MINIREVIEW

The hunt for the most-wanted chemolithoautotrophic spookmicrobes

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One sentence summary: In this review, we highlight the most-wanted methane- and ammonia-oxidizing spookmicrobes discovered in the past quarter century.

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ABSTRACT

Microorganisms are the drivers of biogeochemical methane and nitrogen cycles. Essential roles of chemolithoautotrophic microorganisms in these cycles were predicted long before their identification. Dedicated enrichment procedures, metagenomics surveys and single-cell technologies have enabled the identification of several new groups of most-wanted spookmicrobes, including novel methoxydotrophic methanogens that produce methane from methylated coal compounds and acetoclastic 'Candidatus Methanothrix paradoxum', which is active in oxic soils. The resultant energy-rich methane can be oxidized via a suite of electron acceptors. Recently, 'Candidatus Methanoperedens nitroreducens' ANME-2d archaea and 'Candidatus Methylomirabilis oxyfera' bacteria were enriched on nitrate and nitrite under anoxic conditions with methane as an electron donor. Although 'Candidatus Methanoperedens nitroreducens' and other ANME archaea can use iron citrate as an electron acceptor in batch experiments, the quest for anaerobic methane oxidizers that grow via iron reduction continues. In recent years, the nitrogen cycle has been expanded by the discovery of various ammonium-oxidizing prokaryotes, including ammonium-oxidizing archaea, versatile anaerobic ammonium-oxidizing (anammox) bacteria and complete ammonium-oxidizing (comammox) Nitrospira bacteria. Several biogeochemical studies have indicated that ammonium conversion occurs under iron-reducing conditions, but thus far no microorganism has been identified. Ultimately, iron-reducing and sulfate-dependent ammonium-oxidizing microorganisms await discovery.

GENERAL INTRODUCTION

During Earth's history, a set of metabolic processes that evolved exclusively in anaerobic microorganisms changed the chemical speciation of all major elements (Falkowski, Fenchel and Delong 2008; Stolz 2017). Our present-day environment is thus the integrated result of microbial experimentation that has allowed life to develop and persist, despite major environmental changes documented in the geological record. The recent expansion of microbial genome sequence data combined with increasingly detailed geochemical analyses has yielded insights on how microorganisms became the biogeochemical engineers of life on Earth. Among the most urgent scientific questions are which key groups of microorganisms drive the relevant reactions, how do these microorganisms interact with each other and their geochemical environment, and how do they impact the Earth system (Anantharaman *et al*. 2016; Thompson *et al*. 2017).

In this context, it is important to understand the microbial and geochemical pathways for the conversion of methane (CH_4), hydrogen sulfide (H_2S) and ammonium (NH_4^+), products of the anaerobic degradation of organic matter by a complex web of microorganisms (Fig. 1). Methanogens are responsible for the terminal step in this anaerobic food web and produce an estimated 583 Tg (range: 458–748) of methane per year from natural and agricultural sources (Saunois *et al*. 2016). Methane is a notorious greenhouse gas, and its atmospheric concentration has more than doubled since the start of the Industrial Revolution (Allen 2016). Concentrations of ammonium, a key player in the deterioration of water quality, have increased dramatically worldwide over the past century, and globally the nitrogen cycle in general has long exceeded safe operational boundaries (Rockström *et al*. 2009). H_2S is extremely toxic to all higher life forms, and its release can greatly alter biogeochemical cycling in aquatic environments (Diaz and Rosenberg 2008). Microorganisms, particularly chemolithoautotrophs, play a critical role in modulating the release of methane, hydrogen sulfide and ammonium by driving a range of redox reactions that ultimately transform these detrimental reductants to comparatively less harmful compounds, such as carbon dioxide (CO_2), sulfate (SO_4^{2-}) and dinitrogen gas (N_2) (Fig. 1).

For more than a century, methane and ammonium were thought to be oxidized by microorganisms only in the presence of oxygen. Unequivocal proof of the anaerobic oxidation of these compounds in the presence of sulfate, nitrite (NO_2^-) and nitrate (NO_3^-) was obtained only in recent decades (Boetius *et al*. 2000; Raghoebarsing *et al*. 2006; Ettwig *et al*. 2010; Haroon *et al*. 2013). Attempts to enrich these so-called (impossible) anaerobic microorganisms growing on methane or ammonium were initially not successful, mainly due to their slow growth and highly specific substrate requirements (Table 1). Selecting samples from ecosystems with counter-gradients of ammonium/nitrate or methane/nitrate (Zhu *et al*. 2012; Vaksmaa *et al*. 2017a) and increasing the number of target cells can reduce enrichment times. Bioreactors with effective biomass retention systems (sequencing batch reactor (SBR) or membrane systems) and optimized growth media (e.g. appropriate trace elements like lanthanides, low substrate availability or low nitrite concentrations) can also contribute to successful enrichment (Strous *et al*. 1997; van Kessel *et al*. 2015). Once sufficient cells are available, metagenomics can be combined with single-cell approaches to quickly reveal the genetic blueprint. Together with stable isotope experiments, this blueprint can be used to design crucial experiments to verify the metabolic potential of these 'impossible' microorganisms.

Emerging evidence suggests that there are several important but previously unknown microbial pathways for the oxidation of methane and ammonium involving oxides of iron and manganese (Beal, House and Orphan 2009; Ettwig *et al*. 2016). Despite rapid and continuing technological improvements, a large part of microbial diversity has yet to be discovered. Many, particularly chemolithoautotrophic processes, have been hypothesized or observed based on nutrient profiles and metagenomic inventories. Species-level detail is often lacking, leaving open the question of whether specific microorganisms are responsible for the biochemical conversions observed in the field. The discovery of multiple 'impossible' anaerobic microorganisms has reinforced the idea that a microorganism or combination of microorganisms should exist for each thermodynamically feasible process (Table 1). In this review, we provide an overview of the discoveries of several most-wanted chemolithoautotrophic spookmicrobes that may play significant roles in global methane, sulfur and nitrogen cycles and highlight a few processes that still await detection.

Methane cycle

Methane is a potent greenhouse gas with a warming potential 34 times stronger than that of carbon dioxide over a time period of 100 years (Henry *et al*. 1970; Lacis *et al*. 1981; Myhre *et al*. 2013). Methane is the most reduced one-carbon compound and plays a key role in the global carbon cycle and the greenhouse effect as was stressed by the first IPCC report in 1990 (Watson *et al*. 1990). Many processes in a wide variety of ecosystems control the global methane budget (Heilig 1994; Kirschke *et al*. 2013; Dean *et al*. 2018). The majority of methane released into the atmosphere (70%–80%) is of biogenic origin (Conrad 1996, 2009), and most if not all biogenic methane is produced by methanogenic archaea within the phylum Euryarchaeota. Proposed alternative pathways include methane production by iron-only nitrogenases (Zheng *et al*. 2018), methane release from methylphosphonates in marine ecosystems (Daughton, Cook and Alexander 1979), and *in situ* formation of methane in terrestrial plants (Keppler *et al*. 2006). Methanogenic archaea are obligate anaerobes found in anoxic soils, sediments and water bodies. A fraction of the methane produced directly escapes into the atmosphere via ebullition (Schütz, Seiler and Conrad 1989; Aben *et al*. 2017).

