Thermodynamic energy of anaerobic microbial redox reactions couples elemental biogeochemical cycles

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Abstract

Purpose The thermodynamic energy of redox reactions affects the distribution of microbial redox reactions and cyclic transformation of elements in various anaerobic ecosystems. The principle of thermodynamics is of dramatic significance in understanding the energetics of metabolic processes, the biogeochemical behavior of microorganisms, and mass and energy cycles. The purpose of this paper is to relate the distribution of the coupling reactions between C, N, Fe, and S, the most important elements involved in microbially mediated redox reactions, with their thermodynamic feasibility to provide theoretical foundation of their occurrence.

Results and discussion Anaerobic microorganisms catalyze diverse redox reactions in anoxic environments, driving elemental biogeochemical cycles on the earth. They capture energy from catalyzing these redox reactions in order to support life. The thermodynamic feasibility of these microbe-driven redox reactions is controlled by their energy yields which depend on environmental conditions. Anaerobic microorganisms can oxidize organic carbon with diverse inorganic compounds including nitrate/nitrite, ferric iron, and sulfate as electron acceptors in

various anoxic environments which is referred to anaerobic respiration of organic matter; reversely, inorganic carbon can be reduced to synthesize cell material with ferrous iron and sulfide as an alternative electron donor by phototrophs under different sets of circumstances. Nitrate/nitrite can be microbially reduced by inorganic compounds such as ferrous iron and sulfide under some specific situations; the coupling of anaerobic anammox oxidation and reduction of nitrite (anammox), ferric iron (ferammox), and sulfate (sulfamox) driven by anaerobes occurs in other particular systems.

Conclusions and perspectives Although there are increasing researches investigating the anaerobe-driven coupling of pairs of elements such as C-N, C-Fe, C-S, N-Fe, N-S, and Fe-S, much more intricate situations associating the coupling of multiple elements are still not comprehensively understood. A great many reactions which are thermodynamically feasible have not yet been identified in natural environments or laboratories. Further work focusing on the metabolic pathways from a genetic and enzymatic perspective and the factors controlling the feasibility of the reactions by using updated technical tools and methods is required.

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1 Introduction

Elemental biogeochemical cycles are largely driven by the electron transfer processes mediated by microorganisms, changing the chemistry of the earth's surface profoundly. Despite that the earth's surface is mostly oxic, anoxic environments are vast distributed, including deep marine, freshwater, soils, and sediments, providing habitats for diverse microorganisms. In these anoxic

environments, anaerobic microorganisms perform complex redox reactions, driving the coupling of elements. The distribution of microbial redox reactions is controlled by the thermodynamic energy of redox reactions which depends on environmental conditions. For example, denitrification has been shown to be coupled to the oxidation of organic and inorganic compounds including carbon, ferrous iron, and sulfide in some particular situations (Canfield et al. 1993; Fossing et al. 1995; Laufer et al. 2016). Conversely, anaerobic oxidation of ammonium can be coupled to the reduction of nitrite, ferric iron, and sulfate under different sets of circumstances (Bender et al. 1989; Schrum et al. 2009; Ding et al. 2014). These redox reactions mediated by anaerobic microbes significantly promote the coupling of C-N, Fe-N, and S-N under anoxic environments. Iron undergoes cycles of reduction and oxidation as a terminal electron acceptor for organic carbon oxidation and an electron donor for inorganic carbon reduction under different conditions in anoxic environments making a dramatic contribution to the global biogeochemical coupling of C-Fe (Zhu et al. 2014). Thermodynamics provide a framework for predicting and verifying whether a specific reaction can occur spontaneously and to which extent it can reach the equilibrium. In this paper, we focus on the biogeochemical coupling between C, N, Fe, and S (Fig. 1), the most important elements involved in microbially mediated redox reactions in anoxic environments. We comprehensively review the distribution of these redox reactions and the thermodynamic feasibility of the reactions in environments to provide theoretical evidence of their occurrence.

2 Thermodynamic energy

In order to support life, microbes harness energy released from the redox reactions (Jin and Bethke 2007). They

transfer electrons from electron donors onto electron transport chains inside cell membrane, pumping out protons and fuelling adenosine triphosphate (ATP) synthesis to conserve energy. The electrons are then passed to terminal electron acceptors, and the whole redox reactions are completed (Jin and Bethke 2007). Burgin et al. (2011) proposed the concept of microbial energy economy which was a metaphor referring to the microbial metabolic pathways. Microorganisms capture raw materials from the surroundings to produce goods - biomolecules, such as proteins and nucleic acids, which are then used to supply service-energy production, growth, and biomolecule regeneration. Like a social economy, competitive relationships are involved between different microbial metabolic pathways because of their corresponding thermodynamic feasibility which is controlled by their energy yields (Burgin et al. 2011). Redox reactions proceed sequentially from the highest energy yields towards the lowest, following a thermodynamic ladder. The Gibbs free energy (ΔG) was developed to describe the amount of energy yields of reactions which involves the standard Gibbs free energy of formation ($\Delta_f G^0$) and activities of the substrates and products:

$$\Delta G = \Delta G^0 + RT \ln Q \quad (1)$$

where ΔG^0 can be calculated from Eq. (2):

$$\Delta G^0 = \sum \nu_p \Delta_f G_p^0 - \sum \nu_s \Delta_f G_s^0 \quad (2)$$

where $\Delta_f G_p^0$ and $\Delta_f G_s^0$ are the standard Gibbs free energy of formation of the products and substrates, respectively ($\Delta_f G^0$ values of the studied species in this paper are listed in Table 1), ν_p and ν_s stand for their stoichiometric coefficients. R and T (in Eq. (1)) represent the gas

