

# Methane cycling in a ferruginous tropical lake (Kabuno Bay, East Africa)

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## 1. Abstract

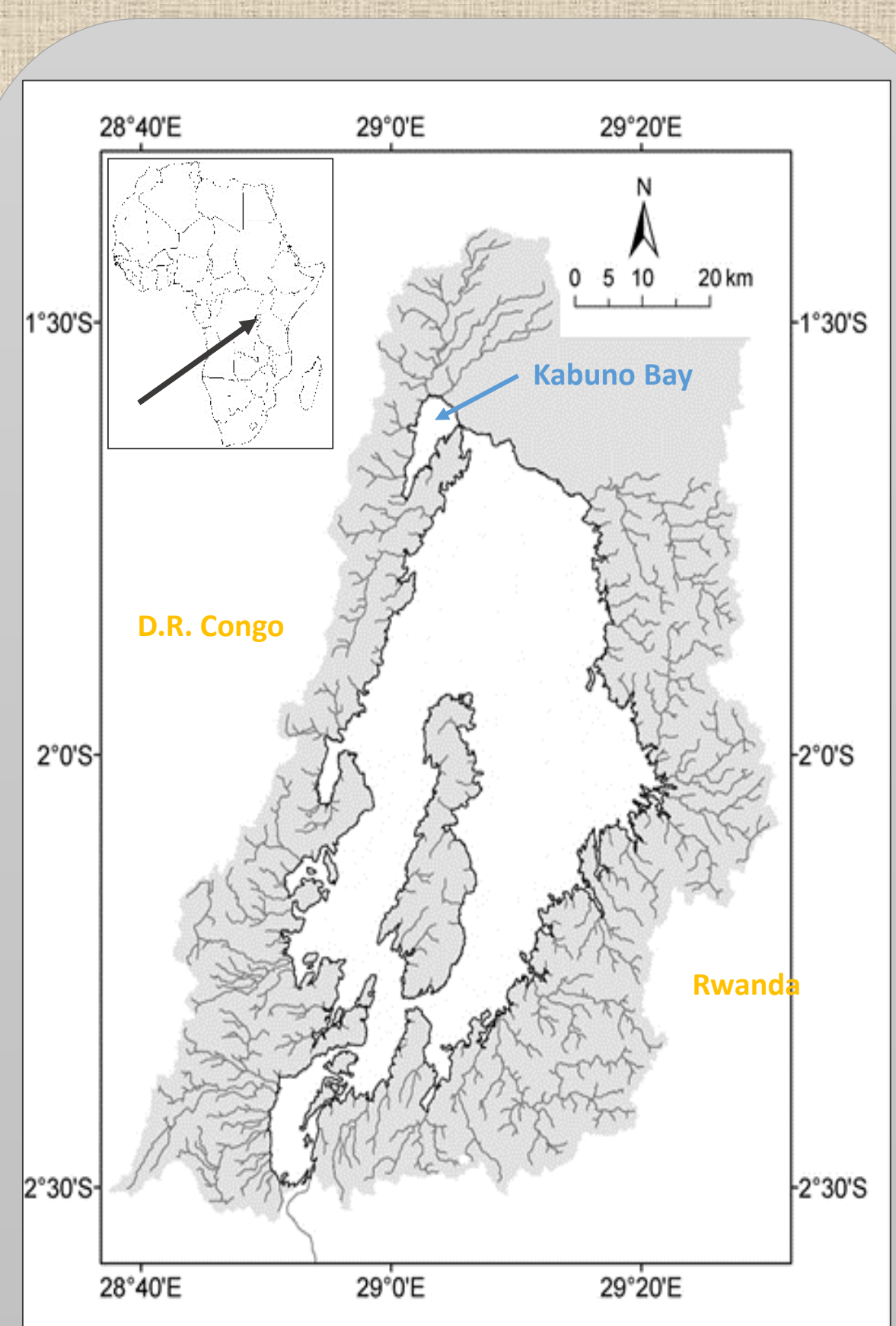
In the ferruginous and anoxic early Earth oceans, photoferroptrophy drove most of the biological production before the advent of oxygenic photosynthesis, but its association with ferric iron ( $\text{Fe}^{3+}$ ) dependent anaerobic methane ( $\text{CH}_4$ ) oxidation (AOM) has never been investigated. We studied AOM in Kabuno Bay, a modern analogue to the Archean Ocean (anoxic bottom waters and dissolved Fe concentrations  $>600 \mu\text{mol L}^{-1}$ ) and its linkage with a variety of electron acceptors. Unlike in most lakes, pelagic  $\text{CH}_4$  oxidation was largely due to AOM that mainly relied on  $\text{Fe}^{3+}$  produced by photoferroptrophs as the main electron acceptor. Ferric iron-driven AOM has not before been envisaged as a possible metabolic process in the Archean ocean, but this can radically change the conceptualization and modelling of metabolic and geochemical processes controlling climate conditions in the Early Earth, and might support the view that low-latitude glaciation events triggered at low atmospheric  $\text{CH}_4$  level.

