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Anaerobic oxidation of methane by manganese oxides in marine sediments: a review

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Anaerobic oxidation of methane (AOM) is a key methane sink in marine sediments, driven by electron acceptors such as sulfate, nitrate, and metal oxides. Manganese (Mn) oxides, owing to their high oxidizing capacity and rapid turnover, are also recognized as critical oxidants in AOM. However, Mn-AOM has not been well reviewed although several relevant studies have been published. In this paper, current results about Mn-AOM are summarized by synthesizing its geochemical characteristics, pathways for manganese activity, and microbial communities involved under certain marine environments. Two dominant pathways have been proposed for microbial involvement in Mn-AOM in marine sediments: direct AOM coupled to Mn oxide reduction, and indirect AOM via Mn oxide-mediated sulfate reduction. Mn-AOM activity is observed in methane-rich cold seeps or continental margins with substantial Mn oxides input. Future research efforts are still needed to prioritize quantifying the role of Mn-AOM in global carbon and marine manganese cycles.

KEYWORDS

manganese oxide, AOM (anaerobic oxidation of methane), Mn-AOM, microbial communities, marine sediments

1 Introduction

Methane is the second-most important greenhouse gas whose global warming potential is 28 times that of carbon dioxide over 100 years (Stocker, 2013). Methane oxidation occurs through both aerobic and anaerobic ways; however, in marine sediments, anaerobic oxidation predominates (Boetius et al., 2000; Reeburgh, 2007; Knittel and Boetius, 2009). In anoxic marine sediments, annual methane production is estimated at 85–300 Tg, with over 90% of this methane being consumed through anaerobic oxidation (Wefer et al., 2003; Reeburgh, 2007; Knittel and Boetius, 2009). Anaerobic oxidation of methane (AOM) is recognized as a key process in limiting atmospheric methane efflux from the ocean (<2% of the global flux) and in mitigating climate change (Reeburgh, 2007; Knittel and Boetius, 2009). Metabolism of organic matter in marine sediments follows a thermodynamic sequence of electron acceptor utilization, with Gibbs free energy yield decreasing in the order: oxygen, nitrate, manganese oxides, iron (oxyhydr)oxides, sulfate, and organic matter itself. This sequence determines the vertical chemical zonation, leading to oxic, nitrogenous, manganous, ferruginous, sulfidic, and methanogenic zones from the sediment surface downwards. Correspondingly, respiration processes occur sequentially as aerobic respiration, nitrate reduction, manganese reduction, iron reduction, sulfate reduction, and methanogenesis (Jørgensen and Kasten, 2006; Canfield and Thamdrup, 2009; Roberts, 2015). Methane generated in the methanogenic zone diffuses upward and reacts with sulfate, resulting in AOM coupled with sulfate reduction (SR) (Barnes and Goldberg, 1976; Beal et al., 2009).

This reaction (SR-AOM) occurs at a typical narrow zone with steep sulfate and methane gradients, called the sulfate-methane transition zone (SMTZ), and the depth at which sulfate is depleted is termed the sulfate-methane interface (SMI) (Iversen and Jørgensen, 1985; Niewöhner et al., 1998). Microorganisms including anaerobic methanotrophs (ANME) and sulfate-reducing bacteria (SRB) are actively involved in SR-AOM (Boetius et al., 2000; Knittel et al., 2005; Niemann et al., 2006; Wegener et al., 2015). In some marine sediments, sulfate reduction rates are not obligately coupled with AOM rates. Studies have demonstrated that even when sulfate has been significantly depleted or at a very low concentration, methane oxidation still occurs at a considerable rate (Joye et al., 2004; Niemann et al., 2006; Parkes et al., 2007; Bowles et al., 2019). Indeed, when methane diffusion rates or fluxes are elevated, sulfate reduction may be insufficient to oxidize all available methane, suggesting that AOM may become reliant on alternative electron acceptors present in marine sediments (Raghoebarsing et al., 2006; Beal et al., 2009; Ettwig et al., 2010; Haroon et al., 2013). Under such sulfate-limited conditions, the extent to which manganese oxides participate in methane oxidation, their specific geochemical signatures, the detailed reaction pathways of Mn-AOM, and certain natural environments where Mn-AOM occurs remain poorly summarized and systematically reviewed.

Manganese, often associated with iron in marine sediments, while present as a trace element, plays a crucial role in AOM. Mn-AOM is speculated to significantly impact the biogeochemical cycling and sink of elements like phosphorus in marine systems (Slomp et al., 2013; Wu et al., 2020), and to have been environmentally critical for methane consumption in sulfate-poor early Earth conditions (Konhauser et al., 2005; Crowe et al., 2011; Norði et al., 2013; Huang et al., 2023). The sources of manganese in marine sediments are diverse, including terrestrial input, aeolian deposition, hydrothermal venting, and ferromanganese nodules on the seafloor (Martin and Meybeck, 1979; Baturin, 1988; Elderfield and Schultz, 1996; Post, 1999; Poulton and Raiswell, 2000; Mahowald et al., 2005; Blöthe et al., 2015; Uramoto et al., 2019; Zhang et al., 2023). Oxidizing manganese in marine sediments is primarily found as Mn(III) and Mn(IV). Mn(III) predominantly exists in pore waters bound to ligands (Madison et al., 2013). Mn (IV) may exist as colloidal (hydr)oxide or manganese oxide particles. Common manganese oxide minerals include amorphous manganese dioxide (MnO_2), lithiophorite, birnessite, todorokite, buserite, pyrolusite (β-MnO_2), and so on (Post, 1999; Neaman et al., 2004; Jones et al., 2011).

Manganese exhibits thermodynamically potent oxidizing properties, enabling it to oxidize methane (Hu et al., 2018; Huang et al., 2023). In marine sediments, microorganisms can mediate the reaction between co-located manganese oxides and methane, driving AOM according to [Equation 1] (Beal et al., 2009):

$$4MnO_2 + CH_4 + 7H^+ \rightarrow 4Mn^{2+} + HCO_3^- + 5H_2O \qquad \Delta G = -556 \ \ kJ/mol \tag{1}$$

Even when manganese oxides and methane are spatially separated, electric currents in marine sediments, conducted by bacterial nanowires combined with pyrite, soluble electron shuttles and outer-membrane cytochromes, can facilitate electron transport. This conductive network enables the oxidation of organic matter in deeper sediments by utilizing electron acceptors in surface sediments (Nielsen et al., 2010; Pfeffer et al., 2012; Nielsen and Risgaard-Petersen, 2015; Burdorf et al., 2017; Bjerg et al., 2018), suggesting that Mn-AOM is not strictly limited by spatial proximity. Furthermore, manganese oxides exhibit rapid turnover rates and a geological battery effect (Canfield et al., 1993), characterized by their capacity for reversible "charging" (electron uptake from organic donors) and "discharging" (electron transfer to acceptors like oxygen). Birnessite, for example, possesses a substantial electron storage capacity, estimated at approximately $2.7\times10^{23}e^-$/mol Mn (Ye et al., 2025). Electron transfer between birnessite and organic matter proceeds via a two-stage, kinetically discontinuous process, exhibiting rapid manganese reduction followed by slow Mn^{2+} release. Reduction of birnessite initially results in a series of metastable phases with accumulated low-valent Mn (Mn(III)/Mn(II)) without immediate Mn^{2+} release; Mn^{2+} ions are released in significant quantities only upon structural destabilization and mineral dissolution (Ye et al., 2025).Thus, even if there is a very small fraction of manganese in the environment, a significant amount of methane can still be oxidized, contributing to the mitigation of global methane emissions.