Fig. 1 Redox reactions between various compounds (C, N, Fe, and S) mediated by anaerobic microorganisms (dotted lines denote abiotic reactions). The redox couples are in an order of increasing standard reduction potential E^0 from left to right. Electrons transfer following the arrows. The number in each square stands for the formula in the

following text. HS_{ox} oxidized humic substances, HS_{red} reduced humic substances. HS_{ox} - HS_{red} has a wide range of standard reduction potential. Here, we put it at an approximate position relative to $Fe(III)$ - $Fe(II)$ and SO_4^{2-}/S^0 - HS^-

Table 1 Gibbs free energy of formation ($\Delta_f G^0$) of the studied constituents

Formula	$\Delta_f G^0$ (kJ/mol)
C ₆ H ₁₂ O ₆	−915.90 ^a
HCO ₃ [−]	−586.77 ^a
CH ₄ (aq)	−34.46 ^b
H ₂ O	−237.10 ^a
H ⁺	0.00 ^a
NO ₃ [−]	−108.74 ^a
NO ₂ [−]	−32.20 ^a
N ₂ (aq)	18.18 ^b
N ₂ O (aq)	113.38 ^b
NH ₄ ⁺	−79.31 ^a
Fe(OH) ₃	−708.50 ^c
α-FeOOH	−489.80 ^d
Fe ²⁺	−78.90 ^a
SO ₄ ^{2−}	−744.53 ^a
S ⁰	0.00 ^a
HS [−]	12.08 ^a

^a Lide (2012)^b Amend and Shock (2001)^c Majzlan et al. (2004)^d Majzlan et al. (2003)

constant (8.314 J/mol) and absolute temperature (298.15 K), respectively. Q denotes the ion activity product according to Eq. (3):

$$Q = \frac{\Pi a_p^{v_p}}{\Pi a_s^{v_s}} \quad (3)$$

where a_p and a_s represent the activities of the products and substrates. We do not differentiate between concentrations and activities of ions because the values of activities in previous reports are often not available.

The value of ΔG reflects the thermodynamic feasibility of the reaction. An exergonic reaction which has a negative value of ΔG has the possibility to proceed spontaneously, while on the contrary, an endergonic reaction which has a positive value of ΔG is difficult to occur under the given conditions. Microbes can catalyze these redox reactions which means raising the reaction rates kinetically by lowering the activation energy to acquire energy for living although cannot change the thermodynamic equilibrium.

Generally, these reactions would not occur close to the limit of thermodynamic equilibrium, i.e., $\Delta G = 0$ for the reason that minimum energy released from the reactions is required to support the growth of microorganisms (Bethke et al. 2011). However, some anaerobic microbes can grow by catalyzing these reactions (ΔG values close to 0) (Conrad et al. 1986; Jackson and McInerney 2002). Different metabolic pathways have different values of minimum energy, with a rough range estimated to be 9–15 kJ/

mol of substrate considering that at least one proton is translocated for the synthesis of ATP when one molecule substrate is oxidized (Hoehler et al. 1994). The minimum energy of a certain metabolic pathway can be determined via pure culture of microbes in the laboratory or estimated from knowledge of the respiratory chain (Jin and Bethke 2003, 2007). Fe(III) reducers need at least 56 kJ to support the oxidation of 1 mol acetate or 11 kJ to support the oxidation of 1 mol H₂ (Jin and Bethke 2009). Methanogens produce methane from acetate with H₂O only when the energy yield exceeds the minimum energy of 11 kJ/mol of acetate (Jin and Bethke 2007). The differing minimum energy required for diverse metabolism pathways influences their energetic efficiency with which substrates are utilized for growth and thus further the thermodynamic feasibility. This minimum energy needs to be considered especially when we judge the thermodynamic feasibility of one reaction with very low energy yield or compare the predominance of two reactions with similar energy generation.

3 Anaerobic organic carbon oxidation

3.1 Anaerobic respiration of organic matter

Anaerobic respiration of organic matter has been a focus of researches for years because this distinct microbial process is ubiquitous in anoxic environments and of significance in decomposing biomass and regenerating nutrients for life (Canfield et al. 1993; Burgin et al. 2011). A vast variety of organic carbon can serve as electron donors with various chemicals as terminal electron acceptors for microorganisms in anoxic environments (Fig. 1). Typically, microbes oxidize organic carbon using electron acceptors in

the order of NO_3^- (Considering that NO_2^- and NO_3^- were not distinguished in some studies, we use NO_3^- to represent NO_3^- and NO_2^- in the formulas in the following discussion if not specially mentioned), Fe(III) , and SO_4^{2-} , yielding progressively decreasing energy (Fig. 2) (Burgin et al. 2011). This energetic hierarchy of reduction processes is present in many natural environments (Froelich et al. 1979; Patrick and Jugsujinda 1992). For example, in a flooded soil with decreasing O_2 diffused into the soil, the microorganisms respire switching from O_2 to NO_3^- as an electron acceptor. Once NO_3^- is depleted, manganese or iron starts to be reduced following a thermodynamic ladder before sulfate reduction (Patrick and Jugsujinda 1992).

