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## 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 Methanotrix 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.

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## 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<sub>4</sub>), hydrogen sulfide (H<sub>2</sub>S) and ammonium (NH<sub>4</sub><sup>+</sup>), 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 (Saunio *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<sub>2</sub>S 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<sub>2</sub>), sulfate (SO<sub>4</sub><sup>2-</sup>) and dinitrogen gas (N<sub>2</sub>) (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<sub>2</sub><sup>-</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>) 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' *Methanotherix soehngeni*, 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 <sub>3</sub> OH	+360	-103	4 CH <sub>3</sub> OH → CO <sub>2</sub> + 3 CH <sub>4</sub> + 2 H <sub>2</sub> O	<i>Methanosarcina semesiae</i>	Brackish sediment	<0.2	-	<5	-	Lyimo, Pol and Op den Camp (2000); Thauer, Jungermann and Decker (1977) and Welte (2018)
CH <sub>3</sub> -R	+193	-56	(CH <sub>3</sub> ) <sub>2</sub> SH + H <sub>2</sub> O → 0.5 CO <sub>2</sub> + 1.5 CH <sub>4</sub> + H <sub>2</sub> S	<i>Methanomethylorans hollandica</i>	Freshwater sediment	<1	-	<30	-	Lomans et al. (1999)
CH <sub>3</sub> COOH	+46	-36	CH <sub>3</sub> COOH → CO <sub>2</sub> + CH <sub>4</sub>	<i>Methanothrix soehngenii</i>	WWTP	7-14	-	500	-	Huser et al. (1982)
				' <i>Candidatus Methanothrix paradoxum</i> '	Wetland soil	-	-	-	-	Angle et al. (2017)
CH <sub>3</sub> O-R	+366	-106	4 CH <sub>3</sub> O-R + 2 H <sub>2</sub> O → 4 R-OH + CO <sub>2</sub> + 3 CH <sub>4</sub>	<i>Methermicoccus shengliensis</i>	Oilfield water	<5	20	-	-	Cheng et al. (2007)
CH <sub>3</sub> OH	+172	-113	CH <sub>3</sub> OH + H <sub>2</sub> → CH <sub>4</sub> + H <sub>2</sub> O	<i>Methanomassiliococcus luminyiensis</i>	Human feces	2	-	-	-	Dridi et al. (2012)
				' <i>Candidatus Methanonatronarchaea</i> '	Hypersaline lake	-	-	-	-	Sorokin et al. (2017)
				' <i>Candidatus Methanofastidiosa</i> '	WWTP	-	-	-	-	Nobu et al. (2016)
Methane (CO <sub>2</sub> /CH <sub>4</sub> at $\Delta E_0' = -240$ mV) as electron donor										
O <sub>2</sub> /H <sub>2</sub> O	+810	-801	CH <sub>4</sub> + 2 O <sub>2</sub> → CO <sub>2</sub> + 2 H <sub>2</sub> O	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						
				<i>Methylocella palustris</i>	Peat					Dedysh et al. (2000)
				<i>Methylocella tundra</i>	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						
				<i>Methylacidiphilum</i>	Geothermal area					Op den Camp et al. (2009)
NO <sub>3</sub> <sup>-</sup> /NO <sub>2</sub> <sup>-</sup>	+430	-503	CH <sub>4</sub> + 4 NO <sub>3</sub> <sup>-</sup> → CO <sub>2</sub> + 4 NO <sub>2</sub> <sup>-</sup> + 2 H <sub>2</sub> O	' <i>Candidatus Methanoperedens nitroreducens</i> '	Freshwater sediment, WWTP	>14	0.57	>1000	<50	Haroon et al. (2013) and Vaksmaa et al. (2017a)
NO <sub>2</sub> <sup>-</sup> /N <sub>2</sub>	+320	-928	3 CH <sub>4</sub> + 8 NO <sub>2</sub> <sup>-</sup> + 8 H <sup>+</sup> → 3 CO <sub>2</sub> + 4 N <sub>2</sub> + 10 H <sub>2</sub> O	' <i>Candidatus Methyloirabilis oxyfera</i> '	Freshwater sediment	>14	0.4-0.2	<50	<10	Raghoebarsing et al. (2006)
Fe <sup>3+</sup> /Fe <sup>2+</sup>	+360	-454	CH <sub>4</sub> + 8 Fe <sup>3+</sup> + 2 H <sub>2</sub> O → CO <sub>2</sub> + 8 Fe <sup>2+</sup> + 8 H <sup>+</sup>	' <i>Candidatus Methanoperedens nitroreducens</i> '	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 <sub>4</sub> <sup>2-</sup> /H <sub>2</sub> S	-210	-21	CH <sub>4</sub> + SO <sub>4</sub> <sup>2-</sup> → HCO <sub>3</sub> <sup>-</sup> + H <sub>2</sub> S + H <sub>2</sub> O	Anaerobic methanotrophic archaea (ANME)	Marine sediment	>50	0.7	>1000	-	Nauhaus et al. (2005); Knittel et al. (2005)
Ammonium (NO <sub>2</sub> <sup>-</sup> /NH <sub>4</sub> <sup>+</sup> at $\Delta E_0' = 340$ mV) as electron donor										
O <sub>2</sub> /H <sub>2</sub> O	+810	-275	NH <sub>4</sub> <sup>+</sup> + 1.5 O <sub>2</sub> → NO <sub>2</sub> <sup>-</sup> + H <sub>2</sub> O + 2 H <sup>+</sup>	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)
				' <i>Candidatus Nitrosopumilus maritimus</i> '	Hot spring					Könneke et al. (2005)
				' <i>Candidatus Nitrosocaldus yellowstonii</i> '	Hot spring					de la Torre et al. (2008)
				' <i>Candidatus Nitrososphaera gargensis</i> '	Garden soil					Hatzenpichler et al. (2008)
				' <i>Candidatus Nitrososphaera viennensis</i> '	Agricultural soil					Tourna et al. (2011)

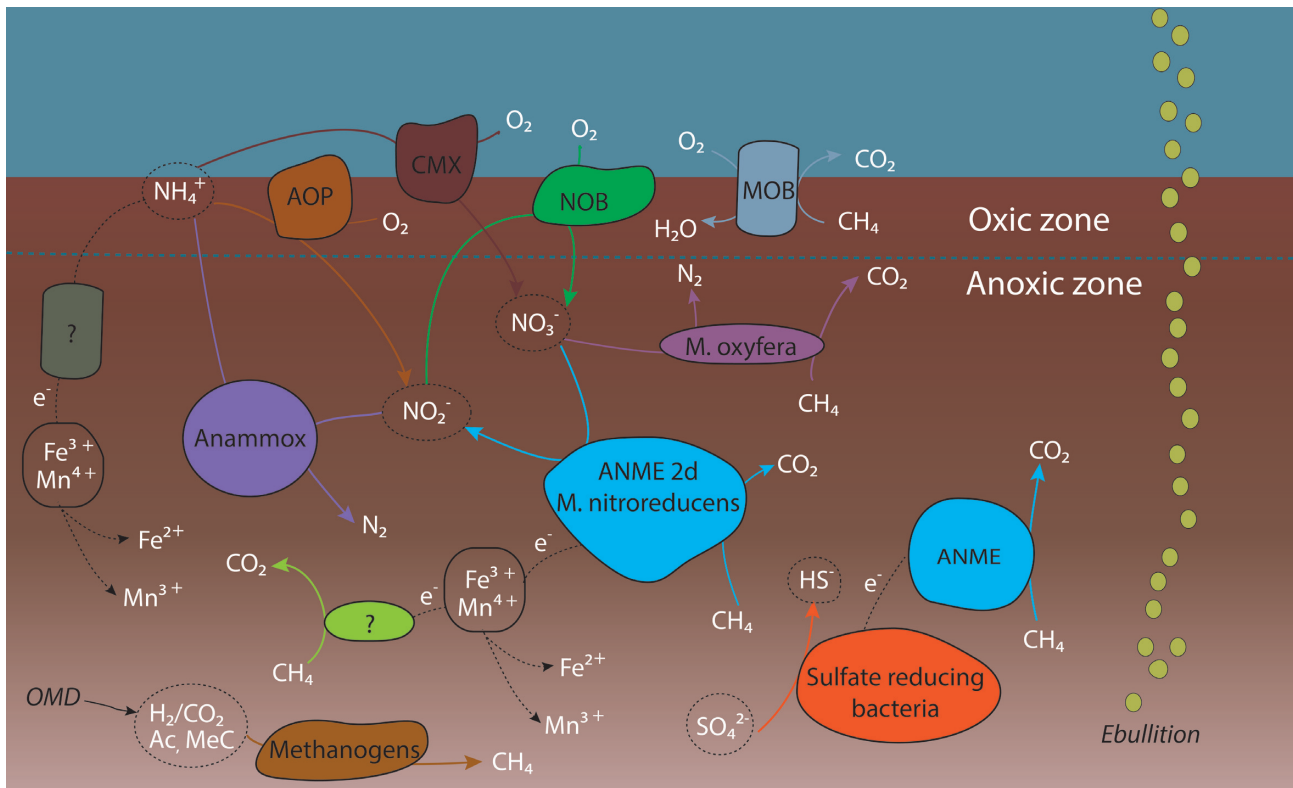
Table 1. Continued

Electron acceptor	$\Delta E_0'$	$\Delta G_0'$	Reaction equation	Micro-organism(s)	Origin	Growth rate	Per cell rate	Ks [S]	Ks [EA]	Reference
Nitrite ( $\text{NO}_3^-/\text{NO}_2^-$ at $\Delta E_0' = 420$ mV) as electron donor $\text{O}_2/\text{H}_2\text{O}$	+810	-74	$\text{NO}_2^- + 0.5 \text{O}_2 \rightarrow \text{NO}_3^-$	' <i>Candidatus Nitrosotalea devanaterrea</i> '	Hot spring					Lehtovirta-Morley, Stoecker and Vilcinskas (2011)
				' <i>Candidatus Nitrosocaldus islandicus</i> '					Daebeler et al. (2018)	
				Nitrite-oxidizing bacteria (NOB)		<1	0.6–13.1	9–544	22–166	Féray and Montuelle (2002) and Nowka, Daims and Spieck (2015)
				Alphaproteobacteria <i>Nitrobacter winogradskyi</i>	Soil			Winslow et al. (1917)		
				Betaproteobacteria ' <i>Candidatus Nitroga arctica</i> '	Permafrost			Alawi et al. (2007)		
				Gammaproteobacteria <i>Nitrococcus mobilis</i>	Ocean water			Watson and Waterbury (1971)		
				Nitrospirae <i>Nitrospira moscoviensis</i>	Heating system			Ehrich et al. (1995)		
				' <i>Candidatus Nitrospira defluvii</i> '	WWTP			Lücker et al. (2010)		
				Nitrospinae <i>Nitrospina gracilis</i>	Ocean water			Watson and Waterbury (1971)		
				Chloroflexi <i>Nitrolancetus hollandicus</i>	Nitrifying reactor			Sorokin et al. (2012)		
Ammonium ( $\text{NO}_3^-/\text{NH}_4^+$ at $\Delta E_0' = 360$ mV) as electron donor $\text{O}_2/\text{H}_2\text{O}$	+810	-349	$\text{NH}_4^+ + 2 \text{O}_2 \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + 2 \text{H}^+$	Comammox <i>Nitrospira</i>		<1	-	0.6	-	van Kessel et al. (2015) and Kits et al. (2017)
