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Drivers of benthic iron fluxes and their iron isotopic signature in sub-Antarctic fjord sediments

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Benthic iron (Fe) fluxes from coastal sediments potentially fuel phytoplankton blooms in downstream regions of subpolar islands. A very light dissolved Fe ($Fe(II)_{aq}$) isotopic composition ($\delta^{56}Fe_{aq}$) in the water column is often interpreted as a benthic signal. Here, we combine geochemical data from the solid-phase and pore water, including the $\delta^{56}Fe_{aq}$, to determine the magnitude and drivers of benthic Fe fluxes in sub-Antarctic fjord sediments of South Georgia. We show a significant positive correlation between the magnitude of benthic Fe fluxes and the mass accumulation rates of total organic carbon (MAR_{TOC}): the MAR_{TOC} mainly controls benthic Fe fluxes by determining the depths of the redox zones. At sites with low benthic Fe fluxes, we found a broad range of $\delta^{56}Fe_{aq}$ (-4.04 ± 0.08‰ to -0.98 ± 0.11‰, n = 3) in the pore-water in the upper oxic zone of the sediments, compared to sites with high benthic fluxes (-3.14 ± 0.06‰ and -1.66 ± 0.04‰, n = 3). The broader range for sites characterized by low Fe fluxes is discussed in terms of a variety of isotope fractionation processes and their respective mass balance of $Fe(II)_{aq}$ and solid-phase Fe ($Fe(III)_{solid}$) distribution, including 1) low rates of microbial Fe reduction, (2) reaction of $Fe(II)_{aq}$ with hydrogen sulfide and precipitation of Fe sulfides and (3) re-oxidation of $Fe(II)_{aq}$ within a comparatively broad oxic and nitrate-containing zone.

In summary, we show that $\delta^{56}Fe_{aq}$ values of the pore water in the upper oxic zone of the sediments are variable and strongly influenced by sedimentary processes. The fact that sites with comparatively high benthic Fe fluxes are characterized by a narrower range of $\delta^{56}Fe_{aq}$ makes us cautiously optimistic about the future application of $\delta^{56}Fe_{aq}$ as a benthic signal. However, the application of the $\delta^{56}Fe_{aq}$ in the water column as a robust indicator of a significant benthic supply of Fe_{aq} into the bottom water that is distinct from other oceanic Fe sources remains challenging. We strongly recommend to take early diagenetic processes in surface sediments into account when using the $\delta^{56}Fe_{aq}$ of the water column as a benthic signal, especially in environments with inhomogeneous depositional conditions.