Different from the distinct interfaces between zones of NO_3^- reduction and Fe(III) reduction, there exist overlaps between zones of reduction of Fe(III) (oxyhydr)oxides and sulfur species (Postma and Jakobsen 1996). The thermodynamic order of Fe(III) reduction and sulfate reduction varies depending on the availability of substrates, concentration of products, and pH. Microbial reduction of Fe(III) (oxyhydr)oxides strongly favors acidic pH, while microbial sulfate reduction is more likely to occur at alkaline pH. We compare the energy yields of the reduction of Fe(III) minerals (taking ferrihydrite and goethite as examples) and sulfur species (S^0 and SO_4^{2-}) (Fig. 2). According to our calculation, at

acidic pH (pH = ~5), reduction of Fe(III) minerals is energetically more favored than sulfur and sulfate reduction. At neutral pH (pH = ~7), both sulfur and sulfate reduction yield similar energy to ferrihydrite reduction but energetically predominate over the reduction of goethite (with higher crystallinity than ferrihydrite). At alkaline pH (pH = ~9), sulfate and sulfur reduction are the favored processes compared with the reduction of ferrihydrite and goethite. Our calculation (data not shown) points out that among the common Fe(III) minerals, only ferrihydrite, the most unstable one, can be reduced at alkaline pH up to 9 which is consistent with previous researches (Wang et al. 2017). Actually, microbial reduction of Fe(III) minerals and sulfur species is often observed to occur simultaneously (Boesen and Postma 1988). Fe(III) - and sulfate-reducing microorganisms are found to live in a mutualistic relationship. The concentrations of reduction products, i.e., free Fe^{2+} and HS^- , can be decreased because of the formation and precipitation of mackinawite (FeS), driving forward both Fe(III) and sulfate reduction (Neal et al. 2001). Moreover, S^0 produced from sulfate reduction can act as an electron shuttle to mediate microbial Fe(III) (oxyhydr)oxide reduction at alkaline environments (Flynn et al. 2014). Under this condition, S^0 can be microbially reduced to HS^- which then abiotically reduces Fe(III) (oxyhydr)oxides (Flynn et al. 2014).

Humic substance can also be electron acceptors of anaerobic respiration (Scott et al. 1998). Humic substances can accept electrons from anaerobic microorganisms and transfer them to solid Fe(III) minerals, facilitating microbial Fe(III) reduction (Newman and Kolter 2000; Huang et al. 2010). Not only dissolved but also particulate humic substances have shown an electron transfer capability (Roden et al. 2010). Quinones have been recognized as the dominant units of redox activities in humic substances (Scott et al. 1998). We calculated the energy yield of the reduction of AQDS, a commonly used quinone containing analogue of humic substances in laboratory, with glucose as an electron donor, and results showed that it is thermodynamically favorable in the range of pH 5–9 (Scott et al. 1998). Considering the complex composition and structures which cannot be totally represented by AQDS, humic substances would have a wide range of reduction potential, i.e., a wide range of standard Gibbs energy change of the half reaction of reduction (Klűpfel et al. 2014). It has been reported that the range of reduction potential over which humic substances can accept electrons overlap those of many other electron acceptors including Fe(III) (oxyhydr)oxides and sulfur species (Klűpfel et al. 2014). Therefore, the segregation between zones of reduction of humic substances and other electron acceptors is diffuse.

Fig. 2 Gibbs free energy ΔG of oxidation of glucose (1 μM) with the reduction of NO_3^- (1 mM) to N_2 ($10^{-3.47}$ M) or NH_4^+ (1 mM), Fe(III) containing minerals including ferrihydrite (Fe(OH)_3) and goethite ($\alpha\text{-FeOOH}$) to Fe^{2+} (10^{-6} – 10^{-4} M), AQDS (1 μM) to AH_2QDS (1 μM), SO_4^{2-} (1 mM) to HS^- (10^{-8} – 10^{-4} M), and S^0 to HS^- (10^{-8} – 10^{-4} M) alternatively in a pH range of 5–9 (corresponding to formula 1–7, values of ΔG are normalized as kJ per mole of e^- transferred). The reactions are thermodynamically feasible below the dotted line at $\Delta G = 0$ (minimum energy not taken into consideration)

3.2 Anaerobic methane oxidation

Anaerobic oxidation of methane (AOM) is a unique microbial process performed mainly by methane-oxidizing archaea. AOM provides a major sink in methane geochemistry, consuming approximately 90% of global methane production (Reeburgh 2007). Up to date, a variety of chemical compounds including sulfate (Moran et al. 2008), nitrate (Haroon et al. 2013), metal (Fe(III) and Mn(IV)) oxides (Beal et al. 2009), and AQDS (Scheller et al. 2016) have been reported to be electron acceptors of AOM. Sulfate-driven AOM, among the pathways with various electron acceptors, was the most investigated one and has been reported to be the dominant pathway for methane removal in ocean sediments (Canfield et al. 1993). Multiple anaerobic methanotrophic archaeal lineages were reported to form syntrophic consortia with sulfate-reducing bacteria to drive AOM in marine habitats though the electron transport mechanism involved is still unclear (McGlynn et al. 2015). But, it has also been reported that anaerobic methanotrophs might couple methane oxidation and sulfate reduction independently (Milucka et al. 2012). At environmental conditions, the coupling of methane oxidation and sulfate reduction is exoergic but yields very small amount energy of only $-5.0 \sim -2.5$ kJ/mol of e^- transferred, leading to a slow growth of 2-month generation times of the AOM consortia (Wegener et al. 2015). Nitrate-dependent methane oxidation is more thermodynamically favorable than sulfate-dependent methane oxidation, yielding -95.3 kJ/mol of e^- transferred at pH 7 at environmental conditions (Zehnder and Brock 1980). However, the process of denitrifying AOM has only been observed in laboratory but not in nature (Raghoebarsing et al. 2006). It was speculated that this process only occurred within millimeters in the oxic/anoxic interface of sediments where methane and nitrate often coexisted, making it difficult to detect (Raghoebarsing et al. 2006). It was shown that methane oxidation and nitrate reduction could be coupled by methanotrophic archaea in concert with denitrifying partner bacteria or methanotrophic archaea alone (Ettwig et al. 2010). Metal (oxyhydr)oxides (birnessite and ferrihydrite) can also be electron acceptors of AOM in marine methane-seep sediments. Birnessite- and ferrihydrite-dependent methane oxidation was reported to have energy