Before dissolved and trapped methane reaches the atmosphere, it can be oxidized by a range of anaerobic and aerobic methanotrophs using a suite of electron acceptors. These methanotrophs include anaerobic methanotrophic (ANME) archaea, and anaerobic and aerobic methanotrophic bacteria. For an extensive overview of methanogenesis and methanotrophy, see Kallistova *et al*. (2017).

Methanogens

Microbial methanogenesis was first described by Omelianski in 1890 and later experimentally confirmed by Söhngen (1906), who was the first to describe the 'fat rod' *Methanothrix soehngenii,* which produces methane from acetate (Huser, Wuhrmann and Zehnder 1982). Methanogens are dependent on fermentative and syntrophic processes that convert

Table 1. Overview of chemolitho(auto)trophic reactions in the conversion of methane, ammonium and nitrite by the microorganisms highlighted in this review.

Electron acceptor	$\Delta E_0'$	$\Delta G_0'$	Reaction equation	Micro-organism(s)	Origin	Growth rate	Per cell rate	Ks [S]	Ks [EA]	Reference
Methane production from various substrates										
CH_3OH	+360	−103	$4\,CH_3OH \rightarrow CO_2 + 3\,CH_4 + 2\,H_2O$	*Methanosarcina semesiae*	Brackish sediment	<0.2	–	<5	–	Lyimo, Pol and Op den Camp (2000); Thauer, Jungermann and Decker (1977) and Welte (2018)
CH_3-R	+193	−56	$(CH_3)_2SH + H_2O \rightarrow 0.5\,CO_2 + 1.5\,CH_4 + H_2S$	*Methanomethylovorans hollandica*	Freshwater sediment	<1	–	<30	–	Lomans et al. (1999)
CH_3COOH	+46	−36	$CH_3COOH \rightarrow CO_2 + CH_4$	*Methanothrix soehngenii*	WWTP	7–14	–	500	–	Huser et al. (1982)
				'Candidatus Methanothrix paradoxum'	Wetland soil	–	–	–	–	Angle et al. (2017)
CH_3O-R	+366	−106	$4\,CH_3O\text{-}R + 2\,H_2O \rightarrow 4\,R\text{-}OH + CO_2 + 3\,CH_4$	*Methermicoccus shengliensis*	Oilfield water	<5	20	–	–	Cheng et al. (2007)
CH_3OH	+172	−113	$CH_3OH + H_2 \rightarrow CH_4 + H_2O$	*Methanomassiliicoccus luminyiensis*	Human feces	2	–	–	–	Dridi et al. (2012)
				'Candidatus Methanonatronarchaeia'	Hypersaline lake	–	–	–	–	Sorokin et al. (2017)
				'Candidatus Methanofastidiosa'	WWTP	–	–	–	–	Nobu et al. (2016)
Methane (CO_2/CH_4 at $\Delta E_0' = -240$ mV) as electron donor										
O_2/H_2O	+810	−801	$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$	Methane-oxidizing bacteria (MOB)		0.5–2	158–240	0.06–12.6	6–37	Ren, Amaral and Knowles (1997); Dunfield and Conrad (2000) and Steenbergh et al. (2010)
				Alphaproteobacteria						
				Methylocella palustris	Peat					Dedysh et al. (2000)
				Methylocella tundra	Peat					Dedysh et al. (2004)
				Upland soil cluster alpha	Soil					Pratscher et al. (2018)
				Gammaproteobacteria						
				Upland soil cluster gamma	Soil					Knief et al. (2003)
				Verrucomicrobia						
				Methylacidiphilum	Geothermal area					Op den Camp et al. (2009)
NO_3^-/NO_2^-	+430	−503	$CH_4 + 4\,NO_3^- \rightarrow CO_2 + 4\,NO_2^- + 2\,H_2O$	'Candidatus Methanoperedens nitroreducens'	Freshwater sediment, WWTP	>14	0.57	>1000	<50	Haroon et al. (2013) and Vaksmaa et al. (2017a)
NO_2^-/N_2	+320	−928	$3\,CH_4 + 8\,NO_2^- + 8\,H^+ \rightarrow 3\,CO_2 + 4\,N_2 + 10\,H_2O$	'Candidatus Methylomirabilis oxyfera'	Freshwater sediment	>14	0.4–0.2	<50	<10	Raghoebarsing et al. (2006)
Fe^{3+}/Fe^{2+}	+360	−454	$CH_4 + 8\,Fe^{3+} + 2\,H_2O \rightarrow CO_2 + 8\,Fe^{2+} + 8\,H^+$	'Candidatus Methanoperedens nitroreducens'	Freshwater sediment, WWTP	–	–	–	–	Ettwig et al. (2009); Ettwig et al. (2016) and Cai et al. (2018)
				ANME-2C	Marine sediment	–	–	–	–	Boetius et al. (2000)
SO_4^{2-}/H_2S	−210	−21	$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + H_2S + H_2O$	Anaerobic methanotrophic archaea (ANME)	Marine sediment	>50	0.7	>1000	–	Nauhaus et al. (2005); Knittel et al. (2005)
Ammonium (NO_2^-/NH_4^+ at $\Delta E_0' = 340$ mV) as electron donor										
O_2/H_2O	+810	−275	$NH_4^+ + 1.5\,O_2 \rightarrow NO_2^- + H_2O + 2\,H^+$	Ammonium-oxidizing bacteria (AOB)		<1	264–552	0.8–112	1–15	Belser and Schmidt (1980) and Laanbroek and Gerads (1993)
				Ammonium-oxidizing archaea (AOA)	Seawater aquarium	<5	0.5–32.2	5–44	–	Kits et al. (2017)
				'Candidatus Nitrosopumilus maritimus'	Hot spring					Könneke et al. (2005)
				'Candidatus Nitrosocaldus yellowstonii'	Hot spring					de la Torre et al. (2008)
				'Candidatus Nitrososphaera gargensis'	Garden soil					Hatzenpichler et al. (2008)
				'Candidatus Nitrososphaera viennensis'	Agricultural soil					Tourna et al. (2011)

