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Biological activity and the Earth's surface evolution: Insights from carbon, sulfur, nitrogen and iron stable isotopes in the rock record

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Abstract

The search for early Earth biological activity is hindered by the scarcity of the rock record. The very few exposed sedimentary rocks have all been affected by secondary processes such as metamorphism and weathering, which might have distorted morphological microfossils and biogenic minerals beyond recognition and have altered organic matter to kerogen. The search for biological activity in such rocks therefore relies entirely on chemical, molecular or isotopic indicators. A powerful tool used for this purpose is the stable isotope signature of elements related to life (C, N, S, Fe). It provides key informations not only on the metabolic pathways operating at the time of the sediment deposition, but more globally on the biogeochemical cycling of these elements and thus on the Earth's surface evolution. Here, we review the basis of stable isotope biogeochemistry for these isotopic systems. Rather than an exhaustive approach, we address some examples to illustrate how they can be used as biosignatures of early life and as proxies for its environment, while keeping in mind what their limitations are. We then focus on the covariations among these isotopic systems during the Archean time period to show that they convey important information both on the evolution of the redox state of the terrestrial surface reservoirs and on co-occurring ecosystems in the Archean. ***To cite this article: C. Thomazo et al., C. R. Palevol 8 (2009).***

Résumé

Apport des isotopes stables (C, N, S, Fe) à l'étude des interrelations entre activités biologiques et conditions physicochimiques de surface de la terre primitive. La recherche et la caractérisation des écosystèmes à la surface de la Terre primitive sont un défi, étant donné le faible degré de préservation des roches archéennes. Les quelques formations sédimentaires disponibles ont, en effet, été modifiées par de nombreux processus secondaires (métamorphisme, altération) qui excluent toute diagnose morphologique robuste des microfossiles et des minéraux associés. La recherche de traces de vie fossile et la caractérisation des environnements contemporains du dépôt reposent ainsi sur des indices chimiques dont les plus robustes sont les isotopes stables. Dans ce manuscrit, nous tenterons de résumer les bases de la biogéochimie des isotopes stables et nous illustrerons comment cette discipline peut permettre d'apporter des contraintes sur la vie primitive et son environnement. Quelques exemples choisis dans différents systèmes isotopiques pertinents pour l'étude de la vie (C, N, S, Fe) et pour l'étude des conditions d'oxydation de surface de la Terre primitive

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(fractionnement indépendant de la masse du soufre) nous permettrons d'illustrer de façon non exhaustive l'approche isotopique et ses limitations dans la recherche de biosignatures. Enfin, nous présenterons les variations séculaires de ces 4 isotopes durant l'Archéen, afin d'illustrer les interrelations biogéochimiques dans les cycles C-S-N-Fe. ***Pour citer cet article : C. Thomazo et al., C. R. Palevol 8 (2009).***

Keywords: Isotopes; Biosignature; Carbon; Nitrogen; Sulfur; Iron; Mass independent fractionation; Archean

Mots clés : Isotopes stables ; Biosignature ; Carbone ; Azote ; Soufre ; Fer ; Archéen

1. Introduction

Life is maintained by a set of chemical reactions called metabolism and organized into pathways, in which one chemical compound (the reagent) is transformed into another (the product) by a sequence of enzymes. Enzymes help living organisms to drive desirable but thermodynamically unfavorable reactions by coupling them to favorable ones. In most cases, for the same reaction (same reagents and same products), biotic and abiotic pathways differ strongly in the mechanisms and number of steps involved, and therefore in speed, yield and – of particular interest here – in the fractionation of stable isotopes.

Most of elements with stable isotopes show variations in the abundances of the minor relative to the major isotope from one chemical species to the other. Their partitioning between two chemical species A and B can be quantitatively described by a fractionation factor ($\alpha_{B/A} = R_B/R_A$), where R represents the ratio between the heavy and the light isotope. In general, isotope effects are small, $\alpha \sim 1$, so that the deviation of α from 1 is used rather than the fractionation factor. For biologically mediated reactions, this quantity, to which we refer as the fractionation, is defined by $\varepsilon_{B/A} = 1000*\ln(\alpha_{B/A}) \approx (\alpha_{B/A}-1)*1000$. Practically, the isotope composition is reported in the usual δ-notation: $\delta = (R/R_{STD}\text{-}1)*1000$, where R and R_{STD} are the sample and standard isotopic ratios respectively. The fractionation can therefore be expressed simply as $\varepsilon_{B/A} = \delta_B - \delta_A$ in parts per thousand.

The validity of using stable isotopes of life-related elements (such as C, N, S or Fe) in the search for early life hinges on the assumptions that early life employed metabolic pathways essentially similar to those observed in the present and exerted similar fractionation effects. Its potential for identifying and characterizing metabolisms in the rock record is illustrated by a rapidly growing number of stable isotope studies on Archean sedimentary rocks. It depends essentially on the difference between biotic and abiotic fractionation factors and the preservation in the rock record of pristine isotopic compositions of reagents and/or products of metabolisms.

In the present contribution, we review four isotopic system of biological interest (C, N, S, Fe). We develop some examples for each, where we evaluate their potential as a proxy for searching life. Finally, we review the temporal isotopic variations of these four isotopic systems to illustrate the interplay of C-S-N-Fe biogeochemical cycling that occurred in ancient Earth.

2. Carbon isotopes

2.1. Biological fractionation of C isotopes

Carbon has two stable isotopes: ^{12}C accounting for 98.9% of the total abundance and ^{13}C, making up the balance of 1.1%. The international standard for $\delta^{13}C$ measurements is the PDB. Autotrophic organisms employ various pathways for inorganic C assimilation (i.e. carboxylation) with specific isotope fractionation (see Table 1), which always favor the lighter isotope. The resulting C_{org} is thus ^{12}C-enriched relative to the inorganic C compounds from which it feeds from [83,85]. In contrast, heterotrophic organisms have the same isotopic composition as the organic matter they feed from. Thus, organic matter derived from heterotrophic organisms records the isotopic composition of the primary producers in a food chain.