				<i>Nitrospira inopinata</i>	Hot water pipe			Daims et al. (2015)		
Ammonium ( $\text{N}_2/\text{NH}_4^+$ at $\Delta E_0' = -280$ mV) as electron donor $\text{NO}_2^-/\text{N}_2$	+320	-358	$\text{NH}_4^+ + \text{NO}_2^- \rightarrow \text{N}_2 + 2 \text{H}_2\text{O}$	Anammox bacteria		4–14	2–20	<5	<5	Lotti et al. (2015) and Zhang et al. (2017)
				Brocadiales ' <i>Candidatus Kuenenia stuttgartiensis</i> '	WWTP			Jetten et al. (2010)		
				' <i>Candidatus Brocadia fulgida</i> '	WWTP			Schmid et al. (2000)		
				' <i>Candidatus Anammoxoglobus propionicus</i> '	WWTP			Kartal et al. (2007)		
				' <i>Candidatus Scalindua profunda</i> '	Marine sediment			van de Vossenberg et al. (2013)		
				' <i>Candidatus Jettenia caeni</i> '	WWTP			Ali et al. (2015)		
				?				Kuypers et al. (2018) and Huang and Jaffé (2018)		
				?				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  $\mu\text{M}$  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  $\text{H}_2/\text{CO}_2$  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 *Methanotrix* (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 semisiae*, *Methanomethylivorans 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 methoxytrophic *Methermicrococcus 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 acetoclastic 'Candidatus Methanoxithrix 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 methyl-coenzyme 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 ( $439 \text{ kJ mol}^{-1}$ ) (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  $-20 \text{ kJ mol}^{-1}$  (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 (Methanococoides-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 Methyloirabilis oxyfera*' (70%–80% of the community). The proposed intra-aerobic pathway for coupling of AOM to nitrite reduction by '*Candidatus Methyloirabilis 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 Methyloirabilis 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 ( $\text{Fe}^{3+}$ ) and oxidized manganese ( $\text{Mn}^{4+}$ ) 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.  $\text{Fe}^{3+}$  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<sub>2</sub> 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)  $\alpha$  and  $\gamma$  (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 USC $\alpha$  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  $\mu$ M) 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 (Treich 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 devanaterrea*' 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).

<sup>15</sup>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 devanaterrea*' 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-tetramethylimidazole-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 defluvi*') generally dominate environments with low substrate availability and hypoxic conditions (Ehrich et al. 1995; Schramm et al. 2000; Lückner 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<sub>2</sub> 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<sub>2</sub>O)) 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 <sup>14</sup>CO<sub>2</sub> 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 <sup>15</sup>N-nitrogen experiments, revealed that the anammox reaction includes the reactive intermediates nitric oxide (NO) and the powerful reductant and 'rocket fuel' hydrazine (N<sub>2</sub>H<sub>4</sub>) (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, February 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  $\text{Fe}^{3+}$  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).  $\text{Fe}^{2+}$  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  $\text{Fe}^{3+}$ , 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 ( $-245 \text{ kJ/mol}$ ) than the generation of nitrite ( $-164 \text{ kJ/mol}$ ) or nitrate ( $-207 \text{ kJ/mol}$ ) (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 ( $1 \mu\text{M Fe}^{2+}$ ,  $1 \mu\text{M NO}_2^-$  and  $\text{NO}_3^-$ ,  $100 \mu\text{M NH}_4^+$ ,  $p\text{N}_2$  0.718 atm,  $p\text{N}_2\text{O}$   $1\text{E-}9$  atm) revealed a Gibbs free energy change of  $-206.9 \text{ kJ/mol}$  (Kiriakis 2015). However, significant accumulation of nitrate up to  $113 \mu\text{M}$  was observed in the incubations, indicating possible nitrifying activity. Isotope tracing studies of Yangtze Estuary sediment slurry incubations showed a potential of  $0.24\text{--}0.36 \text{ mg N kg}^{-1} \text{ d}^{-1}$  (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.  $^{30}\text{N}_2$  production rates) in paddy field soils range from  $0.17$  to  $0.59 \text{ mg N kg}^{-1} \text{ d}^{-1}$  (Ding et al. 2014), comparable to the Feammox rates found for intertidal wetlands ( $0.24\text{--}0.36 \text{ mg N kg}^{-1} \text{ d}^{-1}$ ) (Li et al. 2015) and tropical forest soils (approximately  $0.32 \text{ mg N kg}^{-1} \text{ d}^{-1}$ ) (Yang, Weber and Silver 2012). The Feammox reaction depends on the availability of ammonium and  $\text{Fe}^{3+}$ . 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  $\text{Fe}^{3+}$  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 Methyloirabilis 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 Methyloirabilis 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<sup>3+</sup> possibly using several highly expressed multiheme cytochrome c proteins (Cai et al. 2018).

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### REFERENCES

- Aben RCH, Barros N, van Donk E, et al. Cross continental increase in methane ebullition under climate change. *Nat Commun* 2017;8:1–8.
- Alawi M, Lipski A, Sanders T, et al. Cultivation of a novel cold-adapted nitrite oxidizing betaproteobacterium from the Siberian Arctic. *ISME J* 2007;1:256–64.
- Ali M, Oshiki M, Awata T, et al. Physiological characterization of anaerobic ammonium oxidizing bacterium "Candidatus Jettenia caeni." *Environ Microbiol* 2015;17:2172–89.
- Allen G, Biogeochemistry: Rebalancing the global methane budget. *Nature* 2016;538:46–8.
