

Geomicrobial functional groups: A window on the interaction between life and environments

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Microbes are well-known for their great diversity and abundance in modern natural environments. They also are believed to provide critical links among higher organisms and their associated environments. However, the low diversity of morphological features and structures of ancient microbes preserved in sediments and rocks make them difficult to identify and classify. This difficulty greatly hinders the investigation of geomicrobes throughout Earth history. Thus, most previous paleontological studies have focused on faunal and floral fossils. Here, geomicrobial functional groups (GFGs), or a collection of microbes featured in specific ecological, physiological or biogeochemical functions, are suggested to provide a way to overcome the difficulties of ancient microbe investigations. GFGs are known for their great diversity in ecological, physiological and biogeochemical functions. In addition, GFGs may be preserved as the biogeochemical, mineralogical and sedimentological records in sediments and rocks. We reviewed the functions, origins and identification diagnostics of some important GFGs involved in the elemental cycles of carbon, sulfur, nitrogen and iron. GFGs were further discussed with respect to their significant impacts on paleoclimate, sulfur chemistry of ancient seawater, nutritional status of geological environments, and the deposition of Precambrian banded iron formations.

geomicrobial functional group, carbon-sulfur-nitrogen cycle, iron reduction and oxidation, photosynthesis, molecular fossils, geobiology, critical periods

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It is not straightforward to fully understand all the dynamic processes of major environmental changes throughout the evolution of Earth. However, it is critical to understand the interactions between life and environments during major environmental transitions throughout history. Previous work has focused on environmental impacts on the biosphere, with assumptions made that organisms can only passively adapt to environmental changes. For example, major and rapid volcanic eruptions as a result of mantle plume dynamic processes have been proposed to trigger a series of variations in both the atmosphere and marine environments, which have resulted in major impacts on biosphere evolution [1]. It is notable that the biosphere also alters the phys-

ical and chemical conditions of the Earth's surface system [2–4]. However, less work has been conducted concerning the positive biotic roles played in changing environments. This lack of work greatly prevents us from comprehensively understanding abrupt environmental changes throughout Earth history, as well as the evolution of the Earth as a planet.

Deciphering of positive biotic roles in environments awaits a breakthrough in research on microbial processes in ancient times [4]. Microbes include all bacteria and archaea, as well as a great majority of eukaryotes. However, only a small proportion of eukaryotes have been targeted in past paleontological investigations, leaving the majority of microbes unknown. Within an ecosystem, microbes not only affect fauna and flora, but also the natural environments in

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which these organisms live. Microbes are both producers and decomposers, which impact geological environments via energy flow and material cycles [5]. In this regard, microbial processes are suggested to be one of the critical components in changing the Earth's system in both ancient and modern times. Nevertheless, less is known with regard to geomicrobial roles over geological times. This is partly, if not entirely due to the fact that most geomicrobes preserved in rocks show less diagnostic morphological and structural features, and cannot always be identified and classified to a specific taxon on the basis of the morphological investigations.

It is important to establish strategies to resolve these identification difficulties. Although geomicrobes are not always easy to assign to a specific genus or species, it is the functional groups of the geomicrobes that play a dominant role in most geological processes [6,7]. This implies that geomicrobial functional groups (GFGs) directly interact with natural environments. GFGs are defined as a collection of microbes featured in specific ecological, physiological or biogeochemical functions, such as the well-known nitrogen-fixing functional group. GFGs are entirely different from taxonomic groups, in that they show a close link between functions and associated environments. Thus, it is necessary to focus our investigations on the GFGs among diverse geomicrobes, in particular those capable of metabolizing the chemical species of carbon, nitrogen, sulfur and iron. Furthermore, GFGs link microbial ecology with biogeochemical processes [6,8], providing a unique opportunity to allow preservation of microbial fingerprints in rocks and sediments as the records of molecular fossils, diverse geochemical records, microbial minerals, and microbially-induced sedimentary structures. These records, recovered by advanced isotope techniques and micro-analysis, provide the micro- and macro-indicators for geological processes induced by geomicrobes. Previously, it was difficult to identify specific GFGs preserved in rocks because of poor analytical techniques. These problems are likely to be overcome with recent analytical advances to investigate GFGs and their roles in diverse geological processes. Here, we mainly review some important GFGs closely involved in the biogeochemical cycles of carbon, sulfur, nitrogen and iron, and evaluate the function, origin, identification diagnostics, and roles of these GFGs in changing environments.

1 Functions and origins of some critical GFGs

1.1 Photosynthetic GFGs

Anoxygenic and oxygenic photosynthesis are important metabolic pathways. The emergence of photosynthetic GFGs was a milestone in the evolution of life, and provided more energy sources for carbon fixation [9]. The earliest photosynthetic microbes belong to the domain bacteria, and include halobacteria, purple sulfur bacteria, purple non-

sulfur bacteria, green sulfur bacteria, green non-sulfur bacteria, heliobacteria and cyanobacteria. Among these microbes, cyanobacteria are the only chlorophyll-containing photosynthetic bacteria, and thus the only oxygenic photosynthetic GFGs. Eukaryotes have been shown to have inherited oxygenic photosynthesis from endosymbiosis with cyanobacteria [10].

The origin of photosynthetic microbes is an important scientific issue to be investigated. Here, we provide a brief summary. More relevant information can be found in the literature [11–14]. Evidence from geochemical, molecular biological and paleontological investigations indicates that photosynthesis is an ancient metabolic pathway [14]. Anoxygenic photosynthetic microbes appear to have had a much earlier origin than oxygenic photosynthetic microbes. Based on molecular studies, purple sulfur bacteria may be the oldest of such microbes [15]. The early Earth had a reductive atmosphere and oceans, where photosynthesis was predominantly anoxygenic, using H_2 , S, H_2S and Fe^{2+} as electron donors [14]. Photosynthesis using Fe^{2+} as the electron donor is believed to have already been prevalent long before the appearance of oxygenic photosynthesis. Early cyanobacteria also are suggested to have used Fe^{2+} as the electron donor during photosynthesis [13]. This pathway has been suggested to be one of the mechanisms responsible for production of Precambrian banded iron formations (BIF) [16–19].

The origin of oxygenic photosynthesis is a critically important part of the evolutionary history of life, yet it is still highly debated [12]. Several lines of geochemical evidence indicate the presence of a great oxidation event about 2.4 billion years ago [20] or a transient oxidation event a little before that time [21–23]. This provides the minimum age for oxygenic photosynthesis. Currently, three different viewpoints have been put forth regarding the origination time of the oxygenic photosynthesis. Some scientists believe that oxygenic photosynthesis originated several hundred million years earlier than the first great oxidation event [24]. This is because quite a long time period is needed to allow the oxygen produced by oxygenic photosynthesis to oxidize volcanic reductive gases, hydrothermal fluids and minerals, which enabled the occurrence of the subsequent great oxidation event. Other scientists believe that oxygenic photosynthesis was almost synchronous with the first great oxidation event [25]. Furthermore, other researchers tend to believe that oxygenic photosynthesis appeared much earlier than any geological records reported on the Earth, which allows the possibility for the presence of a highly oxidative atmosphere in the Archean [26]. Diverse records of biogeochemistry, sedimentology, mineralogy and paleontology are further required to precisely constrain the origination time of oxygenic photosynthesis.

Algae originated much later than photosynthetic bacteria. Chlorophyta became important primary producers in the late Proterozoic, while dinoflagellates, coccoliths and dia-

toms did not become important primary producers on the continental shelf until the Mesozoic Era [27].

1.2 GFGs in methane cycling

Terrestrial plant ecosystems are believed to have a great impact on global climate change via regulation of the carbon cycle, which can now be quantitatively evaluated by mathematical modeling. However, GFGs also can play very important roles, by not only producing and consuming CO₂ and CH₄, but also degrading organic matter. Both of these processes dramatically affect carbon sources, sinks and fluxes, and thus regulate the global carbon cycle. For example, methanogens and methanotrophs have been demonstrated to dominantly affect atmospheric CH₄ concentration. In the marine environment, some bacteria, such as aerobic anoxygenic phototrophic bacteria, can transfer bioavailable dissolved organics to recalcitrant dissolved organics, favoring their accumulation in seawater over a long period of time [28]. Great attention has been placed in deciphering the relationship between atmospheric CH₄ concentration and paleoclimate change throughout Earth history. This is because CH₄ is the second most important greenhouse gas, and has a relatively depleted carbon isotopic composition in the geological record. Here, we summarize the general features of CH₄-associated GFGs, mainly methanogens and methanotrophs.

