Metastable iron sulphur mineral phases drive highly dynamic biogeochemical cycles in marine sediments

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Iron (Fe) redox reactions in marine sediments play an important role in biogeochemical cycles of other elements such as sulphur (S). The formation of metastable Fe-S-minerals or pyrite, reductive dissolution of Fe(III) (oxyhydr)oxides or other microbially mediated Fe redox reactions drive the cycling of Fe. In order to determine the Fe stability towards redox changes, intact marine sediment cores (Aarhus Bay, Denmark) were incubated under a 12 h light-dark cycle for 7 days and subsequently rigorously mixed. Geochemical parameters (Fe^{2+}, O_2, dissolved S-species) were quantified at high spatial and temporal resolution using microelectrodes. Sequential extractions of solid phase Fe and ^{57}Fe-specific Mössbauer spectroscopy were performed to identify changes in Fe mineral phases.

We observed a decrease of the initial 300 µM Fe^{2+} concentration in 3 cm sediment depth during the initial 7 days of incubation of the marine sediment cores to only 50 µM. Physical mixing after 7 days (simulation of a storm event or bioturbation) led to extensive re-mobilization of Fe^{2+} into the sediment porewater, up to 250 µM. Fe mineral phases shifted from amorphous/poorly crystalline Fe to higher crystallinity phases within the first 7 days of incubation and shifted back towards less crystalline Fe mineral phases after the mixing event. The relative abundance of a metastable Fe-S-mineral phase increased during the initial 7-day incubation and dropped after mixing. Finally, in the top 2 mm, during the first days of incubation, elevated Fe^{2+} concentrations of up to 75 µM were quantified in light-penetrated surface sediment, probably caused by Fe(III) photoreduction.

Our findings show that the Fe^{2+} distribution in marine sediments is not only controlled by microbial Fe(III) reduction. A significant amount of Fe^{2+} gets released during physical perturbation, as well as by Fe(III) photoreduction. Especially the processes of physical perturbation and Fe(III) photoreduction have so far not been considered to feed the Fe^{2+} budget in natural sediments along redox gradients.