Table 1. Continued

Electron acceptor	$\Delta E_0'$	$\Delta G_0'$	Reaction equation	Micro-organism(s)	Origin	Growth rate	Per cell rate	Ks [S]	Ks [EA]	Reference
				'Candidatus Nitrosotalea devanaterra'	Hot spring					Lehtovirta-Morley, Stoecker and Vilcinskas (2011)
				'Candidatus Nitrosocaldus islandicus'						Daebeler et al. (2018)
Nitrite (NO_3^-/NO_2^- at $\Delta E_0'$ = 420 mV) as electron donor										
O_2/H_2O	+810	–74	$NO_2^- + 0.5\,O_2 \rightarrow NO_3^-$	Nitrite-oxidizing bacteria (NOB)		<1	0.6–13.1	9–544	22–166	Féray and Montuelle (2002) and Nowka, Daims and Spieck (2015)
				Alphaproteobacteria *Nitrobacter winogradskyi*	Soil					Winslow et al. (1917)
				Betaproteobacteria 'Candidatus Nitroga arctica'	Permafrost					Alawi et al. (2007)
				Gammaproteobacteria *Nitrococcus mobilis*	Ocean water					Watson and Waterbury (1971)
				Nitrospirae *Nitrospira moscoviensis* 'Candidatus Nitrospira defluvii'	Heating system WWTP					Ehrich et al. (1995) Lücker et al. (2010)
				Nitrospinae *Nitrospina gracilis*	Ocean water					Watson and Waterbury (1971)
				Chloroflexi *Nitrolancetus hollandicus*	Nitrifying reactor					Sorokin et al. (2012)
Ammonium (NO_3^-/NH_4^+ at $\Delta E_0'$ = 360 mV) as electron donor										
O_2/H_2O	+810	–349	$NH_4^+ + 2\,O_2 \rightarrow NO_3^- + H_2O + 2\,H^+$	Comammox *Nitrospira*		<1	–	0.6	–	van Kessel et al. (2015) and Kits et al. (2017)
				Nitrospira inopinata	Hot water pipe					Daims et al. (2015)
Ammonium (N_2/NH_4^+ at $\Delta E_0'$ = -280 mV) as electron donor										
NO_2^-/N_2	+320	–358	$NH_4^+ + NO_2^- \rightarrow N_2 + 2\,H_2O$	Anammox bacteria		4–14	2–20	<5	<5	Lotti et al. (2015) and Zhang et al. (2017)
				Brocadiales 'Candidatus Kuenenia stuttgartiensis'	WWTP					Jetten et al. (2010) Schmid et al. (2000)
				'Candidatus Brocadia fulgida'	WWTP					Kartal et al. (2008)
				'Candidatus Anammoxoglobus propionicus'	WWTP					Kartal et al.(2007)
				'Candidatus Scalindua profunda'	Marine sediment					van de Vossenberg et al. (2013)
				'Candidatus Jettenia caeni'	WWTP					Ali et al. (2015)
Fe^{3+}/Fe^{2+}	+360	–303	$NH_4^+ + 3Fe(OH)_3 + 5\,H^+ \rightarrow 3\,Fe^{2+} + 9\,H_2O + 0.5\,N_2$	?		–	–	–	–	Kuypers et al. (2018) and Huang and Jaffé (2018)
SO_4^{2-}/H_2S	–210	–22	$8\,NH_4^+ + 3\,SO_4^{2-} \rightarrow 4\,N_2 + 1.5\,H_2S + 12\,H_2O + 2\,H^+$	?		–	–	–	–	Zhang et al. (2009)

Redox potentials of the half-reactions are given at 25°C and pH 7. $\Delta E_0'$ is displayed in mV, $\Delta G_0'$ is displayed in kJ/mol substrate. Growth rates are displayed in days, per cell rates are given in fmol substrate per cell per day and Ks is given in µM substrate [S] and electron acceptor [EA], '–' indicates values have not been determined yet. For MOB, AOB, NOB, and anammox bacteria the range of the ecophysiological parameters is given. WWTP = wastewater treatment plant.

organic compounds to methanogenic substrates (Kotsyurbenko, Nozhevnikova and Zavarzin 1993; Schink 1997). Methanogens that use H_2/CO_2 and methylated compounds as substrates were subsequently isolated and characterized (for an overview, see Plugge and Stams 2010). Acetate usage appears to be limited to the genera *Methanosarcina* and *Methanothrix* (Jetten, Stams and Zehnder 1992). There are seven methanogenic orders: Methanosarcinales, Methanomicrobiales, Methanobacteriales, Methanococcales, Methanopyrales, Methanocellales, and the recently discovered Methanomassiliicoccales (Garrity, Bell and Lilburn 2004; Thauer et al. 2008; Dridi et al. 2012; Iino et al. 2013; Lyu and Lu 2015). Methanomassiliicoccales species (*Methanomassiliicoccus luminyiensis*) were first discovered in human feces and use hydrogen as an electron donor to
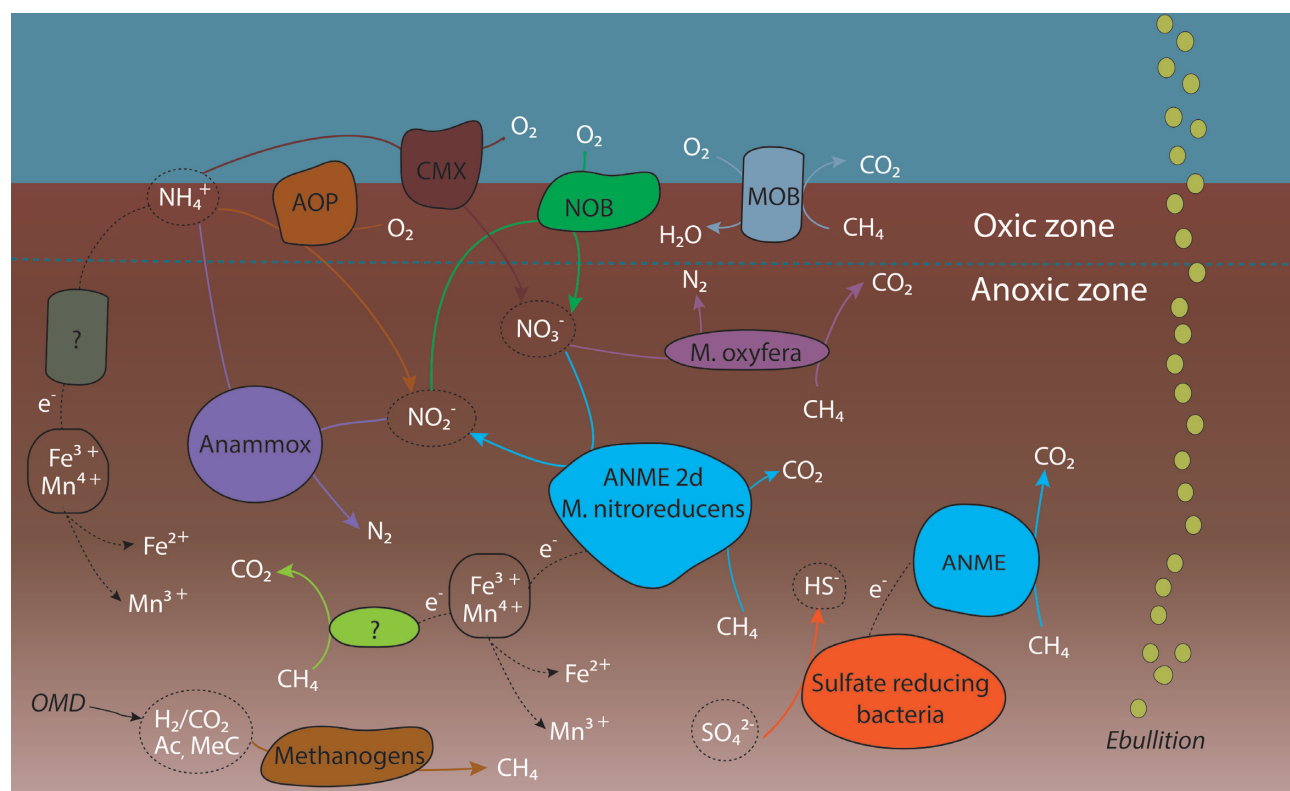
Figure 1. Overview of microbial diversity and possible reactions in the global methane and nitrogen cycles. AOP: ammonium-oxidizing prokaryotes including Thaumarchaeota and AOB, CMX: comammox bacteria, NOB: nitrite-oxidizing bacteria, MOB: methane-oxidizing bacteria, ANME: anaerobic methane-oxidizing archaea. OMD: organic matter degradation. The '?' indicates as-yet undiscovered processes of iron- and manganese-dependent ammonium and methane oxidation (see Table 1).

