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Iron isotope fractionation associated with pyrite formation and redox changes in Holocene Baltic Sea sediments

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Iron isotope fractionations have been demonstrated to be most pronounced in association with redox processes [1,2]. Furthermore, Fe isotope data of authigenic pyrites represent useful indicators for past variations in the redox state of the ocean in response to changes in atmospheric oxygen [3]. Pyrites older than ∼1.8 Ga display larger variations in their Fe isotope composition compared to more recent ones. However, pyrite formation related to modern cyanobacterial mats produces pronounced negative Fe isotope signatures [4]. In order to further investigate whether the formation of anoxic sediments with distinct pyrite formation can influence the isotopic composition of Fe in the marine environment, well-characterized continental shelf sediments of the Baltic Sea were investigated in this study. Sediment samples were selected from a 6.5 m long piston core from the Gotland basin in the Baltic Sea, collected at about 200 m water depth. These sediments were deposited after the last deglaciation during the last ∼10,000 years. The upper part of the core is laminated and enriched in S, organic C and redox sensitive trace elements, deposited under periodically euxinic conditions, whereas the lower part was deposited under more oxidizing conditions [5]. The main Fe bearing minerals are illite, chlorite, pyrite and potentially mackinawite.

Iron isotope data were measured on a GV Instruments Isoprobe MC-ICPMS by the standard sample bracketing method and are reported as δ^{56}Fe (variations in the ^{56}Fe/^{54}Fe ratio relative to the IRMM-14 standard). The reproducibility for sediment samples is about ± 0.07 permil (2s). In bulk samples, the iron isotope composition varies significantly from –0.22 to +0.21 for δ^{56}Fe. The δ^{56}Fe values are correlated with the S content of the samples, whereas no correlation with bulk Fe concentration was observed. These data provide evidence for considerable Fe isotope fractionation at the bulk sample scale in the marine environment. Moreover, they imply that pyrite as the main S-bearing phase has a negative Fe isotope composition of at least –0.4 permil, representing a storage site for isotopically light Fe in the marine environment. Low δ^{56}Fe values have also been reported for recent pyrites from a euxinic basin of the Black Sea [6]. Further work will focus on analyses of pyrite separates in order to determine the degree of Fe isotope fractionation. Additionally, the present samples will be investigated by Mössbauer spectroscopy for potential correlation of the obtained Fe isotope results with the Fe(II)/Fe(III) ratio in the sediments.

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