

Victor A. Melezhik *Editor-in-Chief*
Lee R. Kump · Anthony E. Fallick
Harald Strauss · Eero J. Hanski
Anthony R. Prave · Aivo Lepland *Editors*

Reading the Archive of Earth's Oxygenation

Volume 3: Global Events and the Fennoscandian
Arctic Russia – Drilling Early Earth Project

Frontiers in Earth Sciences

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Volume 3: Global Events and the
Fennoscandian Arctic Russia -
Drilling Early Earth Project

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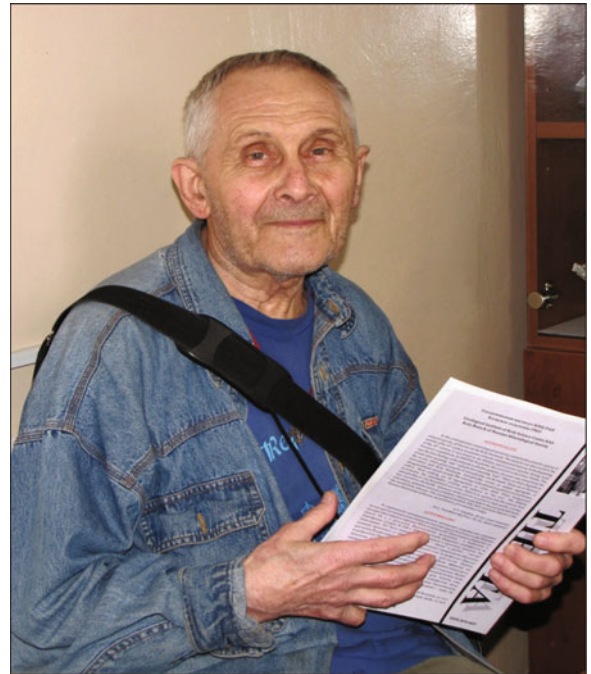
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Dedication

The editors respectfully dedicate this three-volume treatise to Dr. Alexander Predovsky of the Geological Institute of the Russian Academy of Sciences in Apatity. He is one of the earliest explorers of the Precambrian geology in Russian Fennoscandia, and his half century of active work on the geochemistry of sedimentary and igneous rocks provided important foundations for the current understanding of Palaeoproterozoic stratigraphy, geochemistry of sedimentary and volcanic processes and ore formation in the region.



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The three-volume set has three major underpinnings. The first is many years of research in Precambrian geology of the Fennoscandian Shield by many workers, and we acknowledge particularly the support of the Geological Survey of Norway; the University of Oulu, Finland; and the Institute of Geology, Petrozavodsk, Russia.

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Preface to Volume 3

Earth's present-day environments are the outcome of a 4.5-billion-year period of evolution reflecting the interaction of global-scale geological and biological processes. Punctuating that evolution were several extraordinary events and episodes that perturbed the entire Earth system and led to the creation of new environmental conditions, sometimes even to fundamental changes in how planet Earth operated. One of the earliest and arguably the greatest of these events was a substantial increase (orders of magnitude) in the atmospheric oxygen abundance, sometimes referred to as the Great Oxidation Event. Given our present knowledge, this oxygenation of the terrestrial atmosphere and the surface ocean, during the Palaeoproterozoic Era between 2.4 and 2.0 billion years ago, irreversibly changed the course of Earth's evolution. Understanding why and how it happened and what its consequences were are among the most challenging problems in Earth sciences.

The three-volume treatise entitled "Reading the Archive of Earth's Oxygenation" (1) provides a comprehensive review of the Palaeoproterozoic Eon with an emphasis on the Fennoscandian Shield geology; (2) serves as an initial report of the preliminary analysis of one of the finest lithological and geochemical archives of early Palaeoproterozoic Earth history, created under the auspices of the International Continental Scientific Drilling Programme (ICDP); (3) synthesises the current state of our understanding of aspects of early Palaeoproterozoic events coincident with and likely related to Earth's progressive oxygenation with an emphasis on still-unresolved problems that are ripe for and to be addressed by future research. Combining this information in three coherent volumes offers an unprecedented cohesive and comprehensive elucidation of the Great Oxidation Event and related global upheavals that eventually led to the emergence of the modern aerobic Earth System.

The format of these books centres on high-quality photo-documentation of Fennoscandian Arctic Russia – Drilling Early Earth Project (FAR-DEEP) cores and natural exposures of the Palaeoproterozoic rocks of the Fennoscandian Shield. The photos are linked to geochemical data sets, summary figures and maps, time-slice reconstructions of basinal and palaeoenvironmental settings that document the response of the Earth system to the Great Oxidation Event. The emphasis on a thorough, well-illustrated characterisation of rocks reflects the importance of sedimentary and volcanic structures that form a basis for interpreting ancient depositional environments, and chemical, physical and biological processes operating on Earth's surface. Most of the structural features are sufficiently complex as to challenge the description by other than a visual representation, and high-quality photographs are themselves a primary resource for presenting essential information. Although nothing can replace the wealth of information that a geologist can obtain from examining an outcrop first hand, the utility of photographs offers the next best source of data for assessing and evaluating palaeoenvironmental reconstructions. This three-volume treatise will, thus, act as an information source and guide to other researchers and help them identify and interpret such features elsewhere, and will serve as an illustrated guidebook to the Precambrian for geology students.

