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## Sources and input mechanisms of hafnium and neodymium in surface waters of the Atlantic sector of the Southern Ocean

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### Abstract

Radiogenic isotopes of hafnium (Hf) and neodymium (Nd) are powerful tracers for water mass transport and trace metal cycling in the present and past oceans. However, due to the scarcity of available data the processes governing their distribution are not well understood. Here we present the first combined dissolved Hf and Nd isotope and concentration data from surface waters of the Atlantic sector of the Southern Ocean. The samples were collected along the Zero Meridian, in the Weddell Sea and in the Drake Passage during RV Polarstern expeditions ANTXXIV/3 and ANTXXIII/3 in the frame of the International Polar Year (IPY) and the GEOTRACES program. The general distribution of Hf and Nd concentrations in the region is similar. However, at the northernmost station located 200 km southwest of Cape Town a pronounced increase of the Nd concentration is observed, whereas the Hf concentration is minimal, suggesting much less Hf than Nd is released by the weathering of the South African Archean cratonic rocks. From the southern part of the Subtropical Front (STF) to the Polar Front (PF) Hf and Nd show the lowest concentrations (<0.12 pmol/kg and 10 pmol/kg, respectively), most probably due to the low terrigenous flux in this area and efficient scavenging of Hf and Nd by biogenic opal. In the vicinity of landmasses the dissolved Hf and Nd isotope compositions are clearly labeled by terrigenous inputs. Near South Africa Nd isotope values as low as  $\epsilon_{Nd} = -18.9$  indicate unradiogenic inputs supplied via the Agulhas Current. Further south the isotopic data show significant increases to  $\epsilon_{Hf} = 6.1$  and  $\epsilon_{Nd} = -4.0$  documenting exchange of seawater Nd and Hf with the Antarctic Peninsula. In the open Southern Ocean the Nd isotope compositions are relatively homogeneous ( $\epsilon_{Nd} \sim -8$  to  $-8.5$ ) towards the STF, within the Antarctic Circumpolar Current, in the Weddell Gyre, and the Drake Passage. The Hf isotope compositions in the entire study area only show a small range between  $\epsilon_{Hf} = +6.1$  and  $+2.8$  support Hf to be more readily released from young mafic rocks compared to old continental ones. The Nd isotope composition ranges from  $\epsilon_{Nd} = -18.9$  to  $-4.0$  showing Nd isotopes to be a sensitive tracer for the provenance of weathering inputs into surface waters of the Southern Ocean.

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### 1. INTRODUCTION

#### 1.1. Hafnium and neodymium isotopes as tracers in seawater

Dissolved radiogenic hafnium (Hf) and neodymium (Nd) isotope compositions (expressed as  $\epsilon_{Hf}$  and  $\epsilon_{Nd}$  by

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normalizing the  $^{176}\text{Hf}/^{177}\text{Hf}$  and the  $^{143}\text{Nd}/^{144}\text{Nd}$  to that of CHUR in parts per 10,000 (Jacobsen and Wasserburg, 1980; Nowell et al., 1998) in seawater have been shown to provide insights into present and past ocean circulation and weathering conditions on land (e.g. Piotrowski et al., 2000; Frank et al., 2002; van de Flierdt et al., 2002). The global average residence time of Nd in the ocean is between 360 and 1500 years, allowing the use of Nd isotopes as a tracer for advection and mixing of water masses over long distances (Jeandel et al., 1995; Tachikawa et al., 1999; Siddall et al., 2008; Arsouze et al., 2009; Rempfer et al., 2011). Hafnium, on the other hand, has an oceanic residence time, which is most likely on the order of only few hundred years (Rickli et al., 2009; Zimmermann et al., 2009b), implying that radiogenic Hf isotopes are useful tracers for water masses restricted to basin scales. However, there are also estimates for the residence time of Hf in the deeper ocean longer than that of Nd, whereas in the surface ocean the opposite was proposed (Godfrey et al., 2008, 2009). This discrepancy is mainly due to the lack of information available on the distribution of dissolved Hf in seawater and the isotopic range of the input sources. While the Nd input into the ocean is known to be governed by river and groundwater contributions, as well as exchange between sediments and seawater (Elderfield et al., 1990; Greaves et al., 1994; Jeandel et al., 1995; Haley et al., 2004; Lacan and Jeandel, 2005), the inputs contributing to the marine Hf budget are still debated. Hafnium in seawater is possibly delivered mainly by fluvial input (e.g. Bayon et al., 2006; Godfrey et al., 2008) but also partial dissolution of dust (Albarède et al., 1998; David et al., 2001; Pettke et al., 2002; Godfrey et al., 2009; Rickli et al., 2010), exchange with marine sediments similar to Nd (Lacan and Jeandel, 2005), and hydrothermal inputs (Bau and Koschinsky, 2006) may play a role.

Comparison of the relationship between the Hf and Nd isotopes in terrestrial rocks, referred to as the “terrestrial array” (Patchett et al., 1984; Vervoort et al., 1999), with available seawater data (Godfrey et al., 2009; Rickli et al., 2009, 2010; Zimmermann et al., 2009a,b) reveals fundamental differences (Fig. 1A). The Hf and Nd isotope composition of terrestrial rocks is governed by a very similar lutetium–hafnium (Lu/Hf) and samarium–neodymium (Sm/Nd) elemental fractionation during igneous processes. The radiogenic isotope systems of Hf and Nd are controlled by the decay of their respective parent isotopes  $^{176}\text{Lu}$  and  $^{147}\text{Sm}$ : Continental crustal rocks are thus characterized by low Lu/Hf and low Sm/Nd leading to unradiogenic bulk Hf and Nd isotope compositions (low  $\epsilon$ -values) over time. Mafic rocks (i.e. mantle-derived rocks) have higher Lu/Hf and Sm/Nd and are therefore more radiogenic (higher  $\epsilon$ -value) in their bulk Hf and Nd isotope compositions. Compared to the terrestrial array, the available seawater Hf and Nd isotope data (“seawater array”) are shifted to more radiogenic Hf isotope compositions for a given Nd isotope composition. The most plausible explanation is that during incongruent weathering of continental crust, unradiogenic Hf is retained in weathering resistant minerals, such as zircons, a process often referred to as the “zircon effect” (Patchett et al., 1984; Albarède et al., 1998; Piotrowski

et al., 2000; van de Flierdt et al., 2002, 2007). In addition, minerals with highly radiogenic Hf isotope composition have been shown to be more susceptible to weathering, thus causing preferential supply of radiogenic Hf to seawater (Bayon et al., 2006, 2009; van de Flierdt et al., 2007; Chen et al., 2011). Rickli et al. (2010) suggested that areas with high atmospheric dust loads, such as the Sahara region, also act as sources of Hf to seawater. Comparing the surface ocean Hf isotope compositions to those of dust indicates that Hf is preferentially released from traces of radiogenic apatite and clays resulting in a surface water Hf isotope composition, which is  $\sim 10 \epsilon_{\text{Hf}}$  units more radiogenic than the bulk dust composition in the Atlantic Ocean. Therefore, both fluvial and atmospheric inputs are likely to contribute to the radiogenic Hf isotope composition in the ocean. An alternative explanation, although so far not supported by direct data, is the input of radiogenic Hf through hydrothermal venting (Bau and Koschinsky, 2006; White et al., 1986). This source has been shown not to deliver any radiogenic Nd to deep waters (German et al., 1990; Halliday et al., 1992) and thus could also explain the observed offset to more radiogenic Hf isotope compositions of seawater.

Despite of the existence of Hf and Nd isotope data from different parts of the global ocean the continental contributions and their supply pathways are still largely unconstrained, in particular in the Southern Ocean. In addition, the Southern Ocean is characterized by a high biogenic opal productivity, which may play an important role for the cycling of Hf and the rare earth elements (REE). Here we present the first combined surface water Hf and Nd isotope compositions and concentrations complemented by REE distributions from the Atlantic sector of the Southern Ocean. With this new dataset we aim at better understandings of the external inputs of Hf and Nd and of the mechanisms, which control their elemental and isotopic distribution in the surface ocean. Comparison of REE patterns from surface waters with those of potential sources allow the processes governing their distribution to be evaluated.

## 1.2. Study area

The surface waters of the Southern Ocean (Fig. 2) are separated from those of the subtropical region further north by a pronounced meridional temperature and salinity gradient. This hydrographic boundary is referred to as the Subtropical Front (STF, Hofmann, 1985). The STF is the only front in the Southern Ocean that is not circumpolar, given that no subtropical waters are found in the Drake Passage between the Antarctic Peninsula and South America (Sievers and Emery, 1978; Sievers and Nowlin, 1984). The STF marks the transition between the relatively cold and fresh Subantarctic Surface Water (SASW) and the much warmer and saltier Subtropical Surface Water (STSW). The front develops in the western South Atlantic Ocean and is associated with an eastward transport of up to 37 Sv ( $1 \text{ Sv} = 10^6 \text{ m}^3 \text{ s}^{-1}$ ). This flow decreases to less than 15 Sv towards South Africa, commonly called the South Atlantic Current (SAC) where it turns north to feed the

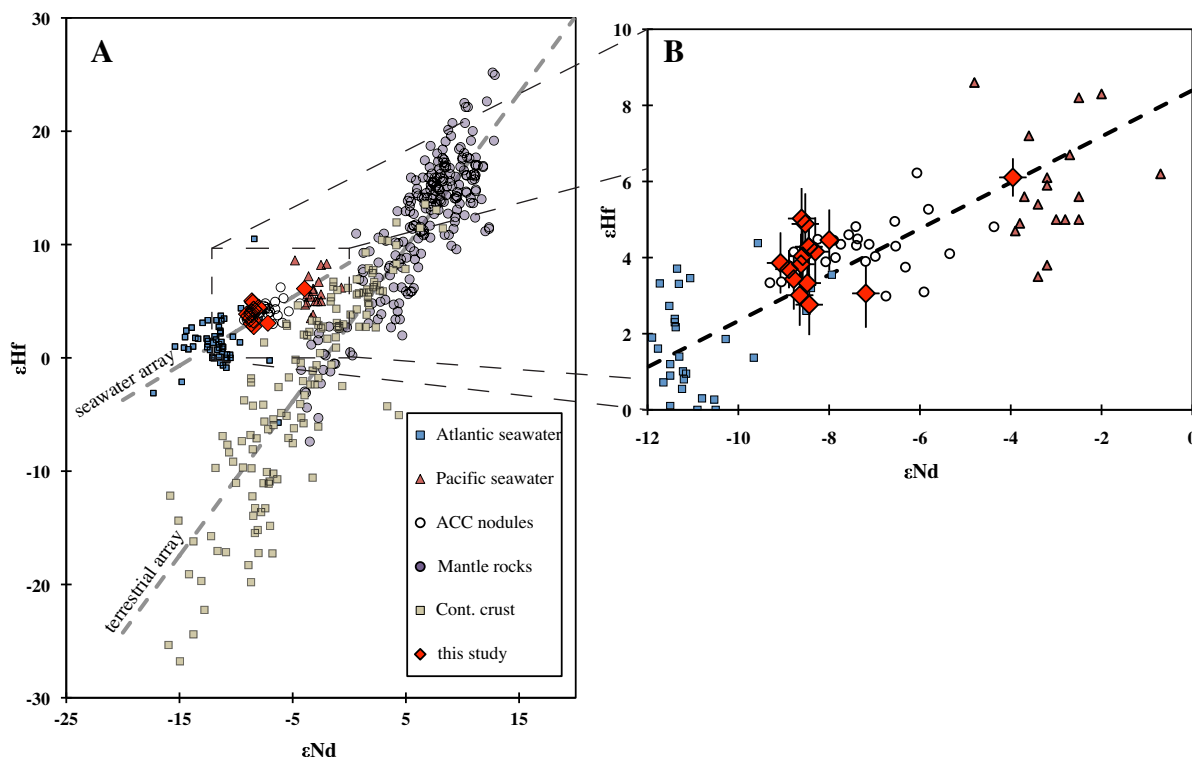


Fig. 1. Hf and Nd isotope compositions of terrestrial rocks (“terrestrial array”), seawater and ferromanganese crusts (“seawater array”). The terrestrial array (Vervoort et al., 1999) is characterized by a larger  $\epsilon_{\text{Hf}}$  variability than that of  $\epsilon_{\text{Nd}}$  (A). The seawater array displays more radiogenic  $\epsilon_{\text{Hf}}$  for a given  $\epsilon_{\text{Nd}}$  value (B). Atlantic Hf isotope compositions (Godfrey et al., 2009; Rickli et al., 2009, 2010) plot at the unradiogenic end of the array, whereas Pacific compositions (Zimmermann et al., 2009a) form the radiogenic part. The Hf and Nd isotope compositions of Southern Ocean seawater as well as of ferromanganese crusts and nodules (van de Fliedert et al., 2006) plot between Atlantic and Pacific compositions.

158 Benguela Current (Stramma and Peterson, 1990). South of  
 159 the STF, a region of weak flow separates the SAC from the  
 160 Antarctic Circumpolar Current (ACC), which dominates  
 161 geostrophic eastward flow around the Antarctic continent.  
 162 The ACC is bound to the south by cyclonically circulating  
 163 gyres, such as the Weddell Gyre (WG, Deacon, 1979; Klatt  
 164 et al., 2005). Within the ACC, bands of pronounced hori-  
 165 zontal density gradients, also associated with strong lateral  
 166 currents, characterize the Subantarctic (SAF) and the Polar  
 167 (PF) Fronts (Emery, 1977; Nowlin and Whitworth, 1977;  
 168 Whitworth, 1980; Peterson and Stramma, 1991). From  
 169 the PF to the Antarctic continent the relatively homoge-  
 170 nous Antarctic Surface Water (AASW) is found, which  
 171 forms the topmost layer above the warmer and saltier  
 172 Upper (U) and Lower (L) Circumpolar Deep Water  
 173 (CDW).