Fractionation during C assimilation is the result of a kinetic isotope effect inherent to irreversible enzymatic CO_2-fixing reactions. In case of the quantitatively dominant carboxylation pathway by ribulose-1.5-bisphosphate (RuBP) carboxylase and the subsequent Calvin–Benson cycle, the magnitude of the isotope effect mostly ranges between 17 and 30‰ (Table 1). This large range derives from the facts that:

- the fractionation in enzymatic reactions varies widely as a function of pH, metal cofactor, temperature and number of other variables [129];
- the different types of RuBisCO enzyme are characterized by different carbon isotope fractionation.

RuBisCO IB and IA give a maximum fractionation of ∼30‰ [111] and ∼24‰ [102], respectively

Table 1
Isotopic effect associated with the fixation of inorganic carbon by autotrophs. (Modified after [53]).
Tableau 1
Effet isotopique associé à la fixation de carbone inorganique par les autotrophes (modifié d'après [53]).

Carboxylation pathway	ε, ‰	Operated by
Calvin cycle/Rubisco (form I)	17–30	C3, C4 and CAM plants, algae
Calvin cycle/Rubisco (form II)	19.5–22	Cynobacteria, purple and chemoautotrohic bacteria
Reductive acetyl-CoA/methanogenese, acetogenese	15–58	Methanogenic bacteria (CO_2 to CH_4)
Reductive acetyl-CoA	16–39	Sulfur reducing bacteria
3-hydroxyprorionate cycle	0–7	Anoxygenic photoautotrophic bacteria
Reductive citric acid cycle	4–13	Anoxygenic photoautotrophic bacteria

and RuBisco II has a smaller fractionation ∼19.5‰ in photoautotrophic purple bacteria [94]. Fractionations are lower for anoxygenic photoautotrophic bacteria that employ either the 3-hydroxypropionate pathway or the reductive tricarboxylic acid cycle (Table 1; [106]). Anaerobes using the acetyl-CoA pathway can produce acetate and/or methane with a fractionation factor comprised between 15 and 58‰. Methane produced by methanogens bacteria using this pathway is probably the most fractionated with extremely ^{13}C-depleted CH_4 relative to CO_2 (∼58‰, [116]). Incorporation of this methane into biomass is performed during methanotrophic assimilation with an associated fractionation of 10 to 34‰ [131]. It produces the isotopically lightest organic carbon observed in the terrestrial biosphere with $\delta^{13}C$ values < -80‰ [39].

2.2. Identifying biological C isotope fractionation in Archean rocks

Two distinct families of C-bearing compounds are found in sedimentary rocks, namely organic carbon (C_{org}) and carbonate (C_{carb}). Carbonates are mainly composed of the skeletal remains of calcite or aragonite secreting organisms, and of inorganically precipitated carbonate crystals in the water column, on the sea floor or as intergrain cements. In any case, carbonates record the isotopic composition of Dissolved Inorganic Carbon (DIC) from which they precipitate, with an offset of the order of 1‰ due to thermodynamic isotopic equilibrium [82]. We can therefore use Archean $\delta^{13}C_{carb}$ values as reliable indicators of the DIC isotope ratios in early Earth environments, i.e., from surface waters to sediment porosity depending on the carbonate type. Sedimentary organic matter originates from residues of living organisms, which have survived remineralization. Several parameters control its $\delta^{13}C_{org}$ ([123] for a review), including source effects (isotopic composition of the DIC), kinetic effects associated to the C assimilation and to a minor extend, the kinetic effects associated to the recycling into biosphere and remineralization in the water column and sediments. When the isotopic composition of the C source is recorded in the $\delta^{13}C_{carb}$, the difference between $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ ($\Delta^{13}C_{org\text{-}carb} = \delta^{13}C_{org} - \delta^{13}C_{carb}$) can be used as a good approximation of the kinetic effects associated to the carbon assimilation pathways and can thus be used as a proxy for life in sedimentary rocks.

2.3. Fischer-Tropsch fractionation of C stable isotope

The most important concern that could invalidate the use of C isotope as a proxy for life would be the existence of inorganic processes able to mimic, in direction and magnitude, metabolic-induced isotopic fractionations. One serious candidate is the Fischer-Tropsch Type reaction (FTT), which produces reduced C from oxidized C (e.g. CO_2) in hydrothermal environments. Hydrothermal alteration of ultramafic rocks (serpentinization) leads to the formation of H_2 and minerals including serpentine, magnetite and brucite. Produced H_2 can reduce CO_2 in hydrothermal fluids to form CH_4 and complex hydrocarbons, including lipids [78]. A recent study has shown that hydrocarbons formed during FTT-synthesis have low $\delta^{13}C$ (ca. −36‰ relative to CO_2-source), which is in the range of most C isotopic signatures observed in Early Archean rocks including those related to hydrothermal precipitation of iron and silica [79]. Therefore, while the C isotope signal is commonly used as a biosignature in sedimentary formation, it could be ambiguous in an Early Archean hydrothermal environment.

2.4. Post-depositional changes of the C isotope composition

In metamorphosed Archean sedimentary rocks, thermal devolatilization of organic matter (production of CH_4 and CO_2) and isotopic exchange between organic C and carbonates may have modified the initial $\delta^{13}C_{org}$. Devolatilization processes can shift C isotope composi-

tion of the residual carbonaceous matter towards higher values due to preferential loss of ^{12}C. The isotopic shift is usually estimated from a relation between $\delta^{13}C_{org}$ and H/C ratio [36,54]. However, in some cases, no isotopic shift is observed (see for example [101]) and corrections should be carefully employed. When both carbonate and organic C co-exist in a rock, metamorphic-driven isotopic exchange between these two phases may occur and decreases the isotope difference between C_{carb} and C_{org} with increasing temperature [119]. The 3.8 Ga sedimentary rocks of Isua Supracrustal belt (Southwest Greenland) offer a good example of extremely ambiguous $\delta^{13}C_{org}$ data in metamorphosed rocks. These rocks experienced amphibolite facies metamorphism (500 °C;