Methanogens are obligate anaerobic and autotrophic archaea, widely occurring in anoxic conditions in a variety of extreme environments, including marine environments [29,30], as well as wetlands, and in particular peatlands [31,32]. The biosynthesis of CH₄ by methanogens includes the pathways involving acetate, H₂/CO₂ and methyl compounds. High CH₄ level has been previously observed over neotropical forests throughout the world, and is now explained by the presence of a diverse community of CH₄-producing archaea. These archaea have been found to multiply in the canopy of belted mouth bromeliads, which enable rainfall to accumulate and form an environment analogous to wetlands [33]. Other potential wet parts in trees (e.g. hollow bamboo internodes, tree holes, non-bromeliad leaf axils) also have been suggested to provide an additional contribution to CH₄ in tropical and subtropical forests.

In contrast to methanogens, which biosynthesize CH₄, the methanotrophs from both bacteria and archaea domains consume CH₄. In deep sea environments, such as in hydrothermal vents and cold seeps, a consortia of anaerobic methane oxidation archaea and sulfate-reducing bacteria complete the anaerobic oxidation of CH₄ [34,35]. To date, the dynamic mechanisms of anaerobic CH₄ oxidation are still debated. A pathway reversing methanogenesis in methanogens is widely accepted with respect to consumption of CH₄ and production of cellular carbon and energy [36]. In freshwater conditions, CH₄-consuming archaea anaerobi-

cally oxidize CH₄ by coupling with the denitrification process [37]. Recently, Ettwig et al. [38] isolated an anaerobic bacterium from freshwater, which can produce oxygen and oxidize CH₄ by using the oxygen produced. This oxygen-producing pathway has great biogeochemical and evolutionary implications.

In peatlands, most biotic oxidation of CH₄ is conducted by aerobic bacteria. In aerobic conditions, CH₄ is transformed to methanal, and then used to biosynthesize organic matter via serine or RuMP pathways. The CH₄-oxidizing bacteria are divided into three types on the basis of morphology, G+C content, metabolic pathways, membrane structure and phospholipid fatty acids. Type I, belonging to the γ -proteobacteria, assimilate CH₄ to form methanal via RuMP pathways. Type II CH₄-oxidizing bacteria include α -proteobacteria, which assimilate CH₄ via serine pathways. Type X CH₄-oxidizing bacteria fall into the Phylum Verrucomicrobia, and they synthesize methanal mainly via RuMP pathways with a very small part of the serine pathway [39].

1.3 GFGs in sulfur cycling

Microbial metabolism within sulfophilic species is one of the main pathways for early organisms to have harvested energy. Barophilic bacteria and archaea, the microbes presumably affiliated with the earliest common ancestor, also obtain energy through sulfur metabolism [40]. Thus, exploring microbes that metabolize sulfur species allows for a better understanding of the origin and evolution of life on Earth and possible exo-life. Sulfate and elemental sulfur reduction, disproportionation of intermediate sulfur compounds and elemental sulfur, and anaerobic and aerobic oxidation of elemental sulfur are the main microbial metabolisms in sulfur cycling. The GFGs metabolizing elemental sulfur and sulfur compounds include sulfate-reducing bacteria and archaea, sulfur-reducing bacteria and archaea, intermediate sulfur disproportionation bacteria, anaerobic sulfur-oxidizing bacteria and aerobic sulfur-oxidizing bacteria (Figure 1).

Sulfate-reducing microbes are dominated by bacteria, with only a few known archaea, both of which are obligatory anaerobic. δ -proteobacteria (Gram-negative bacteria) are the main sulfate-reducing bacteria, with a few Gram-positive bacteria and thermophilic bacteria (*Thermodesulfobacterium* and *Thermodesulfovibrio*) [41]. There are very few sulfate-reducing archaea found to date, and these are mostly high-temperature hot spring archaea (*Archaeoglobus*) [41]. Based on sulfur isotope records, the origin of sulfate-reducing microbes is estimated to be as early as 3.47 Ga [42,43]. It is as yet unclear whether these early sulfate-reducing microbes were bacteria or archaea, although they are assumed to have been bacteria. The sulfur isotope fractionation by sulfate-reducing archaea remains uncertain [44].

Intermediate sulfur disproportionation bacteria are

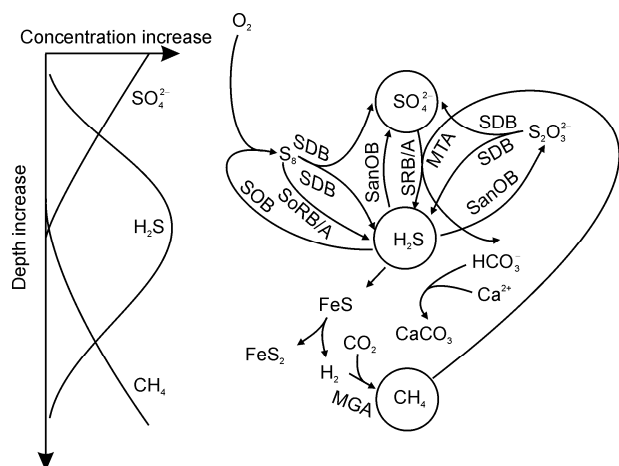


Figure 1 Sulfur cycle and the involved GFGs. SRB/A, sulfate-reducing bacteria/archaea; SDB, sulfur disproportionating bacteria; SanOB, anaerobic sulfur-oxidizing bacteria; SOB, aerobic sulfur-oxidizing bacteria; SoRB/A, sulfur-reducing bacteria/archaea; MGA, methanogenic archaea; MTA, methanotrophic archaea.

anaerobic and autotrophic [45]. These bacteria can produce, via metabolism, a large sulfur isotope fractionation ($\Delta^{34}\text{S} > 46\text{‰}$) [46]. Based on multiple-sulfur isotopic compositions, Johnston et al. [47] postulated that these bacteria would have been present in the Mid-Mesoproterozoic, about 1.3 Ga. Parnell et al. [48] documented a very large (greater than 50‰) sulfur isotope fractionation in some terrestrial strata deposited about 1.18 Ga. They suggested this fractionation was evidence for sulfur disproportionation reduction driven by elevated atmospheric O_2 content at that time. However, micro-analysis on multiple-sulfur isotopes resulted in the hypothesis that microbial sulfate reduction and sulfur disproportionation would have existed about 3.4 Ga [49]. It is notable that microbial sulfate reduction itself also can induce very large sulfur isotopic fractionation [50–52]. All of these data appear to be contradictory with the proposal that sulfur disproportionation is indicative of elevated content of atmospheric O_2 [53].

Anaerobic sulfur-oxidizing bacteria mainly include green sulfur bacteria and purple sulfur bacteria living in the euxinic photic zone, both of which are anoxygenic and photoautotrophic. They can utilize sunlight as an energy source and H_2S as an electron donor for CO_2 fixation. The origination of these microbes was thought to be no later than 1.6 Ga [54]. However, they are scarcely found in Precambrian rocks, but show a frequent occurrence in Phanerozoic anoxic environments [55]. This differentiation may have been caused by high maturity of organic matter in Precambrian rocks, which may have destroyed the diagnostic compounds of these microbes. The low sulfate concentration in Precambrian oceans also may have inhibited the bloom of these microbes.

Aerobic sulfur-oxidizing bacteria generally require O_2 to oxidize elemental sulfur, and are believed to have originated later in Earth history. Biomarkers and paleontological rec-

ords suggest that these aerobic bacteria existed in the ocean about 1.64 Ga [56]. However, these GFGs may not have needed molecular oxygen, and could have an earlier origin. For example, aerobic sulfur-oxidizing bacteria have been found in H_2S -bearing waters below the chemocline in the modern Black Sea [57]. Some studies have shown that these GFGs can use nitrate to replace O_2 as the electron donor during the microbial oxidation of sulfur [58]. Wacey et al. [59] suggested that these GFGs may have existed in the ocean about 3.4 billion years ago.

Sulfur-reducing metabolism is also ancient, but has a low energy yield [41]. Microbes involved in this metabolism include bacteria and archaea, most of which are anaerobic heterotrophic microbes [41]. In addition to sulfur, some oxides, such as the oxides of manganese (IV) and iron (III) [41] can be reduced by these microbes. The sulfur-reducing archaea discovered to date are extremely thermophilic microbes in hot spring systems. Little is known about the origin and evolution of these archaea.

It is clear that all the sulfur-metabolizing GFGs appeared early in Earth history (Early Archean). However, it is still not clear what the causes of their early occurrence may have been, and what is the geological implication. More work is needed to decipher these issues, in particular, investigation of microbial lipids, their compound-specific isotope composition and functional genes of modern analogs.

1.4 GFGs in nitrogen cycling

Nitrogen is more important than phosphorous as an element to determine marine primary productivity [60]. Microbes act as a powerful engine to drive the nitrogen cycle in the global ecological systems, and play significant roles in the transformation of different nitrogen species (NH_4^+ , NO_3^- and N_2 , etc., Figure 2) [8].

