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Os and Pb isotope evolution of Holocene Baltic Fe-Mn precipitates: Divergent tracer for environmental changes and anthropogenic impact

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Osmium (Os) and Lead (Pb) isotope profiles of Baltic ferromanganese precipitates were analyzed in order to decipher their geochemical archive of environmental changes and anthropogenic impacts in the regional scale of a marginal sea over the last 1500 years. The Os isotope system can be used in palaeoceanographic research as tracer for changes in chemical weathering and continental runoff. In the investigated age range the Pb isotope system represents a sensitive monitor for heavy metal pollution and anthropogenic influences. Fe-Mn precipitates from shallow water (20 m depth) of the Mecklenburg Bay (SW-Baltic Sea) have been growing in fine laminated structures since approximately 4300 years at growth rates of up to 0.02 mm/year.

The Os isotopic composition of a homogenized Fe-Mn precipitate (used as a project-internal reference) from the shallow SW-Baltic Sea (^{187}Os/^{188}Os: 1.4795 $\pm$ 0.0038, 1.4798 $\pm$ 0.0038) and of a Fe-Mn precipitate from the Bothnian Bay (70 m depth, N-Baltic, ^{187}Os/^{188}Os: 2.411 $\pm$ 0.005) are in general accordance with former findings of Peucker-Ehrenbrink and Ravizza (1996) with 1.4921 $\pm$ 0.0098 and 2.5567 $\pm$ 0.0042, respectively. For comparison with postglacial Fe-Mn precipitates outside the Baltic Sea system a sample from the Laptev Sea (N-Siberia, 30 m depth) was included in this study. The resulting ^{187}Os/^{188}Os ratio of 1.063 $\pm$ 0.004 is identical with the present-day seawater value of 1.059 $\pm$ 0.007 (Levasseur et al., 1998). Nine age controlled profile steps distributed over the last 1500 years and one prehistoric sub-sample

covering 3000 to 3500 years BP were analyzed for Os isotopes (ages based on the $^{226}Ra_{excess}$/Ba geochronometer; Liebetrau et al., 2002). The latter is characterized by a $^{187}Os/^{188}Os$ ratio of 1.177 $\pm$ 0.005, significantly above seawater values. Palaeoceanographic reconstructions of salinity changes in the central Baltic Sea (Emeis et al ., 2003) indicate for this time interval low salinities. The related increase of freshwater influence corresponds well to the more radiogenic Os signature. The $^{187}Os/^{188}Os$ profile over the last 1500 years documents a significant increase from values close to 1 (0.998 $\pm$ 0.005 , 1.003 $\pm$ 0.005) between 1000 and 1500 years BP to more radiogenic 1.277 $\pm$ 0.003 in the middle of the last century, correlated with a general increase of the Os concentration. For the time interval from 2800 years BP onwards, a general rise in salinity is reconstructed (Emeis et al., 2003) and its pattern correlates with the finding of low $^{187}Os/^{188}Os$ ratios around 1000 years BP, whereas from that period on salinity and Os isotope signature developed in a contrary sense. $^{206}Pb/^{204}Pb$ ratios evolved over the same time interval inversely to the Os isotopes from radiogenic values around 20.2 to less radiogenic signatures of 18.4 in recent times. This observation is interpreted to reflect increasing heavy metal pollution, initiated by Ag and Pb mining in the Harz region (Germany) around 1000 years BP (Liebetrau et al., 2004), suporting a strong atmospheric transport component of Pb.

The opposite implications of Os isotopic composition trend and palaeoceanographic salinity reconstructions for the seawater inflow / riverine input ratio indicate an increasing concentration of radiogenic Os in the latter, at least over the last 1000 years. A general enhancement of weathering and erosion processes as well as a relative shift of the Baltic riverine input towards the highly radiogenic Os sources of the Precambrian Baltic shield could be the controlling factors. The divergent trend in isotopic signatures of Os and Pb are interpreted to reflect differences in transport processes and varying source strengths due to anthropogenic inputs.

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