- Amos RT, Bekins BA, Cozzarelli IM, et al. Evidence for iron-mediated anaerobic methane oxidation in a crude oil-contaminated aquifer. *Geobiology* 2012;10:506–17.
- Anantharaman K, Brown CT, Hug LA, et al. Thousands of microbial genomes shed light on interconnected biogeochemical processes in an aquifer system. *Nat Commun* 2016;7:1–11.
- Angle JC, Morin TH, Solden LM, et al. Methanogenesis in oxygenated soils is a substantial fraction of wetland methane emissions. *Nat Commun* 2017;8:1–9.
- Arshad A, Dalcin Martins P, Frank J, et al. Mimicking microbial interactions under nitrate-reducing conditions in an anoxic bioreactor: enrichment of novel Nitrospirae bacteria distantly related to *Thermodesulfobium*. *Environ Microbiol* 2017;19:4965–77.
- Arshad A, Speth DR, de Graaf RM, et al. A metagenomics-based metabolic model of nitrate-dependent anaerobic oxidation of methane by *Methanoperedens*-like archaea. *Front Microbiol* 2015;6:1–14.
- Babbin AR, Keil RG, Devol AH, et al. Organic matter stoichiometry, flux, and oxygen control nitrogen loss in the ocean. *Science* 2008;320:655–8.
- Bale NJ, Villanueva L, Fan H, et al. Occurrence and activity of anammox bacteria in surface sediments of the southern North Sea. *FEMS Microbiol Ecol* 2014;89:99–110.
- Bao P, Li G-X. Sulfur-driven iron reduction coupled to anaerobic ammonium oxidation. *Environ Sci Technol* 2017;51:6691–8.
- Bartelme RP, McLellan SL, Newton RJ. Freshwater recirculating aquaculture system operations drive biofilter bacterial community shifts around a stable nitrifying consortium of ammonia-oxidizing archaea and comammox Nitrospira. *Front Microbiol* 2017;8:1–18.
- Beal EJ, House CH, Orphan VJ. Manganese- and iron dependent marine methane oxidation. *Science* 2009;184:7.

- Beeckman F, Motte H, Beeckman T, Nitrification in agricultural soils: impact, actors and mitigation. *Curr Opin Biotechnol* 2018;**50**:166–73.
- Beijerinck MW, Die Bakterien der Papilionaceenknöllchen. *Bot Zeitung* 1888;**46**:726–804.
- Belsler LW, Schmidt EL, Growth and oxidation kinetics of three genera of ammonia oxidizing nitrifiers. *FEMS Microbiol Lett* 1980;**7**:213–6.
- Berger S, Frank J, Dalcin Martins P, et al. High-quality draft genome sequence of “Candidatus Methanoperedens sp.” strain BLZ2, a nitrate-reducing anaerobic methane-oxidizing archaeon enriched in an anoxic bioreactor. *Genome Announc* 2017;**5**:1–2.
- Berks BC, Ferguson SJ, Moir JW B et al. Enzymes and associated electron transport systems that catalyse the respiratory reduction of nitrogen oxides and oxyanions. *Biochim Biophys Acta* 1995;**1232**:97–173.
- Bhattacharjee AS, Motlagh AM, Jetten MSM et al. Methane dependent denitrification- from ecosystem to laboratory-scale enrichment for engineering applications. *Water Res* 2016;**99**:244–52.
- Boetius A, Ravensschlag K, Schubert CJ et al. A marine microbial consortium apparently mediating anaerobic oxidation of methane. *Nature* 2000;**407**:623–6.
- Borin S, Mapelli F, Rolli E et al. Anammox bacterial populations in deep marine hypersaline gradient systems. *Extremophiles* 2013;**17**:289–99.
- Broda E. Two kinds of lithotrophs missing in nature. *Z Allg Mikrobiol* 1977;**17**:491–3.
- Cai C, Leu AO, Xie G et al. A methanotrophic archaeon couples anaerobic oxidation of methane to Fe(III) reduction, *ISME J* 2018; **94**:1–11.
- Carere CR, Hards K, Houghton KM et al. Mixotrophy drives niche expansion of verrucomicrobial methanotrophs. *ISME J* 2017;**11**:2599–610.
- Chang Y-H, Cheng T-W, Lai W-J et al. Microbial methane cycling in a terrestrial mud volcano in eastern Taiwan. *Environ Microbiol* 2012;**14**:895–908.
- Chao Y, Mao Y, Yu K et al. Novel nitrifiers and comammox in a full-scale hybrid biofilm and activated sludge reactor revealed by metagenomic approach. *Appl Microbiol Biotechnol* 2016;**100**:8225–37.
- Cheng L, Qiu T-L, Yin X-B et al. *Methermicoccus shengliensis* gen. nov., sp. nov., a thermophilic, methylotrophic methanogen isolated from oil-production water, and proposal of *Methermicoccaceae* fam. nov. *Int J Syst Evol Microbiol* 2007;**57**:2964–9.
- Clark DR, Rees AP, Joint I. Ammonium regeneration and nitrification rates in the oligotrophic Atlantic Ocean: Implications for new production estimates. *Limnol Oceanogr* 2008;**53**:52–62.
- Clément JC, Shrestha J, Ehrenfeld JG et al. Ammonium oxidation coupled to dissimilatory reduction of iron under anaerobic conditions in wetland soils. *Soil Biol Biochem* 2005;**37**:2323–8.
- Conrad R. Soil microorganisms as controllers of atmospheric trace gases (H<sub>2</sub>, CO, CH<sub>4</sub>, OCS, N<sub>2</sub>O, and NO). *Microbiol Rev* 1996;**60**:609–40.
- Conrad R. The global methane cycle: recent advances in understanding the microbial processes involved. *Environ Microbiol Rep* 2009;**1**:285–92.
- Costa E, Pérez J, Kreft J-U. Why is metabolic labour divided in nitrification? *Trends Microbiol* 2006;**14**:213–9.
- Crowe SA, Katsev S, Leslie K et al. The methane cycle in ferruginous Lake Matano. *Geobiology* 2011;**9**:61–78.
- Daebeler A, Herbold CW, Vierheilig J et al. Cultivation and genomic analysis of “Candidatus Nitrosocaldus islandicus,” an obligately thermophilic, ammonia-oxidizing thaumarcaeon from a hot spring biofilm in Graendalur Valley, Iceland. *Front Microbiol* 2018;**9**:193.
- Daffonchio D, Borin S, Brusa T et al. Stratified prokaryote network in the oxic–anoxic transition of a deep-sea halocline. *Nature* 2006;**440**:203–7.
- Daims H, Lebedeva EV, Pjevac P et al. Complete nitrification by Nitrospira bacteria. *Nature* 2015;**528**:504–9.
- Dalsgaard T, Canfield DE, Petersen J et al. N<sub>2</sub> production by the anammox reaction in the anoxic water column of Golfo Dulce, Costa Rica. *Nature* 2003;**422**:606–8.
- Daughton CG, Cook AM, Alexander M. Phosphate and soil binding: factors limiting bacterial degradation of ionic phosphorus-containing pesticide metabolites. *Appl Environ Microbiol* 1979;**37**:605–9.
- de Almeida NM, Maalcke WJ, Keltjens JT, et al.. Proteins and protein complexes involved in the biochemical reactions of anaerobic ammonium-oxidizing bacteria. *Biochem Soc Trans* 2011;**39**:303–8.
- Dean JF, Middelburg JJ, Röckmann T et al. Methane feedbacks to the global climate system in a warmer world. *Rev Geophys* 2018, **56**: 207–50.
- Dedysh SN, Berestovskaya YY, Vasylijeva LV et al. *Methylocella tundrae* sp. nov., a novel methanotrophic bacterium from acidic tundra peatlands. *Int J Syst Evol Microbiol* 2004;**54**:151–6.
- Dedysh SN, Liesack W, Khmelenina VN et al. *Methylocella palustris* gen. nov., sp. nov., a new methane-oxidizing acidophilic bacterium from peat bogs, representing a novel subtype of serine-pathway methanotrophs. *Int J Syst Evol Microbiol* 2000;**50**:955–69.
- de la Torre JR, Walker CB, Ingalls AE et al. Cultivation of a thermophilic ammonia oxidizing archaeon synthesizing crenarchaeol. *Environ Microbiol* 2008;**10**:810–8.
- Diaz RJ, Rosenberg R. Spreading dead zones and consequences for marine ecosystems. *Science* 2008;**321**:926–9.
- Dietl A, Ferousi C, Maalcke WJ et al. The inner workings of the hydrazine synthase multiprotein complex. *Nature* 2015;**527**:394–7.
