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Geochemical proxies of ocean circulation and weathering inputs: Radiogenic isotopes of Nd, Pb, Sr, Hf, and Os

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Abstract. Marine records of the radiogenic isotope composition of the elements neodymium (Nd), lead (Pb), hafnium (Hf), strontium (Sr), and osmium (Os) allow the reconstruction of past continental weathering inputs on different time scales as a function of their respective oceanic residence times. Sr and Os have oceanic residence times significantly longer than the global mixing time of the ocean and are efficiently mixed on a global scale. Their isotope composition changes on long time scales as a function of plate tectonics and major orogenies, which allows their use as precise stratigraphic tools for the entire Phanerozoic. In contrast, Hf, Pb, and in particular Nd, have residence times on the order of or shorter than the global mixing time of the ocean, which results in distinct isotopic signatures of water masses and allows the reconstruction of past water mass mixing and weathering inputs on both long and short time scales. Here applications of these isotopes systems with a focus on the shorter residence time tracers are reviewed (without claiming to be comprehensive) and problems and potential solutions are discussed. **Keywords:** Radiogenic isotopes, paleo-oceanography, ocean circulation, water mass mixing, continental weathering

1. Introduction

The radiogenic isotope signatures in rocks vary because one of the isotopes has changed its abundance over time due to ingrowth caused by decay of a radioactive parent isotope (i.e. ^{143}Nd is the decay product of ^{147}Sm , which means that the ratio between ^{143}Nd and primordial ^{144}Nd is variable). Consequently the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of the rocks changes as a function of their age and the ratio between the concentrations of samarium (Sm) and Nd. The radiogenic isotope composition of dissolved trace metals in the ocean primarily reflects the balance between the radiogenic isotope composition of the continental weathering inputs and mantle derived sources, either weathering of mantle-derived basaltic rocks or hydrothermal contributions (Figure 1) (see [1,2] for a review).

