Archaea in Biogeochemical Cycles

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Abstract

Archaea constitute a considerable fraction of the microbial biomass on Earth.
Like Bacteria they have evolved a variety of energy metabolisms using organic and/or inorganic electron donors and acceptors, and many of them are
able to fix carbon from inorganic sources. Archaea thus play crucial roles in
the Earth's global geochemical cycles and influence greenhouse gas emissions. Methanogenesis and anaerobic methane oxidation are important steps
in the carbon cycle; both are performed exclusively by anaerobic archaea.
Oxidation of ammonia to nitrite is performed by *Thaumarchaeota*. They represent the only archaeal group that resides in large numbers in the global
aerobic terrestrial and marine environments on Earth. Sulfur-dependent
archaea are confined mostly to hot environments, but metal leaching by acidophiles and reduction of sulfate by anaerobic, nonthermophilic methane
oxidizers have a potential impact on the environment. The metabolisms of
a large number of archaea, in particular those dominating the subsurface,
remain to be explored.

Contents

INTRODUCTION

All currently known life forms gain the free energy required to meet the energetic cost of maintenance, growth, and reproduction through enzymatically catalyzed redox reactions. Life exploits many pairs of electron donors and acceptors (redox pairs) for the generation of biochemical energy and the assimilation of nutrients, but single species use only a specific subset of those redox pairs. The survival of all living organisms thus depends on the constant supply of different combinations of electron donors and acceptors, which are present in limited amounts in the biosphere and therefore need to be constantly recycled. The cycling of these chemical substances emerges from geophysical processes and the combined metabolisms of all life forms (96). These self-organized nutrient cycles, which are increasingly influenced by human activities, can be represented as networks of processes, connecting different reservoirs of substances and defining biogeochemical cycles for various chemical elements and molecules. Owing to their versatile metabolisms, microorganisms drive most of the biological fluxes of the elements—particularly the six major building blocks of life, hydrogen, carbon, nitrogen, sulfur, oxygen, and phosphorus—and thus shape the biogeochemistry of our planet (32).

For more than half a century, since Vladimir Vernadsky coined the term biogeochemistry in 1926, only Bacteria and Eukarya were considered to contribute significantly to global nutrient cycles. The Archaea, constituting the third fundamental domain of life, were not described until 50 years later (137). Until the early 1990s, they were perceived mainly as a group of microorganisms thriving in extreme habitats that have, except for the methanogens (130), little influence on global nutrient cycling. However, this view began to change when molecular biological techniques were introduced into microbial ecology. The discovery that archaea are found in oceanic plankton (23, 35) has triggered a huge number of follow-up studies showing that archaea represent an abundant and diverse group of microorganisms in the whole biosphere and suggesting that they have a significant impact on nutrient cycling. In addition to cultivation of novel archaeal strains, culture-independent techniques, in particular molecular biological, biochemical, and isotope-based methods, have since remained instrumental for recognizing and characterizing novel archaeal metabolisms and for estimating their environmental impact. Through these studies it has become increasingly evident that archaea are important players in both carbon and nitrogen cycling. In this review, the distribution of the Archaea in the biosphere and their role in extant biogeochemical cycles are discussed in light of recent discoveries.

THE DOMAIN ARCHAEA

Woese & Fox (137) and Woese et al. (138) provided the first evidence that Archaea constitute a third domain alongside Bacteria and Eukarya within the phylogenetic tree of life. This finding was
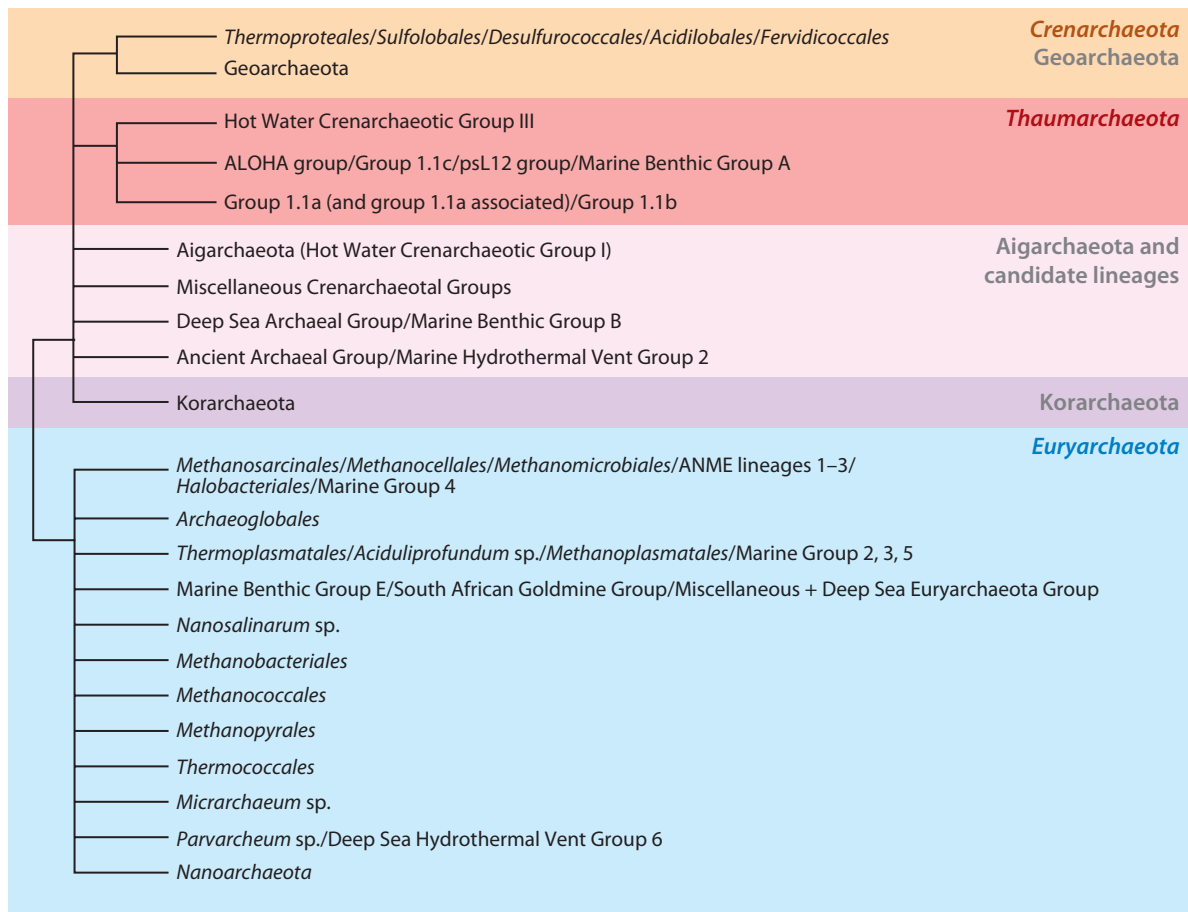
Thermoproteales/Sulfolobales/Desulfurococcales/Acidilobales/Fervidicoccales	***Crenarchaeota***
Geoarchaeota	Geoarchaeota
Hot Water Crenarchaeotic Group III	***Thaumarchaeota***
ALOHA group/Group 1.1c/psL12 group/Marine Benthic Group A	
Group 1.1a (and group 1.1a associated)/Group 1.1b	
Aigarchaeota (Hot Water Crenarchaeotic Group I)	**Aigarchaeota and**
Miscellaneous Crenarchaeotal Groups	**candidate lineages**
Deep Sea Archaeal Group/Marine Benthic Group B	
Ancient Archaeal Group/Marine Hydrothermal Vent Group 2	
Korarchaeota	**Korarchaeota**
Methanosarcinales/Methanocellales/Methanomicrobiales/ANME lineages 1–3/	***Euryarchaeota***
Halobacteriales/Marine Group 4	
Archaeoglobales	
Thermoplasmatales/Aciduliprofundum sp./*Methanoplasmatales*/Marine Group 2, 3, 5	
Marine Benthic Group E/South African Goldmine Group/Miscellaneous + Deep Sea Euryarchaeota Group	
Nanosalinarum sp.	
Methanobacteriales	
Methanococcales	
Methanopyrales	
Thermococcales	
Micrarchaeum sp.	
Parvarcheum sp./Deep Sea Hydrothermal Vent Group 6	
Nanoarchaeota	

Figure 1

Schematic representation of the phylogenetic diversity of archaea with the major lineages as referred to in the text. The multifurcations indicate that the placement of most lineages varies in different phylogenetic analyses. The tree is intended to give a general orientation to readers who are not familiar with archaea. Phyla in gray typeface have not been validated.

overwhelmingly corroborated by genomic and biochemical data showing that all archaea share unique membranes and have cell walls that differ from those of bacteria (36). Furthermore, they use distinctive informational processing machineries (e.g., replication and transcription) considered to be derived from a common ancestor with Eukarya (36). Since their discovery as a separate domain, the number of known taxa within the Archaea has been expanded continuously. As of November 2, 2012, there were 116 archaeal genera representing 450 cultivated and validly described species (**http://www.bacterio.cict.fr**). However, most of the archaeal diversity, currently referenced in public databases, remains uncultivated (117) and is known only from 16S rRNA gene sequences obtained from molecular surveys (24). Many of these uncultivated archaea are only distantly related to their closest cultivated relatives and specify numerous lineages representing a wide range of taxonomic ranks, up to the phylum level. Cultivated and uncultivated archaeal lineages have been classified in a few high-rank taxa (**Figure 1**), and a short overview of currently proposed archaeal phyla is provided below.

MCG: Miscellaneous Crenarchaeotal Group

DSAG: Deep Sea Archaeal Group

Most cultivated archaea are assigned to two major archaeal phyla, *Euryarchaeota* and *Crenarchaeota*, that were originally defined by Woese et al. (138). *Euryarchaeota* include eight taxonomic classes (i.e., *Methanopyri*, *Methanococci*, *Methanobacteria*, *Methanomicrobia*, *Archaeoglobi*, *Halobacteria*, *Thermococci*, and *Thermoplasmata*) that include methanogens, methane-oxidizing archaea, denitrifiers, sulfate reducers, iron oxidizers, and organotrophs (61). Members of this phylum are globally distributed, and some lineages, often uncultivated ones, are abundant in marine waters, soils, and sediments (117, 128), whereas many of the long-known euryarchaeotes inhabit extreme environments and are therefore restricted to specific geographic areas. The hyperthermophilic, parasitic *Nanoarchaeum equitans*, initially suggested to represent a new candidate phylum (49), likely constitutes an additional fast-evolving lineage of the *Euryarchaeota* (14).