- Ding B, Li Z, Qin Y. Nitrogen loss from anaerobic ammonium oxidation coupled to Iron(III) reduction in a riparian zone. *Environ Pollut* 2017;**231**:379–86.
- Ding L-J, An X-L, Li S et al. Nitrogen loss through anaerobic ammonium oxidation coupled to iron reduction from paddy soils in a chronosequence. *Environ Sci Technol* 2014;**48**:10641–7.
- Dridi B, Fardeau M-L, Ollivier B et al. *Methanomassiliicoccus luminyensis* gen. nov., sp. nov., a methanogenic archaeon isolated from human faeces. *Int J Syst Evol Microbiol* 2012;**62**:1902–7.
- Dunfield PF, Conrad R. Starvation alters the apparent half-saturation constant for methane in the type II methanotroph *Methylocystis* strain LR1. *Appl Environ Microbiol* 2000;**66**:4136–8.
- Dunfield PF, Liesack W, Henckel T et al. High-affinity methane oxidation by a soil enrichment culture containing a type II methanotroph. *Appl Environ Microbiol* 1999;**65**:1009–14.
- Dunfield PF, Yuryev A, Senin P et al. Methane oxidation by an extremely acidophilic bacterium of the phylum Verrucomicrobia. *Nature* 2007;**450**:879–82.
- Egger M, Rasigraf O, Sapart CJ et al. Iron-mediated anaerobic oxidation of methane in brackish coastal sediments. *Environ Sci Technol* 2015;**49**:277–83.

- Ehrich S, Behrens D, Lebedeva E et al. A new obligately chemolithoautotrophic, nitrite-oxidizing bacterium, *Nitrospira moscoviensis* sp. nov. and its phylogenetic relationship. *Arch Microbiol* 1995;164:16–23.
- Engström P, Dalsgaard T, Hulth S et al. Anaerobic ammonium oxidation by nitrite (anammox): implications for N<sub>2</sub> production in coastal marine sediments. *Geochim Cosmochim Acta* 2005;69:2057–65.
- Ettwig KF, Butler MK, Paslier D Le et al. Nitrite-driven anaerobic methane oxidation by oxygenic bacteria. *Nature* 2010;464:543–8.
- Ettwig KF, Speth DR, Reimann J et al. Bacterial oxygen production in the dark. *Front Microbio* 2012;3:1–8.
- Ettwig KF, van Alen T, van de Pas-Schoonen KT et al. Enrichment and molecular detection of denitrifying methanotrophic bacteria of the NC10 phylum. *Appl Environ Microbiol* 2009;75:3656–62.
- Ettwig KF, Zhu B, Speth D et al. Archaea catalyze iron-dependent anaerobic oxidation of methane. *Proc Natl Acad Sci USA* 2016;113:12792–6.
- Evans PN, Parks DH, Chadwick GL et al. Methane metabolism in the archaeal phylum Bathyarchaeota revealed by genome-centric metagenomics. *Science* 2015;350:434–8.
- Falkowski PG, Fenchel T, Delong EF. The microbial engines that drive earth's biogeochemical cycles. *Science* 2008;320:1034–9.
- Fdz-Polanco F, Fdz-Polanco M, Fernandez N et al. New process for simultaneous removal of nitrogen and sulphur under anaerobic conditions. *Water Res* 2001;35:1111–4.
- Finster K, King GM, Bak F. Formation of methylmercaptan and dimethylsulfide from methoxylated aromatic compounds in anoxic marine and fresh water sediments. *FEMS Microbiol Lett* 1990;74:295–301.
- Finster K, Tanimoto Y, Bak F. Fermentation of methanethiol and dimethylsulfide by a newly isolated methanogenic bacterium. *Arch Microbiol* 1992;157:425–30.
- Féray C, Montuelle B. Competition between two nitrite-oxidizing bacterial populations: a model for studying the impact of wastewater treatment plant discharge on nitrification in sediment. *FEMS Microbiol Ecol* 2002;42:15–23.
- Füssel J, Lücker S, Yilmaz P et al. Adaptability as the key to success for the ubiquitous marine nitrite oxidizer *Nitrocooccus*. *Sci Adv* 2017;3:1–9.
- Garrity GM, Bell JA, Lilburn TG. Taxonomic outline of the prokaryotes. In: Bergey D, Buchanan R, Gibbons N (eds). *Bergey's Manual of Systematic Bacteriology*. 2nd edn. Baltimore: Williams & Wilkins, 2004.
- Gayon U, Dupetit G. *Recherches Sur La Réduction Des Nitrates Par Les Infinités Petits*. Imprimerie Berger-Levrault et Cie, Nancy, France. 1886.
- Geets J, Boon N, Verstraete W. Strategies of aerobic ammonia-oxidizing bacteria for coping with nutrient and oxygen fluctuations. *FEMS Microbiol Ecol* 2006;58:1–13.
- Gilman A, Fu Y, Hendershott M et al. Oxygen-limited metabolism in the methanotroph *Methylomicrobium buryatense* 5GB1C. *PeerJ* 2017;5:1–12.
- Gilson ER, Huang S, Jaffé PR. Biological reduction of uranium coupled with oxidation of ammonium by *Acidimicrobiaceae* bacterium A6 under iron reducing conditions. *Biodegradation* 2015;26:475–82.
- Gonzalez-Martinez A, Rodriguez-Sanchez A, van Loosdrecht MCM et al. Detection of comammox bacteria in full-scale wastewater treatment bioreactors using tag-454-pyrosequencing. *Environ Sci Pollut Res* 2016;23:25501–11.
- Griffin BM, Schott J, Schink B. Nitrite, an electron donor for anoxygenic photosynthesis. *Science* 2007;316:1870.
- Hamm R, Thompson T. Dissolved nitrogen in the sea water of the Northeast Pacific with notes on the total carbon dioxide and the dissolved oxygen. *J Mar Res* 1941;4:11–27.
- Haroon MF, Hu S, Shi Y et al. Anaerobic oxidation of methane coupled to nitrate reduction in a novel archaeal lineage. *Nature* 2013;500:567–70.
- Hatzenpichler R, Lebedeva EV, Spieck E et al. A moderately thermophilic ammonia-oxidizing crenarchaeote from a hot spring. *Proc Natl Acad Sci* 2008;105:2134–9.
- Hatzenpichler R. Diversity, physiology, and niche differentiation of ammonia-oxidizing archaea. *Appl Environ Microbiol* 2012;78:7501–10.
- Heilig GK. The greenhouse gas methane (CH<sub>4</sub>): sources and sinks, the impact of population growth, possible interventions. *Popul Environ* 1994;16:109–37.
- Henry L, Husson N, Andia R et al. Infrared absorption spectrum of methane from 2884 to 3141 cm<sup>-1</sup>. *J Mol Spectrosc* 1970;36:511–20.
- Herbold CW, Lehtovirta-Morley LE, Jung M-Y et al. Ammonia-oxidizing archaea living at low pH: Insights from comparative genomics. *Environ Microbiol* 2017;19:4939–52.
- Huang, S and Jaffé, PR. Isolation and characterization of an ammonium-oxidizing iron reducer: *Acidimicrobiaceae* sp. A6. *PLoS ONE* 2018; 13:1–12.
- Huang S, Jaffé PR. Characterization of incubation experiments and development of an enrichment culture capable of ammonium oxidation under iron-reducing conditions. *Biogeosciences* 2015;12:769–79.
- Hulth S, Aller RC, Gilbert F. Coupled anoxic nitrification/manganese reduction in marine sediments. *Geochim Cosmochim Acta* 1999;63:49–66.
- Huser BA, Wuhrmann K, Zehnder AJB. *Methanotrix soehngenii* gen. nov. sp. nov., a new acetotrophic non-hydrogen-oxidizing methane bacterium. *Arch Microbiol* 1982;132:1–9.
- Iino T, Tamaki H, Tamazawa S et al. 'Candidatus methanogranum caenicola': a novel methanogen from the anaerobic digested sludge, and proposal of *methanomassiliococcales* fam. nov. and *methanomassiliococcales* ord. nov. for a methanogenic lineage of the class thermoplasmata. *Microb Environ* 2013;28:244–50.
- Isobe K, Ohte N. Ecological perspectives on microbes involved in N-cycling. *Microb Environ* 2014;29:4–16.
- Jadhav DA, Ghangrekar MM. Effective ammonium removal by anaerobic oxidation in microbial fuel cells. *Environ Technol* 2015;36:767–75.
