Earth and Planetary Science Letters 394 (2014) 99–110

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Neodymium and hafnium boundary contributions to seawater along the West Antarctic continental margin

Jörg Rickli [a,b,*], Marcus Gutjahr [c], Derek Vance [a], Mario Fischer-Gödde [d], Claus-Dieter Hillenbrand [e], Gerhard Kuhn [f]

[a] Institute of Geochemistry and Petrology, ETH Zurich, Clausiusstrasse 25, 8092 Zurich, Switzerland
[b] Bristol Isotope Group, School of Earth Sciences, University of Bristol, Wills Memorial Building, Bristol BS8 1RJ, UK
[c] GEOMAR Helmholtz Centre for Ocean Research Kiel, Wischhofstraße 1–3, 24148 Kiel, Germany
[d] Institut für Planetologie, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Strasse 10, 48149 Münster, Germany
[e] British Antarctic Survey, High Cross, Madingley Road, Cambridge CB3 0ET, UK
[f] Alfred Wegener Institute, Columbusstrasse, 27568 Bremerhaven, Germany

ARTICLE INFO

Article history:
Received 4 October 2013
Received in revised form 25 February 2014
Accepted 3 March 2014
Available online 3 April 2014
Editor: G.M. Henderson

Keywords:
neodymium
hafnium
seawater
Southern Ocean
radiogenic isotopes

ABSTRACT

Neodymium and hafnium isotopes and elemental concentrations (Sm, Nd, Hf, Zr) have been measured in three water column profiles south of the Antarctic Circumpolar Current in, and to the east of the Ross Sea, in conjunction with five bottom water samples from the Amundsen Sea Embayment.

Neodymium and hafnium both appear to be released from sediments in the Embayment. In the case of Nd, this is reflected in radiogenic isotope compositions (ε_{Nd} up to −5.4) and highly elevated concentrations (up to 41 pmol/kg). Hafnium isotopes, on the other hand, are only very slightly altered relative to the open ocean sites, and boundary release is most prominently indicated by elevated concentrations (>1 pmol/kg versus ~0.7 pmol/kg). There is also a local input of both Hf and Nd at the Marie Byrd Seamounts, which leads to Nd isotope compositions as radiogenic as −3.1, and hafnium shifted to less radiogenic compositions in local bottom water.

A compilation of the new data with literature data reveals a consistent view of the influence of Antarctica on the Nd isotope composition in Lower Circumpolar Deep Water (LCDW) and Antarctic Bottom Water (AABW). Sector specific Nd addition shifts AABW formed in the Atlantic sector to less radiogenic isotope compositions (average $\varepsilon_{Nd} = -9$) relative to LCDW (average $\varepsilon_{Nd} = -8.4$), whereas AABW in the Pacific sector is shifted to more radiogenic values (average $\varepsilon_{Nd} = -7$). The evolution towards more radiogenic ε_{Nd} with depth in LCDW in the Pacific sector is likely to reflect admixture of AABW but, in addition, is also controlled by boundary exchange with the slope as observed at the Marie Byrd Seamounts.

Hafnium isotopes are relatively homogeneous in the data set, ranging between $\varepsilon_{Hf} = +2$ and +3.8 for most samples, excluding less radiogenic compositions in deep waters close to the Marie Byrd Seamounts. The Hf isotope composition in the Pacific sector is, however, slightly less radiogenic than in the Atlantic, corresponding to an average of +3 relative to an average of +3.8. This probably reflects unradiogenic Hf inputs from Antarctica to the Pacific sector, which are vertically homogenized by reversible scavenging. The Hf isotope heterogeneity in LCDW between both sectors is likely to indicate a shorter seawater residence time for Hf than for Nd, which is consistent with the dissolved – particulate phase partitioning of both elements.

