rock shale data.

A diverse set of redox proxies suggest that atmospheric oxygen levels increased in the Neoproterozoic Era (e.g., Fike et al., 2006; Canfield et al., 2007; Och and Shields-Zhou, 2012; Sahoo et al., 2012; Ader et al., 2014; Sperling et al., 2015b). However, the degree and exact timing of oxygenation are not well understood. Although iron isotope studies may provide valuable insights, few iron isotope data from Neoproterozoic rocks exist so far (Halverson et al., 2011; Fan et al., 2014; Tahata et al., 2015; Zhang et al., 2015; Cox et al., 2016). Iron isotope ratios in Sturtian iron formation deposited during post-glacial transgression show a systematic trend of up-section increasing  $\delta^{56}$ Fe values, which has been interpreted as oxidation of a successively decreasing proportion of the ferrous iron reservoir during deepening of the depositional environment (Halverson et al., 2011; Cox et al., 2016). Sedimentary pyrites in Cryogenian (ca. 717–635 Ma) black shales from South China show a systematic decrease from positive values (ca. 0 to +1%) to values comparable to the hydrothermal iron source (ca. -0.5 + 0%), which Zhang et al. (2015) interpreted to reflect near-quantitative oxidation of the ferrous iron reservoir and, by inference, increasing environmental oxygen levels. Tahata et al. (2015) reported Fe isotope data from pyrites in carbonates, shales, sandstones, and diamictites from the Neoproterozoic succession in Svalbard and suggested that heavy  $\delta^{56}$ Fe values before and after the Sturtian glaciation attest to an anoxic-ferruginous deep ocean. The bulk rock Fe isotopic composition of carbonates, phosphorites, and diagenetic chert from the Ediacaran (ca. 635-541 Ma) Doushantuo Formation in South China were also interpreted to reflect a ferruginous deep ocean (Fan et al., 2014). Although these interpretations are broadly consistent with redox constrains from other proxies (e.g., Canfield et al., 2008; Johnston et al., 2010, 2013; Sperling et al., 2013; Kunzmann et al., 2015; Sperling et al., 2015b), limited data hinders the reconciliation of the iron isotope record with proposed models of oxygenation. The reconstruction of a detailed secular Fe isotope trend is further complicated because previous studies focused on different rock types and either present bulk rock or mineral-specific isotope data. Focus on specific minerals (like pyrite) has the advantage that it yields more pronounced isotopic variations because the biogeochemical signals are undiluted by the detrital sedimentary component. However, a disadvantage of this approach is that specific minerals may not fully capture seawater signals. For example, pyrite formed in non-euxinic environments does not act as quantitative iron sink (Berner, 1984), making it difficult to extract information about changing seawater chemistry. In contrast, bulk rock analyses, although affected by the detrital iron pool, has the advantage of capturing both diagenetic and water column processes. Furthermore, recrystallization during burial does not affect the bulk rock composition, whereas it has the potential to alter individual phases.

Here, we report the bulk rock Fe isotope composition of 124 marine shales from Svalbard, NW Canada, and Siberia deposited between 1050 and 570 Ma. Our first aim is to evaluate the relative importance of isotopic fractionation in the water column versus fractionation during diagenesis on the bulk shale Fe isotope composition. To address this question, we created an isotope mass-balance model, which suggests that water column processes, i.e. the quantitative or non-quantitative oxidation of a ferrous iron reservoir in response to environmental oxygen levels, are more important than fractionation during diagenesis. Based on the conclusion drawn from modelling, we qualitatively interpret our new record of the secular variation of Fe isotopes in Neoproterozoic shales (Fig. 5.1) in terms of atmospheric oxygen levels and compare the Fe isotope record to models of Neoproterozoic oxygenation based on other redox proxies. Although still sparse, the Fe isotope record suggests an increase in atmospheric oxygen before the ca. 635 Ma Marinoan glaciation, which is in contrast to most redox proxies that imply that oxygenation occurred after the Marinoan glaciation.

# 5.2 Background

#### 5.2.1 Sources of iron to the ocean

Iron delivered to the modern ocean in suspended or colloidal form by rivers has a  $\delta^{56}$ Fe composition of ca. -1.0 to +0.3‰ (Beard et al., 2003a; Fantle and DePaolo, 2004; Bergquist and Boyle, 2006; Ingri et al., 2006). However, riverine iron is not a significant source to the open ocean because the ionic strength of seawater neutralizes surface charges of colloidal particles, which causes iron to be removed in near shore environments (e.g., Boyle et al., 1974; Boyle and Edmond, 1977; Sholkovitz et al., 1978; Krachler et al., 2010). Therefore, riverine iron transported to the open ocean is restricted to nanoparticulate Fe-oxyhydroxides (Raiswell, 2011b). Additional sources of bioavailable, continent-derived iron to the oceans are icebergs (Raiswell et al., 2008; Raiswell, 2011a) and dust. The latter is an important iron source to the ocean (e.g., Duce and Tindale, 1991; Fung et al., 2000; Jickells et al., 2005) and has an Fe isotopic composition of -0.1 to +0.3‰ (Zhu et al., 2000; Beard et al., 2003a,b). Dissolved Fe(II) from continental margin sediments has recently been identified as another important iron source to the water column (Elrod et al., 2004, 2008; Lohan and Bruland, 2008; Cullen et al., 2009; Severmann et al., 2010; John et al., 2012; Conway and John, 2014; Dale et al., 2015) and is characterized by a mostly light isotopic composition ranging from -3.5 to -0.5‰ (Bergquist and Boyle, 2006; Severmann et al., 2006; Staubwasser et al., 2006; Homoky et al., 2009; Severmann et al., 2010; Tangalos et al., 2010; Homoky et al., 2013). In some exceptions, non-reductive dissolution of Fe-oxyhydroxides can lead to positive  $\delta^{56}$ Fe values of up to +1.2‰ (Radic et al., 2011; Homoky et al., 2013). Hydrothermal iron ranges from -0.7 to -0.1‰ but the mass-weighted average is likely close to the high end (Beard et al., 2003b; Severmann et al., 2004; Johnson et al., 2008b). Although some recent studies indicate that this flux may be more significant than previously thought (Toner et al., 2009; Saito et al., 2013; Conway and John, 2014), the contribution of hydrothermal iron to the modern ocean is generally considered to be small (Lilley et al., 2004). In contrast, hydrothermal iron was likely the dominant iron source in the anoxic, sulfate-poor Precambrian ocean (e.g., Derry and Jacobsen, 1990; Kump and Seyfried, 2005; Holland, 2006).

#### 5.2.2 Iron isotope fractionation during diagenesis

Particulate iron delivered to modern marine siliciclastic sediments can be subdivided into an unreactive pool (mainly silicate minerals) and a highly reactive pool, which can undergo reductive dissolution on diagenetic timescales (Canfield, 1989; Raiswell and Canfield, 1998; Poulton and Canfield, 2011; Raiswell and Canfield, 2012). Reactive iron-bearing minerals are carbonates, Fe-oxyhydroxides, magnetite, and pyrite. Fe-oxyhydroxides are by far the most important of these minerals and are mainly formed during pyrite dissolution and oxidation during continental weathering (Reinhard et al., 2013). Common Fe-oxyhydroxides are ferrihydrate, lepicrocite, goethite, and hematite, which generally have  $\delta^{56}$ Fe compositions similar to bulk continental crust (0.09±0.05‰; Beard et al., 2003a). Detrital magnetite and carbonate are quantitatively insignificant.

Dissimilatory iron reduction (DIR) is an important pathway of organic matter oxidation in which Fe-oxyhydroxides are used as electron acceptors (e.g., Thamdrup, 2000; Lovley et al., 2004). During DIR, bacteria shuttle electrons to the surface of Fe-oxyhydroxides, either by direct

contact with the mineral surface (e.g., *Geobacter sulfureducens*) or by production of chelators that solubilize Fe(III) and release of low molecular weight compounds (e.g., Shewanella putrefaciens) that shuttle electrons from the cell to the mineral surface (e.g., Lovley et al., 2004). Furthermore, both types of bacteria can produce pili ('nanowires') for transporting electrons to insoluble Fe-oxyhydroxides (e.g., Gorby et al., 2006). DIR produces aqueous ferrous iron (Fe(II)<sub>aq</sub>) that is isotopically up to  $\sim 3\%$  lighter than the ferric iron substrate (Beard et al., 1999, 2003a; Icopini et al., 2004; Crosby et al., 2005; Johnson et al., 2005; Crosby et al., 2007). Detailed studies by Crosby et al. (2005, 2007) demonstrated that isotopically light  $Fe(II)_{aq}$  can be explained by isotope exchange between three iron pools that are formed during DIR:  $Fe(II)_{aq}$ , Fe(II) that is sorbed onto the surface of the Fe(III)-mineral, and Fe(III) that forms an outer, reactive surface layer of the Fe-oxyhydroxide. The dominant isotope effect is an equilibrium fractionation of  $\sim$ -3% between Fe(II)<sub>aq</sub> and the reactive Fe(III) layer (Crosby et al., 2005, 2007). The isotopic composition of  $Fe(II)_{aq}$  depends on the mass balance between the three reactive iron pools, where a maximum isotopic difference is observed in systems with a small  $Fe(II)_{aq}$  pool with most iron residing in the reactive Fe(III) layer (Crosby et al., 2007). With ongoing DIR, the size of the  $Fe(II)_{aq}$  pool increases at the expense of the Fe(III) pool in the surface layer of the mineral, concomitant with an increase in the  $\delta^{56}$ Fe value of Fe(II)<sub>aq</sub> (Crosby et al., 2007). The fractionation between the  $Fe(II)_{aq}$  and reactive Fe(III) layer is independent of the ferric Fe substrate and the bacterial species, such that the role of bacteria in controlling isotope compositions lies in making the Fe(III) of the mineral available for electron and isotopic exchange (Crosby et al., 2007). Indeed, the fractionation of  $\sim$  -3‰ is equivalent to abiological equilibrium fractionation between hexaquo- $Fe(II)_{aq}$  and hexaquo- $Fe(III)_{aq}$  (Johnson et al., 2002; Welch et al., 2003). Isotopic fractionation during sorption of Fe(II)<sub>aq</sub> onto the surface of Fe-oxyhydroxides is mineral specific and is  $\sim -1.24\%$  for goethite (Beard et al., 2010, see references therein for older estimates), about -0.8% for hydrous ferric oxide (Wu et al., 2011), and -0.49 for hematite (Wu et al., 2009, 2010). The effect of DIR and/or abiological Fe-oxyhydroxide reduction in natural environments leads to pore waters with isotopically depleted iron.