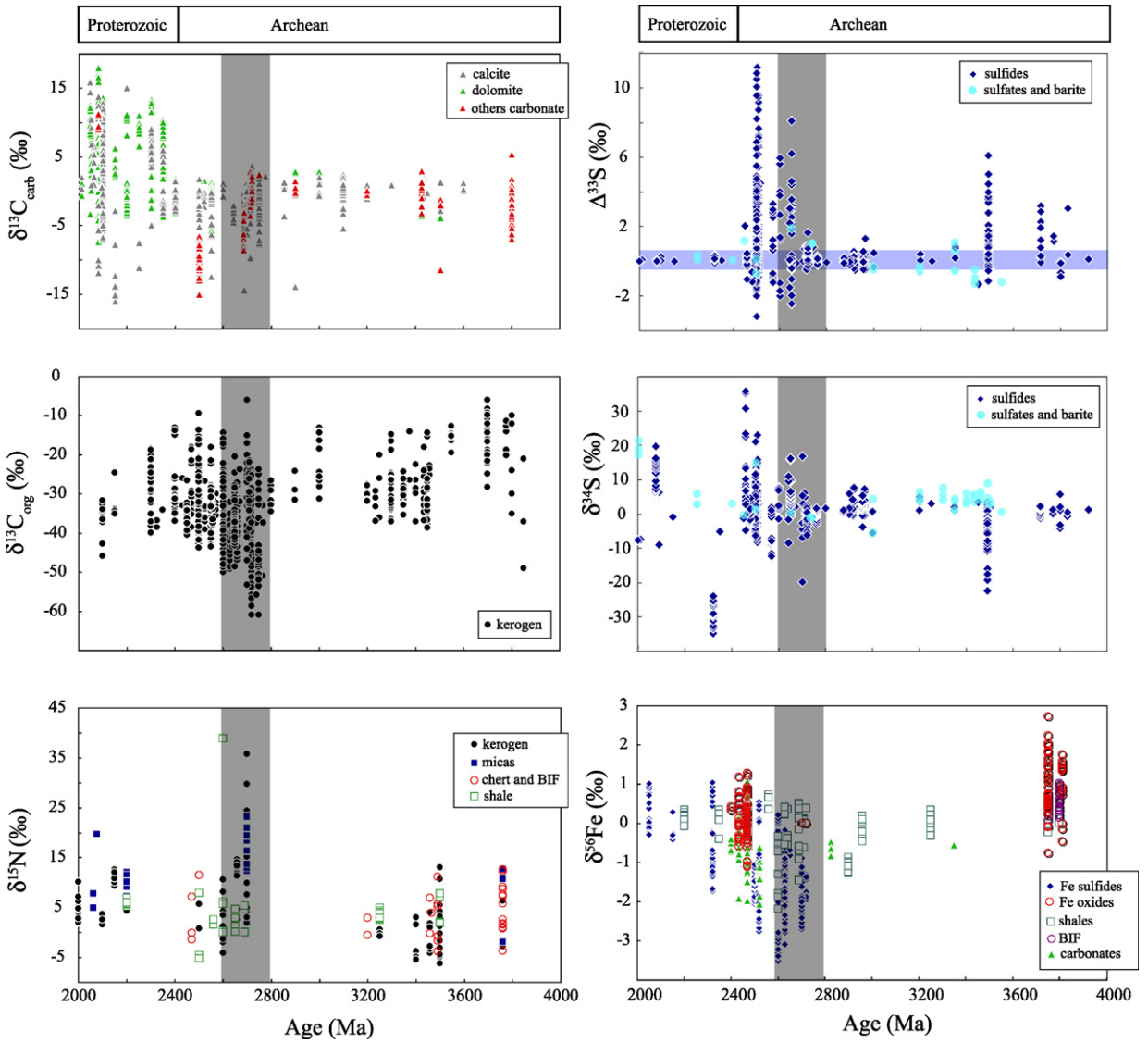

Fig. 1. Secular variations of C (kerogens and carbonates), N (kerogens, micas and bulk shales, cherts and BIF), S (sulfides, sulfate and barite) and Fe (sulfides, Fe oxides from BIF, carbonates, bulk shales and BIF) isotopic compositions through the Archean and Late Proterozoïc eon (3.8 to 2.0 Ga). The gray field underlines transient and extensive variation of C, N, S and Fe isotopic composition around 2.7 Ga. Mass independent fractionation of sulfur is expressed using the conventional $\Delta^{33}S$, and the blue field refers to mass dependent range of $\Delta^{33}S$. Data of the compilation and references are provided in a separate table as supplementary material.

Fig. 1. Variations séculaires des compositions isotopiques du C (kerogènes et carbonates), de l'N (kerogènes, micas, shales, cherts et BIF), du S (sulfures, sulfate et barite) et du Fe (sulfures, oxydes de Fe extraits de BIF, carbonates, shales et BIF), au cours de l'Archéen et du Paléoprotérozoïque (3,8 à 2,0 Ga). La zone grisée souligne une excursion des compositions isotopiques du C, N, S et Fe autour de 2,7 Ga. Le fractionnement indépendant de la masse du soufre est exprimé en utilisant la notation $\Delta^{33}S$ et la zone bleue représente la gamme de variation du $\Delta^{33}S$ masse dépendante. Les données compilées et les références sont fournies sur un tableau séparé en tant que document supplémentaire.

3–5 kbar), so that their carbonaceous matter is present as graphite. In metacarbonates, bulk carbonate and graphite carbon isotope compositions range from −12 to −10‰ and −9 to +1‰, respectively. The low values and the variability of the isotope fractionations between graphite and carbonate, are more compatible with various extent of isotopic exchange during metamorphism than with values inherited from the deposition time [118]. However, graphite globules armored in garnet crystals present lower $\delta^{13}C$ values of ∼ −19‰ [95]. The garnets being supposed to have sheltered to some extent the graphite from isotope exchange, their $\delta^{13}C$ values are the closest known so far to the initial organic matter $\delta^{13}C$, which must have been lower and thus arguably of biological origin.

