

## **Survival of the fittest: phosphorus burial in the sulfidic deep Black Sea**

Peter Kraal, Nikki Dijkstra, Thilo Behrends, and Caroline Slomp

Utrecht University, Earth Sciences - Geochemistry, Utrecht, Netherlands (p.kraal@uu.nl)

The Black Sea is characterized by permanently anoxic and sulfidic deep waters. Studies of the mechanisms of P burial in such a setting can be used to improve our understanding of P cycling in modern coastal systems undergoing eutrophication and ancient oceans during periods of anoxia in Earth's past.

Here, we present phosphorus and iron (Fe) pools as determined in surface sediments along a transect from oxic shallow waters to sulfidic deep waters in the northwestern Black Sea, using a combination of bulk chemical analyses and micro-scale X-ray fluorescence ( $\mu$ XRF) and X-ray absorption spectroscopy ( $\mu$ XAS). We show that under oxic bottom water conditions, ferric iron oxides (Fe(III)ox) in surficial sediment efficiently scavenge dissolved phosphate from pore waters. Under these conditions, Fe(III)ox-bound P constitutes the main P pool at the sediment surface, but rapidly declines with depth in the sediment due to anoxic diagenesis.

The transition from shallow (oxic) to deep (sulfidic) waters along the depth transect is reflected in a slight increase in the fraction of organic P. We also show evidence for authigenic calcium phosphate formation under sulfidic conditions at relatively low dissolved PO<sub>4</sub> concentrations. Furthermore, we provide spectroscopic evidence for the presence of Fe(II)-Mn(II)-Mg-P minerals in sediments of the sulfidic deep basin. We hypothesize that these minerals are formed as a result of input of Fe(III)ox-P from shallower waters and subsequent transformation in either the water column or sediment. This finding suggests an unexpected strength of Fe-P shuttling from the shelf to the deep basin. While the presence of Fe-P species in such a highly sulfidic environment is remarkable, further analysis suggests that this P pool may not be quantitatively significant. In fact, our results indicate that some of the P that is interpreted as Fe-bound P based on chemical extraction may in fact be Ca-associated PO<sub>4</sub> consisting of a combination of fish debris and adsorbed P.