The isotope effects associated with oxidation of  $Fe(II)_{aq}$  to  $Fe(III)_{aq}$  (biologically mediated or abiological), subsequent coupled isotope and electron exchange between aqueous Fe(II) and Fe(III) species, followed by precipitation of ferric Fe minerals, have been studied in experiments

and natural environments (Bullen et al., 2001; Johnson et al., 2002; Skulan et al., 2002; Welch et al., 2003; Croal et al., 2004; Balci et al., 2006; Jang et al., 2008; Beard et al., 2010; Wu et al., 2011; Frierdich et al., 2014a). The equilibrium fractionation between  $Fe(II)_{aq}$  and  $Fe(III)_{aq}$  of  $\sim 3\%$  is the dominant isotope effect, likely overwhelming any effect associated with biological oxidation of  $Fe(II)_{aq}$  (Balci et al., 2006). These studies have shown the equilibrium fractionation between Fe(II)<sub>aq</sub> and different Fe-oxyhydroxides to be between -1.24 and -1.04‰ for goethite (Beard et al., 2010; Frierdich et al., 2014a), and about -3.2% for both hematite (Skulan et al., 2002; Welch et al., 2003; Beard et al., 2010) and hydrous ferric oxide (Wu et al., 2011). Frierdich et al. (2014b) suggested that, at least in the case of goethite, later isotopic equilibration erases the signature of initial kinetic fractionation associated with mineral precipitation. Comparable to the reduction of Fe(III) by DIR, oxidation of Fe(II) and subsequent Fe-oxyhydroxide precipitation involves different iron pools;  $Fe(II)_{aq}$ , Fe(III) of the mineral, Fe(II) sorbed on the mineral surface, and a reactive Fe(III) surface layer (Beard et al., 2010; Wu et al., 2010). Adsorption of Fe(II) on Fe-oxyhydroxide surfaces upon mixing of reduced groundwater with oxic water can lead to significant depletion of heavy isotopes in the aqueous Fe(II) pool (Bullen et al., 2001; Teutsch et al., 2005; Rouxel et al., 2008).

The fate of Fe(II)<sub>aq</sub> that does not become oxidized depends on the chemical conditions of the pore waters and whether it encounters an Fe(III)-oxyhydroxide, dissolved sulfide, or carbonate. In pore waters with low dissolved sulfide concentrations (and anoxic bottom waters), Fe(II)<sub>aq</sub> can escape to the water column (Scholz et al., 2014a,b; Dale et al., 2015). However, if the Fe(II)<sub>aq</sub> ion encounters an Fe(III)-oxydydroxide in anoxic pore waters, magnetite (Fe<sub>3</sub>O<sub>4</sub>) can form abiologically (e.g., Tamura et al., 1983; Schwertmann, 1988; Lovley, 1990). This reaction is associated with an equilibrium fractionation factor of  $\Delta^{56}$ Fe<sub>Fe(II)aq</sub>-magnetite  $\sim -1.6\%$  (Johnson et al., 2005; Frierdich et al., 2014b). Magnetite can also form as a breakdown product of smectite during burial diagenesis (Katz et al., 2000) or can be produced by magnetotactic bacteria (e.g., Blakemore, 1982). However, the amount of magnetite formed by magnetotactic bacteria on a per cell basis is about 5000 times smaller than that produced by DIR (Frankel, 1987).

Isotope effects between  $Fe(II)_{aq}$  and carbonate minerals are poorly studied, but experiments suggest that the fractionation is strongly influenced by the mineralogical composition of carbonate minerals (Johnson et al., 2005). Wiesli et al. (2004) reported an equilibrium fractionation factor for siderite ( $\Delta^{56}$ Fe<sub>Fe(II)aq-siderite</sub>) of 0.48% based on an abiological experiment. In contrast, Johnson et al. (2005) reported no measurable fractionation for siderite precipitation in biological experiments (including DIR). However, these authors noted a fractionation of 0.9% for Ca-substituted siderite and suggested that the substitution of other cations such as Mg and Mn will also result in a significant isotope effect (Johnson et al., 2005).

The isotopic fractionation between aqueous iron species and pyrite under demonstrably equilibrium conditions has not been experimentally determined yet. However, several studies focused on the fractionation between Fe(II)<sub>aq</sub> and mackinawite (FeS), a pyrite precursor mineral (Butler et al., 2005; Guilbaud et al., 2010, 2011a,b; Wu et al., 2012). The most recent experiments by Guilbaud et al. (2011b) and Wu et al. (2012) reported an equilibrium fractionation factor of  $\Delta^{56}$ Fe<sub>Fe(II)aq-FeS</sub> ~ -0.32\%. The fractionation factor is independent of temperature and pH in low temperature environments; however, mackinawite formed at low pH (<4) may partially record an initial positive kinetic isotope fractionation (Butler et al., 2005; Guilbaud et al., 2010, 2011b). Low pH conditions promote particle coarsening via aggregation, which limits isotopic exchange (Wu et al., 2012), but this process is unlikely to be important at near-neutral or alkaline pH conditions of diagenetic environments, and Wu et al. (2012) suggest that the initial kinetic fractionation is erased by later isotopic equilibration. Although the net fractionation between aqueous iron species and pyrite (FeS<sub>2</sub>) has yet to be determined experimentally, theoretical approaches using the reduced partition ratios, or  $\beta$ -factors, suggest that pyrite should be one of the isotopically heaviest minerals (Polyakov et al., 2007; Blanchard et al., 2009).

# 5.3 Materials and Methods

#### 5.3.1 Samples

We measured the bulk rock Fe isotope composition of 124 dark grey to black shales ranging in age from ~1050 Ma to 570 Ma (Tab. 5.2). Samples come from three different areas: Svalbard-East Greenland (n=62), northwestern Canada (n=54) and western Siberia (n=8). Fresh outcrops were sampled routinely during mapping and stratigraphic logging over the course of multiple field seasons. We interpret our Fe isotope data in the context of previously reported and new major element (Fe and Al), and iron speciation data (Tab. 5.3; Kunzmann et al., 2015; Sperling et al., 2015a). New elemental and Fe speciation data were obtained using the methods outlined in Kunzmann et al. (2015).

#### 5.3.2 Sample preparation and Fe isotope measurements

Cleaned and cut samples were powdered in a chrome steel ring mill and combusted at 550°C for 5h (Dean, 1974). Approximately 40 mg powder was digested in a mixture of double-distilled, concentrated HCl-HF-HNO<sub>3</sub>, followed by a second digestion step in aqua regia (see Supplementary Information for details). Iron was purified by anion-exchange chromatography in a HCl medium using Bio Rad AG1 X4 resin (200-400  $\mu$ m mesh) following the steps outlined in Halverson et al. (2011). Iron isotope ratios were measured in a 10 ppm solution on a Nu Plasma II multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS) at the Geotop research center, Montréal. The MC-ICP-MS was operated in high-resolution mode and standard-sample-standard bracketing was used to correct for instrumental mass bias. Measured <sup>56</sup>Fe/<sup>54</sup>Fe and <sup>57</sup>Fe/<sup>54</sup>Fe ratios are reported relative to IRMM-14 using standard delta notation. We routinely prepared and analyzed the certified reference material BHVO-2 (Hawaiian basalt) and obtained average  $\delta^{56}$ Fe and  $\delta^{57}$ Fe values of  $0.06\pm0.03\%$  (1SE) and  $0.11\pm0.04\%$  (1SE), respectively. These values lie within the range reported in the GeoReM data base (Jochum et al., 2005). In addition to BHVO-2, we routinely analyzed an in-house hematite standard and obtained standard errors (1SE) of  $\pm 0.03\%$  for  $\delta^{56}$ Fe and  $\pm 0.04\%$  for  $\delta^{57}$ Fe.

# 5.4 Results

The measured  $\delta^{56}$ Fe values (n=124) span a range from -0.45 to +1.04‰ (mean 0.26‰, Fig. 5.1A). Although significant isotopic variability is observed in every stratigraphic unit (Fig. 5.1A), these data show systematic secular variation spanning the Neoproterozoic (Fig. 5.1B). The mean  $\delta^{56}$ Fe value increases from roughly -0.1‰ in the ca. 1050 Ma Strelnye Gory Formation of Siberia to roughly +0.7‰ in the ca. 800 Ma Ram Head Formation of northwestern Canada. This maximum is followed by a decrease of  $\delta^{56}$ Fe to values below +0.2‰ (i.e., near crustal values) in units younger than the ca. 717 Ma Sturtian glaciation. However, due to a limited number of data for some stratigraphic units, we treat this apparent secular variation with caution. The relationships between  $\delta^{56}$ Fe, total iron/aluminium (FeT/Al) and different iron pools are shown in Figs. 5.2 and 5.3. Following Poulton and Canfield (2005, 2011), we define highly reactive iron (FeHR) as the sum of iron bound in carbonate minerals (FeCarb), oxyhydroxides (FeOx), mixed valence oxides like magnetite (FeMag), and pyrite (FePy). Total iron is the sum of FeHR and an unreactive iron pool (FeUn) comprising mostly silicate minerals.  $\delta^{56}$ Fe values generally show a negative relationship with FeT/Al and FeHR/FeT (Fig. 5.2A, B, D, E, G, H). A clear relationship between FeCarb/FeT and  $\delta^{56}$ Fe is not observable (Fig. 5.2C, F, I). The Russøya Member of Svalbard (Fig. 5.3A) and the Sheepbed, Reefal Assemblage, and Black Canyon Creek formations of northwestern Canada (Fig. 5.3D) show a negative relationship between FeOx/FeT and  $\delta^{56}$ Fe. No clear relationship is observed for the other stratigraphic units. Furthermore, FeMag/FeT and FePy/FeT ratios do not show clear relationships with  $\delta^{56}$ Fe values in any unit (Fig. 5.3B, C, E, F, H, I), with the exception of a minor positive correlation between  $\delta^{56}$ Fe values and FeMag/FeT in the Strelnye Gory Formation of Siberia (Fig. 5.3H).

## 5.5 Discussion

### 5.5.1 Iron systematics in Neoproterozoic shales: the effect of iron shuttling

Negative relationships between  $\delta^{56}$ Fe and FeT/Al suggest a basin-scale transport mechanism of iron with distinct isotopic composition. Samples depleted in iron relative to the continental crust preferentially lost isotopically light iron, driving their  $\delta^{56}$ Fe composition towards heavier values. In contrast, samples with FeT/Al ratios above the crustal range are systematically enriched in isotopically heavy iron, with  $\delta^{56}$ Fe values mostly between 0 and 0.4‰ (for comparison, the continental crust has  $0.09\pm0.05\%$ ). The shuttled iron is isotopically light as observed in modern settings (Severmann et al., 2008; Scholz et al., 2014b) and part of the highly reactive iron pool that can be mobilized during diagenesis as suggested by a negative relationship between  $\delta^{56}$ Fe and FeHR/FeT. The negative correlation between FeOx/FeT and  $\delta^{56}$ Fe is consistent with the notion that the shuttled iron was ultimately sourced from Fe-oxyhydroxides that underwent reductive dissolution during diagenesis. This relationship and lack of correlation of Fe isotope ratios with other highly reactive iron species suggest that Fe-oxyhydroxides in our samples represent the most important iron pool in terms of regulating  $\delta^{56}$ Fe composition.