- Jensen MM, Lam P, Revsbech NP et al. Intensive nitrogen loss over the Omani Shelf due to anammox coupled with dissimilatory nitrite reduction to ammonium. *ISME J* 2011;5:1660–70.
- Jetten M, Op den Camp H, Kuenen J et al. Description of the order Brocadiales. In: Krieg N, Ludwig W, Whitman W et al. (eds). *Bergey's Manual of Systematic Bacteriology*. Berlin: Springer, 2010, 596–603.
- Jetten MSM, Stams AJM, Zehnder AJB. Methanogenesis from acetate: a comparison of the acetate metabolism in *Methanotrix soehngenii* and *Methanosarcina* spp. *FEMS Microbiol Lett* 1992;88:181–98.
- Kallistova AY, Merkel AY, Tarnovetskii IY et al. Methane formation and oxidation by prokaryotes. *Microbiology* 2017;86:671–91.
- Kartal B, Kuenen JG, van Loosdrecht MCM. Sewage treatment with anammox. *Science* 2010;328:702–3.

- Kartal B, Kuypers MMM, Lavik G et al. Anammox bacteria disguised as denitrifiers: nitrate reduction to dinitrogen gas via nitrite and ammonium. *Environ Microbiol* 2007;9:635–42.
- Kartal B, Maalcke WJ, de Almeida NM et al. Molecular mechanism of anaerobic ammonium oxidation. *Nature* 2011;479:127–30.
- Kartal B, Van Niftrik L, Rattray J et al. “*Candidatus Brocadia fulgida*”: an autofluorescent anaerobic ammonium oxidizing bacterium. *FEMS Microbiol Ecol* 2008;63:46–55.
- Keppeler F, Hamilton JTG, Braß M et al. Methane emissions from terrestrial plants under aerobic conditions. *Nature* 2006;439:187–91.
- Khadem AF, van Teeseling MCF, van Niftrik L et al. Genomic and physiological analysis of carbon storage in the verrucosomic microbial methanotroph “*Ca. Methylacidiphilum fomariolicum*” SolV. *Front Microbiol* 2012;3:1–10.
- Kiriazis N, . Evidence for iron-dependent anaerobic ammonium oxidation to nitrate (Feammox) in deep sea sediments, School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA, USA. 2015.
- Kirschke S, Bousquet P, Ciais P et al. Three decades of global methane sources and sinks. *Nat Geosci* 2013;6:813–23.
- Kits KD, Campbell DJ, Rosana AR et al. Diverse electron sources support denitrification under hypoxia in the obligate methanotroph *Methylomicrobium album* strain BG8. *Front Microbiol* 2015;6:1–11.
- Kits KD, Klotz MG, Stein LY. Methane oxidation coupled to nitrate reduction under hypoxia by the Gammaproteobacterium *Methylomonas denitrificans*, sp. nov. type strain FJG1. *Environ Microbiol* 2015;17:3219–32.
- Kits KD, Sedlacek CJ, Lebedeva EV. et al. Kinetic analysis of a complete nitrifier reveals an oligotrophic lifestyle. *Nature* 2017;549:269–72.
- Knief C, Lipski A, Dunfield PF. Diversity and activity of methanotrophic bacteria in different upland soils. *Appl Environ Microbiol* 2003;69:6703–14.
- Knittel K, Boetius A. Anaerobic oxidation of methane: progress with an unknown process. *Annu Rev Microbiol* 2009;63:311–34.
- Knittel K, Losekann T, Boetius A et al. Diversity and distribution of methanotrophic archaea at cold seeps. *Appl Environ Microbiol* 2005;71:467–79.
- Koch H, Galushko A, Albertsen M et al. Growth of nitrite-oxidizing bacteria by aerobic hydrogen oxidation. *Science* 2014;229:717–25.
- Koch H, Lückner S, Albertsen M et al. Expanded metabolic versatility of ubiquitous nitrite-oxidizing bacteria from the genus *Nitrospira*. *Proc Natl Acad Sci USA* 2015;112:11371–6.
- Kolb S, Knief C, Dunfield PF et al. Abundance and activity of uncultured methanotrophic bacteria involved in the consumption of atmospheric methane in two forest soils. *Environ Microbiol* 2005;7:1150–61.
- Kotsyurbenko OR, Nozhevnikova AN, Zavarzin GA. Methanogenic degradation of organic matter by anaerobic bacteria at low temperature. *Chemosphere* 1993;27:1745–61.
- Kuenen JG. Anammox bacteria: from discovery to application. *Nat Rev Micro* 2008;6:320–6.
- Kuypers MMM, Lavik G, Woebken D et al. From The Cover: Massive nitrogen loss from the Benguela upwelling system through anaerobic ammonium oxidation. *Proc Natl Acad Sci* 2005;102:6478–83.
- Kuypers MMM, Marchant HK, Kartal B. The microbial nitrogen-cycling network. *Nat Rev Microbiol* 2018;0:1–14.
- Kuypers MMM, Sliemers AO, Lavik G et al. Anaerobic ammonium oxidation by anammox bacteria in the Black Sea. *Nature* 2003;422:608–11.
- Könneke M, Bernhard AE, de la Torre JR et al. Isolation of an autotrophic ammonia-oxidizing marine archaeon. *Nature* 2005;437:543–6.
- Laanbroek HJ, Gerards S. Competition for limiting amounts of oxygen between *Nitrosomonas europaea* and *Nitrobacter winogradskyi* grown in mixed continuous cultures. *Arch Microbiol* 1993;159:453–9.
- Lacis A, Hansen J, Lee P et al. Greenhouse effect of trace gases, 1970-1980. *Geophys Res Lett* 1981;8:1035–8.
- Lam P, Kuypers MMM. Microbial nitrogen cycling processes in oxygen minimum zones. *Annu Rev Mar Sci* 2011;3:317–45.
- Lam P, Lavik G, Jensen MM et al. Revising the nitrogen cycle in the Peruvian oxygen minimum zone. *Proc Natl Acad Sci* 2009;106:4752–7.
- Lazar CS, , Baker BJ, Seitz K et al. Genomic evidence for distinct carbon substrate preferences and ecological niches of Bathyarchaeota in estuarine sediments, *Environ Microbiol*. 2016;18:1200–11.
- Lebedeva E V, Off S, Zumbrägel S et al. Isolation and characterization of a moderately thermophilic nitrite-oxidizing bacterium from a geothermal spring. *FEMS Microbiol Ecol* 2011;75:195–204.
- Lehtovirta-Morley LE, Ge C, Ross J et al. Characterisation of terrestrial acidophilic archaeal ammonia oxidisers and their inhibition and stimulation by organic compounds. *FEMS Microbiol Ecol* 2014;89:542–52.
- Lehtovirta-Morley LE, Stoecker K, Vilcinskis A et al. Cultivation of an obligate acidophilic ammonia oxidizer from a nitrifying acid soil. *Proc Natl Acad Sci* 2011;108:15892–7.
- Liu S, Yang F, Gong Z et al. Application of anaerobic ammonium-oxidizing consortium to achieve completely autotrophic ammonium and sulfate removal. *Bioresour Technol* 2008;99:6817–25.
- Li X, Hou L, Liu M et al. Evidence of nitrogen loss from anaerobic ammonium oxidation coupled with ferric iron reduction in an intertidal wetland. *Environ Sci Technol* 2015;49:11560–8.
- Li X, Huang Y, Liu H et al. Simultaneous Fe(III) reduction and ammonia oxidation process in anammox sludge. *J Environ Sci* 2018;64:42–50.
- Li X, Yuan Y, Huang Y et al. A novel method of simultaneous NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> removal using Fe cycling as a catalyst: Feammox coupled with NAFO. *Sci Total Environ* 2018;631-632:153–7.
- Lomans BP, Maas R, Luderer R et al. Isolation and characterization of *Methanomethylolorans hollandica* gen. nov., sp. nov., isolated from freshwater sediment, a methylotrophic methanogen able to grow on dimethyl sulfide and methanethiol. *Appl Environ Microbiol* 1999;65:3641–50.
- Lotti T, Kleerebezem R, Abelleira-Pereira JM et al. Faster through training: the anammox case. *Water Res* 2015;81:261–8.
- Luesken FA, Wu ML, Op den Camp HJM et al. Effect of oxygen on the anaerobic methanotroph “*Candidatus Methylomirabilis oxyfera*”: kinetic and transcriptional analysis. *Environ Microbiol* 2012;14:1024–34.
- Luther GW, Sundby B, Lewis BL et al. Interactions of manganese with the nitrogen cycle: alternative pathways to dinitrogen. *Geochim Cosmochim Acta* 1997;61:4043–52.
