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Accumulation of Peptides and Deaminated Peptides in Sediment Porewaters Under Different Redox Conditions.

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Sediment early diagenesis acts as an interface between the short and long organic carbon cycles. Examining porewater dissolved organic matter (DOM) composition and dynamics provides a deeper mechanistic understanding of organic matter degradation in sediments. Evidence to date suggests that oscillating redox conditions have a major impact on both DOM cycling in sediments as well as on the benthic DOM flux. This work will examine porewater DOM accumulation under anoxic and mixed redox conditions with a primary focus on the degradation of proteins within the sediment column. Incomplete hydrolysis of proteins and peptides to free amino acids leads to catabolic deamination of non-hydrolyzed peptides, and we hypothesize that products of deamination are refractory and accumulate in sediment porewaters. We will elucidate the structures of accumulated peptides across four sites in the central and southern California continental margin. These sites are fine-grained and relatively organic-rich, yet vary in their degrees of oxygenation, bioturbation and bioirrigation, and organic carbon burial efficiency. We will compare the distribution of different peptides and deaminated peptides across these sites. Amino acid sequences of deaminated peptides show enrichments in specific amino acids that have been found to inhibit/limit the activities of many peptidases (e.g., proline, tyrosine, and phenylalanine). This work helps fill the knowledge gap on the connection between sediment DOM dynamics and the oceanic DOM cycle and sheds light on addressing how refractory DOM is produced in sediments, using state-of-the-art mass spectroscopy analytical techniques.