yields (-33.8 and -69.5 kJ/mol of e^- transferred at in situ conditions) higher than sulfate-dependent methane oxidation, but much slower rates (14 and $6 \mu\text{mol}/\text{year}/\text{cm}^3_{\text{sed}}$) than sulfate methane oxidation ($52 \mu\text{mol}/\text{year}/\text{cm}^3_{\text{sed}}$) (Beal et al. 2009). The rates of Mn(IV)- and Fe(III)-driven methane oxidation may be limited by the solid phase manganese and iron (oxyhydr)oxides which are relatively difficult to utilize for microorganisms. It has been recently found that microorganisms could use humic acids and quinone-containing humic acids AQDS (2,6-AQDS), 1,5-AQDS, and 2,7-AQDS to oxidize methane directly without syntrophic interaction in a methane seep sediment (Scheller et al. 2016). The rate of AQDS-driven AOM was comparable with sulfate-driven AOM in the incubation. It indicated that AOM would also have the ability to reduce solid metal (oxyhydr)oxides with humic acids or other soluble compounds as electron shuttles which supported the finding of AOM-coupled Fe(III) reduction (Scheller et al. 2016). Direct evidence of Fe(III)-driven AOM in cold seep sediments in the northern Okinawa was provided by Peng et al. (2017) from the geological record. They illustrated a model that Fe(III)-driven AOM occurred in the zone where methane and reducible Fe(III) (oxyhydr)oxides were both abundant, while sulfate was completely consumed because of sulfate-driven AOM above this zone. Dissolved Fe^{2+} generated from Fe-driven AOM would migrate with upwelling seep fluids to the zone of sulfate-driven AOM and react with sulfide to form the precipitation of pyrites or mackinawite. Therefore, sulfate-driven AOM and Fe(III)-driven AOM may contribute together to prevent methane emission from seeps (Peng et al. 2017).

4 Anaerobic HCO_3^- reduction by inorganic compounds

4.1 Anaerobic HCO_3^- reduction by Fe(II)

(where (CH_2O) represents simplified composition of cell material)

Photoferrotrophs can use Fe(II) to reduce HCO_3^- for assimilation into cell material in HCO_3^- - and Fe^{2+} -rich environments. Phototrophs utilize solar electromagnetic radiation for energy generation; therefore, they only live in habitats exposed to light. Photoautotrophic Fe(II)-oxidation has been

used to explain the appearance of Fe(III) (oxyhydr)oxides in ancient banded iron formations (BIFs) (Widdel et al. 1993; Miot et al. 2009) and the primary production of organic matter (Canfield et al. 2006) before the occurrence of oxygenic phototrophs (including plants, algae, and cyanobacteria who are responsible for most of the primary production on the present earth) on the early earth (ca. 3.8–2.2 Ga) (Kasting 1993). Photoautotrophic Fe(II) oxidation happened when downward diffusion of CO₂ from shallow, CO₂-rich layer caused by the activity of microbial mats intercepted Fe(II) upwelling from deep waters (Tice and Lowe 2004). Anoxygenic phototrophs were evidenced to thrive within a ferruginous chemocline in modern environments such as Lake Matano (Crowe et al. 2008). A previous research indicated that photoferrotrophs produce poorly crystalline ferric (oxyhydr)oxides (ferrihydrite), which then age into crystalline minerals goethite or lepidocrocite (Kappler and Newman 2004). The reaction tends to occur at high pH as the reaction is proton-producing. But, it has also been reported that photoferrotrophs could oxidize Fe(II) only in dissolved phase, thus setting an upper limit to pH (Martin 1990). The pH dependence of the feasibility of photoautotrophic Fe(II) oxidation, in turn, may explain why photoferrotrophs usually grow at such a narrow pH range (strain L7 grows at pH 6.0 to 7.5, with an optimum pH at 7.0; SW2 grows at pH 5.5 to 7.0, with an optimum pH at 6.5) (Ehrenreich and Widdel 1994).

4.2 Anaerobic HCO₃[−] reduction by HS[−]

Bacteria can also play the roles of primary producers to use sulfide as an electron donor in anoxygenic photosynthesis in sulfide- and bicarbonate-rich freshwater, marine, and particularly hot springs where anoxygenic phototrophic oxidation of sulfide is the dominant way of primary production (Blankenship et al. 1995). In this process, sulfide is oxidized to elemental sulfur or further oxidized to sulfate. Photoautotrophic sulfur oxidation is also a candidate contributor to early earth primary production (Canfield and Raiswell 1999). Sulfide derived from sub-aerial volcanic and terrestrial hydrothermal systems would enter the early earth surface and get involved in primary production (sulfide flux from the deep-ocean hydrothermal systems would have not made an important contribution to early earth primary production because it would have probably precipitated with dissolved Fe²⁺ in the oceans which is mentioned above).