reduce methanol to methane (Dridi *et al.* 2012). In anoxic sediments, the concerted action of acetogens and methanogens can result in the breakdown of methoxylated aromatic compounds like trimethoxybenzoate (Finster, King and Bak 1990). The acetogens cleave off the methoxy-groups and produce dimethylsulfide and methanethiol, which can subsequently be used by methylotrophic methanogens (*Methanosarcina semesiae*, *Methanomethylovorans hollandica*) employing several unique methyltransferases (Finster, Tanimoto and Bak 1992; Lomans *et al.* 1999; Lyimo *et al.* 2000). The list of methanogenic substrates was recently expanded to include the direct use of methoxylated aromatic compounds by methoxydotrophic *Methermicoccus shengliensis* (Methanosarcinales) found in coal beds (Cheng *et al.* 2007; Mayumi *et al.* 2016). Two novel candidate classes, '*Candidatus* Methanonatronarchaeia' and '*Candidatus* Methanofastidiosa', were also recently discovered (Nobu *et al.* 2016; Sorokin *et al.* 2017). '*Candidatus* Methanonatronarchaeia', which are most closely related to *Halobacterium*, were detected in a metagenomic dataset of hypersaline lakes (Sorokin *et al.* 2017). '*Candidatus* Methanofastidiosum methylthiophilus' has the metabolic potential for methanogenesis through methylated thiol reduction using a methylated-thiol:coenzyme M methyltransferase (Nobu *et al.* 2016). These findings indicate that methanogenic archaea might include more extremophilic and metabolically versatile members than those currently known.

The recent observation of the aceticlastic '*Candidatus* Methanothrix paradoxum' in oxygenated soils (Angle *et al.* 2017) and indications of methanogenesis under oxic conditions (Wagner 2017) are striking since methanogens are considered obligate anaerobes. The occurrence of methane production in oxic environments might dramatically alter our view of methanogenic ecosystems.

Whether methanogenesis occurs outside Euryarchaeota remains a matter of debate. The discovery of Bathyarchaeota and Verstraetearchaeota genome bins including methylcoenzyme M reductase (MCR) genes indicates that methanogenesis might be more widespread in the archaeal domain than previously thought (Evans *et al.* 2015; Vanwonterghem *et al.* 2016). Other studies consider Bathyarchaeota anaerobic heterotrophs that assimilate sedimentary organic carbon compounds (Lazar *et al.* 2016; Xiang *et al.* 2017). Verstraetearchaeota also appear to utilize sugars as carbon compounds (Vanwonterghem *et al.* 2016). For an overview and discussion of potential methanogens outside the Euryarchaeota phylum see Welte (2018).

Methane oxidation

Before methane produced by methanogens reaches the atmosphere, first anaerobic methanotrophs oxidize methane using a suite of electron acceptors, and the methane that passes this anoxic filter can ultimately be converted by aerobic methane-oxidizing bacteria.

Sulfate-dependent anaerobic methane oxidation

The anaerobic oxidation of methane (AOM) was long considered impossible due to the high activation energy needed to break the C-H bonds (439 kJ mol^{-1}) (reviewed in Thauer and Shima 2008). The discovery of counter-gradients of sulfate and

methane changed this view and indicated habitats with active AOM (Reeburgh and Heggie 1977). The coupling of AOM to sulfate reduction in marine sediments appeared to be mediated by a microbial consortium (Boetius et al. 2000). Sulfate-dependent anaerobic oxidation of methane (S-AOM) is particularly intriguing since the reaction has a relatively low Gibbs free energy change of approximately -20 kJ mol^{-1} (Table 1) in most habitats (for a discussion of kinetics and thermodynamics, see Thauer (2011)). In marine ecosystems, S-AOM is carried out by a consortium of ANME archaea in cooperation with sulfate-reducing bacteria or possibly by ANME alone (Knittel and Boetius 2009; Milucka et al. 2012; Scheller et al. 2016). An inverted and modified methanogenesis pathway has been proposed for the catalysis of AOM by ANME (McGlynn et al. 2015; Timmers et al. 2017). ANMEs are divided into three distinct groups: ANME-1 (Methanosarcinales-related and Methanomicrobiales), ANME-2 (Methanosarcinales) and ANME-3 (Methanococcoides-related) (Knittel et al. 2005; Nauhaus et al. 2005; Stadnitskaia et al. 2005). The 16S rRNA gene phylogeny indicates that ANME groups are not monophyletic with each other, and the phylogenetic distance between subgroups is large, with nucleotide sequence similarities of 75%–92% (Knittel and Boetius 2009).

Nitrite- & nitrate-dependent methane oxidation

After the discovery of S-AOM in marine sediments, the hunt for nitrate- and nitrite-dependent methane oxidation (N-AOM) intensified. Based on redox calculations, both nitrate and nitrite are suitable electron acceptors for methane oxidation and, compared to sulfate, have much higher energy yields per mole of methane (Table 1). In 2006, Raghoebarsing et al. (2006) reported the first enrichment culture coupling AOM to denitrification. The enrichment culture contained archaea (10%–20% of the community) distantly related to ANME-2, and an NC10 phylum bacterium named 'Candidatus Methylomirabilis oxyfera' (70%–80% of the community). The proposed intra-aerobic pathway for coupling of AOM to nitrite reduction by 'Candidatus Methylomirabilis oxyfera' produces oxygen and dinitrogen gas from two molecules of nitric oxide (NO) (Ettwig et al. 2010, 2012). A major implication of this proposed pathway is that aerobic pathways might have been present before oxygenic photosynthesis arose. Despite this proposed intra-aerobic pathway of 'Candidatus Methylomirabilis oxyfera', oxygen exposure as low as 2% has inhibitory effects on methane and nitrite conversion rates (Luesken et al. 2012). A recent survey based on primer-based detection of NO dismutase showed that these genes do occur in many anoxic aquifers (Bhattacharjee et al. 2016; Zhu et al. 2017). Surveys of both 16S rRNA and pmoA genes (which encode the beta subunit of particulate methane monooxygenase) revealed a wide environmental distribution of N-AOM from wetlands to marine sediments and mud volcanos (Welte et al. 2016).

The role of the ANME-2 archaea in the first enrichment culture was resolved much later. In a bioreactor fed with nitrate, methane and ammonium, a stable co-culture of anaerobic ammonium-oxidizing (anammox) bacteria ('Candidatus Kuenenia stuttgartiensis') and ANME-2d archaea was established (Haroon et al. 2013). These archaea were identified as 'Candidatus Methanoperedens nitroreducens' (70%–80% of the community), which are capable of coupling nitrate reduction to methane oxidation (Haroon et al. 2013). ANME-2d archaea have subsequently been co-enriched a number of times with NC10 phylum and anammox bacteria, which probably scavenge the nitrite and convert it to dinitrogen gas. Analyses of several genomes of 'Candidatus Methanoperedens nitroreducens' have revealed

that all genes of the (reverse) methanogenic pathway are present (Haroon et al. 2013; Arshad et al. 2015; Berger et al. 2017; Narrowe et al. 2017; Vaksmaa et al. 2017a). The best-characterized gene for methanogenesis and AOM is mcrA, which encodes for the alpha subunit of Methyl-coenzyme M reductase. An environmental primer-based study based on 16S rRNA and mcrA genes showed that 'Candidatus Methanoperedens nitroreducens' is abundantly present in paddy fields (9% relative abundance of the archaeal community), river sediments and even marine sediments (Vaksmaa et al. 2016, 2017b).

