



Experimental Oxidation of Iron Sulphides from Intertidal Surface Sediments: Stable Isotope Effects (S, O, C)

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Top intertidal sediments show a pronounced zone of activities of sulphate-reducing bacteria. Iron sulfides may be formed, but a substantial part is reoxidized to sulfate. Microbial or chemical reoxidation can be further enhanced by a resuspension of surface sediments by tidal currents or storms. The rates of the different processes depend on the site-specific sedimentological properties (e.g., grain size, iron and sulphur contents etc.). In the present study 3 different areas of the German Wadden Sea were studied: a mud flat in the Jade Bay, and sandy sediments in the intertidals of Spiekeroog and Sylt islands. The latter site is part of an in-situ lugworm-exclusion experiment. The goal was the experimental and field investigation of the fate of iron sulfides and the formation of sulphate upon resuspension of intertidal surface sediments in oxygenated seawater.

All sites were geochemically analyzed for dissolved and solid phase iron, manganese, sulphur and carbon phases/species, and sulphate reduction rates were measured using radiotracers. Dissolved chloride and grain sizes analysis were additionally carried out. TOC, S and metal phase contents were higher in mud compared to sandy sediments. Field results demonstrate gross but only minor net sulphide production and a downcore increases in FeS contents, due to intense sulphide oxidation at the surface. Pyrite, on the other hand, was abundant through the sediments due to continuous sediment reworking.

The fate of iron-sulphides and accumulation of sulphate as a function of time was followed in batch experiments using dark suspensions of surface sediments in site-bottom waters at room temperature. During the experiments, each sample was shaken continuously under exposition to oxygen, and sub-samples were taken at the beginning and after discrete time intervals. A very fast oxidation rate of AVS led to a complete exhaustion within a day, whereas Cr(II)-reducible sulfur was initially built up and then decreased. This observation can be explained by a formation of S° and FeOOH, followed by the oxidation of pyrite. The dissolved species (SO_4/Cl ratios) reflected the continuous accumulation of sulphate as an oxidation product. Dissolved inorganic carbonate (DIC) concentrations decreased upon reaction progress, due to the liberation of protons upon iron sulphide oxidation and degassing of carbon dioxide. The $^{13}C/^{12}C$ ratio of the residual DIC increased due to the preferential desorption of $^{12}CO_2$. ^{34}S and ^{18}O contents of dissolved sulphate further show process specific isotope discrimination.

The experiments demonstrate the importance of oxidation on the fate of FeS, but less pyrite and the formation of sulphate from resuspended intertidal surface sediments.

Acknowledgements: The authors gratefully acknowledge discussions and field advice by N. Volkenborn, and financial support from Deutsche Forschungsgemeinschaft during DFG-SPP 'BioGeoChemistry of the Wadden Sea' (JO 307/4, BO 1584/4), Max Planck Society, and Leibniz-IO Warnemünde.