Studies of two different modern environments have shown evidence for the shuttling of isotopically distinct iron between depositional sites. In euxinic basins, diagenetic reactions such as DIR mobilize reactive and isotopically light iron in suboxic shelf sediments. The iron is transported to the more distal, euxinic basin, where it is quantitatively trapped during syngenetic pyrite formation in the water column, and buried with sediments in the deep basin (Wijsman et al., 2001: Anderson and Raiswell, 2004: Lyons and Severmann, 2006: Severmann et al., 2008). This iron shuttle leads to depleted FeT/Al ratios and high  $\delta^{56}$ Fe values of shelf sediments relative to the detrital flux and enriched FeT/Al ratios with negative  $\delta^{56}$ Fe in euxinic sediments (Severmann et al., 2008). Thus, the iron shuttle in euxinic basins can be identified, by a negative relationship between FeT/Al and  $\delta^{56}$ Fe (Fehr et al., 2008; Severmann et al., 2008; Duan et al., 2010; Fehr et al., 2010; Owens et al., 2012). This pattern is similar to what we see in Neoproterozoic shales (Fig. 5.2); however, our samples were deposited in continental margin settings, not restricted basins, and iron speciation and other redox data (Kunzmann et al., 2015; Sperling et al., 2015a) imply deposition under non-euxinic conditions (Fig. 5.9). Furthermore,  $\delta^{56}$ Fe is decoupled from the abundance of pyrite (Fig. 5.3C, F, I), suggesting that a euxinic iron shuttle was not responsible for the FeT/Al –  $\delta^{56}$ Fe relationships in our Neoproterozoic sample set.

In modern, open marine settings, reactive and isotopically light iron is mobilized from sediments where the oxygen minimum zone (OMZ) impinges on the shelf, causing depleted FeT/Al ratios and heavier  $\delta^{56}$ Fe values than the detrital flux (Scholz et al., 2014b). The mobilized iron is transported laterally in the oxygen-deficient part of the water column and partly precipitated in sediments below the OMZ (Scholz et al., 2014b). This oxidative trapping leads to enriched FeT/Al, but in contrast to euxinic basins, it is associated with heavier  $\delta^{56}$ Fe values (Scholz et al., 2014b) because Fe-oxyhydroxide formation preferentially consumes the heavy isotope and the reaction is locally non-quantitative. This generally leads to a positive correlation between FeT/Al and  $\delta^{56}$ Fe. This contrast with the observed negative relationship seen in our data set. Furthermore, it is unlikely to find such FeT/Al –  $\delta^{56}$ Fe patterns in Neoproterozoic marine sediments because the redox structure of the Neoproterozoic ocean was likely characterized by an oxic surface mixed layer and a ferruginous deep ocean (Canfield et al., 2008; Lyons et al., 2014; Sperling et al., 2015b).

To the extent that anoxic deep oceans prevailed through most of the Proterozoic Eon, the
formation of the OMZ as prominent feature of the ocean may not have occurred until the Ediacaran or later (Ader et al., 2014; Lyons et al., 2014; Kunzmann et al., 2015). However, modern OMZ settings provide an example of a mechanism for significant loss of iron from the sediment to the water column. Therefore, we interpret samples with depleted FeT/Al and high  $\delta^{56}$ Fe values to have lost Fe to an anoxic-ferruginous water column. However, loss of Fe to the water column requires a concentration gradient similar to the suboxic OMZ off the coast of Peru (Noffke et al., 2012). Hence, even when anoxic deep waters are considered ferruginous as opposed to euxinic, this distinction does not imply high Fe concentrations. Indeed, a long-lived, low-Fe ferruginous ocean during the Proterozoic is consistent with the disappearance of banded iron formation from the geological record ca. 1.8 Ga ago.

Although the mechanism by which iron was lost from our samples during diagenesis is relatively straightforward, identifying an iron sink in an oceanographic setting dominated by an oxic surface and anoxic-ferruginous deep ocean is more difficult. We envision two possible mechanisms by which isotopically light iron might be concentrated in shales. The first is fluctuation in the depth of the chemocline (due, for example, to seasons or cyclical variations in the intensity of mixing of the surface ocean), where lowering of the chemocline (or upwelling of ferruginous waters) exposes dissolved iron to oxidants, leading to precipitation of isotopically light iron. The second potential mechanism involves transport of dissolved iron into deeper parts of the basin, where local or intermittently euxinic conditions trapped the iron as pyrite, but where no signature is left in the iron speciation record.

An important difference between data from modern samples and our data set is a significantly larger range in  $\delta^{56}$ Fe values and FeT/Al ratios in Neoproterozoic shales. This testifies to more intense iron cycling in an anoxic ocean compared to the mostly oxygenated modern ocean.

### 5.5.2 Model of the isotopic composition of highly reactive iron

This study is the first attempt towards a bulk rock Fe isotope record for the Neoproterozoic. Therefore, we did not analyze individual iron speciation pools to investigate the isotopic composition of highly reactive iron and provide a modeling approach instead. However, future analyses of individual iron pools will be able to provide an important test of our model and the conclusions drawn from it.

#### Model set-up

To better understand the controls on the Fe isotope composition of Neoproterozoic shales, we created a steady state isotope mass-balance model that describes the fluxes ( $\phi$ ) and isotopic effects ( $\epsilon$ ) associated with the transport and reaction pathways of highly reactive iron in anoxic marine sediments (Fig. 5.4). The aim of our model is to predict the  $\delta^{56}$ Fe composition of highly reactive iron ( $\delta^{56}$ Fe<sub>HR-model</sub>). These values can be compared to our measured bulk rock  $\delta^{56}$ Fe after correcting for the unreactive iron content (Fig. 5.5). The relationship between measured bulk rock  $\delta^{56}$ Fe and the isotopic composition of highly reactive iron in the same sample can be described as

$$\delta^{56} Fe = FeHR/FeT \times \delta^{56} Fe_{HR-calc} + (1 - FeHR/FeT) \times \delta^{56} Fe_{Un}$$
(5.1)

where  $\delta^{56}$ Fe is the measured bulk rock value,  $\delta^{56}$ Fe<sub>HR-calc</sub> is the calculated  $\delta^{56}$ Fe value for highly reactive iron after correction, and  $\delta^{56}$ Fe<sub>Un</sub> is the isotopic composition of unreactive iron, which we assume to have crustal values (~0.09‰; Beard et al., 2003a). The calculated isotopic composition of highly reactive iron in our samples varies between ca. -1 and +8‰; however, >90% of our data fall in the range between -1 and 3‰ (Fig. 5.5). Samples with extremely high  $\delta^{56}$ Fe<sub>HR-calc</sub> have FeHR/FeT ratios <0.15. With our model, we focus on re-producing the >90% of our data that have  $\delta^{56}$ Fe values below +3‰. For these samples, the ratio of the precipitated minerals in our model (Fig. 5.4; magnetite, carbonate, pyrite, Fe-oxyhydroxides) was set to reflect the average composition of the measured Neoproterozoic shales based on our iron speciation data (Tab. 5.3).

A full description of the model is provided in the Supplementary Information; here we provide a brief overview, with an emphasis on the assumptions and simplifications that are built into the model. First, we assume that the diagenetic cycling of highly reactive iron is fueled by the delivery of Fe-oxyhydroxide minerals to the sediment, and that the detrital flux of carbonate, pyrite, and magnetite is negligible. Consistent with generally low pyrite abundance in our samples, we assume that dissimilatory iron reduction is the major pathway of Fe-oxyhydroxide reduction (e.g., Thamdrup, 2000), not the reaction with hydrogen sulfide (e.g., Canfield, 1989). Furthermore, we assume that magnetite formed in sediments did not get re-oxidized. The formation of magnetite in our model occurs through the reaction of one  $Fe(II)_{aq}$  ion with hydrous ferric oxide (e.g., Lovley, 1990). Other pathways such as the breakdown of smectite during burial (Katz et al., 2000) and formation by magnetotactic bacteria (Blakemore, 1982) are considered negligible. Other Fe-bearing minerals such as vivianite (a group of ferrous phosphate minerals) are not considered. Moreover, we model all fluxes out of the  $Fe(II)_{aq}$  pool to be simultaneous rather than continuous.

We varied the isotopic composition of incoming Fe-oxyhydroxides ( $\delta_{in}$ ) between -1 and +3‰ (Tab. 5.1). The minimum value would reflect oxyhydroxides that precipitate upon quantitative oxidation of hydrothermally derived ferrous iron with a composition of -1‰ (reported values for hydrothermal iron range from -0.7 to -0.1; Sharma et al., 2001; Beard et al., 2003b; Severmann et al., 2004). The maximum value reflects oxidation of a minor proportion of the ferrous iron pool with an initial  $\delta^{56}$ Fe value of 0‰—roughly the high end of reported compositions for hydrothermal iron.

Microbial reduction of Fe-oxyhydroxides (in our model collectively referred to as FeOx; Fig. 5.4) is limited to amorphous and poorly crystalline compounds, whereas more crystalline minerals like goethite and hematite cannot be efficiently reduced by DIR in natural environments (Lovley and Phillips, 1986a,b; Thamdrup, 2000). Amorphous and poorly crystalline FeOx phases generally make up less than 20% of the total FeOx reservoir in sediments (Thamdrup, 2000), consistent with results from sulfate-poor natural environments that indicate that generally less than 20-30% of the available FeOx is microbially reducible (Lovley and Phillips, 1986a). Furthermore, Fe(II) adsorption onto the surface of FeOx may further hinder efficient reduction of FeOx (Roden, 2004). However, Fe(III) in some clay minerals is also microbially reducible (e.g., Stucki et al., 1987; Kostka et al., 1996; Vorhies and Gaines, 2009) and Fe(III) from clay may represent about 10% of the microbially reducible iron (Wallmann et al., 1993; Thamdrup, 2000). Therefore, we varied the proportion of microbially reducible FeOx in our model runs between 10 and 30% (Tab. 5.1), but also perform runs with 100% to test the most extreme scenario (Tab. 5.1). The significant amounts of preserved FeOx remaining in our samples (Tab. 5.3) is consistent with limited reduction by bacteria.