1. Introduction

The reconstruction of past ocean circulation using seawater-derived neodymium (Nd) isotope compositions has a longstanding tradition on Quaternary and longer timescales (see reviews in Frank, 2002 and Goldstein and Hemming, 2003). The application often relies on the assumption of "quasi-conservative" behaviour of Nd isotopes as a water mass tracer, which assumes that the seawater Nd isotope composition at a given location primarily reflects the relative contribution of Nd from the mixing of water masses rather than non-advective processes such as scavenging and vertical regeneration in the water column or fluxes from sediment (Goldstein and Hemming, 2003; Siddall et al., 2008). A variety

* Corresponding author. Tel.: +41 44 632 35 62.
E-mail addresses: joerg.rickli@erdw.ethz.ch (J. Rickli), mgutjahr@geomar.de (M. Gutjahr), derek.vance@erdw.ethz.ch (D. Vance), m.fischer-goedde@uni-muenster.de (M. Fischer-Gödde), hilc@bas.ac.uk (C.-D. Hillenbrand), Gerhard.Kuhn@awi.de (G. Kuhn).

http://dx.doi.org/10.1016/j.epsl.2014.03.008
0012-821X/

of studies have, however, shown that Nd can be released or exchanged along continental margins from shallow to abyssal settings (Carter et al., 2012; Lacan and Jeandel, 2001, 2005a, 2005b; Rickli et al., 2009; Wilson et al., 2012), implying non-conservative behaviour at least close to the seabed. In addition, inherited continental FeMn oxyhydroxides and sediment redistribution processes, for example along ridges, can also obscure authigenic seawater records (Bayon et al., 2004; Gutjahr et al., 2008). Some locations, such as parts of the Atlantic sector of the Southern Ocean, appear to be unaffected by these processes and yield robust information on the temporal variability of North Atlantic Deep Water formation between glacials and interglacials (Piotrowski et al., 2005; Rutberg et al., 2000). In summary, it should be considered as observationally established that studies using Nd isotopes need to evaluate, on a site-by-site basis, to which degree temporal variations in sediment-derived ε_{Nd} can be ascribed to changes in ocean circulation.

Hafnium isotope variations in seawater have only been explored recently (Godfrey et al., 2009; Rickli et al., 2010, 2009; Stichel et al., 2012a, 2012b; Zimmermann et al., 2009a, 2009b) due to the low concentration of Hf in seawater and resulting analytical difficulties. The interest in Hf isotopes as a paleoceanographic tool is twofold. Early observations of Hf isotopes in FeMn crust and nodules, which record ambient seawater isotopic compositions (Zimmermann et al., 2009b), have suggested that Hf isotopes are positively correlated with Nd isotopes on a global scale (Albarède et al., 1998; David et al., 2001). Hafnium isotopes have thus been used to complement Nd isotopes as a water mass tracer in the past (Chen et al., 2012; van de Flierdt et al., 2004). Furthermore, time series of Hf isotopes in FeMn crust have led to the suggestion that the congruency in Hf isotope weathering could vary with the intensity of physical weathering on the continents (Piotrowski et al., 2000; van de Flierdt et al., 2002). Therefore, the Hf isotopic evolution of seawater may carry information on variations in physical weathering intensity in the past. A few initial studies on Hf isotopes in rivers, however, suggest that the presence (or absence) of phosphates, as well as the hydrological conditions, may actually be more important for the congruency in Hf weathering than physical grinding of rocks by glacial activity (Bayon et al., 2006; Rickli et al., 2013). In general, the sources of seawater Hf are poorly constrained to date (e.g., Vervoort et al., 2011). For instance, it is not well documented whether Hf is released or exchanged along continental margins, as observed for Nd.

Whether and to which degree Nd or Hf behave conservatively in seawater can be tested through measurement of elemental and/or isotopic exchange fluxes along ocean margins. Such fluxes, if present, can affect Nd and Hf isotope records of past ocean circulation (a point previously made in Carter et al., 2012), as these records are obtained from sedimentary phases, which record Nd and Hf in ambient bottom water (e.g., Piotrowski et al., 2005; Zimmermann et al., 2009b). There is a need for a better understanding of such boundary processes to characterize their effect on the distribution of Nd and Hf isotopes on a larger scale, and to help quantify their contribution to the seawater elemental budgets of Hf and Nd. Modelling studies of the oceanic distribution of Nd isotopes indicate that the seawater budget may actually be dominated by boundary related processes, which could account for up to 90% of seawater Nd (Rempfer et al., 2011; see also Arsouze et al., 2007). For simplicity, we will refer to this interface generally as the ocean boundary, independently of the nature of the seafloor (soft sediments, hard ground) or the oceanographic setting (open ocean, continental shelf).

