

The role of deep-water glauconitization in the sedimentary iron cycle

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The iron bioavailability significantly influences biological processes in modern (deep sea) ecosystems and in particular in superficial marine sediments, and has been of major significance throughout the geological record. Reservoir-flux models are currently used to examine mass balance relationships in the marine iron cycle, assuming steady-state between continental iron sources and marine sulfidic sediment sinks. However, the characterization and quantification of iron uptake by glauconitization has not been included and therefore its importance in the marine sedimentary iron cycle remains uncertain.

In the modern, deep-sea environment of ODP Site 959, Ivory Coast-Ghana Marginal Ridge (eastern equatorial Africa) most of the highly reactive, (nano)particulate ferrihydrite input was directly used to form early diagenetic Fe(III)-smectite, glauconite-smectite (Gl-S) and finally evolved glauconite minerals (Baldermann et al., 2013). The latter phases occur together with late diagenetic pyrite overgrowths. We present here new rates of iron sequestration attributed to deep-water glauconitization and pyritization, based on combined electron energy-loss spectroscopy data, high-resolution transmission electron microscopy images and chemical composition data of separated green grain sub-fractions and bulk sediment samples that were taken from the top 25 m of sediments. In the near-surface sediments (≤ 3 mbsf) iron uptake related to green-clay authigenesis ranged from 23 to 204 $\mu\text{MFe}/\text{cm}^2/\text{ky}$ (76 $\mu\text{MFe}/\text{cm}^2/\text{ky}$ on average), which is 3 to 37 times faster (10 times on average) than that of the pyritization reaction (2 to 29 $\mu\text{MFe}/\text{cm}^2/\text{ky}$). During advanced stages of early diagenesis (≥ 5 mbsf) pyritization becomes more important (28 to 131 $\mu\text{MFe}/\text{cm}^2/\text{ky}$) but iron sequestration by glauconitization remains 1 to 5 times faster (36 to 167 $\mu\text{MFe}/\text{cm}^2/\text{ky}$ with an average rate of 72 $\mu\text{MFe}/\text{cm}^2/\text{ky}$). Our observations clearly reveal that green-clay authigenesis significantly limits the iron bioavailability in modern, deep-sea sediments and should be considered in future models of the marine iron cycle.

Baldermann, A., Warr, L.N., Grathoff, G.H. and Dietzel, M. (2013) The rate and mechanism of deep-sea glauconite formation at the Ivory Coast - Ghana Marginal Ridge. *Clays and Clay Minerals*, **61**, 258-276.