We varied the  $\Delta^{56}$ Fe between the initial FeOx and Fe(II)<sub>aq</sub> between -3 and 0‰ to reflect the possible range in fractionation occurring during DIR and to match typical pore water Fe(II)<sub>aq</sub> compositions (Bergquist and Boyle, 2006; Severmann et al., 2006; Homoky et al., 2009; Severmann et al., 2010; Tangalos et al., 2010; Homoky et al., 2013). Although theoretical determinations

of fractionation factors are significantly improved by refined methods of calculating  $\beta$ -factors (Rustad et al., 2010; Polyakov and Soultanov, 2011), we have chosen to use the most recent experimentally determined fractionation factors for fluid-mineral pairs in our model (Tab. 5.1; see also section 2.2), which are the most realistic values when compared to the rock record.

In our model runs presented in Fig. 5.6, we assume that the flux of Fe out of the sediments  $(\phi_{esc})$  is never less than 50% of the reduced iron and that the re-oxidation rate  $(\gamma_{re-ox})$ , i.e., the oxidation of Fe(II)<sub>aq</sub> back to Fe(III) within sediment pore waters is never less than 20%. However, significant flux of Fe(II) out of sediments simultaneous with re-oxidation of Fe(II)<sub>aq</sub> to Fe(III) may not be likely for most settings as they generally require different redox conditions. To allow for a benthic Fe flux (i.e. anoxic conditions), the oxidation of Fe(II)<sub>aq</sub> must occur primarily through anaerobic NO<sub>3</sub><sup>-</sup> reduction catalyzed by bacteria (e.g., Konhauser et al., 2011). Although NO<sub>3</sub><sup>-</sup> concentrations are generally expected to be low in an anoxic ocean, N isotope data suggest that NO<sub>3</sub><sup>-</sup> was probably stable in much of the middle to late Neoproterozoic ocean (Ader et al., 2014). We stress that the reason for our modeling is to estimate the potentially highest influence of diagenetic iron cycling on the composition of highly reactive iron. This encourages us to assume  $\gamma_{re-ox}$  and  $\phi_{esc}$  that may be slightly to high. However, lowering them will only decrease the importance of diagenetic iron cycling on the isotopic composition of highly reactive iron.

#### Model results

Our model results confirm the expectation that the release of dissolved iron from sediments to the water column leaves behind an isotopically enriched iron pool (Fig. 5.6). As expected from mass-balance considerations, it also demonstrates that the importance of diagenetic iron cycling for the overall isotopic composition increases with increasing proportion of incoming iron that is reducible ( $\phi_{in}$ ; Fig. 5.6A-C). However, even if all of the incoming Fe-oxyhydroxides are reducible (Fig. 5.6C), diagenetic iron cycling still does not lead to significant isotopic enrichment of highly reactive iron. Even assuming that all of the incoming FeOx is reducible ( $\phi_{in}=1$ ) and that 75% of the reduced iron is lost to the water column ( $\phi_{esc}=0.75$ )—unrealistically high values— the  $\delta^{56}$ Fe value of highly reactive iron only changes by ~ 0.9‰ (Fig. 5.6F). Therefore, we conclude that diagenetic iron cycling is only of second order importance in setting the isotopic composition of highly reactive iron. Increasing the re-oxidation rate only leads to a minor increase in  $\delta^{56}$ Fe when the proportions of formed minerals and their amount (i.e., flux of Fe out of sediments) is held constant (Fig. 5.6D). As predicted from mass-balance relationships, increasing the flux of dissolved iron out of the sediments leads to progressive enrichment of the highly reactive iron pool but cannot increase the  $\delta^{56}$ Fe of highly reactive iron by more than 0.3% (Fig. 5.6E). In summary, the isotopic composition of the incoming Fe-oxyhydroxides is the major control on the  $\delta^{56}$ Fe composition of highly reactive iron and bulk shale (if FeHR represents most of the total iron pool). Our  $\delta^{56}$ Fe<sub>HR-calc</sub> (Fig. 5.5) can only be reproduced if  $\delta_{in}$  is varied substantially. Therefore, our model results suggest that water column processes, i.e. quantitative or non-quantitative oxidation of a ferrous iron reservoir, is the most important process in setting the  $\delta^{56}$ Fe composition of highly reactive iron.

# 5.5.3 The Neoproterozoic iron isotope record: implication for the oxygenation of Earth's surface environments

Our modeling indicates that the isotopic composition of the incoming Fe-oxyhydroxides is the major control on the Fe isotopic composition of highly reactive iron in marine shales. Because deposition under anoxic conditions leads to enrichment of highly reactive iron, the bulk shale isotopic composition can be significantly modified (i.e., from crustal composition) if incoming Feoxyhydroxides are isotopically heavy. The two potential sources of Fe-oxyhydroxides to sediments in an anoxic ocean are those delivered with the detrital flux, and oxyhydroxides that formed through (partial) oxidation of dissolved ferrous iron in seawater (although Fe-oxyhydroxides need to be deposited relatively fast to escape reduction in the anoxic water column). Fe-oxyhydroxides delivered by modern rivers can be slightly heavier than the continental crust (up to 0.31‰; Ingri et al., 2006) and oxyhydroxides formed in estuaries by partial oxidation of  $Fe(II)_{aq}$  in groundwater have been shown be isotopically heavy, up to 1.5% (Rouxel et al., 2008). However, the latter oxyhydroxides stay in the sediment where they form and are unlikely to be dispersed across the shelf. Similarly, colloidal iron in rivers does not reach the middle and outer shelf (where our samples were deposited) because it is trapped in coastal environments (e.g., Boyle and Edmond, 1977; Poulton and Raiswell, 2002). Therefore, (partial) oxidation of a ferrous seawater iron reservoir is the most likely source of Fe-oxyhydroxides in our samples. This ferrous iron reservoir originates from hydrothermal sources, which have a bulk composition of ca. -0.1‰ (Beard et al., 2003b; Severmann et al., 2004; Johnson et al., 2008b). Environmental oxygen levels control to what degree this reservoir becomes oxidized (non-quantitative or near-quantitative), which in turn controls the Fe isotopic composition of precipitated Fe-oxyhydroxides. Because they exert a strong control on the isotopic composition of highly reactive iron, we can use our data (Figs. 5.1, 5.5) to qualitatively evaluate first order changes in environmental oxygen levels.

Our bulk shale Fe isotope data set (Fig. 5.1) represents only the first step towards a global Fe isotope record for the Neoproterozoic. It is far from complete: few samples (n=<10) were analyzed for most stratigraphic units and the sampled units come from only three regions. Hence the record and our interpretations are provisional and likely to be revised as new data emerge. Nevertheless, they merit consideration within the context of the progressive oxygenation of the Precambrian oceans and atmosphere.

The ca. 1050 Ma Siberian samples from the Strelnye Gory Formation (Fig. 5.1) have on average negative  $\delta^{56}$ Fe values, i.e. lighter than the continental crust (0.09±0.05%; Beard et al., 2003a). However, the data are too few and too far separated temporally from the remaining data to draw any robust conclusion as to their significance. The remaining data can broadly be divided into two stages (Figs. 5.1B, 5.7). Stage 1 comprises all pre-Sturtian units and is characterized by average  $\delta^{56}$ Fe values ranging mostly from 0.3 to 0.5% (Figs. 5.1B, 5.7). These values are heavier than the continental crust (0.09±0.05‰) and hydrothermal iron (ca. -0.1‰), implying delivery of isotopically heavy Fe-oxyhydroxides to the sediments, which in turn suggests non-quantitative oxidation of the ferrous seawater iron reservoir. In contrast, Stage 2 comprises all post-Sturtian units, which have average  $\delta^{56}$ Fe values between +0.05 and +0.2‰ (Figs. 5.1B, 5.7). These values overlap with the composition of the continental crust and are slightly higher than the assumed bulk composition of hydrothermal iron (ca. -0.1‰), suggesting near-quantitative oxidation of the ferrous iron reservoir and hence higher environmental oxygen levels.

These results are consistent with interpretations based on an Fe isotope data set from South China suggesting a Cryogenian increase in oxygen levels (Zhang et al., 2015). They are also consistent with constraints from N isotope data that show no difference between Cryogenian and Ediacaran samples (Ader et al., 2014) and imply a stable nitrate reservoir. However, the hypothesis of significant Cryogenian oxygenation is inconsistent with other data sets, namely iron speciation and redox-sensitive trace element data, which imply that significant oxygenation of the Neoproterozoic ocean was strictly a post-Ediacaran phenomenon (Partin et al., 2013; Kunzmann et al., 2015; Sperling et al., 2015b). This discrepancy highlights the need to better understand the fundamental controls on each individual paleoredox proxy and its sensitivity to ambient redox. Such advances will require calibration of proxies in modern environments (e.g., Severmann et al., 2008; Busigny et al., 2014) and will be informed both by constraints on individual fluid-mineral fractionation factors and results of diagenetic and mass balance modeling. Furthermore, our Fe isotope results only allow interpretations about first-order changes in oceanic redox conditions and atmospheric oxygen levels. In addition, they do not allow us to constrain the rise of oxygen. Significant variation in the isotopic composition of individual post-Sturtian shales demonstrate redox heterogeneity and are consistent with recent models of an overall anoxic Ediacaran ocean with fluctuating redox conditions (Kendall et al., 2015; Sahoo et al., 2016).

### 5.6 Conclusion

The presented data set is the first step towards a bulk shale Fe isotope record for the Neoproterozoic. Systematic variation of  $\delta^{56}$ Fe values with FeT/Al and iron speciation indicates basin-scale shuttling of Fe similar to that seen in modern sub-oxic to anoxic environments. However, a larger range of Fe isotope ratios in Neoproterozoic shales suggest more intense iron cycling in a world with lower oxygen concentrations and mostly anoxic oceans. Isotopic modeling suggests that fractionation associated with the (partial) oxidation of the ferrous seawater iron reservoir is much more important in setting the isotopic composition of shales than diagenetic iron cycling. Therefore, the Fe isotopic composition of marine shales can be used to qualitatively evaluate environmental oxygen levels if one assumes that the isotopic composition of hydrothermal iron did not significantly change through time. Our preliminary Fe isotope record suggests a shift in the mode of iron cycling in the marine realm that is increase of oxygen levels before the 635 Ma Marinoan glaciation. This conclusion is inconsistent with constrains from other redox studies (e.g., Canfield et al., 2007; Kunzmann et al., 2015; Sperling et al., 2015b) and highlights the need to better understand the fundamental controls on different redox proxies and their sensitivity to incremental changes in environmental redox conditions. Furthermore, it demonstrates the need to quantify atmospheric oxygen levels as inconsistent constrains drawn from different proxies might

be reconcilable if we better understand what oxygen thresholds are required to cause a different behavior of a certain proxy.

