

Iron sequestration during green-clay authigenesis – a limiting factor for the benthic fluxes of iron?

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Recent advances in the study of iron biogeochemistry have greatly improved our understanding of the processes and environmental controls affecting the benthic fluxes of iron at the sediment-seawater interface. The increasing evidence of substantial sequestration of dissolved Fe²⁺ during reverse weathering in oceanic sediments challenges our long-standing conceptual view that the early diagenetic formation of Fe-rich clay minerals, also-called green-clay authigenesis, is only of little importance in the benthic cycle of iron [1-2]. Herein, we show that microbial-catalyzed dissolution of highly labile Fe-(oxyhydr)oxides in suboxic subsurface sediments creates a secondary reservoir of dissolved Fe²⁺ that is limited by the competing formation of green-clay and pyrite. The rate of Fe deposition by green-clay authigenesis amounts to 76-127 $\mu\text{mol Fe cm}^{-2}\cdot\text{kyr}^{-1}$ for modern deep-sea sediments, which is significantly higher than the global burial rate of iron related to pyrite in organic-poor, deep-sea sediments ($\sim 30 \mu\text{mol Fe cm}^{-2}\cdot\text{kyr}^{-1}$; [2]). In modern and ancient continental shelves, which are characterized by higher temperature, an elevated supply and reflux of dissolved and particulate Fe, enhanced microbial activity, and increased hydrodynamic energy, compared to deep-sea environments, the rate of iron burial by green-clay is ~ 50 -200 times faster and can amount up to ~ 7 -16 $\text{mmol Fe cm}^{-2}\cdot\text{kyr}^{-1}$. We therefore propose that green-clay authigenesis is a limiting factor for the benthic fluxes of iron occurring in modern sediments, and is thus controlling a huge variety of biogeochemical processes taking place on the ocean floor.

[1] Baldermann, A., Dietzel, M., Mavromatis, V., Mittermayr, F., Warr, L.N., Wemmer, K., 2017. The role of Fe on the formation and diagenesis of interstratified glauco-nite-smectite and illite-smectite: A case study of Upper Cretaceous shallow-water carbonates. *Chem. Geol.* 453, 21-34.

[2] Baldermann, A., Warr, L.N., Letofsky-Papst, I., Mavromatis, V., 2015. Substantial iron sequestration during green-clay authigenesis in modern deep-sea sediments. *Nat. Geosci.* 8, 885-889.