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The impact of depositional conditions on biogeochemical cycling of iron and stable iron signatures in sediments of the Argentina Continental Margin

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The Argentina Continental Margin represents a unique geologic setting to study interactions between bottom currents and sediment deposition as well as their impact on (bio)geochemical processes, particularly the cycling of iron (Fe). Our aim was to determine (1) how different depositional conditions control post-depositional (bio)geochemical processes and (2) how stable Fe isotopes (δ^{56}Fe) of pore water and solid phases are affected accordingly. Furthermore, we (3) evaluated the applicability of δ^{56}Fe of solid Fe pools as a proxy to trace past diagenetic alteration of Fe, which might be decoupled from current redox conditions. Sediments from two different depositional environments were sampled during RV SONNE expedition SO260: a site dominated by contouritic deposition on a terrace (Contourite Site) and the lower continental slope (Slope Site) dominated by hemipelagic sedimentation. Sequentially extracted sedimentary Fe [1] and δ^{56}Fe analyses of extracts and pore water [2,3] were combined with sedimentological, radioisotope, geochemical and magnetic data. Our study presents the first sedimentary δ^{56}Fe dataset at the Argentina Continental Margin.

The depositional conditions differed between and within both sites as evidenced by variable grain sizes, organic carbon contents and sedimentation rates. At the Contourite Site, non-steady state pore-water conditions and diagenetic overprint occurs in the post-oxic zone and the sulfate-methane transition (SMT). In contrast, pore-water profiles at the Slope Site suggest that currently steady-state conditions prevail, leading to a strong diagenetic overprint of Fe oxides at the SMT. Pore-water δ^{56}Fe values at the Slope Site are mostly negative, which is typical for on-going microbial Fe reduction. At the Contourite Site the pore-water δ^{56}Fe values are mostly positive and range between -0.35‰ to 1.82‰. Positive δ^{56}Fe values are related to high sulfate reduction rates that dominate over Fe reduction in the post-oxic zone. The HS^- liberated during organoclastic sulfate reduction or sulfate-mediated anaerobic oxidation of methane (AOM) reacts with Fe^{2+} to form Fe sulfides. Hereby, light Fe isotopes are preferentially removed from the dissolved pool. The

isotopically light Fe sulfides drive the acetate-leached Fe pool towards negative values. Isotopic trends were absent in other extracted Fe pools, partly due to unintended dissolution of silicate Fe masking the composition of targeted Fe oxides. Significant amounts of reactive Fe phases are preserved below the SMT and are possibly available for reduction processes, such as Fe-mediated AOM [4]. Fe^{2+} in the methanic zone is isotopically light at both sites, which is indicative for a microbial Fe reduction process.

Our results demonstrate that depositional conditions exert a significant control on geochemical conditions and dominant (bio)geochemical processes in the sediments of both contrasting sites. We conclude that the applicability of sedimentary $\delta^{56}Fe$ signatures as a proxy to trace diagenetic Fe overprint is limited to distinct Fe pools. The development into a useful tool depends on the refining of extraction methods or other means to analyse $\delta^{56}Fe$ in specific sedimentary Fe phases.

References:

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