# Acknowledgments

We thank Silke Severmann for informative discussions. MK acknowledges financial support through scholarships awarded by the Department of Earth & Planetary Sciences, McGill University, and Geotop. This project was further supported by the Yukon Geological Survey and grants to GPH from Natural Sciences and Engineering Research Council (NSERC) and the American Chemical Society (Petroleum Research Fund).

## **Figures and tables**



Fig. 5.1 Bulk shale iron isotope data from late Proterozoic units in Svalbard, northwestern Canada, and Siberia. Analytical error (1SE) is smaller than the symbols. A)  $\delta^{56}$ Fe shows significant variation within stratigraphic units. B) Box plot of  $\delta^{56}$ Fe for every measured stratigraphic unit. Ediacaran units (Dracoisen, Sheepbed, Blueflower, June Beds) have mean  $\delta^{56}$ Fe values comparable to the continental crust (ca. 0.09‰). Older units (with the exception of the Strelnye Gory and Arena formations) are dominated by heavier  $\delta^{56}$ Fe values. The number of samples analyzed for each unit is shown in parentheses. Note that the x-axis in B) does not exactly show the age (as in A)), although units are organized from older (left) to younger (right).



Fig. 5.2 Relationship between  $\delta^{56}$ Fe and different iron pools. Analytical error (1SE) is smaller than the symbols. A) and B) Negative relationship of FeT/Al and FeHR/FeT with  $\delta^{56}$ Fe in samples from Svalbard. Grey shaded area in A) represents typical FeT/Al ratios of the continental crust. Grey shaded field in B) represents FeHR/FeT ratios that do not distinguish oxic from anoxic conditions (Poulton and Canfield, 2011). C) The same samples show no clear relationship between  $\delta^{56}$ Fe and FeCarb/FeT. D) and E) Samples from Canada also show a negative relationship between  $\delta^{56}$ Fe and FeT/Al and FeHR/FeT, respectively. F) FeCarb/FeT ratios in shales from Canada are very low and show no systematic relationship with  $\delta^{56}$ Fe. G) and H) Samples from Siberia also show a negative relationship between  $\delta^{56}$ Fe and FeT/Al and FeHR/FeT, respectively. I) No clear relationship between FeCarb/FeT and  $\delta^{56}$ Fe in shales from Siberia.



Fig. 5.3 Relationship between  $\delta^{56}$ Fe and different iron speciation pools. Analytical error (1SE) is smaller than the symbols. A)-C) The samples from Svalbard show no clear relationship between  $\delta^{56}$ Fe, FeOx/FeT, FeMag/FeT, and FePy/FeT. One exception is a minor negative relationship between  $\delta^{56}$ Fe and FeOx/FeT in the Russøya Member. D) Shales from Canada (in particular Reefal Assemblage, Sheepbed, and Black Canyon Creek) show a negative relationship between FeOx/FeT and  $\delta^{56}$ Fe. E) and F) Samples from Canada show no clear relationship between  $\delta^{56}$ Fe and FeMag/FeT and FePy/FeT, respectively. G) Siberian samples show no correlation between FeOx/FeT and  $\delta^{56}$ Fe. H) Weak positive relationship between  $\delta^{56}$ Fe and FeMag/FeT in samples from Siberia. I) The same samples generally have low FePy/FeT ratios, which show no relationship to  $\delta^{56}$ Fe.



Fig. 5.4 Summary of important pathways involved in transport and isotopic fractionation of highly reactive iron in sediments. Each pathway is characterized by a specific flux ( $\phi$ ) and isotopic fractionation ( $\epsilon$ ). The fluxes of individual pathways are defined as proportion of the flux in ( $\phi_{in}$ ), which is the reducible fraction of incoming Fe-oxyhydroxides.  $\delta_{in}$  defines the isotopic composition of incoming oxyhydroxides and is varied in our model to reflect water column processes. Anoxic (ferruginous) bottom waters and sulfide-poor pore waters allow escape of some Fe(II)<sub>aq</sub>. Grey boxes represent iron pools that are removed from the system; the  $\delta^{56}$ Fe<sub>HR-model</sub> composition reflects the isotopic compositions of individual boxes, considering their respective flux (dictated by the average iron speciation composition). Abbreviations are: Ox-Mag, oxyhydroxide-magnetite; Red, reduction; re-ox, re-oxidation; Ox-burial, oxyhydroxide burial; Mag, magnetite; esc, escape; Carb, carbonate; Py, pyrite.



Fig. 5.5 Bulk rock  $\delta^{56}$ Fe plotted against the calculated composition of highly reactive iron ( $\delta^{56}$ Fe<sub>HR-calc</sub>) following equation 1. More than 90% of data have highly reactive iron compositions between -1 and 3‰.



Fig. 5.6 Results for model runs with different parameter settings. Modeled isotopic composition of highly reactive iron (x-axis) is plotted against different values for isotopic fractionation associated with reduction of FeOx and production of pore water Fe(II)<sub>aq</sub>. The five lines represent different starting compositions of incoming Fe-oxyhydroxides. Mineral compositions remained constant and was set to average iron speciation composition (Supplementary Information; 60% Fe-oxyhydroxides, 20% carbonate, 10% magnetite, 10% pyrite). A)–C) Following mass-balance, increase of  $\phi_{in}$  increases the importance of diagenetic iron cycling and isotope exchange results in residual highly reactive iron with successively heavier  $\delta^{56}$ Fe values. D) Increasing the re-oxidation rate ( $\gamma_{re-ox}$ ) without changing  $\phi_{esc}$  or mineral proportions, does not significantly change isotopic compositions (compare to B)). E) The residual highly reactive iron becomes progressively heavier with increasing iron flux to the water column ( $\phi_{esc}$ ; compare to B)). F) The largest influence of diagenetic iron cycling on the isotopic composition of highly reactive iron occurs when all Fe-oxyhydroxides are reducible and re-oxdiation rate and flux out of sediments are high. Although these parameter settings are unrealistic for natural environments, this model run demonstrates that diagenetic processes are not as important for the isotopic composition as the starting composition of incoming Fe-oxyhydroxides, i.e. water column processes.



Fig. 5.7 Simplified evolution of the  $\delta^{56}$ Fe composition of Neoproterozoic shales (see Fig. 5.1 for data). Stage 1 is characterized by  $\delta^{56}$ Fe values mostly ranging from 0.3 to 0.5%. Samples from Stage 2 are mostly in the range from 0.05 to 0.2%, overlapping the composition of the crust. This implies more quantitative oxidation of the ferrous seawater iron reservoir, and by inference an increase in oxygen levels after the Sturtian glaciation.

**Tab. 5.1** Summary of applied fractionation factors in our model (Fig. 5.4). References: 1, Johnson et al. (2002); 2, Welch et al. (2003); 3, Crosby et al. (2005); 4, Crosby et al. (2007); 5, Skulan et al. (2002); 6, Wu et al. (2011); 7, Johnson et al. (2005); 8, Frierdich et al. (2014b); 9, Wiesli et al. (2004); 10, Guilbaud et al. (2011b); 11, Wu et al. (2012)

Pathway	fractionation factor ( $^{56}\varepsilon)$	Reference
$\mathrm{FeOx}{\rightarrow}\mathrm{Fe(II)_{aq}}~(\varepsilon_{\mathrm{Red}})$	-3-0‰	1-4
$\mathrm{FeOx}{\rightarrow}\mathrm{FeMag}~(\varepsilon_{\mathrm{Ox-Mag}})$	0‰	_
$\mathrm{FeOx}{\rightarrow}\mathrm{FeMag}\;(\varepsilon_{\mathrm{Ox\text{-}burial}})$	0‰	_
$\mathrm{Fe}(\mathrm{II})_{\mathrm{aq}}{\rightarrow}\mathrm{FeOx}~(\varepsilon_{\mathrm{re-ox}})$	-3‰	5,  6
$\mathrm{Fe}(\mathrm{II})_{\mathrm{aq}}{\rightarrow}\mathrm{FeMag}~(\varepsilon_{\mathrm{FeMag}})$	-1.6‰	7, 8
$\mathrm{Fe}(\mathrm{II})_{\mathrm{aq}} {\rightarrow} \mathrm{water \ column} \ (\varepsilon_{\mathrm{esc}})$	0‰	_
$\mathrm{Fe}(\mathrm{II})_{\mathrm{aq}}{\rightarrow}\mathrm{Fe}\mathrm{Carb}~(\varepsilon_{\mathrm{Carb}})$	0.5%	7, 9
$\mathrm{Fe}(\mathrm{II})_{\mathrm{aq}}{\rightarrow}\mathrm{FePy}~(\varepsilon_{\mathrm{Py}})$	-0.32‰	10, 11

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# 5.7 Supplementary Information

### 5.7.1 Methods and data

### Sampling, cleaning, crushing

Dark grey to black shales were sampled during mapping and stratigraphic section logging. Fresh samples without obvious weathered surfaces were targeted. All samples were cleaned with water and a hand brush, and finally cut with a diamond saw to remove weathered edges. If necessary, remaining weathered parts were removed with sand paper. Dried samples were crushed and ground in a chrome steel ring mill, which was cleaned with ethanol and pre-contamianted with sample material between samples. Possible iron contamination during grinding has previously been evaluated to be negligible for soft rock samples like shales (Hickson and Juras, 1986; Sperling et al., 2013).

#### Sample preparation and measurements

About 1 g of sample material was combusted at 550°C for at least 5 hours to oxidize organic carbon complexes and determine loss on ignition.

Sample digestion was carried out in a clean lab at Geotop, Montreal. All acids were double distilled. Approximately 40 mg of combusted powder was weighted into Savillex<sup>TM</sup> teflon beaker and digested in a mixture of 2 ml 6 M HCl : 1 ml 50% HF : 0.5 ml 7 M HNO<sub>3</sub> for 48 hours at ~80°C. The samples were dried down but ~ 0.5 ml 7 M HNO<sub>3</sub> was added just before complete drying to prevent the formation of apatite group minerals. Samples were taken up again in a mixture of 2 ml 6 M HCl : 0.65 ml 7 M HNO<sub>3</sub> and left on the hot plate for 24–48 hours at ca. 80°C. After the samples were dried down again, they were taken up in 2 ml of 6 M HCl. An aliquot was taken for element analyses and the remaining 1 ml of sample solution was loaded on teflon columns containing Bio Rad AG 1 X4 resin (200–400  $\mu$ m mesh). Iron purification followed the procedure described in Halverson et al. (2011).

Isotopic measurements were performed on a Nu Plasma II multicollector-inductively coupled plasma mass spectrometer at Geotop, Montreal. The instrument was operated in high-resolution and wet mode. Standard-sample-standard bracketing was used to correct for internal mass bias. Results (Tab. 5.2) are reported relative to IRMM-14. We routinely prepared and measured the certified reference material BHVO-2 (basalt), as well as an in-house hematite standard. We obtained mean standard errors (1SE) of  $\pm 0.03\%$  for  $\delta^{56}$ Fe and  $\pm 0.04$  for  $\delta^{56}$ Fe.