5 Anaerobic NO₃[−]/NO₂[−] reduction by inorganic compounds

5.1 Anaerobic NO₃[−] reduction by Fe(II)

Fe(II) commonly accumulated as an end product of microbial Fe(III) reduction in natural environments has been observed to be re-oxidized in many pure cultures and sediment enrichments (Benz et al. 1998; Blöthe and Roden 2009; Laufer et al. 2016), accompanied by NO₃[−]/NO₂[−] reduction to N₂. NO₂[−] can chemically oxidize Fe(II) without catalysis, but the abiotic reaction of NO₃[−] with Fe(II) only occurs in the presence of microorganisms or surface catalysis such as lepidocrocite and green rust or trace metals like Cu²⁺ (Sørensen and Thorling 1991; Hansen et al. 1996; Ottley et al. 1997; Picardal 2012). In the process of Fe(II)-dependent NO₃[−] reduction, diverse species of Fe(II) including soluble Fe(II) or Fe(II) containing minerals like siderite and magnetite can act as electron donors (Benz et al. 1998; Chaudhuri et al. 2001). In addition to N₂, N₂O was reported to be one of the products of Fe(II)-dependent NO₃[−] reduction (Muehe et al. 2009). Based on our thermodynamic calculation, reduction of NO₃[−] to N₂ or N₂O coupled to Fe(II) oxidation is exoergic generating −75.5~−61.7 or −61.3~−47.1 kJ/mol of e[−] transferred at pH 7.0. It is controversial whether the couple of Fe(II) oxidation and NO₃[−] reduction is directly enzymatically catalyzed in the microcosm incubations (Canfield and Raiswell 1999; Straub et al. 1996). One of the intermediates of microbial denitrification, NO₂[−], can chemically oxidize Fe(II); therefore, the observed coupling of NO₃[−] reduction and Fe(II) oxidation in the microcosm incubations might just be a by-product of denitrification. Most known Fe(II)-oxidizing NO₃[−]-reducing microbes live mixotrophically and therefore require an organic carbon source for the oxidation of Fe(II) over a long period (Hansen et al. 1996; Straub et al. 2004). Recently, researchers confirmed that NO₃[−] reduction coupled to Fe(II) oxidation can be catalyzed by microorganisms (Robertson et al. 2016). They determined stoichiometries of Fe(II) oxidation and nitrate reduction in microcosm incubations and the incorporation of ¹⁴C from labeled bicarbonate and proved the existence of autotrophic Fe(II)-oxidizing NO₃[−]-reducing bacteria in marine sediments. Nevertheless, genetic and enzymatic evidence for the presence of enzymatically catalyzed Fe(II)-oxidizing NO₃[−]-reducing pathway is still lacking (Chakraborty et al. 2011). The actual existence

of autotrophic nitrate-dependent Fe(II) oxidation in the natural environments also needs to be investigated.

5.2 Anaerobic $\text{NO}_3^-/\text{NO}_2^-$ reduction by sulfide

Nitrate/nitrite-reducing bacteria can also use sulfide as an electron donor besides organic carbon or Fe(II) under anoxic environments (Ottley et al. 1997). In these ecosystems, nitrate/nitrite can be microbially reduced to nitrogen or ammonia when sulfide is oxidized to elemental sulfur or further sulfate (Burgin and Hamilton 2008; Payne et al. 2009). Microbial nitrate/nitrite reduction coupled to sulfide oxidation was first documented in marine ecosystems where sulfide is rich (Fossing et al. 1995). It has been increasingly revealed that the coupling of nitrate/nitrite reduction and sulfide oxidation plays an important biogeochemical role in freshwater systems with low sulfide as well (Burgin and Hamilton 2008; Payne et al. 2009; Yang et al. 2012a). Based on our thermodynamic calculation, nitrate reduction to nitrogen coupled to sulfide oxidation to sulfate is thermodynamically feasible yielding $-88.4 \sim -84.7$ kJ/mol of e^- transferred. Because the primary source of sulfide is usually microbial sulfate reduction, sulfide-driven nitrate/nitrite reduction tends to contribute significantly to nitrate/nitrite removal mainly in suboxic zones with sufficient sulfate inputs and high carbon inputs which supports microbial sulfate reduction (Ottley et al. 1997). It was reported that quinones can facilitate simultaneous removal of sulfide and nitrate/nitrite by abiotically oxidizing sulfide and transferring electrons to denitrifying microorganisms (Aranda-Tamaura et al. 2007). Thus, quinones may also play the role of electron shuttles in mediating the couple of sulfide oxidation and nitrate/nitrite reduction. Sulfide oxidation was reported to attribute to 30% of the overall nitrate removal in a stratified lake in Spain and 10–40% in freshwater ecosystems (15–40% in lakes, 15–25% in streams, and 10–15% in wetlands) in Michigan (Burgin and Hamilton 2008).

6 Anaerobic anammox oxidation by inorganic compounds

Ammonia was naturally produced by microorganisms in water and soils as an end product of plant and animal waste decomposition. A large amount of ammonia enters the environment, on the other hand, through nitrogen-based fertilizers applied in agricultural fields for purpose of high productivity. The excess ammonia has caused various environmental problems, such as water eutrophication and habitat degradation (Bond and Lovley 2002; Balci and Dincel 2002).