Crenarchaeota contain only one taxonomic class (i.e., *Thermoprotei*) and five taxonomic orders (i.e., *Acidilobales*, *Desulfurococcales*, *Fervidicoccales*, *Sulfolobales*, and *Thermoproteales*), two of which (*Acidilobales* and *Fervidicoccales*) were discovered only recently (100, 106). All crenarchaeotes have been found in hot environments such as acidic terrestrial hot springs and submarine hydrothermal vents, as well as smoldering refuse piles (61).

Few organisms of the recently defined phylum *Thaumarchaeota* have been cultivated (124), all of which gain energy by ammonia oxidation. Organisms of this phylum are globally distributed and are found in high numbers in marine and freshwater environments, soils, and sediments and also occur in extreme environments including hot springs.

On the basis of genomic data, additional archaeal phyla have recently been proposed. They include Korarchaeota (5, 29), Aigarchaeota (94), and Geoarchaeota (67). The affiliation of several deep-branching lineages such as the Miscellaneous Crenarchaeotal Group (MCG), Deep Sea Archaeal Group (DSAG), and Ancient Archaeal Group (AAG) is still unclear (43). Members of these new phyla have been found in the terrestrial and marine subsurface (128) but also in hot springs and deep-sea hydrothermal systems, and no representative has yet been obtained in pure culture.

ARCHAEAL METABOLISMS AND BIOGEOCHEMICAL CYCLES

Archaeal metabolisms sustain the production of the archaeomass and determine the biogeochemical impact of the Archaea. On the basis of cell counts and molecular studies, archaea account for more than 20% of all prokaryotes in ocean waters (56), about 1–5% in upper soil layers (6, 95), and probably represent the dominant group of microorganisms in marine subsurface sediments (76) and in most geothermal habitats. Their involvement in major geochemical cycles is discussed below.

Carbon Cycle

Archaea dominate the biogenic production of methane (CH_4) but are also key to the oxidation of this important hydrocarbon. Archaeal organisms also play significant roles in the production and mineralization of organic matter.

Carbon assimilation. Many cultivated representatives of the *Crenarchaeota*, *Thaumarchaeota*, and *Euryarchaeota* are capable of autotrophic growth (**Supplemental Table 1**; follow the **Supplemental Material link** from the Annual Reviews home page at **http://www.annualreviews.org**), as they assimilate carbon from oxidized inorganic compounds, i.e., carbon dioxide (CO_2) or bicarbonate (HCO_3^-), reducing those substrates to form simple organic molecules (9) (**Figure 2a**). Investigation of the genome sequence of "*Candidatus* Caldiarchaeum subterraneum" (94) indicates
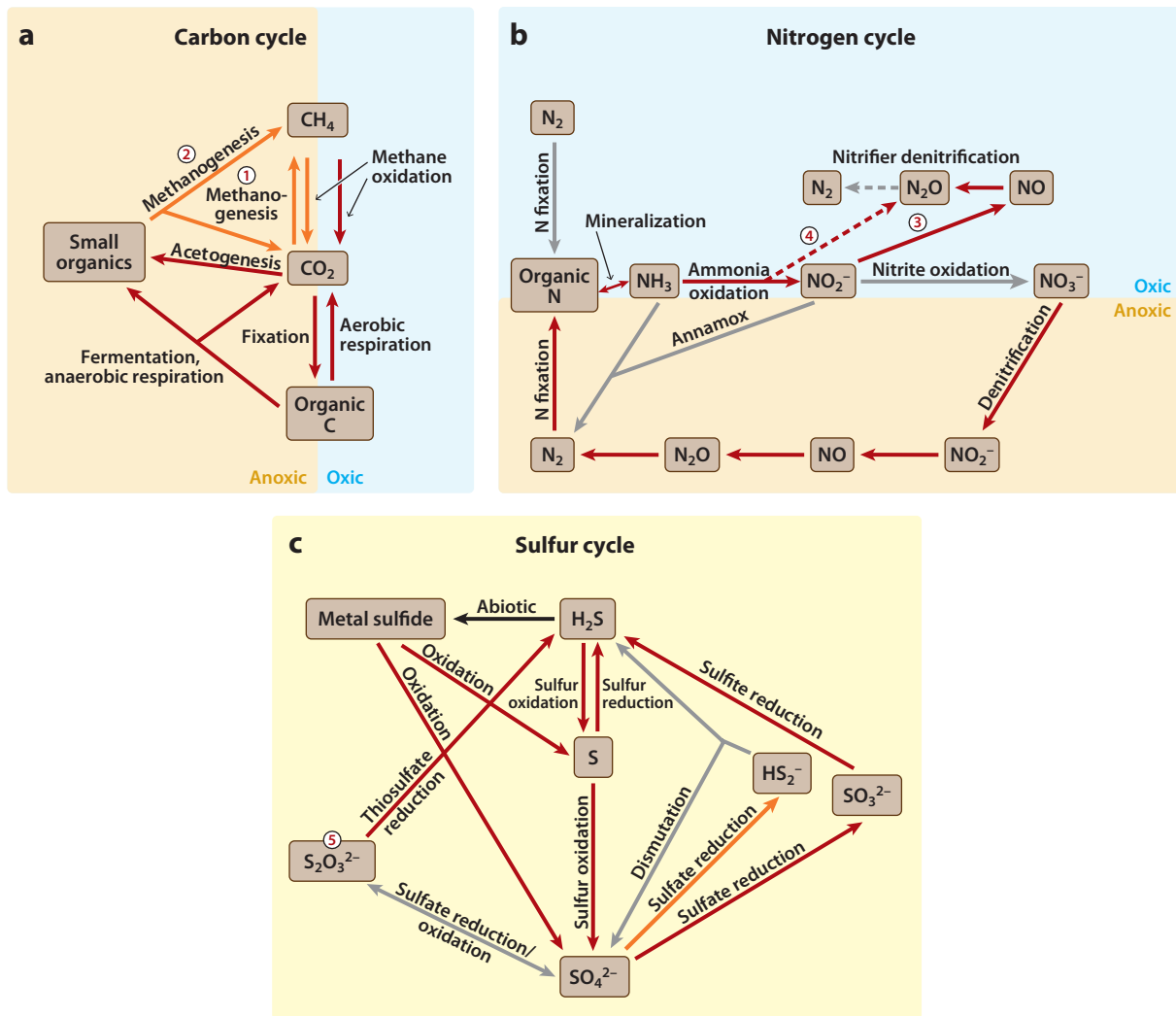
⏵ Supplemental Material

Figure 2

Schematic representation of the involvement of archaea in (*a*) carbon, (*b*) nitrogen, and (*c*) sulfur cycles. Red arrows indicate metabolic steps found in archaea and bacteria; orange arrows indicate metabolic pathways present exclusively in archaea; and gray arrows indicate metabolisms known only from bacteria. Circled numbers can be defined as follows: 1, hydrogenotrophic methanogenesis is a lithotrophic process resulting from the reduction of CO_2 with H_2 as electron donor; 2, formatotrophic, acetotrophic, and methylotrophic methanogenesis are organotrophic processes supported by the degradation of formate, acetate, and methylated compounds, respectively; 3, nitrifier denitrification is thought to occur under low oxygen conditions; 4, N_2O might be a direct side product of the ammonia-oxidizing pathway; 5, $S_2O_3{}^{2-}$ is produced in several different ways including abiotic processes not presented here.

that members of the Aigarchaeota might also be able to assimilate inorganic carbon. Three different metabolic pathways for autotrophic carbon fixation have been characterized in cultivated archaeal autotrophs, and these were reviewed recently (9).

Many autotrophic members of the Archaea grow mixotrophically; i.e., they coassimilate small organic compounds under suitable conditions or switch between an autotrophic and a heterotrophic lifestyle (61). Whereas *Thaumarchaeota* as described thus far depend on inorganic

carbon for assimilation, some lineages of *Euryarchaeota* and *Crenarchaeota* include several facultative autotrophic organisms but also obligate heterotrophs, such as the representatives of the *Halobacteriales* and *Thermococcales* (61).

The determination of the growth mode of most archaea is based on in vitro experiments, which might not reflect the lifestyle of these organisms in their natural habitats and limits the current knowledge of those organisms that have been successfully cultivated. However, some environmental studies using natural radiocarbon content, stable isotope probing (SIP) techniques, or microautoradiography combined with catalyzed reporter deposition–fluorescence in situ hybridization (MICRO-CARD-FISH) have been performed to reveal the lifestyle of particular archaea in natural populations and microcosms. For example, the natural radiocarbon content of archaeal lipids indicates that *Thaumarchaeota* in ocean waters predominately grow autotrophically (50, 99, 140). Modeled estimates of archaeal biomass production in deep waters range from 0.7 to 0.8 Gt C/year, suggesting that *Thaumarchaeota* might contribute ~1% of the annual primary production in the ocean (47, 50) and could provide, at least in some instances, most of the reduced carbon for heterotrophic microorganisms in oxygen minimum zones (45). Similarly, evidence for autotrophic growth of at least some phylotypes of *Thaumarchaeota* has been provided in soil microcosms using SIP (105, 144). In contrast, representatives of the MCG and DSAG lineages, dominant groups of archaea in the ocean subsurface sediments (11, 68, 128), were shown to grow heterotrophically in ocean margin sediments (11). Dual SIP, i.e., a quantitative stable isotope probing approach, suggested that euryarchaeal anaerobic methanotroph (ANME) lineages are also autotrophs (59).

Organic carbon mineralization. The catabolic degradation of organic substrates by chemoorganotrophs usually results in the production of CO_2 as the main end product (**Figure 2a**). However, the absence of external electron acceptors (fermentative conditions) or a limitation in respiratory capacity is associated with the excretion of partially oxidized compounds, e.g., organic acids or alcohols, in addition to CO_2. Numerous archaeal organisms, including aerobes and anaerobes, can grow organotrophically (see below for a discussion of organotrophic methanogens and methane-oxidizing archaea). Those organisms that have been cultivated thus far are extremophiles, which belong to the *Euryarchaeota* and *Crenarchaeota* (**Supplemental Table 1**). A comprehensive description of the various organotrophic metabolisms supporting cultivated archaeal organisms can be found in Reference 61. On the basis of the genome sequence of uncultivated extremophilic archaea, representatives of the Korarchaeota, Geoarchaeota, Aigarchaeota, the provisional euryarchaeal class *Nanohaloarchaea*, and ARMAN lineages might also grow organotrophically (4, 29, 37, 67, 93, 94). Recent metagenomic studies suggest that euryarchaeal phototrophic organotrophs (Marine group II) could be ubiquitous in the global ocean (34, 51), but currently there is no proof that archaeal organisms present in moderate environments play a major role in organic carbon mineralization.