Most Fe and Al concentrations and iron speciation data were previously published (**Sperlinginpress**; Tab. 5.3; Kunzmann et al., 2015). New data were obtained following the procedure described in Kunzmann et al. (2015).

### Data

All Fe isotope data are listed in Tab. 5.2. Iron speciation data, Fe and Al concentrations, and FeT/Al ratios are listed in Tab. 5.3. Iron isotope data follow the mass-dependent fractionation line as shown in Fig. 5.8. Iron speciation data indicate that shales were deposited under anoxic-ferruginous or oxic conditions (Fig. 5.9). Euxinic conditions did not prevail during deposition of any shale samples.

### 5.7.2 Model

For the simplified system presented in Fig. 5.4 (main text), the fluxes and isotopic compositions can be treated in terms of two branch points, FeOx and  $Fe(II)_{aq}$ . The pathways of highly reactive iron in and out of the FeOx reservoir must match in terms of fluxes and isotopic compositions

$$\phi_{\rm in}\delta_{\rm in} + \phi_{\rm re-ox}(\delta Fe(II) + \epsilon_{\rm re-ox}) = \phi_{\rm Red}(\delta FeOx + \epsilon_{\rm Red})$$

$$+2/3\phi_{\rm Mag}(\delta FeOx + \epsilon_{\rm Ox-Mag}) + \phi_{\rm Ox-burial}(\delta FeOx + \epsilon_{\rm Ox-burial})$$
(5.2)

where the subscripts *re-ox*, *Red*, *Mag*, *Ox-Mag*, and *Ox-burial* stand for *re-oxidation*, *reduction*, magnetite, oxide to magnetite, and oxyhydroxide burial, respectively. Correspondingly, flows of highly reactive iron in and out of the  $Fe(II)_{aq}$  pool must balance in terms of fluxes and isotopic composition

$$\begin{split} \varphi_{\text{Red}}(\delta FeOx + \epsilon_{\text{Red}}) &= 1/3\varphi_{\text{Mag}}(\delta Fe(II)_{\text{aq}} + \epsilon_{\text{Mag}}) + \varphi_{\text{esc}}(\delta Fe(II)_{\text{aq}} + \epsilon_{\text{esc}}) \\ &+ \varphi_{\text{Carb}}(\delta Fe(II)_{\text{aq}} + \epsilon_{\text{Carb}}) + \varphi_{\text{Py}}(\delta Fe(II)_{\text{aq}} + \epsilon_{\text{Py}}) \\ &+ \varphi_{\text{re-ox}}(\delta Fe(II)_{\text{aq}} + \epsilon_{\text{re-ox}}) \end{split}$$
(5.3)

where the subscripts *esc*, *Carb*, and *Py* represent *escape*, *carbonate*, and *pyrite*, respectively. The isotopic composition of individual pools is controlled by the sizes of the individual fluxes, which together equal  $\phi_{in}$ , and the isotope effects associated with each pathway. Applied fractionation factors are listed in Tab. 5.1 in the main text.

### Figures and tables

![](_page_249_Figure_2.jpeg)

Fig. 5.8 Plot of  $\delta^{56}$ Fe versus  $\delta^{57}$ Fe of all analyzed Neoproterozoic shale samples. Data follow the theoretical mass-dependent fractionation line with a slope of ~1.5 (e.g., Beard and Johnson, 2004).

![](_page_250_Figure_1.jpeg)

Fig. 5.9 Iron speciation data of all analyzed Neoproterozoic shales (grouped by geographical location). Samples were deposited in anoxic-ferruginous and oxic environments. Horizontal grey bar reflects ambiguous samples that could have been deposited in oxic or anoxic environments (see Poulton and Canfield (2011) for recent review).

Tab. 5.2 Iron isotope composition of measured Neoproterozoic shales. Isotopic composition of highly reactive iron
$(\delta^{56} \text{FeHR}_{\text{calc}})$ calculated following equation 1 in the main text. Abbreviations: Drac., Dracoisen Formation; Mac.,
Macdonaldryggen Member; Are., Arena Formation; Rus., Russøya Member; Sva., Svanbergfjellet Formation, Oxf.,
Oxfordbreen Formation; AP, Abraham Plains Formation; RH, Ram Head Formation; G; Gayne Formation; BCC,
Black Canyon Creek Formation; JB, June Beds Formation; Bf, Blueflower Formation; She., Sheepbed Formation;
RA, Reefal Assemblage formation; SG, Strelnye Gory.

Sample		Unit	Age	$\delta^{57} \mathrm{Fe}$	1SE	$\delta^{56} \mathrm{Fe}$	1SE	$\delta^{56}$ FeHR <sub>calc</sub>
section	height		Ma	‰	%0	‰	‰	%0
Svalbard								
G306	159.0	Drac.	630.31	0.47	0.02	0.31	0.01	0.36
G306	156.0	Drac.	630.4	-0.16	0.01	-0.08	0.02	
G306	150.0	Drac.	630.6	0.51	0.09	0.37	0.05	
G306a	143.0	Drac.	630.82	-0.17	0.02	-0.11	0.01	-0.18
G306	131.0	Drac.	630.99	0.03	0.03	0.01	0.01	-0.03
G436	138.0	Drac.	630.77	0.68	0.03	0.36	0.02	0.94
G436	120.0	Drac.	631.4	0.76	0.12	0.51	0.07	2.94
G436	105.0	Drac.	631.8	-0.12	0.02	-0.10	0.02	-0.51
G436	101.5	Drac.	632.0	1.22	0.24	0.83	0.16	2.04
G436	95.5	Drac.	632.1	0.66	0.02	0.45	0.00	2.05
G436	64.0	Drac.	633.2	0.08	0.03	0.03	0.02	0.02
G436	42.0	Drac.	633.9	0.12	0.07	0.06	0.06	0.09
G436	10.5	Drac.	634.88	0.75	0.06	0.44	0.02	2.34
G411	72.0	Drac.	632.96	0.18	0.04	0.12	0.01	0.39
G411	45.0	Drac.	633.83	0.06	0.00	0.05	0.01	0.05
G411	41.0	Drac.	633.96	0.47	0.05	0.34	0.03	0.50
G411	37.0	Drac.	634.09	0.41	0.02	0.31	0.01	0.83
G419	2.6	Mac.	645.59	0.09	0.01	0.08	0.02	0.08
G419	6.7	Mac.	646.05	0.08	0.02	0.06	0.01	0.06
G419	12.3	Mac.	646.68	0.60	0.08	0.40	0.08	0.70
G435	18.0	Mac.	647.3	1.28	0.02	0.94	0.05	
G435	25.0	Mac.	648.1	-0.38	0.01	-0.35	0.01	-0.69
G435	35.0	Mac.	649.2	0.13	0.04	0.08	0.03	0.12
G435	45.0	Mac.	650.4	1.18	0.13	0.79	0.10	1.81
G435	56.0	Mac.	651.6	0.95	0.16	0.41	0.05	0.98
G435	66.0	Mac.	652.7	0.79	0.04	0.50	0.03	0.93
G435a	76.0	Mac.	653.9	0.19	0.06	0.13	0.03	0.25
G435	79.5	Mac.	654.3	0.29	0.02	0.18	0.00	0.40
G407	278.0	Mac.	654.74	0.30	0.02	0.19	0.01	0.73
G407	261.0	Mac.	656.66	0.04	0.03	0.01	0.02	-0.04
G407	245.0	Mac.	658.46	0.07	0.03	0.02	0.00	0.01
G407	233.0	Mac.	659.81	0.08	0.02	0.00	0.02	-0.05
GR12	78.0	Are.	659.39	0.08	0.00	0.05	0.00	0.24
GR12	71.0	Are.	659.89	0.22	0.03	0.16	0.03	0.53
GR12	64.5	Are.	659.36	-0.05	0.09	-0.01	0.01	-0.09
GR12	15.9	Are.	661.86	0.02	0.01	0.04	0.00	0.08
GR12	10.5	Are.	662.24	-0.04	0.04	-0.03	0.03	-0.18
GR12	8.5	Are.	662.39	0.14	0.02	0.09	0.01	0.19
GR12	3.3	Are.	662.77	-0.21	0.12	-0.12	0.05	-0.17
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G519a	-	Rus.	715	0.29	0.03	0.15	0.01	0.37
G519b	-	Rus.	715	0.09	0.05	0.08	0.03	0.38
G521	46.0	Rus.	740.39	0.81	0.15	0.52	0.11	1.30
G521	44.4	Rus.	740.55	-0.21	0.02	-0.22	0.03	-0.45
G521	40.5	Rus.	740.94	0.56	0.01	0.35	0.01	1.60
G521	30.0	Rus.	741.99	0.36	0.03	0.26	0.05	0.49
G521	26.4	Rus.	742.35	0.11	0.06	0.07	0.02	0.10
G521	23.4	Rus.	742.65	0.34	0.10	0.10	0.00	0.47
G521	19.6	Rus.	743.02	1.21	0.03	0.84	0.02	2.54
G521	13.2	Rus.	743.66	1.21	0.06	0.84	0.04	1.97
G521	3.7	Rus.	744.61	0.98	0.03	0.69	0.02	
P5014	52.0	Rus.	742.1	0.36	0.09	0.29	0.08	
P5014	30.5	Rus.	744.17	0.30	0.04	0.23	0.03	
G517	-	Bac.	780.4	0.85	0.01	0.56	0.02	1.23
G155	149.3	Sva.	802.15	0.14	0.01	0.14	0.01	0.51
G155	149.1	Sva.	802.2	-0.23	0.07	-0.17	0.06	-0.19
G155	133.5	Sva.	802.57	1.00	0.10	0.71	0.07	
G155	100.6	Sva.	803.36	0.41	0.16	0.29	0.10	
G155	83.6	Sva.	803.77	0.56	0.00	0.36	0.00	0.37
G471	8.3	Sva.	801.96	0.49	0.12	0.26	0.00	
G471	6.1	Sva.	802.23	0.72	0.04	0.43	0.04	1.60
G426a	-	Oxf.	835	0.24	0.03	0.17	0.02	1.27
G426b	-	Oxf.	835	0.39	0.05	0.30	0.03	1.73
NW Canada								
G14		AP	860	-0.01	0.03	0.02	0.01	0.27
G23	45.0	$\mathbf{RH}$	799.6	0.83	0.05	0.57	0.03	3.69
G23	25.0	$\mathbf{RH}$	800.8	0.80	0.02	0.52	0.00	4.68
G12	1118.0	$\mathbf{RH}$	810.5	1.54	0.02	1.04	0.01	3.37
G12	958.0	G	817.8	0.75	0.05	0.48	0.00	0.87
G0233	189.3	BCC	902.2	-0.09	0.04	-0.23	0.03	-0.44
G0233	105.6	BCC	910.1	0.81	0.05	0.60	0.04	7.41
G0233	95.0	BCC	911.1	0.79	0.05	0.65	0.01	7.04
G0233	37.0	BCC	916.5	0.51	0.21	0.36	0.12	2.86
F1161	196.2	$_{\mathrm{JB}}$	570	-0.12	0.12	-0.10	0.06	-0.26
F1161	31.2	$_{\mathrm{JB}}$	570	0.35	0.00	0.28	0.00	0.39
F1161	28.5	$_{\mathrm{JB}}$	570	-0.10	0.07	0.01	0.03	-0.02
F1163	103.5	Bf	585	0.06	0.10	0.11	0.04	0.52
F1164	84.2	$\operatorname{Bf}$	585	-0.27	0.04	-0.20	0.02	-0.34
F1164	64.0	$\operatorname{Bf}$	585	0.12	0.07	0.08	0.02	0.10
F1164	8.9	$\operatorname{Bf}$	585	0.62	0.04	0.41	0.04	0.81
F1165	237.0	She.	625	0.08	0.09	0.08	0.01	0.71
F1165	205.0	She.	625	0.07	0.01	0.04	0.02	0.13
M106	490	She.	620	-0.02	0.01	0.02	0.01	0.03
M106	107	Cha	699.7	0.54	0.06	0.39	0.03	2.96
	407	one.	022.1	0.04	0.00	0.00	0.00	<b>=</b> .00
M106	$\frac{407}{365}$	She.	624	-0.02	0.00 0.01	0.02	0.00	-0.01
M106 M106	$407 \\ 365 \\ 258$	She. She. She.	622.7 624 627.5	-0.02 -0.09	$0.00 \\ 0.01 \\ 0.02$	0.02 -0.07	0.00 0.02 0.04	-0.01 -0.23

