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Reliable extraction of a deepwater trace metal isotope signal from Fe–Mn oxyhydroxide coatings of marine sediments

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Abstract

The extraction of a deepwater radiogenic isotope signal from marine sediments is a powerful, though under-exploited, tool for the characterisation of past climates and modes of ocean circulation. The radiogenic and radioactive isotope compositions (Nd, Pb, Th) of ambient deepwater are stored in authigenic Fe–Mn oxyhydroxide coatings in marine sediments, but the unambiguous separation of the isotopic signal in this phase from other sedimentary components is difficult and measures are needed to ensure its seawater origin. Here the extracted Fe–Mn oxyhydroxide phase is investigated geochemically and isotopically in order to constrain the potential and the limitations of the reconstruction of deepwater radiogenic isotope compositions from marine sediments.

Our results show that the isotope compositions of elements such as Sr and Os obtained from the Fe–Mn oxyhydroxide fraction are easily disturbed by detrital contributions originating from the extraction process, whereas the seawater isotope compositions of Nd, Pb and Th can be reliably extracted from marine sediments in the North Atlantic. The main reason is that the Nd, Pb and Th concentrations in the detrital phase of pelagic sediments are much lower than in the Fe–Mn oxyhydroxide fractions. This is reflected in Al/Nd, Al/Pb and Al/Th ratios of the Fe–Mn oxyhydroxide fractions, which are as low as or even lower than those of hydrogenetic ferromanganese crusts. Mass balance calculations illustrate that the use of the $^{87}Sr/^{86}Sr$ isotope composition to confirm the seawater origin of the extracted Nd, Pb and Th isotope signals is misleading. Even though the $^{87}Sr/^{86}Sr$ in the Fe–Mn oxyhydroxide fractions is often higher than the seawater Sr isotope composition, the corresponding detrital contribution does not translate into altered seawater Nd, Pb and Th isotope compositions due to mass balance constraints. Overall the rare earth element patterns, elemental ratios, as well as the mass balance calculations presented here highlight the potential of using authigenic Fe–Mn oxyhydroxide coatings as paleoceanographic archives for the analysis of past seawater Nd, Pb and Th isotope compositions.

Keywords: Neodymium; Lead; Thorium; Fe–Mn oxyhydroxides; Leaching; Mass balance

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1. Introduction

The chemical extraction (leaching) of the seawater-derived Nd, Pb and Th isotope signal in the authigenic and early diagenetic Fe–Mn oxyhydroxide phase of marine sediments offers great potential for paleoceanographic and paleoclimatic purposes because it can yield essential information on sub-millennial fluctuations of marine environmental conditions. The benefit of using these seawater-derived radiogenic or radioactive trace metal isotope signatures is that they are not biased by biological processes, unlike other stable isotope or elemental ratio proxies. The analytical approach, however, is not trivial and an inherent caveat of the leaching of Fe–Mn oxyhydroxide coatings from marine sediments is the lack of unambiguous evidence for its unbiased deepwater origin.

Due to its residence time in seawater of 600 to 2000 years, Nd isotopes are increasingly used as a quasi-conservative water mass tracer for the present and past ocean (Frank, 2002; Goldstein and Hemming, 2003; Piotrowski et al., 2005). Lead is removed much faster from the water column, with an average residence time of only about 50 years in the Atlantic (Henderson and Maier-Reimer, 2002). Therefore, dissolved Pb isotope records are suitable archives for the detection of changes in local input sources (Frank, 2002; van de Flierdt et al., 2003; Foster and Vance, 2006). Dissolved Th isotopes in seawater are, as yet, a largely unemployed tool for the determination of changes in particle fluxes from the continents to the oceans because the ^{232}Th/^{230}Th is strongly controlled by the presence or absence of particulates in seawater (Guo et al., 1995; Robinson et al., 2004). As a consequence, higher particle fluxes from the continents to the open ocean should result in elevated seawater ^{232}Th/^{230}Th. Considering the repeated deposition of ice rafted debris (IRD) layers during Heinrich events over the last glacial cycle, ^{232}Th/^{230}Th might serve as a good proxy for the correlation of North Atlantic sediment cores in the absence of conspicuous IRD layers.

Rare Earth Element (REE) porewater profiles of marine pelagic sediments suggest that under oxic to suboxic conditions trace metals (Sr, Nd, Os, Pb, Th) are scavenged from porewaters and incorporated into Fe–Mn oxyhydroxide coatings within the uppermost few centimetres below seafloor (Haley et al., 2004). These authors found most elevated REE concentrations in the upper 5 cm below seafloor, which indicates that most trace metals are incorporated into Fe–Mn oxyhydroxides within this zone or slightly below. Haley et al. (2004) also illustrated the effect of anoxic porewaters, where Fe–Mn oxyhydroxides are dissolved leading to trace metal concentrations in the pore waters, which are an order of magnitude higher than those found under oxic conditions (see also Elderfield and Sholkovitz, 1987; Thomson et al., 1993, 1995). Therefore, in studies employing the Fe–Mn oxyhydroxide fraction as paleoceanographic archives it is crucial to assess whether pore water anoxia prevailed at any time, which may have obliterated the original seawater signal.

It has also been suggested that, locally, the original authigenic Fe–Mn oxyhydroxide signal in marine sediments can be disturbed through pre-formed riverine Fe–Mn oxides on detrital material (Bayon et al., 2004). These authors concluded that the authigenic Fe–Mn oxyhydroxide signal in a sediment core from the Angola basin was biased through pre-formed detrital Fe oxide component associated with Congo river material transferred to the sedimentation site (Bayon et al., 2004). This issue is difficult to quantify in the interpretation of past seawater trace metal isotope compositions derived from Fe–Mn oxyhydroxide coatings. Core-top calibrations, directly comparing the extracted authigenic fraction with direct seawater measurements, are the best tool to date to detect such pre-formed oxides in the case of Nd and Th isotopes. For Pb isotopes, however, this test cannot be conducted because of anthropogenic disturbance of the natural seawater Pb isotope compositions (Schaule and Patterson, 1981; Alleman et al., 1999).

Measures are required to assess the reliability of the chemically extracted authigenic trace metal isotope signal. For this purpose, in previous studies using the Nd isotope composition of Fe–Mn oxyhydroxide coatings in pelagic sediments, the Sr isotope composition of the same fraction was measured to confirm the pure seawater origin of the Nd in the oxyhydroxide leachate (Rutberg et al., 2000; Piotrowski et al., 2004, 2005). Strontium is a conservative element in seawater with a residence time on the order of millions of years (Palmer and Elderfield, 1985; Henderson et al., 1994). The Sr isotope composition extracted from Fe–Mn oxyhydroxides in pelagic sediments of the past 100 kyr should thus reproduce the present-day seawater ^{87}Sr/^{86}Sr of 0.70918 (Henderson et al., 1994) if no significant Sr was leached from the detrital fraction. This test was successfully used in earlier studies carried out in the Southern Atlantic, where a seawater Sr isotope composition was indeed measured in the leachates. In contrast, the application of this monitor indicated significant detrital contributions to the leachates of Fe–Mn oxyhydroxides from several sites in the North Atlantic (Piotrowski, 2004). These offsets in Sr isotopes were not accompanied by obvious alterations of the Nd isotope compositions. Using core-top Nd isotope compositions measured in Fe–Mn oxyhydroxide leaches, in conjunction with the dissolved