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Metal-dependent anaerobic oxidation of methane in Eastern Mediterranean mud volcanoes and its potential link to anoxic silicate weathering

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Marine sediments are a vast reservoir of global CH_4, yet only a small fraction of CH_4 escapes from the sedimentary reservoirs to the water column and atmosphere. It is generally accepted that sulfate-reduction (SR) coupled anaerobic oxidation of methane (AOM) mediated by microbial communities plays an important barrier role in regulating marine methane emission, profoundly influencing the global carbon-sulfur cycle. Trace elements participate in microbial activities in the form of metal enzymes or coenzymes, but the coupling relationship between trace elements and AOM process remains unclear. To bridge this knowledge gap, we analyzed a series of sediments collected from mud volcanoes and pockmarks in the Eastern Mediterranean Sea (EMS) by combining sediment lipid biomarkers and trace element geochemistry of bulk sediment, sediment detrital fractions and lipid fractions. Results showed that the bulk sediments in pockmarks and reference stations obviously inherit the characteristics of hemipelagic sediments in the EMS, with higher contents of CaO and MgO. The bulk sediments from mud volcanoes were significantly enriched in SiO_2, Fe_2O_3, and Na_2O, which is derived from the mud breccia in mud volcano system. Surprisingly, lipid biomarkers associated with anaerobic methanotrophic archaea were detected but sulfate-reducing bacteria were absent, implying that SR was decoupled with AOM while metal-dependent AOM may be widely present in the mud volcanoes of the EMS. Transition metal elements are depleted in sediment detrital fractions, these trace elements were apparently released from detrital fractions through the process of anoxic silicate weathering, the enrichment of these elements in the corresponding lipid fractions is the direct evidence that confirm the utilization of trace elements by microbes. As the most common detrital mineral in the EMS, smectite alteration (anoxic silicate weathering) can provide trace elements such as V, Co, Ni and Zn to accelerates various biogeochemical processes in mud volcano area. At last, our research emphasizes the promotion of high temperature on smectite alteration and provides a case of the influence of clay mineral phase transition on biogeochemical process of cold seep system for the first time, which is considered to be an effective analogy with the methane-rich and sulfate-poor Archean ocean.