Methanogenesis. Methane, a major greenhouse gas but also an important source of energy for humans, is the predominant hydrocarbon in Earth's atmosphere. Methanogenic archaea are strict anaerobes that produce methane (CH_4) as the major product of their energy-conserving metabolism (**Figure 2a**). All methanogenic archaea characterized so far belong to the *Euryarchaeota* (**Supplemental Table 1**) and are distributed among five taxonomic classes, i.e., *Methanopyri*, *Methanococci*, *Methanobacteria*, *Methanomicrobia*, and *Thermoplasmata* (26, 79, 98).

Several methanogenic pathways that rely on various substrates have been described (**Figure 2a** and **Supplemental Table 1**): CO_2 reduction with hydrogen (hydrogenotrophic methanogens) or formate (formatotrophic methanogens) as electron donors; methanol reduction with hydrogen; fermentation of acetate (acetotrophic methanogens); and dismutation of methylated compounds

Stable isotope probing (SIP): a substrate highly enriched in a stable isotope (e.g., ^{13}C) is given to an environmental sample to detect metabolically active organisms inside a complex microbial consortium

ANME: anaerobic methanotroph

Chemoorganotroph: organism that uses organic compounds as electron donors and energy sources

(methylotrophic methanogens) such as methanol, methylamines, dimethylsulfide (DMS), or methanethiol (33, 79). Whereas most cultivated methanogens reduce CO_2 with hydrogen, only members of *Methanosarcinales* have the ability to produce methane from the fermentation of acetate and the dismutation of methylated compounds. The recently discovered methanogenic *Thermoplasmata* reduce methanol with hydrogen (26, 98) and might also use methylamines as methanogenic substrate (104). Currently, none of these methanogenic metabolisms have been found in bacteria or eukaryotes. Although acetate fermentation is performed by only a few cultivated methanogens, this process could account for up to two-thirds of the methane released to the atmosphere by archaeal methanogenesis; the reduction of CO_2 accounts for the rest of the archaeal contribution to atmospheric methane, with minor amounts of methane produced by the dismutation of methyl compounds (33).

Methanogens have been isolated from various anoxic environments (20, 79) (e.g., rice paddies and peat bogs; freshwater, marine, and hypersaline sediments; hydrothermal vents; deep-subsurface habitats; the gastrointestinal tract of various animals) and are usually abundant where electron acceptors such as NO_3^-, Fe^{3+}, and SO_4^{2-} are in short supply. Hydrogenotrophic methanogens and acetogenic bacteria have similar requirements, including anoxic conditions, a source of H_2 as electron donor, and a source of CO_2 as electron acceptor (**Figure 2a**). But methanogenesis occurs preferentially at low H_2 concentrations and at a pH lower than 7; it can also be performed at high temperatures (2, 65, 130). Interestingly, methanogenic archaea have also been found in oxic environments, i.e., various aerated soils (3, 102) and the oxygenated water column of an oligotrophic lake (40). The methanogens in aerated soils became active under wet anoxic conditions (3), and those in oxygenated lake waters were attached to photoautotrophs, which might enable anaerobic growth and supply of methanogenic substrates (40). Several other processes, such as the microbial decomposition of methylphosphonate (55, 88), could be responsible for methane production in oxygenated waters (60), and fungi (74) and plants (15) are possible sources of methane in aerated soils. The global significance of these alternative aerobic methanogenic pathways remains to be assessed.

Archaeal methanogenesis produces about 1 Gt of methane every year (111, 130) and accounts for a significant fraction of the net annual emissions of methane to the atmosphere, with some estimates as high as 74% (79). Methanogenic archaea also produce methane that stays locked in underground reservoirs by taking part in the biodegradation of crude oil (52) and coal (126). Methane production by methanogenic archaea is suspected to rise considerably in arctic soils because of climate warming and is thus a major focus of current arctic research (82).

Methanogenic syntrophies. Methanogenic archaea engage in various syntrophic partnerships (121) that involve the transfer of electrons from a fermentative organism to the methanogen via a carrier molecule, such as H_2 or acetate. The methanogens use the carrier molecule as electron donor for energy conservation, and the fermentative organism gains energy from the redox reaction that produces the electron carrier only if the methanogens oxidize the carrier molecule, keeping the carrier at a low concentration. Methanogens might also receive electrons directly (121) via conductive pili or nanowires (112) or across conductive iron-oxide minerals (58). Syntrophic interactions enable methanogenesis when methanogenic substrates are limiting, and their establishment can also lead to increased methane production rates (58, 120). The global biogeochemical impact of syntrophic interactions involving methanogenic *Euryarchaeota* is considerable as they enable the complete degradation of complex organic molecules to carbon dioxide and methane in methanogenic habitats (121). Acetotrophic methanogens can also produce hydrogen and support the hydrogen-dependent dechlorination of xenobiotic compounds by dehalorespiring

Syntrophic partnerships: electron transfers between two organisms enabling growth on otherwise thermodynamically unfavorable reactions

microorganisms (46), further broadening the biogeochemical significance of interactions involving methanogenic archaea.

Methane oxidation. Methanogenic archaea are a major source of CH_4 emissions, but some of their closest relatives in turn play a critical role in controlling these emissions by oxidizing CH_4 back to CO_2 (**Figure 2a**). Methane-oxidizing archaea, also called methanotrophic archaea, are strict anaerobes that gain energy by coupling the oxidation of methane to the reduction of sulfate (SO_4^{2-}) (129, 131). These organisms belong to the *Euryarchaeota* and all are representatives of a single taxonomic class, the *Methanomicrobia*, along with various methanogenic archaea. The 16S rRNA gene sequences of the euryarchaeal ANMEs determine three sequence clusters, namely ANME-1, ANME-2, and ANME-3 (**Supplemental Table 1**), which are distantly related to each other (16S sequence similarity of 75–92%) and do not form a monophyletic lineage (63). Representatives of the ANME lineages have not been obtained in pure culture; therefore, their taxonomy has not been formally established. These archaea often, but not always, form microbial consortia with sulfate-reducing *Deltaproteobacteria* (reviewed in 63), which led to the suggestion that the sulfate-dependent anaerobic oxidation of methane (AOM) is a syntrophic process. The very low energy yield of this metabolism, however, led researchers to question the viability of these putative syntrophies (129, 131), and a recent breakthrough study (89) showed that ANME-2 organisms alone perform AOM coupled to dissimilatory sulfate reduction (see Sulfidogenesis, below). No other organism, bacterial or eukaryotic, is known to perform a similar process.

The environmental distribution of ANME organisms has been reviewed extensively by Knittel & Boetius (63), and a short account of their report is presented here. Methanotrophic archaea thrive in anoxic environments where both methane and sulfate are present, which often occurs in marine benthic systems. Accordingly, ANME organisms are widely distributed in methane seep ecosystems as well as in marine sediments, where their habitat is restricted to the sulfate-methane transition zone. The abundance of methanotrophic archaea often mirrors the rates of anaerobic methane oxidation measured in those habitats; i.e., dense populations (up to densities greater than 10^{10} cells cm^{-3}) are found at methane seeps, hotspots of AOM, and small populations ($<10^6$ cells cm^{-3}) occur in marine sediments, where process rates are lower. Methane-oxidizing archaea have also been detected in anoxic water columns, hydrothermal vents, soils, aquifers, and freshwater habitats, the physicochemical settings of which differ widely, further indicating that archaeal methanotrophs are physiologically diverse. The habitat ranges of the ANME-1, ANME-2, and ANME-3 lineages are not identical. ANME-1 and ANME-2 are globally distributed and present in similar environments, but one of these two groups usually dominates at a specific geographic location. ANME-3 organisms are essentially present at submarine mud volcanoes sites. The physiological and metabolic bases of these differences, if any, are not clear.

Iron (as ferrihydrite) and manganese (as birnessite) are alternative electron acceptors suitable for AOM, and there is evidence that these processes may occur in marine sediments where SO_4^{2-}-dependent AOM may also take place (7). The potential rate of SO_4^{2-}-driven AOM was reported to be 4 and 10 times as fast as birnessite- and ferrihydrite-dependent AOM in Eel River Basin sediments, respectively, but the global co-occurrence of these processes, their relative contribution to in situ rates of AOM, and the identity of the microorganisms responsible for the iron- and manganese-dependent processes remain to be determined. AOM can also be coupled in a fundamentally different biochemical pathway to the denitrification from nitrite (NO_2^-), a process occurring in freshwater habitats (31, 145) and performed by recently discovered bacteria belonging to the NC10 candidate division (30), but there is no indication that NO_2^-- and SO_4^{2-}-driven AOM can occur in the same environment (see, e.g., 25).

AOM exerts a strong control over ocean CH_4 emissions, which account for only 2% of the CH_4 released to the atmosphere. Global estimates of the rate of AOM in oceanic environments suggest that a large fraction (>50%) of the gross annual production of CH_4 in marine systems is consumed by anaerobic methanotrophs before CH_4 is even released to ocean waters (111). The AOM in marine sediments has been attributed to the CH_4-oxidizing activity of ANME archaea, but other microorganisms may be involved (7) and their identity and contribution to the global CH_4 budget need to be determined. There are, however, some uncertainties about the ability of ANME archaea to respond to a potential increase in ocean methane production, which could result from an accelerated melting of the massive reservoir of methane hydrates present in the seabed (13).

Carbonate precipitation. Anaerobic methanotrophic archaea promote the precipitation of carbonates from the inorganic carbon dissolved in the sediment pore water by locally increasing the alkalinity and inorganic carbon concentration of the water (16, 134). Because carbonates are relatively stable in sediments, their formation results in the long-term storage of carbon in the lithosphere. The carbon of carbonate rocks is re-emitted to the atmosphere only slowly over geological timescales through volcanism associated with tectonic plate subductions, which is part of the long-term carbon cycle (10). Anaerobic methane-oxidizing archaea buffer the global climatic impact of marine CH_4 production not only by oxidizing CH_4 to CO_2 but also by transferring to the lithosphere some of the carbon cycled on a short timescale by living organisms.

Nitrogen Cycle

Archaea are central to the oxidation of ammonia (NH_3) to nitrite (NO_2^-) but are also involved in the fixation of dinitrogen (N_2) gas and denitrification process. The mineralization of organic nitrogen compounds by archaeal organotrophs is not discussed.

Nitrogen fixation. Most organisms, including the great majority of archaea, assimilate nitrogen either from inorganic nitrogen sources, such as NH_3 and nitrate (NO_3^-), or from nitrogen-containing organic compounds (17). These organic and inorganic nitrogen sources, however, are in short supply within the biosphere, and the maintenance of most life forms is dependent on processes that continuously produce suitable nitrogen compounds from the large reservoir of N_2 in the atmosphere. The atmospheric nitrogen enters the food chain essentially via a biogeochemical process called nitrogen fixation, which consists of the reduction of N_2 to NH_3 (**Figure 2b**). This process is performed naturally by a number of bacterial and archaeal microorganisms, but the industrial fixation of nitrogen through the Haber-Bosch process produces similarly large quantities of ammonia used as fertilizers in agriculture, which is currently strongly disturbing the nitrogen cycle (19, 41).