Nitrogen gas cannot be used directly by most organisms. However, nitrogen-fixing microorganisms can convert nitrogen gas into bio-available ammonia, the fundamental constituents for the biosynthesis of proteins and nucleic acids [8]. The nitrogen-fixing microbial functional group differs significantly in marine and terrestrial environments. The diazotrophic microorganisms in open oceans are primarily from the cyanobacterium genus *Trichodesmium*. However, some unicellular cyanobacteria (e.g. *Crocosphaera watsonii*) have been discovered recently in the oligotrophic regions of open oceans at high latitudes and deep waters, with both biomass and nitrogen-fixing rate comparable with those of *Trichodesmium*. These widely-distributed unicellular cyanobacteria have made a major contribution to the marine nitrogen budget, and have become important organisms to help understand the marine nitrogen cycle [61]. Cyanobacterial nitrogen-fixation is primarily regulated by the *nifH* gene [62], which can encode the key protein, iron and molybdenum nitrogenase. The bioavailability of metals, such as iron and molybdenum can,

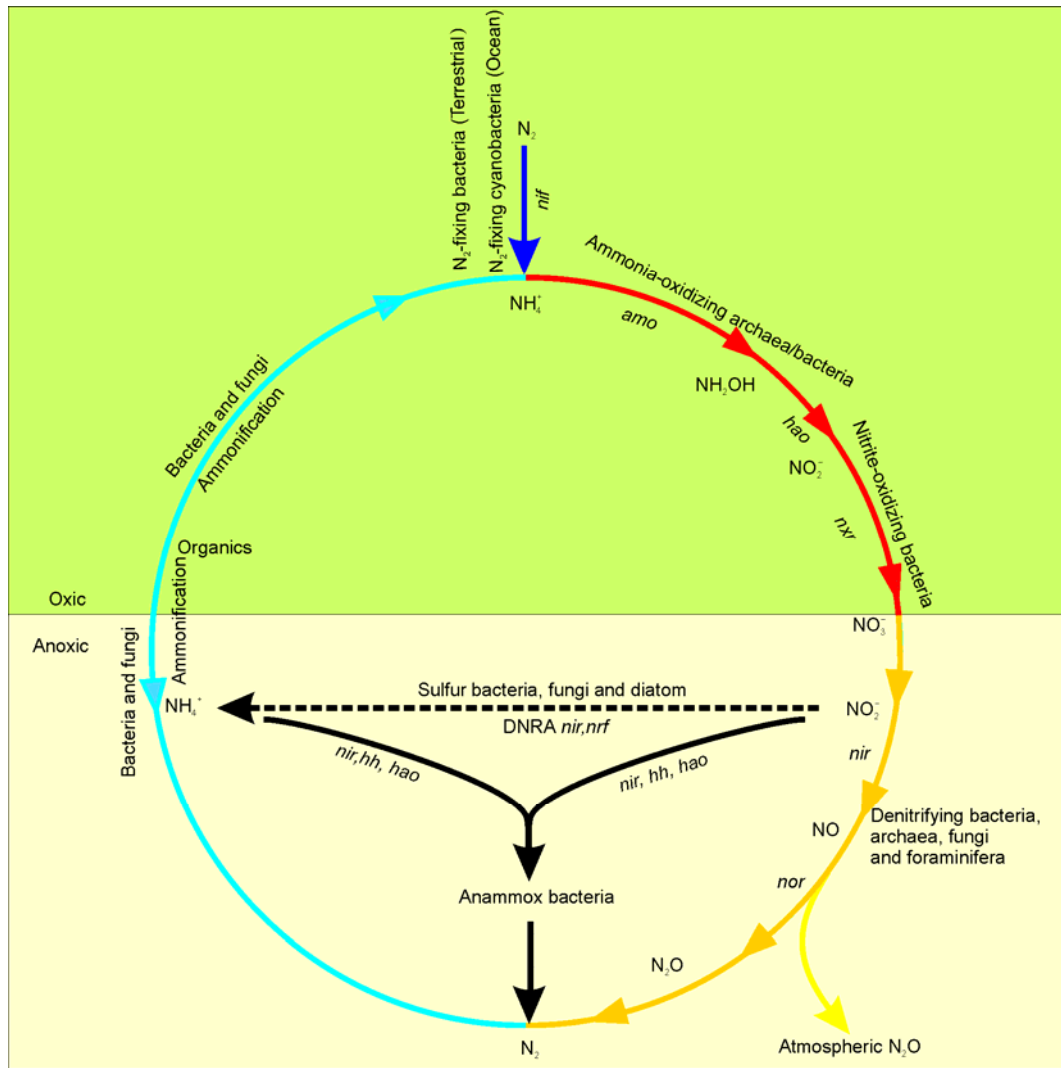


Figure 2 Nitrogen cycle and the related GFGs. *nif*, nitrogenase; *amo*, ammonia monooxygenase; *hao*, hydroxyl-amine oxidoreductase; *nrx*, nitrite oxidoreductase; *hh*, hydrazine hydrolase; *nor*, NO reductase. The purple, red, yellow, blue and black lines or curves denote, respectively, the nitrogen-fixing process, nitrification, denitrification, ammonification and anammox processes. The dashed line represents dissimilatory nitrate reduction to ammonium.

to some extent, affect microbial nitrogen-fixing processes [63]. In terrestrial environments, the primary diazotrophic microorganisms are rhizobia and some free-living nitrogen-fixing bacteria and archaea. In modern microbial mats, cyanobacteria and γ -proteobacteria can co-occur in the same microbial community, and collectively constitute the N_2 -fixing GFGs. Nevertheless, the primary nitrogen-fixation in these microbial mats is regulated by different microbes at different time. Cyanobacteria primarily fix nitrogen from day time to midnight, whereas γ -proteobacteria become the dominant nitrogen-fixer from midnight to dawn [64].

Biologically fixed ammonia can be consumed by organisms or further oxidized to nitrate by ammonia-oxidizing GFGs (Figure 2). The ammonia oxidizers were first believed to be obligatory aerobic and chemolithotrophic ammonia-oxidizing bacteria (AOB), phylogenetically within β - and γ -proteobacteria [65]. However, Leininger et al. [66]

found that on the basis of quantitative Q-PCR measurement of the ammonia monooxygenase gene (*amoA*; key gene regulating ammonia-oxidation), ammonia-oxidizing archaea (AOA) were clearly more abundant than AOB in modern soils. AOA also were found to dominate over AOB in most other environments, including marine or lacustrine water columns and sediments [67]. AOA are phylogenetically affiliated with Crenarchaeota group 1.1. They are aerobic and chemolithotrophic, and fix carbon dioxide via acetyl/propionyl-coenzyme A carboxylase [68,69]. AOA occur in a variety of environments in great abundance, implying that they play an important role in the global nitrogen cycle. The purely cultured strains of AOA can maintain a high ammonia oxidation rate comparable with the AOA in the oligotrophic regions of open oceans, and have a remarkably high affinity to reduced nitrogen. This indicates that AOA can compete over heterotrophs and algae in oligotrophic environments by the preferential acquisition of ammonia [70].

Nitrification rates of AOA and AOB can be influenced by environmental conditions (e.g. pH). In acidified oceans, ammonia oxidation rates can slow down [71], and may thereby result in a fluctuating marine nitrogen pool, which also is observed in past Earth conditions, when the atmospheric P_{CO_2} was relatively high.

To date, no microorganism has been demonstrated to be capable of directly oxidizing ammonium to nitrate. The nitrification process usually includes two steps; AOA or AOB first transform ammonium to nitrite, and then nitrite-oxidizing bacteria further oxidize nitrite into bio-accessible nitrate. Different from nitrification, denitrification can be triggered by bacteria, archaea or fungi. Even some benthic foraminifera have been demonstrated to perform the complete denitrification process from nitrate to nitrogen gas [72]. Denitrifiers are generally facultatively anaerobic heterotrophs, and use nitrate as the final electron acceptor. NO_3^- reduction during denitrification is catalyzed by nitrite reductase (*nir*) and NO reductase (*nor*) with the intermediate product of N_2O , a kind of greenhouse gas. The atmospheric N_2O concentration has been found to be usually greater in interglacial periods than in glacial periods, suggesting that the denitrification process possibly exerts an impact on global climate change via N_2O emission [60]. Nitrification and denitrification can balance the dynamics of the global nitrogen cycle. However, an estimate of nitrogen budget reveals that nitrogen loss is clearly greater than nitrogen inputs in modern marine environments [73]. In addition to denitrification, anammox, a process that converts ammonium and nitrite into nitrogen gas [74], may contribute 30%–50% of the nitrogen loss. The anammox bacteria, phylogenetically falling into Planctomycetes, are characterized by slow growth, but a diverse occurrence in anoxic marine or lacustrine environments or even high-temperature petroleum reservoirs [75,76]. In-depth investigations of anammox bacteria will re-shape our understanding of the nitrogen cycle throughout Earth history.