Finally, the three-volume treatise provides a link to the FAR-DEEP core collection archived at the Geological Survey of Norway. These drillcores are a unique resource that can be used to solve the outstanding problems in understanding the causes and consequences of the multiple processes associated with the progressive oxygenation of terrestrial environments. It is anticipated that the well-archived core will provide the geological foundation for future research aimed at testing and generating new ideas about the Palaeoproterozoic Earth. The three-volume treatise will be of interest to researchers involved directly in studying this hallmark period in Earth history, as well as professionals and students interested in Earth System evolution in general.

Volume 3: “Global Events and the Fennoscandian Arctic Russia – Drilling Earth Project” represents another kind of illustrated journey through the early Palaeoproterozoic, provided by syntheses, reviews and summaries of the current state of our understanding of a series of global events that resulted in a fundamental change of the Earth System from an anoxic to an oxic state. The book discusses traces of life and possible causes for the Huronian-age glaciations; addresses radical changes in carbon, sulphur and phosphorus cycles during the Palaeoproterozoic; and provides a comprehensive description and a rich photo-documentation of the early Palaeoproterozoic supergiant, petrified oil-field. Terrestrial environments are characterised through a critical review of available data on weathered and calcified surfaces and travertine deposits. Potential implementation of Ca, Mg, Sr, Fe, Mo, U and Re-Os isotope systems for deciphering Palaeoproterozoic seawater chemistry and a change in the redox state of water and sedimentary columns are discussed. The volume considers in detail the definition of the oxic atmosphere, possible causes for the oxygen rise, and considers the oxidation of terrestrial environment not as a single event but a slow-motion process lasting over hundreds of millions of years. Finally, the book provides a roadmap as to how the FAR-DEEP cores may facilitate future interesting science and provide a new foundation for education in earth-science community.

Welcome to the illustrative journey through one of the most exciting periods of planet Earth!

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Part VII

**Earth's Oxygenation and Associated Global Events:
The FAR-DEEP Perspective**



7.1 The End of Mass-Independent Fractionation of Sulphur Isotopes

M. Reuschel, H. Strauss, and A. Lepland

7.1.1 Introduction

The Archaean-Proterozoic transition is marked by a number of fundamental upheavals in respect to geological, tectonic, geochemical, biological and climatic aspects. Of these, the most significant change appears to be a substantial increase in atmospheric oxygen concentration initiating the irreversible oxygenation of our planet. It has been proposed that a major oxygenation event occurred during the early Palaeoproterozoic some 2.3 Ga ago, widely termed the “Great Oxidation Event” (“GOE”, Holland 1999, 2006). Evidence for this generally accepted view (but see Ohmoto 1999; Ohmoto et al. 2006, for a different view) stems from geological, mineralogical and geochemical data. Of these, the study of multiple sulphur isotopes, i.e. the analysis of all four stable isotopes of sulphur (^{32}S , ^{33}S , ^{34}S and ^{36}S) developed recently into the central approach for reconstructing the chemical composition of Earth’s early atmosphere, and secular variations thereof. Specifically, it has been suggested that mass-independently fractionated sulphur isotopes, archived in sediments of Archaean and early Palaeoproterozoic age, provide a reliable tool for reconstructing past atmospheric oxygen concentrations (Farquhar et al. 2000; Pavlov and Kasting 2002; Ueno et al. 2009).

The time interval archived in the FAR-DEEP drill cores straddles this crucial time of Earth’s initial oxygenation. This chapter reviews the temporal record of mass-independently fractionated sulphur as a proxy for atmospheric oxygen. We will proceed by briefly introducing the relevant systematics of stable isotope geochemistry including the analysis of multiple sulphur isotopes. This will lead into a discussion about the implications for reconstructing the temporal evolution of atmospheric oxygen abundance.

Finally, the FAR-DEEP rock record that archives the termination of mass-independently fractionated sulphur isotopes will be introduced.

7.1.2 Multiple Sulphur Isotope Systematics

The geochemistry of light stable isotopes (i.e. H, C, N, O, S) has witnessed a long history of applications in earth and life sciences (e.g. Hoefs 2009). For decades, variations in the stable isotopic composition of geomaterials have been utilised for reconstructing environmental conditions and/or for tracing physical, chemical or biological processes in the low- and high-temperature realm. Most frequently, the ratio of a rare over a major stable isotope was considered. Given their natural abundances, the two stable sulphur isotopes ^{34}S (natural abundance of 4.21 %) and ^{32}S (natural abundance of 95.01 %) are generally considered with results reported in the so-called delta notation:

$$\delta^{34}\text{S} [\text{‰}, \text{V} - \text{CDT}] = \left[\left(\frac{{}^{34}\text{S}/{}^{32}\text{S}_{\text{sa}} - {}^{34}\text{S}/{}^{32}\text{S}_{\text{std}}}{\text{}} \right) / \frac{{}^{34}\text{S}/{}^{32}\text{S}_{\text{std}}}{\text{}} \right] \times 1,000 \quad (1)$$

Variations in isotopic composition are based on the fact that two different isotopes of the same element (here ^{34}S and ^{32}S) react differently during a given reaction/process. This is a consequence of different numbers of neutrons for a given number of protons, expressed in their differing isotope mass. The observation that the isotopic composition of a given element prior to (reactant) and after (product) a given reaction is different is termed isotopic fractionation.