Terrestrial agriculture-affected ecosystems that receive high concentrations of nitrogen compounds are also facilitating environments for nitrite- and nitrate-dependent methanotrophy. However, little is known about the relevance of N-AOM in terrestrial ecosystems, particularly those with prolonged anoxic conditions, such as natural or restored peatlands. For an extensive overview of N-AOM, see Welte et al. (2016).

Iron- and manganese-dependent methane oxidation

In addition to nitrate and nitrite, oxidized iron (Fe^{3+}) and oxidized manganese (Mn^{4+}) should be suitable electron acceptors for AOM based on Gibbs free energy (Table 1). Iron is the most abundant metal in the Earth's crust and can serve as both an electron donor and acceptor in microbial metabolism. Iron forms stable minerals in both the divalent and trivalent states depending on geochemical conditions. Fe^{3+} is most stable under oxic conditions (Raiswell and Canfield 2012). The reduction-oxidation cycle is coupled to other elements, including carbon, nitrogen, oxygen and sulfur. Conversion in the iron cycle can be abiotic or mediated by microorganisms (Weber et al. 2006; Melton et al. 2014). Iron bioavailability is generally low due to the poor solubility of iron minerals at neutral pH, but microorganisms have developed strategies to mediate electron exchange with insoluble iron forms (Weber, Achenbach and Coates 2006). Although a wide variety of organisms are known to reduce iron, the microorganisms responsible for the reduction of metal-oxides coupled to AOM (here abbreviated as Fe-AOM) have remained elusive.

Geochemical profiling and stable isotope tracer studies have demonstrated the occurrence of Fe-AOM in lake sediments (Sivan et al. 2011; Norði, Thamdrup and Schubert 2013; Torres et al. 2014), marine sediments (Beal, House and Orphan 2009; Wankel et al. 2012; Riedinger et al. 2014; Egger et al. 2015), paddy field sediments (Miura et al. 1992; Murase and Kimura 1994), lake water (Crowe et al. 2011), a terrestrial mud volcano (Chang et al. 2012), and in a contaminated aquifer (Amos et al. 2012). However, the responsible microorganisms were not identified in these studies. ANME archaea have been implicated in Fe-AOM in marine and volcanic systems (Beal, House and Orphan 2009; Chang et al. 2012). A recent study demonstrated that 'Candidatus Methanoperedens nitroreducens' can use various electron acceptors, including iron citrate, and thus may be capable of Fe-AOM (Ettwig et al. 2016). Fe-AOM by ANME-2C with iron citrate has been shown in mesocosm experiments using deep-sea methane seep sediment (Scheller et al. 2016). Wegener et al. (2015) observed that ANME archaea, under thermophilic AOM conditions, overexpress genes for extracellular cytochrome production and form nanowire-like cell-to-cell connections, suggesting an important role of direct interspecies electron transfer. However, microbial growth on Fe-AOM has yet not been demonstrated. Identifying the responsible microorganism(s) therefore remains a primary interest.

Aerobic methane oxidation

Methane that is not oxidized by anaerobic methanotrophs can reach the oxic layer of sediment or soil and undergo conversion by aerobic methanotrophs. Aerobic microbial oxidation of methane was first described in 1906 (Söhngen 1906). Based on the isolation and description of numerous aerobic methane-oxidizing bacteria (MOB), it was long assumed that microbial methane oxidation was only possible under oxic conditions (Whittenbury, Phillips and Wilkinson 1970). MOB belong to Alphaproteobacteria (type II), Gammaproteobacteria (type I) and the phylum Verrucomicrobia (Trotsenko and Murrell 2008; Op den Camp *et al.* 2009; Semrau, DiSpirito and Yoon 2010). Aerobic methanotrophs are found in virtually all ecosystems, from acidic permafrost-affected peatlands (*Methylocella palustris* (Dedysh *et al.* 2000); *Methylocella tundrae* (Dedysh *et al.* 2004)) to volcanic mud pots with temperatures up to 70°C and pH values as low as 1 (Dunfield *et al.* 2007; Pol *et al.* 2007). These volcanic aerobic *Methylacidiphilum* methanotrophs belong to the phylum Verrucomicrobia (Op den Camp *et al.* 2009; van Teeseling *et al.* 2014). The verrucomicrobial methanotrophs use the Calvin cycle for CO_2 fixation (Khadem *et al.* 2012) and are able to grow as Knallgas bacteria on hydrogen and oxygen (Carere *et al.* 2017; Mohammadi *et al.* 2017a). These methanotrophs express hydroxylamine oxidoreductase, nitrite reductase and nitric oxide reductase to counteract the nitrosative stress induced by high ammonium concentrations in mud volcanoes (Mohammadi *et al.* 2017b). The growth of verrucomicrobial methanotrophs is dependent on rare earth elements (lanthanides), which are incorporated into the active center of an XoxF-type methanol dehydrogenase (Pol *et al.* 2014). The unique properties of verrucomicrobial MOB are a striking example of the breadth of microbial diversity and physiology that remains to be explored and discovered.

Atmospheric methane levels were long considered too low to sustain microbial methanotrophy, but methane oxidation at atmospheric levels has been described in upland soils (Dunfield *et al.* 1999). Culture-independent studies of these soils, which have high-affinity methane oxidation capacity, detected novel methanotrophic bacteria within Alpha- and Gammaproteobacteria named upland soil cluster (USC) α and γ (Knief, Lipski and Dunfield 2003; Kolb *et al.* 2005; Ricke *et al.* 2005). Recently, Pratscher *et al.* (2018) obtained a 85% complete draft genome of the USCα genus within *Beijerinckiaceae* using combined metagenomics and targeted cell enrichments with fluorescence *in situ* hybridization-fluorescence activated cell sorting. In addition, recent studies have indicated that classic MOB can thrive under extremely low oxygen conditions by apparently coupling fermentative metabolism to nitrate reduction (Kits *et al.* 2015; Kits, Klotz and Stein 2015; Oswald *et al.* 2016; Gilman *et al.* 2017). Together with the observations of methanogenesis under oxic conditions, these findings may alter our understanding of controls on methane fluxes.

Nitrogen cycle

Historically, the nitrogen cycle was thought to include only a few processes: (i) the fixation of dinitrogen gas into ammonium by free-living or symbiotic microorganisms (Beijerinck 1888); (ii) nitrification, in which ammonium is oxidized via nitrite to nitrate (Winogradsky 1890); (iii) denitrification, in which oxidized nitrogen species are reduced to dinitrogen gas by heterotrophic and/or autotrophic bacteria (Gayon and Dupetit 1886) and (iv) nitrate/nitrite dissimilation and assimilation, which

provides many microorganisms with ammonium (Berks *et al.* 1995). In 1977, Broda calculated that several nitrogen processes could sustain as-yet undiscovered microorganisms (Broda 1977). However, it was not until 1995 that one of these processes, anammox (Table 1), was observed, and in 1999, the responsible anammox bacteria were identified as novel Planctomycetes (Mulder *et al.* 1995; Strous *et al.* 1999). In 2005, marine Thaumarchaeota (previously named Crenarchaeota) capable of oxidizing ammonium at oceanic concentrations (1 nM to 10 μM) were isolated and characterized (Könneke *et al.* 2005; Lam and Kuypers 2011). The complete ammonium-oxidizing (comammox) bacteria predicted by Costa *et al.* in 2006 were later identified as *Nitrospira* bacteria (Daims *et al.* 2015; van Kessel *et al.* 2015).