174 The Atlantic sector of the Southern Ocean is bounded  
 175 by the landmasses of South Africa in the east, the Antarctic  
 176 continent in the south and South America in the west  
 177 (Fig. 2). The geology of South Africa mainly comprises  
 178 the Archaean Kaapvaal Craton, which is surrounded by  
 179 several orogenic belts of Proterozoic and Paleozoic age.  
 180 On top of this old basement the sedimentary Karoo Basin  
 181 developed during the Paleozoic (Cole, 1992). The geological  
 182 structure of the Antarctic continent (Fig 2A) can be broadly  
 183 divided into the three tectonic domains comprising the East

184 Antarctic Shield (EAS), the Transantarctic Mountains  
 185 (TAM) and West Antarctica (WA). The EAS comprises a  
 186 Precambrian to Ordovician igneous and sedimentary base-  
 187 ment overlain by Devonian to Jurassic sediments. East Ant-  
 188 arctica, in particular the Dronning Maud Land (DML),  
 189 consists of approximately the same tectonic facies as South  
 190 Africa, in both cases originating from the Pan-African  
 191 orogeny which formed during the collision of East and  
 192 West Gondwana about 600–500 Ma ago (Thomas et al.,  
 193 1993; Rogers et al., 1994). The TAM mark the boundary  
 194 between East and West Antarctica. They consist of sedi-  
 195 mentary deposits from the Late Cambrian Ross orogeny,  
 196 Devonian to Permian sediment covers of Gondwana, and  
 197 Jurassic tholeiites. The TAM underwent uplift since the  
 198 early Cretaceous (Dalziel, 1992; Fitzsimons, 2000). West  
 199 Antarctica has five crustal blocks, of which three are rele-  
 200 vant for this study: the Haag Nunataks (HN), the Ellsworth  
 201 Whitmore Mountains (EWM) and the Antarctic Peninsula  
 202 (AAP). The HN represents a small crustal block between  
 203 the AAP and the EWM consisting of Proterozoic amphibol-  
 204 ites and orthogneisses (Millar and Pankhurst, 1987). The  
 205 EWM form a 415 km long, NNE–SSW trending mountain  
 206 chain being a terrane once situated at the margin of  
 207 Gondwana prior to its break-up during the Jurassic  
 208 (Dalziel, 1992; Storey, 2005). The AAP mainly consists of  
 209 magmatic rocks of varying origin and is interpreted as a

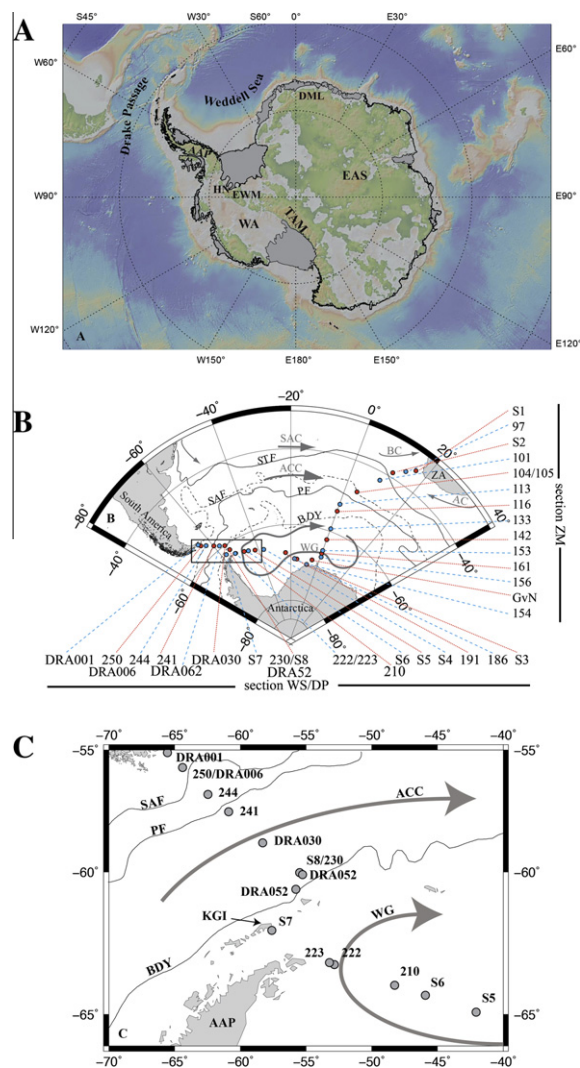


Fig. 2. Overview of the study area. The upper map (A) shows the bedrock configuration of Antarctica together with the major shelf ice contours (grey areas). The main geologic terrains are displayed: Antarctic Peninsular (AAP), East Antarctic Shield (EAS), Ellsworth Whitmore Mountains (EWM), Dronning Maud Land (DML), Haag Nunataks (HN), Transantarctic Mountains (TAM) and West Antarctica (WA). The map was constructed using GeoMapApp© (<http://www.geomapp.org>) with the topography after Ryan et al. (2009). (B) Shows the sample sites and the hydrographic surface conditions and (C) is an enlargement of the area near the Antarctic Peninsula and King George Island (KGI). The main hydrographic features are the Agulhas Current (AC), the Antarctic Circumpolar Current (ACC), the Benguela Current (BC), the South Atlantic Current (SAC) and the Weddell Gyre (WG). The dashed and dotted lines in (B) and (C) represent the approximate locations of the Southern Ocean frontal system from north to south: the Subtropical Front (STF), the Subantarctic Front (SAF), the Polar Front (PF) and the Southern ACC boundary (BDY) as described in Orsi et al. (1995).

magmatism, and back-arc sequences on the eastern side of the Peninsula bounded by the Weddell Sea. Across the Drake Passage to the north these back-arc sequences continue as the southern part of South America (Patagonia). Together with the AAP, Patagonia forms one of the largest igneous provinces on Earth (Pankhurst et al., 1998).

## 2. METHODS

### 2.1. Sample collection and onboard procedures

Most samples were collected during the International Polar Year (IPY) cruise ANTXXIV/3 on the German research vessel *FS Polarstern* from February to April 2008. This cruise was also part of the international GEOTRACES program and all samples were collected and measured for their Nd and Hf concentrations and isotope compositions according to the agreed GEOTRACES protocols (<http://www.obs-vlfr.fr/GEOTRACES/libraries/documents/Intercalibration/Cookbook.pdf>). Between 100 and 130 L of seawater were taken for each sample mostly when the ship was underway. The collection was carried out in three different ways: (1) using a towed stainless steel fish with a Teflon head, through which surface water was pumped directly into the ship's laboratory under trace metal clean conditions, (2) using the ship's own seawater intake system made of polypropylene tubes, or (3) using Niskin bottles on a CTD rosette collecting water from 25 to 480 m water depth during station time (Table 1 and Fig. 2). For this study we refer to samples shallower than 100 m as *surface samples*. All samples were filtered through a 142 mm Millipore® filter disc with a pore size of 0.45 µm into acid cleaned LDPE cubitainers. Filtration was performed within 12 h after collection or directly during collection when possible. The samples were then acidified to pH ~2 with double distilled, concentrated HNO<sub>3</sub>. From each sample an aliquot of 2 L was kept for concentration analysis. About 500–600 mg iron (Fe), in the form of previously cleaned dissolved Fe-chloride, was added to the large volume samples and left for 24 h for equilibration. In a second step, ammonia solution (25%, Merck Suprapur®) was added to bring the pH back to 8 in order to co-precipitate the dissolved trace metals (i.e. Hf and Nd) with Fe hydroxide (FeOOH). The supernatant was discarded and the residual FeOOH precipitate was transferred into pre-cleaned 2 L LDPE-bottles.

In addition, five Nd samples collected in the Drake Passage during the expedition ANTXXIII/3 on *Polarstern* were included in this study (see Table 1). For each of these samples 10 L of seawater were filtered and acidified as described above. The pre-concentration was realized by co-precipitation with manganese hydroxide (MnOOH) after increasing the pH to ~8. The MnOOH precipitate was filtered on board in a laminar flow hood and the filters were stored away for further analysis on shore.

### 2.2. Further procedures in the home laboratory

The FeOOH precipitates obtained during ANTXXIV/3 were centrifuged in the home laboratory of GEOMAR in Kiel (Germany) and were rinsed at least twice with de-

210 long-lived magmatic arc partly built on Cambrian continental crust (Millar et al., 2001). Most of the exposed rocks, 211 however, are of Mesozoic and younger ages resulting from 212 subduction on the western margin of the Peninsula. These 213 consist of the AAP Batholith, which reflects central arc 214

ionized water (MilliQ, 18.2 M $\Omega$ ) to wash out major ions. The precipitate was removed from the centrifuge tubes and transferred into 60 ml Teflon vials with 5 ml 6 M HCl (quartz distilled). After evaporation, 4 ml of aqua regia were added and the closed vials were heated at 110 °C for at least 24 h to destroy organic compounds. The samples were then transformed to Cl-form and finally dissolved in 4 ml of 6 M HCl. The majority (more than 99%) of the Fe was removed prior to chromatographic separation by solvent extraction with di-ethyl ether (Stichel et al., 2014). The residual was then evaporated and re-dissolved in 4 ml 3 M HCl.

Most of the samples formed a jelly-like silica gel in HCl, which scavenged about 90% of the Hf from the sample. This silica gel was isolated and dissolved with 2 M HF. After evaporation of the 2 M HF, this fraction was recombined with the HCl soluble fraction of the same sample. The purification of Hf and separation of REE followed a modified recipe of M $\ddot{u}$ nkler et al. (2001). Some remaining traces of ytterbium (Yb), which would have caused an isobaric interference on <sup>176</sup>Hf, were subsequently removed on an additional column loaded with 1.4 ml of cation-exchange resin (Biorad<sup>®</sup> AG50W-X8, 200–400  $\mu$ m mesh-size) using 1 M HCl and 0.05 M HF to elute Hf before the rare earth elements (REE). Purification after M $\ddot{u}$ nkler et al. (2001) also allowed the separation of the REE from most of the sample matrix. The REE were eluted in 6 M HCl immediately after loading the sample. The REE cut was further processed using LN-Spec resin following Pin and Zalduegui (1997). The respective Hf and Nd cuts were treated with 100  $\mu$ l HNO<sub>3</sub> (concentrated, quartz distilled) and 100  $\mu$ l H<sub>2</sub>O<sub>2</sub> (30 wt.%, Merck Suprapur<sup>®</sup>) in preparation for mass spectrometry to avoid potentially disturbing matrix effects by traces of resin or other residual organic compounds. Finally the samples were dissolved in 0.5 M HNO<sub>3</sub> (Nd) and 0.5 M HNO<sub>3</sub> + 0.1 M HF (Hf) for measurement on the MC-ICPMS.

The filtered MnOOH precipitates from the additional samples from expedition ANTXXIII/3 were dissolved and further treated at LEGOS in Toulouse (France). Extraction of the “REE fraction” from the MnOOH co-precipitate was conducted on an anion exchange resin following the procedure described in Jeandel et al. (2011). Neodymium was then purified following the two-step procedure of Lacan and Jeandel (2001).

### 2.3. Concentration measurements

Hafnium and neodymium concentrations were obtained by isotope dilution (ID) similar to the method described by Rickli et al. (2009). For the five additional samples, only Nd concentrations were determined following Lacan and Jeandel (2001). Weighed spike solutions of <sup>178</sup>Hf and a mixture of <sup>150</sup>Nd/<sup>149</sup>Sm were added to an acidified 0.5 L aliquot of each sample. The samples were left for 4–5 days to completely equilibrate. Subsequently FeCl<sub>3</sub> was added to the samples and Hf and Nd were co-precipitated with FeOOH by adding ammonia to raise the pH to 8. For mass spectrometric analysis, purification of Hf and Nd using a single cation chromatographic separation step (1.4 ml resin bed,

Biorad<sup>®</sup> AG50W-X8, 200–400  $\mu$ m mesh-size) was sufficient. Hafnium was loaded and collected in a mixture of 1 M HCl and 0.05 M HF (0.5 ml loading solution, 2 additional ml for elution), whereas Nd was collected in 5 ml 6 M HNO<sub>3</sub>, following the elution of barium in 12 ml of 2 M HNO<sub>3</sub>. The respective cuts containing Nd and Hf were evaporated to dryness and then oxidized by adding 200  $\mu$ l of a 1:1 mixture of 0.5 M HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> (30 wt.%) to destroy remaining organic compounds originating from the resin before measurement on the MC-ICPMS. Replicates for each element were processed and yielded an external reproducibility of better than 1% for Nd and between 3% and 10% for Hf depending on concentration. Laboratory blanks were quantified by processing 0.5 L of MQ-water in the same way as the samples and corresponded to less than 1% for Nd, where no blank corrections were applied. The Hf content of the samples being very low was closer to the blank level. The blank amounted to  $5 \pm 0.7$  pg ( $n = 11$ , corresponding to 50% of the smallest sample), which was subtracted from all samples to achieve a correct seawater concentration.

The concentrations of all the naturally occurring rare earth elements (REE) concentrations were determined using a seaFAST system (Elemental Scientific Inc.) connected to an Agilent 7500ce ICP-MS. The seaFAST system performs preconcentration, matrix removal and online elution into the ICP-MS enabling direct analysis of trace metals from 4 ml of undiluted seawater (Hathorne et al., 2012). The overall reproducibility for all REE concentrations was better than 8% (1 SD), estimated from repeated measurements of a seawater sample ( $n = 10$ ). The agreement for Nd concentrations between the seaFast measurements and isotope dilution is better than 10% for most of the samples except for stations S3, S7 and 222 (180 m), where the seaFAST produced 13.7%, 13.0% and 15.3% higher concentrations.

### 2.4. Isotope measurements

The Hf isotope compositions were measured on a Nu Plasma HR MC-ICPMS at GEOMAR applying manual time resolved data acquisition. The samples were dissolved in 250–500  $\mu$ l 0.5 M HNO<sub>3</sub>/0.1 M HF to obtain a Hf concentration of  $\sim$ 20 ppb corresponding to a total beam of at least 4 V. The measured Hf isotope ratios were integrated over the time of analysis (3–5 min) and corrected for instrumental mass fraction to <sup>179</sup>Hf/<sup>177</sup>Hf = 0.7325 applying an exponential mass fractionation law. All <sup>176</sup>Hf/<sup>177</sup>Hf ratios were normalized to the accepted value for JMC 475 of 0.28216 (Nowell et al., 1998) using the average of repeated measurements of the JMC 475 standard in each session. The external reproducibility for the set of samples in this study was  $\pm 0.8$   $\epsilon_{\text{Hf}}$  (2 SD) and was estimated by 4–6 repeated measurements of the JMC 475 Hf standard during every session at the same concentration as the samples. The Nd isotope composition was either also measured on the Nu plasma instrument, though in automatic mode, or on a Thermo Scientific Triton1 TIMS. The measured isotopic composition was corrected for instrumental mass bias to <sup>146</sup>Nd/<sup>144</sup>Nd = 0.7219 applying an exponential mass fractionation law. All <sup>143</sup>Nd/<sup>144</sup>Nd ratios were normalized to

the JNdi-1 standard with the accepted ratio of 0.512115 (Tanaka et al., 2000) using the average of the repeatedly measured standard of the respective session. The external reproducibility was between  $\pm 0.3 \epsilon_{\text{Nd}}$  and  $\pm 0.39 \epsilon_{\text{Nd}}$  (2 SD) estimated by repeated measurements of the JNdi-1 standard, as well as of an internal laboratory standard. Duplicates measured on both instruments resulted in the same value within this error. The blanks for both elements (laboratory work only) were  $\sim 20$  pg (Hf) and  $\sim 50$  pg (Nd), which in both cases was less than 1% of the smallest sample.