Reviews synthesizing Mn-AOM with specific consideration of manganese properties are currently limited, though several reviews on AOM or metal-AOM exist (Riedinger et al., 2014; Oni and Friedrich, 2017; Liang et al., 2019; Vuillemin et al., 2023; Chen et al., 2024; Zhao et al., 2024). This review provides a comprehensive synthesis of the current understanding of Mn-AOM. The main goal is to consolidate existing knowledge, critically discuss inconsistencies and limitations in current findings, and thereby provide researchers with a clear overview of this emerging field.

Abbreviations: AOM, anaerobic oxidation of methane; SR, sulfate reduction; SR-AOM, sulfate reduction coupled with anaerobic oxidation of methane; Metal-AOM, metal reduction coupled with anaerobic oxidation of methane; Fe-AOM, iron oxide reduction coupled with anaerobic oxidation of methane; Mn-AOM, manganese oxide reduction coupled with anaerobic oxidation of methane; MnR-AOM, direct AOM coupled to Mn oxide reduction; MnR-S-AOM, indirect AOM via Mn oxide-mediated sulfate reduction; ANME, anaerobic methanotrophs; SRB, sulfate-reducing bacteria; MRB, metal-reducing bacteria.

This review achieves this by synthesizing current knowledge on: (i) the geochemical characteristics of Mn-AOM in marine sediments and the pathways of manganese activity; (ii) the associated microbial communities and their interactions with electron acceptors; and (iii) the documented natural environments and the conditions that favor the process. Ultimately, this work seeks to stimulate further research interest and offer enlightening suggestions for future directions about Mn-AOM in marine sediments.

2 Geochemical understanding of Mn-AOM

2.1 Geochemical signatures of Mn-AOM in sediments

Initial research suggesting a microbially mediated reaction between manganese oxides and methane in the natural environment can be traced back to Hein et al.'s (1987) investigation into the formation of ^{13}C-depleted rhodochrosite ($MnCO_3$) deposits in the California Coast Ranges. Beal et al.'s (2009) landmark investigation, involving the introduction of birnessite and ferrihydrite to marine seep sediment from the Eel River Basin, significantly illuminated the potential for metal-dependent AOM (manganese and iron) in marine settings. While their study did not conclusively ascertain the direct reaction of manganese with methane, it prompted numerous investigations into the role of metals (Fe and Mn) in AOM processes.

Among metal-AOM reactions, Fe-AOM has attracted more extensive attention than Mn-AOM (Crowe et al., 2011; Sivan et al., 2011; Egger et al., 2015b; Rooze et al., 2016; Cai et al., 2018; Yang et al., 2023). However, studies have revealed Mn involvement in AOM alongside Fe, with observable geochemical signatures. Dissolved inorganic carbon (DIC) produced by AOM and the authigenic carbonates precipitated from it typically inherit the isotopically light carbon signature of methane (Paull et al., 1992; Kastner et al., 2008; Tong et al., 2013). In porewater profiles, high concentrations of Mn^{2+} below the SMI, together with increasing $\delta^{13}C\text{-}CH_4$, rising DIC levels, and lower δ^{13}C-DIC values at corresponding depths, can be attributed to manganese reduction coupled to AOM (Figure 1) (Riedinger et al., 2014; Xiao et al., 2019, 2023). Decoupling of sulfate reduction and AOM, characterized by high methane-to-sulfate ratios or higher AOM rates relative to sulfate reduction rates, suggests the use of alternative electron acceptors (Segarra et al., 2013; Su et al., 2020). The authigenic precipitation of rhodochrosite, or elevated concentrations of Mn(II) in carbonate phases exhibiting depleted δ^{13}C signatures, has been interpreted as diagnostic evidence for manganese-coupled AOM (Xiao et al., 2019). Furthermore, Mn(III/IV) oxides or manganese micronodules in the solid phase have also been documented in hydrate-bearing or cold seep environments, providing suggestive evidence for Mn-AOM (Segarra et al., 2013; Xiao et al., 2019; Yang et al., 2023).

AOM driven by manganese is thermodynamically favorable and presumed to occur preferentially (Riedinger et al., 2014; Xu et al., 2021). Manganese oxide reduction as an electron acceptor provides substantially more energy (~20 times) than sulfate reduction, and also more than iron oxide reduction, in AOM process (Table 1) (Beal et al., 2009; Segarra et al., 2013; Ettwig et al., 2016). The high redox potential of manganese oxides enables them to act as terminal electron acceptors in organic matter oxidation, potentially oxidizing methane through HS^- and Fe(II) acting as electron shuttles (Wang and Van Cappellen, 1996; Thomsen et al., 2004; De Schamphelaire et al., 2007). Evidence from post-Marinoan Doushantuo cap dolostone formation, where δ^{34}S values of authigenic pyrite correlate positively with carbonate manganese content, suggests manganese reduction influences the HS^- pool. This implies manganese oxides can serve as terminal electron acceptors for methane oxidation by oxidizing HS^- to SO_4^{2-} (Cai et al., 2023).