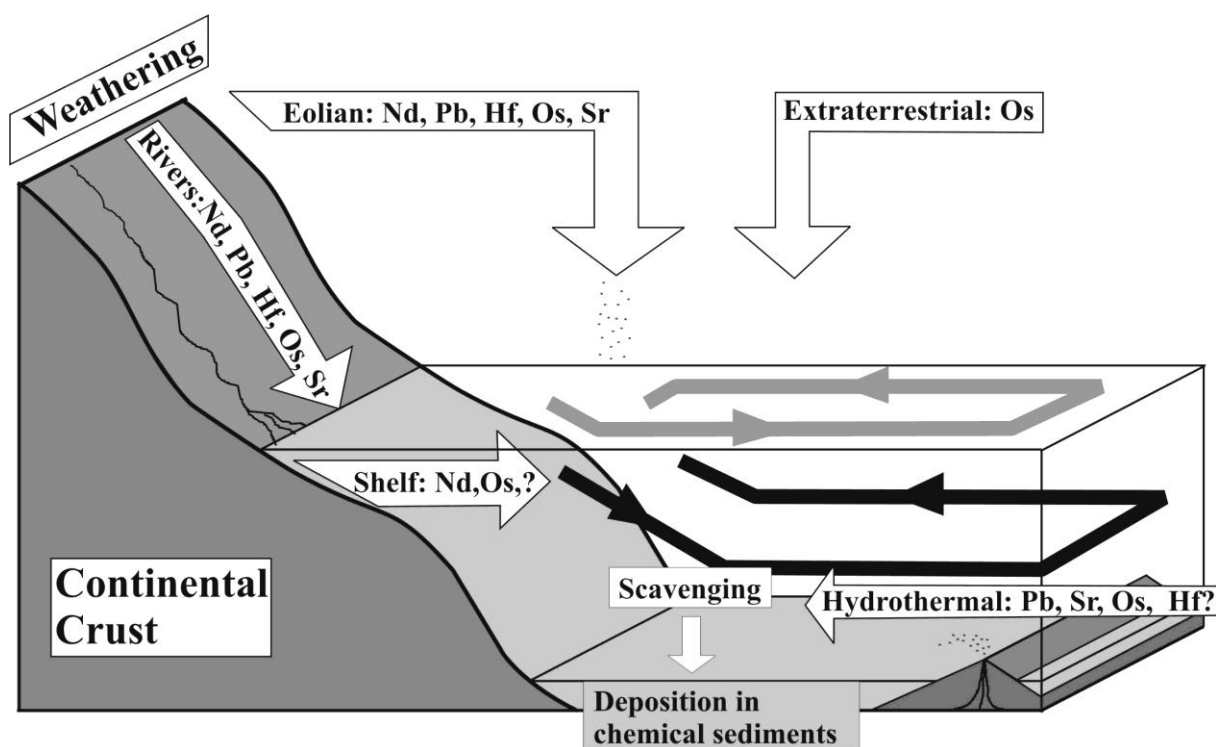


Figure 1. Sources, sinks and pathways of trace metals with radiogenic isotope signatures.

Strontium and osmium have long oceanic residence times between about 10,000 years and 2 million years, respectively. Their radiogenic isotope compositions are consequently homogeneously distributed in global seawater. Stored in authigenic carbonates, such as microfossil shells Sr and Os isotope records provide information about long term changes in weathering inputs as a function of tectonic changes, such as major orogenies or changes in the production rate of oceanic crust as a consequence of the break-up of continents. Due to these systematic global variations, which have been recorded at many locations and on many geological time scales, Sr isotopes have successfully been used for establishing a reliable marine stratigraphy over the entire Phanerozoic [3]. The global data base for variations in the Os isotope composition of global seawater is currently much smaller (e.g. [4]) but the data base is constantly growing [5] and Os isotopes have for example successfully been used for dating marine hydrogenetic ferromanganese crusts [6], in which Sr isotope variations are not reliably preserved (e.g. [7,8]).

In contrast, Nd, Hf and Pb are particle reactive in seawater and thus their concentrations and radiogenic isotope compositions are not homogeneously mixed in global seawater. These elements have residence times between 50-200 years (Pb, [9]) and 400 to 2000 years (Nd, Hf, [10,11,12]) which is on the order of or shorter than the global ocean mixing time. In the open ocean, where these metals are not directly influenced by weathering inputs, the radiogenic isotope systems of Nd and Hf can serve as isotopic fingerprints of water masses and thus quasi-conservative tracers of water mass mixing [12,13,14,15,16,17]. The water masses acquire their isotopic signatures in the source areas of the water masses through weathering inputs and subsequently only change their isotope composition by mixing with other water masses if circulation is vigorous enough, as is the case for Nd isotopes in the present day Atlantic Basin (Figure 2). These radiogenic isotope signatures are not influenced by any biological fractionation, which makes them valuable paleo proxies of past ocean circulation and weathering inputs provided that suitable archives are available.