The additional samples from ANTXXIII/3 were measured on a MAT 261 TIMS (Observatoire Midi-Pyrénées, Toulouse, France), using the same method as described above to correct for instrumental mass bias. These samples were normalized to the La Jolla Nd standard with the accepted  $^{143}\text{Nd}/^{144}\text{Nd}$  value of 0.511859, yielding an external reproducibility between  $\pm 0.2$  and  $0.6 \epsilon_{\text{Nd}}$  units (2 SD). Both laboratories participated in the 2008–2010 GEOTRACES intercalibration efforts and their results agreed well within the overall 2 SD variation of  $\epsilon_{\text{Nd}} \pm 0.6$  (van de Flierdt et al., 2012).

## 2.5. Particles

We compared our data to results for Nd isotopes and REE concentrations in particulates from the Southern Ocean published by Hegner et al. (2007), whose study area largely overlapped with ours. Hafnium concentrations for marine particulates, which were measured on the same samples as in Hegner et al. (2007), have not been published in that study. Therefore, we analyzed these Hf concentrations for samples that were most proximal to our study sites. The methodology followed the one described in Hegner et al. (2007).

## 3. RESULTS

The results for dissolved Hf and REE concentrations and Hf and Nd isotope compositions from this study are presented in Tables 1 and 2. The previously published particulate Nd concentrations (Hegner et al., 2007) and the new particulate Hf concentrations are listed together in Table 3. This table also shows those stations of ANTXXIV/3 closest to those of Hegner et al. (2007).

### 3.1. Hf and Nd concentrations in the dissolved fraction

Both Hf and Nd concentrations show similar distribution patterns in the studied area (Fig. 3) with some distinct exceptions as will be detailed below. The Zero Median section displays the following elemental distributions from north to south (Fig. 3A): the highest Nd concentration of 24.2 pmol/kg is observed at station S1, about 200 km southwest of Cape Town. This high Nd concentration is in marked contrast to the very low Hf concentration at this station with only 0.06 pmol/kg (Table 1). The Nd concentration decreases southward to a minimum value 6.7 pmol/kg at the STF (station S2). Towards the SAF, the concentrations for both elements remain at a low level corresponding to  $\sim 6$  pmol/kg for Nd and  $\sim 0.05$  pmol/kg

for Hf, respectively. A pronounced southward increase in the concentrations of both elements is observed between the SAF (station 104/105) and the BDY (station 113 and 116). From there onwards, the Hf and Nd concentrations remain relatively constant across the Weddell Gyre (WG) yielding typical concentrations of  $\sim 0.2$  pmol/kg for Hf and  $\sim 15$  pmol/kg for Nd.

The elemental distribution in the section through the Weddell Sea (east to west) and the Drake Passage (south to north) is characterized (Fig. 3B) by Hf and Nd concentrations in the Weddell Sea that are similar to those observed around the Zero Meridian in the WG. Starting approximately at station S6 the Hf concentrations, and, to a lesser extent, the Nd concentrations, rise continuously until station S7 north of the AAP. This broad maximum in concentrations with a peak value of 0.38 pmol/kg Hf and 22.6 pmol/kg Nd at station 7 occurs near King George Island. Further north in the Drake Passage Hf and Nd concentrations drop again to values similar to those found in the eastern Atlantic sector of the ACC.

### 3.2. REE patterns of the dissolved fraction

Fig. 4 shows PAAS-normalized (Post-Archean Average Shale, Taylor and McLennan, 1985) REE patterns for the 30 analyzed surface seawater samples (see data in Table 2). With the exception of two samples, the surface waters show shale normalized REE patterns similar to previous studies with heavy REE (HREE) enrichment compared to the light REE (LREE, e.g. Elderfield and Greaves, 1982; de Baar et al., 1983, 1985; Piepgras and Jacobsen, 1992; German et al., 1995). Stations S2 and particularly S1 show only small enrichments of the HREEs. The cerium anomalies  $\text{Ce}/\text{Ce}^*$  ( $\text{Ce}/\text{Ce}^* = \log [3 \times \text{Ce}_\text{N}/(2 \times \text{La}_\text{N} + \text{Nd}_\text{N})]$ ), whereby values  $< 0$  represent negative anomalies and  $\text{REE}_\text{N}$  is normalized to that of PAAS, Taylor and McLennan, 1985) of all samples are negative between  $-1.31$  and  $-0.24$  (Table 2). The smallest negative Ce anomaly was measured at station S1, close to South Africa. The most negative  $\text{Ce}/\text{Ce}^*$  values of  $-1.31$  to  $-1.03$  and  $-1.13$  to  $-0.61$  were found at stations within the Weddell Gyre and the ACC, respectively. The pronounced negative anomalies in the WG weaken close to Antarctica and only correspond to  $-0.56$  at station 222 west of the AAP and to  $-0.76$  at station 154 close to the DML. PAAS-normalized La–Yb ratios ( $\text{La}_\text{N}/\text{Yb}_\text{N}$ ) range from 0.19 to 0.68 (Fig. 3 and Table 2). The highest  $\text{La}_\text{N}/\text{Yb}_\text{N}$  ratios were measured at S1 (0.68) and S2 (0.53). South of the STF, in the ACC and the Weddell Gyre, these ratios drop to 0.19–0.38. Like the  $\text{Ce}/\text{Ce}^*$ , the  $\text{La}_\text{N}/\text{Yb}_\text{N}$  ratios close to the AAP are similar to those in the Weddell Gyre (0.28–0.36).

### 3.3. Dissolved Hf and Nd isotope composition

Overall, the Hf isotope composition of the surface waters is relatively constant and most samples are between  $\epsilon_{\text{Hf}} = +2.8$  and  $+5.0$ , whereas the range of Nd isotopes is almost 15  $\epsilon_{\text{Nd}}$  units ( $\epsilon_{\text{Nd}} = -18.9$  to  $-4.0$ , Fig. 3). It should be noted that for the stations north of the Polar Front (PF) the Hf concentration in the samples was too low for Hf



Table 1

Dissolved trace metal data from ANTXXIV/3 and ANTXXIII/3. The hydrographic data (temperature and salinity) are from the ships own PODAS system.

| Station             | Device                    | Depth (m) | Temperature (°C) | Salinity | $\epsilon_{Nd}$ | Error (2 $\sigma$ ) | Nd (pmol/kg) | $\epsilon_{Hf}$ | Error (2 $\sigma$ ) | Hf (pmol/kg) |      |
|---------------------|---------------------------|-----------|------------------|----------|-----------------|---------------------|--------------|-----------------|---------------------|--------------|------|
| S1                  | 34° 53.15' S 16° 40.70' E | Fish      | 5                | 21.03    | 35.47           | -18.9               | 0.3          | 24.2            |                     | 0.06         |      |
| 97                  | 36° 59.60' S 12° 45.40' E | CTD       | 100              | 18.23    | 35.55           | -15.9               | 0.4          |                 |                     |              |      |
| S2                  | 38° 48.00' S 11° 35.80' E | Fish      | 5                | 17.53    | 34.92           | -11.0               | 0.3          | 6.7             |                     | 0.04         |      |
| 101                 | 42° 20.60' S 8° 59.20' E  | CTD       | 75               | 10.21    | 34.55           | -9.7                | 0.4          | 8.6             |                     |              |      |
| 104                 | 47° 39.80' S 4° 16.20' E  | CTD       | 75               | 6.41     | 33.72           | -7.9                | 0.4          | 8.2             |                     |              |      |
| 105                 | 47° 39.00' S 4° 16.60' E  | Fish      | 5                | 6.50     | 33.71           | -7.9                | 0.3          | 7.4             |                     | 0.08         |      |
| 113                 | 52° 59.80' S 0° 02.00' E  | CTD       | 75               | 1.22     | 33.79           | -7.9                | 0.4          | 16.1            |                     |              |      |
| 113                 | 52° 59.80' S 0° 02.00' E  | CTD       | 150              | 0.20     | 34.02           | -8.0                | 0.4          | 15.0            |                     |              |      |
| 116                 | 54° 21.00' S 0° 01.00' E  | Fish      | 5                | 1.04     | 33.80           | -8.0                | 0.3          | 15.8            | 4.5                 | 0.8          | 0.18 |
| 133                 | 59° 14.00' S 0° 02.00' E  | Fish      | 5                | 0.21     | 33.95           | -8.6                | 0.3          | 18.2            |                     | 0.19         |      |
| 142                 | 62° 20.00' S 0° 00.00' E  | Fish      | 5                | 0.53     | 33.94           | -8.6                | 0.3          | 17.3            | 5.0                 | 0.8          | 0.11 |
| 153                 | 65° 19.00' S 0° 00.00' E  | Fish      | 5                | -0.18    | 33.97           | -8.5                | 0.3          | 17.3            | 4.9                 | 0.8          | 0.18 |
| 154                 | 70° 34.50' S 8° 07.38' W  | CTD       | 135              | -1.69    | 34.02           | -9.9                | 0.4          | 19.4            |                     | 0.22         |      |
| 156                 | 67° 08.00' S 0° 24.00' E  | Fish      | 5                | -0.67    | 33.97           | -8.6                | 0.3          | 19.5            | 3.0                 | 0.8          | 0.25 |
| 161                 | 66° 29.20' S 0° 00.00' E  | CTD       | 100              | 0.77     | 34.64           | -8.7                | 0.4          | 17.9            |                     | 0.40         |      |
| GvN                 | 68° 31.80' S 4° 39.00' W  | Fish      | 5                | -1.18    | 33.84           | -8.8                | 0.3          | 16.8            | 3.4                 | 0.8          | 0.20 |
| S3                  | 69° 02.00' S 15° 42.00' W | Snorkel   | 5                | -        | -               | -8.6                | 0.3          | 16.9            | 4.0                 | 0.8          | 0.16 |
| 186                 | 69° 03.00' S 17° 25.00' W | CTD       | 25               | -1.84    | 33.93           | -8.4                | 0.3          | 17.2            | 4.3                 | 0.8          | 0.20 |
| 191                 | 67° 21.00' S 23° 38.00' W | CTD       | 25               | -1.85    | 34.12           | -8.5                | 0.3          | 18.5            | 4.3                 | 0.8          | 0.21 |
| S4                  | 65° 34.00' S 36° 46.00' W | Snorkel   | 5                | -1.44    | 34.15           | -9.0                | 0.3          | 18.5            |                     | 0.18         |      |
| S5                  | 64° 59.00' S 42° 00.00' W | Snorkel   | 5                | -1.55    | 33.91           | -8.4                | 0.3          | 18.3            | 2.8                 | 0.8          | 0.16 |
| S6                  | 64° 20.00' S 46° 04.40' W | Snorkel   | 5                | -1.76    | 33.25           | -8.6                | 0.3          | 18.1            | 3.8                 | 0.8          | 0.22 |
| 210                 | 64° 02.80' S 48° 15.40' W | CTD       | 25               | -1.83    | 33.79           | -8.5                | 0.3          | 18.3            | 3.3                 | 0.8          | 0.27 |
| 222                 | 63° 21.00' S 52° 51.00' W | CTD       | 25               | -1.82    | 34.08           | -8.9                | 0.3          | 19.9            | 3.7                 | 0.5          | 0.25 |
| 222                 | 63° 21.00' S 52° 51.00' W | CTD       | 50               | -1.82    | 34.10           | -8.9                | 0.4          | 21.2            |                     | 0.29         |      |
| 222                 | 63° 21.00' S 52° 51.00' W | CTD       | 100              | -1.58    | 34.37           | -8.9                | 0.4          | 19.9            |                     | 0.30         |      |
| 222                 | 63° 21.00' S 52° 51.00' W | CTD       | 180              | -1.22    | 34.49           | -8.7                | 0.4          | 20.4            |                     | 0.32         |      |
| 222                 | 63° 21.00' S 52° 51.00' W | CTD       | 280              | -0.90    | 34.54           | -8.7                | 0.4          | 21.3            |                     | 0.35         |      |
| 222                 | 63° 21.00' S 52° 51.00' W | CTD       | 400              | -0.90    | 34.56           | -9.1                | 0.3          | 22.5            | 3.9                 | 0.8          | 0.34 |
| 223                 | 63° 17.00' S 53° 13.00' W | CTD       | 25               | -1.82    | 34.18           | -8.3                | 0.3          | 21.1            | 4.2                 | 0.9          | 0.31 |
| S7                  | 62° 08.00' S 57° 31.00' W | Snorkel   | 5                | 1.04     | 34.06           | -4.0                | 0.3          | 22.6            | 6.1                 | 0.5          | 0.38 |
| S8                  | 60° 03.00' S 55° 24.00' W | Snorkel   | 5                | 1.78     | 33.85           | -7.2                | 0.3          | 14.3            | 3.1                 | 0.9          | 0.20 |
| 230                 | 60° 06.00' S 55° 16.40' W | CTD       | 50               | 0.79     | 34.17           | -6.9                | 0.4          | 18.9            |                     | 0.31         |      |
| 230                 | 60° 06.00' S 55° 16.40' W | CTD       | 150              | 0.57     | 34.34           | -6.4                | 0.4          | 19.9            |                     | 0.35         |      |
| 241                 | 57° 37.20' S 60° 53.80' W | CTD       | 50               | 2.84     | 33.79           | -8.4                | 0.4          | 11.8            |                     | 0.17         |      |
| 244                 | 56° 53.80' S 62° 28.00' W | CTD       | 25               | 5.38     | 33.92           | -8.2                | 0.4          | 10.2            |                     | 0.12         |      |
| 244                 | 56° 53.80' S 62° 28.00' W | CTD       | 50               | 5.38     | 33.92           | -8.2                | 0.4          | 9.6             |                     | 0.09         |      |
| 250                 | 55° 45.50' S 64° 26.20' W | CTD       | 150              | 3.64     | 34.02           | -8.2                | 0.4          | 9.7             |                     |              |      |
| DRA001 <sup>a</sup> | 55° 07.00' S 65° 35.04' W | CTD       | 50               | 8.32     | 33.74           | -5.7                | 0.6          | 8.5             |                     |              |      |
| DRA006 <sup>a</sup> | 55° 45.00' S 64° 30.00' W | CTD       | 20               | 5.10     | 33.90           | -8.6                | 0.3          | 8.9             |                     |              |      |
| DRA030 <sup>a</sup> | 58° 52.00' S 58° 18.00' W | CTD       | 20               | 2.50     | 33.89           | -8.2                | 0.5          | 14.7            |                     |              |      |
| DRA052 <sup>a</sup> | 61° 50.00' S 55° 26.00' W | CTD       | 31               | -        | -               | -6.3                | 0.3          | 21.4            |                     |              |      |
| DRA062 <sup>a</sup> | 60° 39.00' S 55° 47.00' W | CTD       | 20               | 0.62     | 34.33           | -7.2                | 0.4          | 17.7            |                     |              |      |

<sup>a</sup>Samples from ANTXXIII/3 (see text).

isotope measurements. For Nd, stations north of the STF close to South Africa have the least radiogenic Nd isotope compositions between  $\epsilon_{Nd} = -18.9$  and  $-11.0$  (Fig. 3A). Another distinctly unradiogenic Nd isotope value of  $\epsilon_{Nd} = -9.9$  is observed in the WG at the southernmost station 154 close to the Antarctic continent. The unique deviation from the above range of Hf isotope compositions is observed at station S7, where the most radiogenic value of  $\epsilon_{Hf} = +6.1$  occurs close to King George Island (KGI, Figs. 2 and 3B). At the same station a similar excursion to more radiogenic values is also observed for Nd isotopes ( $\epsilon_{Nd} = -4.0$ ). At the nearby stations DRA 052, 062 and S8

north of King George Island, Nd isotope compositions between  $\epsilon_{Nd} = -6.3$  to  $-7.2$  were measured. The Hf isotope compositions on nearby stations, on the other hand, are not elevated. A further radiogenic Nd isotope excursion in the ACC to  $\epsilon_{Nd} = -5.7$  is measured at station DRA001, close to the southern tip of Chile. Apart from these deviations the Nd isotope compositions, similar to Hf, are rather uniform within the ACC and the WG at values between  $\epsilon_{Nd} = -7.8$  and  $-8.6$ .