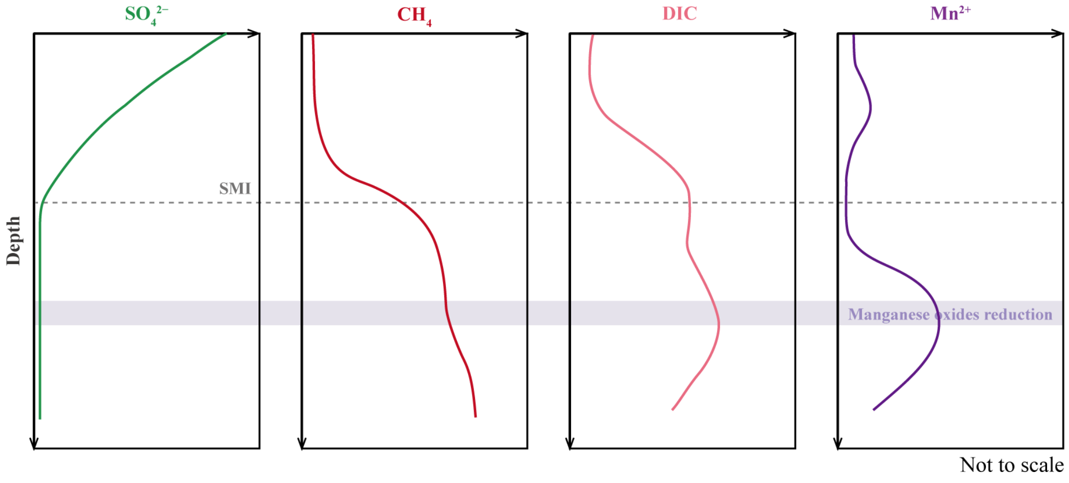


FIGURE 1
Schematic diagram of pore water geochemical profiles illustrating manganese reduction coupled to AOM.

TABLE 1 Gibbs free energy changes under standard conditions ($\Delta G^{0'}$) and the calculated *in situ* ΔG of different electron acceptors.

Electron Acceptor	Reaction	$\Delta G^{0'}$ (kJ mol^{-1} CH_4)	*in situ* ΔG (kJ mol^{-1} CH_4)	AOM rate (μmol CH_4 cm^{-3} yr^{-1})	Reference
Mn(IV): Birnessite	$CH_4 + 4MnO_2 + 7H^+ \rightarrow HCO_3^- + 4Mn^{2+} + 5H_2O$	N.A.	-383	N.A.	Leu et al., 2020
		-494	-556	14	He et al., 2018; Beal et al., 2009
		-790	-594 ± 4 /-577 ± 2	N.A.	Segarra et al., 2013
Fe(III): Ferric Citrate	$CH_4 + 8Fe^{3+} + 2H_2O \rightarrow CO_2 + 8Fe^{2+} + 8H^+$	-454	N.A.	N.A.	Ettwig et al., 2016
Fe(III): Ferrihydrite	$CH_4 + 8Fe(OH)_3 + 15H^+ \rightarrow HCO_3^- + 8Fe^{2+} + 21H_2O$	-81.6 (pH = 7)	-270.3	6	He et al., 2018; Beal et al., 2009
		-571	-175 ± 8 /-192 ± 8	N.A.	Segarra et al., 2013
SO_4^{2-}	$CH_4 + SO_4^{2-} \rightarrow HCO3^- + HS^- + H2O$	-16.6	-14 ~ -35	52	Liang et al., 2019; Beal et al., 2009

N.A. means not available.

2.2 Experiments for Mn-AOM pathway

In order to reveal the specific role of manganese in AOM, researchers have conducted controlled incubation experiments to manipulate key variables and subsequently elucidate the underlying pathways of Mn-AOM (Table 2). Laboratory incubations of freshwater and brackish tidal wetland sediments amended with manganese oxides (birnessite) showed a significant increase in the Mn(II) content of the carbonate phase. A greater rate of AOM than SR was also observed, suggesting that AOM may be linked to the reduction of birnessite (Segarra et al., 2013).

Some studies added both manganese oxides and molybdate (a sulfate reduction inhibitor) to determine whether sulfate reduction to HS^- occurred under experimental conditions. Xu et al. (2021) observed a significant decrease in the SR rate after the addition of birnessite, but an obvious increase in the AOM rate, and found that the molybdate did not affect the AOM rate. These results suggested that birnessite and sulfate might compete for the electron acceptor of AOM, and that birnessite here can act directly with methane (Xu et al., 2021). However, a similar experiment performed by Su et al. (2020) observed an evident decrease in the AOM rate after the addition of vernadite (δ-MnO_2) and molybdate. This observation suggests that SO_4^{2-} remains a significant factor in AOM, and further implies that manganese oxides may indirectly facilitate AOM by oxidizing reduced sulfur species, potentially linking manganese reduction to SR-AOM (Yao and Millero, 1996; Schippers and Jørgensen, 2001). The discrepancy in experimental results may be attributed to the specific mineral types of the added manganese oxides (birnessite vs. vernadite), which exhibit distinct kinetic and thermodynamic properties that can significantly influence reaction occurrence and rates (Neumann Wallheimer et al., 2025). Additionally, differences in the sediment source environments (marine for Xu et al. (2021); sulfate-rich lake for Su et al. (2020)) likely host different dominant microbial communities, potentially leading to variations in reaction pathways. In marine sediments, a cryptic sulfur cycle beneath the SMTZ, wherein manganese oxides are capable of oxidizing sulfides to sulfate [Equations 2–4], has been previously proposed as a pathway for this indirect involvement in SR-AOM (Jones et al., 2011; Treude et al., 2014):

$$MnO_2 + H_2S \rightarrow Mn^{2+} + S^0 + 2OH^- \tag{2}$$

$$3MnO_2 + S^0 + 4H^+ \rightarrow 3Mn^{2+} + SO_4^{2-} + 2H_2O \tag{3}$$

$$4MnO_2 + H_2S + 6H^+ \rightarrow 4Mn^{2+} + SO_4^{2-} + 4H_2O \tag{4}$$

Beyond sediment enrichments, bioreactor studies have examined Mn-AOM geochemistry (Table 2). A freshwater enrichment culture obtained under anaerobic, nitrate-reducing conditions with a continuous supply of methane showed that the reduction of environmentally relevant forms of Fe(III) and Mn(IV) was coupled with the oxidation of methane (Ettwig et al., 2016). Another freshwater sediment experiment used methane and birnessite to feed the bioreactor, and biochemical profiling of the system revealed Mn(IV)-dependent AOM (Leu et al., 2020). Both studies support the direct coupling of manganese reduction to AOM.

Extant research delineates two dominant pathways of Mn-AOM: (1) direct AOM coupled to Mn oxide reduction (MnR-AOM) (Figure 2A) and (2) indirect AOM via Mn oxide-mediated sulfate reduction (MnR-S-AOM) (Figure 2B).

MnR-AOM, while thermodynamically advantageous, is kinetically less favorable than SR-AOM. The solid-phase nature of manganese minerals limits the reactive surface area compared to dissolved sulfate, resulting in slower reaction rates with methane than those observed with sulfate (Table 1). This kinetic factor may promote Mn-AOM pathways that utilize sulfur as an intermediate. In addition, 1 mol of methane requires 4 mol of MnO_2 [Equation 1],

TABLE 2 Incubation experiments exploring the coupling between manganese oxide reduction and AOM.