Aerobic ammonium oxidation

Ammonium oxidation to nitrate via nitrite

Since the description and isolation of *Nitrosomonas*-like aerobic ammonium oxidizers by Winogradsky at the end of the 19th century, this process was attributed to chemolithoautotrophic bacteria (ammonium-oxidizing bacteria, AOB). In marine environments, ammonium oxidation was thought to be limited to the deeper water layers due to light inhibition and ammonium concentrations below the threshold level for AOB activity (Yool *et al.* 2007). This view was challenged by two metagenomics-based studies surveying the microbial diversity of seawater (Venter *et al.* 2004) and soil (Treusch *et al.* 2005), which identified archaeal ammonia monooxygenase (*amoA*) genes phylogenetically affiliated with the phylum Thaumarchaeota. The link between archaea and ammonium oxidation was established by Könneke *et al.* (2005) with the isolation of 'Candidatus Nitrosopumilus maritimus', a marine group I.1a representative, from a saltwater aquarium in Seattle, Washington. In recent years, many more ammonium-oxidizing Thaumarchaeota (AOA) representatives have been isolated or enriched, including 'Candidatus Nitrososphaera viennensis' soil group I.1b from soil, 'Candidatus Nitrososphaera gargensis' soil group I.1b from the Garga hot spring, 'Candidatus Nitrosocaldus islandicus' from an Icelandic hot spring, and 'Candidatus Nitrosocaldus yellowstonii' and 'Candidatus Nitrosotalea devanaterra' soil group I.1a-associated enrichments from soil (de la Torre *et al.* 2008; Hatzenpichler *et al.* 2008; Lehtovirta-Morley *et al.* 2011, 2014; Stieglmeier *et al.* 2014; Daebeler *et al.* 2018). Recently, 'Candidatus Nitrosotalea' species were also enriched from acidic soils with pH values as low as 3.2 (Herbold *et al.* 2017).

[15]N stable isotope experiments have confirmed that nitrification, most likely by Thaumarchaeota, occurs in the photic zone of marine ecosystems (Clark, Rees and Joint 2008). In terrestrial ecosystems, acidiphilic 'Candidatus Nitrosotalea devanaterra' grows optimally between pH 4 and 5 (Zhang *et al.* 2010; Lehtovirta-Morley *et al.* 2011). However, determining the relative contributions of either AOB or AOA in ecosystems is quite challenging due to the large differences in growth rates, K_s for ammonia and oxygen, and sensitivity to inhibitors such as 2-phenyl-4,4,5,5,-tetramethylimidazoline-1-oxyl-3-oxide (PTIO) and allylthiourea (ATU) (Geets, Boon and Verstraete 2006; Yan *et al.* 2012; Martens-Habbena *et al.* 2015; Beeckman, Motte and Beeckman 2018). For a critical view on the importance of bacterial versus archaeal ammonium oxidation, see reviews by Prosser and Nicol (2008), Pester, Schleper and Wagner (2011), Hatzenpichler (2012) and Stahl and de la Torre (2012).

In many ecosystems, the nitrite produced by ammonium-oxidizing prokaryotes (AOP = AOB and AOA) is subsequently

oxidized by nitrite-oxidizing bacteria (NOB). Nitrite oxidation is a widespread trait that is found in six phyla: Alpha-, Beta- and Gammaproteobacteria, Nitrospirae, Nitrospinae and Chloroflexi (Nowka, Daims and Spieck 2015). *Nitrobacter winogradskyi* (Winslow *et al*. 1917) was the first nitrite oxidizer to be studied in extensive detail. *Nitrobacter* species tend to dominate nutrient-rich and oxygen-saturated environments. *Nitrospina* was discovered together with *Nitrococcus* in 1971 in marine ecosystems (Watson and Waterbury 1971). *Nitrospina gracilis* appears to be a major marine nitrite-oxidizing species. In general, *Nitrospina* species are quite well-adapted to low environmental nitrite concentrations (Maixner *et al*. 2006). *Nitrococcus mobilis* has a much more versatile metabolism, including nitrate reduction and sulfide oxidation (Füssel *et al*. 2017). *Nitrospira* species (i.e. *Nitrospira moscoviensis* and '*Candidatus* Nitrospira defluvii') generally dominate environments with low substrate availability and hypoxic conditions (Ehrich *et al*. 1995; Schramm *et al*. 2000; Lücker *et al*. 2010). They are more versatile than initially assumed and can use hydrogen and urea as substrates (Koch *et al*. 2014, 2015). Among betaproteobacterial nitrite oxidizers, the novel *Nitrotoga* species '*Candidatus* Nitrotoga arctica' was highly enriched from permafrost soils (Alawi *et al*. 2007). NOB can also use cyanate for energy and as a nitrogen source. Cyanate-encoding genes clustered with NOB have also been found in *Nitrososphaera gargensis* and *Scalindua* anammox bacteria (Palatinszky *et al*. 2015). Sorokin *et al*. (2012) isolated a nitrite oxidizer that belongs to the widespread phylum Chloroflexi, *Nitrolancetus hollandicus*, from a nitrifying reactor. *Nitrolancetus hollandicus* has a broad temperature range (25°C–63°C) but a low affinity for nitrite ($K_s = 1$ mM) and can use formate as a source of energy and fix CO_2 via the Calvin cycle. *Thiocapsa* species can couple the anaerobic oxidation of nitrite directly to phototrophy (Griffin, Schott and Schink 2007). Intriguingly, although the disproportionation of nitrite (into nitrate and nitrous oxide (N_2O)) would yield sufficient Gibbs free energy to sustain growth, no organisms capable of carrying out this reaction have been identified (Kuypers, Marchant and Kartal 2018).

Comammox: complete ammonium oxidation to nitrate

Ammonium oxidation to nitrate was once assumed to be a two-step reaction carried out by the subsequent action of ammonium and nitrite oxidizers. Despite a lack of biological proof for complete nitrification by a single organism, its existence and potential competitive advantage in biofilms with low substrate concentrations were proposed in 2006, based on modeling of the trade-off between growth rate (short pathways are faster) and growth yield (more complete pathways result in a higher energy yield) (Costa, Pérez and Kreft 2006). In 2015, the first comammox *Nitrospira* species were discovered in two different ecosystems (Daims *et al*. 2015; van Kessel *et al*. 2015). These observations expanded the metabolic potential of the *Nitrospira* clade, which was thought to contain only strict canonical aerobic NOB (Watson *et al*. 1986; Ehrich *et al*. 1995; Lebedeva *et al*. 2011). Since its discovery, comammox *Nitrospira* have been detected in several wastewater treatment reactors using metagenomics and primer-based approaches (Chao *et al*. 2016; Gonzalez-Martinez *et al*. 2016), drinking water systems (Pinto *et al*. 2016; Bartelme, McLellan and Newton 2017) and a variety of natural systems using a *pmoA* primer-targeted approach (Pjevac *et al*. 2017). Very recently, Kits *et al*. (2017) experimentally determined that the half saturation constant (K_s) for ammonium (0.65–1.1 μM) of *Nitrospira inopinata* was two orders of magnitude lower than that of any other cultured ammonium oxidizer, suggesting that *N.*

inopinata is very competitive in environments with low ammonium concentrations.