Combined Hf and Nd isotope compositions show that surface waters from the Southern Ocean are shifted towards more radiogenic Hf values for given Nd values when

Table 2

Dissolved REE concentration in pmol/kg, together with PAAS-normalized La/Yb ratios and Ce-anomalies ( $Ce/Ce^*$ ). The REE concentrations were measured with a seaFAST system (see Section 2.3). For comparison the Nd concentration in pmol/kg obtained by isotope dilution is also provided.

| Station                     | Depth (m) | Latitude     | Longitude    | La   | Ce   | Pr   | Nd   | Sm   | Eu   | Gd   | Tb   | Dy   | Ho   | Er   | Tm   | Yb   | Lu   | La/Yb (norm) | Ce/Ce* | Nd (ID) |
|-----------------------------|-----------|--------------|--------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|--------------|--------|---------|
| SAC & ACC on Zero Meridian: |           |              |              |      |      |      |      |      |      |      |      |      |      |      |      |      |      |              |        |         |
| S1                          | 0         | 34° 53.15' S | 16° 40.7' E  | 29.5 | 35.3 | 6.02 | 25.1 | 4.68 | 1.24 | 5.54 | 0.75 | 4.97 | 1.11 | 3.64 | 0.46 | 2.57 | 0.43 | 0.68         | -0.24  | 24.2    |
| S2                          | 0         | 38° 48' S    | 11° 35.8' E  | 12.1 | 6.47 | 1.52 | 6.77 | 1.53 | 0.29 | 2.00 | 0.29 | 2.25 | 0.71 | 2.03 | 0.24 | 1.43 | 0.17 | 0.50         | -0.53  | 6.68    |
| 101                         | 75        | 42° 20.60' S | 8° 59.20' E  | 12.3 | 5.90 | 2.05 | 8.99 | 2.14 | 0.34 | 2.49 | 0.43 | 3.00 | 0.94 | 3.18 | 0.37 | 2.52 | 0.45 | 0.29         | -0.61  | 8.56    |
| 104                         | 75        | 47° 39.80' S | 4° 16.20' E  | 14.1 | 3.53 | 1.95 | 8.61 | 1.82 | 0.49 | 2.60 | 0.45 | 3.63 | 1.05 | 3.74 | 0.55 | 3.54 | 0.70 | 0.24         | -0.87  | 8.16    |
| 105                         | 0         | 47° 39.00' S | 4° 16.60' E  | 11.9 | 2.60 | 1.54 | 7.21 | 1.41 | 0.42 | 1.99 | 0.42 | 3.83 | 1.12 | 3.81 | 0.51 | 3.73 | 0.64 | 0.19         | -0.93  | 7.38    |
| 113                         | 70        | 52° 59.80' S | 0° 02.00' E  | 23.6 | 5.64 | 3.34 | 15.1 | 2.80 | 0.87 | 4.59 | 0.74 | 5.73 | 1.47 | 5.37 | 0.81 | 5.26 | 0.97 | 0.27         | -0.90  | 16.1    |
| 116                         | 0         | 54° 21.00' S | 0° 01.00' E  | 24.5 | 8.34 | 3.69 | 16.6 | 2.77 | 0.76 | 4.68 | 0.64 | 5.71 | 1.49 | 5.16 | 0.90 | 5.39 | 0.94 | 0.27         | -0.75  | 15.8    |
| Weddell Gyre:               |           |              |              |      |      |      |      |      |      |      |      |      |      |      |      |      |      |              |        |         |
| 133                         | 0         | 59° 14.00' S | 0° 02.00' E  | 31.9 | 3.74 | 4.50 | 19.8 | 3.60 | 0.93 | 4.86 | 0.85 | 6.22 | 1.63 | 5.91 | 0.88 | 6.01 | 1.05 | 0.31         | -1.20  | 18.2    |
| 142                         | 0         | 62° 20.00' S | 0° 00.00' E  | 30.3 | 3.60 | 4.08 | 18.3 | 3.41 | 0.86 | 4.61 | 0.76 | 5.95 | 1.73 | 5.64 | 0.88 | 6.02 | 1.04 | 0.30         | -1.20  | 17.3    |
| 153                         | 0         | 65° 19' S    | 0° 00.00' E  | 28.7 | 3.63 | 3.94 | 18.0 | 3.19 | 0.83 | 4.50 | 0.70 | 5.94 | 1.57 | 5.77 | 0.80 | 5.62 | 1.15 | 0.30         | -1.17  | 17.3    |
| 154                         | 135       | 70° 34.50' S | 8° 07.38' W  | 33.9 | 11.0 | 4.95 | 20.9 | 3.46 | 0.91 | 5.08 | 0.88 | 6.02 | 1.65 | 5.97 | 0.97 | 6.71 | 1.14 | 0.30         | -0.76  | 19.4    |
| 156                         | 5         | 67° 08.00' S | 0° 24.00' E  | 28.4 | 3.75 | 4.03 | 19.5 | 2.95 | 0.80 | 5.00 | 0.71 | 6.05 | 1.62 | 5.80 | 0.84 | 5.45 | 1.01 | 0.31         | -1.16  | 19.5    |
| 161                         | 100       | 66° 29.20' S | 0° 00.00' E  | 31.1 | 4.53 | 4.40 | 18.6 | 3.19 | 1.02 | 4.67 | 0.81 | 6.24 | 1.72 | 6.43 | 0.89 | 6.50 | 1.23 | 0.28         | -1.11  | 17.9    |
| GvN                         | 5         | 68° 31.80' S | 4° 39.00' W  | 29.5 | 3.37 | 4.01 | 16.8 | 3.04 | 0.71 | 6.06 | 0.70 | 6.10 | 1.58 | 5.37 | 0.91 | 5.09 | 1.05 | 0.34         | -1.21  | 16.8    |
| S3                          | 0         | 69° 02.00' S | 15° 42.00' W | 30.6 | 4.72 | 4.25 | 19.2 | 3.14 | 0.84 | 5.01 | 0.77 | 6.28 | 1.57 | 5.84 | 0.94 | 5.98 | 1.00 | 0.30         | -1.09  | 16.9    |
| 186                         | 0         | 69° 03.00' S | 17° 25.00' W | 29.9 | 4.14 | 4.11 | 19.0 | 3.06 | 0.88 | 5.10 | 0.71 | 5.44 | 1.65 | 6.02 | 0.84 | 5.86 | 0.97 | 0.30         | -1.13  | 17.2    |
| 191                         | 5         | 67° 21.00' S | 23° 38.00' W | 32.1 | 4.01 | 4.43 | 18.9 | 3.70 | 0.90 | 5.72 | 0.84 | 6.23 | 1.72 | 6.00 | 0.96 | 4.96 | 1.09 | 0.38         | -1.17  | 18.5    |
| S4                          | 0         | 65° 34.00' S | 36° 46.00' W | 32.6 | 2.92 | 4.36 | 18.7 | 3.48 | 0.87 | 5.05 | 0.80 | 5.97 | 1.77 | 6.03 | 0.92 | 6.06 | 1.10 | 0.32         | -1.31  | 18.5    |
| S5                          | 0         | 64° 59.00' S | 42° 00.00' W | 31.0 | 3.43 | 4.48 | 20.2 | 3.73 | 0.96 | 5.65 | 0.74 | 6.55 | 1.88 | 6.11 | 0.83 | 5.98 | 1.05 | 0.31         | -1.23  | 18.3    |
| S6                          | 0         | 64° 20.00' S | 46° 04.40' W | 30.9 | 3.48 | 4.30 | 19.2 | 3.43 | 0.84 | 5.66 | 0.83 | 5.75 | 1.66 | 5.91 | 0.84 | 6.21 | 1.06 | 0.29         | -1.22  | 18.1    |
| 210                         | 0         | 64° 02.80' S | 48° 15.40' W | 30.9 | 5.45 | 4.75 | 20.0 | 3.69 | 0.84 | 4.55 | 0.78 | 5.95 | 1.80 | 5.71 | 0.92 | 6.26 | 1.13 | 0.29         | -1.03  | 18.3    |
| AAP & Drake passage:        |           |              |              |      |      |      |      |      |      |      |      |      |      |      |      |      |      |              |        |         |
| 222                         | 50        | 63° 21.00' S | 52° 51.00' W | 39.1 | 19.3 | 5.41 | 21.0 | 3.73 | 0.98 | 5.27 | 0.75 | 6.43 | 1.74 | 6.29 | 0.90 | 6.52 | 1.14 | 0.36         | -0.56  | 21.2    |
| 222                         | 180       | 63° 21.00' S | 52° 51.00' W | 34.2 | 9.49 | 4.96 | 23.6 | 4.03 | 0.92 | 4.95 | 0.87 | 6.22 | 1.80 | 6.22 | 0.92 | 6.37 | 1.18 | 0.32         | -0.84  | 20.4    |
| 222                         | 280       | 63° 21.00' S | 52° 51.00' W | 36.1 | 14.1 | 5.19 | 22.1 | 4.11 | 1.05 | 5.89 | 0.94 | 6.97 | 1.83 | 6.72 | 0.99 | 6.61 | 1.18 | 0.32         | -0.68  | 21.3    |
| 222                         | Bottom    | 63° 21.00' S | 52° 51.00' W | 37.4 | 10.1 | 5.58 | 23.2 | 4.49 | 0.95 | 5.72 | 0.95 | 7.16 | 1.90 | 6.54 | 0.99 | 7.10 | 1.29 | 0.31         | -0.84  | 22.5    |
| S7                          | 0         | 62° 08.00' S | 57° 31.00' W | 33.6 | 16.2 | 5.80 | 25.6 | 4.98 | 1.19 | 6.49 | 0.96 | 7.24 | 1.99 | 6.60 | 1.08 | 7.22 | 1.29 | 0.28         | -0.61  | 22.6    |
| S8                          | 0         | 60° 03.00' S | 55° 24.00' W | 26.3 | 4.70 | 3.44 | 15.6 | 2.74 | 0.78 | 3.90 | 0.69 | 5.00 | 1.47 | 5.04 | 0.74 | 4.41 | 0.82 | 0.35         | -1.02  | 14.3    |
| 230                         | 50        | 60° 06.00' S | 55° 16.40' W | 30.0 | 9.18 | 4.55 | 20.8 | 3.85 | 1.09 | 4.99 | 0.78 | 6.39 | 1.75 | 6.05 | 0.88 | 5.96 | 1.17 | 0.30         | -0.80  | 18.9    |
| 230                         | 150       | 60° 06.00' S | 55° 16.40' W | 31.8 | 9.46 | 4.58 | 21.0 | 3.81 | 1.11 | 5.56 | 0.98 | 6.59 | 1.93 | 6.55 | 1.02 | 6.77 | 1.22 | 0.28         | -0.81  | 19.9    |
| 241                         | 50        | 57° 37.20' S | 60° 53.80' W | 20.1 | 3.75 | 2.95 | 12.4 | 2.21 | 0.63 | 3.44 | 0.60 | 4.68 | 1.41 | 4.80 | 0.70 | 4.39 | 0.82 | 0.27         | -1.00  | 11.8    |
| 244                         | 25        | 56° 53.80' S | 62° 28.00' W | 14.7 | 2.06 | 2.09 | 9.5  | 1.69 | 0.46 | 2.94 | 0.46 | 3.73 | 1.21 | 3.98 | 0.64 | 3.79 | 0.70 | 0.23         | -1.13  | 10.2    |
| 244                         | 50        | 56° 53.80' S | 62° 28.00' W | 16.3 | 2.78 | 2.23 | 9.47 | 1.69 | 0.40 | 3.08 | 0.52 | 3.97 | 1.19 | 3.98 | 0.66 | 4.21 | 0.72 | 0.23         | -1.03  | 9.57    |

520 compared to the “terrestrial array” (Fig. 1B). Similar to  
521 previously published seawater data (Godfrey et al., 2009;  
522 Rickli et al., 2009, 2010; Zimmermann et al., 2009a,b),  
523 the surface waters in this study plot on the “seawater  
524 array”, as previously also derived from analyses of ferro-  
525 manganese crust and nodule surfaces (Albarède et al.,  
526 1998; David et al., 2001; van de Flierdt et al., 2006). All  
527 samples form an isotopically tightly constrained field, with  
528 the only exception of the samples collected in the vicinity of  
529 KGI, which plot on the more radiogenic part of the seawater  
530 array.