Sample location	Incubation condition	Mn-AOM kinetics	Mainly functional microorganism	Pathway	Reference
Methane-seep sediments from Eel River Basin, California	Artificial sulfate-free seawater, $[CH_4]$ = 1.5 mM, [birnessite MnO_2] = 10 mM, $[Mn^{2+}]$ = 0.2 mM, $[H^+] = 10^{-8}$ mM, $[HCO_3^-]$ =11 mM, $[CH_4]$ = 1.5 mM, temperature at 10°C	$^{13}CH_4$: 14 µmol CH_4 cm^{-3} yr^{-1}	ANME-1 and/or *Methanococcoides*/ANME-3 with a bacterial partner (e.g. *Bacteroides*, Proteobacteria including *Geobacter*, Acidobacteria, and Verrucomicrobia)	MnR-AOM	Beal et al., 2009
Marine sediments from Shenhu area of the northern South China Sea	Anaerobic artificial seawater with sediment (1:1), [birnessite MnO_2] = 10 mM, [molybdate] = 30 mM	$^{14}CH_4$: above 0.45 nmol cm^{-1} d^{-1}	ANME-2a/b	MnR-AOM	Xu et al., 2021
Brackish coastal sediments from Dover Bluff salt marsh, Georgia	Sterile-filtered anoxic artificial porewater with sediment (1:3), [birnessite MnO_2] = 10 mM, salinity = 21–28 PSU, pH = 7.1, temperature at 20°C	$^{14}CH_4$: 2.4 CH_4 nmol cm^{-3} slurry d^{-1}	N.A.	MnR-AOM	Segarra et al., 2013
Marine sediments from north and east of Barrow, Alaskan Beaufort Sea continental margin	Artificial seawater medium with sediment (1:10), Na-birnessite, dark, temperature at 13°C	$^{14}CH_4$: PC12: ~0.8 nmol cm^{-3} d^{-1} (max) PC13: ~2.7 nmol cm^{-3} d^{-1} (max)	N.A.	MnR-S-AOM	Treude et al., 2014
Marine sediments from Haima cold seep, South China Sea	No Incubation	Modeling: 0.32 CH_4 µmol cm^{-2} y^{-1}	ANME-1,2c; ETH-SRB1 (ethane-dependent sulfate-reducing bacteria)	MnR-AOM	Xiao et al., 2023
Coastal freshwater sediments from Hammersmith Creek River, Georgia	Sterile-filtered anoxic artificial porewater with sediment (1:3), [birnessite MnO_2] = 10 mM, salinity = 0–1 PSU, pH = 7.0, temperature at 20°C	$^{14}CH_4$: 3.6 CH_4 nmol cm^{-3} slurry d^{-1}	N.A.	MnR-AOM	Segarra et al., 2013
Sediments from a sulfate-rich lake (Lake Cadagno) in the southern Alps of Switzerland	Experiment 1, [vernadite] = 10 mmol L^{-1}; Experiment 2, Slurries from Experiment 1 reamended with either [vernadite or [sulfate], plus [molybdate] = 20 mmol L^{-1}; dark, anoxic, temperature = 25°C, 20 mL $^{13}CH_4$	$^{13}CH_4$: ca. 1.67 µmol CO_2 L^{-1} d^{-1}	*Candidatus* Methanoperedens or with potential sulfate-reducing partners Desulfobulbaceae	MnR-S-AOM	Su et al., 2020
Culture of nitrate-AOM enrichment from canal Twentekanaal, Netherlands	At room temperature, pH=7.5 (± 0.15)	$^{13}CH_4$: 21 nmol CO_2 mg (protein)$^{-1}$ h^{-1}	ANME-2d and an *M. oxyfera*-like microorganism	MnR-AOM	Ettwig et al., 2016
Culture of Fe-AOM enrichment from Gold Creek Reservoir in Brisbane, Queensland, Australia	Artificial seawater, CH_4 = 0.6–1.2 atm (90% CH_4, 5% CO_2, 5% N_2), birnessite = ~1–2 g dry weight (added per 2–4 months), pH = 6.8–7.5, temperature = 22 ± 2°C	44.5 µmol CH_4 l^{-1} d^{-1}	*Candidatus* Methanoperedens manganicus and *Candidatus* Methanoperedens manganireducens	MnR-AOM	Leu et al., 2020
Culture from a lab-scale constructed wetland with natural Mn ores	Synthetic anaerobic medium (N_2-flushed), $[CH_4]$ = pure, [δ-MnO_2] = 100–120 mg Mn/L, pH ≈ 7.0 (1 M HCl), temperature = 30 ± 2°C, O_2< 0.002% (N_2 headspace)	$^{13}CH_4$: 0.2 to 0.6 pmol CH_4 day^{-1} cell^{-1}	*Candidatus* Methanoperedens sp. BLZ1, *Luteitalea pratensis*	MnR-AOM	Liu et al., 2023

N.A. means not available.

four times the amount of SO_4^{2-} needed for SR-AOM, which means that MnO_2 needs a higher rate of supply.

While both pathways are recognized, the specific environmental and microbial determinants that govern their relative importance and spatial distribution in natural sediments are not yet fully understood. Electron acceptor availability is likely a significant influencing factor, encompassing the supply and bioavailability (mineral form) of manganese oxides (Neumann Wallheimer et al., 2025), as well as the concentrations of sulfate and sulfide (see section 4 for environmental conditions favoring Mn-AOM in marine sediments). The composition and metabolic preferences of microbial communities may also be crucial determinants; their preference for specific electron acceptors or metabolic strategies likely dictates the pathway utilized (see Section 3.2). For instance, microbial consortia adapted to long-term SR-AOM might preferentially utilize sulfur-mediated pathways (MnR-S-AOM)

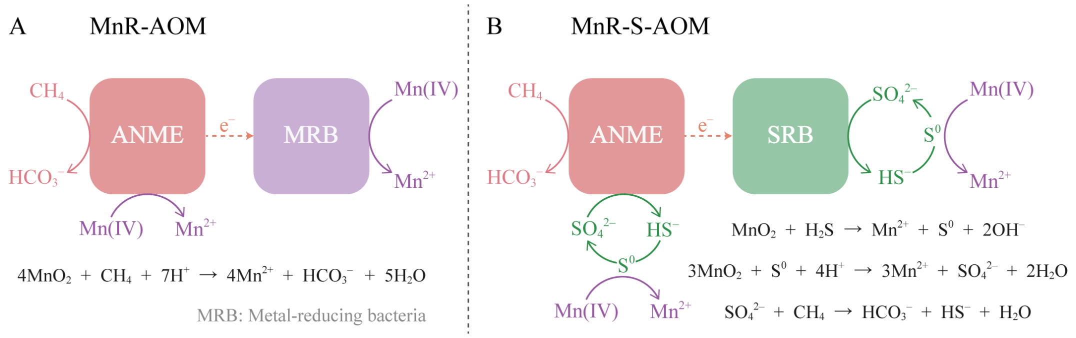


FIGURE 2
Two pathways of Mn-AOM (modified from He et al., 2018). **(A)** MnR-AOM, the reduction of manganese oxides directly drives AOM; **(B)** MnR-S-AOM, where manganese oxides oxidize HS^- to produce SO_4^{2-}, which is then reduced by methane.

when sulfate is becoming limiting, rather than immediately switching to direct MnR-AOM (e.g., Cai et al., 2023). Additionally, ambient geochemical conditions (e.g., pH, Eh, temperature, salinity), which can significantly impact reaction kinetics and microbial activity, are likely candidates influencing pathway selection (He et al., 2018; Cai et al., 2021b; Zhao et al., 2024). Detailed and systematic studies investigating how these potential determinants influence Mn-AOM pathway selection are needed in future research.