6.1 Anammox

Ammonium in the soils was reported to be anaerobically oxidized coupled with nitrate and nitrite reduction (anammox) as a mechanism of N removal in natural ecosystems. At first, both nitrite and nitrate were assumed to function as electron acceptors (Bender et al. 1989; Zhu et al. 2008; Shen et al. 2014):

But, anammox bacteria were found to prefer nitrite rather than nitrate (Zhu et al. 2008). Anammox is thermodynamically favorable at typical environments, such as marine sediments, freshwater sediments, and paddy soils, where the concentrations of both NH_4^+ and $\text{NO}_3^-/\text{NO}_2^-$ are much higher than the minimum requirement for the anammox reaction (Fig. 3) (Hamersley et al. 2009; Rich et al. 2008; Zhu et al. 2015). Anammox in natural environments was first observed in sediments from the Baltic-North Sea transition (Dalsgaard and Thamdrup 2002). It was surprising that anammox contributed to 24–67% of the total N_2 production in continental shelf sediments, whereas the remainder was related to denitrification (Dalsgaard and Thamdrup 2002). Besides the common marine ecosystem, anammox also occurred in fresh water and terrestrial ecosystems (Zhu et al. 2015), especially in the suboxic water layer in a lacustrine system, like Lake Tanganyika, where anammox rates was up to 10 nM N_2/h , comparable to the marine water column (Schubert et al. 2006). The anammox reaction was estimated to contribute to 19–35 and 19% of total N_2 production in anoxic water column of Golfo Dulce, Costa Rica and in ice floe from the Greenland respectively (Dalsgaard et al. 2003; Rysgaard and Glud 2004). Bacteria responsible for anammox was firstly identified in the Black Sea and identified as

Fig. 3 The relationship between NO_2^- and NH_4^+ when anammox reaches the thermodynamic equilibrium indicated by the solid line. Above the line, the reaction is thermodynamically feasible (minimum energy not taken into consideration). Shaded areas and dots in different colors reflect field data with the occurrence of anammox taken from previous literatures (Zhu et al. 2015; Schmid et al. 2007; Dale et al. 2009; Jaeschke et al. 2007; Rich et al. 2008; Hamersley et al. 2009; Jaeschke et al. 2009a, b; Engstrom et al. 2009)

Planctomycetales, similar to those isolated in bioreactors through fluorescently labeled RNA probes and the detection of ladderane membrane lipids unique to the bacterial anammoxosome (Kuyper et al. 2003).

6.2 Feammox

Fe(III) can also act as an electron acceptor of anaerobic ammonia oxidation which process was named as feammox. In recent years, there have been increasing researches on feammox (Clément et al. 2005; Shrestha et al. 2009; Yang et al. 2012b). Ammonia can be microbially oxidized to N_2 , NO_2^- , or NO_3^- coupled with the reduction of Fe(III) minerals (Fe(III) is written in the form of ferrihydrite ($\text{Fe}(\text{OH})_3$)) (Yang et al. 2012b):

Direct evidence of feammox- NO_2^- process was firstly provided in soils (from a forested riparian wetland in New Jersey, pH 4.8) amended with urea (Clément et al. 2005). It was confirmed that ammonia could be oxidized to nitrogen coupled to iron reduction in the absence of initial $\text{NO}_3^-/\text{NO}_2^-$ (Shrestha et al. 2009). Ammonia was observed to be oxidized to nitrogen in upland soils, paddy soils, intertidal wetland (Yang et al. 2012b; Ding et al. 2014; Li et al. 2015), nitrite in wetland soils (Shrestha et al. 2009), and nitrate in anaerobic sludge via feammox (Sawayama 2006; Park et al. 2009). The bacteria responsible for feammox has not been isolated so far, but researchers have identified an uncultured *Acidimicrobiaceae* bacterium A6 as potential because it was one of the dominate microbes in a feammox system (Huang et al. 2014).

Feammox are much more favored at acidic conditions than at alkaline conditions (Fig. 4). It was estimated that feammox can only occur under the circumstance of pH < 6.5 (Yang et al. 2012b). High accumulation of free Fe^{2+} would lower the reaction free energy yield thus impeding the forward proceeding of the reactions as well. According to our calculation, ferrihydrite-driven ammonia ($\text{NH}_4^+ = 10^{-3} \text{ M}$) oxidation to N_2 and NO_3^- can proceed when Fe^{2+} is under $\sim 10^{-2.9}$ and $10^{-12.6} \text{ M}$ at pH 7, the latter of which is much lower than the common cases, indicating that feammox- NO_3^- is thermodynamically unfavorable at neutral pH (Fig. 4). Huang et al. (2014) applied different iron sources including 6-line ferrihydrite, goethite, ferric chloride, and ferric citrate to investigate the possibilities of them to serve as electron acceptors of ammonia oxidation. They confirmed that feammox only occurred in samples amended with ferrihydrite and goethite. The possible explanation was that the concentration of produced ferrous ion was low due to its adsorption to ferrihydrite and goethite, which might create the condition for the feasibility of feammox reaction, or feammox bacteria might only have the ability to reduce iron (oxyhydr)oxides, as is the case for some iron reducers (Huang et al. 2014). Investigation by Park et al. (2009), however, showed that ferric citrate drove feammox process in anaerobic sludge from a piggery wastewater. Chelators such as citrate may raise the Fe(III)/Fe(II) reduction potential, therefore driving forward the reaction of feammox. Many organic molecules such as dissolved humic substances can chelate and solubilize Fe(III). Therefore,

Fig. 4 The relationships between Fe^{2+} and NH_4^+ when feammox- N_2 and NO_3^- reach the thermodynamic equilibrium at different pHs (pH = 5, 7, 9) indicated by the corresponding solid lines. Below the corresponding lines, the reactions are thermodynamically feasible (minimum energy not taken into consideration). Field or laboratory data with the occurrence of feammox are not available

chelated Fe(III) may have the potential to play a role in feammox in the nature. But, evidence remains to be provided whether and to which extent chelated Fe(III) in the nature can drive anaerobic ammonia oxidation.

