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Aragonite precipitation induced by anaerobic oxidation of methane in shallow-water seeps, Tyrrhenian Sea, Italy

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In the shallow-water organic-poor silicate sands off the West coast of Elba, Italy, we found aragonite precipitates within a radius of 10 cm to methane seeps in 20 - 40 cm sediment depth. The shallow seep site was mapped by SCUBA diving and in an area of 100 m^2 nine gas emission spots were observed. The gas emission, containing 73 Vol. % methane, was measured to be 0.72 L m^{-2} d^{-1}. Findings of anaerobic methane oxidizing archea (ANME 1, 2, 2a, 2b) and sulphate reducing bacteria (SRB) as well as in vitro rate measurements of anaerobic oxidation of methane (AOM) with a maximum of 67 ± 7 nmol CH_4 cm^{-3} d^{-1} led to the hypothesis that carbonate precipitation is coupled to these microbial processes.

Porewater analysis showed elevated concentrations of dissolved inorganic carbon (DIC) (up to 15.5 mmol L^{-1}) and hydrogen sulfide (up to 6.6 mmol L^{-1}). The presence of bicarbonate and the ambient temperature (14 – 25 °C) facilitate the precipitation of needle-shaped aragonite. Oxygen isotope compositions of the mineral are consistent with the ambient temperatures and may indicate a recent diagenetic formation of this mineral.

Although precipitation should not be preserved in these sandy permeable sediments, influenced by seasonality, wave action, and fluid flow, we found up to 10-50 cm^3 irregular pieces of cemented sand grains, very often encrusting dead seagrass rhizomes.

Commonly known carbonate structures, especially from the deep sea, are chimneys, mounds, hardgrounds and nodules. These structures are well known from seep and vent sites, usually showing the same range of stable carbon isotope fractionation as the escaping methane.

The permeable sediment at the Elba site possibly allows the gas to frequently change its pathway to the sediment surface and thus precipitation can occure at several spots and more irregular than in the reported sites. Preservation of precipitates, however, requires sufficient authigenic aragonite to be formed before fluid dynamics changed the flow path.

The Elba aragonites, showed a carbon isotope signature of -14.9‰ vs. VPDB, mirroring the isotopic signature of the pore-water DIC at this sediment depth. Similar δ^{13}C-compositions of -15.3‰ were obtained for the discharging methane, giving room for discussion about the origin of the gas.

We suppose that AOM is the main driver for aragonite precipitation in the permeable sands at the shallow-water seeps because of (1) very low organic carbon contents (0.5 mg/g) in the sediment, (2) ^{13}C enrichment in the methane gas, (3) elevated DIC concentrations in the pore-water, and (4) AOM in vitro activity. Thus, aragonite precipitates of the seep site near Elba may represent a unique system to study ongoing abiogenic seep carbonate formation at shallow depth as a modern analogue for seep carbonates occurring in the geological record.