#### 531 4. DISCUSSION

##### 532 4.1. Weathering inputs of Hf and REEs

##### 533 4.1.1. South Africa

534 While the general distribution of Hf and REE concen-  
535 trations, as well as Hf and Nd isotopes are similar in most  
536 parts of the study area, the data are distinctly different close

537 to South Africa. At station S1 the Nd concentration of  
538 24.2 pmol/kg is the highest measured in this study, whereas  
539 Hf is at its lowest level (0.06 pmol/kg). The high Nd con-  
540 centration together with the shale-normalized  $La_N/Yb_N$  of  
541 0.68 and an only slightly negative Ce anomaly ( $Ce/Ce^*$   
542  $= -0.24$ ) suggest enhanced terrigenous inputs from  
543 the South African continent. A shale-normalized REE pat-  
544 tern comparable to that of particulate data (Hegner et al.,  
545 2007) further supports increased contributions to the dis-  
546 solved REEs originating from terrigenous material, proba-  
547 bly via partial dissolution of particles (Fig. 4). A  
548 continental input is also indicated by the very negative sea-  
549 water Nd isotope composition of  $\varepsilon_{Nd} = -18.9$  at S1. How-  
550 ever, the isotope composition of suspended particles  
551 yielding  $\varepsilon_{Nd}$  of  $-14.5$  (Hegner et al., 2007) is too radiogenic  
552 to explain the low seawater Nd isotope composition at S1.  
553 Surface sediments deposited around the South African  
554 coast are on average also more radiogenic ( $\varepsilon_{Nd} = -14$  to  
555  $-12$ , Franzese et al., 2006). Therefore, an additional source  
556 supplying unradiogenic Nd is necessary to explain the

Table 3  
Particulate Hf, Nd and biogenic opal data from Hegner et al. (2007) closest to the sample sites of this study.

| Sample <sup>a</sup> | LAT <sup>a</sup><br>(degrees N) | LON <sup>a</sup><br>(degrees E) | Biogen.<br>SiO <sub>2</sub> <sup>a</sup> (%) | Particulate Nd <sup>a</sup><br>(pmol/l) | Error<br>(%) | Particulate Hf <sup>b</sup><br>(pmol/l) | Error<br>(%) | Nd/Hf<br>particles | Closest station to<br>ANTXXIV/3 <sup>c</sup> |
|---------------------|---------------------------------|---------------------------------|--|---|--------------|---|--------------|--------------------|--|
| z137                | −39.53                          | 18.84                           |  | 0.460                                   | 4.2          | 0.015                                   | 13.7         | 30.9               | S2   |
| z01                 | −49.75                          | 5.87                            | 29   | 1.145                                   | 3.5          | 0.080                                   | 7.1          | 14.2               | 105  |
| z02                 | −53.47                          | 9.00                            | 42   | 0.405                                   | 4.4          | 0.039                                   | 6.4          | 10.4               | 116  |
| z04                 | −60.58                          | 3.00                            | 17   | 4.635                                   | 1.8          |   |              |                    | 133  |
| z05                 | −63.63                          | −0.31                           | 8  | 4.028                                   | 2.6          | 0.148                                   | 5.9          | 27.2               | 142/153                                      |
| z06                 | −67.27                          | −3.93                           | 9  | 1.170                                   | 3.3          | 0.056                                   | 9.3          | 21.1               | 156/GvN                                      |
| z71 (2)             | −68.40                          | −26.14                          | 58   | 0.231                                   | 12.3         | 0.042                                   | 14.2         | 5.4                | 191  |
| z72                 | −66.81                          | −32.00                          | 47   | 0.156                                   | 12.0         |   |              |                    | S4   |
| z75                 | −63.03                          | −44.17                          | 37   | 0.675                                   | 3.1          | 0.092                                   | 5.4          | 7.3                | S5/S6  |
| z76                 | −61.86                          | −52.42                          | 27   | 0.076                                   | 6.0          | 0.009                                   | 7.5          | 8.5                | 210  |
| z77                 | −62.23                          | −55.47                          |  | 0.100                                   | 7.0          | 0.010                                   | 7.7          | 9.7                | 222/223                                      |
| z84                 | −62.30                          | −58.65                          |  | 24.438                                  | 3.1          | 2.882                                   | 3.7          | 8.5                | S7   |
| z87                 | −59.81                          | −59.69                          | 42   | 0.195                                   | 3.8          | 0.027                                   | 14.2         | 7.2                | S8   |
| z89                 | −56.68                          | −63.21                          | 29   | 0.142                                   | 3.6          | 0.010                                   | 6.7          | 14.8               | 244  |

<sup>a</sup>From Hegner et al. (2007).

<sup>b</sup>From the same samples of Hegner et al. (2007).

<sup>c</sup>This study.

557 unradiogenic value at S1, most plausibly surface waters ad-  
558 ducted by the Agulhas Current. The Agulhas waters may  
559 have been influenced by particle dissolution close to the  
560 eastern coast of South Africa and carry unradiogenic Nd  
561 into the Atlantic, which is supported by the provenance  
562 of deposited detritus in the southern Cape Basin (Rutberg  
563 et al., 2005; Franzese et al., 2006). Unfortunately, there  
564 are no further data available on the marine particle compo-  
565 sition from the Indian Ocean side of South Africa to sup-  
566 port this assumption. As mentioned above, the Hf  
567 concentration at S1 is one of the lowest of the entire sample  
568 set, which does not support an additional input from partic-  
569 cle dissolution for Hf in that area. Thus, a release of Hf  
570 from particles appears to be of no importance or Hf is sim-  
571 ply scavenged more readily. Unfortunately the lack of a Hf  
572 isotope value at this station does not allow to investigate if  
573 boundary exchange has been involved instead, through  
574 which the radiogenic isotope signature can change but not  
575 necessarily the concentration (e.g. Lacan and Jeandel,  
576 2005). Possibly, Hf is largely retained in refractory miner-  
577 als, such as zircon, which make it less available during par-  
578 ticle dissolution. If Hf scavenging was high at S1, the effect  
579 on the REEs seems to be very low given the high concentra-  
580 tion of these elements. Even though recent studies have  
581 shown that Hf is scavenged in surface waters more readily  
582 than e.g. Nd, the overall scavenging behavior of these two  
583 elements is similar (Godfrey et al., 2009; Rickli et al.,  
584 2010). Thus, it seems rather unlikely that a very high Nd  
585 concentration accompanied with a very low Hf concentra-  
586 tion is only the result of different scavenging behavior be-  
587 tween both elements.

588 Further south at station S2, just north of the STF, the  
589 HREE are 40% lower while the LREE are between 60%  
590 and 84% lower, and Hf is at its minimum value of  
591 0.04 pmol/kg. The REE pattern shifts from a flatter shale  
592 normalized shape at S1 to a steeper seawater-like pattern  
593 at S2 with LREEs relatively depleted compared to HREEs  
594 ( $La_N/Yb_N = 0.5$ ) and a lower  $Ce/Ce^*$  of −0.53 (Fig. 4 and

Table 2). Although not very pronounced, this pattern, to-  
gether with the overall low abundance of the REEs suggest  
either a low contribution from the dissolution of terrige-  
nous material or enhanced scavenging due to higher pro-  
ductivity at the STF, most likely a combination of both  
processes. Hegner et al. (2007) reported low aluminum  
(Al) and thorium (Th) concentrations in particles docu-  
menting very low terrigenous inputs to this area thus pro-  
viding an explanation for the low dissolved REE  
concentrations. These authors also proposed that scaveng-  
ing of Nd from seawater on the order of only 5–10% of  
the available dissolved load would be sufficient to yield  
the observed Nd concentrations adsorbed to the particles.  
However, the slightly lower  $La_N/Yb_N$  ratios from our study  
between 0.19 and 0.29 from the STF to the BDY compared  
to the ones from the Weddell Gyre (~0.29 to 0.38) may  
indicate more ample scavenging, since LREE are preferen-  
tially scavenged to biogenic particles (e.g. Elderfield and  
Greaves, 1982). The low dissolved Nd concentrations in  
our surface water samples from the ACC can thus be ex-  
plained by limited supply but additional scavenging also  
seems to be involved.

#### 4.1.2. Antarctica and South America

The elemental distribution of the sampled stations near  
the Antarctic continent does not indicate strong terrigenous  
supply. Within the entire Weddell Gyre Hf and REE con-  
centrations are elevated relative to the ACC but with no sig-  
nificant increases similar to those observed for S1 close to  
the Antarctic continent (Figs. 3 and 4). However, at sta-  
tions S7 and 222, close to the volcanic King George Island  
(KGI, Fig. 2C) and east of the Antarctic Peninsula (AAP),  
respectively, the Hf and REE concentrations are clearly ele-  
vated. In particular, at S7 the Hf concentration of  
0.38 pmol/kg is almost twice as high as it is on average in  
the Weddell Gyre, whereas the REE concentrations are  
on average only about 10–50% higher. At station 222 no  
significant increase of the Hf concentration in the surface

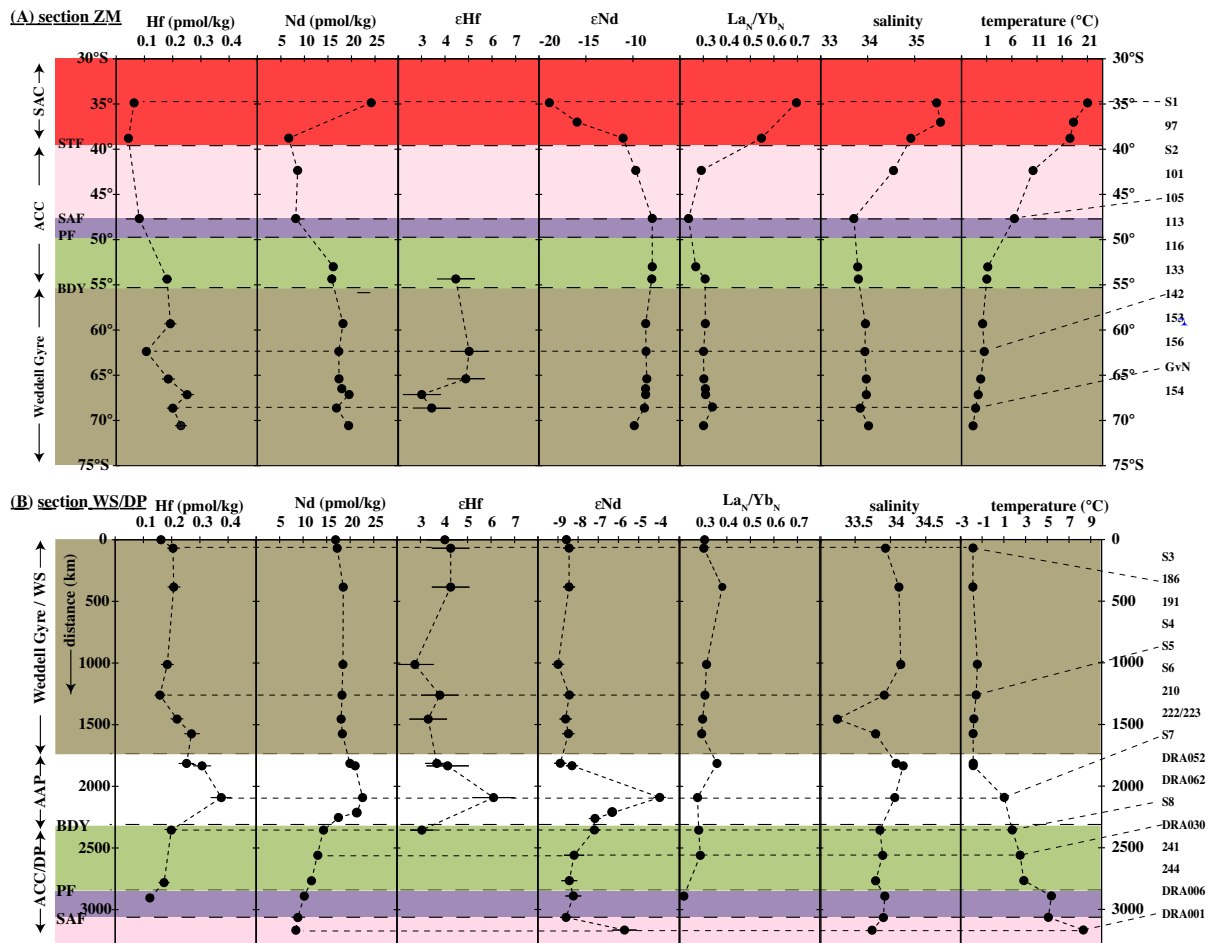


Fig. 3. Geochemical composition of the surface samples (<100 m water depth) along the Zero Meridian (A) and through the Weddell Sea and the Drake Passage (B), note the different scales in  $\epsilon_{Nd}$  and temperature between (A) and (B). Major hydrographic transitions are marked by horizontal dashed lines (see text). Hafnium and Nd concentrations largely follow a similar pattern in both sections with the exception that S1 in (A) shows a significantly elevated Nd concentration. The Hafnium and Nd isotope compositions also follow similar trends where combined data are available. The only exceptions are stations 156 and GvN, where the  $\epsilon_{Hf}$  drops to less radiogenic values, whereas  $\epsilon_{Nd}$  does not. The La/Yb ratios are normalized to PAAS (Taylor and McLennan, 1985). Horizontal bars indicate the analytical uncertainties, which in most cases are smaller than symbol size.