The ability to fix N_2 gas, or diazotrophy, is a widespread feature of methanogenic archaea and is also present in anaerobic methane-oxidizing euryarchaea (**Supplemental Table 1**), but is expressed only in the absence of other nitrogen sources as for bacterial nitrogen fixers (17, 22, 72). Diazotrophic methanogens belong to three major taxonomic classes, i.e., *Methanobacteria*, *Methanococci*, and *Methanomicrobia* (**Supplemental Table 1**), and have been isolated from various environments (17, 72, 87), suggesting a widespread occurrence in anoxic habitats (**Figure 2b**). Diazotrophic methanotrophs belong to the ANME-2 lineage (22, 101) and are known only from methane seep sediments. Cultivation experiments have shown that methanotrophic diazotrophs not only fix but also share nitrogen with bacterial partners in AOM consortia (22). The prevalence of in situ diazotrophic growth by methanogenic and methanotrophic archaea, however, is

uncertain, and the importance of archaeal nitrogen fixation in providing reduced nitrogen for anaerobic microbial communities remains to be assessed.

Lithoautotrophic:
describes an organism that uses inorganic compounds as energy sources and fixes carbon from inorganic compounds

AOA:
ammonia-oxidizing archaea

Nitrification. Not only is ammonia taken up by most organisms and immobilized in their biomass, it is also oxidized to NO_3^- in oxic environments via the nitrification process (**Figure 2b**), which consists of two steps, i.e., the oxidation of NH_3 to NO_2^- and its further conversion to NO_3^-. Each step is catalyzed by different guilds of microorganisms, namely the ammonia and nitrite oxidizers, respectively. Until recently, it was assumed that only lithotrophic bacteria (66) and, to a limited extent, heterotrophic microorganisms (125) are involved in nitrification. The discovery that lithoautotrophic archaea thriving in oxic and moderate habitats have the capacity to oxidize NH_3 to NO_2^- (64, 133) was unexpected, and their high numbers in marine and freshwaters, soils and surface sediments, and thermally heated environments suggest a prominent role in global nitrogen cycling (73, 118, 139).

A handful of ammonia-oxidizing archaea (AOA), all belonging to *Thaumarchaeota* (**Supplemental Table 1**), have been obtained in pure culture or enrichments. They stem from marine and continental habitats and are assigned to four different thaumarchaeal lineages: group 1.1a, group 1.1a associated, group 1.1b, and ThAOA/HWCG III (for a recent review, see 124). Physiological studies have recently shown that the ammonia-oxidizing soil thaumarchaeon "*Candidatus* Nitrososphaera viennensis" (132) is able to grow on urea as an alternative source of NH_3 (**Supplemental Table 1**), and there is evidence suggesting that urea is an important substrate for archaeal ammonia oxidation in polar waters (1). Furthermore, analysis of the "*Candidatus* Nitrososphaera gargensis" genome indicated that cyanate (OCN^-) might be used as substrate for archaeal ammonia oxidation (123) (**Supplemental Table 1**). However, thaumarchaeal relatives of cultivated AOA might not always grow by oxidizing NH_3 (91) or they might use different electron acceptors (54, 128).

The relative contribution of archaeal and bacterial ammonia oxidizers to the NH_3 oxidation process is uncertain, and their respective ecological niches have been discussed (107). Cultivated AOA are characterized by a low tolerance to high NH_3 concentrations, and the highest growth inhibitory concentration reported for an AOA, i.e., 20 mM NH_4^+ (pH 7.5) for "*Ca*. N. viennensis" (132), is similar to the lowest inhibitory concentration reported for an ammonia-oxidizing bacterium (AOB), i.e., 21.4 mM NH_4^+ for the JL21 strain (127). However, according to very few studies, AOA also have lower substrate threshold and half-saturation constant (K_m) for ammonium uptake than AOB (85, 107). Together these data suggest that AOA outcompete AOB at low substrate concentrations, such as those in ocean waters, where AOA might be responsible for most of the ammonia oxidation (85). Microcosm experiments indicate that AOA can also play a major role in soil NH_3 oxidation (42, 97), even in fertilized soils (116, 135), which could be explained by an uneven distribution of fertilizer in the soil pore space, defining a mosaic of high- and low-ammonia niches. Other studies have also indicated that archaeal ammonia oxidation in soils might be fueled by the mineralization of organic nitrogen compounds (75), suggesting interactions with ammonifying microorganisms. Furthermore, AOA seem to be responsible for most of the ammonia oxidation in some acidic soils (42, 81, 143), and the first acidophilic ammonia oxidizer, the thaumarchaeon "*Candidatus* Nitrosotalea devanaterra," was cultivated only recently (71).

Ammonia oxidation is the rate-limiting step of the nitrification process and supports the oxidation of NO_2^- to NO_3^- (**Figure 2b**) by nitrite-oxidizing bacteria (NOB), but the nature of the interactions between AOA and NOB is still unclear. In the marine environment, especially in oxygen minimum zones, AOA might also support the anaerobic oxidation of NH_4^+ with NO_2^- (anammox) (**Figure 2b**) by supplying nitrite and consuming oxygen (69, 141).

Nitrification has a global impact on the form of inorganic nitrogen (NH_3 or NO_3^-) available in ecosystems. The assimilation of NO_3^- has a higher energetic cost than that of NH_3 because

NO_3^- is first reduced to NH_3 before assimilation. Nevertheless, NO_3^- is a primary nitrogen source for many phototrophs such as phytoplankton and crops. In soils, nitrification is also responsible for losses of nitrogen (including nitrogen fertilizers), as NO_2^- and NO_3^- are easily leached to groundwater. High nitrification activity supported by heavy fertilization of agricultural soils may then cause groundwater pollution and ecosystem eutrophication at groundwater resurgence points.

Denitrification. The existence of processes regenerating atmospheric N_2 gas from oxidized inorganic nitrogen compounds, i.e., NO_2^- and NO_3^-, is essential for the long-term survival of continental ecosystems, as all earth nitrogen would otherwise accumulate in the ocean due to ongoing nitrification activity. Dinitrogen production occurs mainly via two processes (**Figure 2b**), namely denitrification (17, 146) and the anaerobic oxidation of NH_4^+ with NO_2^- (anammox) (57). The relative contribution of these two processes on a global scale remains unclear. The anammox is performed solely by bacteria and is not further discussed. Denitrification is a form of anaerobic respiration that uses NO_3^- or NO_2^- as electron acceptor and results in the sequential formation of gaseous nitrogen compounds, i.e., nitric oxide (NO), nitrous oxide (N_2O), and/or N_2. The process does not always produce N_2 as final product, which can lead to the release of significant amounts of NO, a major ozone-depleting substance, and N_2O, a potent greenhouse gas and source of NO (109). Denitrification occurs in many environments including soils, oceans, and freshwaters and is usually performed by facultative anaerobes growing under microaerophilic or anoxic conditions (146). Denitrifiers include various bacteria, some archaea, and even eukaryotes (17, 146).

Only a few cultivated archaea are capable of denitrification (**Supplemental Table 1**). The prevalence of this metabolism in the archaeal domain and the biogeochemical significance of archaeal denitrification have been little investigated. All denitrifying archaea characterized thus far are either organotrophic halophiles or lithoautotrophic (facultative or obligate) hyperthermophiles using NO_3^- as electron acceptor (12, 44, 83, 136). The exception is *Pyrobaculum aerophilum*, which accepts both NO_3^- and NO_2^- (136). Archaeal denitrifiers produce various mixtures of NO_2^-, NO, N_2O, and N_2, and *Pyrolobus fumarii* releases NH_4^+ in a biochemically unrelated process called nitrate ammonification (12). A metagenomic analysis suggested that the uncultivated archaeon "*Ca*. C. subterraneum" might also be able to use NO_3^- as electron acceptor (94).

The ammonia-oxidizing thaumarchaeon "*Candidatus* Nitrosopumilus maritimus" and thaumarchaeal enrichment cultures obtained from pelagic waters were shown to produce N_2O (80, 115) (**Supplemental Table 1**), and the comparison of the isotopic signature of the N_2O emitted by cultures and ocean waters indicated that AOA could account for most of the oceanic production of this greenhouse gas (115), which represents up to 30% of the worldwide emissions of N_2O to the atmosphere. Whether this finding represents a form of nitrifier denitrification as performed by AOB (119) remains unclear, and the biochemical basis of this process has not been determined.

Sulfur Cycle

Archaea influence the cycling of sulfur through a variety of processes, which result in the production or the oxidation of sulfidic compounds.

Sulfidogenesis. Sulfidogenesis describes the production of hydrogen sulfide (H_2S), a by-product of the metabolism of various facultative and obligate anaerobes, including many archaea. Hydrogen sulfide is also a component of volcanic exhalations, particularly in hydrothermal fields and submarine vents (62). Although sulfidogenesis is a major biogeochemical process, H_2S is a reactive molecule and therefore does not always accumulate in environments where it is produced. It can react with metal ions to form metal sulfides; be oxidized in air, resulting in sulfur deposition; or

Hyperthermophiles: organisms with optimal growth temperature at or above 80°C

Supplemental Material

be used as electron donor by various microorganisms (see Sulfide Oxidation, below). Cultivated archaeal sulfidogens belong to *Euryarchaeota* and *Crenarchaeota* (**Supplemental Table 1**), and there is no indication that members of other archaeal phyla release H_2S as a main product of their metabolism. Archaeal sulfidogens produce H_2S essentially by the dissimilatory reduction of elemental sulfur (S^0 most often present as S_8), sulfite (SO_3^{2-}), thiosulfate ($S_2O_3^{2-}$), or sulfate (SO_4^{2-}).

The ability to use elemental sulfur as electron acceptor (**Figure 2c**) is widespread, though not universal, in cultivated representatives of the hyperthermophilic *Crenarchaeota* as well as in those of *Thermococci* and *Thermoplasmata* (*Euryarchaeota*) (62, 78, 113). Elemental sulfur may be either respired with H_2 or organic compounds as electron donors, as performed by various members of *Crenarchaeota* and *Thermoplasmata*, or used as electron sinks in fermentation processes carried out by many *Thermococci* and some representatives of *Desulfurococcales* (**Supplemental Table 1**). Some methanogenic archaea, e.g., *Methanopyrus* and *Methanobacterium*, produce significant quantities of H_2S when grown with elemental sulfur but do not conserve energy from the reaction (77, 78). All sulfur-reducing archaea, with the exception of H_2S-producing mesophilic methanogens, are (hyper)thermophiles thriving in geothermal environments, high-temperature oil reservoirs (38, 84), and coal beds (126), and they are even associated with deep-sea animals (48). Several bacteria are able to reduce elemental sulfur to H_2S, including members of the *Deltaproteobacteria* and *Epsilonproteobacteria*, which are present, for example, in marine and freshwater sediments, continental hot springs, deep-sea hydrothermal vents, and subsurface environments (18, 92). Archaeal and bacterial sulfur reducers therefore can inhabit similar environments, although archaea prevail at higher temperature, lower pH, and in more reducing conditions. The global rate of elemental sulfur reduction to H_2S and the relative contribution of archaeal and bacterial organisms to this process have not been assessed, and the impact of sulfur-reducing archaea on the functioning of microbial communities remains largely unknown.