Fractionation of stable sulphur isotopes is associated with inorganic as well as biologically mediated reactions and reflects thermodynamic equilibrium and/or kinetic isotope effects (for a recent review, see e.g. Canfield 2001). In principle, isotopic fractionation is a consequence of the relative mass difference between the stable isotopes,

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resulting in different behaviour during physical, chemical and/or biological processes. For sulphur, the mass difference between ^{32}S and ^{33}S is 1 amu (atomic mass unit), which is half of the mass difference between ^{32}S and ^{34}S (2 amu). Consequently, mass dependency dictates the following fractionation relationships between the four different stable sulphur isotopes:

$$\delta^{33}\text{S} = 0.515 \times \delta^{34}\text{S} \quad (2)$$

and

$$\delta^{36}\text{S} = 1.9 \times \delta^{34}\text{S}. \quad (3)$$

Empirical and experimental observations resulted in the general notion that all reactions/processes occurring on Earth, whether physical, chemical or biological, result in **mass-dependent isotopic fractionation (MDF)**. As a consequence, researchers have concentrated for decades on determining the $\delta^{34}\text{S}$ value of a given sulphur-bearing compound, accepting that mass-dependency would allow calculation of the other isotope ratios (if needed).

In strong contrast to these observations in terrestrial materials, it was discovered early on that extraterrestrial materials are characterised by a clearly different behaviour in isotopic fractionation and exhibit so-called mass-independently fractionated isotopes (e.g. sulphur: Hulston and Thode 1965; oxygen: Clayton et al. 1977). In addition, Thiemens and Heidenreich (1983) observed the existence of similar mass-independent (oxygen) isotope fractionation during ozone production reflecting photochemically induced processes in Earth's present atmosphere.

Following this reasoning, **mass-independent fractionation of sulphur isotopes (MIF-S)** means that:

$$\delta^{33}\text{S} \neq 0.515 \times \delta^{34}\text{S} \quad (4)$$

and

$$\delta^{36}\text{S} \neq 1.9 \times \delta^{34}\text{S}. \quad (5)$$

Renewed interest in the study of multiple sulphur isotopes and the application to geological and biological questions required the formulation of a (now commonly accepted) way for reporting results, notably as $\Delta^{33}\text{S}$ (respectively $\Delta^{36}\text{S}$). This term quantifies the deviation of a measured $\delta^{33}\text{S}$ ($\delta^{36}\text{S}$) value from the calculated $\delta^{33}\text{S}$ ($\delta^{36}\text{S}$) value if mass-dependent fractionation (MDF) would have happened (Farquhar et al. 2000):

$$\Delta^{33}\text{S} = \delta^{33}\text{S} - 1,000 \times \left((1 + \delta^{34}\text{S}/1,000)^{0.515} - 1 \right) \quad (6)$$

and:

$$\Delta^{36}\text{S} = \delta^{36}\text{S} - 1,000 \times \left((1 + \delta^{34}\text{S}/1,000)^{1.9} - 1 \right). \quad (7)$$

In general, studies on modern geo- and biomaterials revealed that variations in $\Delta^{33}\text{S}$ of $\pm 0.3 \text{ ‰}$ are attributed to mass-dependent sulphur isotope fractionation (given an external precision for $\Delta^{33}\text{S}$ of $\pm 0.008 \text{ ‰}$, Zerkle et al. 2009, 2010). In contrast, deviations from this array (i.e. a $\Delta^{33}\text{S}$ that is larger than $\pm 0.3 \text{ ‰}$) reflect the presence of mass-independent fractionation processes. Currently, no threshold value has been agreed for $\Delta^{36}\text{S}$, which allows a distinction between MDF or MIF-S as known for $\Delta^{33}\text{S}$, but we note that external precision for $\Delta^{36}\text{S}$ is $\sim 0.3 \text{ ‰}$ (e.g. Bao et al. 2007).