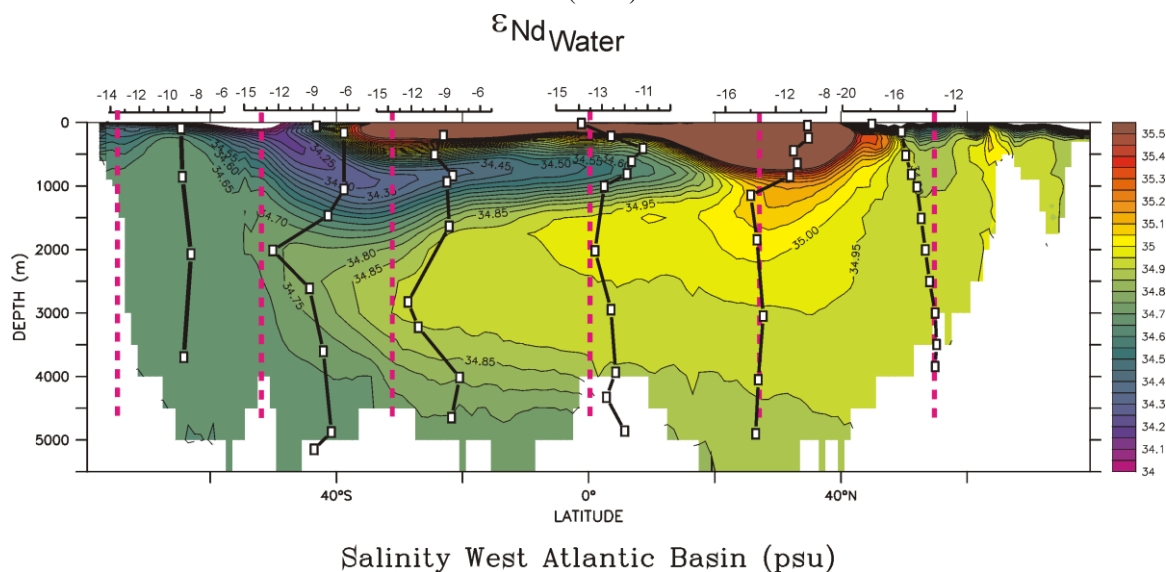


Figure 2. Water mass distribution on a N-S transect in the present day Atlantic Ocean as characterized by salinity (in ‰) [18]. North Atlantic Deep Water (NADW) flowing south is characterized by its high salinity and is compensated by northward flowing cold Antarctic Bottom Water (AABW) and warmer low salinity Antarctic Intermediate Water (AAIW). Water column ϵ_{Nd} data are superimposed, which clearly reflect this distribution of the water masses [14,15,16] (ϵ_{Nd} values represent the deviation of the measured $^{143}\text{Nd}/^{144}\text{Nd}$ of a sample from that of the Chondritic Uniform Reservoir (CHUR) in parts per 10,000). The figure has been reprinted with permission from [16]. Copyright 1999 American Association for the Advancement of Science

The radiogenic isotope composition of past seawater is either recorded in chemical sediments or seawater-derived chemical components, which incorporate the radiogenic isotope composition of seawater during their growth. Suitable chemical sediments recording long term changes in the radiogenic isotope composition of past deep waters are hydrogenetic ferromanganese crusts or nodules (see [1] for a review). Records from these chemical precipitates are generally restricted to a relatively coarse time resolution due to their extremely low growth rates on the order of few millimeters per million years. Advances in resolution of these archives were achieved through laser ablation measurements of Pb and Nd isotopes [19,20], which, however, still only allow a resolution on the order of 10,000 years per measurement making it difficult to reliably reconstruct glacial-interglacial variations.

More recent efforts have therefore been focussed on the extraction of the radiogenic isotope signatures of seawater from archives permitting higher time resolution records. It has been shown for Nd isotopes that foraminiferal shells deposited in marine pelagic sediments can serve as archives for deep water [21] and even surface water Nd isotope signatures of the past [22,23,24,25]. The paleo surface water records have for example been used to reconstruct changes in riverine inputs or erosional signals in the Labrador Sea or the Bay of Bengal on millennial to million year time scales. The extraction of the Nd isotope signatures, in particular those of surface waters, is, however, complicated by the fact that the concentrations within the foraminiferal carbonate itself are extremely low. Despite the fact that several recent studies have suggested that the methods to acquire surface water data of the past are now reliable [e.g. 26] the method still needs further studies to determine the effects of potential diagenetic additions of Nd from deep waters with a different isotope signature [27].

Other archives that have been successfully and reliably used to reconstruct the past Nd isotope composition of deep waters are fossil fish teeth, which incorporate the deep water Nd isotope composition during early diagenesis of the phosphate at the sediment water interface [28,29,30], and more recently deep water corals, which incorporate the Nd into their carbonate skeleton [31,32,33,34]. In the past ten years the most commonly used archive to extract deep water radiogenic isotope compositions for reconstructions of past weathering inputs and ocean circulation has been thin ferromanganese coatings on foraminifera or other sediment particles, which form through early diagenetic processes at the sediment water interface [35,36,37]. At particular locations the reliability

of this archive is also currently under debate due to effects of sediment redistribution or partial dissolution of volcanic glasses during leaching of the sediments.

