

The imprint of methane seepage on geochemical processes in cold-water coral mounds on Pen Duick Escarpment, Gulf of Cadiz

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The production of hydrogen sulfide during anaerobic oxidation of methane (AOM) strongly imprints the geological record of cold-water coral mounds on Pen Duick Escarpment, Gulf of Cadiz. This study examines mechanisms of carbonate dissolution and precipitation in coral-containing, hydrocarbon-influenced, siliciclastic sediments on cores from Alpha and Beta Mound retrieved during R/V Marion Dufresne Cruise 169 MICROSYSTEMS. Analyses of solid-phase iron minerals, multi-element pore-water composition and carbonate mineralogy combined with $\delta^{34}\text{S}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotope measurements reveal a strong coupling between post-depositional diagenetic changes with respect to the S and Fe cycle and alternations in the sedimentary carbonate composition. The sediments exhibit an almost complete consumption of reactive Fe-mineral phases due to the formation of iron-sulfide minerals with average degree of pyritization (DOP) values > 0.7 . $\delta^{34}\text{S}_{\text{pyrite}}$ values of up to -2% indicate that this process is driven by the upward diffusion of ^{34}S -enriched hydrogen sulfide produced during AOM in deeper sediment layers. In the top part of the mounds, this lack of reactive Fe-minerals combined with ongoing, in-situ organoclastic sulfate reduction (non-AOM) leads to a net increase in proton production that is not compensated by Fe-oxide reduction and iron-sulfide precipitation processes, but induces coral dissolution. Additionally, Ca^{2+} and Mg^{2+} pore-water profiles and carbonate mineralogy data suggest the precipitation of high-Mg calcite in deeper layers. Authigenic carbonate precipitation is promoted by the contemporaneous production of DIC from AOM as evidenced by depleted $\delta^{13}\text{C}_{\text{carbonate}}$ signals.