7.1.3 The Multiple Sulphur Isotope Record of Precambrian Sedimentary Rocks

For decades, our understanding of the Precambrian global sulphur cycle was based on temporal records of the traditional $\delta^{34}\text{S}$ value measured in sedimentary sulphates and sulphides (for reviews, see e.g. Strauss 2002, 2004; Lyons et al. 2004; Kah et al. 2004; Canfield 2004). These records suggest a low-sulphate Precambrian ocean (e.g. Lyons and Gill 2010), a non-linear increase in $\delta^{34}\text{S}_{\text{sulphate}}$, as a consequence of the growing importance of biological sulphur cycling in the sedimentary realm (e.g. Strauss 2004; Guo et al. 2009; Lyons and Gill 2010), and the onset of bacterial sulphate reduction in the early Palaeoproterozoic (e.g. Strauss 2002) or in the Neoproterozoic (e.g. Grassineau et al. 2001) or possibly as early as in the Palaeoarchaeon (e.g. Shen et al. 2009). These conclusions are based on two simple observations, notably (1) a sizeable difference in the sulphur isotopic composition between (reconstructed) seawater sulphate and sedimentary sulphide, and (2) a substantial deviation in $\delta^{34}\text{S}$ from the crustal average value. Given the paucity of preserved sulphate occurrences in the Precambrian sedimentary record (see Chap. 7.5), the interpretation in respect to early sulphur cycling is largely based on the sedimentary sulphide record. Here, special emphasis is placed on detecting the activity of sulphur-utilising microbes, specifically bacterial sulphate reduction. Today, this form of microbial sulphur cycling is associated with substantial isotope fractionation. Sulphate reducing bacteria preferentially metabolise $^{32}\text{SO}_4$ causing a proposed maximum fractionation of 45 ‰ between seawater sulphate and hydrogen sulphide (Canfield 2001). Pyrite, which is formed if reduced iron is available, is depleted in ^{34}S and its burial leads to an enrichment of ^{34}S in the seawater sulphate pool. The Precambrian record of sulphide $\delta^{34}\text{S}$ is characterised by

near zero $\delta^{34}\text{S}$ values during the Archaean (with few exceptions, e.g. Grassineau et al. 2001; Philippot et al. 2007; Shen et al. 2009), indicating the apparent absence of microbial turnover of sulphate. Unquestionable evidence for bacterial sulphate reduction, based on high-magnitude isotope fractionation, with strongly negative $\delta^{34}\text{S}$ as low as -34.7‰ (Bekker et al. 2004) at seawater sulphate sulphur isotopic compositions between $+10$ and $+20\text{‰}$ (Schröder et al. 2008; Guo et al. 2009) does not occur in the rock record before 2.3 Ga. This increase in microbially induced sulphur isotope fractionation between parent seawater sulphate and produced hydrogen sulphide (deposited as pyrite) is suggested to be the result of increasing oceanic sulphate concentrations, connected to the rise in atmospheric oxygen concentration and subsequent onset of oxidative weathering of sulphides.

The discovery of MIF-S in terrestrial sedimentary sulphides and sulphates of Precambrian age by Farquhar et al. (2000) strongly stimulated the field of stable sulphur isotope geochemistry. Multiple sulphur isotope studies over the past 10 years (e.g. Farquhar et al. 2000, 2007; Mojzsis et al. 2003; Ono et al. 2003, 2009a, b; Ohmoto et al. 2006; Guo et al. 2009; Thomazo et al. 2009) revealed a distinct MIF-S signature in sedimentary sulphides and sulphates of Archaean and early Palaeoproterozoic age (Fig. 7.1). During this time the $\Delta^{33}\text{S}$ values display a spread between -2.5 and $+11.2\text{‰}$ with clearly discernible temporal variations in the range of $\Delta^{33}\text{S}$ values. While the Eoarchaeon and Palaeoarchaeon sediments yielded $\Delta^{33}\text{S}$ values between -1.7 and $+6.1\text{‰}$, the subsequent Mesoarchaeon time interval between 3.2 and 2.7 Ga displays only minimal anomalies in $\Delta^{33}\text{S}$ for sedimentary sulphides. In strong contrast, high-magnitude fractionations between -2.5 and $+11.2\text{‰}$ characterise the MIF-S record for the Neoarchaeon and early Palaeoproterozoic. Finally, the distinct MIF-S signature disappears from the sedimentary rock record in the early Palaeoproterozoic between 2.3 and 2.5 Ga ago (e.g. Guo et al. 2009). Younger Proterozoic and Phanerozoic rocks through to the modern world display exclusively mass-dependently fractionated sulphur isotope values.

MIF-S is thought to originate from photochemical reactions of sulphur dioxide, induced by short-wave UV rays in an oxygen-free atmosphere (e.g. Farquhar et al. 2001). Under the modern oxidising atmospheric conditions, sulphur is only present as aerosol of sulphuric acid with a homogenous sulphur isotopic composition. However, given a chemically reducing atmosphere as suggested for the Archaean and early Palaeoproterozoic (prior to the GOE), isotopically different sulphur species (such as elemental sulphur and aerosols of sulphate) would have been generated, preserved, and subsequently transferred to Earth's surface (Kasting et al. 1989; Pavlov and Kasting 2002; Ono et al. 2003). This way, distinct MIF-S signatures

were archived in the ancient sedimentary rock record as sulphate and sulphide.