## 2. Introduction

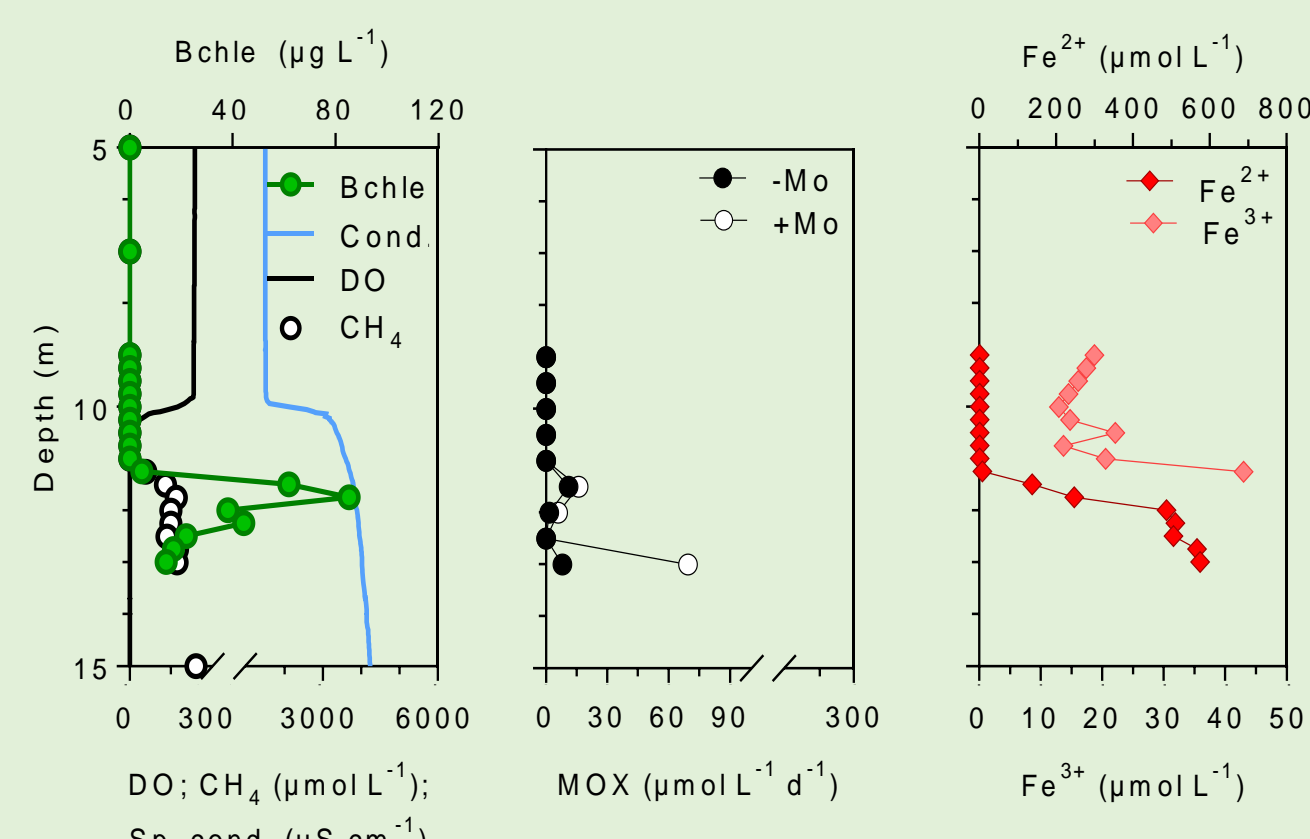
Tropical inland waters and wetlands have been recognized as major sources of methane ( $\text{CH}_4$ ) to the atmosphere. In modern marine sediments where  $\text{SO}_4^{2-}$  is more abundant by several orders of magnitude than any other electron acceptor, most of the  $\text{CH}_4$  removal is due to anaerobic  $\text{CH}_4$  oxidation (AOM) coupled to  $\text{SO}_4^{2-}$  reduction. However,  $\text{SO}_4^{2-}$  abundance is typically much lower in freshwaters, so that  $\text{CH}_4$  oxidation in anoxic hypolimnion or sediments of lakes might be linked to the reduction of thermodynamically more favorable electron acceptors such as nitrite ( $\text{NO}_2^-$ ), nitrate ( $\text{NO}_3^-$ ), manganese IV ( $\text{Mn}^{4+}$ ) and ferric iron ( $\text{Fe}^{3+}$ ).