- Lyimo TJ, Pol A, Op Den Camp HJM et al. *Methanosarcina semesiae* sp. nov., a dimethylsulfide-utilizing methanogen from mangrove sediment. *Int J Syst Evol Microbiol* 2000;50:171–8.
- Lyu Z, Lu Y. Comparative genomics of three *Methanocellales* strains reveal novel taxonomic and metabolic features. *Environ Microbiol Rep* 2015;7:526–37.
- Lückner S, Wagner M, Maixner F et al. A *Nitrospira* metagenome illuminates the physiology and evolution of globally

- important nitrite-oxidizing bacteria. *Proc Natl Acad Sci* 2010;**107**:13479–84.
- Lüke C, Speth DR, Kox MAR et al. Metagenomic analysis of nitrogen and methane cycling in the Arabian Sea oxygen minimum zone. *PeerJ* 2016;**4**:e1924.
- Maixner F, Noguera DR, Anneser B et al. Nitrite concentration influences the population structure of *Nitrospira*-like bacteria. *Environ Microbiol* 2006;**8**:1487–95.
- Martens-Habbena W, Qin W, Horak REA et al. The production of nitric oxide by marine ammonia-oxidizing archaea and inhibition of archaeal ammonia oxidation by a nitric oxide scavenger. *Environ Microbiol* 2015;**17**:2261–74.
- Mayumi D, Mochimaru H, Tamaki H et al. Methane production from coal by a single methanogen. *Science* 2016;**354**:222–5.
- McGlynn SE, Chadwick GL, Kempes CP et al. Single cell activity reveals direct electron transfer in methanotrophic consortia. *Nature* 2015;**526**:531–5.
- Melton ED, Swanner ED, Behrens S et al. The interplay of microbially mediated and abiotic reactions in the biogeochemical Fe cycle. *Nat Rev Micro* 2014;**12**:797–808.
- Milucka J, Ferdelman TG, Polerecky L et al. Zero-valent sulphur is a key intermediate in marine methane oxidation. *Nature* 2012;**491**:541–6.
- Miura Y, Watanabe A, Murase J et al. Methane production and its fate in paddy fields. *Soil Sci Plant Nutr* 1992;**38**:673–9.
- Mohammadi S, Pol A, van Alen TA et al. *Methylacidiphilum fumarolicum* SolV, a thermoacidophilic “Knallgas” methanotroph with both an oxygen-sensitive and -insensitive hydrogenase. *ISME J* 2017;**11**:945–58.
- Mohammadi SS, Pol A, van Alen T et al. Ammonia oxidation and nitrite reduction in the verrucomicrobial methanotroph *Methylacidiphilum fumarolicum* SolV. *Front Microbiol* 2017b;**8**:1–11.
- Mulder A, van de Graaf AA, Robertson LA et al. Anaerobic ammonium oxidation discovered in a denitrifying fluidized bed reactor. *FEMS Microbiol Ecol* 1995;**16**:177–84.
- Murase J, Kimura M. Methane production and its fate in paddy fields. *Soil Sci Plant Nutr* 1994;**40**:505–14.
- Myhre G, Shindell D, Bréon F-M et al. Anthropogenic and natural radiative forcing. In: Stocker T, Qin D, Plattner G-K et al. (eds). *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge, UK and New York, NY, USA: Cambridge University Press, 2013, 659–740.
- Narrowe AB, Angle JC, Daly RA et al. High-resolution sequencing reveals unexplored archaeal diversity in freshwater wetland soils. *Environ Microbiol* 2017;**19**:2192–209.
- Nauhaus K, Treude T, Boetius A et al. Environmental regulation of the anaerobic oxidation of methane: a comparison of ANME-I and ANME-II communities. *Environ Microbiol* 2005;**7**:98–106.
- Neumann S, Wessels HJCT, Rippstra WIC et al. Isolation and characterization of a prokaryotic cell organelle from the anammox bacterium *Kuenenia stuttgartiensis*. *Mol Microbiol* 2014;**94**:794–802.
- Nobu MK, Narihiro T, Kuroda K et al. Chasing the elusive Euryarchaeota class WSA2: genomes reveal a uniquely fastidious methyl-reducing methanogen. *ISME J* 2016;**10**:2478–87.
- Norøi KÅ, Thamdrup B, Schubert CJ. Anaerobic oxidation of methane in an iron-rich Danish freshwater lake sediment. *Limnol Oceanogr* 2013;**58**:546–54.
- Nowka B, Daims H, Spieck E. Comparison of oxidation kinetics of nitrite-oxidizing bacteria: nitrite availability as a key factor in niche differentiation. *Appl Environ Microbiol* 2015;**81**:745–53.
- Op den Camp HJM, Islam T, Stott MB et al. Environmental, genomic and taxonomic perspectives on methanotrophic *Verrucomicrobia*. *Environ Microbiol Rep* 2009;**1**:293–306.
- Oshiki M, Ishii S, Yoshida K et al. Nitrate-dependent ferrous iron oxidation by anaerobic ammonium oxidation (anammox) bacteria. *Appl Environ Microbiol* 2013;**79**:4087–93.
- Oswald K, Milucka J, Brand A et al. Aerobic gamma-proteobacterial methanotrophs mitigate methane emissions from oxic and anoxic lake waters. *Limnol Oceanogr* 2016;**61**:S101–18.
- Palatinszky M, Herbold C, Jehmlich N et al. Cyanate as an energy source for nitrifiers. *Nature* 2015;**524**:105–8.
- Pester M, Schleper C, Wagner M. The Thaumarchaeota: an emerging view of their phylogeny and ecophysiology. *Curr Opin Microbiol* 2011;**14**:300–6.
- Pinto AJ, Marcus DN, Ijaz UZ et al. Metagenomic evidence for the presence of comammox *Nitrospira*-like bacteria in a drinking water system. *mSphere* 2016;**1**:1–8.
- Pitcher A, Villanueva L, Hopmans EC et al. Niche segregation of ammonia-oxidizing archaea and anammox bacteria in the Arabian Sea oxygen minimum zone. *ISME J* 2011;**5**:1896–904.
- Pjevac P, Schaubberger C, Poghosyan L et al. AmoA-targeted polymerase chain reaction primers for the specific detection and quantification of comammox *Nitrospira* in the environment. *Front Microbiol* 2017;**8**:1–11.
- Plugge CM, Stams AJM. The microbiology of methanogenesis. In: Smith P, Reay D, Van Amstel A (eds). *Methane and Climate Change*. Oxford, Taylor & Francis Group, 2010, 1–13.
- Pol A, Barends TRM, Dietl A et al. Rare earth metals are essential for methanotrophic life in volcanic mudpots. *Environ Microbiol* 2014;**16**:255–64.
- Pol A, Heijmans K, Harhangi HR et al. Methanotrophy below pH 1 by a new *Verrucomicrobia* species. *Nature* 2007;**450**:874–8.
- Pratscher J, Vollmers J, Wiegand S et al. Unravelling the identity, metabolic potential and global biogeography of the atmospheric methane-oxidizing upland soil cluster  $\alpha$ . *Environ Microbiol* 2018, **20**:1–14.
- Prosser JI, Nicol GW. Relative contributions of archaea and bacteria to aerobic ammonia oxidation in the environment. *Environ Microbiol* 2008;**10**:2931–41.
- Qu B, Fan B, Zhu S et al. Anaerobic ammonium oxidation with an anode as the electron acceptor. *Environ Microbiol Rep* 2014;**6**:100–5.
- Raghoebarsing AA, Pol A, van de Pas-Schoonen KT et al. A microbial consortium couples anaerobic methane oxidation to denitrification. *Nature* 2006;**440**:918–21.
- Raiswell R, Canfield D. The iron biogeochemical cycle past and present. *Geochem Persp* 2012;**1**:1–220.
- Reeburgh WS, Heggie DT. Microbial methane consumption reactions and their effect on methane distributions in freshwater and marine environments. *Limnol Oceanogr* 1977;**22**, 1–9.
- Ren T, Amaral JA, Knowles R. The response of methane consumption by pure cultures of methanotrophic bacteria to oxygen. *Can J Microbiol* 1997;**43**:925–928.
- Reyes C, Dellwig O, Dähnke K et al. Bacterial communities potentially involved in iron-cycling in Baltic Sea and North Sea sediments revealed by pyrosequencing. *FEMS Microbiol Ecol* 2016;**92**:1–9.
