Vivianite formation and the role of Fe-mediated anaerobic oxidation of methane in deep-sea sediments

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Methane is a powerful greenhouse gas and the most abundant hydrocarbon in the atmosphere. Anaerobic oxidation of methane (AOM) plays a key role in preventing the release of methane from marine sediments. Sulfate typically represents the most important electron acceptor for AOM in marine sediments. However, recent studies provided evidence that AOM can also be coupled to the reduction of iron (Fe) oxides. Importantly, the Fe-mediated anaerobic oxidation of methane (Fe-AOM) can facilitate the formation of reduced Fe-phosphate minerals (e.g. vivianite) by releasing phosphate and ferrous Fe to the pore water.

In this study, we combined microscopic and spectroscopic analyses of handpicked mineral aggregates with sediment geochemical analyses to characterize the distribution and mineralogy of Fe-phosphate minerals present in methane-rich sediments from the South China Sea. We demonstrate that authigenic vivianite formation occurs in the Fe oxide-rich sediments below the sulfate-methane transition zone (SMTZ). Our results reveal that vivianite acts as an important burial phase for both Fe and P below the SMTZ at our study site. The high handpicked vivianite concentrations of up to 1.58 wt.‰ indicate that Fe reduction coupled to AOM drives a sink-switching from P associated with Fe-oxides to vivianite below the SMTZ. Thus, while Fe-AOM likely consumes only a relatively small percentage of methane compared to sulfate-driven AOM in modern marine sediments, our study supports recent findings that it may have broad implications for the deep Fe, P cycling and related biogeochemical processes. Vivianite formation can be an indicator for the occurrence of Fe-AOM under low-sulfate but high-methane, ferric conditions which are widely observed in many different sediments. Considering that such sulfate-poor but methane-rich conditions also prevailed in the Archean ocean replete with Fe oxide-rich deposits known as banded iron formations (BIFs), it is possible that Fe-AOM was important for Fe, P and methane cycling on the early Earth.