The origin of nitrogen-cycling GFGs has not yet been understood well. Oxygen may play a critical role in the origin and evolution of these GFGs. The nitrogenase genes are common in bacteria and archaea, but nitrogenase can be inactivated by free oxygen. The early anaerobic microbes capable of nitrogen-fixation may be located at the root of the phylogenetic tree, and occur before the great oxygenation events (ca. 2.4 Ga ago) [20,77]. After molecular oxygen accumulated in the atmosphere and oceans, the nitrogen-fixing microbes were able to develop a number of special strategies (e.g. heterocyst and photosystem I) to separate nitrogenase from free oxygen [78]. In the early evolution of Earth, the scarcity of nitrate and ammonium may have triggered a selection pressure, favoring the evolution of nitrogenase in anaerobic microorganisms (e.g. methanogens, green sulfur bacteria and purple sulfur bacteria) to balance the nitrogen budget [79,80]. AOB and AOA use molecular oxygen to oxidize ammonium, whereas denitrifi-

cation and anammox require nitrate produced in nitrification. It was not until the presence of oxygenic photosynthetic microorganisms, such as cyanobacteria, that these nitrogen-cycling GFGs could originate and establish the framework of the modern nitrogen cycle. In fact, $\delta^{15}N$ in sedimentary kerogen reveals that nitrification and denitrification may have occurred in the late Archean (ca. 2.72 Ga) [81].

Another important environmental factor influencing the origin and evolution of nitrogen-cycling GFGs is the concentration of some metals (e.g. iron and molybdenum) in marine oceans. Iron and molybdenum are the fundamental elements in nitrogenase, and can be more efficient than other substitutions, such as vanadium and nickel. They also can act as clear indicators of marine redox conditions in the early history of the Earth [82]. In reduced Archean oceans, a large amount of Fe^{2+} may have existed in seawater, but the reduced species of molybdenum can only be trapped in sediments, where they are not be available to organisms. In the sulfidic Proterozoic oceans, iron appears to have been depleted in seawater but Mo had a relatively high content at that time, relative to Archean oceans. The oxic seawater in Phanerozoic oceans may have freed enough molybdenum, but still may show a depletion of iron [83]. The effective Fe/Mo nitrogenase only could occur at ca. 0.5–0.6 Ga, when deep ocean water was oxic and more molybdenum in oxidized form could have been released to seawater. Thereafter, the marine nitrogen cycle was significantly accelerated.

1.5 GFGs in iron cycling

It is well recognized that iron plays a fundamental role in microbial metabolism. Acting as an essential element, iron can be acquired by microbial cells to constitute a versatile family of cytochrome hemes, the metalloenzymes catalyzing various oxidative reactions. Iron also can be used to form intracellular minerals by magnetotactic bacteria [84,85]. These nano-scale minerals, generally termed magnetosomes, benefit the mobility of magnetotactic bacteria aligned along geomagnetic field lines [84,85]. Conversely, some microorganisms obtain energy by triggering the external iron redox cycle, in which ferrous iron is used as an electron donor and ferric iron as an electron acceptor.

A variety of microbes are intimately involved in Fe(II)-Fe(III) redox conversions (Figure 3). Under conditions with nearly neutral pH, Fe(II) easily can be oxidized to Fe(III) in the presence of free oxygen. However, in plant rhizosphere and hydrothermal vents, the bacteria mainly are from three genera (*Gallionella*, *Leptothrix* and *Matinobacter*), and can enzymatically oxidize Fe(II) through the following reaction, $2Fe(II) + O_2 + 4H_2O \rightarrow 2Fe(OH)_3 + 2H^+$ [86,87]. In neutral anoxic environments, it has become clear that anoxygenic photosynthetic bacteria and nitrate-reducing bacteria are the two major functional groups to oxidize iron [86,87]. The anoxygenic photosynthetic bacteria (photoferrotrophy) are phylogenetically diverse, including the purple sulfur

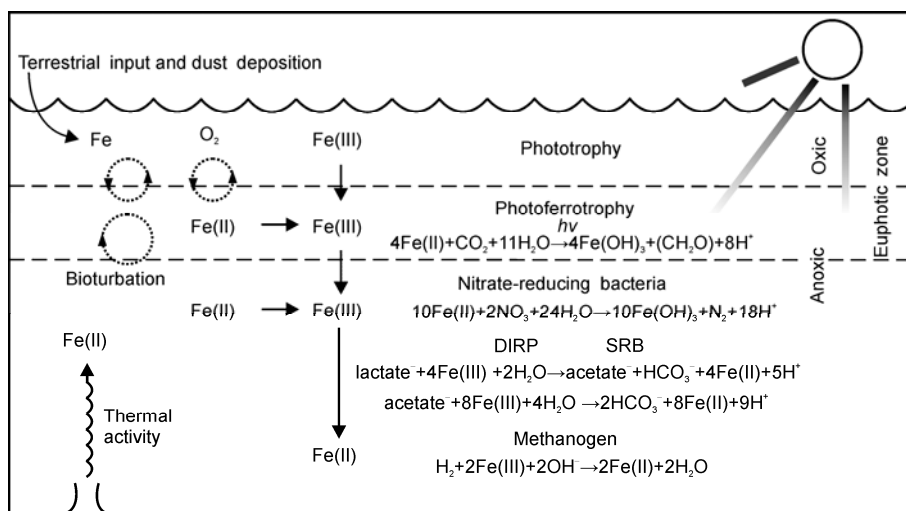


Figure 3 Iron cycle and related GFGs.

bacterium *Thiodictyon* sp. from γ -proteobacteria, purple non-sulfur bacterium *Rhodobacter ferrooxidans* in α -proteobacteria, and green sulfur bacterium *Chlorobium ferrooxidans* in δ -proteobacteria [86–89]. However, all photoferrotrophy shows a similar pathway involved in Fe(II) oxidation, which is linked to respiratory systems coupled with CO₂ fixation [86–89]. More evidence has emphasized the importance of nitrate-dependent iron-oxidizing bacteria (e.g. *Ferroglyphus placidus*) in anoxic Fe(II) oxidation around circumneutral pH, which are capable of reducing nitrate to nitrogen gas using Fe(II) as an electron donor [86]. This process can be of enzymatic catalysis or indirect chemical reactions in which the intermediate nitrite generated from nitrate reduction can chemically oxidize Fe(II) ($4\text{Fe(II)} + 2\text{NO}_2^- + 6\text{H}^+ \rightarrow 4\text{Fe(III)} + \text{N}_2\text{O} + 3\text{H}_2\text{O}$) [90]. During Fe(II) oxidation, various Fe(III)-minerals, including hydrous ferric oxide, goethite and lepidocrocite, formed at the cost of soluble or solid-phase Fe(II) (siderite, vivianite, magnetite, iron sulfide) [86,88,90].

Since the isolation of dissimilatory Fe(III)-reducing prokaryotes (DIRP) more than 20 years ago (e.g. *Geobacter metallireducens* [91]; *Shewanella oneidensis* [92]), microbial Fe(III) reduction has received considerable attention. In DIRP, electrons are generated after the oxidation of hydrogen gas or low-molecular organic matter, and then are transferred from cellular membranes to Fe(III)-minerals outside the cell [93]. Understanding of the Fe(III) reduction by DIRP has been improved greatly with regard to the types of microorganisms, metabolic processes and electron transferring mechanisms [93]. In addition to the well-known DIRP, a wide variety of anaerobes also are considered to conduct Fe(III) reduction in natural settings (e.g. some fermentative microorganisms [94], sulfate-reducing bacteria [95,96], and some methanogens [97,98]). In contrast to soluble electron acceptors (e.g. nitrate and sulfate) present in anoxic environments, Fe(III) occurs as solid phases (oxides or silicate), leaving dissimilatory Fe(III) reduction as the

preferred pathway. Various minerals (e.g. magnetite, vivianite, siderite) can be formed during this process, depending on the initial minerals and geochemical conditions. It has been proposed that microbial Fe(III) reduction may be one of the earliest respiration pathways in Earth history [99].

In comparison with nearly neutral environments, iron-cycling GFGs are quite different in acidic conditions (i.e. acid mine drainages). In acidic environments, *Thiobacillus* and *Leptospirillum* have been found to predominate during aerobic Fe(II) oxidation [100], whereas *Acidobacterium* shows a predominance in the anaerobic reduction of Fe(III)-minerals [101].