Cultivated archaea able to perform the dissimilatory reduction of SO_4^{2-} to H_2S (**Figure 2c**) belong to only three genera: *Archaeoglobus* (*Euryarchaeota*), *Caldivirga* (*Crenarchaeota*), and *Thermocladium* (*Crenarchaeota*) (**Supplemental Table 1**). *Archaeoglobus* spp. use H_2 as electron donors and, in some instances, simple organic acids, while *Caldivirga* spp. and *Thermocladium* spp. use complex organic substrates (62, 78). Thiosulfate ($S_2O_3^{2-}$) can also be used as electron acceptor by members of all three genera and SO_3^{2-} by *Archaeoglobus* spp. (**Figure 2c** and **Supplemental Table 1**). A few additional genera belonging to *Archaeoglobi*, *Desulfurococcales*, and *Thermoproteales* can also respire SO_3^{2-} and/or $S_2O_3^{2-}$ (**Supplemental Table 1**). Whereas all these organisms are hyperthermophiles, bacterial sulfate reducers form an abundant and diverse group of microorganisms that occurs in a broad range of anoxic habitats and may account for most of the global biogenic H_2S production (92). Nevertheless, *Archaeoglobus* spp. thrive in high-temperature oil reservoirs (8, 38), where they may contribute to crude oil souring, which has detrimental impacts on the cost and safety of oil exploitation and its market value.

A new perspective on the contribution of archaeal organisms to dissimilatory sulfate reduction and sulfidogenesis has emerged from research showing that ANME-2 archaea (see Methane Oxidation, above) use sulfate as electron acceptor, reducing it to zero valent sulfur, possibly in the form of disulfide (HS_2^-) (**Figure 2c** and **Supplemental Table 1**), a completely new process in the sulfur cycle (89). The authors suggest that bisulfide (HS^-, i.e., dissociated H_2S) is produced from the dismutation of HS_2^- (**Figure 2c**), also a new process, performed by *Deltaproteobacteria* often growing in consortia with ANME archaea, and that bisulfide could also be produced, to some extent, directly by the archaeal methanotroph. These processes, if proven to be general features of ANME archaea, including ANME-1 and ANME-3 lineages, and associated *Deltaproteobacteria*, imply that archaea could have a significant role in the dissimilatory reduction of sulfate and in the biogenesis of sedimentary metal sulfides, and will also force a revision of our view of carbon

and sulfur cycling in marine sediments. Although the final products of sulfate reduction in deep marine sediments are metal sulfides, essentially pyrite (FeS_2), the production of H_2S/HS^- from AOM at methane seeps occurs in near-surface sediments and supports entire ecosystems, including macrofauna, that are based on the lithoautotrophic oxidation of H_2S (53).

Dimethylsulfide (DMS), a volatile organic sulfide (thioether), is another important intermediate in the sulfur cycle. DMS is biogenically produced and released in significant amounts to the atmosphere from aquatic environments. Processes controlling the production of DMS in marine surface waters have received special attention owing to the potential effect of DMS on cloud formation and global climate (21, 70, 108). Various archaeal organisms have the ability to produce but also oxidize DMS (for DMS oxidation, see Methanogenesis, above). All DMS-producing archaea belong to the *Euryarchaeota* (**Supplemental Table 1**), including representatives of *Halobacteria* (78, 90) and possibly members of the uncultivated Marine group II (86). *Halobacteria* produce DMS via the dissimilatory reduction of dimethylsulfoxide (DMSO) as a form of anaerobic respiration (78, 90), and representatives of Marine group II, widespread in ocean waters, might have a similar ability (86). DMSO is abundant in aquatic environments and could act as an important precursor to the production of DMS (70), but the significance of archaeal DMSO reduction remains to be clarified.

Sulfide oxidation. A number of acidophilic archaea (and bacteria) are able to oxidize sulfide minerals (**Figure 2c**) such as pyrite (FeS_2), marcasite (FeS_2), and chalcopyrite ($CuFeS_2$) (28, 39, 110). The oxidation of these metal sulfides can result from the direct enzymatic attack of the mineral surface (110), in which case the sulfide compound constitutes the source of electrons and energy of the oxidizing microorganism. However, microorganisms can oxidize metal sulfides indirectly via the production of an oxidant, i.e., Fe^{3+}, which is generated from the biooxidation of Fe^{2+} ions dissolved in the water surrounding the mineral particle (110). Archaeal organisms able to oxidize sulfide minerals belong to *Sulfolobales* (*Crenarchaeota*) and *Thermoplasmatales* (*Euryarchaeota*) (**Supplemental Table 1**). These organisms and their bacterial counterparts have been found in geothermal environments and mining areas and are thought to pervade in sulfide ore deposits (39, 110). Crenarchaeotes often have the ability to oxidize elemental sulfur (**Figure 2c** and **Supplemental Table 1**), like many bacterial sulfide oxidizers, but grow only at high (>65°C) temperatures, whereas *Thermoplasmatales* (euryarchaeotes) include mesophiles that can withstand extreme acidity (pH 0). The exposure of sulfide minerals to moisture and air at mining sites results in increased rates of metal sulfide bio-oxidation, which lead to the production of significant amounts of sulfuric acid, causing serious environmental pollution in the form of acid mine drainage. The relative contributions of bacterial and archaeal organisms to metal sulfide oxidation are unclear, but archaeal organisms can dominate acid mine drainage communities and have an important role in pyrite oxidation (27). Furthermore, bioreactor experiments have shown that archaeal organisms can be more efficient than bacteria in solubilizing sulfide minerals (110, 114), which points to the importance of archaeal organisms for the biomining industry.

Although H_2S often reacts with metal ions to form insoluble metal sulfides, H_2S can accumulate in significant amounts in a number of environments (e.g., Black Sea, meromictic lakes, swamps, solfataras). Despite its toxicity toward most living organisms, H_2S supports the growth of many bacteria and few hyperthermophilic archaea (**Figure 2c**) by serving as electron donor and energy source. Archaeal H_2S oxidizers (**Supplemental Table 1**) are poorly characterized and include representatives of only two genera: *Acidianus* (103) and *Ferroglobus* (44). Growth on H_2S occurs anaerobically with Fe^{3+} and NO_3^- as electron acceptors. Some *Acidianus* strains are also able to grow on carbon disulfide (CS_2), a component of volcanic exhalations, by enzymatically converting CS_2 to H_2S (122). In contrast, diverse H_2S-oxidizing bacteria are known, including phototrophs,

chemotrophs, aerobes, anaerobes, autotrophs, and heterotrophs, which are thought to play a significant role in the formation of biogenic sulfur deposits (28).

CONCLUSIONS AND PERSPECTIVES

Archaea have taken center stage in modern ecology and biogeochemistry research, although they were long seen as an assemblage of extremophilic organisms without a major role in the Earth system. Archaea are now recognized to have important roles in global biogeochemical cycles while being diverse and truly ubiquitous in the biosphere. At least two metabolisms essential for global nutrient cyclings are carried out exclusively by archaea: methanogenesis and sulfate-dependent anaerobic methane oxidation. The third archaeal metabolism of global importance is aerobic ammonia oxidation. Although both archaea and bacteria contribute to this process and their metabolic and ecological differences need to be clarified, the wide distribution of ammonia-oxidizing archaea in virtually all investigated aerobic habitats indicates a prominent role for these organisms. A full appreciation of the contribution of Archaea to Earth's biogeochemistry still lies far ahead, and a minimum of two fundamental issues need to be addressed: the inventory of all biogeochemical processes carried out by archaeal organisms and the quantification of archaeal biomass, production, and nutrient cycling activities in natural environments.

Characterization of the physiology and metabolism of uncultivated archaea is likely to identify new players of known biogeochemical processes but might also reveal novel nutrient cycling activities. Besides metagenomic studies and single-cell genomics, distribution patterns of microbial groups across physicochemical gradients have been used to raise hypotheses about biogeochemical reactions performed by currently uncultivated archaeal lineages (54). This approach led, for example, to the suggestion that representatives of DSAG could be heterotrophs using ferric iron (Fe^{3+}) as electron acceptor (11, 54). Such hypotheses, however, need to be experimentally tested in order to ascertain the biogeochemical function of these organisms. Furthermore, the full appreciation of the biogeochemical impact of an organism can only be achieved by taking into account the whole set of its metabolic pathways. For example, the recent discovery of a pathway for methylphosphonate biosynthesis in "*Ca*. Nitrosopumilus maritimus" (88) illustrated that this ammonia-oxidizing thaumarchaeon is not only involved in the nitrogen cycle but also takes part in the redox cycling of phosphorus, a poorly characterized component of the global phosphorus cycle.

A better understanding of the biogeochemical function of the Archaea will also emerge from progress in our ability to predict and measure biogeochemical fluxes resulting from the metabolic activities of archaeal organisms in their natural environment. This requires tackling the intricate nature of microbial communities to decipher archaeal signatures within a multitude of overlapping processes. Two opposite and complementary paths, i.e., systems ecology and synthetic ecology, also called top-down and bottom-up approaches, respectively, are currently being developed to characterize microbial metabolism on a community-wide scale (142).

SUMMARY POINTS

1. Archaea have evolved a number of energy metabolisms using inorganic and organic electron donors and acceptors.

2. Like bacteria, archaea play crucial roles in biogeochemical cycles, particularly the carbon and nitrogen cycles.

3. Methanogenesis and anaerobic methane oxidation are two processes of global importance that are performed exclusively by archaea.

4. Ammonia oxidation, the first step of nitrification, is performed by aerobic *Thaumarchaeota*, as well as by some bacterial lineages.

5. *Thaumarchaeota* represent one of the largest populations in oceanic plankton; they also occur in high numbers in terrestrial environments.

6. Sulfate reduction to disulfide as performed by ANME organisms may have a large impact on ocean seafloor sulfur cycling.

7. Leaching of metal sulfide by extreme acidophilic archaea in acidic coal mines contributes to the formation of acid mine drainage but may also help recover commercially important metals from sulfide ores.

8. Molecular techniques in addition to classical physiological characterization of isolated strains are indispensable for estimating the role of archaea in geochemical cycles.