M106	218	She.	628.8	-0.17	0.05	-0.11	0.02	-0.43
M106	159	She.	630.6	-0.08	0.07	-0.06	0.04	-0.19
M106	88.5	She.	632.9	0.00	0.09	-0.02	0.04	-0.08
M106	86.5	She.	633	0.38	0.06	0.28	0.04	0.90
M103	455.3	$\mathbf{R}\mathbf{A}$	825	1.10	0.01	0.74	0.01	4.18
M103	454.8	$\mathbf{R}\mathbf{A}$	825	0.99	0.01	0.66	0.01	2.27
M103	454.3	$\mathbf{R}\mathbf{A}$	825	0.98	0.10	0.73	0.10	1.34
M103	453.8	$\mathbf{R}\mathbf{A}$	825	0.40	0.02	0.31	0.02	0.32
M103	453.3	$\mathbf{R}\mathbf{A}$	825	0.59	0.01	0.43	0.01	1.25
M103	452.8	$\mathbf{R}\mathbf{A}$	825	0.10	0.02	0.11	0.02	0.13
M103	452.3	$\mathbf{R}\mathbf{A}$	825	0.91	0.03	0.64	0.03	1.59
M103	451.8	$\mathbf{R}\mathbf{A}$	825	0.55	0.02	0.39	0.02	0.96
M103	451.3	$\mathbf{R}\mathbf{A}$	825	0.78	0.06	0.53	0.06	2.51
M103	450.8	$\mathbf{R}\mathbf{A}$	825	0.87	0.06	0.58	0.06	2.40
M103	450.3	$\mathbf{R}\mathbf{A}$	825	0.75	0.04	0.51	0.04	2.74
M103	398.8	$\mathbf{R}\mathbf{A}$	830	0.59	0.02	0.41	0.02	0.55
M103	397.8	$\mathbf{R}\mathbf{A}$	830	0.27	0.04	0.11	0.04	0.13
M103	394.4	$\mathbf{R}\mathbf{A}$	830	0.25	0.05	0.21	0.05	0.29
M103	393.9	$\mathbf{R}\mathbf{A}$	830	0.63	0.02	0.44	0.02	0.73
M103	393.4	$\mathbf{R}\mathbf{A}$	830	0.20	0.03	0.18	0.03	0.21
M103	392.9	$\mathbf{R}\mathbf{A}$	830	0.27	0.04	0.31	0.04	0.45
M103	392.4	$\mathbf{R}\mathbf{A}$	830	1.05	0.03	0.84	0.03	5.70
M103	391.9	$\mathbf{R}\mathbf{A}$	830	0.67	0.05	0.53	0.05	2.02
M103	391.4	$\mathbf{R}\mathbf{A}$	830	0.53	0.02	0.37	0.02	0.83
M103	390.9	$\mathbf{R}\mathbf{A}$	830	0.76	0.04	0.57	0.04	1.80
M103	390.4	$\mathbf{R}\mathbf{A}$	830	1.05	0.17	0.65	0.17	4.74
M103	389.9	$\mathbf{R}\mathbf{A}$	830	0.70	0.02	0.53	0.02	4.39
M103	389.4	$\mathbf{R}\mathbf{A}$	830	1.18	0.09	0.79	0.02	2.20
M103	386.0	$\mathbf{R}\mathbf{A}$	830	0.84	0.02	0.57	0.02	4.41
M103	381.0	$\mathbf{R}\mathbf{A}$	830	0.30	0.03	0.20	0.03	0.34
M104	380.3	$\mathbf{R}\mathbf{A}$	830	0.54	0.02	0.39	0.02	1.72
Siberia								
GS2	212.0	$\operatorname{SG}$	1045.2	-0.15	0.05	-0.06	0.04	-0.18
GS2	176.0	$\operatorname{SG}$	1046.9	0.19	0.07	0.15	0.04	0.41
GS2	143.0	$\operatorname{SG}$	1048.4	-0.46	0.11	-0.27	0.05	-0.84
GS2	116.0	$\operatorname{SG}$	1049.7	-0.69	0.02	-0.45	0.02	-0.71
GS4	39.2	$\operatorname{SG}$	1046.3	0.06	0.12	0.04	0.03	0.07
GS4	28.5	$\operatorname{SG}$	1046.8	-0.10	0.07	0.01	0.03	-0.03
GS4	24.5	$\operatorname{SG}$	1047.0	0.02	0.12	0.03	0.07	0.01
GS5	98.8	$\operatorname{SG}$	1048.5	-0.06	0.20	-0.11	0.09	-0.34

Sample		Unit	Fe	Al	FeT/Al	FeCarb	FeOx	FeMag	FePy	FeHR/FeT	FePy/FeHR	Reference
section	height		wt.%	wt.%	-	wt. $\%$	wt. $\%$	wt.%	wt. $\%$	~	2	
Svalbard												
$\mathbf{Svalbard}$												
G306	159.0	Drac.	1.43	6.78	0.21	0.21	0.58	0.03	0.35	0.82	0.30	1
G306	156.0	Drac.										
G306	150.0	Drac.		4.40	1.12							1
G306a	143.0	Drac.	3.96	7.12	0.90	1.15	0.63	0.06	0.98	0.71	0.35	1
G306	131.0	Drac.	3.53	6.92	0.51	0.24	0.85	0.07	0.69	0.52	0.37	1
G436	138.0	Drac.	2.63	7.12	0.37	0.73	0.12	0.06	0.04	0.36	0.04	1
G436	120.0	Drac.	4.26	8.33	0.51	0.38	0.13	0.19	0.02	0.17	0.03	1
G436	105.0	Drac.	5.19	7.34	0.71	0.37	0.13	0.13	0.55	0.23	0.47	1
G436	101.5	Drac.	3.31	7.92	0.42	0.34	0.15	0.11	0.72	0.40	0.54	1
G436	95.5	Drac.	3.82	8.42	0.45	0.31	0.14	0.19	0.18	0.21	0.22	1
G436	64.0	Drac.	3.46	7.96	0.44	0.56	0.24	0.11	0.66	0.45	0.42	1
G436	42.0	Drac.	3.04	7.53	0.40	0.23	0.64	0.11	0.28	0.41	0.22	1
G436	10.5	Drac.	3.71	7.60	0.49	0.38	0.13	0.11	0.05	0.18	0.08	1
G411	72.0	Drac.	3.81	6.80	0.56	0.25	0.53	0.19	0.06	0.27	0.06	1
G411	45.0	Drac.	3.38	4.88	0.69	1.30	0.66	0.08	0.02	0.61	0.01	1
G411	41.0	Drac.	4.37	3.81	1.15	1.71	0.71	0.07	0.27	0.63	0.10	1
G411	37.0	Drac.	4.42	6.71	0.66	0.54	0.77	0.19	0.04	0.35	0.02	1
G419	2.6	Mac.	1.63	4.19	0.39	0.61	0.17	0.01	0.47	0.78	0.37	1
G419	6.7	Mac.	2.23	4.41	0.51	0.72	0.17	0.03	0.72	0.74	0.44	1
G419	12.3	Mac.	2.41	5.52	0.44	0.48	0.12	0.03	0.68	0.54	0.52	1
G435	18.0	Mac.		6.96	0.32							1
G435	25.0	Mac.	2.48	5.83	0.43	0.55	0.47	0.05	0.29	0.55	0.21	1
G435	35.0	Mac.	3.37	7.08	0.48	0.30	0.65	0.05	0.57	0.47	0.36	1
G435	45.0	Mac.	4.18	7.56	0.55	0.50	0.49	0.14	0.65	0.42	0.37	1