2 Identification diagnostics of GFGs in sediments and rocks

2.1 Photosynthetic GFGs

As stated earlier, photosynthetic GFGs preserved in rocks are hard to identify by morphological examination. The commonly used geochemical and mineralogical records can indicate redox potential of the water column, and thus provide indirect inference for the presence of photosynthetic GFGs. In the past several decades, a variety of biomarkers have been found to be specific for modern photosynthetic GFGs, which can be extrapolated to ancient times. Cyanobacteria can be inferred by the presence of 2-methylhopanoids, including 2-methylhopanepolyols and 2-methylhopanes, especially those with a carbon number >31 [102]. Some cyanobacteria also can biosynthesize specific branched alkanes, such as 7-methylheptacosane and 8-methylheptacosane [103]. Green sulfur bacteria also have some specific biomarkers, such as maleimides (1H-pyrrole-2,5-diones) [104], 2-alkyl-1,3,4-trimethylbenzene and C₄₀ isorenieratene [105]. The biomarkers specific for diatoms include C₂₅ and C₃₀ highly branched isoprenoids (HBI) [106] and 24-nor-cholesterols [107]. Dinoflagellates can biosyn-

thesize dinosterol (4 α ,23,24-trimethyl-5 α -cholan-22-en-3 β -ol), while coccolithes are the dominant precursors of long chain alkenones [108]. However, caution should be taken when using biomarkers to interpret origins. For example, 2-methylhopanoids also have been detected in bacteria other than cyanobacteria. Thus, multiple lines of evidence are needed for the robust confirmation of specific GFGs.

2.2 GFGs in methane cycling

Microbes involved in CH₄ cycling usually have diagnostic lipid compounds and/or depleted carbon isotopic composition, which can be used as indicators of the related GFGs in ancient times. In cold seeps of modern seas, methanotrophic archaea encompass the following three clades: ANME-1, ANME-2 and ANME-3 [109]. ANME-1 lipids are featured by GDGTs dominated by 0–3 cyclopentane rings, while ANME-2 biosynthesizes mainly *sn*2-hydroxyarchaeol and crocetane (2,6,11,15-tetramethylhexadecane). ANME-3 is characterized by *sn*2-hydroxyarchaeol and PMI (2,6,10,15,19-pentamethylcosane) [110]. In contrast, aerobic methanotropic bacteria of Group I synthesize 3-methylhopanoids [111] and C₁₆ mono-saturated fatty acids, while those of Group II synthesize C₁₈ mono-saturated fatty acids.

Furthermore, lipids derived from methanotrophs normally show a highly depleted carbon isotope composition, which is inherited from ¹³C-depleted biogenic CH₄. Methane produced via the acetate pathway has a $\delta^{13}\text{C}$ range from –50‰ to –65‰, and the CO₂/H₂ pathway will result in CH₄ with more depleted $\delta^{13}\text{C}$ values (–60‰ to –110‰) [112]. Integration of diagnostic biomarkers with ¹³C-depleted isotope records will allow a robust confirmation of CH₄-cycling GFGs present in Earth history.

In addition to lipid biomarkers and carbon isotopes, some specific minerals also can provide a clue for the activity of CH₄-cycling GFGs. In cold seeps of the modern sea floor, great abundances of chemoautotrophic microorganisms have been found. HCO₃[–], produced by anaerobic CH₄ oxidation, is oversaturated in seawater, and interacts with Ca²⁺ to precipitate calcium carbonate. These minerals, known as cold seep carbonates, often contain thrombolite with aragonite cements of radial and concentric structures, or brecciated carbonates from overpressured gas movements. Associated with these carbonate minerals are barite and gypsum, forming encrustations, mound and slabs of various sizes, with thicknesses of meters to tens of meters [113]. Presence of over-saturated HS[–] facilitates the deposition of framboidal pyrite. The authigenic carbonates formed in cold seeps normally show a depletion of ¹³C, while barite has a relative ³⁴S enrichment. Some of the sedimentary structures and isotope compositions can help to identify events related to gas hydrate release and their impact on the Earth environments and ecosystems [114,115]. In contrast with cold seeps, hydrothermal vents are mainly composed of sulfide, such as pyrite, chalcopyrite, pyrrhotine and blende. Massive sulfide

ores containing microfossils are commonly regarded as remains of ancient black smoker systems [116].

2.3 GFGs in sulfur cycling

Precise identification of the GFGs related to sulfur metabolism is the key to unravel the sulfur cycle and oceanic geochemistry throughout Earth history. Current diagnostics include biomarkers, iron geochemistry and sulfur isotope compositions. Green sulfur bacteria (Chlorobiaceae) and purple sulfur bacteria (Chromatiaceae) are two important anaerobic microbes which utilize H₂S, and are good indications for euxinic oceans, if found in ancient deposits. They both have particular biomarkers. Chlorobactane, isorenieratane and trimethyl aryl isoprenoids are the main biomarkers of green sulfur bacteria, while okenane is diagnostic of purple sulfur bacteria [54]. As the carbon fixation pathway in green sulfur bacteria is the Krebs cycle featured by only small isotope fractionation, the organic compounds biosynthesized by these bacteria show a ¹³C-enriched isotopic composition. The carbon isotopic composition of trimethyl aryl isoprenoids and other potential compounds, such as farnesane, also can be diagnostic of green sulfur bacteria. Sulfate-reducing microbes identified in modern environments show some biomarkers, such as short-chained (C₁₅, C₁₇) *iso*- and *anteiso*-fatty acids [117]. Unfortunately, these fatty acids are transformed very easily during early diagenesis to other more geologically stable compounds, but of less specific biotic diagnostic value (i.e. *iso*- and *anteiso*-alkanes). Other potential biomarkers of ancient sulfate-reducing bacteria are yet to be explored.

It is known that H₂S is an important by-product of microbial sulfate reduction, and can react with iron (II) to form pyrite that is ultimately preserved in ancient deposits. It is interesting to note that pyrite grains show a size variation related to their sedimentary environmental conditions. In extremely anoxic or euxinic environments, microbial sulfate reduction occurs in the water column where the iron concentration is very low. In this case, the pyrite grains formed are framboidal with a small but homogeneous size range (mean value of 4–5 μm) [118]. The size distribution pattern of framboidal pyrite grains and the iron geochemical features are useful tools to explore sulfidic oceans and associated GFGs in ancient times [119].

Sulfur isotopic composition of pyrite could be an effective record for the sulfur cycle and the related GFGs [42]. A large kinetic fractionation of sulfur isotopes exists during microbial sulfate reduction, resulting in ³²S-depleted pyrite. When the oceanic sulfate concentration is very low, pyrite formed tends to yield very high $\delta^{34}\text{S}$ values, such as those found in Precambrian rocks [120]. The sulfur isotopic composition of pyrite also can be used to locate the redox boundary in ancient oceans. When the redox boundary is located below the sediment-water interface, pyrite $\delta^{34}\text{S}$ is featured by high values with a very large variation range.

Both ^{33}S and ^{36}S of low contents can be measured precisely by advanced techniques. This refinement in techniques makes it possible to discriminate microbial sulfate reduction from sulfur disproportionation in ancient times because of their distinct ^{33}S fractionation coefficient ($^{33}\lambda$) [47,121,122].

2.4 GFGs in nitrogen cycling

The identification of nitrogen-metabolizing GFGs in sediments and rocks is the key to decipher the nitrogen cycle in geological history, and can only rely on microbial membrane lipids and nitrogen isotopic signatures. Some diazotrophic cyanobacteria (e.g. *Anabaena cylindrical*) can biosynthesize specific biomarkers (e.g. glycolipids in heterocysts), which can protect the O_2 -sensitive nitrogenase from inactivation. The heterocyst glycolipids can be preserved in sediments for a long time because of their resistance to degradation, and can be used as biomarkers to trace nitrogen-fixation cyanobacteria in ancient oceans [78]. Specific unsaturated bacteriohopanepolyols with four hydroxyl side chains are diagnostic of nitrogen-fixing cyanobacteria, *Trichodesmium*, the dominant microbes in modern oceans [123].

Ammonia-oxidizing crenarchaeota possess a unique biomarker (i.e. crenarchaeol with cyclopentyl rings), which has been preserved even in Cretaceous marine strata [124,125]. The number of cyclopentyl rings in the lipids of marine ammonia-oxidizing crenarchaeota shows a strong positive correlation with sea surface temperatures (SST). Based on this observation, a paleothermometer (TEX_{86}) was established and widely applied to ancient SST reconstruction [126]. The biomarkers of anammox bacteria (ladderanes) are the membrane lipids of anammoxosome, a compartment that prevents the poisonous hydrazine from entering the cell [127]. Ladderanes have been used to trace the anammox process in the Arabian Sea over the last glaciation [128], which is currently the only known way to identify the presence of anammox in geological history.