Kabuno Bay is a ferruginous sub-basin of Lake Kivu (RD Congo) with a marked and distinct physico-chemistry, so being considered as an independent lake. Due to high hydrothermal activity, a strong and stable stratification is established within Kabuno bay water column throughout the year, with waters being anoxic below  $\sim 11$  m depth. A consequence of this strong stratification is the occurrence of a particularly steep gradient in  $\text{CH}_4$  and iron ( $\text{Fe}^{2+}/\text{Fe}^{3+}$ ) concentrations in the chemocline. Also, anoxic waters of Kabuno Bay are characterized by low sulfide ( $\text{HS}^-$ ) concentrations. These combined features are rarely encountered in modern environments, while they were widespread in the Archean ocean. Lirós et al. (2015) reported the occurrence of a particularly active pelagic Fe cycle driven by photoferroptrophy in Kabuno Bay, with little net Fe oxidation, meaning that Fe reduction processes are tightly coupled to photoferroptrophic Fe oxidation. In the present study, we measured  $\text{CH}_4$  oxidation rates in the water column of Kabuno Bay, and investigated the potential importance of Fe as a terminal electron acceptor for AOM. We hypothesized that  $\text{Fe}^{3+}$  could be the main electron acceptor for AOM given the high abundance of Fe species in the water column and the high *in situ* photoferroptrophic rates previously reported in Kabuno Bay.

