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The influence of a diffusive boundary layer on early organic matter and calcium carbonate diagenesis

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The diffusive boundary layer (DBL) is a thin fluid layer that extends a few hundred microns to millimeters above the sediment-water interface. In the DBL, molecular diffusion is the dominant mode of solute transport and laboratory experiments of sediment calcium carbonate ($CaCO_3$) dissolution in seawater suggest that diffusion through the DBL is the rate-limiting step for $CaCO_3$ dissolution at the seafloor. Nevertheless, earlier assessments of in situ $CaCO_3$ dissolution at the sediment-water interface in the central equatorial Pacific indicated that DBL thickness does not impact overall dissolution rates (Berelson et al., 1994). Here, using a diagenetic model that incorporates the latest $CaCO_3$ dissolution kinetics, organic-matter degradation, and a DBL above the sediment-water interface, we examine reasons for this apparent inconsistency.

We show that DBL control of benthic $CaCO_3$ dissolution is a function of both organic matter flux to the seafloor and bottom-water saturation state with respect to $CaCO_3$. In shallower, supersaturated waters, thicker DBLs trap organic-matter degradation by-products in sediment porewaters and in most cases favor $CaCO_3$ dissolution. In deeper, undersaturated waters, thicker DBLs maintain sediment porewater near equilibrium with respect to $CaCO_3$ and thus facilitate $CaCO_3$ preservation. Regardless of the bottom-water saturation state with respect to $CaCO_3$, DBL thickness strongly affects the depth distribution of porewater solutes and should be taken into account when interpreting measured or reconstructed sedimentary pH profiles. More broadly, our modeling results stress that the DBL is a diffusion barrier that acts in both directions. In sediments subject to a strong organic matter delivery, thicker DBLs can inhibit oxygen penetration and promote porewater anoxia, thus affecting both sediment chemistry and biology.

Reference:

Berelson, W.M., Hammond, D.E., McManus, J. and Kilgore, T.E. (1994) Dissolution kinetics of calcium carbonate in equatorial Pacific sediments. Global Biogeochemical Cycles 8, 219-235.