In addition to these diagnostic lipids preserved in sediments, nitrogen isotopes ($\delta^{15}\text{N}$) also can reflect the presence of nitrogen-related GFGs. Cyanobacteria can induce fractionation of nitrogen isotopes with organic $\delta^{15}\text{N}$ values ranging from -3‰ to 1‰ . Nitrogen isotopic fractionation during nitrogen-fixation and non nitrogen-fixation has been discriminated clearly in supratidal and intertidal microbial mats. Organic nitrogen isotope composition was clearly more negative in supratidal than in intertidal microbial mats, and heterocyst glycolipids, the biomarkers of some nitrogen-fixing cyanobacteria, were identified only in supratidal microbial mats [78]. The negative shifts of $\delta^{15}\text{N}$ during Cretaceous oceanic anoxic events and across the Permian-Triassic boundary both indicate past blooms of cyanobacteria [129,130], consistent with the occurrence of enhanced cyanobacterial biomarkers [131]. Nitrogen fixation needs more energy than nitrate-assimilating metabolism, and mi-

croorganisms, even cyanobacteria, prefer nitrate uptake to nitrogen-fixation. Thus, at some critical periods in geologic history, enhanced nitrogen fixation, shown by $\delta^{15}\text{N}$ due to marine cyanobacteria blooms, may indirectly indicate low nitrate concentrations and anoxic conditions in ancient sea water.

Denitrification, including anammox, can cause a great fractionation of nitrogen isotopes. The ^{15}N -enriched nitrate left after denitrification can be assimilated by primary producers, such as algae, to biosynthesize organic matter with relatively positive $\delta^{15}\text{N}$, averaging between 7‰ and 9‰ [132]. Elevated $\delta^{15}\text{N}$ values may indicate the presence of relatively strong denitrification, and *vice versa*. For example, relatively higher $\delta^{15}\text{N}$ values and higher N_2O concentrations observed in interglacial ice cores, reveal stronger denitrification in interglacial compared to glacial periods. The nitrogen loss may become more severe because of the much stronger denitrification during interglacial periods, and further cause the decline of marine primary productivity [60]. However, pure culture experiments of some diazotrophic cyanobacteria have revealed that $\delta^{15}\text{N}$ records cannot discriminate nitrogen-fixation from non nitrogen-fixation [78], with both nitrate uptake and nitrogen fixation showing negative $\delta^{15}\text{N}$ values. In addition, the $\delta^{15}\text{N}$ values also may be affected by microbial degradation of organic matter, terrestrial organic input and diagenesis. Thus, caution should be taken when interpreting the nitrogen cycle on the basis of $\delta^{15}\text{N}$ records throughout geologic history.

2.5 GFGs involved in iron redox cycle

GFGs related to the iron redox cycle are hard to preserve in rocks and, if preserved, they are difficult to classify into a specific group. It was widely assumed that both the branched (i.e. 10-methyl $\text{C}_{16:0}$) and *iso*- (*iC* $_{17:107c}$) fatty acids could be used as indicators of DIRP. However, these fatty acids also are biosynthesized by sulfate-reducing bacteria [133]. To date, a series of diagnostics of these GFGs are proposed, including mineral types and assemblages, and iron isotope compositions.

Magnetite is one of the typical products formed during microbial Fe(III) reduction. Biogenic and inorganic magnetite cannot be differentiated by morphological features [134], but rather by other properties. In an experimental study on *Shewanella oneidensis*, Perez-Gonzalez et al. [135] found that cell fragments and metabolic materials can co-precipitate with magnetite. On the basis of analysis of precipitated magnetite by thermogravimetry and FT-IR, the authors revealed that organic matter enclosed in biogenic magnetite can be of diagnostic use to differentiate inorganic magnetite. In contrast to chemically-synthesized magnetite, biogenic analogs are characterized as poor crystallinity [135,136] and excess Fe^{2+} content, with an $\text{Fe}^{2+}/\text{Fe}_{\text{total}}$ ratio of 0.4–0.6 [136–138] which, in turn, results in the presence of distinct lattice parameters [136] and the shifting of vibrating adsor-

bent peaks in Raman spectra toward higher frequency [135].

In addition to oxides and hydroxides, clay minerals are another important reservoir of structural Fe(III), which can be used as an electron acceptor by Fe(III)-reducing microorganisms [139]. Upon microbial reduction, Si, Al and other elements in clay minerals can be released into aquatic systems, favoring the precipitation of silica, Fe(II)-minerals (sulfides), calcite and other secondary minerals [96,139]. The silica and iron sulfide formed could be transformed to more stable phases (quartz and pyrite, respectively). Consequently, the mineral assemblages (e.g. aggregates of quartz and pyrite, calcite intergrown with phyllosilicate) and other geochemical records (e.g. sulfur isotope composition) help to identify the presence of Fe(III)-reducing microorganisms [140,141].

It is notable that, in the past decade, iron isotope composition has had a rapid application in the detection of microbial activities. The growing evidence suggests that hydrous ferric oxide induced by photoferrotrophy indicates $\delta^{56}\text{Fe}$ values greater than aqueous Fe^{2+} values (by ca. 1.5 ‰), which is caused by both equilibrium fractionation (ca. 2.9‰) between Fe^{3+} and Fe^{2+} in aquatic system, and kinetic fractionation during the co-precipitation of oxides and Fe(III)aq ($\sim -1.4\text{‰}$) [142,143]. In contrast, the iron oxides produced by nitrate-dependent iron-reducing bacteria show a $\delta^{56}\text{Fe}$ value 3‰ greater than aquatic Fe^{2+} , but close to the equilibrium fractionation between Fe^{3+} and Fe^{2+} in aquatic systems at room temperature [144]. An experimental study by Crosby et al. [145] indicated that soluble Fe^{2+} produced by the DIRP, *Geobacter sulfurreducens*, shows $\delta^{56}\text{Fe}$ values 3‰ more depleted than reactive Fe(III) on iron oxide surfaces, which was caused by fractionation during atomic and electron exchanges between them.

3 GFGs roles over major environmental changes

Photosynthetic GFGs are some of the most important microbes in the evolution of the Earth's environments. These GFGs enable the biosynthesis of organics using CO_2 and sunlight energy. Thus, they exert an important effect on the Earth system via regulation of the carbon cycle. In addition, the molecular oxygen released in photosynthesis further changes the Earth's environments via influencing the cycles of carbon, sulfur, nitrogen and iron which, in turn, cause a significant impact on the origin and evolution of other organisms. Photosynthesis is believed to be the dominant dynamic process that triggered the evolution of the Earth from oxygen-free to oxygenic system, which is the prerequisite of the presence of metazoans. Photosynthetic GFGs are, to some extent, the most significant driver to change the Earth's environments. Photosynthesis has been discussed in detail elsewhere [14,146], and will not be discussed further here.

The GFGs involved in the carbon cycle have a great im-

act on marine environments as well as on the atmosphere, and cause the association of abnormal paleoclimate with carbon cycle variation. The roles of these GFGs are archived in rocks in the form of organics and inorganics, such as minerals. The GFGs metabolizing sulfur species also can influence the atmosphere via release of sulfur-containing organics which are quickly transformed into dimethyl sulfide in the air, among other mechanisms. While it is difficult to identify and confirm such processes in ancient times, we can demonstrate the roles played by these GFGs in changing marine environments by exploring the sulfur isotope composition in rocks. Nitrogen-metabolizing GFGs mainly impact organisms and environments by changing their nutritional status, which may be recorded in the nitrogen isotope composition of organic compounds.

It is notable that a variety of GFGs interacted during environmental change across critical periods in Earth history. For example, nitrogen-fixing microbes (mainly cyanobacteria), sulfur-metabolizing microbes (green sulfur bacteria) and CH_4 -oxidizing bacteria (Type I) all have been documented to have caused blooms during the transitional period from the Permian to Triassic. Associated with these microbial blooms was the presence of a sulfidic ocean, low sulfate concentration in seawater, abnormal paleoclimate, fluctuating carbon cycle, and mass extinction of both marine and terrestrial fauna and flora. The co-occurrence of these events shows interactions not only among GFGs, but also with the paleoenvironments of that interval.