Though feammox is less thermodynamically feasible compared with anammox (see Fig. 7), feammox cannot be overlooked when considering nitrogen loss from soils. Feammox was estimated to occur at the rate of 0.17–0.59 mg N/kg/day in paddy soils in China (Ding et al. 2014) and approximately 0.32 mg N/kg/day in tropical forest soils (Yang et al. 2012b). Feammox drove a nitrogen loss of 7.8–61 kg N/ha/year in (0–10 cm depth) paddy soils in China which accounted for about 3.9–31% of the N fertilizer applied to paddy soils comparable to 23% reported for anammox in paddy soils (Ding et al. 2014).

It was reported that AQDS can function as an electron shuttle to facilitate feammox, which indicates that bacterial AQDS reduction is also coupled to ammonia oxidation (Zhou et al. 2016). Therefore, humic substances, which are rich in quinone moieties like AQDS, are likely to be potential electron acceptors of bacterial ammonia oxidation despite no evidence yet. We calculated the thermodynamic feasibility of the reduction of common quinones (Table 2) coupled to ammonia oxidation and found that a large portion of the quinones can be candidates as electron acceptors of ammonia oxidizers (Fig. 5). Theoretically, reduction of quinones in humic acids to hydroquinones can proceed when E^0 is above ca. -0.22 V at

Fig. 5 Gibbs free energy ΔG (normalized as kJ per mole of e^- transferred) of oxidation of ammonia (1 mM) with diverse quinone species (1 μM) commonly used in researches for the studies of humic substances as an electron acceptor alternatively in a pH range of 5–9. The reactions are thermodynamically feasible below the dotted line at $\Delta G = 0$ (minimum energy not taken into consideration)

pH 7.0. At this point, the anaerobic ammonium oxidizing reaction ought to be more widely distributed than supposed previously considering the vast distribution of humic substances in natural environments (Aiken et al. 1985). However, as mentioned above, AQDS is not a surrogate which is equivalent to much more complex humic substances. It remains to be studied whether humic substances can act as electron acceptors of microbial ammonia oxidation.

6.3 Suramox

The process of sulfate reduction coupled to anaerobic ammonia oxidation was observed in many bioreactors and named as suramox (FdZ-Polanco et al. 2001; Liu et al. 2008; Zub et al. 2008). The mechanism of the process has been controversial since the reaction was first discovered in an anaerobic fluidized bed reactor in 2001 (FdZ-Polanco et al. 2001). The mostly accepted mechanism can be written as

In suramox reaction, NH_4^+ was presumed to be oxidized to NO_2^- and then reduced to N_2 by anammox bacteria as follows:

These two formulas could be integrated as formula 27. Therefore, the whole suramox reaction observed in previous

Table 2 Structures and standard reduction potentials ($X^0 + 2 H^+ + 2 e^- \rightleftharpoons XH_2$) at pH 7.0 (E^0) of quinone species

Name	Abbreviation	Formula	Structure	E^0 (V)
9,10-anthraquinone-2,6-disulfonic acid	AQ26DS (AQDS)	$C_{14}H_8O_8S_2$		-0.184
9,10-Anthraquinone-1,5-disulfonic acid	AQ15DS	$C_{14}H_8O_8S_2$		-0.175
9,10-anthraquinone-2-sulfonic acid	AQS	$C_{14}H_8O_5S$		-0.225
7-R-D-glucopyranosyl-9,10-dihydro-3,5,6,8-tetrahydroxy-1-methyl-9,10-dioxo-2-anthracenecarboxylic	Car	$C_{22}H_{20}O_{13}$		-0.5
9,10-dihydro-4,5-dihydroxy-9,10-dioxo-2-anthracene carboxylic acid (Rhein)	Rhe	$C_{15}H_8O_6$		-0.27
9,10-anthraquinone-2-carboxylic acid	AQC	$C_{15}H_8O_4$		-0.254
1,2-dihydroxy-9,10-anthraquinone (Alizarin)	Ali	$C_{14}H_8O_4$		-0.344
5,8-dihydroxy-1,4-naphthoquinone (Naphthazarin)	5,8-DHNQ	$C_{10}H_6O_4$		-0.050

5-hydroxy-1,4-naphthoquinone (Juglon)	5-HNQ	C ₁₀ H ₆ O ₄		-0.003
2-hydroxy-1,4-naphthoquinone (Lawsone)	2-HNQ	C ₁₀ H ₆ O ₃		-0.137
o-Benzoquinone	oBQ	C ₆ H ₄ O ₂		0.389
Chloro-p-benzoquinone	CpBQ	C ₆ H ₃ O ₂ Cl		0.298
p-Benzoquinone	pBQ	C ₆ H ₄ O ₂		0.285
Benzoquinonacetic acid	BQA	C ₈ H ₆ O ₄		0.273
2,5-Dimethyl-p-benzoquinone	2,5-DpBQ	C ₈ H ₈ O ₂		0.179
1,2-Naphthoquinone - 4-sulfonate	NQSA	C ₁₀ H ₆ O ₅ S		0.214