2. Applications and case studies: Progress and problems

2.1. Pb and Hf isotopes: Tracing past weathering regimes and continental inputs

Pb has a very short average residence time in seawater due to its high particle reactivity and consequently cannot be transported very far without vertical additions. The isotopic composition of Pb shows a large range of variations in continental rocks and is thus a suitable tracer for nearby continental weathering inputs in the past and with some restrictions also for short range water mass exchange in the past [38,39]. While the Nd isotope composition of a source rock is essentially transferred into seawater without large changes, the Pb and Hf isotope compositions are fractionated during weathering on land (incongruent weathering) and therefore also carry information about the prevailing weathering regime near the source regions of particular water masses. In the case of Pb, the controlling process has been the preferential release of highly radiogenic Pb, which is weakly bound in the mineral lattices due to radiation damage, from rock surfaces freshly eroded by glaciers [40]. Based on this process, Pb isotope time series from sediments in the western North Atlantic have for example been used to reconstruct the past retreat of the Laurentide ice sheet since the Last Glacial Maximum and thus the transition from dominantly glaciated landscapes with reduced chemical weathering to the modern weathering regime [41].

The fractionation of Hf isotopes, in contrast, predominantly occurs because weathering-resistant zircons contain large amounts of unradiogenic Hf, which are not released during chemical weathering, but can only significantly be introduced into seawater when glacial grinding of rocks releases a significant fraction of the Hf contained in the zircons (see [42] for a review). This process, together with preferential release of radiogenic Hf from some labile minerals [43,44] and potential hydrothermal inputs of Hf [45] are mainly responsible for the fact that seawater and its archives for a given Nd isotope signature show a more radiogenic Hf isotope composition if compared to expected values from bulk rock analyses. In addition, the weathering effects result in a reduction of the global range of Hf isotope ratios in seawater compared with bulk rock signatures. A trend towards more congruent weathering in the North Atlantic Ocean over the past 2-3 million years has been revealed by combined Hf-Nd isotope analyses of ferromanganese crusts from the western North Atlantic, which has been interpreted as a consequence of weathering conditions increasingly controlled by physical weathering during glacial periods since the major intensification of Northern Hemisphere Glaciation at 2.7 million years ago [46].

2.2. Nd isotopes: Reconstructing past ocean circulation

The main interest in radiogenic isotope systems for paleo-oceanography, however, arises from the fact that radiogenic isotope systems can be used to constrain past water mass mixing on ocean basin scales. The most suitable system for this purpose is that of Nd, which can be measured precisely both in seawater and sedimentary archives and can provide clear information about the water mass structure, such as for example in the Atlantic Ocean (Figure 2).

As a case study the evolution of the export of NADW from the North Atlantic to the Southern Ocean, one of the key currents of the global thermohaline circulation system, is discussed here. Such reconstructions have been carried out on different time scales. On the million years time scale ferromanganese crust records in the North Atlantic have revealed a substantial shift of the Nd isotope signature of NADW to less radiogenic values over the past 3 million years [38,47], probably mainly caused by increased supply of unradiogenic Nd from Northern Canada and Greenland in the course of the major intensification of Northern Hemisphere Glaciation [47]. Over the same period of time this shift was not mirrored by similar changes of the Southern Ocean's main water mass, the Circumpolar Deep Water (CDW) [48], into which NADW is ultimately entrained and which today constitutes about 50-70 % of the Nd in CDW, the other 30-50 % being of Pacific origin with much

higher Nd isotope signatures [49]. This absent shift was interpreted as an overall decrease of NADW export by 15-35% over the past 3 million years although the observed Nd isotope variations of the Southern Ocean crusts may entirely have been caused by a progressively stronger decrease of NADW export only during glacial periods because samples from ferromanganese crusts integrate over several 10,000 years of growth history [48].