3.1 GFGs involved in abnormal climate

Both CO_2 and CH_4 are the most important greenhouse gases, and also are critical components in the global carbon cycle. As a result, an abnormal carbon cycle usually is associated with abnormal climate change, such as cold and warm periods. In ancient times, enhanced activities of methanogens and methanotrophs have been documented to closely correlate with paleoclimate change. These CH_4 -related GFGs, independently or in cooperation with other GFGs, played positive roles on paleo-environments. For example, endophytic methanotrophic bacteria have been found to have lived in symbiosis with *Sphagnum* species in peatlands [147]. This symbiotic phenomenon is believed to have been dominant in the global *Sphagnum* peatlands. Methanotrophic bacteria, of high diversity [148], oxidize CH_4 to CO_2 , which is then fixed by *Sphagnum* as the carbon source for photosynthesis. This symbiotic process allows CH_4 to cycle within peatland organisms, mitigating CH_4 release to the atmosphere. In the northern hemisphere, *Sphagnum* species cover an area of $1.5 \times 10^6 \text{ km}^2$, and it could be estimated that this symbiosis will reduce the release of CH_4 from peatlands to the atmosphere [149]. However, since the last glaciation, the circum-arctic peatlands have been observed to have expanded explosively between 12 and 8 ka, in agreement with the sustained peak in concentration of at-

atmospheric CH₄ [150,151]. This reveals the importance of peatland contribution to atmospheric CH₄, although reduced by microbial symbiosis. Massive release of deep-sea CH₄ also was found to occur during the warm intervals of the last glaciation [152–154], though remained further confirmation. It appears that peatlands are probably not one of the major contributors to the progressive increase of atmospheric CH₄ concentration during the recent 5 ka [150,155]. It has been found that, of all the CO₂ fixed by *Sphagnum* species, the relative CO₂ proportion derived from methanotrophic oxidation is related to peatland hydrological conditions [147,156]. Consequently, precipitation impacts the symbiosis of methanotrophs with *Sphagnum* species, and the release of peatland CH₄. We should pay particular attention to this with regard to the current situation of increasing global warming [157].

In Earth history, some warm periods that occurred immediately after major glaciations have been found to be associated with massive releases of CH₄ from sea floor gas hydrates. One typical example is the Doushantuo warm period after the Nantuo glaciation in Neoproterozoic. Cap carbonates from several sections show extremely ¹³C depleted carbon isotopic values (as low as −48‰), previously suggesting a widespread CH₄ release in this warm period in south China [115]. However, this explanation awaits further investigation because different interpretation was recently proposed for the ¹³C depleted cap carbonate [158]. The Paleocene-Eocene thermal maximum (55 Ma) is a well-documented thermal interval. Atmospheric temperature is believed to have increased by 5–9°C within a very short period (several thousand years) [159,160]. The greenhouse effect from oxidation of CH₄ released from a tremendous volume of gas hydrate has been proposed widely to have triggered this warm event [161,162], although this hypothesis is rejected by other researchers [163]. Pancost et al. [164] identified the bloom of methanotrophic bacteria in wetlands across the Paleocene-Eocene boundary, indicated by the occurrence of ¹³C-depleted hopanes. These studies revealed a potential causal connection among CH₄-related GFGs, gas hydrate release and the thermal climate, in which GFGs might show positive or negative feedback to climate change by regulating the CH₄ cycle. Association of warm climate with elevated atmospheric CO₂ concentration also was commonly present in the Mesozoic, such as in the interval across Triassic-Jurassic boundary, early Toarcian in the Jurassic and early Aptian in the Cretaceous. However, it remains unclear how GFGs show a response to the events observed in these warm intervals.

Abnormal carbon cycles shown by carbon isotope excursions also are associated with biotic mass extinctions (e.g. end Permian and end Cretaceous), in addition to the associated major climate change [165,166]. Stanley [167] proposed that the dominant cause for carbon isotope excursions was associated with the Phanerozoic mass extinctions is change in the respiration rate of marine bacteria. The tem-

perature variations occurring during these biotic crises would likely have strongly affected microbial respiration rate which, in turn, influences the amount of ¹³C-depleted organic matter buried and the δ¹³C value of the marine inorganic carbon pool. This infers a linkage among microbes, abnormal carbon cycle, climate change and biotic crisis, which awaits further investigation. Luo et al. [168] discovered that blooms of cyanobacteria or green sulfur bacteria show a strong link with carbon isotope excursion across the Permian-Triassic boundary at the Meishan section. They stated that GFGs variations immediately following the faunal mass extinction could have strongly affected carbon isotope fractionation.

3.2 GFGs in sulfidic oceans

It is well known that anoxic seawater environments mainly develop through the O₂ consumed in the water column by abundant organics derived from blooming microbes. The euxinic ocean is characterized by an anoxic condition enriched in H₂S. A well-known ancient euxinic ocean was that of the Late Palaeoproterozoic to Late Neoproterozoic or the so called Canfield Ocean, proposed by Canfield [169], which lasted for more than 1 Ga. Elevated atmospheric O₂ content of early Earth promoted continental erosion and thus allowed an increase in oceanic sulfate content. Microbial reduction of elevated sulfate led to hydrogen sulfide surpassing Fe (II) volume, and H₂S began to accumulate in the ocean. As a result, the ferruginous ocean was replaced by the euxinic ocean, occurring about 1.84 Ga ago [170]. In the Phanerozoic, euxinic oceans also occurred frequently, and interrupted the normal oxic oceanic sedimentation. The main intervals known with euxinic conditions in the Phanerozoic are Late Cambrian [171], the transition from Ordovician to Silurian [172], Late Devonian [173], late Permian to early Triassic [55,174] and several intervals in the Cretaceous known as the Anoxic Ocean Events [175]. It remains unclear whether these euxinic oceans were global, or caused by local restricted sedimentary basin conditions (e.g. as in the Black Sea).

The typical GFGs in euxinic oceans are characterized by microbes capable of reducing sulfate, and oxidizing H₂S in anaerobic and aerobic pathways. Sulfate-reducing bacteria or archaea are the main microbes that carry out sulfate reduction. This metabolism produces a great amount of H₂S to cause euxinic oceans, leaving the sulfate residue enriched in heavy sulfur isotopes [54,176]. Anaerobic H₂S-oxidizing microbes mainly include green sulfur bacteria and purple sulfur bacteria. The two microbes, requiring both sunlight and H₂S in a sulfidic photic zone, oxidize H₂S to sulfate [54,55]. Aerobic H₂S-oxidizing bacteria may reside in the same horizon, or much shallower than, anaerobic H₂S-oxidizing bacteria [57], and they mainly produce elemental sulfur [177].

In euxinic oceans, some GFGs are capable of denitrifica-

tion, anaerobic ammonia oxidation and nitrogen-fixation [178]. These GFGs convert most of the biologically available nitrogen (NH_3 , NH_4^+ , NO_3^- , NO_2^-) to inert nitrogen gas in euxinic conditions. This means that euxinic oceans would be deficient in bioavailable nitrogen and would promote microbial nitrogen fixation dominantly driven by cyanobacteria [178,179]. Some archaea with unknown functions also could play important roles in development of euxinic oceans [180,181].

3.3 GFGs in seawater with low sulfate concentration

Sulfate concentration is very high (about 29 mmol/L) in modern oceans. However, oceanic sulfate concentration in geological history varied frequently, and was characterized by several intervals with extremely low values. The Precambrian ocean, for example, had very low sulfate concentrations [44,182]. In the Phanerozoic, the oceans also were characterized by the alternation of high and low sulfate concentrations [183,184], with low values being reported from the Late Cambrian to Early Devonian, Permian-Triassic transition and Triassic-Jurassic transitional period [176,185].

Methanogens are the main GFGs in the oceans with low sulfate concentration. Methanogens will compete with sulfate-reducing bacteria for H_2 and acetate [186]. Decline in oceanic sulfate concentration facilitates methanogen bloom by obtaining much more H_2 and acetate [54]. In addition, because more than 50% of organics are mineralized through sulfate reduction [187], low sulfate concentrations allow more organics to remain unmineralized and present in the methanogenesis zone, which in turn causes the methanogen blooms.

Methanotrophs, particularly aerobic methanotrophs, also are dominant GFGs in oceans with low sulfate content. The enhanced metabolism of methanogens illustrated above promotes the production of CH_4 . It is well known that most (80%) methane [188] is oxidized by the consortium of anaerobic methanotrophs and sulfate-reducing bacteria using sulfate as an important electron acceptor [35]. Low oceanic sulfate content and high production of CH_4 clearly promotes the metabolism of aerobic methanotrophs, including type I, II and X. Type I methanotrophs, indicated by definite biomarkers such as 3-methylhopanepolyols, are abundant in modern lacustrine environments with low sulfate content, but scarce in modern oceanic environments [123]. Type I methanotrophs also were found to be abundant in Precambrian strata, in particular in the late Archean when oceanic sulfate concentration is believed to have been low [54,189]. Recently, extremely low oceanic sulfate concentrations [176] also were found in association with high abundance of type I methanotrophs [174] in strata straddling the Permian-Triassic transition. Consequently, typical GFGs in environments with low sulfate content are methanogens and aerobic methanotrophs, along with some others, such as photosyn-

thetic GFGs.