632 water is observed. The more radiogenic Hf and Nd isotope  
 633 compositions at S7 ( $\epsilon_{Hf} = +6.1$  and of  $\epsilon_{Nd} = -4.0$ , respec-  
 634 tively) clearly document external inputs of these elements  
 635 from the basaltic rocks of KGI. The observed radiogenic  
 636 Nd isotope composition accompanied only by a small in-  
 637 crease of the REE concentrations implies a boundary ex-  
 638 change process with the KGI. A similar, though not as  
 639 pronounced exchange of Nd isotopes has obviously influ-  
 640 enced station 154, which has been sampled in 135 m wa-  
 641 ter depth close to the seafloor at the Antarctic ice shelf. Here  
 642 the Nd isotope composition of  $\epsilon_{Nd} = -9.9$  is more than 1  
 643  $\epsilon$ -unit lower than those in the nearby surface stations  
 644 (Fig. 3B). A simple mass balance calculation, using the  
 645 Nd isotope composition of station 154 ( $\epsilon_{Nd} = -9.9$ ), the  
 646 average isotope composition of the Weddell Sea and that  
 647 of glacio-marine sediments ( $\epsilon_{Nd} = -8.6$  and  $-15.0$ , respec-  
 648 tively, this study; Roy et al., 2007; Stichel et al., 2014), sug-  
 649 gests that about 20% of the Nd must be derived from shelf  
 650 sediments off Dronning Maud Land. However, the increase

of the Nd concentration and most of the REEs is less than  
 10% compared to the average surface concentration of  
 17.9 pmol/kg. In order to test if processes other than parti-  
 cle or sediment release are involved, we simply calculate a  
 hypothetical  $\epsilon_{Nd}$  signature only caused by exchange with  
 particles based on the above considerations and compare  
 it with the measured value. This is an approach similar to  
 the one of Lacan and Jeandel (2001) using the following  
 equation:  $\epsilon_{Nd-calc} = ([Nd]_{initial} * \epsilon_{Nd-initial} + \Delta[Nd] * \epsilon_{Nd-  
 SED}) / [Nd]_{meas}$ , where  $[Nd]_{initial}$  is the average concentration  
 of surface waters in the Weddell Sea (18 pmol/kg),  $[Nd]_{meas}$   
 the one of station 154 (19.4 pmol/kg),  $\Delta[Nd]$  the difference  
 in concentration (1.4 pmol/kg) and  $\epsilon_{Nd-initial}$  is the average  
 isotope composition of the Weddell Sea surface waters  
 ( $\epsilon_{Nd} = -8.6$ ). The isotope composition of the sediment  
 ( $\epsilon_{Nd-SED} = -15.0$ ) is taken from Roy et al. (2007) close to  
 station 154 of our study. If the calculated value is the same  
 as the one observed, the difference in the isotope composi-  
 tion between these waters seems to be derived entirely by

particle or sediment release. The calculated isotope composition of  $\epsilon_{\text{Nd}} = -9.1$ , however, is about 0.8  $\epsilon_{\text{Nd}}$  units more radiogenic, which is just about higher than the external reproducibility of  $\pm 0.4$ , but still suggests that boundary exchange processes do influence the isotope composition at this location. If particle dissolution was the only process to explain the isotope composition at station 154, the corresponding  $\Delta[\text{Nd}]$  must be  $\sim 4.5$  pmol/kg, whereas the observed  $\Delta[\text{Nd}]$  is only 1.4 pmol/kg.

The only significant drop towards less radiogenic Hf isotope compositions is observed at station 153 ( $\epsilon_{\text{Hf}} = +4.9$ ) and stations 156 and GvN nearest to Dronning Maud Land ( $\epsilon_{\text{Hf}} = +3.0$  and  $\epsilon_{\text{Hf}} = +3.4$ , respectively; Fig. 3A). The proximity of these stations to the Antarctic shelf suggests an unradiogenic Hf input from the Dronning Maud Land (e.g. van de Flierdt et al., 2006, 2007). Although a shift to unradiogenic Nd is not observed for these stations the unradiogenic Nd isotope composition at the southernmost station 154 ( $\epsilon_{\text{Nd}} = -9.9$ ,  $\epsilon_{\text{Hf}}$  is not available) also suggests Nd inputs from the Dronning Maud Land. In general, Nd isotopes in the WG are slightly less radiogenic than in the ACC (Table 1), also pointing at some Nd fluxes from Antarctica to the Weddell Sea. The less radiogenic Hf signatures observed in the vicinity of Dronning Maud Land may be a consequence of a relatively congruent release of Hf from the exposed rocks on land due to the glacial grinding of weathering resistant zircons. Evidence for a more congruent release of Hf under physical weathering conditions has previously been found in ferromanganese crusts, which recorded less radiogenic Hf isotope compositions than those of the seawater array in regions and during periods of prevailing enhanced physical weathering (Piotrowski et al., 2000; van de Flierdt et al., 2002, 2007). These authors concluded that the onset of Northern Hemisphere Glaciation and the accompanying enhanced physical weathering led to a more congruent release of Hf isotopes from the old continental crust in northern Canada and Greenland. However, the shift of the Hf isotope compositions in these studies was several  $\epsilon_{\text{Hf}}$  units compared to only 1  $\epsilon_{\text{Hf}}$  unit in our case. Our data from the Weddell Sea in the proximity of Dronning Maud Land thus suggest that the local Hf isotope composition in this case is not a sensitive tracer for physical weathering inputs. Furthermore, the combined Hf and Nd isotope data do not plot significantly closer to the terrestrial array (Fig. 1).

The exchange with Antarctica is clearly more prominent at station S7, close to King George Island (KGI). Like most of the South Sandwich Islands, KGI is composed of relatively young, mafic island arc rocks (see Section 1.2). Previous studies on James Ross Island, which has the same geological origin as KGI (e.g. Machado et al., 2005) reported Hf and Nd isotope compositions of the bulk rocks of  $\epsilon_{\text{Hf}} \sim +7$  (Sims et al., 2008) and  $\epsilon_{\text{Nd}} \sim +5$  (Hole et al., 1994; Kosler et al., 2009). Enhanced weathering input from these rocks is also indicated by the high particulate concentrations of Hf and Nd (Hegner et al., 2007; Table 3), which are likely to modify the isotope composition of the surface waters. We thus also calculated the hypothetical Nd isotope composition only controlled by partial dissolution of particles at station S7, analogous to the approach above. We

used the Nd isotope composition and concentration of station 230/50 m ( $\epsilon_{\text{Nd}} = -8.2$ ; 18.9 pmol/kg) as a representative value of surface waters from the Drake Passage. The isotope composition of KGI ranges from  $\epsilon_{\text{Nd}} = +1$  to  $+5$  (Hole et al., 1994; Kosler et al., 2009), from which a hypothetical Nd isotope composition of  $\epsilon_{\text{Nd}} = -6.7$  to  $-6.0$  is calculated. This is  $2-2.7$   $\epsilon_{\text{Nd}}$  units less radiogenic than the observed signatures (Fig. 3B). The observed Nd isotope composition of  $\epsilon_{\text{Nd}} = -4.0$  is therefore largely a result of boundary exchange rather than dissolution of weathered volcanic material. The REE pattern of S7 is similar to that of LCDW (Hathorne et al., 2012) and also suggests that elemental input derived from volcanic material (REE values from Machado et al., 2005) is of minor importance (Fig. 4).

The observed radiogenic Hf isotope composition at KGI of  $\epsilon_{\text{Hf}} = +6.1$  (S7) also indicates a significant influence from weathering inputs on the surface water isotope composition. The Hf concentration of 0.38 pmol/kg is also significantly higher than the average in the Weddell Sea or the ACC (Fig. 3 and Table 1). Applying the same approach as for Nd reveals that the hypothetical Hf isotope composition should be between  $+3.8$  and  $+5.4$ , using average compositions of the Weddell Gyre and the ACC ( $\epsilon_{\text{Hf-initial}} = +3$  to  $+4$  and  $[\text{Hf}]_{\text{initial}} = 0.2$  to  $0.3$  pmol/kg). The observed Hf isotope composition at S7, however, is  $\epsilon_{\text{Hf}} = +6.1$ , indicating again that boundary exchange processes govern the isotope composition rather than addition of dissolved Hf from particles or weathered material.

The peak radiogenic Hf and Nd isotope values sharply decrease towards less radiogenic levels of  $\epsilon_{\text{Nd}} = -6.3$  (DRA052) and  $\epsilon_{\text{Nd}} = -7.2$ ;  $\epsilon_{\text{Hf}} = +3$  (S8 and DRA062) towards the Drake Passage, implying that the influence of KGI is locally limited and that the boundary exchange signals are rapidly diluted by surface ocean waters from the Drake Passage. The imprint on the Hf isotope compositions is even more locally confined and is only detected at station 7. This is explained by the lower isotopic contrast for Hf between station 7 ( $\epsilon_{\text{Hf}} = +6.1$ ) and the “typical” ACC surface ocean ( $\epsilon_{\text{Hf}} \sim +4$ , Fig. 3B) relative to the contrast observed for Nd isotopes, but may also reflect a shorter surface ocean residence time for Hf than for Nd as suggested before (Rickli et al., 2010). A more radiogenic Nd isotope signal is again observed in the northern part of the Drake Passage (Fig. 3B). At station DRA001 the Nd isotope composition of  $\epsilon_{\text{Nd}} = -5.7$  implies radiogenic input from the southern tip of South America, possibly derived from the Pali Aike Volcanic Field, which consist of lavas with a Nd isotope composition as radiogenic as  $\epsilon_{\text{Nd}} \sim +5$  (D’Orazio et al., 2000). The imprint is only observed close to the coast and the Nd isotope composition of the open Drake Passage is indistinguishable from the ACC  $\epsilon_{\text{Nd}}$  signatures of  $\sim -8$  along the Zero Meridian.

#### 4.2. Cycling of Hf and Nd in the Southern Ocean

Previous studies have suggested that Hf and REEs are prone to scavenging by biogenic opal in the Southern Ocean (e.g. Rickli et al., 2009; Stichel et al., 2011). It was suggested that the large specific surface area of diatom frustules acts as an effective scavenger for Hf and Nd. Stichel

et al. (2011) found that Hf and Nd concentrations correlate well with dissolved Si content in the Southern Ocean and suggested that the observed linear increase of Nd concentration with water depth represents a steady release of Nd, while the frustules dissolve. This feature was not observed for Hf, indicating a different remineralization behavior. A comparison of particulate Nd/Hf ratios from our study with the particulate opal content in the eastern Atlantic sector of the ACC indicates a strong negative correlation between these parameters (Nd and opal data from Hegner et al. (2007); Fig. 5 and Table 3). This suggests that Hf is more efficiently scavenged from surface waters than Nd when siliceous frustules of diatoms are present. This means that diatom productivity acts as a more effective sink for Hf than for Nd in the Southern Ocean given that a significant fraction of the opal is buried in the sediment. However, one would expect that such an effect would influence the dissolved fraction as well, which is not observed (Fig. 5B). Except for stations S1, S2 and 142 the elemental distribution of Hf and Nd is very similar and does not support any fractionation by scavenging. One plausible explanation is that the particulate and dissolved fractions were collected separately on different expeditions. The particulate samples were taken between November 1997 and March 1998 (Hegner et al., 2007), whereas the dissolved fraction was sampled from February to April 2008. To estimate if and to what extent the diatoms contribute to a preferential scavenging or elemental fractionation, parallel collection of the particulate and dissolved fractions is required in future studies.

South of the ACC the dissolved concentrations for both elements are elevated and rather homogenous, with the exception of station 142, where the Hf concentration amounts to only 0.11 pmol/kg, i.e. only half of the average Hf concentration observed for other samples in this area. Hegner et al. (2007) also observed higher particulate Nd concentrations in the WG (more than 2 pmol/L) together with unradiogenic detrital Nd isotope compositions and high Al concentrations of up to 7.2 nmol/L, supporting supply of terrigenous material by icebergs. However, the elevated concentrations of Nd (~18 pmol/kg) and Hf (~0.21 pmol/kg) observed within the Weddell Gyre in our study compared to those north of the PF are more likely caused by accumulation of deep sourced Hf and Nd rather than derived from icebergs, as discussed below. The highest dissolved Hf and Nd concentrations south of the STF of 0.38 pmol/kg and 22.1 pmol/kg, respectively, were measured near the volcanic King George Island. This matches the highest concentrations in particulate Hf and Nd (2.88 pmol/L and 24.44 pmol/L, respectively, Hegner et al., 2007; Table 3), implying a strong input from this or adjacent islands.

Terrigenous influence is further supported by the isotope composition of particles in the Weddell Gyre yielding values  $\epsilon_{Nd} = -15$  or lower, suggesting an enhanced input of material from East Antarctica via ice rafting (Hegner et al., 2007). Alternatively, the Weddell Gyre's average dissolved Nd and Hf isotope composition is nearly identical to that of CDW ( $\epsilon_{Nd} = -8.5 \pm 0.3$ ,  $\epsilon_{Hf} = +4.4 \pm 0.6$ , Stichel et al., 2011) in the studied area. This similarity may suggest that the isotope compositions of surface waters are the result

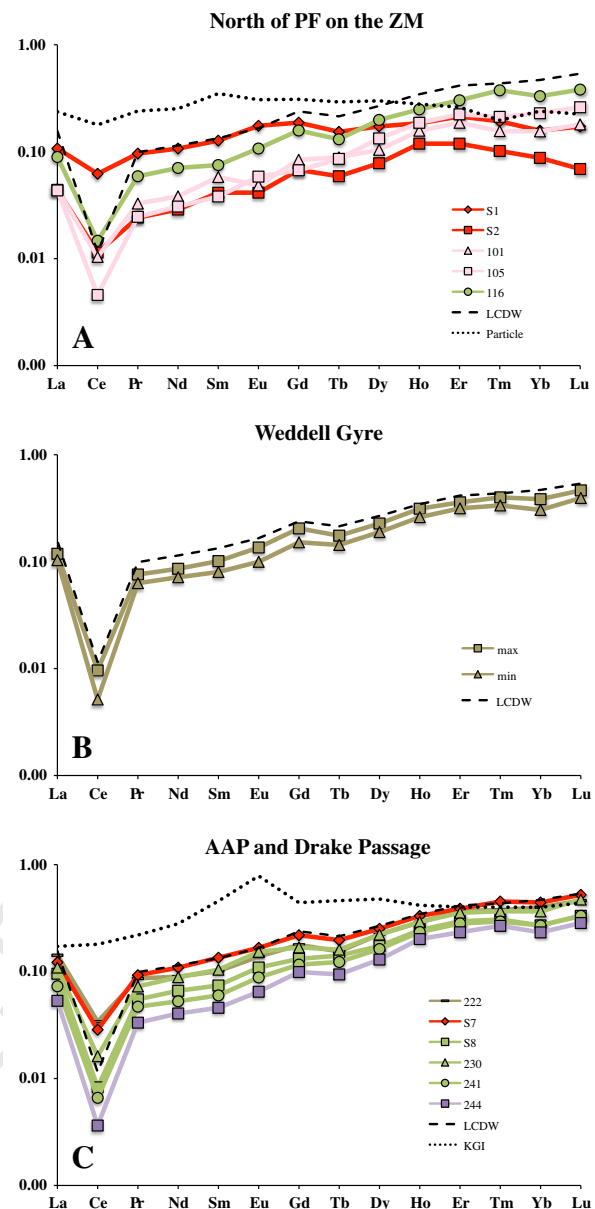


Fig. 4. Shal-normalized REE patterns of surface samples (<100 m depth) from north of the Polar Front on the Zero Meridian (A), the Weddell Gyre (B) and the Antarctic Peninsula including the Drake Passage (C). The color-coding corresponds to the zones illustrated in Fig. 3. Additional patterns are shown for comparison: The composition of suspended particles close to South Africa (A, Hegner et al., 2007), Lower Circumpolar Deep Water (LCDW) at 2000 m in the Weddell Gyre (A–C, Hathorne et al., 2012) and the composition of volcanic rocks of King George Island (C, Machado et al., 2005). Seawater values are normalized to PAAS multiplied by  $10^6$ , whereas the normalized particulate values are multiplied by 0.01 to fit on the same scale.

of vigorous mixing and accumulation of these elements 848  
within the WG rather than reflecting the result of low terrigenous 849  
input. A supply of Hf and Nd from deeper waters is 850  
supported by relatively high surface water concentrations 851  
of ~0.2 pmol/kg and ~18 pmol/kg, respectively. Addition- 852

ally, the REE patterns in the Weddell Gyre are very similar to the pattern of LCDW in Hathorne et al. (2012). On the basis of the distribution of the highly particle reactive elements Th and protactinium (Pa) in the Weddell Gyre, Rutgers van der Loeff and Berger (1993) documented that particle export and thus scavenging is very low leading to their accumulation in the water column of the Weddell Gyre. The general homogeneity of Hf and REE within the Weddell Gyre also suggests accumulation of these elements. This observation can be used to estimate the minimum residence time of Hf and REE in surface waters within the Weddell Gyre. The average residence time of a parcel of surface water there is around 2.5 years (Gordon and Huber, 1990; Hoppema et al., 1995), implying that the residence times of Hf and the REEs is at least in that order.