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1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1			1	1	1	Η	-
0.54	0.47	0.46	0.44	0.02	0.01	0.02	0.01	0.13	0.38	0.33	0.39	0.53	0.65	0.17	0.00	0.02	0.01	0.01	0.01	0.00	0.00	0.00	0.01	0.00				0.08	0.01	0.14		
0.39	0.52	0.42	0.40	0.24	0.28	0.29	0.28	0.16	0.27	0.22	0.27	0.28	0.36	0.76	0.35	0.18	0.38	0.55	0.21	0.48	0.49	0.18	0.32	0.41				0.44	0.24	0.91		
0.94	1.05	0.83	0.73	0.02	0.01	0.03	0.01	0.14	0.72	0.61	0.83	1.10	1.57	0.43	0.00	0.01	0.01	0.02	0.02	0.00	0.01	0.00	0.01	0.00				0.02	0.01	0.13		
0.14	0.17	0.11	0.16	0.18	0.24	0.20	0.20	0.32	0.39	0.45	0.47	0.30	0.21	0.06	0.34	0.09	0.21	0.25	0.32	0.20	0.47	0.22	0.13	0.04				0.04	0.16	0.03		
0.17	0.33	0.23	0.12	0.35	0.47	0.60	0.56	0.19	0.35	0.20	0.27	0.17	0.19	0.17	1.02	0.17	0.69	1.97	1.06	0.51	2.19	0.39	0.57	0.47				0.18	0.49	0.59		
0.51	0.68	0.61	0.66	0.51	0.56	0.49	0.47	0.46	0.46	0.57	0.55	0.50	0.46	1.93	0.12	0.23	0.22	0.18	0.18	0.20	0.20	0.27	0.27	0.12				0.06	0.23	0.17		
0.58	0.57	0.62	0.61	0.65	0.72	0.72	0.72	0.93	0.99	1.09	1.03	0.99	0.95		0.48	0.57	0.37	0.55	0.97	0.27	0.84	0.66	0.45	0.22	0.34			0.15	0.66	1.37		
7.69	7.55	6.89	6.95	6.77	6.42	6.31	6.15	7.70	7.37	7.51	7.48	7.41	7.07		8.69	4.97	7.93	7.98	7.67	7.07	7.03	7.60	6.77	6.86	7.88			4.71	5.54	0.74	0.14	0.24
4.44	4.32	4.24	4.22	4.41	4.60	4.56	4.40	7.15	7.26	8.17	7.70	7.34	6.69	3.39	4.20	2.84	2.95	4.40	7.42	1.92	5.89	5.02	3.05	1.54	2.66			0.71	3.67	1.01		
Mac.	Mac.	Mac.	Mac.	Mac.	Mac.	Mac.	Mac.	Are.	Rus.	Rus.	Rus.	Rus.	Rus.	Rus.	Rus.	Rus.	Rus.	Rus.	Rus.	Rus.	Rus.	Bac.	Sva.	Sva.	Sva.	Sva.						
56.0	66.0	76.0	79.5	278.0	261.0	245.0	233.0	78.0	71.0	64.5	15.9	10.5	8.5	3.3	ı	ı	46.0	44.4	40.5	30.0	26.4	23.4	19.6	13.2	3.7	52.0	30.5	ı	149.3	149.1	133.5	100.6
G435	G435	G435a	G435	G407	G407	G407	G407	GR12	G519a	G519b	G521	P5014	P5014	G517	G155	G155	G155	G155														

Sva. 0.19 0.24 0.78 0.06 Sva. 3.52 10.15 0.35	0.78 0.06 0.35	0.06	0.07	0.01	0.04	0.96	0.23	1
Sva. 3.16 9.84 0.32 0.08	0.32 $0.08$	0.08	0.57	0.16	0.00	0.26	0.00	1
Oxf. 8.74 6.51 1.34 0.27	1.34  0.27	0.27	0.33	0.49	0.01	0.13	0.01	1
Oxf. 5.57 9.54 0.58 0.27	0.58 0.27	0.27	0.21	0.45	0.00	0.17	0.00	1
AP / 10 13 00 0 39 0 00	0 39 0 00	0.00	0 1 R	0.01	0.00	0.06	000	this study
RH 2.83 7.81 0.36 0.10	0.36 0.10	0.10	0.25	0.07	0.00	0.15	0.01	this study
RH 2.66 7.47 0.36 0.08	0.36 $0.08$	0.08	0.13	0.08	0.00	0.11	0.00	this study
RH 0.73 9.88 0.07 0.04	0.07 $0.04$	0.04	0.16	0.02	0.01	0.30	0.03	this study
G 1.77 9.23 0.19 0.06	0.19 $0.06$	0.06	0.82	0.04	0.00	0.52	0.00	this study
BCC 1.24 5.93 0.21 0.12	0.21 $0.12$	0.12	0.53	0.02	0.02	0.56	0.03	this study
BCC 2.22 8.59 0.26 0.06	0.26 $0.06$	0.06	0.08	0.03	0.01	0.08	0.03	this study
BCC 1.95 8.41 0.23 0.07	0.23 $0.07$	0.07	0.08	0.03	0.00	0.09	0.01	this study
BCC 3.20 9.30 0.34 0.06	0.34 $0.06$	0.06	0.26	0.06	0.01	0.12	0.02	this study
JB 3.17 12.20 0.26 0.09	0.26 $0.09$	0.09	1.31	0.05	0.06	0.48	0.04	2
JB $2.96$ $2.85$ $1.04$ $0.72$	1.04  0.72	0.72	1.01	0.03	0.21	0.67	0.11	2
JB $3.72 \ 10.20 \ 0.36 \ 0.24$	0.36 $0.24$	0.24	1.34	0.03	0.53	0.57	0.25	2
Bf 2.51 10.20 0.25 0.06	0.25 $0.06$	0.06	0.33	0.05	0.02	0.18	0.04	2
Bf 1.04 1.52 0.68 0.34	0.68  0.34	0.34	0.23	0.01	0.09	0.64	0.13	2
Bf 4.84 13.20 0.37 0.06	0.37 $0.06$	0.06	2.64	0.07	0.03	0.58	0.01	2
Bf 0.80 13.10 0.06 0.04	0.06  0.04	0.04	0.35	0.00	0.00	0.48	0.01	2
She. 6.51 9.34 0.70 0.19	0.70  0.19	0.19	0.31	0.19	0.00	0.11	0.00	2
She. 5.03 8.94 0.56 0.10	0.56 $0.10$	0.10	0.95	0.05	0.00	0.22	0.00	2
She. 3.98 9.14 0.44 0.05	0.44 $0.05$	0.05	0.45	0.08	0.04	0.16	0.07	this study
She. 4.45 10.79 0.41 0.13	0.41 $0.13$	0.13	0.36	0.08	0.00	0.13	0.01	this study
She. 3.99 9.57 0.42 0.09	0.42 $0.09$	0.09	1.09	0.09	0.01	0.32	0.01	this study
She. 3.36 9.78 0.34 0.19	0.34 $0.19$	0.19	1.02	0.09	0.01	0.39	0.01	this study
She. 3.72 8.80 0.42 0.61	0.42 $0.61$	0.61	1.36	0.12				this study
She. 3.42 7.05 0.48 0.12	0.48 $0.12$	0.12	0.78	0.06	0.11	0.31	0.11	this study
She. 3.89 8.01 0.49 0.10	0.49 $0.10$	0.10	1.33	0.07	0.14	0.42	0.09	this study
She. 4.07 7.84 0.52 0.21	0.52 $0.21$	0.21	1.73	0.09	0.12	0.53	0.06	this study
She. 2.68 4.00 0.67 0.16	0.67 $0.16$	0.16	0.38	0.04	0.21	0.29	0.26	this study

this study	this study	this study	this study	this study	this study	this study	this study	this study	this study	this study	this study	this study	this study	this study	this study	this study	this study	this study	this study	this study	this study	this study	this study	this study	this study	this study		this study				
0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00		0.51	0.04	0.00	0.66	0.02
0.17	0.28	0.53	0.98	0.32	0.65	0.39	0.38	0.20	0.23	0.18	0.71	0.75	0.67	0.57	0.75	0.64	0.15	0.25	0.42	0.31	0.14	0.12	0.35	0.13	0.52	0.22		0.46	0.32	0.35	0.66	0.28
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.81	0.06	0.00	1.98	0.02
0.02	0.06	0.06	0.16	0.04	0.07	0.05	0.06	0.03	0.05	0.03	0.12	0.20	0.22	0.34	0.15	0.14	0.04	0.03	0.03	0.08	0.02	0.04	0.07	0.10	0.21	0.09		0.16	0.49	0.78	0.18	0.30
0.23	0.50	1.10	9.18	0.61	3.35	0.96	0.85	0.18	0.42	0.24	3.12	3.92	2.47	3.15	3.62	2.60	0.17	0.32	0.64	0.38	0.06	0.19	0.44	0.28	1.32	0.35		0.40	0.48	0.48	0.50	0.50
0.01	0.01	0.02	0.01	0.02	0.02	0.02	0.02	0.01	0.00	0.01	0.04	0.02	0.01	0.00	0.01	0.01	0.04	0.00	0.00	0.02	0.02	0.00	0.02	0.03	0.04	0.02		0.20	0.33	0.82	0.34	0.10
0.15	0.19	0.25	0.96	0.20	0.42	0.23	0.24	0.17	0.20	0.16	0.44	0.56	0.36	0.56	0.48	0.39	0.15	0.17	0.16	0.17	0.11	0.21	0.18	0.24	0.39	0.27		0.48	0.56	0.95	0.67	0.44
9.99	10.74	8.91	9.98	10.13	12.48	11.54	10.19	6.54	9.81	9.54	10.43	9.84	11.08	10.87	10.48	11.03	11.29	7.98	10.02	9.32	7.31	9.19	8.41	13.60	7.63	7.84		7.19	7.71	6.27	6.73	7.39
1.53	2.04	2.23	9.60	2.06	5.28	2.66	2.47	1.14	2.01	1.53	4.62	5.53	4.04	6.09	5.03	4.31	1.75	1.36	1.63	1.55	0.77	1.91	1.51	3.30	2.99	2.13		3.42	4.33	5.94	4.50	3.27
$\mathbf{RA}$	$\operatorname{RA}$	$\operatorname{RA}$	$\operatorname{RA}$	$\operatorname{RA}$	$\mathbf{RA}$	$\mathbf{RA}$	$\operatorname{RA}$	$\mathbf{RA}$	$\operatorname{RA}$	$\operatorname{RA}$	$\mathbf{RA}$	$\operatorname{RA}$	$\operatorname{RA}$	$\operatorname{RA}$	$\operatorname{RA}$	$\operatorname{RA}$	$\operatorname{RA}$	$\mathbf{RA}$	$\operatorname{RA}$	$\operatorname{RA}$		SG	SG	SG	SG	SG						
455.3	454.8	454.3	453.8	453.3	452.8	452.3	451.8	451.3	450.8	450.3	398.8	397.8	394.4	393.9	393.4	392.9	392.4	391.9	391.4	390.9	390.4	389.9	389.4	386.0	381.0	380.3		212.0	176.0	143.0	116.0	39.2
M103	M103	M103	M103	M103	M103	M103	M103	M103	M103	M103	M103	M103	M103	M103	M103	M103	M103	M103	M103	M103	M103	M103	M103	M103	M103	M104	Siberia	GS2	GS2	GS2	GS2	GS4

this study	this study	this study
0.01	0.01	0.01
0.49	0.44	0.38
0.02	0.01	0.01
0.30	0.34	0.25
1.15	1.08	0.88
0.20	0.19	0.25
0.50	0.54	0.32
6.89	6.76	11.41
3.43	3.67	3.68
SG	$S_{\rm C}$	SG
28.5	24.5	98.8
GS4	GS4	GS5

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