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LITERATURE CITED

1. Alonso-Sáez L, Waller AS, Mende DR, Bakker K, Farnelid H, et al. 2012. Role for urea in nitrification by polar marine Archaea. *Proc. Natl. Acad. Sci. USA* 109:17989–94

2. Amend JP, Shock EL. 2001. Energetics of overall metabolic reactions of thermophilic and hyperthermophilic Archaea and Bacteria. *FEMS Microbiol. Rev.* 25:175–243

3. **Angel R, Claus P, Conrad R. 2012. Methanogenic archaea are globally ubiquitous in aerated soils and become active under wet anoxic conditions. *ISME J.* 6:847–62**

4. Baker BJ, Comolli LR, Dick GJ, Hauser LJ, Hyatt D, et al. 2010. Enigmatic, ultrasmall, uncultivated Archaea. *Proc. Natl. Acad. Sci. USA* 107:8806–11

5. Barns SM, Delwiche CF, Palmer JD, Pace NR. 1996. Perspectives on archaeal diversity, thermophily and monophyly from environmental rRNA sequences. *Proc. Natl. Acad. Sci. USA* 93:9188–93

6. Bates ST, Berg-Lyons D, Caporaso JG, Walters WA, Knight R, Fierer N. 2011. Examining the global distribution of dominant archaeal populations in soil. *ISME J.* 5:908–17

7. **Beal EJ, House CH, Orphan VJ. 2009. Manganese- and iron-dependent marine methane oxidation. *Science* 325:184–87**

8. Beeder J, Nilsen RK, Rosnes JT, Torsvik T, Lien T. 1994. *Archaeoglobus fulgidus* isolated from Hot North Sea oil field waters. *Appl. Environ. Microbiol.* 60:1227–31

9. Berg IA, Kockelkorn D, Ramos-Vera WH, Say RF, Zarzycki J, et al. 2010. Autotrophic carbon fixation in archaea. *Nat. Rev. Microbiol.* 8:447–60

10. Berner RA. 2003. The long-term carbon cycle, fossil fuels and atmospheric composition. *Nature* 426:323–26

11. Biddle JF, Lipp JS, Lever MA, Lloyd KG, Sørensen KB, et al. 2006. Heterotrophic Archaea dominate sedimentary subsurface ecosystems off Peru. *Proc. Natl. Acad. Sci. USA* 103:3846–51

3. Shows that methanogenic archaea are ubiquitous in aerated soils and become active under anoxic conditions.

7. First evidence for the existence of iron- and manganese-dependent anaerobic methane oxidation.

12. Blöchl E, Rachel R, Burggraf S, Hafenbradl D, Jannasch HW, Stetter KO. 1997. *Pyrolobus fumarii*, gen. and sp. nov., represents a novel group of archaea, extending the upper temperature limit for life to 113°C. *Extremophiles* 1:14–21

13. Boswell R, Collett TS. 2011. Current perspectives on gas hydrate resources. *Energy Environ. Sci.* 4:1206–15

14. Brochier C, Gribaldo S, Zivanovic Y, Confalonieri F, Forterre P. 2005. Nanoarchaea: representatives of a novel archaeal phylum or a fast-evolving euryarchaeal lineage related to Thermococcales? *Genome Biol.* 6:R42

15. Bruhn D, Møller IM, Mikkelsen TN, Ambus P. 2012. Terrestrial plant methane production and emission. *Physiol. Plant.* 144:201–9

16. Budai JM, Martini AM, Walter LM, Ku TCW. 2002. Fracture-fill calcite as a record of microbial methanogenesis and fluid migration: a case study from the Devonian Antrim Shale, Michigan Basin. *Geofluids* 2:163–83

17. Cabello P, Roldán MD, Moreno-Vivián C. 2004. Nitrate reduction and the nitrogen cycle in archaea. *Microbiology* 150:3527–46

18. Campbell BJ, Engel AS, Porter ML, Takai K. 2006. The versatile ϵ-proteobacteria: key players in sulphidic habitats. *Nat. Rev. Microbiol.* 4:458–68

19. Canfield DE, Glazer AN, Falkowski PG. 2010. The evolution and future of Earth's nitrogen cycle. *Science* 330:192–96

20. Chaban B, Ng SYM, Jarrell KF. 2006. Archaeal habitats—from the extreme to the ordinary. *Can. J. Microbiol.* 52:73–116

21. Charlson RJ, Lovelock JE, Andreae MO, Warren SG. 1987. Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature* 326:655–61

22. Dekas AE, Poretsky RS, Orphan VJ. 2009. Deep-sea archaea fix and share nitrogen in methane-consuming microbial consortia. *Science* 326:422–26

23. DeLong EF. 1992. Archaea in coastal marine environments. *Proc. Natl. Acad. Sci. USA* 89:5685–89

24. DeLong EF, Pace NR. 2001. Environmental diversity of bacteria and archaea. *Syst. Biol.* 50(4):470–78

25. Deutzmann JS, Schink B. 2011. Anaerobic oxidation of methane in sediments of Lake Constance, an oligotrophic freshwater lake. *Appl. Environ. Microbiol.* 77:4429–36

26. Dridi B, Fardeau M-L, Ollivier B, Raoult D, Drancourt M. 2012. *Methanomassiliicoccus luminyensis* gen. nov., sp. nov., a methanogenic archaeon isolated from human faeces. *Int. J. Syst. Evol. Microbiol.* 62:1902–7

27. Edwards KJ, Bond PL, Gihring TM, Banfield JF. 2000. An archaeal iron-oxidizing extreme acidophile important in acid mine drainage. *Science* 287:1796–99

28. Ehrlich HL, Newman DK. 2009. *Geomicrobiology*. Boca Raton, FL: CRC Press. 5th ed. 628 pp.

29. Elkins JG, Podar M, Graham DE, Makarova KS, Wolf Y, et al. 2008. A korarchaeal genome reveals insights into the evolution of the Archaea. *Proc. Natl. Acad. Sci. USA* 105:8102–7

30. **Ettwig KF, Butler MK, Le Paslier D, Pelletier E, Mangenot S, et al. 2010. Nitrite-driven anaerobic methane oxidation by oxygenic bacteria. *Nature* 464:543–48**

31. Ettwig KF, van Alen T, van de Pas-Schoonen KT, Jetten MSM, Strous M. 2009. Enrichment and molecular detection of denitrifying methanotrophic bacteria of the NC10 phylum. *Appl. Environ. Microbiol.* 75:3656–62

32. Falkowski PG, Fenchel T, DeLong EF. 2008. The microbial engines that drive Earth's biogeochemical cycles. *Science* 320:1034–39

33. Ferry JG. 2010. How to make a living by exhaling methane. *Annu. Rev. Microbiol.* 64:453–73

34. Frigaard N-U, Martinez A, Mincer TJ, DeLong EF. 2006. Proteorhodopsin lateral gene transfer between marine planktonic Bacteria and Archaea. *Nature* 439:847–50

35. Fuhrman JA, McCallum K, Davis AA. 1992. Novel major archaebacterial group from marine plankton. *Nature* 356:148–49

36. Garrett RA, Klenk HP, eds. 2007. *Archaea: Evolution, Physiology and Molecular Biology*. Oxford: Blackwell

37. Ghai R, Pašić L, Fernández AB, Martin-Cuadrado A-B, Mizuno CM, et al. 2011. New abundant microbial groups in aquatic hypersaline environments. *Sci. Rep.* 1:135

30. First evidence for nitrite-dependent anaerobic methane oxidation.

38. Gittel A, Sørensen KB, Skovhus TL, Ingvorsen K, Schramm A. 2009. Prokaryotic community structure and sulfate reducer activity in water from high-temperature oil reservoirs with and without nitrate treatment. *Appl. Environ. Microbiol.* 75:7086–96

39. Golyshina OV, Timmis KN. 2005. *Ferroplasma* and relatives, recently discovered cell wall-lacking archaea making a living in extremely acid, heavy metal-rich environments. *Environ. Microbiol.* 7:1277–88

40. Grossart H-P, Frindte K, Dziallas C, Eckert W, Tang KW. 2011. Microbial methane production in oxygenated water column of an oligotrophic lake. *Proc. Natl. Acad. Sci. USA* 108:19657–61

41. Gruber N, Galloway JN. 2008. An Earth-system perspective of the global nitrogen cycle. *Nature* 451:293–96

42. Gubry-Rangin C, Nicol GW, Prosser JI. 2010. Archaea rather than bacteria control nitrification in two agricultural acidic soils. *FEMS Microbiol. Ecol.* 74:566–74

43. Guy L, Ettema TJG. 2011. The archaeal "TACK" superphylum and the origin of eukaryotes. *Trends Microbiol.* 19:580–87

44. Hafenbradl D, Keller M, Dirmeier R, Rachel R, Roßnagel P, et al. 1996. *Ferroglobus placidus* gen. nov., sp. nov., a novel hyperthermophilic archaeum that oxidizes Fe^{2+} at neutral pH under anoxic conditions. *Arch. Microbiol.* 166:308–14

45. Hansman RL, Griffin S, Watson JT, Druffel ERM, Ingalls AE, et al. 2009. The radiocarbon signature of microorganisms in the mesopelagic ocean. *Proc. Natl. Acad. Sci. USA* 106:6513–18

46. Heimann AC, Batstone DJ, Jakobsen R. 2006. *Methanosarcina* spp. drive vinyl chloride dechlorination via interspecies hydrogen transfer. *Appl. Environ. Microbiol.* 72:2942–49

47. Herndl GJ, Reinthaler T, Teira E, van Aken H, Veth C, et al. 2005. Contribution of Archaea to total prokaryotic production in the deep Atlantic Ocean. *Appl. Environ. Microbiol.* 71:2303–9

48. Holden JF, Takai K, Summit M, Bolton S, Zyskowski J, Baross JA. 2001. Diversity among three novel groups of hyperthermophilic deep-sea *Thermococcus* species from three sites in the northeastern Pacific Ocean. *FEMS Microbiol. Ecol.* 36:51–60

49. Huber H, Hohn MJ, Rachel R, Fuchs T, Wimmer VC, Stetter KO. 2002. A new phylum of Archaea represented by a nanosized hyperthermophilic symbiont. *Nature* 417:63–67

50. Ingalls AE, Shah SR, Hansman RL, Aluwihare LI, Santos GM, et al. 2006. Quantifying archaeal community autotrophy in the mesopelagic ocean using natural radiocarbon. *Proc. Natl. Acad. Sci. USA* 103:6442–47

51. Iverson V, Morris RM, Frazar CD, Berthiaume CT, Morales RL, Armbrust EV. 2012. Untangling genomes from metagenomes: revealing an uncultured class of marine Euryarchaeota. *Science* 335:587–90