3 Microbial processes in Mn-AOM

3.1 Microbial communities involved in Mn-AOM

The SR-AOM, which is the major pathway of AOM, is typically mediated by syntrophic microbial consortia of ANME and sulfate-reducing bacteria (SRB) in the natural environment (Boetius et al., 2000; Niemann et al., 2006; Wegener et al., 2015). ANME encompass three distinct phylogenetic clades: ANME-1 (subgroups a and b), ANME-2 (subgroups a, b, c, and d), and ANME-3 (Ruff et al., 2015; Cai et al., 2021b). Mn-AOM in natural systems appears to necessitate the involvement of ANME alongside some metal-reducing bacteria (MRB) partners such as *Desulfuromonas* and *Pelobacter* members, although thermochemical oxidation of methane by manganese oxides without microbes has also been observed in environments like hydrothermal sediments (Chang et al., 2012; Huang et al., 2023).

Investigation into microbial communities involved in Mn-AOM in marine sediments employs both direct molecular analysis (DNA/RNA extraction and sequencing) of sediment samples and cultivation-based methods aimed at enriching key microorganisms (Beal et al., 2009; Liu et al., 2023; Xiao et al., 2023). Despite the persistent lack of representative pure cultures for Mn-AOM and the resulting unclear identification of the specific microbial populations responsible, shifts in microbial community structure following manganese addition offer valuable insights into potential functional groups (Table 2). For example, a 10-month culture experiment presented by Beal et al. (2009) indicated a substantial increase in manganese reducers within the bacterial community upon birnessite incubation, suggesting a vital role of bacteria in Mn-AOM. These results imply that Mn-AOM may be mediated by ANME-1 and/or *Methanococcoides*/ANME-3 in association with bacterial partners. House et al. (2011), using FISH and FISH-SIMS, identified that archaea-bacteria mixed aggregates were the most metabolically active entities during Mn-AOM, resembling those involved in SR-AOM. Direct DNA/RNA sequencing and analysis of sediment samples by Xiao et al. (2023) indicated that in methanic sediments, abundant active ANME groups (ANME-1 and ANME-2c) and potential dissimilatory metal reducers (e.g., ETH-SRB1) are potentially involved in metal-AOM *in situ*. Some studies have illuminated the capacity of ANME to perform the entire process without bacterial partners. Metagenomic sequencing has revealed that ANMEs capable of utilizing manganese solely are ANME-2a/b (Xu et al., 2021), "*Ca. M. nitroreducens*"-like archaea (Ettwig et al., 2016), "*Ca. M. manganireducens*" and "*Ca. M. manganicus*"; the latter three are assigned to ANME-2d (Leu et al., 2020; Cai et al., 2021b). In contrast to Leu et al.'s (2020) research, a recent bioreactor study by Liu et al. (2023) found Mn-AOM to be mediated by an anaerobic consortium comprising *Candidatus Methanoperedens* sp. BLZ1 and a distinct bacterial partner (*Luteitalea pratensis*).

Beyond direct Mn-AOM, the microbial functional roles in the MnR-S-AOM pathway are also complex. In the sediments of Cadagno Lake, where manganese is coupled to AOM through the sulfur cycle, the interdependence of ANME and SRB is likely facultative (Su et al., 2020). Analysis of microbial abundance revealed that SRB, specifically members of the *Desulfobulbus* group, exhibited peak abundance coinciding with only one of the two observed ANME maxima. This observation hints that ANME may engage in collaborative interactions with SRB or, alternatively, possess the capacity to execute AOM independently in MnR-S-AOM (Su et al., 2020).

It is important to note that the utilization of different parental substrates in cultivation experiments contributes to their variable effectiveness in representing *in situ* marine sediment conditions. Some employ a mixture of sampled marine sediment and artificial seawater, which can relatively better simulate *in situ* marine conditions (Beal et al., 2009; House et al., 2011; Segarra et al., 2013; Treude et al., 2014). In contrast, studies involving bioreactors primarily focused on the Mn-AOM reaction itself may diverge considerably from natural settings (Ettwig et al., 2016; Leu et al., 2020; Liu et al., 2023). Compared to cultivation experiments, results obtained from direct DNA/RNA extraction and sequencing of sediment samples provide more robust evidence for demonstrating the natural occurrence or ecological significance of microorganisms in marine sediments (Chang et al., 2012; Xu et al., 2021; Xiao et al., 2023). Therefore, future research incorporating *in situ* analysis of microbial communities and functions in sampled areas is essential for achieving a deeper understanding and stronger evidence of Mn-AOM.

3.2 Interactions between microorganisms and electron acceptors

Manganese oxides occur predominantly in solid phase in natural environments, so Mn-AOM microbes have to possess several strategies for transferring electrons between the cells and the minerals. Existing evidence suggests several potential strategies for this electron transfer process: direct contact between microbial cells and manganese oxide minerals; indirect electron transfer by electron shuttles; and direct electron transfer by nanowires (He et al., 2018; Liang et al., 2019; Leu et al., 2020; Dang et al., 2021) (Figure 3).

Numerous multiheme c-type cytochrome-encoding genes are found in abundance in ANME-2d members. The genome of "*Ca.* M. nitroreducens" encodes a great number of multiheme c-type cytochromes that may contribute to electron transfer in Mn-AOM (Haroon et al., 2013; Arshad et al., 2015). However, "*Ca.* M. nitroreducens" has yet to be directly confirmed to have an intermediate interspecies electron transfer. Besides, 43 and 25 putative multiheme c-type cytochromes were found to be encoded in "*Ca.* M. manganicus" and "*Ca.* M. manganireducens," respectively. In the transcriptomes of "*Ca.* M. manganicus" and "*Ca.* M. manganireducens," 23 and 9 multiheme c-type cytochromes were substantially expressed, respectively (Leu et al., 2020). These c-type cytochromes were previously found to transfer electrons from intracellular to extracellular and therefore facilitate the direct electron transfer between microorganisms and minerals (Cai et al., 2021b). They also have been recognized as shuttles for extracellular electron transfer (Shi et al., 2007; Wang et al., 2014), and it is hypothesized that they perform a similar function in ANME-2d members (Ettwig et al., 2016).