Anaerobic ammonium oxidation by anammox bacteria

Hamm and Thompson (1941) reported that much less ammonium accumulated in anoxic water than expected based on stoichiometric calculations, providing the first indications of anammox. Chemical observations by Richards (1965) indicated the presence of alternative nitrogen loss pathways. In 1977, Broda famously proposed two types of lithotrophs based on Gibbs free energy calculations of the reactions. The predicted phototrophic anaerobic ammonium oxidizers have yet to be identified. The other hypothesized 'missing' process was anaerobic oxidation of ammonium with nitrite/nitrate as the oxidant. Subsequent field observations also indicated higher ammonium losses than expected (Smith, Howes and Duff 1991). In the early 1990s, Mulder *et al*. (1995) reported on the biological N-loss in an anoxic wastewater treatment plant at the Gist-Brocades yeast factory in Delft, The Netherlands. To prevent hydrogen sulfide production from the high-sulfate wastewaters, copious amounts of calcium nitrate were added to suppress sulfate reduction. Inadvertently, the presence of sufficient ammonium, nitrite and nitrate under anoxic conditions created a suitable niche for anammox bacteria. Recordings of the ammonium concentrations in the influent and effluent revealed that after 8 months, ammonium disappeared under anoxic conditions (Mulder *et al*. 1995). After the manuscript on the study was rejected by numerous journals for not being relevant with respect to applied or environmental aspects of microbiology, the editor of FEMS Microbiology Ecology was brave enough to accept and publish the story (Mulder *et al*. 1995). The microbial nature and initial characterization of the biomass of the process were investigated by Gijs Kuenen and co-workers at TU Delft (Kuenen 2008). A few years after its discovery, a highly enriched anammox culture was obtained by continuous cultivation in an SBR system with substrate limitation and effective biomass retention (Strous *et al*. 1997). The anammox cells were further purified by density gradient centrifugation. These purified cells produced dinitrogen gas from ammonium and nitrite while incorporating $^{14}CO_2$ into biomass (Strous *et al*. 1999). 16S rRNA analysis showed that the anammox bacteria belonged to the order Brocadiales within the phylum Planctomycetes (Jetten *et al*. 2010). For reviews on anammox biochemistry, physiology, application and ecosystem relevance, see Kartal, Kuenen and van Loosdrecht (2010), van Niftrik and Jetten (2012), and Kuypers, Marchant and Kartal (2018).

In 2006, the first genetic blueprint of anammox bacteria was elucidated, which, together with sophisticated ^{15}N-nitrogen experiments, revealed that the anammox reaction includes the reactive intermediates nitric oxide (NO) and the powerful reductant and 'rocket fuel' hydrazine (N_2H_4) (van de Graaf *et al*. 1997; Schalk *et al*. 1998). The mechanism, structure and biophysical properties of the key metabolic hydrazine synthase enzyme were recently elucidated (Kartal *et al*. 2011; Dietl *et al*. 2015). Anammox bacteria appear to fix carbon through the Wood-Ljungdahl (reductive acetyl-CoA) pathway with electrons derived from the oxidation of nitrite to nitrate (Schouten *et al*. 2004; de Almeida *et al*. 2011).

Five genera (*Kuenenia, Brocadia, Anammoxoglobus, Scalindua* and *Jettenia*) of anammox bacteria are known, and 10 species have been described. For an extensive overview, see van Niftrik and Jetten (2012). None of these are available as pure culture, and current enrichments using bioreactors with planktonic cells or aggregates/granules reach up to 95% (Kartal *et al*. 2011). Electron

microscopic analyses have indicated a unique intracytoplasmic compartment named the 'anammoxosome' with a membrane composed of a single layer of ladderane lipids (van Niftrik et al. 2004; Neumann et al. 2014). Genomic analysis (Strous et al. 2006) and subsequent experimental confirmation (van Teeseling et al. 2015) revealed that anammox bacteria do possess a peptidoglycan cell wall and thus should be considered Gram-negative bacteria. Nearly 28 thousand anammox-related 16S rRNA gene sequences have been identified thus far (NCBI, NLM, Bethesda, MA, USA, Feburary 2018), indicating that likely only a fraction of anammox diversity is known. Anammox bacteria have been detected in freshwater environments, including anoxic wastewater, sediments and agricultural soils and in marine systems, including coastal and estuarine sediments, anoxic basins, mangrove sediments and oxygen minimum zones (OMZs) (Isobe and Ohte 2014).

From an ecosystem perspective, anammox bacteria contribute significantly to the oceanic nitrogen cycle (Dalsgaard et al. 2003; Kuypers et al. 2005; Lam et al. 2009; Pitcher et al. 2011; Bale et al. 2014; Lüke et al. 2016). Lüke et al. (2016) reported the co-occurrence of Scalindua, Nitrospina and novel microorganisms with dissimilatory nitrate reduction to ammonium (DNRA) potential (novel nrfA gene) in the Arabian Sea. The role of anammox bacteria in nitrogen loss has been investigated in global major OMZs, including the Black Sea, the Chilean and Peruvian OMZ, the Namibian OMZ and the Arabian Sea, where they are estimated to contribute to 50% of N loss (Kuypers et al. 2003, 2005; Lam et al. 2009; Jensen et al. 2011; Kuypers, Marchant and Kartal 2018). In continental shelf sediments, their estimated contribution reaches 79% (Thamdrup and Dalsgaard 2002; Engström et al. 2005). Quantifying the contribution of anammox bacteria and denitrifiers to total oceanic nitrogen loss is an ongoing challenge (Babbin et al. 2008). Anammox bacteria have been shown to perform DNRA with formate as an electron donor (Kartal et al. 2007). Furthermore, the use of volatile fatty acids in anammox has been shown for 'Candidatus Anammoxoglobus propionicus', which co-oxidizes propionate, acetate and formate with ammonium and 'Candidatus Brocadia fulgida', 'Candidatus Jettenia caeni' and 'Candidatus Scalindua profunda', which co-oxidize acetate and formate with ammonium (Kartal et al. 2007; Kartal, Kuenen and van Loosdrecht 2010; van de Vossenberg et al. 2013; Ali et al. 2015). Caution is needed since experimental data on environmental factors and in situ species activity and regulation of metabolism are scarce. For a relevant perspective, see Voss and Montoya (2009).