52. Jones DM, Head IM, Gray ND, Adams JJ, Rowan AK, et al. 2008. Crude-oil biodegradation via methanogenesis in subsurface petroleum reservoirs. *Nature* 451:176–80

53. Jørgensen BB, Boetius A. 2007. Feast and famine—microbial life in the deep-sea bed. *Nat. Rev. Microbiol.* 5:770–81

54. Jorgensen SL, Hannisdal B, Lanzén A, Baumberger T, Flesland K, et al. 2012. Correlating microbial community profiles with geochemical data in highly stratified sediments from the Arctic Mid-Ocean Ridge. *Proc. Natl. Acad. Sci. USA* 109:2846–55

55. Karl DM, Beversdorf L, Björkman KM, Church MJ, Martinez A, Delong EF. 2008. Aerobic production of methane in the sea. *Nat. Geosci.* 1:473–78

56. Karner MB, DeLong EF, Karl DM. 2001. Archaeal dominance in the mesopelagic zone of the Pacific Ocean. *Nature* 409:507–10

57. Kartal B, Van Niftrik L, Keltjens JT, Op den Camp HJM, Jetten MSM. 2012. Anammox—growth physiology, cell biology, and metabolism. *Adv. Microb. Physiol.* 60:211–62

58. Kato S, Hashimoto K, Watanabe K. 2012. Methanogenesis facilitated by electric syntrophy via (semi)conductive iron-oxide minerals. *Environ. Microbiol.* 14:1646–54

59. Kellermann MY, Wegener G, Elvert M, Yoshinaga MY, Lin Y-S, et al. 2012. Autotrophy as a predominant mode of carbon fixation in anaerobic methane-oxidizing microbial communities. *Proc. Natl. Acad. Sci. USA* 109:19321–26

60. Keppler F, Boros M, Frankenberg C, Lelieveld J, McLeod A, et al. 2009. Methane formation in aerobic environments. *Environ. Chem.* 6:459–65

40. Suggests methanogens are active in anaerobic microniches within the oxic water column of a lake.

61. Kletzin A. 2007. General characteristics and important model organisms. In *Archaea: Molecular and Cellular Biology*, ed. R Cavicchioli, pp. 14–92. Washington, DC: ASM

62. Kletzin A. 2007. Metabolism of inorganic sulfur compounds in Archaea. In *Archaea: Evolution, Physiology, and Molecular Biology*, ed. RA Garrett, H-P Klenk, pp. 261–74. Malden, MA: Blackwell

63. Knittel K, Boetius A. 2009. Anaerobic oxidation of methane: progress with an unknown process. *Annu. Rev. Microbiol.* 63:311–34

64. Könneke M, Bernhard AE, de la Torre JR, Walker CB, Waterbury JB, Stahl DA. 2005. Isolation of an autotrophic ammonia-oxidizing marine archaeon. *Nature* 437:543–46

65. Kotsyurbenko OR, Glagolev MV, Nozhevnikova AN, Conrad R. 2001. Competition between homoacetogenic bacteria and methanogenic archaea for hydrogen at low temperature. *FEMS Microbiol. Ecol.* 38:153–59

66. Kowalchuk GA, Stephen JR. 2001. Ammonia-oxidizing bacteria: a model for molecular microbial ecology. *Annu. Rev. Microbiol.* 55:485–529

67. Kozubal MA, Romine M, deM Jennings R, Jay ZJ, Tringe SG, et al. 2013. Geoarchaeota: a new candidate phylum in the Archaea from high-temperature acidic iron mats in Yellowstone National Park. *ISME J.* 7:622–34

68. Kubo K, Lloyd KG, Biddle JF, Amann R, Teske A, Knittel K. 2012. Archaea of the miscellaneous crenarchaeotal group are abundant, diverse and widespread in marine sediments. *ISME J.* 6:1949–65

69. Lam P, Jensen MM, Lavik G, McGinnis DF, Muller B, et al. 2007. Linking crenarchaeal and bacterial nitrification to anammox in the Black Sea. *Proc. Natl. Acad. Sci. USA* 104:7104–9

70. Lee PA, De Mora SJ, Levasseur M. 1999. A review of dimethylsulfoxide in aquatic environments. *Atmosphere-Ocean* 37:439–56

71. Lehtovirta-Morley LE, Stoecker K, Vilcinskas A, Prosser JI, Nicol GW. 2011. Cultivation of an obligate acidophilic ammonia oxidizer from a nitrifying acid soil. *Proc. Natl. Acad. Sci. USA* 108:15892–97

72. Leigh JA. 2000. Nitrogen fixation in methanogens: the archaeal perspective. *Curr. Issues Mol. Biol.* 2:125–31

73. Leininger S, Urich T, Schloter M, Schwark L, Qi J, et al. 2006. Archaea predominate among ammonia-oxidizing prokaryotes in soils. *Nature* 442(7104):806–9

74. Lenhart K, Bunge M, Ratering S, Neu TR, Schüttmann I, et al. 2012. Evidence for methane production by saprotrophic fungi. *Nat. Commun.* 3:1046

75. Levičnik-Höfferle Š, Nicol GW, Ausec L, Mandić-Mulec I, Prosser JI. 2012. Stimulation of thaumarchaeal ammonia oxidation by ammonia derived from organic nitrogen but not added inorganic nitrogen. *FEMS Microbiol. Ecol.* 80:114–23

76. Lipp JS, Morono Y, Inagaki F, Hinrichs K-U. 2008. Significant contribution of Archaea to extant biomass in marine subsurface sediments. *Nature* 454:991–94

77. Liu Y, Beer LL, Whitman WB. 2012. Methanogens: a window into ancient sulfur metabolism. *Trends Microbiol.* 20:251–58

78. Liu Y, Beer LL, Whitman WB. 2012. Sulfur metabolism in archaea reveals novel processes. *Environ. Microbiol.* 14:2632–44

79. Liu Y, Whitman WB. 2008. Metabolic, phylogenetic, and ecological diversity of the methanogenic archaea. *Ann. N. Y. Acad. Sci.* 1125:171–89

80. Loescher CR, Kock A, Koenneke M, LaRoche J, Bange HW, Schmitz RA. 2012. Production of oceanic nitrous oxide by ammonia-oxidizing archaea. *Biogeosci. Discuss.* 9:2095–122

81. Lu L, Han W, Zhang J, Wu Y, Wang B, et al. 2012. Nitrification of archaeal ammonia oxidizers in acid soils is supported by hydrolysis of urea. *ISME J.* 6:1978–84

82. Mackelprang R, Waldrop MP, DeAngelis KM, David MM, Chavarria KL, et al. 2011. Metagenomic analysis of a permafrost microbial community reveals a rapid response to thaw. *Nature* 480:368–71

83. Mancinelli RL, Hochstein LI. 1986. The occurrence of denitrification in extremely halophilic bacteria. *FEMS Microbiol. Lett.* 35:55–58

84. Mardanov AV, Ravin NV, Svetlitchnyi VA, Beletsky AV, Miroshnichenko ML, et al. 2009. Metabolic versatility and indigenous origin of the archaeon *Thermococcus sibiricus*, isolated from a Siberian oil reservoir, as revealed by genome analysis. *Appl. Environ. Microbiol.* 75:4580–88

85. Martens-Habbena W, Berube PM, Urakawa H, de la Torre JR, Stahl DA. 2009. Ammonia oxidation kinetics determine niche separation of nitrifying Archaea and Bacteria. *Nature* 461:976–79

86. Martin-Cuadrado A-B, Rodriguez-Valera F, Moreira D, Alba JC, Ivars-Martínez E, et al. 2008. Hindsight in the relative abundance, metabolic potential and genome dynamics of uncultivated marine archaea from comparative metagenomic analyses of bathypelagic plankton of different oceanic regions. *ISME J.* 2:865–86

87. Mehta MP, Baross JA. 2006. Nitrogen fixation at 92°C by a hydrothermal vent archaeon. *Science* 314:1783–86

88. **Metcalf WW, Griffin BM, Cicchillo RM, Gao J, Janga SC, et al. 2012. Synthesis of methylphosphonic acid by marine microbes: a source for methane in the aerobic ocean. *Science* 337:1104–7**

89. **Milucka J, Ferdelman TG, Polerecky L, Franzke D, Wegener G, et al. 2012. Zero-valent sulphur is a key intermediate in marine methane oxidation. *Nature* 491:541–46**

90. Müller JA, DasSarma S. 2005. Genomic analysis of anaerobic respiration in the archaeon *Halobacterium* sp. strain NRC-1: dimethyl sulfoxide and trimethylamine *N*-oxide as terminal electron acceptors. *J. Bacteriol.* 187:1659–67

91. Mußmann M, Brito I, Pitcher A, Damsté JSS, Hatzenpichler R, et al. 2011. Thaumarchaeotes abundant in refinery nitrifying sludges express *amoA* but are not obligate autotrophic ammonia oxidizers. *Proc. Natl. Acad. Sci. USA* 108:16771–76

92. Muyzer G, Stams AJM. 2008. The ecology and biotechnology of sulphate-reducing bacteria. *Nat. Rev. Microbiol.* 6:441–54

93. Narasingarao P, Podell S, Ugalde JA, Brochier-Armanet C, Emerson JB, et al. 2012. De novo metagenomic assembly reveals abundant novel major lineage of Archaea in hypersaline microbial communities. *ISME J.* 6:81–93

94. Nunoura T, Takaki Y, Kakuta J, Nishi S, Sugahara J, et al. 2011. Insights into the evolution of Archaea and eukaryotic protein modifier systems revealed by the genome of a novel archaeal group. *Nucleic Acids Res.* 39:3204–23

95. Ochsenreiter T, Selezi D, Quaiser A, Bonch-Osmolovskaya L, Schleper C. 2003. Diversity and abundance of Crenarchaeota in terrestrial habitats studied by 16S RNA surveys and real time PCR. *Environ. Microbiol.* 5:787–97

96. Odum HT. 1988. Self-organization, transformity, and information. *Science* 242:1132–39

97. Offre P, Prosser JI, Nicol GW. 2009. Growth of ammonia-oxidizing archaea in soil microcosms is inhibited by acetylene. *FEMS Microbiol. Ecol.* 70:99–108

98. Paul K, Nonoh JO, Mikulski L, Brune A. 2012. "Methanoplasmatales," Thermoplasmatales-related Archaea in termite guts and other environments, are the seventh order of methanogens. *Appl. Environ. Microbiol.* 78:8245–53

99. Pearson A, McNichol AP, Benitez-Nelson BC, Hayes JM, Eglinton TI. 2001. Origins of lipid biomarkers in Santa Monica Basin surface sediment: a case study using compound-specific Δ14C analysis. *Geochim. Cosmochim. Acta* 65:3123–37

100. Perevalova AA, Bidzhieva SK, Kublanov IV, Hinrichs K-U, Liu XL, et al. 2010. *Fervidicoccus fontis* gen. nov., sp. nov., an anaerobic, thermophilic crenarchaeote from terrestrial hot springs, and proposal of *Fervidicoccaceae* fam. nov. and *Fervidicoccales* ord. nov. *Int. J. Syst. Evol. Microbiol.* 60:2082–88

101. Pernthaler A, Dekas AE, Brown CT, Goffredi SK, Embaye T, Orphan VJ. 2008. Diverse syntrophic partnerships from deep-sea methane vents revealed by direct cell capture and metagenomics. *Proc. Natl. Acad. Sci. USA* 105:7052–57

102. Peters V, Conrad R. 1995. Methanogenic and other strictly anaerobic bacteria in desert soil and other oxic soils. *Appl. Environ. Microbiol.* 61:1673–76

103. Plumb JJ, Haddad CM, Gibson JAE, Franzmann PD. 2007. *Acidianus sulfidivorans* sp. nov., an extremely acidophilic, thermophilic archaeon isolated from a solfatara on Lihir Island, Papua New Guinea, and emendation of the genus description. *Int. J. Syst. Evol. Microbiol.* 57:1418–23

104. Poulsen M, Schwab C, Jensen BB, Engberg RM, Spang A, et al. 2013. Methylotrophic methanogenic *Thermoplasmata* implicated in reduced methane emissions from bovine rumen. *Nat. Commun.* 4:1428

88. Proves that thaumarchaeal representatives produce methylphosphonate, a substrate for aerobic methanogenesis in the ocean.