- Richards F. Anoxic basins and fjords. In: Ripley J, Skirrow G (eds). *Chemical Oceanography*. London, 1965, Washington University, Seattle Department of Oceanography, 611–45.
- Ricke P, Kube M, Nakagawa S et al. First genome data from uncultured upland soil cluster alpha methanotrophs provide further evidence for a close phylogenetic relationship to *Methylcapsa acidiphila* B2 and for high-affinity methanotrophy

- involving particulate methane monooxygenase. *Appl Environ Microbiol* 2005;**71**:7472–82.
- Riedinger N, Formolo MJ, Lyons TW et al. An inorganic geochemical argument for coupled anaerobic oxidation of methane and iron reduction in marine sediments. *Geobiology* 2014;**12**:172–81.
- Rockström J, Steffen W, Noone K et al. A safe operating space for humanity. *Nature* 2009;**461**:472–5.
- Rooze J, Egger M, Tsandev I et al. Iron-dependent anaerobic oxidation of methane in coastal surface sediments: Potential controls and impact. *Limnol Oceanogr* 2016;**61**:S267–82.
- Rooze J, Meile C. The effect of redox conditions and bioirrigation on nitrogen isotope fractionation in marine sediments. *Geochim Cosmochim Acta* 2016;**184**:227–39.
- Russ L, Speth DR, Jetten MSM et al. Interactions between anaerobic ammonium and sulfur-oxidizing bacteria in a laboratory scale model system. *Environ Microbiol* 2014;**16**:3487–98.
- Saunio M, Bousquet P, Poulter B et al. The global methane budget 2000–2012. *Earth Syst Sci Data* 2016;**8**:697–751.
- Schalk J, Oustad H, Kuenen JG et al. The anaerobic oxidation of hydrazine: a novel reaction in microbial nitrogen metabolism. *FEMS Microbiol Lett* 1998;**158**:61–67.
- Scheller S, Yu H, Chadwick GL et al. Artificial electron acceptors decouple archaeal methane oxidation from sulfate reduction. *Science* 2016;**351**:703–7.
- Schink B. Energetics of syntrophic cooperation in methanogenic degradation. *Microbiol Mol Biol Rev* 1997;**61**:262–80.
- Schmid M, Twachtmann U, Klein M et al. Molecular evidence for genus level diversity of bacteria capable of catalyzing anaerobic ammonium oxidation. *Syst Appl Microbiol* 2000;**23**:93–106.
- Schouten S, Strous M, Kuypers MMM et al. Stable carbon isotopic fractionations associated with inorganic carbon fixation by anaerobic ammonium-oxidizing bacteria. *Appl Environ Microbiol* 2004;**70**:3785–8.
- Schramm A, De Beer D, Gieseke A et al. Microenvironments and distribution of nitrifying bacteria in a membrane-bound biofilm. *Environ Microbiol* 2000;**2**:680–6.
- Schrum HN, Spivack AJ, Kastner M et al. Sulfate-reducing ammonium oxidation: a thermodynamically feasible metabolic pathway in subseafloor sediment. *Geology* 2009;**37**:939–42.
- Schütz H, Seiler W, Conrad R. Processes involved in formation and emission of methane in rice paddies. *Biogeochemistry* 1989;**7**:33–53.
- Semrau JD, DiSpirito AA, Yoon S. Methanotrophs and copper. *FEMS Microbiol Rev* 2010;**34**:496–531.
- Shrestha J, Rich JJ, Ehrenfeld JG et al. Oxidation of ammonium to nitrite under iron-reducing conditions in wetland soils. *Soil Sci* 2009;**174**:156–64.
- Sivan O, Adler M, Pearson A et al. Geochemical evidence for iron-mediated anaerobic oxidation of methane. *Limnol Oceanogr* 2011;**56**:1536–44.
- Smith RL, Howes BL, Duff JH. Denitrification in nitrate-contaminated groundwater: occurrence in steep vertical geochemical gradients. *Geochim Cosmochim Acta* 1991;**55**:1815–25.
- Sorokin DY, Lückner S, Vejmelkova D et al. Nitrification expanded: discovery, physiology and genomics of a nitrite-oxidizing bacterium from the phylum Chloroflexi. *ISME J* 2012;**6**:2245–56.
- Sorokin DY, Makarova KS, Abbas B et al. Discovery of extremely halophilic, methyl-reducing euryarchaea provides insights into the evolutionary origin of methanogenesis. *Nat Microbiol* 2017;**2**:1–11.
- Speth DR, Lagkouvardos I, Wang Y et al. Draft genome of *Scalindua rubra*, obtained from the interface above the discovery deep brine in the Red Sea, sheds light on potential salt adaptation strategies in anammox bacteria. *Microb Ecol* 2017;**74**:1–5.
- Stadnitskaia A, Muyzer G, Abbas B et al. Biomarker and 16S rDNA evidence for anaerobic oxidation of methane and related carbonate precipitation in deep-sea mud volcanoes of the Sorokin Trough, Black Sea. *Mar Geol* 2005;**217**:67–96.
- Stahl DA, de la Torre JR. Physiology and diversity of ammonia-oxidizing archaea. *Annu Rev Microbiol* 2012;**66**:83–101.
- Steenbergh AK, Meima MM, Kamst M et al. Biphasic kinetics of a methanotrophic community is a combination of growth and increased activity per cell. *FEMS Microbiol Ecol* 2010;**71**:12–22.
- Stieglmeier M, Klingl A, Alves RJE et al. *Nitrososphaera viennensis* gen. nov., sp. nov., an aerobic and mesophilic, ammonia-oxidizing archaeon from soil and a member of the archaeal phylum Thaumarchaeota. *Int J Syst Evol Microbiol* 2014;**64**:2738–52.
- Stolz JF. Gaia and her microbiome. *FEMS Microbiol Ecol* 2017;**93**:1–13.
- Strous M, Fuerst JA, Kramer EHM et al. Missing lithotroph identified as new planctomycete. *Nature* 1999;**400**:446–9.
- Strous M, Pelletier E, Mangenot S et al. Deciphering the evolution and metabolism of an anammox bacterium from a community genome. *Nature* 2006;**440**:790–4.
- Strous M, Van Gerven E, Zheng P et al. Ammonium removal from concentrated waste streams with the anaerobic ammonium oxidation (Anammox) process in different reactor configurations. *Water Res* 1997;**31**:1955–62.
- Söhngen NL. Het ontstaan en verdwijnen van waterstof en methaan onder den invloed van organisch leven. 1906.
- Thamdrup B, Dalsgaard T. Production of N<sub>2</sub> through anaerobic ammonium oxidation coupled to nitrate reduction in marine sediments. *Appl Environ Microbiol* 2002;**68**:1312–8.
- Thamdrup B, Dalsgaard T. The fate of ammonium in anoxic manganese oxide-rich marine sediment. *Geochim Cosmochim Acta* 2000;**64**:4157–64.
- Thauer RK, Jungermann K, Decker K. Energy conservation in chemotrophic anaerobic bacteria. *Bacteriol Rev* 1977;**41**:100–80.
- Thauer RK, Kaster A-K, Seedorf H et al. Methanogenic archaea: ecologically relevant differences in energy conservation. *Nat Rev Micro* 2008;**6**:579–91.
- Thauer RK, Shima S. Methane as fuel for anaerobic microorganisms. *Ann N Y Acad Sci* 2008;**1125**:158–70.
- Thauer RK. Anaerobic oxidation of methane with sulfate: on the reversibility of the reactions that are catalyzed by enzymes also involved in methanogenesis from CO<sub>2</sub>. *Curr Opin Microbiol* 2011;**14**:292–9.
- Thompson LR, Sanders JG, McDonald D et al. A communal catalogue reveals Earth's multiscale microbial diversity. *Nature* 2017;**551**:457–63.
- Timmers PHA, Welte CU, Koehorst JJ et al. Reverse methanogenesis and respiration in methanotrophic archaea. *Archaea* 2017;**2017**:1–22.
- Torres NT, Och LM, Hauser PC et al. Early diagenetic processes generate iron and manganese oxide layers in the sediments of Lake Baikal, Siberia. *Environ Sci: Processes Impacts* 2014;**16**:879–89.
- Tourna M, Stieglmeier M, Spang A et al. *Nitrososphaera viennensis*, an ammonia oxidizing archaeon from soil. *Proc Natl Acad Sci* 2011;**108**:8420–5.



- Treusch AH, Leininger S, Kletzin A et al. Novel genes for nitrite reductase and Amo-related proteins indicate a role of uncultivated mesophilic crenarchaeota in nitrogen cycling. *Environ Microbiol* 2005;7:1985–95.