Data of standard reduction potentials at pH 7.0 (E^0') of quinone species were calculated from standard reduction potentials E^0 or directly from references (Aeschbacher et al. 2011; Rau et al. 2002; Uchimiya and Stone 2006)

Fig. 6 The relationship between SO_4^{2-} and NH_4^+ when suramox reaches the thermodynamic equilibrium indicated by the solid line. Above the line, the reaction is thermodynamically feasible (minimum energy not taken into consideration). Shaded areas and dots in different colors reflect data with the occurrence of suramox within reactors taken from previous reports (Fdz-Polanco et al. 2001; Liu et al. 2008; Zub et al. 2008; Yang et al. 2009; Zhang et al. 2009; Cai et al. 2010; Rikmann et al. 2012; Yuan et al. 2013)

studies might be consisted of a series of reactions rather than a simple continual reaction (Liu et al. 2008; Yuan et al. 2013). Schrum et al. (2009) first provided evidence that sulfate-reducing ammonium oxidation occurred when upward-diffusing ammonium contacted the downward-diffusing sulfate in Bay of Bengal sediment. Reported data from these experiments (Fig. 6) indicated that almost all conditions in the experiments were favorable for the suramox reaction. It can be inferred that the suramox reaction can only occur at high substrate concentrations due to its relatively low energy yield, which was corresponded with the result of Zhang et al. (2009).

The existence of anaerobic ammonia oxidation coupled with sulfate reduction has been recognized, but the microorganisms involved have not yet been identified clearly so far. Liu et al. (2008) discovered a new species named *Anammoxoglobus sulfate*, belonging to Planctomycetales holding a critical role in the first-step reaction (formula 28) of suramox process and showed that the Planctomycete bacteria might have a more versatile metabolism than previously assumed. Cai et al. (2010) isolated a strain named ASR related to *Bacillus benzoovorans* from an anaerobic ammonia and sulfate removing reactor and identified its ability to

Fig. 7 Gibbs free energy ΔG of oxidation of ammonia (1 mM) to N_2 ($10^{-3.47}$ M) or $\text{NO}_3^-/\text{NO}_2^-$ (1 mM) with reduction of NO_2^- (1 mM) (anammox), $\text{Fe}(\text{OH})_3$, Fe^{3+} (1 mM) to Fe^{2+} (10^{-6} – 10^{-4} M) (feammox), and SO_4^{2-} (10 mM) to S^0 (suramox) alternatively in a pH range of 5–9 (corresponding to formulas 21, 23, 25, and 27, values of ΔG are normalized as kJ per mole of e^- transferred). The reactions are thermodynamically feasible below the dotted line at $\Delta G = 0$ (minimum energy not taken into consideration)

perform the whole suramox reaction, further widening the knowledge about the structure of potential functional microbial communities implicated in the suramox process. Similarly, in the study of Liu et al. (2015), the dominant bacteria changed from *Candidatus brocadia* to *Bacillus benzoovorans* when the process transformed from nitrite-reducing anaerobic ammonium oxidation to sulfate-reducing anaerobic ammonium oxidation in the sludge reactor.

The discovery of suramox has brought forward a novel high-efficient and low-cost route for the biological removal of ammonium and sulfate in the application of wastewater treatment, compared with traditional separately removing ammonia and sulfate (Zhang et al. 2009). Suramox is usually less thermodynamically feasible than anammox according to our thermodynamic calculation (Fig. 7). Suramox can only happen at high concentrations of SO_4^{2-} and NH_4^+ (Fig. 6), which explains why suramox process was usually only observed in anthropogenic waste water. Though suramox has only been found in few natural environments, this novel reaction widens our knowledge about the biogeochemical cycle between the element nitrogen and sulfur.

7 Conclusions

Anaerobic microorganisms mediate a variety of redox reactions, on the one hand gaining energy for their growth and on the other hand driving the biogeochemical cycling of elements in earth's environment. The couplings of

elements driven by anaerobes are extremely complex since different chemical compounds of different species and activities are linked together. Although we summarize the anaerobe-driven coupling of each pair of elements of C-N, C-Fe, C-S, N-Fe, N-S, and Fe-S in this review, the actual situation will be much more intricate because all elements can be microbially associated together, forming a global huge cycle of multiple elements.

Advanced technical tools and methods have been revealing novel microbial reactions truly present on the earth at an amazing rate. However, the mechanism of the reactions and the metabolism and physiology of the associate microbes are far from understanding. Many reactions have been predicted to exist from a thermodynamic perspective but have not yet been identified in natural environments or laboratories. Kinetic constraints of redox reactions need to be taken into consideration for the reason that certain reactions which are possible based on thermodynamic prediction may occur very slowly if the activation energy is high and efficient enzymes are lacking. Further work is required to focus on the metabolic pathways genetically and enzymatically and the factors controlling the feasibility of the reactions. Moreover, the dynamic balance between the various redox processes needs to be explored for a better understanding how microbes transition metabolic strategies to adapt to changing geochemical conditions. Especially, more work has to be carried out on organic carbon such as the molecular composition, structure, and properties of organic carbon and how organic carbon is involved in microbial activities because carbon is the most abundant element in organisms and the geochemical cycle of carbon is extremely important to all living organisms on the earth.

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Compliance with ethical standards

Conflict of interest The authors declare no competing financial interest.

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