89. Shows that ANME-2 organisms alone couple the AOM with the reduction of sulfate to disulfide.

105. Pratscher J, Dumont MG, Conrad R. 2011. Ammonia oxidation coupled to CO_2 fixation by archaea and bacteria in an agricultural soil. *Proc. Natl. Acad. Sci. USA* 108:4170–75

106. Prokofeva MI, Kostrikina NA, Kolganova TV, Tourova TP, Lysenko AM, et al. 2009. Isolation of the anaerobic thermoacidophilic crenarchaeote *Acidilobus saccharovorans* sp. nov. and proposal of *Acidilobales* ord. nov., including *Acidilobaceae* fam. nov. and *Caldisphaeraceae* fam. nov. *Int. J. Syst. Evol. Microbiol.* 59:3116–22

107. A critical look at the ecological niche differentiation between archaeal and bacterial ammonia oxidizers.

107. Prosser JI, Nicol GW. 2012. Archaeal and bacterial ammonia-oxidisers in soil: the quest for niche specialisation and differentiation. *Trends Microbiol.* 20:523–31

108. Quinn PK, Bates TS. 2011. The case against climate regulation via oceanic phytoplankton sulphur emissions. *Nature* 480:51–56

109. Ravishankara AR, Daniel JS, Portmann RW. 2009. Nitrous oxide (N_2O): the dominant ozone-depleting substance emitted in the 21st century. *Science* 326:123–25

110. Rawlings DE. 2002. Heavy metal mining using microbes. *Annu. Rev. Microbiol.* 56:65–91

111. Reeburgh WS. 2007. Oceanic methane biogeochemistry. *Chem. Rev.* 107:486–513

112. Reguera G, McCarthy KD, Mehta T, Nicoll JS, Tuominen MT, Lovley DR. 2005. Extracellular electron transfer via microbial nanowires. *Nature* 435:1098–101

113. Reysenbach A-L, Liu Y, Banta AB, Beveridge TJ, Kirshtein JD, et al. 2006. A ubiquitous thermoacidophilic archaeon from deep-sea hydrothermal vents. *Nature* 442:444–47

114. Rohwerder T, Gehrke T, Kinzler K, Sand W. 2003. Bioleaching review part A: progress in bioleaching: fundamentals and mechanisms of bacterial metal sulfide oxidation. *Appl. Microbiol. Biotechnol.* 63:239–48

115. Provides evidence for a major role of thaumarchaeal organisms in marine N_2O production.

115. Santoro AE, Buchwald C, McIlvin MR, Casciotti KL. 2011. Isotopic signature of N_2O produced by marine ammonia-oxidizing Archaea. *Science* 333:1282–85

116. Schauss K, Focks A, Leininger S, Kotzerke A, Heuer H, et al. 2009. Dynamics and functional relevance of ammonia-oxidizing archaea in two agricultural soils. *Environ. Microbiol.* 11:446–56

117. Schleper C, Jurgens G, Jonuscheit M. 2005. Genomic studies of uncultivated archaea. *Nat. Rev. Microbiol.* 3:479–88

118. Schleper C, Nicol GW. 2010. Ammonia-oxidising archaea—physiology, ecology and evolution. *Adv. Microb. Physiol.* 57:1–41

119. Shaw LJ, Nicol GW, Smith Z, Fear J, Prosser JI, Baggs EM. 2006. *Nitrosospira* spp. can produce nitrous oxide via a nitrifier denitrification pathway. *Environ. Microbiol.* 8:214–22

120. Shimoyama T, Kato S, Ishii S, Watanabe K. 2009. Flagellum mediates symbiosis. *Science* 323:1574

121. Sieber JR, McInerney MJ, Gunsalus RP. 2012. Genomic insights into syntrophy: the paradigm for anaerobic metabolic cooperation. *Annu. Rev. Microbiol.* 66:429–52

122. Smeulders MJ, Barends TRM, Pol A, Scherer A, Zandvoort MH, et al. 2011. Evolution of a new enzyme for carbon disulphide conversion by an acidothermophilic archaeon. *Nature* 478:412–16

123. Spang A, Poehlein A, Offre P, Zumbrägel S, Haider S, et al. 2012. The genome of the ammonia-oxidizing *Candidatus* Nitrososphaera gargensis: insights into metabolic versatility and environmental adaptations. *Environ. Microbiol.* 14:3122–45

124. Stahl DA, De la Torre JR. 2012. Physiology and diversity of ammonia-oxidizing archaea. *Annu. Rev. Microbiol.* 66:83–101

125. Stein LY. Heterotrophic nitrification and nitrifier denitrification. In *Nitrification*, ed. BB Ward, DJ Arp, MG Klotz, pp. 95–114. Washington, DC: ASM Press

126. Strąpoć D, Mastalerz M, Dawson K, Macalady J, Callaghan AV, et al. 2011. Biogeochemistry of microbial coal-bed methane. *Annu. Rev. Earth Planet. Sci.* 39:617–56

127. Suwa Y, Imamura Y, Suzuki T, Tashiro T, Urushigawa Y. 1994. Ammonia-oxidizing bacteria with different sensitivities to $(NH_4)_2SO_4$ in activated sludges. *Water Res.* 28:1523–32

128. Teske A, Sørensen KB. 2008. Uncultured archaea in deep marine subsurface sediments: Have we caught them all? *ISME J.* 2:3–18

129. Thauer RK. 2011. Anaerobic oxidation of methane with sulfate: on the reversibility of the reactions that are catalyzed by enzymes also involved in methanogenesis from CO_2. *Curr. Opin. Microbiol.* 14:292–99

130. Thauer RK, Kaster A-K, Seedorf H, Buckel W, Hedderich R. 2008. Methanogenic archaea: ecologically relevant differences in energy conservation. *Nat. Rev. Microbiol.* 6:579–91

131. Thauer RK, Shima S. 2008. Methane as fuel for anaerobic microorganisms. *Ann. N. Y. Acad. Sci.* 1125:158–70

132. Tourna M, Stieglmeier M, Spang A, Könneke M, Schintlmeister A, et al. 2011. *Nitrososphaera viennensis*, an ammonia oxidizing archaeon from soil. *Proc. Natl. Acad. Sci. USA* 108:8420–25

133. Treusch AH, Leininger S, Kletzin A, Schuster SC, Klenk H-P, Schleper C. 2005. Novel genes for nitrite reductase and AMO-related proteins indicate a role of uncultivated mesophilic Crenarchaeota in nitrogen cycling. *Environ. Microbiol.* 7:1985–95

134. Ussler W III, Paull CK. 2008. Rates of anaerobic oxidation of methane and authigenic carbonate mineralization in methane-rich deep-sea sediments inferred from models and geochemical profiles. *Earth Planet. Sci. Lett.* 266:271–87

135. Verhamme DT, Prosser JI, Nicol GW. 2011. Ammonia concentration determines differential growth of ammonia-oxidising archaea and bacteria in soil microcosms. *ISME J.* 5:1067–71

136. Völkl P, Huber R, Drobner E, Rachel R, Burggraf S, et al. 1993. *Pyrobaculum aerophilum* sp. nov., a novel nitrate-reducing hyperthermophilic archaeum. *Appl. Environ. Microbiol.* 59:2918–26

137. Woese CR, Fox GE. 1977. Phylogenetic structure of the prokaryotic domain: the primary kingdoms. *Proc. Natl. Acad. Sci. USA* 74:5088–90

138. Woese CR, Kandler O, Wheelis ML. 1990. Towards a natural system of organisms: proposal for the domains Archaea, Bacteria, and Eucarya. *Proc. Natl. Acad. Sci. USA* 87:4576–79

139. Wuchter C, Abbas B, Coolen MJ, Herfort L, van Bleijswijk J, et al. 2006. Archaeal nitrification in the ocean. *Proc. Natl. Acad. Sci. USA* 103(33):12317–22

140. Wuchter C, Schouten S, Boschker HTS, Sinninghe Damsté JS. 2003. Bicarbonate uptake by marine Crenarchaeota. *FEMS Microbiol. Lett.* 219:203–7

141. Yan J, Haaijer SCM, Op den Camp HJM, Van Niftrik L, Stahl DA, et al. 2012. Mimicking the oxygen minimum zones: stimulating interaction of aerobic archaeal and anaerobic bacterial ammonia oxidizers in a laboratory-scale model system. *Environ. Microbiol.* 14:3146–58

142. Zengler K, Palsson BO. 2012. A road map for the development of community systems (CoSy) biology. *Nat. Rev. Microbiol.* 10:366–72

143. Zhang L-M, Hu H-W, Shen J-P, He J-Z. 2012. Ammonia-oxidizing archaea have more important role than ammonia-oxidizing bacteria in ammonia oxidation of strongly acidic soils. *ISME J.* 6:1032–45

144. Zhang L-M, Offre PR, He J-Z, Verhamme DT, Nicol GW, Prosser JI. 2010. Autotrophic ammonia oxidation by soil thaumarchaea. *Proc. Natl. Acad. Sci. USA* 107:17240–45

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

146. Zumft WG. 1997. Cell biology and molecular basis of denitrification. *Microbiol. Mol. Biol. Rev.* 61:533–616

**Annual Review of
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Contents

Index

Errata

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