- Trotsenko YA, Murrell JC. Metabolic aspects of aerobic obligate methanotrophy. *Adv Appl Microbiol* 2008;63:183–229.
- Vaksmaa A, Guerrero-Cruz S, van Alen TA et al. Enrichment of anaerobic nitrate-dependent methanotrophic ‘*Candidatus Methanoperedens nitroreducens*’ archaea from an Italian paddy field soil. *Appl Microbiol Biotechnol* 2017;101:7075–84.
- Vaksmaa A, Jetten MSM, Ettwig KF et al. McrA primers for the detection and quantification of the anaerobic archaeal methanotroph ‘*Candidatus Methanoperedens nitroreducens*’. *Appl Microbiol Biotechnol* 2017;101:1631–41.
- Vaksmaa A, Lücke C, van Alen T et al. Distribution and activity of the anaerobic methanotrophic community in a nitrogen-fertilized Italian paddy soil. *FEMS Microbiol Ecol* 2016;92:1–11.
- van de Graaf AA, de Bruijn P, Robertson LA et al. Metabolic pathway of anaerobic ammonium oxidation on the basis of <sup>15</sup>N studies in a fluidized bed reactor. *Microbiology* 1997;143:2415–21.
- van de Vossenberg J, Woebken D, Maalcke WJ et al. Early diagenetic processes generate iron and manganese oxide layers in the sediments of Lake Baikal, Siberia. *Environ Microbiol* 2013;15:1275–89.
- van Kessel MAHJ, Speth DR, Albertsen M et al. Complete nitrification by a single microorganism. *Nature* 2015;528:555–9.
- van Niftrik L, Jetten MSM. Anaerobic ammonium-oxidizing bacteria: unique microorganisms with exceptional properties. *Microbiol Mol Biol Rev* 2012;76:585–96.
- van Niftrik LA, Fuerst JA, Sinninghe Damsté JS et al. The anammoxosome: an intracytoplasmic compartment in anammox bacteria. *FEMS Microbiol Lett* 2004;233:7–13.
- van Teeseling MCF, Mesman RJ, Kuru E et al. Anammox Planctomycetes have a peptidoglycan cell wall. *Nat Commun* 2015;6:1–6.
- van Teeseling MCF, Pol A, Harhangi HR et al. Expanding the verucomicrobial methanotrophic world: description of three novel species of *Methylacidimicrobium* gen. nov. *Appl Environ Microbiol* 2014;80:6782–91.
- Vanwonterghem I, Evans PN, Parks DH et al. Methylophilic methanogenesis discovered in the archaeal phylum Verstraetearchaeota. *Nat Microbiol* 2016;1:1–9.
- Venter JC, Remington K, Heidelberg JF et al. Environmental genome shotgun sequencing of the Sargasso Sea. *Science* 2004;30:66–74.
- Voss M, Montoya JP. Oceans apart. *Nature* 2009;461:49–50.
- Wagner D. Effect of varying soil water potentials on methanogenesis in aerated marshland soils. *Sci Rep* 2017;7:1–9.
- Wankel SD, Adams MM, Johnston DT et al. Anaerobic methane oxidation in metalliferous hydrothermal sediments: influence on carbon flux and decoupling from sulfate reduction. *Environ Microbiol* 2012;14:2726–40.
- Watson RT, Rodhe H, Oeschger H et al. Greenhouse gases and aerosols. In: Houghton JT, Jenkins GJ, Ephraums JJ (eds). *Climate Change, The IPCC Scientific Assessment*. Cambridge: Cambridge University Press, 1990, 18–22.
- Watson SW, Bock E, Valois FW et al. *Nitrospira marina* gen. nov. sp. nov.: a chemolithotrophic nitrite-oxidizing bacterium. *Arch Microbiol* 1986;144:1–7.
- Watson SW, Waterbury JB. Characteristics of two marine nitrite oxidizing bacteria, *Nitrospina gracilis* nov. gen. nov. sp. and *Nitrococcus mobilis* nov. gen. nov. sp. *Archiv Mikrobiol* 1971;77:203–30.
- Weber KA, Achenbach LA, Coates JD. Microorganisms pumping iron: anaerobic microbial iron oxidation and reduction. *Nat Rev Micro* 2006;4:752–64.
- Weber KA, Urrutia MM, Churchill PF et al. Anaerobic redox cycling of iron by freshwater sediment microorganisms. *Environ Microbiol* 2006;8:100–13.
- Wegener G, Krukenberg V, Riedel D et al. Intercellular wiring enables electron transfer between methanotrophic archaea and bacteria. *Nature* 2015;526:587–90.
- Welte CU, Rasigraf O, Vaksmaa A et al. Nitrate- and nitrite-dependent anaerobic oxidation of methane. *Environ Microbiol Rep* 2016;8:941–55.
- Welte CU. Revival of archaeal methane microbiology. *mSystems* 2018;3:e00181–17.
- Whittenbury R, Phillips KC, Wilkinson JF. Enrichment, isolation and some properties of methane-utilizing bacteria. *J Gen Microbiol* 1970;61:205–18.
- Winogradsky S. Recherches sur les Organismes de la Nitrification. *Ann Inst Pasteur (Paris)* 1890;4:215–811.
- Winslow CE, Broadhurst J, Buchanan RE et al. The families and genera of the bacteria: preliminary report of the committee of the society of american bacteriologists on characterization and classification of bacterial types. *J Bacteriol* 1917;2:505–66.
- Xiang X, Wang R, Wang H et al. Distribution of Bathyarchaeota communities across different terrestrial settings and their potential ecological functions. *Sci Rep* 2017;7:1–11.
- Yang J, Jiang H, Wu G et al. Co-occurrence of nitrite-dependent anaerobic methane oxidizing and anaerobic ammonia oxidizing bacteria in two Qinghai-Tibetan saline lakes. *Front Earth Sci* 2012;6:383–91.
- Yang WH, Weber KA, Silver WL. Nitrogen loss from soil through anaerobic ammonium oxidation coupled to iron reduction. *Nat Geosci* 2012;5:538–41.
- Yan J, Haaijer SCM, Op den Camp HJM et al. Mimicking the oxygen minimum zones: stimulating interaction of aerobic archaeal and anaerobic bacterial ammonia oxidizers in a laboratory-scale model system. *Environ Microbiol* 2012;14:3146–58.
- Yool A, Martin AP, Fernández C et al. The significance of nitrification for oceanic new production. *Nature* 2007;447:999–1002.
- Zecchin S, Mueller RC, Seifert J et al. Rice paddy Nitrospirae encode and express genes related to sulfate respiration: proposal of the new genus ‘*Candidatus Sulfoibium*.’ *Appl Environ Microbiol* 2017;0:1–34.
- Zhan G, Zhang L, Tao Y et al. Anodic ammonia oxidation to nitrogen gas catalyzed by mixed biofilms in bioelectrochemical systems. *Electrochim Acta* 2014;135:345–50.
- Zhang L, Narita Y, Gao L et al. Maximum specific growth rate of anammox bacteria revisited. *Water Res* 2017;116:296–303.
- Zhang L, Zheng P, He Y et al. Performance of sulfate-dependent anaerobic ammonium oxidation. *Sci China Ser B-Chem* 2009;52:86–92.
- Zhang L-M, Offre PR, He J-Z et al. Autotrophic ammonia oxidation by soil Thaumarchaea. *Proc Natl Acad Sci* 2010;107:17240–5.
- Zhao R, Zhang H, Li Y et al. Research of iron reduction and the iron reductase localization of anammox bacteria. *Curr Microbiol* 2014;69:880–7.
- Zheng Y, Harris DF, Yu Z et al. A pathway for biological methane production using bacterial iron-only nitrogenase. *Nat Microbiol* 2018;3:281–6.
- Zhou G-W, Yang X-R, Li H et al. Electron shuttles enhance anaerobic ammonium oxidation coupled to iron(III) reduction. *Environ Sci Technol* 2016;50:9298–307.

Zhu B, Bradford L, Huang S et al. Unexpected diversity and high abundance of putative nitric oxide dismutase (Nod) genes in contaminated aquifers and wastewater treatment systems. Voordouw G (ed.). *Appl Environ Microbiol* 2017;**83**:1–13.

Zhu B, van Dijk G, Fritz C et al. Anaerobic oxidization of methane in a minerotrophic peatland: enrichment of nitrite-dependent methane-oxidizing bacteria. *Appl Environ Microbiol* 2012;**78**:8657–65.