Iron- and manganese-dependent ammonium oxidation

Several anammox species can reduce Fe^{3+} at the expense of formate or acetate (Strous et al. 2006; van de Vossenberg et al. 2013; Zhao et al. 2014; Ali et al. 2015). Fe^{2+} can be used as an electron donor for nitrate reduction by anammox and several denitrifiers (Strous et al. 2006; Oshiki et al. 2013). Contradictory reports on nitrification coupled to metal-oxide reduction appeared in the 1990s (Luther et al. 1997; Hulth, Aller and Gilbert 1999; Thamdrup and Dalsgaard 2000). The coupling of iron and/or manganese reduction to anaerobic ammonium oxidation should be feasible at physiologically relevant concentrations based on thermodynamic calculations (Table 1). Similar to Fe-AOM, the so-called Feammox process could be important in sediments with relatively low sulfate concentrations (Rooze and Meile 2016; Rooze et al. 2016). A number of field observations suggest that oxidation of ammonium can be coupled to the reduction of Fe^{3+}, with

dinitrogen gas, nitrite, or nitrate as the end product. Acidimicrobiaceae may oxidize ammonium under iron-reducing conditions (Gilson, Huang and Jaffé 2015; Huang and Jaffé 2015). The Feammox process has been observed in riparian wetlands (Clément et al. 2005; Shrestha et al. 2009; Ding, Li and Qin 2017), forested wetlands (Huang and Jaffé 2015), tropical forest soils (Yang et al. 2012), paddy field soils (Ding et al. 2014; Zhou et al. 2016), intertidal wetlands (Li et al. 2015) and anammox sludge (Li et al. 2018a, b). During the Feammox process, the generation of dinitrogen gas is more favorable (−245 kJ/mol) than the generation of nitrite (−164 kJ/mol) or nitrate (−207 kJ/mol) (Luther et al. 1997; Clément et al. 2005; Shrestha et al. 2009; Kuypers, Marchant and Kartal 2018). Thermodynamic calculations of the Feammox process under natural conditions in Congo lobe sediments (1 μM Fe^{2+}, 1 μM NO_2^- and NO_3^-, 100 μM NH_4^+, pN_2 0.718 atm, pN_2O 1E-9 atm) revealed a Gibbs free energy change of −206.9 kJ/mol (Kiriazis 2015). However, significant accumulation of nitrate up to 113 μM was observed in the incubations, indicating possible nitrifying activity. Isotope tracing studies of Yangtze Estuary sediment slurry incubations showed a potential of 0.24–0.36 mg N kg^{-1} d^{-1} (Li et al. 2015). Li et al. (2015) suggested that the effects of tidal fluctuations on ferric iron reduction could mediate Feammox activity and nitrogen loss in intertidal wetland ecosystems.

These findings imply alternative pathways of N loss from soils and sediments. Potential Feammox rates (i.e. $^{30}N_2$ production rates) in paddy field soils range from 0.17 to 0.59 mg N kg^{-1} d^{-1} (Ding et al. 2014), comparable to the Feammox rates found for intertidal wetlands (0.24–0.36 mg N kg^{-1} d^{-1}) (Li et al. 2015) and tropical forest soils (approximately 0.32 mg N kg^{-1} d^{-1}) (Yang, Weber and Silver 2012). The Feammox reaction depends on the availability of ammonium and Fe^{3+}. The oxidized form of iron is affected by pH, which regulates the reactivity of iron oxide minerals and iron redox reactions. However, iron-reducing bacteria can affect the Feammox process by controlling Fe^{3+} reduction in anoxic environments. The iron-reducing bacteria Geobacteraceae spp. and Shewanella spp. may be directly or indirectly involved in ammonium oxidation (Clément et al. 2005; Shrestha et al. 2009; Li et al. 2015). Although these studies support the occurrence of Feammox in various environments, the key microbial organisms responsible for this process must be convincingly identified. Anoxic microbial fuel cells fed solely with ammonium could be a good model system to investigate the occurrence of Feammox in sediments but have received limited attention (Qu et al. 2014; Zhan et al. 2014; Jadhav and Ghangrekar 2015; Li et al. 2015; Reyes et al. 2016).

Sulfate-dependent ammonium oxidation

Sulfate-dependent ammonium oxidation is thermodynamically very challenging under biologically relevant conditions (Table 1) and would barely yield sufficient Gibbs free energy even at molar concentrations of ammonium. Very few field observations are available (Schrum et al. 2009), and there is no genomic evidence that anammox bacteria can use sulfate instead of nitrite as an electron acceptor. In 2008, the anammox bacterium 'Candidatus Anammoxoglobus sulfate' was presumably enriched from an anammox reactor biomass fed with ammonium sulfate under anoxic conditions (Liu et al. 2008). Fdz-Polanco et al. (2001) proposed a two-stage sulfate-reducing ammonium oxidation (SRAO) in which sulfate is reduced to elemental sulfur. Zhang et al. subsequently proposed an alternative route in which sulfate is reduced to sulfide (Zhang et al. 2009). Furthermore, sulfur-driven iron reduction coupled to anaerobic ammonium

oxidation was recently described by Bao and Li (2017). The interfaces of anoxic deep-sea brine pools may represent a possible ecosystem where very high ammonium and sulfate concentrations can be found (Daffonchio *et al.* 2006; Borin *et al.* 2013). Metagenomic surveys indicated a high diversity of microorganisms, including anammox bacteria, at these interfaces (Daffonchio *et al.* 2006; Speth *et al.* 2017). Dedicated high-pressure salt-resistant reactor equipment would be needed to successfully establish enrichment cultures on ammonium and sulfate from these ecosystems.

Microbial interactions in the methane, sulfur and nitrogen cycles

While the enrichment and characterization of individual 'impossible' anaerobic chemolithoautotrophic microorganisms is of great interest to microbiologists, these organisms do not live in isolation. In ecosystems, these microorganisms must collaborate to remove toxic intermediates or compete for limiting resources. Recently, the fate of ammonium, sulfide and methane under nitrate-reducing conditions similar to those in estuarine ecosystems was elegantly investigated in a bioreactor system (Russ *et al.* 2014; Arshad *et al.* 2017). Over time, an enrichment culture developed in which '*Candidatus* Methanoperedens nitroreducens', '*Candidatus* Methylomirabilis oxyfera' and anammox bacteria coexisted with sulfide oxidizers. '*Candidatus* Methanoperedens nitroreducens' converted 53% of the supplied methane while reducing 69% of the nitrate to nitrite. Sulfide oxidizers contributed 31% to nitrite production. The nitrite was converted to dinitrogen gas by anammox bacteria (53%) at the expense of ammonium, by '*Candidatus* Methylomirabilis oxyfera' (37%) at the expense of methane, and by sulfide oxidizers (10%). Surprisingly, the metagenome of this anaerobic community was dominated by a new Nitrospirae species, '*Candidatus* Nitrobium versatile'. Based on the retrieved genome, '*Candidatus* Nitrobium versatile' might produce ammonium from nitrite by sulfur disproportionation or utilize other one-carbon excretion products. Relatives of these Nitrospirae with similarly versatile potential have since been detected in gypsum-fertilized paddy fields (Zecchin *et al.* 2017).

CONCLUSIONS

Taken together, these studies and examples emphasize the fascinating diversity of the most-wanted spookmicrobes. Future detailed field studies using state-of-the-art biogeochemical and microbiology methods in selected environments with counter gradients of iron oxides and ammonium and/or methane are needed to identify suitable niches and samples for the discovery of new methane- or ammonium-dependent iron reducers. We expect that such samples will yield many more exciting discoveries of chemolithoautotrophic spookmicrobes when the microbial ecology and interactions are investigated under controlled substrate-limited conditions in bioreactor systems. During the page proof stage two studies (Table 1) appeared online. Huang and Jaffé reported the isolation of an *Acidimicrobiaceae* strain that can convert ammonium to nitrite at pH 4 with ferrihydrite as electron acceptor (Huang and Jaffé 2018). Cai *et al.* described a 1100 day enrichment of '*Candidatus* Methanoperedens ferrireducens' that use methane to reduce Fe^{3+} possibly using several highly expressed multiheme cytochrome *c* proteins (Cai *et al.* 2018).

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