## 3. Results

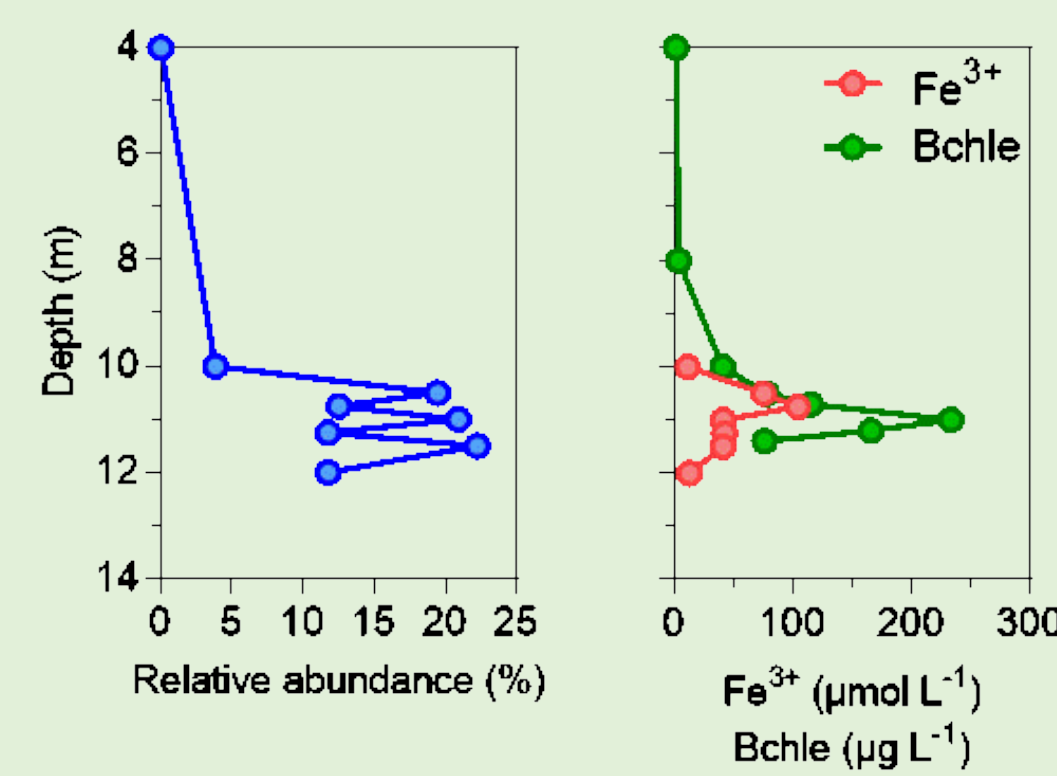


### 3.1 $\text{CH}_4$ oxidation



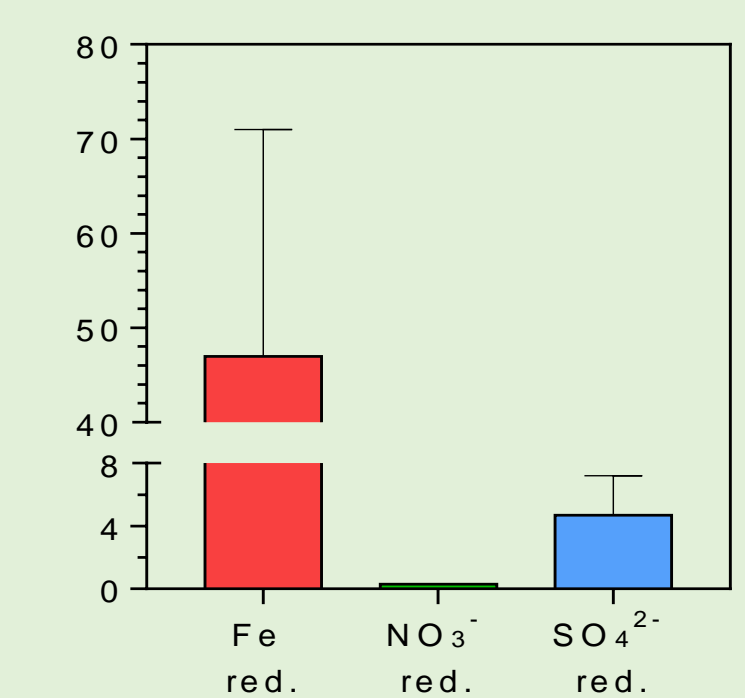
- $\text{CH}_4$  oxidation (MOX) is higher when  $\text{SO}_4^{2-}$  reducing bacteria activity is inhibited  $\Rightarrow$   $\text{SO}_4^{2-}$  is not the main electron acceptor
- Maximum AOM rates and Bchle (specific biomarker of photoferroptrophs) concentrations, and Fe oxidation/reduction zone co-occur

### 3.2 Genomic evidence



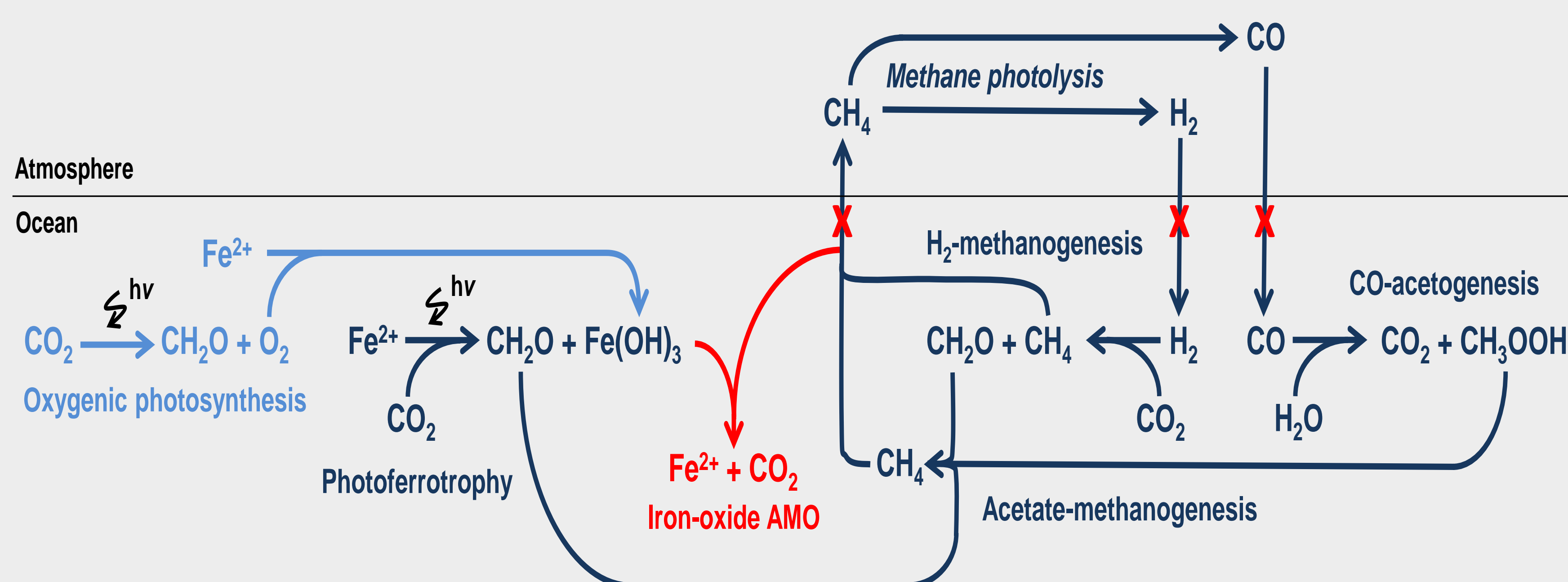
The relative abundance of *Candidatus Methanoperedens*, an Archaea capable of AOM coupled to Fe oxides reduction, is higher in the Fe reduction zone. Also, Bchle concentrations are higher in the same zone, suggesting a coupling between photoferroptrophy and Fe reduction-linked AOM.

