Goldschmidt 2026 Abstract
https://doi.org/10.46427/gold2026.36789

Carbonate dynamics in brackish methane-bearing Baltic Sea shelf sediment

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Continental shelf sediments of the southeastern Baltic Sea exhibit pronounced variability in carbonate dynamics under contrasting redox and hydrological regimes. Three settings were investigated: (1) anoxic brackish sediments dominated by organoclastic sulfate reduction (OSR; REF), (2) methane-bearing nearshore sediments (MET), and (3) methane-bearing sediments influenced by submarine groundwater discharge (MET-W). The study integrates dissolved inorganic carbon (DIC), total alkalinity (TA), methane cycling, and authigenic carbonate formation.

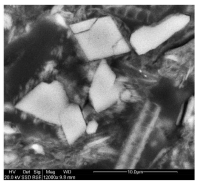
In REF sediments, sulfate persists throughout the profile and methane is absent, indicating OSR as the principal pathway of organic matter degradation. DIC and TA increase with depth and exceed bottom-water concentrations. Downcore decreases in δ^{13}C-DIC reflect DIC production from marine and terrestrial organic matter oxidation. Sediment pore waters are supersaturated with respect to calcite and dolomite. Authigenic carbonates co-occur with pyrite. Elevated H_2S and limited reactive Fe constrain pyrite formation, promoting sulfide accumulation and localized carbonate dissolution. Benthic fluxes indicate net export of DIC and alkalinity to the overlying water.

In MET sediments, methane increases with depth and isotopic signatures confirm a microbial origin. $\Delta DIC:\Delta SO_4^{2-}$ ratios (~1 to >4) indicate combined contributions from OSR, sulfate-dependent anaerobic oxidation of methane (AOM), and methanogenesis. A δ^{13}C-DIC minimum at the sulfate–methane transition confirms active AOM. Elevated DIC and TA drive carbonate supersaturation, and authigenic calcite, dolomite, and siderite occur. Methane cycling enhances alkalinity production and carbonate precipitation.

In MET-W sediments, high methane concentrations coincide with freshwater seepage, reflected by downcore decreases in Cl^-, Ca^{2+}, and Mg^{2+}. AOM rates exceed those at other sites by two orders of magnitude and dominate DIC production. δ^{13}C-DIC signatures indicate isotopic buffering during carbonate precipitation. High DIC and TA generate strong supersaturation: euhedral dolomite is common. Authigenic carbonates constitute an efficient inorganic carbon sink, with carbonate accumulation rates highest at MET-W (484 ± 13 µmol m^{-2} d^{-1}), compared to MET (254 ± 58) and REF (60 ± 35).

Carbonate dynamics are governed by interactions among OSR, methanogenesis, AOM, sulfate availability, and freshwater input. Methane oxidation, particularly under groundwater influence strongly promotes carbonate precipitation and inorganic carbon sequestration.

Project funded by the National Science Centre, Poland (grant 2022/45/B/ST10/00395).


Authigenic dolomite. SEM image.

