How did ferruginous Archean oceans make methane?

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Reactive Fe(III) minerals can reduce CH_4 emissions by inhibiting microbial methanogenesis and stimulating anaerobic CH_4 oxidation. Thus, it is puzzling how ferruginous Archean oceans supported high CH_4 fluxes that warmed the early Earth under the Faint Young Sun. In this study, we examined the effects of Fe(III) speciation on CH_4 cycling in month-long anoxic incubations of ferruginous sediment from the Archean ocean analogue, Lake Matano, Indonesia, amended with $^{13}CH_4$ and ferrihydrite or goethite. Initially, an endogenous crystalline Fe(III) mineral was reduced, and headspace CH_4 concentrations declined (4-8 Fe(III) reduced per 1 CH_4 consumed). After four days, the native reactive crystalline phase was depleted, and reduction of endogenous and/or synthetic ferrihydrite began, along with CH_4 production (20x higher with endogenous vs. synthetic ferrihydrite). The offset between the initial period of CH_4 consumption and subsequent appearance of ^{13}C label in DIC suggests that CH_4 was initially assimilated into biomass and subsequently remineralized. 16S rRNA sequences with highest similarity to Bathyarchaeota (Miscellaneous Crenarchaeota Group), with recently discovered methylotrophic methanogenic capacity, were most abundant in the sediment used to inoculate the incubations. After two weeks, 16S rRNA sequences with highest similarity to Fe(III)-reducing Deltaproteobacteria (Desulfuromonadaceae and Geobacteraceae, in ferrihydrite vs. goethite enrichments, respectively) became dominant. The decline in Bathyarchaeota 16S rRNA sequences during the incubation as well as the presence of *mcrA* sequences with highest similarity to Euryarchaeota in two metagenomes from day 15 suggests that methanogenesis in the enrichments was likely performed by Euryarchaeota. The rapid shift from CH_4 consumption to production based on availability of endogenous Fe(III) oxides suggests that Fe(III) phase and aggregate size could have exerted important controls on CH_4 fluxes from Archean oceans. *This research was funded by NASA Exobiology grant NNX14AJ87G, the NASA Astrobiology Institute (Alternative Earths team NNA15BB03A), and a small research grant from the Center for Dark Energy Biosphere Investigations (C-DEBI).*