

## **Impacts of ocean acidification on the carbonate system at the sediment-water interface: a case-study in the NW Mediterranean Sea**

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According to common predictions, carbon dioxide (CO<sub>2</sub>) uptake from the atmosphere into the oceans will decrease the average pH of seawater by 0.06-0.32 pH units by 2100. Ocean acidification alters chemical equilibria in seawater and thus potentially impacts marine ecosystem structure and functioning. Shelf regions play a key role for an important fraction of marine life and represent an important part of the global carbon cycle. Due to shallow water depth, chemistry in the water column is strongly coupled with biogeochemistry in the sediments. The aim of the present work is to investigate the impact of ocean acidification on carbonate chemistry. It focuses especially on exchange fluxes of dissolved inorganic carbon (DIC), total alkalinity (TA) and calcium through the sediment-water interface, and its impact on calcium carbonate precipitation or dissolution. For this purpose, sediment cores were incubated *ex situ* with an open flow of CO<sub>2</sub> enriched seawater for 22 days (pHT=7.4, pH reported on the total proton scale). In parallel, sediment cores were incubated as a control with untreated seawater. Incubations took place in a water bath in a dark room with controlled temperature (14°C). Oxygen and pH microprofiles were recorded in the top first mm of the sediment during the whole experiment every 3 days. On 7 occasions, cores were isolated and incubated for 12 hours to estimate fluxes of DIC, TA, oxygen and nutrients. Porewater profiles of DIC, TA, calcium and nutrients were analyzed before and after incubation. On the solid phase, the content of particulate organic carbon, the C:N ratio and its isotopic  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  signature have been determined. In addition, total carbon contents have been measured and X-Ray diffraction was used to look for phase shifts between calcite and aragonite. A net decrease of pH was observed in the upper sediment layers, as well as an increase of DIC and TA pore water concentrations. The acidified cores showed higher DIC and TA exchange fluxes during the incubations in isolation, whereas oxygen exchange fluxes were independent of pH. Significant changes in the solid phase of the sediments could not be identified and the calcium pore water concentrations seemed not to be affected by acidification of the overlying waters during the given time scale. These results are put in the framework of coastal ocean acidification and are used to understand how the acidification changes the carbonate chemistry in the pore waters and constrain dissolution/precipitation of calcium carbonate.