## 5. SUMMARY AND CONCLUSIONS

In this study the first combined surface water Hf and Nd isotope compositions and Hf and REE concentrations of surface waters from the Atlantic sector of the Southern Ocean are presented. The data set comprises a wide range of Hf and Nd concentrations from low values in the South Atlantic Current (0.04 and 6.7 pmol/kg) to maximum values near King George Island (0.38 and 22.6 pmol/kg).

- (1) The highest Nd concentrations were found in surface waters southwest of Cape Town. In the same sample, a very low Hf concentration indicates restricted release of Hf from the South African continental crust. High  $La_N/Yb_N$  ratios between 0.50 and 0.68 and markedly flat PAAS-normalized REE patterns support enhanced terrigenous input from South Africa. This is accompanied by the least radiogenic Nd isotope composition as low as  $\epsilon_{Nd} = -18.9$ , which was probably advected via the Agulhas Current and documents inputs from weathering of Archean cratonic rocks exposed in South Africa.
- (2) The low elemental concentrations just north of the Subantarctic Front most likely result from a combination of limited terrigenous supply and high biological productivity. A good correlation of the particulate Nd/Hf ratio with biogenic  $SiO_2$  content suggests a preferential scavenging of Hf onto siliceous frustules. The Hf and Nd concentrations are lower north of the PF and increase southward to more constant values within the WG indicating accumulation resulting from low biogenic particle fluxes and thus a weak scavenging efficiency of trace metals.
- (3) We observe the influence of volcanic rocks by marked increases of Hf and Nd concentrations in the vicinity of King George Island. These are, accompanied by a pronounced excursion to more radiogenic isotope compositions for both elements ( $\epsilon_{Hf} = +6.1$ ;  $\epsilon_{Nd} = -4.0$ ). Mass balance considerations suggest that not only elemental release originating from particle dissolution but also boundary exchange processes govern the isotope composition of surface waters. A similar influence from mantle-

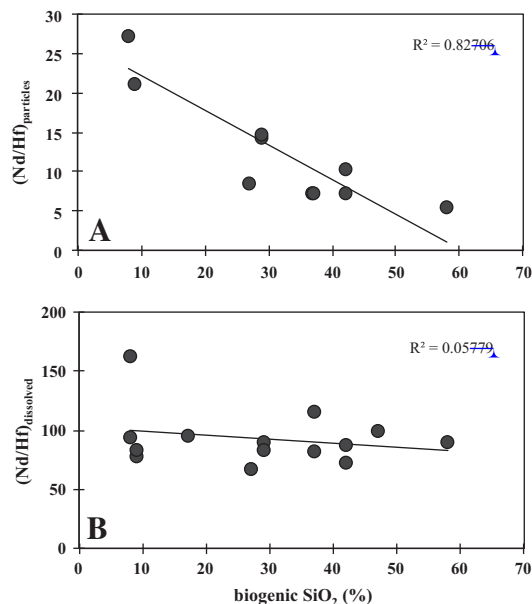


Fig. 5. Nd/Hf ratio in particles (A) and in the dissolved fraction (B) plotted against the biogenic opal content in particles (Hegner et al., 2007).

derived rocks is observed at the southern tip of Chile. Boundary exchange processes most likely also take place on the Antarctic shelf where less radiogenic Nd than the average composition of the Weddell Gyre is found at 135 m water depth close to the seafloor.

- (4) The Hf and Nd isotope compositions of the surface samples are shifted towards more radiogenic Hf values for given Nd values when compared to the “terrestrial array” and plot on the “seawater array”.
- (5) The majority of the studied areas comprising the ACC and the Weddell Gyre shows essentially homogenous isotope compositions of  $\epsilon_{Hf} \sim +4$  and  $\epsilon_{Nd} \sim -8.5$ , which is similar to the deep water compositions studied previously and documents strong vertical and lateral mixing of Hf and Nd south of the Polar Front, indicating a residence time at least as long as the turnover time of surface waters in the Weddell Gyre.

## UNCITED REFERENCES

Boebel et al. (2003), Jacobs et al. (1992), Richardson et al. (2003), You et al. (2003).

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- 945 **REFERENCES**
- 946 Albarède F., Simonetti A., Vervoort J. D., Blichert-Toft J. and  
 947 Abouchami W. (1998) A Hf-Nd isotopic correlation in ferro-  
 948 manganese nodules. *Geophys. Res. Lett.* **25**, 3895–3898.
- 949 Arsouze T., Dutay J.-C., Lacan F. and Jeandel C. (2009)  
 950 Reconstructing the Nd oceanic cycle using a coupled dynamical  
 951 – biogeochemical model. *Biogeosciences* **6**, 2829–2846.
- 952 Bau M. and Koschinsky A. (2006) Hafnium and neodymium  
 953 isotopes in seawater and in ferromanganese crusts: the “element  
 954 perspective”. *Earth Planet. Sci. Lett.* **241**, 952–961.
- 955 Bayon G., Vigier N., Burton K. W., Jean Carignan A. B.,  
 956 Etoubleau J. and Chu N.-C. (2006) The control of weathering  
 957 processes on riverine and seawater hafnium isotope ratios.  
 958 *Geology* **34**, 433.
- 959 Bayon G., Burton K. W., Soulet G., Vigier N., Dennielou B.,  
 960 Etoubleau J., Ponzevera E., German C. R. and Nesbitt R. W.  
 961 (2009) Hf and Nd isotopes in marine sediments: constraints on  
 962 global silicate weathering. *Earth Planet. Sci. Lett.* **277**, 318–326.
- 963 Boebel O., Lutjeharms J., Schmid C., Zenk W., Rossby T. and  
 964 Barron C. (2003) The Cape Cauldron: a regime of turbulent  
 965 inter-ocean exchange. *Deep Sea Res. Part II: Topical Stud.*  
 966 *Oceanogr.* **50**, 57–86.
- 967 Cole D. I. (1992) Evolution and development of the Karoo Basin.  
 968 In *Inversion Tectonics of the Cape Fold Belt* (eds. M. J. de Wit  
 969 and I. G. D. Ransome). Karoo and Cretaceous Basins of  
 970 Southern Africa, Balkema, Rotterdam, pp. 87–100.
- 971 Chen T.-Y. et al. (2011) Zircon effect alone insufficient to generate  
 972 seawater Nd-Hf isotope relationships. *Geochem. Geophys.*  
 973 *Geosyst.* **12**, Q05003. <http://dx.doi.org/10.1029/2010GC003363>.
- 974 Dalziel I. W. D. (1992) Antarctica – a tale of 2 supercontinents.  
 975 *Annu. Rev. Earth Planet. Sci.* **20**, 501–526.
- 976 David K., Frank M., O’Nions R. K., Belshaw N. S. and Arden J.  
 977 W. (2001) The Hf isotope composition of global seawater and  
 978 the evolution of Hf isotopes in the deep Pacific Ocean from Fe–  
 979 Mn crusts. *Chem. Geol.* **178**, 23–42.
- 980 de Baar H. J. W., Bacon M. P. and Brewer P. G. (1983) Rare-earth  
 981 distributions with a positive Ce anomaly in the Western North  
 982 Atlantic Ocean. *Nature* **301**, 324–327.
- 983 de Baar H. J. W., Bacon M. P., Brewer P. G. and Bruland K. W.  
 984 (1985) Rare earth elements in the Pacific and Atlantic. *Oceans*  
 985 **49**, 1943–1959.
- 986 Deacon G. E. R. (1979) The Weddell gyre. *Deep Sea Res. Part A.*  
 987 *Oceanogr. Res. Papers* **26**, 981–995.
- 988 D’Orazio M., Agostini S., Mazzarini F., Innocenti F., Manetti P.,  
 989 Haller M. J. and Lahsen A. (2000) The Pali Aike Volcanic  
 990 Field, Patagonia: slab-window magmatism near the tip of South  
 991 America. *Tectonophysics* **321**, 407–427.
- 992 Elderfield H. and Greaves M. J. (1982) The rare earth elements in  
 993 seawater. *Nature* **296**, 214–219.
- 994 Elderfield H., Upstillgoddard R. and Sholkovitz E. (1990) The rare  
 995 earth elements in rivers, estuaries, and coastal seas and their  
 996 significance to the composition of ocean waters. *Geochim.*  
 997 *Cosmochim. Acta* **54**, 971–991.
- 998 Emery W. J. (1977) Antarctic polar frontal zone from Australia to  
 999 the Drake Passage. *J. Phys. Oceanogr.* **7**, 811–822.
- 1000 Fitzsimons I. (2000) A review of tectonic events in the East  
 1001 Antarctic Shield and their implications for Gondwana and  
 1002 earlier supercontinents. *J. Afr. Earth Sci.* **31**, 3–23.
- Frank M., Whiteley N., Kasten S., Hein J. R. and O’Nions K. 1003  
 (2002) North Atlantic Deep Water export to the Southern 1004  
 Ocean over the past 14 Myr: evidence from Nd and Pb isotopes 1005  
 in ferromanganese crusts. *Paleoceanography* **17**, 1022. [http://](http://dx.doi.org/10.1029/2000pa000606) 1006  
[dx.doi.org/10.1029/2000pa000606](http://dx.doi.org/10.1029/2000pa000606). 1007
- Franzese A. M., Hemming S., Goldstein S. and Anderson R. (2006) 1008  
 Reduced Agulhas Leakage during the Last Glacial Maximum 1009  
 inferred from an integrated provenance and flux study. *Earth* 1010  
*Planet. Sci. Lett.* **250**, 72–88. 1011
- German C. R., Klinkhammer G. P., Edmond J. M., Mitra A. and 1012  
 Elderfield H. (1990) Hydrothermal scavenging of rare-earth 1013  
 elements in the ocean. *Nature* **345**, 516–518. 1014
- German C. R., Masuzawa T., Greaves M. J., Elderfield H. and 1015  
 Edmond J. M. (1995) Dissolved Rare-Earth Elements in the 1016  
 Southern-Ocean - Cerium Oxidation and the Influence of 1017  
 Hydrography. *Geochim. Cosmochim. Acta* **59**, 1551–1558. 1018
- Godfrey L. V., Field M. P. and Sherrill R. M. (2008) The estuarine 1019  
 distributions of Zr, Hf and Ag in the Hudson River, and the 1020  
 implications for their continental and anthropogenic sources to 1021  
 seawater. *Geochem. Geophys. Geosyst.* **9**, Q12007. [http://](http://dx.doi.org/10.1029/2008GC002123) 1022  
[dx.doi.org/10.1029/2008GC002123](http://dx.doi.org/10.1029/2008GC002123). 1023
- Godfrey L. V., Zimmermann B., Lee D. C., King R. L., Vervoort J. 1024  
 D., Sherrill R. M. and Halliday A. N. (2009) Hafnium and 1025  
 neodymium isotope variations in NE Atlantic seawater. *Geo-* 1026  
*chem. Geophys. Geosyst.* **10**, Q08015. [http://dx.doi.org/10.1029/](http://dx.doi.org/10.1029/2009GC002508) 1027  
[2009GC002508](http://dx.doi.org/10.1029/2009GC002508). 1028
- Greaves M., Statham P. and Elderfield H. (1994) Rare earth 1029  
 element mobilization from marine atmospheric dust into 1030  
 seawater. *Mar. Chem.* **46**, 255–260. 1031
- Haley B. A., Klinkhammer G. P. and McManus J. (2004) Rare 1032  
 earth elements in pore waters of marine sediments. *Geochim.* 1033  
*Cosmochim. Acta* **68**, 1265–1279. 1034
- Halliday N., Davidson P., Owen M. and Olivarez M. (1992) 1035  
 Metalliferous sediments and the scavenging residence time of 1036  
 Nd near hydrothermal vents. *Geophys. Res. Lett.* **19**, 761– 1037  
 764. 1038
- Hathorne E., Haley B. A., Stichel T., Grasse P., Zieringer M. and 1039  
 Frank M. (2012) Online preconcentration ICP-MS analysis of 1040  
 rare earth elements in seawater. *Geochem. Geophys. Geosyst.* **13**, 1041  
 Q01020. <http://dx.doi.org/10.1029/2011GC003907>. 1042
- Hegner E., Dauelsberg H. J., Rutgers van der Loeff M. M., Jeandel 1043  
 C. and de Baar H. J. W. (2007) Nd isotopic constraints on the 1044  
 origin of suspended particles in the Atlantic Sector of the 1045  
 Southern Ocean. *Geochem. Geophys. Geosyst.* **8**, Q10008. [http://](http://dx.doi.org/10.1029/2007GC001666) 1046  
[dx.doi.org/10.1029/2007GC001666](http://dx.doi.org/10.1029/2007GC001666). 1047
- Hofmann E. E. (1985) The large-scale horizontal structure of the 1048  
 Antarctic circumpolar current from FGGE drifters. *J. Geophys.* 1049  
*Res.* **90**, 7087–7097. 1050
- Hole M. J., Saunders A. D., Rogers G. and Sykes M. A. (1994) The 1051  
 relationship between alkaline magmatism, lithospheric exten- 1052  
 sion and slab window formation along continental destructive 1053  
 plate margins. *Spec. Publ. Geol. Soc. London* **81**, 265–285. 1054
- Jacobs S. S., Hellmer H. H., Doake C. S. M., Jenkins A. and 1055  
 Frolich R. M. (1992) Melting of ice shelves and the mass 1056  
 balance of Antarctica. *J. Glaciol.* **38**, 375–387. 1057
- Jacobsen S. B. and Wasserburg G. J. (1980) Sm–Nd isotopic 1058  
 evolution of chondrites. *Earth Planet. Sci. Lett.* **50**, 139–155. 1059
- Jeandel C., Bishop J. K. and Zindler A. (1995) Exchange of 1060  
 neodymium and its isotopes between seawater and small and 1061  
 large particles in the Sargasso Sea. *Geochim. Cosmochim. Acta* 1062  
**59**, 535–547. 1063
- Jeandel C., Venchiarutti C., Bourquin M., Pradoux C., Lacan F., 1064  
 van Beek P. and Riotte J. (2011) Single column sequential 1065  
 extraction of Ra, Nd, Th, Pa and U from a natural sample. 1066  
*Geostand. Geoanal. Res.* **1–9**. [http://dx.doi.org/10.1111/j.1751-](http://dx.doi.org/10.1111/j.1751-908X.2010.00087.x) 1067  
[908X.2010.00087.x](http://dx.doi.org/10.1111/j.1751-908X.2010.00087.x). 1068