Conductive nanowires constitute another Mn-AOM electron transfer mechanism (Figure 3) (Leu et al., 2020). These conductive structures of "*Ca.* M. manganicus", similar to the "*Ca.* M. nitroreducens" Mnv1 strain (Guerrero-Cruz and Cremers, 2018), show upregulation of archaellum-related genes under oxidative stress. Nanowires are suggested to allow electrons to transfer over greater distances relative to multiheme c-type cytochromes independently (Krukenberg et al., 2018). Mn-AOM-related microbes "*Ca.* M. manganicus" and "*Ca.* M. manganireducens" genomes encode for genes of the principal subunit flagellin (*flaB*), a component of the archaellum. During Mn-AOM experiments in "*Ca.* M. manganicus," 2 of the 4 *flaB* genes were significantly expressed, suggesting the involvement of these conductive appendages in electron transfer (Leu et al., 2020).

In terms of electron acceptor utilization, ANME populations are recognized as versatile methanotrophs, exhibiting metabolic flexibility depending on environmental availability (Wankel et al., 2012; Ettwig et al., 2016; Scheller et al., 2016). While ANME-1, -2, and -3 clades are primarily associated with SR-AOM (Milucka et al., 2012), evidence indicates their involvement in Mn-AOM as well (Beal et al., 2009; Chang et al., 2012; Xu et al., 2021). However, studies suggest a preferential utilization of sulfate over metal oxides by these ANME clades (Riedinger et al., 2014; Egger et al., 2015b). Modeling of the Haima cold seep by Xiao et al. (2023) further supports this preference, indicating a minor contribution of Mn-AOM and Fe-AOM (1.5% each) relative to the dominant SR-AOM (97%). In contrast to these findings, laboratory experiments have demonstrated that some anaerobic methanotrophs prefer metals over sulfate as electron acceptors. Enriched from freshwater sediment, "*Ca.* M. ferrireducens," "*Ca.* M. manganicus," and "*Ca.* M. manganireducens" performed Fe(III)- or Mn(IV)-dependent AOM over a prolonged period, even in the presence of sulfate (Cai

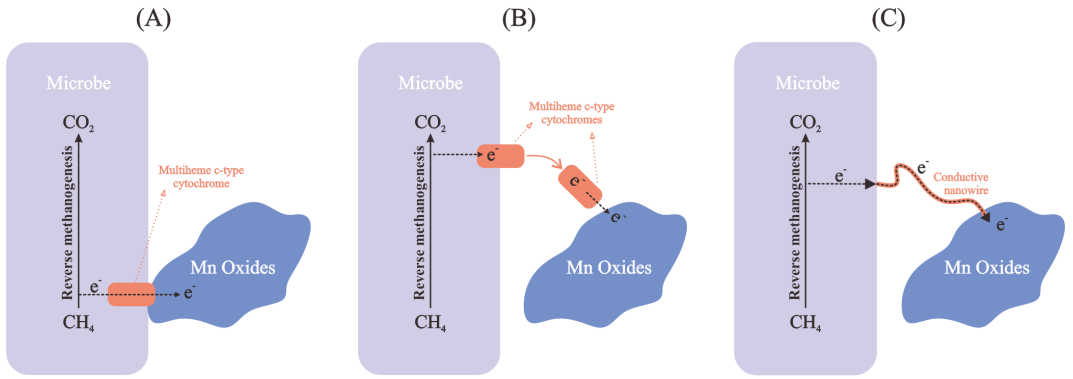


FIGURE 3
Mechanisms of electron transfer between microbes and Mn oxides. **(A)** Direct contact with Mn oxides; **(B)** Indirect electron transfer by electron shuttles; **(C)** Direct electron transfer by nanowires.

et al., 2018; Leu et al., 2020). Likewise, "*Ca*. M. nitroreducens" and "*Ca*. M. oxyfera" exhibit a preference for nitrate/nitrite reduction, irrespective of sulfate availability in culture media (Haroon et al., 2013; Ettwig et al., 2009).

The versatility of ANME to utilize electron acceptors is likely to be greatly affected by the availability of electron acceptors in the environment. Alterations in external environmental conditions not only induce functional adaptations within existing microbial populations but also contribute to shifts in community composition. For instance, the nitrate-dependent AOM archaeon "*Ca*. M. nitroreducens" is able to execute Fe- and Mn-AOM when nitrate concentrations are limiting (Haroon et al., 2013; Ettwig et al., 2016). Furthermore, laboratory bioreactor experiments, with conditions modified from initial incubations, further revealed significant shifts in dominant microbial types and the emergence of novel Mn-AOM microbes (e.g., *Ca*. M. manganicus and *Ca*. M. manganireducens) (Leu et al., 2020). It is hypothesized that microorganisms in these systems may mutate and/or evolve in response to variations in electron acceptor supply (Guerrero-Cruz et al., 2021). These findings underscore the complexity and under-exploration of microbial diversity and function in Mn-AOM.

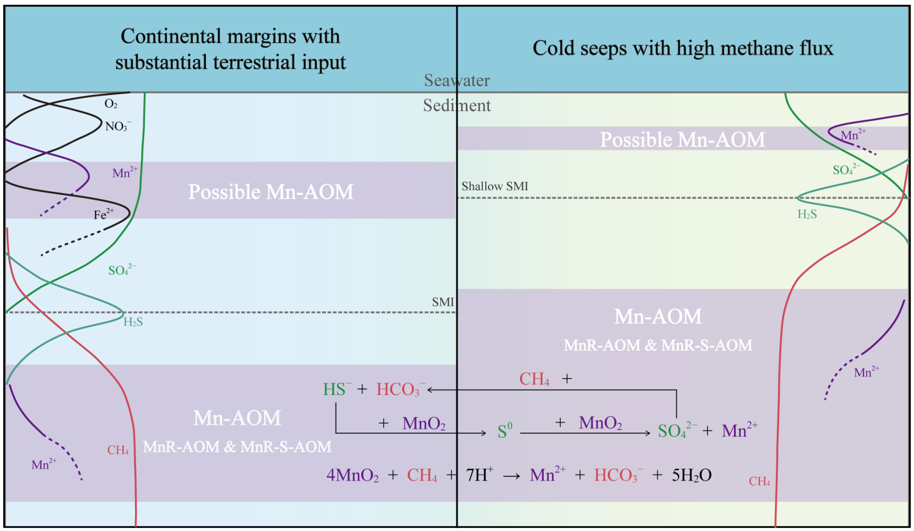
4 Environmental conditions for Mn-AOM occurrence