2.5. The isotope record of a life operated C cycle in the Archean

A systematic difference in the isotope composition of organic and carbonate C reservoirs (Fig. 1) – with $\Delta^{13}C_{org\text{-}carb} \sim -30‰$ – has been observed in most organic-rich sediments of different ages from 3.5 to 2.0 Ga (Fig. 1). This carbon isotope record is an important, uninterrupted evidence for the presence of a substantial biosphere over geological time down to ∼3.5 Ga [54,99]. The $\delta^{13}C_{org}$ record shows a negative excursion between ∼2.7 and 2.6 Ga (Fig. 1), with $\delta^{13}C$ values as low as −60‰, while carbonate $\delta^{13}C$ values remain close to 0‰ [35,52,113]. This transitory $\Delta^{13}C_{org\text{-}carb} \sim -60‰$ suggests that methanotrophy, and hence methanogenesis, was contributing significantly to the C cycling during this period.

3. Nitrogen isotopes

Nitrogen – a common element in proteins and nucleic acids – has two stable isotopes: ^{14}N (99.6337%) and ^{15}N (0.3663%) [103]. The international standard for $\delta^{15}N$ measurements is Air. Nitrogen mainly occurs in rocks as organic nitrogen in the carbonaceous matter and *fixed ammonium* (NH_4^+), derived from the decomposition of organic molecules during diagenesis and early stages of metamorphism. *Fixed* NH_4^+ is firmly bound in the lattice structure of K-bearing minerals, where it can replace K^+ ions [10,56]. The $\delta^{15}N$ value of *fixed* NH_4^+ can be considered as a relatively good proxy of the isotopic composition of organic N [100,128], the isotope effect associated with diagenesis being usually smaller than a few per mill [97]. The $\delta^{15}N$ in modern marine bulk sediments is indeed of +7 ± 1‰ [88], close to that measured in the oceanic organic matter influx +5‰ [3].

3.1. N isotopes fractionation in biological systems

The first step in N cycling is biological *fixation* of atmospheric N_2 by aerobic or anaerobic autothrophs, such as cyanobacteria, which have the nitrogenase enzyme that combines gaseous N with hydrogen to produce ammonia (NH_3) with little isotopic fractionation ($\varepsilon \leq 2‰$; [105]). Ammonia is quickly assimilated and incorporated into proteins and other organic N compounds, through the process of *uptake*. Organic-N is often converted back into inorganic N by *mineralization*. This process produces an enzymatic breakdown of organic matter to release amine groups (-NH_2) of amino acids and subsequently NH_4^+ through *ammonification* with little isotopic fractionation ($\varepsilon \leq -5$ to +0‰; [105]). Under aerobic conditions, NH_4^+ is rapidly oxidized to nitrite (NO_2^-) and subsequently to nitrate (NO_3^-) in a two-step process called *nitrification*, where a strong isotopic fractionation is produced ($\varepsilon = -17‰$; [105]). Marine organisms can recycle nitrates by:

- *nitrate uptake* or *assimilation* with a relatively constant ε of +5‰ [105];
- in suboxic environments, nitrate is stepwise reduced to gaseous N_2 by heterotrophic bacteria that can use NO_3^- as alternative electron acceptor when O_2 is not readily available.

This process, called *denitrification* is characterized by a much larger isotope effect ($\varepsilon = -25‰$) [105], which is responsible for the enrichment in ^{15}N of oceanic nitrate (relative to atmospheric N).

The $\delta^{15}N$ of nitrate resulting from this multistep kinetic metabolic fractionation is ∼ +5‰ [105]. Because nitrate is utilized by primary producers, the $\delta^{15}N$ of the sinking flux (and of organic matter prior to diagenesis) will be close to 5‰ [88]. Diagenesis should have little isotopic effect on the N of fixed ammonium as disclosed by the isotopic similarity of oceanic N_{org} ($\delta^{15}N = +5‰$) with the bulk sedimentary N ($\delta^{15}N = +7 \pm 1‰$) [3,88].

3.2. The Archean biogeochemical cycling of nitrogen

Beaumont and Robert [8] showed an evolution of the N isotopic signature of kerogens with $\delta^{15}N_{kerogen}$ from −6.2‰ in the Early Archean to +10‰ in the Late Proterozoic. This evolution was interpreted as changes in the redox potential of the Earth towards more oxidizing condition around the Great Oxidation Event [55]. The increase of atmospheric O_2 at the end

of the Archean would have encouraged the biological production of NO_3^- and its use as a source for organic ^{15}N-enriched nitrogen.

Earlier negative $\delta^{15}N$ values during Archean might reflect a metabolic isotopic fractionation in anoxic conditions, when the oceanic nitrate pool was scarce. Bacteria might have used reduced, inorganic forms of nitrogen through NH_4^+ uptake [43] and NH_3 assimilation [7], which are able to produce some negative isotopic shift. Alternatively, Beaumont and Robert [8] argued that atmospheric N_2 could have been isotopically lighter than today ($\delta^{15}N = -5‰$) if derived from an Enstatite Chondrite source [60] and thus, simple *biological fixation* of that N could have been reflected in the organic pool.

Pinti and Hashizume [90] and Pinti et al. [91] challenged the interpretation of Beaumont and Robert [8], suggesting that their kerogens represented an environmentally biased sample of the Archean biota, in that many were extracted from silica precipitated from hydrothermal fluids. In such anoxic setting, metabolic processes are regulated by chemosynthetic biota [26]. *Chemoautolithotrophy* describes the synthesis of organic C compounds from CO_2 using energy and reducing power derived from the oxidation of inorganic compounds, such as NH_4^+, which support microbial chemosynthesis [59]. The N isotopic signature of the biomass produced by chemosynthesis, via N fixation [70,80] is significantly depleted in ^{15}N, with $\delta^{15}N$ values ranging from −9.6 to +0.9‰ [25,26,70,86,117].