Following the early observations by Farquhar et al. (2000) and subsequent experimental work (Farquhar et al. 2001), different atmospheric sulphur-bearing phases are thought to carry distinct MIF-S signals. Elemental sulphur is regarded as the main carrier of a positive $\Delta^{33}\text{S}$ signature whereas sulphate aerosols are thought to be the carrier for a corresponding negative $\Delta^{33}\text{S}$ signal (e.g. Farquhar and Wing 2003; Ono et al. 2003). However, modelling by Ueno et al. (2009) revealed that sulphate aerosols might also acquire positive $\Delta^{33}\text{S}$ values. In their model, all SO_2 that enters the atmosphere is converted into carbonyl sulphide (OCS). This would lead to high levels (>1 ppm) of atmospheric OCS given a volcanic sulphur flux that is three times higher than today (Bluth et al. 1993; Ueno et al. 2009). Due to the high UV shielding effect of OCS, the sulphate acquires a negative $\Delta^{33}\text{S}$ signature, a feature consistent with MIF-S data for the Archaean sulphate occurrences. A decrease in the volcanic sulphur flux could, hence, explain the positive $\Delta^{33}\text{S}$ recorded in carbonate-associated sulphate (CAS; for a detailed description about CAS as palaeoproxy see Chap. 7.5) from the Transvaal Supergroup (South Africa) and Hamersley Basin (Western Australia) (Guo et al. 2009; Domagal-Goldman et al. 2008).

Considering the different magnitudes of the MIF-S signal and the apparent temporal variation of it, the MIF-S record has been interpreted to reflect differences in the chemical composition of the atmosphere. Most conspicuous in that respect are sedimentary sulphides of Mesoarchaeon age between 3.2 and 2.7 Ga that display attenuated $\Delta^{33}\text{S}$ values only minimally above the threshold for non-zero $\Delta^{33}\text{S}$, i.e. $0 \pm 0.3\text{‰}$. Respective data have been interpreted to reflect an early oxic atmosphere (Ohmoto et al. 2006). However, subsequent studies regard even these greatly attenuated $\Delta^{33}\text{S}$ values to reflect MIF-S (Farquhar et al. 2007; Domagal-Goldman et al. 2008; Thomazo et al. 2009). This interpretation is based on considering $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ relationships. On a plot of $\Delta^{36}\text{S}$ versus $\Delta^{33}\text{S}$, the Archaean and earliest Palaeoproterozoic samples plot along a regression line with a slope of around -1 . This is quite different for Phanerozoic sulphides, which define a slope varying between -4.4 and -9.8 in a $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ diagram, with an average slope of $\Delta^{36}\text{S}/\Delta^{33}\text{S} = -6.9$ (Fig. 7.2, Ono et al. 2006). The fact that observational data agree with respective multiple sulphur isotope results from experimental studies performed under simulated anoxic atmospheric conditions (Farquhar et al. 2001) indicates the significance of $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ relationships in identifying MIF-S even when $\Delta^{33}\text{S}$ is substantially minimised (Farquhar et al. 2007; Ono et al. 2006). Consequently, low yet clearly non-zero $\Delta^{33}\text{S}$ values cannot be considered as evidence for an early oxygenation of Earth's atmosphere.