Mn-AOM in natural marine sediments is primarily documented in cold seep and continental margin settings (Table 3). Cold seeps, characterized by exceedingly high methane flux and transport rate, facilitate the interaction of methane with the diverse electron acceptors present in sediments (Liu et al., 2022). High methane flux drives the SMI upwards to near seafloor surface in marine sediments, resulting in shallower redox zones and increased overlap of geochemical zones. This SMI shift enhances the probability of methane encountering manganese oxides above the SMI depth, thus promoting Mn-AOM (Figure 4). Studies in high methane flux regions like the Shenhu area reveal that concentrations of methane can be high up to 15 mM –80 mM and that AOM rates exceeding the SR rate at high methane concentrations (>5 mM), indicating the importance of alternative electron acceptors like manganese oxides (Lapham et al., 2013; Bowles et al., 2019). Incubation experiments further corroborate this, demonstrating simultaneous birnessite and sulfate involvement in AOM (Su et al., 2020). Therefore, in high methane flux settings, SMI upward migration and the resulting increased methane-manganese oxides interaction might drive Mn-AOM reaction. Furthermore, with a shallow SMI, the geological battery effect of manganese minerals may significantly contribute to Mn-AOM, as Mn(II) from manganese oxide reduction can be re-oxidized by oxygen near the surface, potentially establishing a manganese cycle for sustained methane oxidation (Ye et al., 2025). This phenomenon is likely more prevalent in shallow sediments, but further research is needed to fully understand the efficient charge-discharge properties of manganese minerals in natural marine sediments. Moreover, high methane flux environments can exacerbate sulfate depletion, further diminishing sulfate availability and creating conditions conducive

TABLE 3 Documented occurrences of Mn-AOM in marine sediments, freshwater sediments (natural environments), and paleo-environmental settings.

Ecosystem	Environment	Sample origin	Pathway	Reference
Marine	Cold seep with high methane flux	Methane-seep sediments from Eel River Basin, California	Mn-AOM*	Beal et al., 2009
		Marine sediments from Haima cold seep, South China Sea	MnR-AOM	Zhang et al., 2023
		Marine sediments from Haima cold seep, South China Sea	MnR-AOM	Xiao et al., 2023
	Continental margin with substantial terrestrial input	Marine sediments from east of the Rio de la Plata, Argentine Basin	Mn-AOM*	Riedinger et al., 2014
		Marine sediments from north and east of Barrow, Alaskan Beaufort Sea continental margin	MnR-S-AOM	Treude et al., 2014
		Marine sediments from the Shenhu area of the northern South China Sea	MnR-AOM	Xu et al., 2021
		Marine sediments from Taixinan Basin, Dongsha area, South China Sea	Mn-AOM*	Xiao et al., 2019
	Coastal zone	Brackish coastal sediments from Dover Bluff salt marsh, Georgia	MnR-AOM	Segarra et al., 2013
	Paleo-marine facies	Post-Marinoan Doushantuo cap dolostone of South China	MnR-S-AOM	Cai et al., 2023
Freshwater		Coastal freshwater sediments from Hammersmith Creek River, Georgia	MnR-AOM	Segarra et al., 2013
		Sediments from a mud volcano in eastern Taiwan	MnR-AOM	Chang et al., 2012
		Sediments from a sulfate-rich lake (Lake Cadagno) in the southern Alps of Switzerland	MnR-S-AOM	Su et al., 2020
	Paleo-lacustrine facies	Triassic sandy conglomerates from the Junggar Basin, northwestern China	MnR-AOM	Cai et al., 2021a

Mn-AOM* pathway: study lacks detailed pathway of manganese activity in AOM.



$$\mathrm{CH_4} + \mathrm{SO_4^{2-}} \rightarrow \mathrm{HS^-} + \mathrm{HCO_3^-}$$

$$\mathrm{HS^-} \xrightarrow{+\ \mathrm{MnO_2}} \mathrm{S^0} \xrightarrow{+\ \mathrm{MnO_2}} \mathrm{SO_4^{2-}} + \mathrm{Mn^{2+}}$$

$$\mathrm{4MnO_2} + \mathrm{CH_4} + \mathrm{7H^+} \rightarrow \mathrm{Mn^{2+}} + \mathrm{HCO_3^-} + \mathrm{5H_2O}$$

Not to scale

FIGURE 4
Observed Mn-AOM environments and potential distribution in marine sediment.

to MnR-AOM. Sulfate-depleted conditions are commonly observed in methanogenic zones (beneath the SMI) in marine sediment profiles, where manganese oxide minerals, if present, can react with methane (Figure 4). In addition, vigorous sulfate consumption, fueled by abundant methane, leads to hydrogen sulfide (HS^-) production. Subsequently, manganese oxides can facilitate the MnR-S-AOM reaction through HS^- mediation just below the SMI (Treude et al., 2014; Su et al., 2020). Observations of Mn-AOM in sediments from hydrate-bearing area of the South China Sea may also be linked to methane supply (Xiao et al., 2019). Hydrate formation necessitates methane saturation in porewater, thus ensuring a sustained methane supply for cold seep formation, although cold seep environments and hydrate zones are not always entirely congruent (Zhang et al., 2021b).

Continental margins with substantial terrigenous input and dynamic deposition provide favorable conditions for Mn-AOM (Figure 4). Abundant organic matter, derived from high surface productivity and terrestrial inputs, fuels methanogenesis and accelerates the consumption of dissolved electron acceptors, such as nitrate and sulfate (Chen et al., 2003). Continental margins are significant depositional zones for terrestrial manganese inputs. The continental margin is generally an unsteady marine depositional environment, where frequent mass movements and accompanying turbidity currents can transport large amounts of manganese and reworked organic matter to deep marine sediments (Hensen et al., 2003; Riedinger et al., 2005). High sedimentation rates in these regions can limit the exposure of reactive metal oxides to oxygenated water, thereby preserving significant amounts of manganese oxide phases within methanogenic zones (Riedinger et al., 2014). In these sulfate-depleted zones below the SMI, preserved manganese minerals become available to react with methane. Additionally, continental slopes often host ferromanganese nodules, and common manganese minerals like birnessite and todorokite, occurring as reactive coatings and fine-grained aggregates, are considered potential oxidants for methane (Zhong et al., 2017; Xu et al., 2021; Zhang et al., 2023). Different manganese species exhibit marked variations in chemical reactivity (Neaman et al., 2004), which directly influence reaction prioritization and pathways (Wang et al., 2018; Cai et al., 2023). However, characterization of manganese mineral types and structures in natural marine sediments remains challenging due to manganese's trace element status and limited mineral formation. Consequently, most studies only rely on selective chemical extraction methods to isolate operationally defined manganese fractions, thereby elucidating manganese speciation and associated geochemical processes (Yang et al., 2018). Sequential extraction analyses reveal four distinct manganese phases in marine sediments: (1) carbonate-associated manganese (e.g., rhodochrosite $MnCO_3$), (2) easily reducible amorphous manganese oxides (e.g., birnessite $Na_{0.7}Ca_{0.3}Mn_7O_{14}{\cdot}2.8H_2O$, vernadite δ-$MnO_2$, nsutite γ-$MnO_2$, and pyrolusite β-$MnO_2$), (3) reducible crystalline manganese oxides (e.g., manganite γ-MnOOH and bixbyite α-Mn_2O_3), and (4) recalcitrant manganese oxides (e.g., hausmannite Mn_3O_4) (Brookins, 1988; Glasby and Schulz, 1999; Poulton and Canfield, 2005). Specifically, carbonate-associated manganese represents a reduced form, whereas manganese oxides in groups (2) and (3) exhibit oxidative capacity and are thus likely to be reactive in Mn-AOM processes.