N isotopic ratios measured in Late Archean (2.7 Ga) shales and kerogens by Jia and Kerrich [62,63] and Kerrich et al. [71] showed exclusively positive $\delta^{15}N$ values from +5 to +24‰. They interpreted the high $\delta^{15}N$ values as a fossil residual signature of a veneer atmosphere having an initial CI-chondritic composition with $\delta^{15}N$ values from +30 to +42‰. The isotopic shift from +24 at 2.7 Ga to 0‰ at present was interpreted as the combination of three processes:

- degassing of ^{15}N-depleted mantle N ($\delta^{15}N = -5 \pm 2‰$);
- progressive sequestration of atmospheric chondritic-like N in sedimentary rocks by fixing organisms;
- return flux of ^{15}N-depleted nitrogen to the atmosphere as a byproduct of some sort of metabolism.

However, the occurrence of an isotopically heavier atmosphere during Archean can be dismissed by the presence of very variable negative $\delta^{15}N$ values in Archean diamonds from −5 to −10‰ and down to −25‰ [22] which possibly reflect the mixing of a crustal component and an atmospheric component recycled into the mantle with isotopically lighter (rather than heavier) primeval N inherited from prototerrestrial material [114].

3.3. N secular variations, redox conditions and the emergency of metabolisms

In Fig. 1, we reported all published (and unpublished data from D. Pinti internal database) N isotopic data measured in bulk rocks and kerogens, plotted against time since Earth formation. Paleoarchean (3.8–3.2 Ga) N isotopic signatures exhibit a bimodal distribution, with $\delta^{15}N$ values from −7 to +7‰ [92]. Nitrogen from Neoarchean organic matter (3.2–2.5 Ga) is much more ^{15}N-enriched, with a $\delta^{15}N_{mean}$ value around +11‰. In a restricted range of age clustered around 2.7 Ga, kerogens, cherts and particularly BIF show an extreme enrichment in ^{15}N (from +24‰ up to +35‰; [8,62]). Proterozoic kerogens and cherts show lower $\delta^{15}N$, with an average of +5.6‰, close to the value of modern ocean nitrates. It is worth noting that the large positive shift in the N isotopic composition measured in kerogens and rocks is reached before the Great Oxidation Event (2.35 Ga; [9]), during the largest deposition of Banded Iron Formation (BIF) ever on Earth, between 2.7 and 2.6 Ga [58]. The deposition of BIF requires the presence of little oxygen, possibly 10^{-2} Present Atmospheric Level (PAL) or less [57]. If these conditions were sufficient to have limited the amount of nitrates in the ocean, we could speculate that the observed elevated $\delta^{15}N$ values were obtained by enhanced *denitrification* [2,3]. The degree of N kinetic isotope fractionation depends on the nitrate availability as a reactant: the lower the reactant availability, the higher the isotopic effect that can be produced by Rayleigh distillation [105]. In a nitrate-poor Archean ocean, the *nitrification-denitrification-assimilation* processes could have easily produced a higher nitrate $\delta^{15}N$ than in the modern ocean. With the increase in oceanic nitrate content following the oxygenation of the ocean at the end of Archean, the nitrate isotopic composition would have decreased to the modern average value of +5‰.

3.4. Limits in the use of N isotopes as a reliable biotic signature

Post-depositional changes of the pristine, metabolic-induced N isotopic fractionation are difficult to evaluate. Studies on thermal metamorphism showed that the $\delta^{15}N_{NH_4+}$ measured in mica increased progressively with the metamorphic grade up to +15‰. This isotope shift was interpreted as a progressive devolatilization of the rock (with preferential loss of lighter ^{14}N compared

to ^{15}N) by increasing temperature [49]. Dauphas and Marty [30] showed that devolatilization could have caused large isotopic shift ($\geq 15‰$) in some Archean hydrothermal mica. However, recent studies have shown that during regional metamorphism (high pressure, high temperature) the $\delta^{15}N_{NH_4+}$ shift is limited to $+2-3‰$ (e.g., [14,61]), while the $\delta^{15}N_{kerogen}$ shift is null [1]. Moreover, as for carbon, the most important concern that could invalidate the use of N isotopes as biosignature would be abiotic processes mimicking metabolic-induced isotopic fractionations. The few experimental data existing on N isotopic fractionation during FTT synthesis of N-based polymers and amino acids gave contradictory results. Miller–Urey reactions of CH_4–NH_3–H_2 mixtures have produced N-containing nonvolatile soluble organics (amino acids, organic acids) and polymers with $\delta^{15}N$ values 8 to 11‰ greater than the starting NH_3 [75]. Plasma-discharge of CO–N_2–H_2 produced carbonaceous materials with $\delta^{15}N$ values of -3 to $-17‰$ relative to the reactant N_2 [72]. These few experimental evidences do not allow estimating whether FTT reactions could have an important role in N isotopic fractionation in Precambrian rocks.

4. Sulfur isotopes

Sulfur has four stable isotopes 32, 33, 34 and 36. The most abundant is ^{32}S, representing $\sim 95\%$ of the total sulfur on Earth. The ^{34}S contributes to 4.22%, ^{33}S to 0.76% and ^{36}S contributes only to 0.0136% of the total [103]. The international standard for $\delta^{34}S$ and $\delta^{33}S$ measurements is V-CDT. Sulfur has a wide range of redox states, spanning from oxidized sulfate (SO_4^{2-}: +VI) to reduced hydrogen sulfide (H_2S: -II). This range of redox states promotes cycling in surface environments and catalyzes the production of a large range of isotopic fractionations from – 60 to +130‰ in $\delta^{34}S$ [27].

4.1. Biological sulfur isotopic fractionations

The Earth surface cycle of S is dominated by biological processes, which utilize the eight-electron S redox gradient and impart large S isotopic fractionations.

Organisms generally use S according to three main processes:

- bacterial sulfate reduction (BSR), where sulfate acts as an electron acceptor during organic C oxidation (i.e. respiration) or H_2 oxidation;
- sulfides oxidation, where sulfides species act as an electron donor associated to O_2, NO_3^- or CO_2 reduction;
- disproportionating metabolisms which obtain energy from the hydrolysis of elemental S, thiosulfates or sulfites.