As discussed above, oceanic sulfate in low contents could exert important impacts on the Earth's environments and biogeochemical cycles. Enhanced methanogenesis and declining anaerobic oxidation of methane allow an elevated flux of methane to the surface ocean and to the atmosphere. Enhanced release of methane, a strong greenhouse gas, tends to increase atmospheric temperature and continental erosion, causing enhanced input of nutrients and sulfate into the ocean, affecting other biogeochemical cycles. Quantification or semi-quantification of these fluxes is needed to decipher these changes in the Earth's system.

Although oceanic sulfate plays an important role on microbial geochemical cycles, its concentration remains largely unknown in ancient times, in particular with controversial data reported for the Precambrian. It was recently found that H_2S was present only in a very small portion of the shallow waters on the continental margin, with most being dominated by Fe (II) in the end-Palaeoproterozoic and end-Neoproterozoic oceans [190,191], indicative of low sulfate concentration. This situation could well have continued into the Late Cambrian [192]. However, little is known about the evolution of this pattern and the causes of low concentrations of oceanic sulfate during the two intervals.

3.4 GFGs related to nutritional status

Nitrogen, phosphorous and iron are important nutrients that control growth in organisms. In shallow marine environments, these nutrients can be input from the continents to the oceans via surface runoff and wind dust. Across the Paleocene-Eocene and Permian-Triassic boundaries, enhanced terrestrial weathering contributed more N, P and Fe to marine environments. The marine photosynthetic GFGs and diazotrophic GFGs flourished, and led to negative shifts of $\delta^{15}\text{N}$ [130,131,174]. In most cases, the GFGs cannot only passively respond to nutrient change, but they also positively impact marine environments. For example, the degradation of dead primary producers in eutrophic oceans may consume most free oxygen in the water column, and result in anoxic conditions. Accordingly, green sulfur and purple sulfur bacteria may flourish in photic zones [174], and enhanced denitrification may emit the greenhouse gas N_2O into the atmosphere [193]. Accumulation of organic matter and anoxic conditions may favor flourishing of methanogens, and enhance the methane emissions [194]. Thus, nutrient exchange in the water column can trigger a series of biogeochemical processes among different GFGs, which significantly affect marine environments. The presence of a variety of GFGs and the associated marine environmental changes across the Permo-Triassic boundary represented such a case in Earth history [130,131,165,174].

In the pelagic oligotrophic regions, nitrate is limited and the bioavailable nitrogen species can only be provided

through cyanobacterial nitrogen-fixation. The nitrogen species fixed may then directly control marine primary productivity [195]. In oligotrophic conditions, the nitrogen cycle driven by nitrogen-related GFGs may be the key factor to determine marine nutrient conditions. It is estimated that nitrogen fixed is $(0.06\text{--}25)\times 10^{12}$ mol per year in modern marine environments [196]. This nitrogen pool becomes indispensable in supporting the vast marine food chains. However, nitrogen-fixation rates can be restricted by Fe, Mo and P inputs by wind dust [63,197,198]. During glacial periods featured by relatively strong wind dust, increased inputs of iron could potentially have enhanced cyanobacterial nitrogen-fixation and promoted marine primary productivity in pelagic regions [199].

It should be noted that an acidified ocean induced by elevated atmospheric P_{CO_2} may reduce ammonia-oxidation rates of AOA and AOB, but promote cyanobacterial nitrogen-fixation [200]. For example, across the Permian-Triassic boundary, volcanic eruptions contributed more CO_2 to the atmosphere, which may have favored diazotrophic cyanobacteria to compete over phytoplankton in low nitrate environments [201]. Ocean acidification also may prevent diatoms and coccolithes from acquiring more soluble iron, which further makes iron more restricted for marine primary producers [202]. Thus, during geological periods with elevated atmospheric P_{CO_2} , diazotrophic cyanobacteria would be the dominant primary producers and may play an important role in the marine ecological systems.

An excess of nutrient elements (e.g. N and P) can favor blooms of some GFGs which, in turn, lead to formation of black shales occurring widely in the geologic history. The black shales are of economic significance since they host a variety of ores, oils and gases, and also can provide insight into the nutrient conditions and seawater chemistry in ancient times [129,132,203]. For example, the lower Cambrian black shales widely distributed on the Yangtze Platform in south China are characterized by the occurrence of geomicrobes and enrichment of polymetallic elements, including Mo and Ni. Enhanced upwelling of nutrient elements (e.g. N and P) at that time may have facilitated the flourishing of cyanobacteria-dominated photosynthetic microbial groups, which contributed abundant organics to the black shales. Sulfate-reducing bacteria may have released hydrogen sulfide in the euxinic waters and resulted in the precipitation and enrichment of metal sulfides [204]. Thus, photosynthetic GFGs and sulfur-metabolizing GFGs may have played key roles in the formation of black shales and associated ores and oil resources throughout Earth history.

3.5 GFGs involved in the deposition of Precambrian banded iron formation

Microbes play important roles in facilitating surface energy flow, as well as affecting various geological processes and associated environmental changes via involvement in the

iron redox cycle. Through these processes, they impact the carbon cycle, the migration of life elements, and the transportation and transformation of metals and nuclides [86,93]. Here, their contribution to the deposition of Precambrian banded iron formations (BIFs) is specifically reviewed.

BIFs are unique marine sedimentary rocks featured by rhythmic layers of chert and iron-rich minerals (e.g. magnetite, hematite), deposited from 3.6 to 1.8 Ga with a maximum deposition at 2.5 Ga [205]. It is believed that the ocean water during this period was characterized by extremely low sulfate concentration and enriched ferrous iron [206]. To date, the mechanism driving ferrous iron oxidation to form ferric iron in BIFs is still highly debated. Fe^{2+} oxidation in the ocean was suggested to have been caused by free oxygen generated by cyanobacterial photosynthesis. However, the chemical oxidation of Fe^{2+} by free oxygen appears to be limited. This is particularly true when we consider the low atmospheric partial pressure of oxygen, which was 10^{-5} to 10^{-3} times less than present values before the first Great Oxidation (2.45 Ga) [207], allowing localized "oxygen oases" in coastal settings [87], and was still 0.02 to 0.04 times the present atmosphere even in the age of 2.45–1.8 Ga [207], with oxic surface water but anoxic bottom water. BIFs were thus formed in anoxic waters, and this excludes the dominant contribution of cyanobacteria [208]. Fe^{2+} could be photo-oxidized by ultraviolet photons, but modern laboratory simulations exclude this as a dominant contribution [209]. It is further proposed that photoferrotrophy could accelerate, and thus dominantly contribute to, ferrous iron oxidation in O_2 -free conditions [19,208,209]. It is notable that the presence of photoferrotrophy in slightly oxic shallow water in ca. 1.9 Ga was confirmed by a negative Ce anomaly and positive $\delta^{56}\text{Fe}$ values found in Gunflint and iron-stromatolites in Biwabik BIFs in North America [210].

It is believed that heterotrophic microbes were ubiquitous in the BIFs [87] because of the precipitation of a huge amount of Fe(III), the presence of anoxic bottom water and the organics biosynthesized by photosynthetic plankton (e.g. anoxygenic photosynthetic Fe(II)-oxidizing bacteria). In fact, the negative $\delta^{56}\text{Fe}$ values found in 2.5-Ga BIFs in Hamersley Basin in Australia and in Transvaal Craton in South Africa support the presence of dissimilatory Fe(III)-reducing bacteria [143]. More recently, Li et al. [211] proposed that the GFGs related to iron redox were dominated by photosynthetic plankton and dissimilatory Fe(III)-reducing bacteria on the basis of the co-occurrence of magnetite and apatite, and features observed using Mössbauer spectroscopy and crystal lattice parameters of magnetite.

4 Conclusions

Extensive investigation of the GFGs involved in the elemental cycles of carbon, sulfur, nitrogen and iron has been conducted in modern natural environments, allowing a deep

understanding of the functions of these particular microbes. These GFGs were found to play significant roles in ancient environments, such as the abnormal climates, sulfidic oceans, seawater with low sulfate concentrations, nutritional status of ecosystems, and the deposition of Precambrian banded iron formations. Nevertheless, the significant roles the GFGs have played throughout Earth history are far from being fully deciphered. This situation results from poor preservation and taxonomic challenges in identifying geomicrobes, which show less diversity in morphology and structures in comparison with fauna and flora preserved in rocks. It is notable that geomicrobes are discriminated by diverse functions of ecology, physiology, metabolism and biogeochemistry, making new breakthroughs possible by targeting their functional groups. It is impossible to identify the entire range of geomicrobes, but it is critical to focus on the GFGs, which were preserved in rocks as diagnostic molecular fossils, geochemical fingerprints, and mineral indications. Some advancement in recognizing the diagnostic records has been made in the past, and needs to be continued in the future. The GFGs are proposed here to be the critical geomicrobes in deciphering the interaction between life and environments throughout Earth history.

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