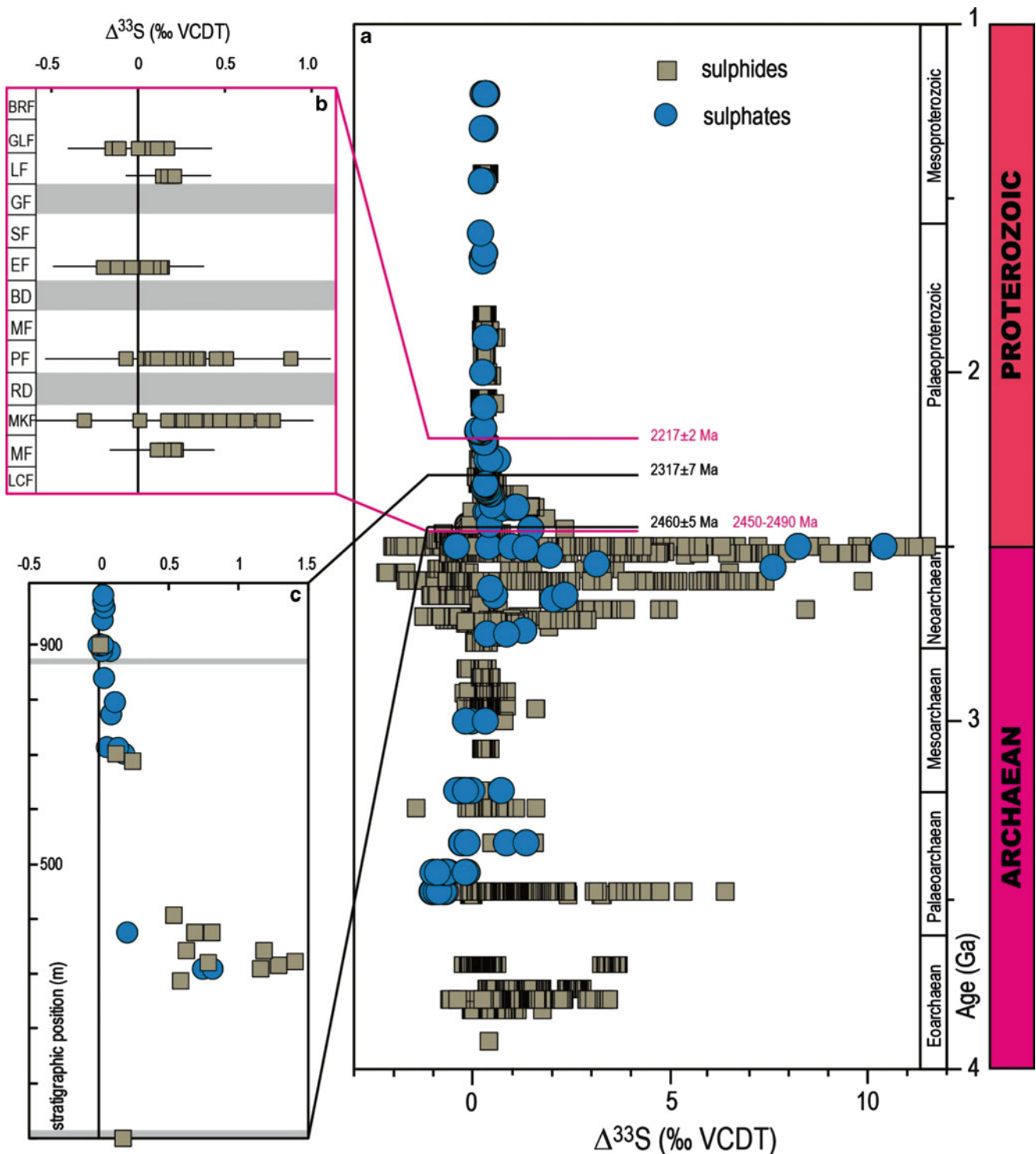


Fig. 7.1 (a) Temporal evolution of $\Delta^{33}\text{S}$ recorded in sedimentary sulphides and sulphates (Source of data: Domagal-Goldman et al. 2008; Guo et al. 2009; Ono et al. 2009a,b; Shen et al. 2009; Thomazo et al. 2009; Johnston et al. 2005, 2006, 2008; Partridge et al. 2008; Bao et al. 2007; Farquhar et al. 2007; Hou et al. 2007; Kamber and Whitehouse 2007; Kaufman et al. 2007; Papineau et al. 2005, 2007; Papineau and Mojzsis 2006; Philippot et al. 2007; Cates and Mojzsis

2006; Jamiesson et al. 2006; Ohmoto et al. 2006; Whitehouse et al. 2005; Hu et al. 2003; Mojzsis et al. 2003; Ono et al. 2003; Farquhar et al. 2002, 2000). (b) Variations in $\Delta^{33}\text{S}$ within the Huronian Supergroup after Papineau et al. (2007); Formation names are listed in Fig. 7.3. (c) Temporal variations in $\Delta^{33}\text{S}$ of carbonate-associated sulphates and sulphides of the Duitsland Formation (Transvaal Supergroup/South Africa) after Guo et al. (2009)

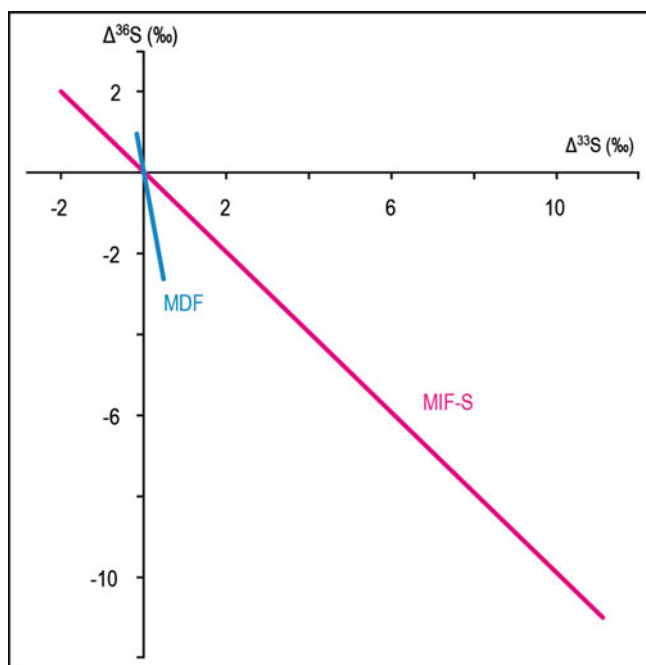


Fig. 7.2 Generalised plot for $\Delta^{36}\text{S}$ and $\Delta^{33}\text{S}$ relationships. The blue line shows the regression line observed for Palaeo-, Meso-, and Neoproterozoic and Phanerozoic sulphur species with an average slope of -6.9 (MDF = mass-dependent sulphur isotope fractionation; variations in the slope between -4.4 and -9.9 have been observed; Ono et al. 2006, 2007; Johnston et al. 2006). Archaean and earliest Palaeoproterozoic sulphur species are typically plotting on a regression line with a slope of -1 (MIF-S = mass-independent fractionated sulphur isotopes; Farquhar et al. 2001; Ono et al. 2003, and references of Fig. 7.1), shown by the red line