We describe below the S isotope fractionations associated with these three processes. The fractionation (ε^{34}) imposed by BSR between initial sulfate and produced sulfides varies from 4 to 46‰ [23,50,68]. It depends on:

- the organism involved [34];
- the sulfate concentration [17,48];
- the sulfate reduction rates [16,34,47].

At high sulfate concentrations, the biological sulfur isotope fractionation of natural populations of sulfate reducers is typically comprised between 20 and 40‰, independently of temperature and reduction rate [16,46]. At low sulfate concentrations (less than 200 μM), it is greatly reduced [16,50].

The biological pathways of sulfides oxidation in nature are diverse and poorly known. They include phototrophic and non-phototrophic oxidation of various sulfide species such as H_2S, S^0, $S_2O_3^{2-}$ and SO_3^{2-}. The fractionations produced during phototrophic oxidation are small or negligible (between -2 and 0‰ [41,42]). Small fractionation also accompanies the non-phototrophic oxidation between -1 and 1‰ [68].

Three different disproportionation reactions involving intermediate S compounds are known: S^0 ($4S^0 + 4H_2O \rightarrow 3H_2S^+ + SO_4^{2-} + 2H^+$), $S_2O_3^{2-}$ ($S_2O_3^{2-} + H_2O \rightarrow H_2S + SO_4^{2-}$), and SO_3^{2-} ($4SO_3^{2-} + 2H^+ \rightarrow H_2S + 3SO_4^{2-}$). The fractionation associated with the disproportionation of elemental S shows a narrow range, where sulfide is depleted in ^{34}S by $6.1 \pm 0.4‰$, and sulfate is enriched in ^{34}S by $18.3 \pm 1.3‰$ [21]. ^{34}S depletions higher than 70‰ recorded in natural sulfides derive from multistep sulfide oxidation of sulfur intermediate subsequently disproportionated, and so on [20]. Inorganic disproportionation involves only a minor $< 3‰$ kinetic isotope fractionation [108].

4.2. Abiotic sulfur isotopic fractionations

High temperature hydrothermal processes ($> 100\,^\circ C$) promote the abiological thermo sulphate reduction (TSR) to sulfides [44]. The maximum isotopic fractionation associated to TSR is $\sim 20‰$ at $100\,^\circ C$. Therefore, while the S isotope signal is commonly used as a biosignature of BSR and disproportionation in sedimentary formations, it could be ambiguous in Early Archean hydrothermal formations [77]. Sulfides could also derive from H_2S released from NSO-compounds,

with kinetic sulfur isotope fractionation lower than −2‰ [77]. Hence, sulfides produced by organic matter thermal cracking should present much heavier $\delta^{34}S$ values than those formed by BSR.

4.3. Identifying biological sulfur isotope fractionation in the rock record

Sulfur isotope measurements are performed essentially on three families of sulfur-bearing compounds which can be found in the rock record. Evaporite sulfate minerals (gypsum, anhydrite, barite), carbonate-associated sulfates (CAS) and sulfur minerals (essentially pyrite). Both evaporites and CAS record faithfully the isotopic composition of the dissolved sulfate they originate from, and pyrite precipitates from dissolved sulfide with a small isotope fractionation (∼1‰, [93]). Thus, the difference between sedimentary sulfate (evaporite or CAS) and pyrite isotope compositions can be used as an indicator of BSR and S disproportionation pathways.

Between 3.5 and 2.4 Ga, sulfate $\delta^{34}S$ secular evolution seems to be centered on 0‰. It is however poorly constrained so far because of the lack of evaporite sulfates minerals in the rock record, and the scarcity of available $\delta^{34}S$ data on CAS (Fig. 1). Pyrite $\delta^{34}S$ Archean secular evolution is better constrained and is also centered around 0‰, except for the Dresser Formation (western Australia) at ∼3.49 Ga, where $\delta^{34}S_{pyrite}$ are lower than −20‰ (Fig. 1) and interpreted as a biological signature in spite of the fact that they belong to a hydrothermal system [89,104] (see § 5.4). The range of $\delta^{34}S_{pyrite}$ around 0 ± 5‰ observed in most Archean pyrites can thus be interpreted either as an absence of evidence for the operation of BSR/disproportionation [109], or, assuming that these sulfur metabolisms were operating [46,104], as the evidence for a sulfate-poor ocean [17]. At ∼2.4 Ga, the increasing range of $\delta^{34}S_{pyrite}$ provides indisputable evidences both for the involvement of BSR and/or disproportionation in the sulfur cycling and for an increasing ocean sulfate concentration. Assuming that the sulfate concentration in the oceans depends on the rate of pyrite oxidative weathering [18,110], this increase in sulfate concentration is interpreted as a response to a rise in the atmospheric O_2 content known as the Great Oxidation Event (see [55] for a review).

4.4. Combined multiple sulfur isotope study: a window to Archean sulfur metabolisms

More recently, combined isotopic measurements of $\delta^{33}S$, $\delta^{34}S$ and $\delta^{36}S$ from Archean sulfides and sulfates have provided new insights into the Archean sulfur metabolisms and oxygenation history. The multiple S isotope studies revealed S anomalous mass-independent fractionation (MIF-S) [9,37,81,87]. MIF-S is expressed by the $\Delta^{33}S$ (i.e. $\Delta^{33}S = \delta^{33}S\text{-}1000*[1 + \delta^{34}S/1000]^{0.515} - 1$) and refers to any chemical or physical process that acts to separate isotopes, where the amount of separation does not scale in proportion with the difference in the masses of the isotopes (see review in [112]). Most isotopic fractionations (including typical kinetic fractionations and equilibrium fractionations) are mass dependent since they are caused by the effects of the mass of an isotope on atomic or molecular velocities, diffusivities or bond strengths. MIF processes are less common, and for sulfur isotopes are known to occur during UV photolysis of SO_2 and SO. In its most basic form, photolysis produces two isotopically-distinct types of sulfur bearing aerosols that are likely to rain out to Earth's surface environments and transfer positive $\Delta^{33}S$ via reduced sulfur species (S^0) and negative $\Delta^{33}S$ via oxidized sulfur species (H_2SO_4) to the sedimentary record. MIF-S are thought to be produced and preserved in the sediments only when atmospheric partial pressure of O_2 is lower than 10^{-5} PAL, thus preventing both oxygen UV shielding effect and re-homogenization of atmospheric sulfur species through oxidation [38,69,98]. MIF-S are significant (i.e. different from 0‰) from 3.8 to 2.4 Ga (Fig. 1) and therefore, provide evidence for a low atmospheric O_2 content before 2.4 Ga [9], and for a very different atmospheric S chemistry in the Archean. Moreover, the sign of $\Delta^{33}S$ can be used to trace the oxidation state of the source of the sedimentary S component. This approach was recently used to re-evaluate the significance of the strongly negative $\delta^{34}S_{pyrite}$ observed in the 3.49 Ga Dresser Formation (Pilbara, western Australia), which was suggested to reflect the first evidence of BSR in a locally sulphate-rich Early Archean environment [104]. Combined observation of negative $\delta^{34}S$ and positive $\Delta^{33}S$ of sulfides was interpreted as evidence for reduced S conversion to sulfides by S disproportionating microorganisms [89].