The major interest in past changes of the export of NADW is on much shorter millennial to centennial time scales. The first higher resolution record of CDW for the past 70,000 years was obtained from the ferromanganese coatings of a sediment core in the Cape Basin, which clearly revealed much more Pacific-like Nd isotope signatures of CDW during glacial Marine Isotope Stages (MIS) 4 and 2 [50]. In agreement with previously obtained benthic carbon isotope records this was interpreted as a significant decrease in NADW export to the Southern Ocean during glacial periods. Further work on the same sediment core at even higher, up to centennial scale resolution revealed similarly marked decreases in NADW export during the cold episodes (stadials) of MIS 3 [51]. While these stadial/interstadial excursions in Nd isotopes occurred synchronously with the benthic carbon isotope changes measured on the same samples, thus excluding uncertainties arising from the chronostratigraphy of the core, a phase lag has been observed at the main MIS transitions, in particular when going from warm to cold stages [51]. The records indicate that benthic oxygen isotope signatures and thus global ice volume started to change first, followed by benthic carbon isotopes some 2,000-3,000 years later, which were affected by changes in the carbon cycle. Lastly, Nd isotopes changed, again about 2,000 years later, indicating that changes of the ocean circulation cannot have triggered the sequence of events at these major climatic transitions but were only a consequence of other forcing factors [51].

A major prerequisite for the validity of these conclusions is that the Nd isotope composition and concentration of Nd of the water masses from the Pacific and of NADW contributing to CDW have remained constant over at least the past 100,000 years. In the case of the Pacific mixing endmember, this is hard to prove by data due to a lack of suitable archives but given the size of the Pacific Basin and its dominant weathering inputs from mantle-derived rocks the assumption of a near constant endmember composition for this period of time seems justified. For the NADW, archives are available to reconstruct its Nd isotope composition at high time resolution. A laser ablation Nd isotope record of two ferromanganese crusts that grew in the water depth of present day NADW was just sufficient to resolve glacial and interglacial Nd isotope signatures of NADW and did not indicate major changes over the past 500,000 years [20]. A similar conclusion was obtained from Nd isotope data of deep sea corals collected within present-day NADW in the western North Atlantic [31], although it was not possible to find corals that grew during the last glacial maximum. A third set of records was also generated from ferromanganese coatings of sediments from Blake Nose on the western North Atlantic continental slope [52]. These drift sediments deposited under vigorous current speeds were strongly affected by sediment redistribution (focusing). Sediment particles deposited in water depths of highest along slope velocities showed least influence by sediment focusing and closely reflected present day Nd isotope signatures of NADW at a nearby location [15], whereas the shallower last glacial main boundary current indicated Nd isotope values of $\epsilon\text{Nd} = -10$. This either reflects a significantly less radiogenic signature of the glacial equivalent of NADW, the Glacial North Atlantic Intermediate Water (GNAIW) [52], or a periodically stronger influence of intermediate waters from the Southern Ocean [53], or a combination of both. The reason for these discrepant results on the past Nd isotope composition of NADW is not yet clear but the reconstruction of past water masses from continental slope sediments may at least partly be influenced by exchange of the bottom waters with the slope sediments themselves, a phenomenon described as boundary exchange [54].

At the same time, glacial deep waters in the western Atlantic have become significantly less radiogenic in their Nd isotope composition due to enhanced northward flow of deep water masses of Southern Ocean origin [52,55]. The study of [55] also revealed that leaching of bulk sediments may at some locations in the North Atlantic result in too radiogenic Nd isotope compositions and that leaching of only the carbonate fraction may lead to more reliable results depending on location.

In summary, it is obvious that more groundtruthing studies are required in this rapidly emerging field of chemical oceanography/paleoceanography. This in particular, is the case for the methods applied to extract the radiogenic isotope signature of past water mass signatures from marine sediments, which need to be developed further in order to be able to exploit their full potential in paleoceanography. While at many locations, even with complex detrital sediment compositions, bulk sediment leaching worked well and provided reliable results [see above,56,57], this is not the case for others. In addition, sediment redistribution and downslope transport may bias a reliable reconstruction of water masses for example from sediments on continental slopes [52,58]. There is, however, also a clear need for a significant increase in the global data base for the present day dissolved and particulate Nd and Hf isotope distribution in the ocean, both in the frame of process studies at the margins of the oceans, but maybe more importantly along basin wide ocean sections. This is required to better understand the relationships of these isotope systems to present day water mass distribution and ocean circulation and is currently being investigated by the international GEOTRACES program [59].

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