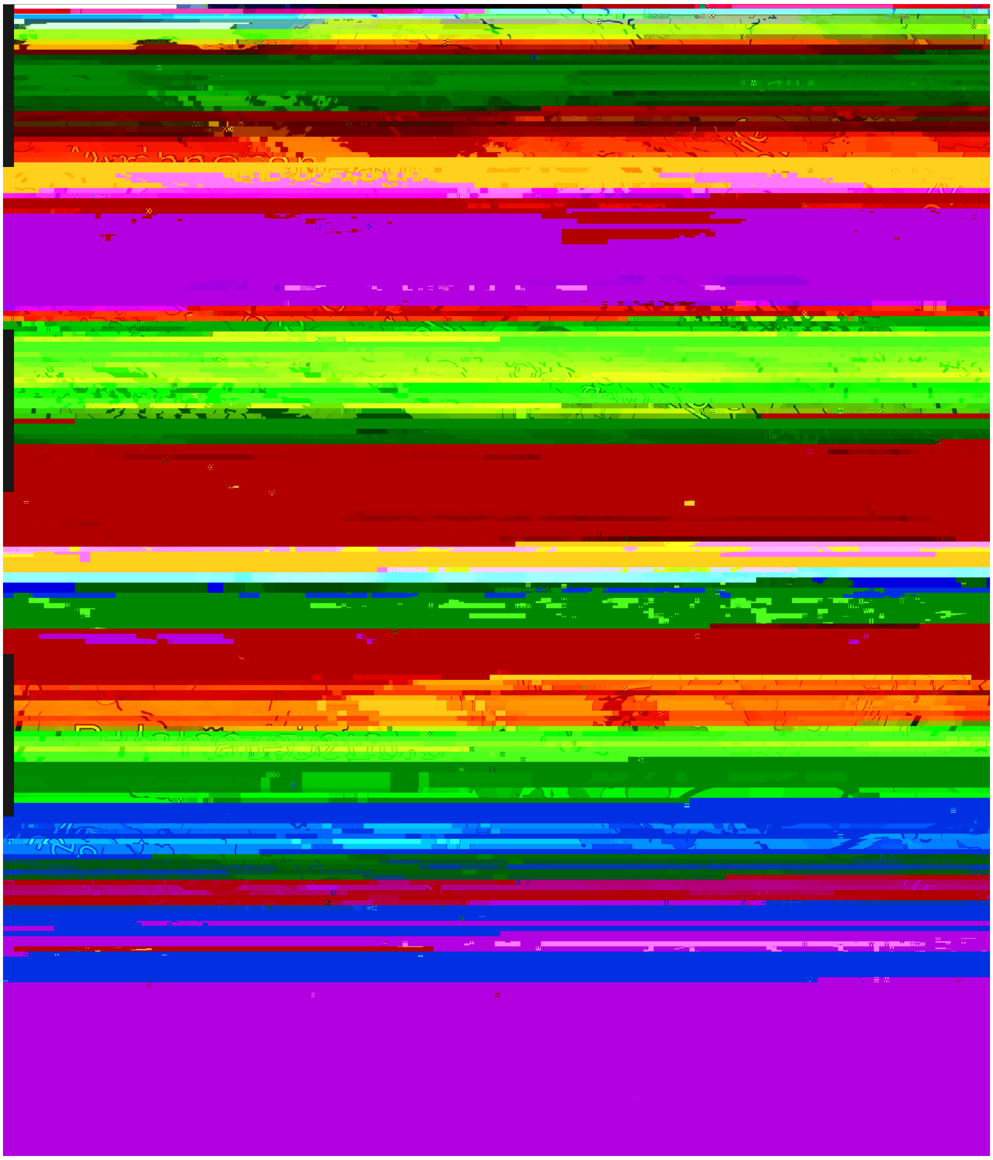

3. SAMPLING AND METHODS

Water samples were collected in the central Baltic Sea at 6 depth profiles and 3 surface water sites during the GEOTRACES cruise on RV Oceania in November 2011. Stichel et al. (2012a,b) provided a detailed description of the sampling procedures, REE/Hf pre-concentration, chromatography, and mass spectrometric measurements. We will therefore describe these only briefly here given that we basically followed the same protocols in the same laboratory at GEOMAR, Kiel, procedures that are identical to the agreed GEOTRACES protocols (http://www.obs-vlfr.fr/GEOTRACES/libraries/documents/Intercalibration/Cookbook.pdf). Sixty liters of seawater were sampled using 3 acid-cleaned 20 L LDPE-collapsible cubitainers for each sample. The deep and surface water samples were taken from a standard rosette equipped with Niskin bottles and a surface pump, respectively. Immediately after collection, samples were filtered through 0.45 µm nitro-cellulose acetate filters. The two river water samples were taken from the Kalix river, Sweden, in June 2012 and the Schwentine river, Germany in July 2012. Both samples were very rich in particles. The Kalix river is characterized by low concentrations of suspended detrital particles but relatively high

bottom waters, while the bottom water sample of the Land-

2009

from 110 to 220 m water depth at the Gotland Deep had initial concentrations as low as at the surface (e.g., 21.1 pmol/kg) and initial ε_{Nd} similar to the inflowing signature of the North Sea ($\varepsilon_{Nd} = \sim-10$, Andersson et al., 1992 associated with the hydrous Fe oxide component (Bau and Koschinsky, 2006). However, it is intriguing that the Hf concentrations increase by a factor of only 1.7 from oxygen-depleted to euxinic waters, while dissolved Fe concentrations increase by up to an order of magnitude in euxinic waters (Turnewitsch and Pohl, 2010). In addition, the Landsort Deep even shows a decrease in Hf concentration of bottom waters. From our data we cannot make a isotopes for a given Nd isotope composition compared to terrestrial rocks and are generally consistent with the global seawater Nd–Hf isotope trend. Note that the central Baltic Sea is essentially dominated by continental inputs without hydrothermal influence. Our data thus provide additional support for the suggestion that hydrothermal influence is probably not a significant source for the seawater Hf two observations strongly suggest that the oceanic residence time of Hf is likely to be much shorter than that of Nd.

The heterogeneously distributed signatures of dissolved Hf isotope signatures in the Baltic Sea seem to contradict the homogeneity of Hf isotope compositions in the open ocean (Rickli et al., 2009; Zimmermann et al., 2009b; Stichel et al., 2012a). Our preferred interpretation is that: (1) the continental Baltic drainage systems have been under the influence of glacial weathering regimes of very different time scales and lithology (e.g., Lundqvist, 1986), which may result in highly variable degrees of incongruent weathering. Therefore, the central Baltic region is not representative of the global continental source heterogeneity in terms of Hf isotope compositions. (2) Mixing within the source areas, such as reflected by large rivers and eolian dust, effectively erase the large local Hf isotopic variability before entering the open ocean.

6. CONCLUSIONS

The first combined Nd–Hf isotope compositions and concentrations in a marginal brackish basin with anoxic bottom waters (the central Baltic Sea) are presented in this study. While Nd is distinctly enriched in bottom anoxic waters, the overall variability of Hf concentrations is rather small. In a high resolution profile at the Gotland Deep, the different geochemical behavior between Hf and Nd is revealed. We propose that Hf is rapidly removed by particles, which prevents Hf accumulation in anoxic waters, while Nd is closely associated with Mn and Fe redox cycling.

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