In contrast, the low $\Delta^{33}\text{S}$ signal in the Mesoarchaeal samples is viewed to reflect either changing atmospheric chemistry (i.e. different mechanism for MIF production) or the occurrence of an organic haze layer in the troposphere due to the activity of methanotrophs that prevents deep UV penetration of the atmosphere (Domagal-Goldman et al. 2008; Thomazo et al. 2009). A shield of organic haze, in addition to preventing the SO_2 photochemistry of short-wave UV rays, may also lead to a global cooling of the Earth's surface. Diamictites within the 2.9 Ga South African Witwatersrand Supergroup and faceted clasts within the coeval Pongola Supergroup are thought to be of glacial origin (Young 1988; Crowell 1999), which would yield a consistent environmental picture if the glaciation was of global nature. The disappearance of the organic haze and thus a return to greenhouse climate conditions could have led to the final rise of the variations in $\Delta^{33}\text{S}$ (Ono et al. 2009a, b; Kaufman et al. 2007) until the large magnitude MIF-S disappears seemingly abruptly after ~ 2.4 Ga (Farquhar et al. 2000; Farquhar and Wing 2003; Papineau et al. 2005).

Neoarchaeal sulphides from the Transvaal Supergroup and the Hamersley Basin display the largest variation in

$\Delta^{33}\text{S}$ throughout the Archaean and include the highest positive anomaly with a $\Delta^{33}\text{S}$ value of 11.2 ‰ (Kaufman et al. 2007). Zahnle et al. (2006) argue that a decrease in the atmospheric methane concentration could have led to the decrease in elemental sulphur production and this would explain subsequent vanishing of the highly positive $\Delta^{33}\text{S}$ anomalies. Within temporal resolution, the largest documented positive $\Delta^{33}\text{S}$ signal (Kaufman et al. 2007) is followed by a sharp decline and ultimate loss of the MIF-S signature in the sedimentary rock record. This change from the mass-independent signal to solely mass-dependent fractionation of sulphur isotopes is associated with the rise in atmospheric oxygen above 10^{-5} PAL (present atmospheric level, Pavlov and Kasting 2002). Few systematic studies provide a record of this temporal window between 2.50 and 2.35 Ga ago, but most prominent are those of the Huronian Supergroup in North America (between 2.5 and 2.2 Ga) and the Transvaal Supergroup in South Africa (between 2.4 and 2.3 Ga).

The Palaeoproterozoic Huronian Supergroup represents a more than 10-km-thick volcano-sedimentary succession that is presently best exposed north of Lake Huron, Ontario, Canada. The age of the succession is constrained between 2.49 and 2.45 Ga (basal Copper Cliff Rhyolite; Krogh et al. 1984) and 2.219 Ga (intrusive Nipissing diabase; Corfu and Andrews 1986). The Huronian Supergroup comprises three stratigraphic units containing sedimentary rocks of glacial origin (from bottom to top: Ramsay Lake Formation, Bruce Formation, Gowganda Formation), separated by respective interglacial units (for a detailed description see Chap. 7.2). Ion microprobe multiple sulphur isotope analyses for sulphides from the Huronian Supergroup were presented in Papineau et al. (2005, 2007). The characterization of authigenic sedimentary or hydrothermal sulphides, and detrital pyrite, and their mass-independent as well as mass-dependent isotopic fractionation patterns have been used in these studies to reconstruct the evolution of atmospheric oxygen abundance, and to trace the activity of sulphate-reducing bacteria within the depositional environment. Most notably, the record of mass-independently fractionated sulphur isotopes indicates that oxygen levels increased irreversibly in the aftermath of the Huronian glaciations (Fig. 7.3). The sedimentary rocks of the Pectors Formation that post-date the Ramsay Lake glacials and represent the first interglacial interval still show small magnitude MIF-S. In contrast, the strata above the second glacial (Bruce Formation) level only show large-range mass-dependent fractionation (Papineau et al. 2007). This indicates that atmospheric oxygen levels increased enough to prevent further mass-independent sulphur isotope fractionation. Increasing atmospheric oxygen levels would have triggered oxidative continental weathering, enhancing weathering rates and likely delivering more nutrients to the ocean, which would have