### 3.3 Chemical evidence



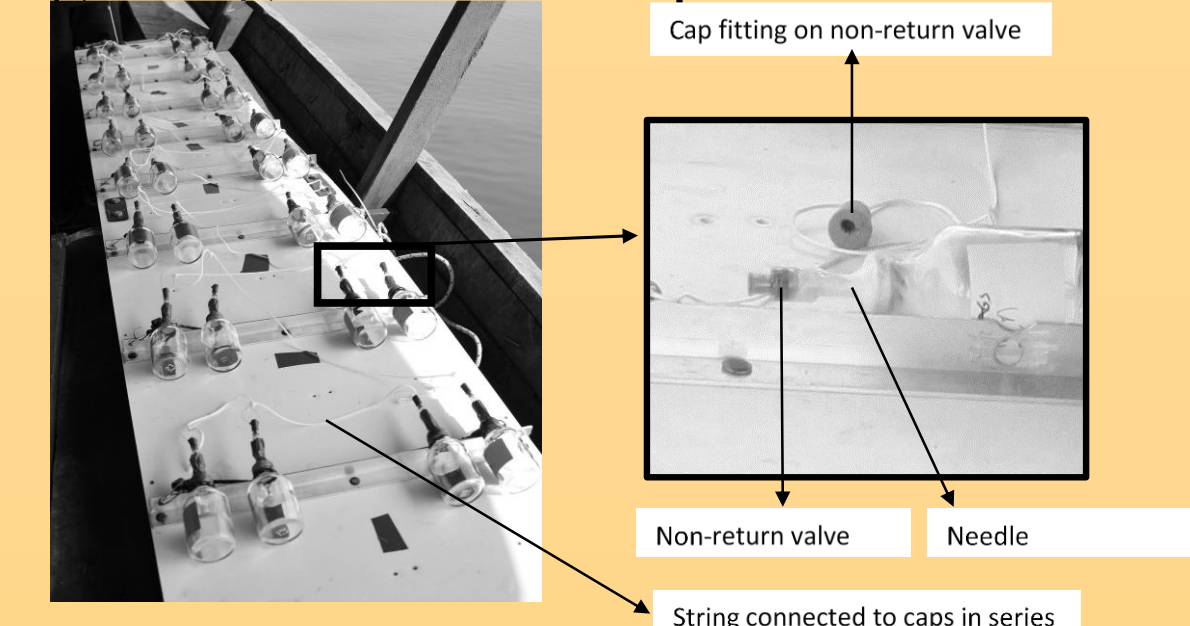
The fraction of the integrated AOM rates potentially sustained by Fe reduction,  $\text{NO}_3^-$  reduction and  $\text{SO}_4^{2-}$  reduction shows that Fe reduction is the main process occurring in Kabuno Bay, suggesting that Fe oxides is the main electron acceptor for AOM

## 4. Conclusion: Consequences on representation of the Archean ocean metabolism



## 5. Methods

- 3 sampling campaigns (May 2013, September 2013, August 2014), in dry and rainy season
- A home-made sampler was designed to avoid degassing from the deep waters



- $\text{CH}_4$  oxidation is measured by the decrease of  $\text{CH}_4$  concentrations in incubations, without and with addition of an inhibitor of sulfate-reducing bacteria activity (molybdate)
- Other parameters measured: nutrients ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ ),  $\text{SO}_4^{2-}$ ,  $\text{H}_2\text{S}$ , dissolved Fe and Mn, Fe and Mn oxides, pigments, archaeal diversity, etc