The release of Nd at a boundary can be compensated by a capture of similar magnitude by scavenging (e.g., Lacan and Jeandel, 2005b). Hence the generic term "boundary exchange" has been introduced (Lacan and Jeandel, 2005a). Little is known about the importance of this process so far with respect to Hf. Observed Hf and zirconium (Zr) concentration profiles across the Celtic Sea shelf in the northeastern Atlantic Ocean indicated no boundary source for both elements (Godfrey et al., 1996). Boundary release of Hf was, however, suggested to happen in the Bay of Biscay based on one single anomalous observation of Hf isotopes and concentrations at 2000 m depth (Rickli et al., 2009). Release of Hf to the surface ocean from basaltic ocean islands seems to be common (Rickli et al., 2010; Stichel et al., 2012b). Boundary fluxes may also explain deep-water maxima in Zr concentrations observed in the open Pacific Ocean (McKelvey and Orians, 1998, 1993). In addition, mixing considerations using Hf isotopes have been used to argue for the release of Hf from the shelf of the Canadian Basin in the Arctic Ocean (Zimmermann et al., 2009a). The mixing end-member compositions of Pacific inflow and riverine inputs were, however, relatively poorly constrained.

The aim of the present study is to constrain processes of Nd and Hf release and exchange at the seawater/seafloor interface off and on the West Antarctic continental margin, using radiogenic isotope and concentration data. This study area is particularly suitable since continent-derived glacial sediments deposited along the margin likely experienced very little chemical alteration preceding deposition, therefore representing reactive immature sediments (e.g., (Anderson, 2007; Hillenbrand et al., 2013; Wadham et al., 2010)). Hence, compared with other near-continental marine settings, elemental and isotopic exchange may be particularly pronounced offshore West Antarctica.

2. Regional setting and hydrography

2.1. Hydrography

The circulation of the Southern Ocean is dominated by the eastward flowing Antarctic Circumpolar Current (ACC), which is bounded to the north by the Subtropical Front (STF) and to the south by its southern boundary (SBACC, Fig. 1, Orsi et al., 1995). The ACC essentially extends from the surface to abyssal depths and eastward transport is mainly concentrated in the Subantarctic and the Polar Front (SAF, PF, Talley et al., 2011 and references therein). Beneath Antarctic Surface Water (AASW), the ACC is divided into Upper Circumpolar Deep Water (UCDW), Lower Circumpolar Deep Water (LCDW) and Antartic Bottom Water (AABW). Upwelling of LCDW south of the SBAAC and modification by sea ice formation processes on the shelf of the Weddell Sea, the Ross Sea and Adélie coast and further less significant shelf areas leads to the formation of AABW (Orsi et al., 1999). In contrast to LCDW, AABW is not a circumpolar water mass. There is no free exchange of bottom waters between the Atlantic, Pacific and Indian sectors, due to several sills between the basins (Orsi et al., 1999). As a result the regional bottom waters, including Weddell Sea, Adélie and Ross Sea Bottom waters, are characterized by specific salinity-temperature properties (Orsi and Whitworth, 2005; Orsi et al., 1999).

The area of the study is situated south of the SBACC, within and east of the Ross Sea Gyre (Fig. 1). Three major water masses can be distinguished, namely AASW, LCDW and AABW (Fig. 2). The water mass transitions as used here follow Whitworth et al. (1998) and are based on neutral densities γ^n. The boundary between AASW and underlying LCDW corresponds to a neutral density isopycnal of 28.00 kg/m^3, which is in a depth range between 100 and 250 m (Talley et al., 2011). The vast majority of the water column beneath AASW is occupied by LCDW ($28.00 < \gamma^n < 28.27$) or modifications of it on the shelf (Arneborg et al., 2012; Orsi et al., 1995; Whitworth et al., 1998). Throughout the deep Pacific basin LCDW is underlain by Antarctic Bottom Water (AABW, $\gamma^n > 28.27$), predominantly formed in the Ross Sea (Jacobs et al., 1970;