5. Fe isotopes

5.1. Fe isotopes fractionation in biological systems

Iron has four stable isotopes, ^{54}Fe, ^{56}Fe, ^{57}Fe and ^{58}Fe, with natural abundances of 5.84, 91.75, 2.12 and 0.28%, respectively. The isotope ratio $^{56}Fe/^{54}Fe$ used by most authors is expressed as $\delta^{56}Fe$, referred to the IRMM-014 standard. The most important parameters controlling Fe isotope fractionations in natural

environment are oxidation state and bonding. In aqueous system, ferric iron (Fe[III]) is soluble under acidic and oxidizing conditions but is insoluble under near neutral-pH conditions. Ferrous iron (Fe[II]) is soluble over a large range of pH under anoxic conditions. Cycling of Fe is not only controlled by Eh-pH conditions but also by living organisms that derive energy through changes in Fe redox state [76,84]. Organisms generally use Fe according to three main processes:

- Fe(II) oxidation, where Fe(II) acts as an electron donor for energy generation;
- dissimilatory iron reduction (DIR), where Fe(III) acts as an electron acceptor for respiration;
- assimilatory Fe metabolism, where Fe is incorporated into biomolecules.

We describe below Fe isotope fractionation associated with these three processes.

The oxidation of Fe(II) under anoxic condition can be performed by phototrophic or chemotrophic metabolisms. Fe(II) can also be oxidized indirectly by microorganisms when reacting with O_2 released from oxygenic photosynthesis. The oxidation of $Fe(II)_{aq}$ into $Fe(III)_{aq}$ leads to insoluble species such as Fe oxihydroxide that evolve ultimately into goethite, hematite and/or magnetite. Isotopic studies of Fe oxides and hydroxides stored in sedimentary rocks may thus reveal the signature of life. Unfortunately, experimental works showed that the oxidation of $Fe(II)_{aq}$ to $Fe(III)_{aq}$ enriches $Fe(III)_{aq}$ in the heavy isotopes by ∼1 to 3.4‰, regardless on whether this oxidation is biologically mediated or not [4,5,64,122]. The enrichment in heavy Fe isotopes during oxidation is usually counterbalanced by a kinetic isotope fractionation during precipitation, enriching the precipitate in the light isotopes [107]. Overall, the net isotopic fractionation is modulated by the rate of precipitation but, in most cases, it produces a precipitate enriched in the heavy isotopes of Fe.

Bacterial DIR is a widespread process in anaerobic marine sediments and may be one of the oldest forms of respiration [120]. This process couples the oxidation of organic matter to the reduction of solid Fe(III). In addition to the production of $Fe(II)_{aq}$, the end-products of DIR may include Fe carbonates (siderite and ankerite) and magnetite [76]. Microbial DIR produces Fe isotope fractionation enriching $Fe(II)_{aq}$ in the light isotopes relative to the initial Fe(III) substrate [6,12,28,65]. In experiments of bacterial DIR, the Fe isotope fractionation between $Fe(II)_{aq}$ and a reactive Fe(III) component on a Fe(III) oxide surface was found constant at −2.95‰ over long timescales, for various Fe(III) substrates and bacterial species [28]. Bacterially-mediated Fe dissolution is thus associated with large isotope fractionation. Abiotic dissolution of minerals seems to be more complex. Some experiments as well as natural environment study illustrate that abiotic dissolution of minerals did not produce significant Fe isotope fractionation [11,12,15,107]. Abiotic goethite dissolution shows different results depending on the mechanism of dissolution. Proton-promoted dissolution produces no fractionation, while ligand-controlled and reductive dissolution enrich the produced $Fe(II)_{aq}$ in the light isotopes by 1.7‰ relative to reactive surface [126]. These abiotic fractionations were significant for the first steps of substrate dissolution but were negligible after only ∼2% of the initial substrate dissolved. Accordingly, abiotic mineral dissolution produces either no or limited fractionation of Fe isotopes. While the direction of the fractionation is the same for biotic and abiotic dissolution, the amplitude is much larger (by at least ∼1‰) in the case of microbial dissolution. When microorganisms have intense metabolic activity, they can produce a large amount of $Fe(II)_{aq}$ with very light Fe isotope signature under conditions out of equilibrium.

Iron assimilation in microorganisms is largely due to the two stable valencies that impart considerable range to the reactivity of Fe. When inserted into organic ligand, Fe can be used to catalyze a wide range of chemical reactions essential to the cell. Fe is also the active component of the O_2 carrier proteins. Only few studies have examined Fe isotope fractionation during uptake by microorganisms [11,12,121]. Experimental work indicates that bacterial Fe assimilation favors uptake of heavy isotope into the cell, with a fractionation of ∼1.1‰ [121]. This fractionation cannot be explained by a simple kinetic process (since lighter isotopes should be favored) and requires at least one step in isotopic equilibrium. However, whether it reflects active microbial assimilation or passive adsorption of Fe on cell walls is still unknown.