- 1069 Klatt O., Fahrbach E., Hoppema M. and Rohardt G. (2005) The  
1070 transport of the Weddell Gyre across the Prime Meridian. *Deep*  
1071 *Sea Res. Part II: Topical Stud. Oceanogr.* **52**, 513–528.
- 1072 Kosler J., Magna T., Mlcoch B., Mixa P., Nyvlt D. and Holub F.  
1073 (2009) Combined Sr, Nd, Pb and Li isotope geochemistry of  
1074 alkaline lavas from northern James Ross Island (Antarctic  
1075 Peninsula) and implications for back-arc magma formation.  
1076 *Chem. Geol.* **258**, 207–218.
- 1077 Lacan F. and Jeandel C. (2001) Tracing Papua New Guinea  
1078 imprint on the central Equatorial Pacific Ocean using neodym-  
1079 ium isotopic compositions and Rare Earth Element patterns.  
1080 *Earth Planet. Sci. Lett.* **186**, 497–512.
- 1081 Lacan F. and Jeandel C. (2005) Neodymium isotopes as a new tool  
1082 for quantifying exchange fluxes at the continent–ocean inter-  
1083 face. *Earth Planet. Sci. Lett.* **232**, 245–257.
- 1084 Machado A., Lima E. F., Chemale F., Morata D., Oteiza O.,  
1085 Almeida D. P. M., Figueiredo A. M. G., Alexandre F. M. and  
1086 Urrutia J. L. (2005) Geochemistry constraints of Mesozoic–  
1087 Cenozoic calc-alkaline magmatism in the South Shetland arc,  
1088 Antarctica. *J. S. Am. Earth Sci.* **18**, 407–425.
- 1089 Millar I. L. and Pankhurst R. J. (1987) Rb–Sr geochronology of  
1090 the region between the Antarctic Peninsula and the Transant-  
1091 arctic Mountains: Haag Nunataks and Mesozoic granitoids. In  
1092 *Gondwana Six: Structure, Tectonics, and Geophys* (ed. G. D.  
1093 McKenzie). Monogr. Ser. AGU, Washington, DC, pp. 151–  
1094 160.
- 1095 Millar I. L., Willan R. C. R., Wareham C. D. and Boyce A. J.  
1096 (2001) The role of crustal and mantle sources in the genesis of  
1097 granitoids of the Antarctic Peninsula and adjacent crustal  
1098 blocks. *J. Geol. Soc.* **158**, 855–867.
- 1099 Munker C., Weyer S., Scherer E. and Mezger K. (2001) Separation  
1100 of high field strength elements (Nb, Ta, Zr, Hf) and Lu from  
1101 rock samples for MC-ICPMS measurements. *Geochem. Geo-*  
1102 *phys. Geosyst.* **2**. <http://dx.doi.org/10.1029/2001GC000183>.
- 1103 Nowell G. M., Kempton P. D., Noble S. R., Fitton J. G., Saunders  
1104 A. D., Mahoney J. J. and Taylor R. N. (1998) High precision  
1105 Hf isotope measurements of MORB and OIB by thermal  
1106 ionisation mass spectrometry: insights into the depleted mantle.  
1107 *Chem. Geol.* **149**, 211–233.
- 1108 Nowlin, Jr., W. D. and Whitworth, III, T. (1977) Structure and  
1109 transport of the Antarctic circumpolar current at Drake  
1110 Passage from short-term measurements. *J. Phys. Oceanogr.* **7**,  
1111 788–802.
- 1112 Pankhurst R. J. et al. (1998) The Chon Aike province of Patagonia  
1113 and related rocks in West Antarctica: a silicic large igneous  
1114 province. *J. Volcanol. Geoth. Res.* **81**, 113–136.
- 1115 Patchett P. J., White W. M., Feldmann H., Kielinczuk S. and  
1116 Hofmann A. W. (1984) Hafnium rare-earth element fractiona-  
1117 tion in the sedimentary system and crustal recycling into the  
1118 earths mantle. *Earth Planet. Sci. Lett.* **69**, 365–378.
- 1119 Peterson R. and Stramma L. (1991) Upper-level circulation in the  
1120 South Atlantic Ocean. *Prog. Oceanogr.* **26**, 1–73.
- 1121 Piepgras D. J. and Jacobsen S. B. (1992) The behavior of rare earth  
1122 elements in seawater: precise determination of variations in the  
1123 North Pacific water column. *Geochim. Cosmochim. Acta* **56**,  
1124 1851–1862.
- 1125 Pin C. and Zalduegui J. F. S. (1997) Sequential separation of light  
1126 rare-earth elements, thorium and uranium by miniaturized  
1127 extraction chromatography: Application to isotopic analyses of  
1128 silicate rocks. *Anal. Chim. Acta* **339**, 79–89.
- 1129 Piotrowski A. M., Lee D.-C., Christensen J. N., Burton K. W.,  
1130 Halliday A. N., Hein J. R. and Gunther D. (2000) Changes in  
1131 erosion and ocean circulation recorded in the Hf isotopic  
1132 compositions of North Atlantic and Indian Ocean ferroman-  
1133 ganese crusts. *Earth Planet. Sci. Lett.* **181**, 315–325.
- Rempfer J., Stocker T. F., Joos F., Dutay J.-C. and Siddall M. 1134  
(2011) Modelling Nd-isotopes with a coarse resolution ocean 1135  
circulation model: Sensitivities to model parameters and 1136  
source/sink distributions. *Geochim. Cosmochim. Acta* **75**, 1137  
5927–5950. 1138
- Richardson P., Lutjeharms J. and Boebel O. (2003) Introduction to 1139  
the “Inter-ocean exchange around southern Africa”. *Deep Sea* 1140  
*Res. Part II: Topical Stud. Oceanogr.* **50**, 1–12. 1141
- Rickli J., Frank M. and Halliday A. N. (2009) The hafnium– 1142  
neodymium isotopic composition of Atlantic seawater. *Earth* 1143  
*Planet. Sci. Lett.* **280**, 118–127. 1144
- Rickli J., Frank M., Baker A. R., Aciego S., de Souza G., Georg R. 1145  
B. and Halliday A. N. (2010) Hafnium and neodymium 1146  
isotopes in surface waters of the eastern Atlantic Ocean: 1147  
implications for sources and inputs of trace metals to the ocean. 1148  
*Geochim. Cosmochim. Acta* **74**, 540–557. 1149
- Rogers J. J. W., Unrug R. and Sultan M. (1994) Tectonic assembly 1150  
of Gondwana. *J. Geodyn.* **19**, 1–34. 1151
- Roy M., van de Fliedert T., Hemming S. R. and Goldstein S. L. 1152  
(2007) <sup>40</sup>Ar/<sup>39</sup>Ar ages of hornblende grains and bulk Sm/Nd 1153  
isotopes of circum-Antarctic glacio-marine sediments: Implica- 1154  
tions for sediment provenance in the southern ocean. *Chem.* 1155  
*Geol.* **244**, 507–519. 1156
- Rutgers van der Loeff M. M. and Berger G. W. (1993) Scavenging 1157  
of <sup>230</sup>Th and <sup>231</sup>Pa near the Antarctic polar front in the South 1158  
Atlantic. *Deep-Sea Res.* **40**, 339–357. 1159
- Ryan W. B. F. et al. (2009) Global multi-resolution topography 1160  
synthesis. *Geochem. Geophys. Geosyst.* **10**, Q03014. [http://](http://dx.doi.org/10.1029/2008GC002332) 1161  
[dx.doi.org/10.1029/2008GC002332](http://dx.doi.org/10.1029/2008GC002332). 1162
- Siddall M., Khatiwala S., van de Fliedert T., Jones K., Goldstein S., 1163  
Hemming S. and Anderson R. (2008) Towards explaining the 1164  
Nd paradox using reversible scavenging in an ocean general 1165  
circulation model. *Earth Planet. Sci. Lett.* **274**, 448–461. 1166
- Sievers A. and Emery J. (1978) Variability of the Antarctic Polar 1167  
frontal zone in the Drake Passage?? Summer 1976–1977. *J.* 1168  
*Geophys. Res.* **83**, 3010–3022. 1169
- Sievers H. A. and Nowlin W. D. (1984) The stratification and water 1170  
masses at Drake Passage. *J. Geophys. Res. Oceans* **89**, 489– 1171  
514. 1172
- Sims K., Blichert-Toft J., Kyle P., Pichat S., Gauthier P., Blusztajn 1173  
J., Kelly P., Ball L. and Layne G. (2008) A Sr, Nd, Hf, and Pb 1174  
isotope perspective on the genesis and long-term evolution of 1175  
alkaline magmas from Erebus volcano, Antarctica. *J. Volcanol.* 1176  
*Geoth. Res.* **177**, 606–618. 1177
- Stichel T., Frank M., Rickli J. and Haley B. (2014) The hafnium 1178  
and neodymium isotope composition of the Atlantic sector of 1179  
the Southern Ocean. *Earth Planet. Sci. Lett.* **317–318**, 282–294. 1180
- Storey B. C. (2005) Antarctic. In *Encyclopedia of Geology* (eds R. 1181  
C. Selley, L. R. M. Cocks and Ian R. Plimer). Elsevier, Oxford, 1182  
pp. 132–140. 1183
- Stramma L. and Peterson R. G. (1990) The South Atlantic current. 1184  
*J. Phys. Oceanogr.* **20**, 846–859. 1185
- Tachikawa K., Jeandel C. and Roy-Barman M. (1999) A new 1186  
approach to the Nd residence time in the ocean: the role of 1187  
atmospheric inputs. *Earth Planet. Sci. Lett.* **170**, 433–446. 1188
- Tanaka T., Togashi S., Kamioka H., Amakawa H., Kagami H., 1189  
Hamamoto T., Yuhara M., Orihashi Y., Yoneda S., Shimizu 1190  
H., Kunimaru T., Takahashi K., Yanagi T., Nakano T., 1191  
Fujimaki H., Shinjo R., Asahara Y., Tanimizu M. and 1192  
Dragusanu C. (2000) JNd-1: a neodymium isotopic reference 1193  
in consistency with LaJolla neodymium. *Chem. Geol.* **168**, 279– 1194  
281. 1195
- Taylor S. R. and McLennan S. M. (1985) *The Continental Crust: 1196*  
*Its Composition and Evolution*. Blackwell Scientific, Boston, 1197  
Mass. 1198

- 1199 Thomas R. J., von Veh M. W. and McCourt S. (1993) The tectonic  
1200 evolution of southern Africa: an overview. *J. Afr. Earth Sc.* **16**,  
1201 5–24. 1220
- 1202 van de Flierdt T., Frank M., Lee D.-C. and Halliday A. N. (2002)  
1203 Glacial weathering and the hafnium isotope composition of  
1204 seawater. *Earth Planet. Sci. Lett.* **201**, 639–647. 1221
- 1205 van de Flierdt T., Hemming S. R., Goldstein S. L. and Abouchami  
1206 W. (2006) Radiogenic isotope fingerprint of Wilkes Land–  
1207 Adélie Coast Bottom Water in the circum-Antarctic Ocean.  
1208 *Geophys. Res. Lett.* **33**, L12606. [http://dx.doi.org/10.1029/](http://dx.doi.org/10.1029/2006GL026020)  
1209 [2006GL026020](http://dx.doi.org/10.1029/2006GL026020). 1222
- 1210 van de Flierdt T., Goldstein S., Hemming S., Roy M., Frank M.  
1211 and Halliday A. (2007) Global neodymium–hafnium isotope  
1212 systematics — revisited. *Earth Planet. Sci. Lett.* **259**, 432–441. 1223
- 1213 van de Flierdt T. and Pahnke K. Geotraces intercalibration  
1214 participants (2012) GEOTRACES intercalibration of neodymium  
1215 isotopes and rare earth elements in seawater and marine  
1216 particulates – Part 1: international intercomparison. *Limnol.*  
1217 *Oceanogr. Methods* **10**, 234–251. 1224
- 1218 Vervoort J. D., Patchett P. J., Blichert-Toft J. and Albarède F.  
1219 (1999) Relationships between Lu–Hf and Sm–Nd isotopic  
1220 systems in the global sedimentary system. *Earth Planet. Sci.*  
1221 *Lett.* **168**, 79–99. 1222
- White W., Patchett J. and BenOthman D. (1986) Hf isotope ratios  
1223 of marine sediments and Mn nodules: evidence for a mantle  
1224 source of Hf in seawater. *Earth Planet. Sci. Lett.* **79**, 46–54. 1225
- Whitworth, III, T. (1980) Zonation and geostrophic flow of the  
1226 Antarctic circumpolar current at Drake Passage. *Deep Sea Res.*  
1227 *Part A. Oceanogr. Res. Papers* **27**, 497–507. 1228
- You Y., Lutjeharms J. R. E., Boebel O. and de Ruijter W. P. M.  
1229 (2003) Quantification of the interocean exchange of intermedi-  
1230 ate water masses around southern Africa. *Deep Sea Res. Part*  
1231 *II: Topical Stud. Oceanogr.* **50**, 197–228. 1232
- Zimmermann B., Porcelli D., Frank M., Rickli J., Lee D. and  
1233 Halliday A. (2009a) The hafnium isotope composition of Pacific  
1234 Ocean water. *Geochim. Cosmochim. Acta* **73**, 91–101. 1235
- Zimmermann B., Porcelli D., Frank M., Andersson P. S., Baskaran  
1236 M., Lee D.-C. and Halliday A. N. (2009b) Hafnium isotopes in  
1237 Arctic Ocean water. *Geochim. Cosmochim. Acta* **73**, 3218–3233. 1238
- Associate editor: Sidney Hemming 1239