Apart from marine sediments, some coastal areas with severe eutrophication also provide an ideal conditions for Mn-AOM (Table 3) (Segarra et al., 2013; Egger et al., 2015b; Wallenius et al., 2021). Eutrophication exacerbates the depletion of easily reactive dissolved electron acceptors in the upper layers of the sediment, causing the SMI to move upward (Egger et al., 2015b). As a result, manganese oxides in the sediment are exposed to the methanogenic zone, where sulfate, nitrate, and nitrite are depleted. Thus, metal oxides appear to be the only available electron acceptors for these deep methane oxidations. Mn-AOM also occurs in some freshwater sediments (Table 3) (Segarra et al., 2013). The lower sulfate content in the freshwater environment compared to the marine environment and the sufficient terrestrial input of reducible manganese as well as the presence of methane production in the sediments provide favorable conditions for Mn-AOM. Furthermore, direct oxidation of biogenic methane by manganese oxides (MnR-AOM) has been documented in a sulfate-poor paleo-lacustrine facies deposits during early diagenesis in the Triassic sandy conglomerates from the Junggar Basin, northwestern China (Cai et al., 2021a). Redox reactions between manganese oxides and methane have also been observed in the water column [e.g., Lake Matano, Indonesia (Jones et al., 2011)].

No consistent conclusion has been reached regarding the requirement for sulfur mediation in the reaction between manganese oxides and methane in natural environments, nor the conditions that dictate its role. Sulfur-mediated manganese reduction coupled anaerobic oxidation of methane (MnR-S-AOM) has been observed in marine continental margin sediments, sulfate-rich lake sediments, and paleo-marine facies deposits. Direct manganese reduction coupled anaerobic oxidation of methane (MnR-AOM) has been reported in marine cold seep sediments, continental margin sediments, coastal sediments, and paleo-lacustrine facies deposits. Some existing Mn-AOM studies have not definitively elucidated the precise pathways of manganese involvement in the anaerobic oxidation of methane (Table 3).

Overall, Mn-AOM has been identified both in marine and freshwater sediments (Beal et al., 2009; Su et al., 2020; Xu et al., 2021; Xiao et al., 2023), with documented evidence spanning historical periods and contemporary environments (Riedinger et al., 2014; Cai et al., 2021a, 2023). To illustrate the broad scope of Mn-AOM reactions, manganese oxides have been successfully applied for methane removal in constructed wetlands (Liu et al., 2020; Zhang et al., 2021a).

5 Conclusions and outlook

This review synthesizes current research on manganese oxides reduction coupled to anaerobic oxidation of methane (Mn-AOM), covering its geochemical characteristics, reaction pathways, and the microbial species involved. Key points include:

- Geochemical Signatures: Widespread Mn-AOM is recognized in natural marine sediments by distinctive geochemical profiles, typically showing the co-occurrence of sulfate depletion, methane consumption, and increased dissolved Mn^{2+} concentrations, and/or the presence of manganese-enriched carbonate phases at corresponding depths.
- Reaction Pathways: Mn-AOM proceeds via two dominant, microbially mediated pathways involving anaerobic methanotrophic archaea (ANME) and potentially synergistic bacterial partners: (1) direct AOM coupled to Mn oxide reduction (MnR-AOM); and (2) indirect AOM via Mn oxide-mediated sulfate reduction (MnR-S-AOM).
- Environmental Conditions: Mn-AOM activity is commonly observed in methane-rich cold seeps or/and continental margins with substantial Mn oxides input, typically below the sediment sulfate-methane interface (SMI).

Despite current advancements, significant knowledge gaps necessitate focused future research. Key aspects include:

- Environmental Controls on Mn-AOM Reactivity: Future research should systematically explore the impact of environmental factors on Mn-AOM, particularly manganese oxide mineral properties (structure, reactivity, transformations) using techniques such as µXRF, EXAFS, XANES, and LA-ICP-MS (Lenz et al., 2014, 2015; Egger et al., 2015a; Hermans et al., 2021; Lenstra et al., 2021), and parameters like salinity, temperature, and pH (Cai et al., 2021b).
- Microbial Ecology and Mn-AOM Pathway: Future studies should intensify research into the microbial ecology by identifying key microorganisms and their metabolic strategies (especially via *in situ* detection). Importantly, studies should also aim to differentiate between direct AOM coupled to Mn oxide reduction (MnR-AOM) and indirect AOM via Mn oxide-mediated sulfate reduction (MnR-S-AOM), which are frequently obscured by overlapping geochemical signals. Research must also systematically identify and quantify the environmental, geochemical, and microbial factors controlling their relative importance and spatial distribution.
- Environmental Distribution, Prevalence, and Significance: Investigations should be broadened to assess the environmental distribution and prevalence of Mn-AOM across diverse natural systems. Quantifying its contribution to global carbon and marine manganese cycles is a key priority, which can be achieved through methodologies such as regional flux estimations (e.g., Crowe et al., 2011; Slomp et al., 2013), model simulations (e.g. Xiao et al., 2023; Neumann Wallheimer et al., 2025), incubation experiments (e.g., Bowles et al., 2019), and analysis of geological records (e.g., Hu et al., 2018).

In conclusion, future research efforts directed towards these areas will be crucial for a comprehensive understanding of Mn-AOM and its significance in global methane dynamics and biogeochemical cycles.

Author contributions

YX: Conceptualization, Writing – review & editing, Writing – original draft, Visualization, Methodology. HL: Supervision, Conceptualization, Writing – review & editing, Funding acquisition. YL: Writing – review & editing. HY: Funding acquisition, Writing – review & editing, Methodology. YT: Writing – review & editing. YHL: Writing – review & editing.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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