5.2. *The Archean biogeochemical cycling of iron*

The earliest photosynthetic metabolism on Earth was probably anoxigenic. Because Fe(II) was the most important electron donor available in the Archean ocean, anaerobic Fe(II) oxidation may have been the main metabolic pathway [19,125]. This biogenic oxidation of $Fe(II)_{aq}$ into $Fe(III)_{aq}$ produces insoluble Fe oxihydroxide and is often considered to explain the deposition of BIF in the Archean [51,73]. Other hypotheses to explain the formation of BIF include Fe(II) oxidation through increase in ambient O_2 by photosynthetic activity [24]

and abiotic Fe photo-oxidation by UV photons [13]. As noted above, Fe isotopes alone cannot differentiate biotic from abiotic oxidation. However, a recent study coupling laboratory experiments with thermodynamic modeling seems to rule out the possibility of a photo-oxidation [74]. If this is true, the two other scenarios involve living organisms, either as oxygenic or anoxygenic photosynthetic metabolism.

Before deciphering biogeochemical index of life from Fe isotopes, it is crucial to understand the cycling of Fe in the Archean. Large variations in the Fe isotope record were identified during Archean and Early Proterozoic by analyzing sedimentary pyrites [96]. Fig. 1 plots a compilation of Fe isotope data available in the literature for Archean rocks. The most significant variation is a large negative excursion of δ^{56}Fe values between 2.7 and 2.3 Ga flanked by near zero or slightly positive δ^{56}Fe values before 2.7 Ga and after 2.3 Ga. It was primarily interpreted as reflecting changes in the Fe isotopes signature of seawater [29,96]. However, this interpretation is weakened by the observation of large Fe isotope heterogeneity (> 2‰) at the cm-scale in Archean rocks, which cannot be explained by secular variation in seawater, because of the high Fe residence time in the Archean ocean [65]. Although such a small scale variability has only been reported once and still needs some confirmation, an alternate hypothesis has been proposed which is that the δ^{56}Fe of sedimentary rocks might reflect mainly biogeochemical cycling during sediment diagenesis [66,67,130]. The large negative excursion of δ^{56}Fe values between 2.7 and 2.3 Ga would result from an extensive activity of DIR metabolism in response to increase Fe(III) and organic carbon delivery to the ocean [65]. If true, this exciting alternative would indicate that Fe isotopes do record the signature of iron based metabolic pathways.

5.3. *Limits in the use of Fe isotopes in Archean rocks*

The drawback with studying old Precambrian rocks is that most of them experienced metamorphism. An important question is thus whether Fe isotope composition reflects processes in water column, sediment diagenesis or metamorphism. Several works on Eoarchean metamorphic rocks demonstrated that Fe isotopes can be used to distinguish protolith signature from metamorphic overprint [31–33]. Whitehouse and Fedo [124] observed small-scale isotopic heterogeneity in magnetite from very small areas within single bands of Eoarchean BIF, indicating a range of fractionation within single depositional event. This is unlikely to have resulted from water column chemistry or later metamorphic disturbance, which should produce isotopic homogeneization. In contrast, Fe isotope heterogeneity likely derives from isotopic reservoir effect during diagenetic reactions in pore waters isolated from the ocean [124]. In Biwabik Iron Formation, Fe isotope fractionation between coexisting minerals decreases with increasing metamorphic grade, indicating that isotopic exchange occurred during metamorphism [115]. Isotopic exchange was limited to the mineral-scale but bulk rock behaved as closed-system and preserved primary Fe isotope composition [40,115]. Any potential isotopic re-equilibration could be avoided by analyzing metamorphic rocks or layers with single Fe-bearing mineralogy, which may be particularly useful for searching isotopic traces of early life.

6. Conclusion

Major changes of C, N, S and Fe isotopic compositions are recorded between ∼2.8 and ∼2.5 Ga (Fig. 1) and can be interpreted in terms of environmental and associated-metabolic changes. The δ^{13}C measured in organic matter shows a large negative isotopic shift from −30‰ down to −60‰ and back to −30‰, while δ^{56}Fe values, which are mainly around 0‰ over the last 4 Ga show in this particular period a decrease down to −4‰ (Fig. 1). MIF-S show variations from −0.5 to +1.4‰ between 3.2 and 2.8 Ga, and a larger range, from −2.5 to +11.2‰, between 2.7 and 2.45 Ga before disappearing after 2.4 Ga [9]. Negative δ^{34}S values < −17‰ are also recorded at 2.7 Ga in the Belingwe belt (Zimbabwe) [45]. Finally, the δ^{15}N shows an extreme enrichment in ^{15}N (from +24 up to +35‰; [8,62]) around 2.7 Ga compared to Paleoarchean δ^{15}N (between −7 and +7‰ [92]) and Proterozoic δ^{15}N (average of +5.6‰).

The isotopic covariations around 2.7 Ga are probably related to a change of the ocean redox conditions [65] and point to the development of metabolisms using oxidized species in the oceans. Low $\delta^{13}C_{org}$ and $\delta^{34}S_{pyrite}$ observed in the Belingwe belt (Zimbabwe) and in the Tumbiana Formation (western Australia) suggest that, *at least locally*, sulfate concentration was high enough to support anaerobic oxidation of methane and BSR [45,113]. The same conclusion in favor of a more oxidizing oceanic environment arises from N and Fe isotopic variations that may reflect the use of a limited pool of nitrates for nitrification-denitrification processes and the use of Fe(III) by DIR activity [67], respectively. Rising of oxidant in the ocean at around 2.65 to 2.5 Ga is also supported by recent development of Mo isotopic study [127]. Despite indication of oceanic oxygenation, significant Δ^{33}S around 2.7 Ga suggests that the

atmosphere remained free of oxygen [113]. This oxygenation was thus likely limited to shallow water environments, either lacustrine or oceanic. The present conclusions illustrate that coupling stable isotope systems can be used as a powerful tracer to identify and characterize the "co-evolution" of metabolisms and early Earth surfaces environment.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.crpv.2009.02.003.

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