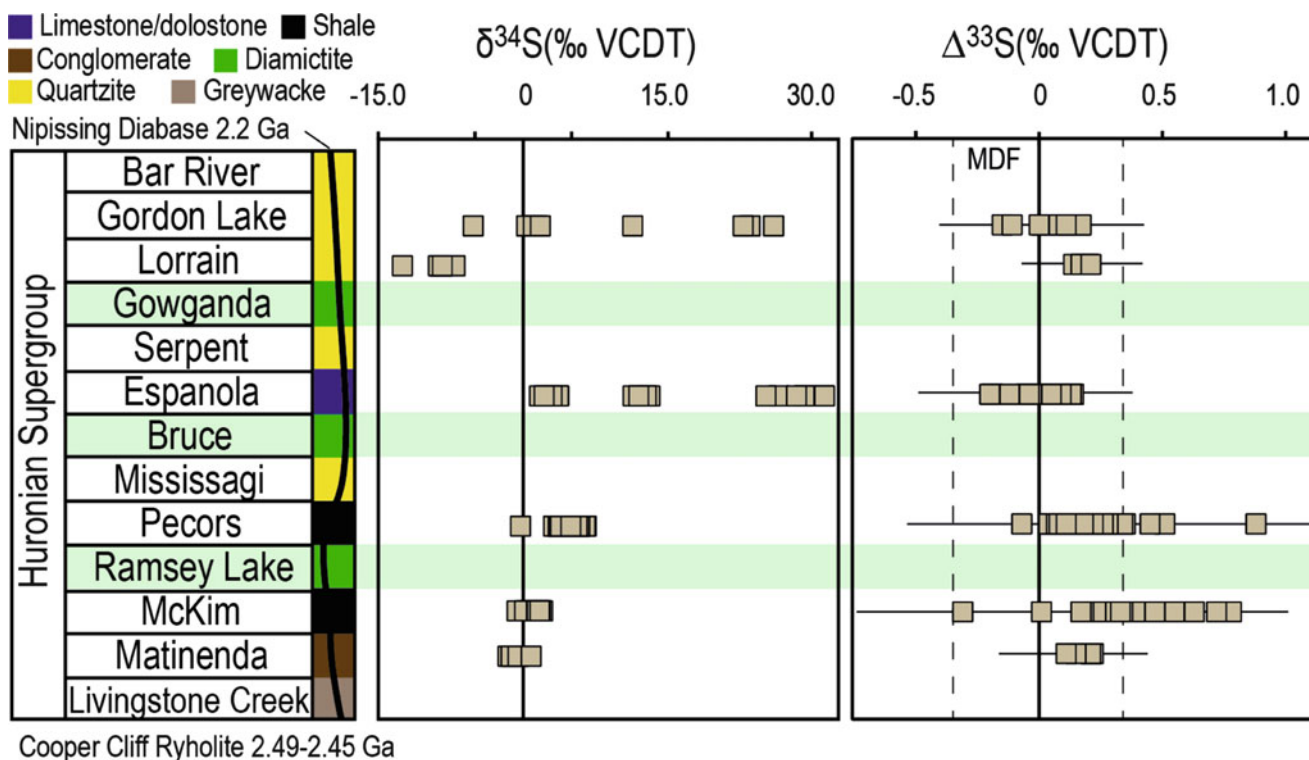


Fig. 7.3 Stratigraphic evolution of $\Delta^{33}\text{S}$ across the Huronian glaciations (Modified after Papineau et al. 2007)

further stimulated oxygenic photosynthesis. Further, such weathering would have also activated the oxidative decomposition of continental sulphide minerals resulting in an enhanced delivery of dissolved sulphate to the ocean, which likely stimulated bacterial sulphate reduction. In this respect, the large range in $\delta^{34}\text{S}$ for sulphides of the second and third glacial and interglacial strata is thought to result from the enhanced microbial turnover of sulphate under variable seawater sulphate concentrations (see Chap. 7.5). This change from MIF to MDF sulphur isotope pattern is not only visible in the sedimentary record from North America, but also in post-glacial strata from Finland and South Africa (Papineau et al. 2005).

The Transvaal Supergroup in South Africa also captures the critical time window of the Archaean-Palaeoproterozoic transition. Here, the Duitsland Formation, which is sandwiched between glaciogenic deposits, is suggested to record the increase of the oceanic sulphate reservoir and the coeval loss of the MIF-S signature archived in sedimentary sulphur, both connected to the rise in atmospheric oxygen. Guo et al. (2009) presented a record of paired multiple sulphur isotope measurements ($\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$) from sulphides and carbonate-associated sulphate. Multiple sulphur isotope data reveal that the Duitsland Formation records the demise of MIF-S, in parallel with an increase

in the range of mass-dependent sulphur isotope fractionation (Fig. 7.4). Although a global correlation of the glacial events of the Huronian glaciation remains speculative, the loss of MIF-S within the upper Duitsland Formation is consistent with the data from the Huronian Supergroup described above. Positive $\delta^{34}\text{S}$ values in the upper Duitsland Formation also point to an increase in the seawater sulphate concentration with progressive bacterial sulphate reduction linked to an enhanced nutrient delivery during the interglacial period.

At present, strata from the Huronian Supergroup in North America and from the Transvaal Supergroup in South Africa are exclusive recorders of the termination of mass-independent sulphur isotope fractionation. They indicate that an irreversible increase in atmospheric oxygen occurred between the first and second glacial event of the Huronian Glaciation (Papineau et al. 2007; Guo et al. 2009). Following Pavlov and Kasting (2002), the disappearance of the MIF-S signature indicates that atmospheric oxygen levels rose from less than 10^{-5} PAL to more than 10^{-2} PAL during the early Palaeoproterozoic. The sulphur cycling after this first rise in atmospheric oxygen is associated exclusively with mass-dependent sulphur isotope fractionation and $\delta^{34}\text{S}$ values that clearly reflect the activity of sulphate reducing bacteria (Bekker et al. 2004; Papineau et al. 2005; Guo et al. 2009).