

# Global neodymium–hafnium isotope systematics — revisited

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## Abstract

Global Nd–Hf isotope systematics can be mainly described with two linear arrays, the global silicate Earth array (“the terrestrial array”) and the global ferromanganese crust and nodule array (“the seawater array”). The offset between these two arrays provides evidence for the sources and mechanisms by which these elements are added to ocean water. However, the reason for this offset is under debate, with the two preferred hypotheses being (i) incongruent release of Hf during continental weathering and (ii) hydrothermal contribution of Hf to the seawater budget.

Here we present new Nd and Hf isotope data on glacio-marine core-top sediments from around the perimeter of the Antarctic continent. The results range from  $\varepsilon_{\text{Hf}} = -30.0$  to  $\varepsilon_{\text{Hf}} = +3.9$  and  $\varepsilon_{\text{Nd}} = -21.3$  to  $\varepsilon_{\text{Nd}} = +0.9$ , reflecting the large range of basement ages and lithologies around the Antarctic continent. In Nd–Hf isotope space, they confirm the systematic correlations found in rocks from other parts around the world and provide valuable insights into the previously underrepresented group of sediments with very old provenance.

In this paper we revisit the cause for the offset of the seawater array from the terrestrial array using simple mass balance considerations. We use these calculations to test to what degree the seawater array could be a product of preferential weathering of “non-zircon portions” of the upper continental crust, implying retention of zircons in the solid residue of weathering. Lutetium–Hf and Sm–Nd evolution and mixing calculations show that the global seawater array can be generated with continental sources only. On the other hand, a predominantly hydrothermal origin of Hf in the ocean is not possible because the seawater Hf isotopic composition is significantly less radiogenic than hydrothermal sources, and requires a minimum fraction of 50% continental Hf. While hydrothermal sources may contribute some Hf to seawater, continental contributions are required to balance the budget.

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## 1. Introduction

Combined Nd and Hf isotope analyses have become widely used in studies of solid Earth geochemistry, but their application to the low-temperature environment is

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still limited (for a recent review see van de Flierdt et al., 2004a). Both elements show variable compositions in seawater and their residence times in the ocean are thought to be similar (500–2000 yr; Jeandel, 1993; McKelvey, 1994; Jeandel et al., 1995; Godfrey et al., 1996, 1997; McKelvey and Orians, 1998; Lee et al., 1999; Tachikawa et al., 1999; David et al., 2001; Tachikawa et al., 2003). A number of studies have recently addressed the sources of Nd and Hf in the ocean and internal cycling processes (e.g., Lacan and Jeandel, 2005; Bau and Koschinsky, 2006; Bayon et al., 2006; Jacobson and Holmden, 2006). In the case of Nd, these studies have been accompanied by a growing number of applications of Nd isotopes as a tracer for past water mass mixing and ocean circulation given that various archives in the ocean have been shown to record the Nd isotopic composition of ambient seawater (e.g., Rutberg et al., 2000; Frank, 2002; Goldstein and Hemming, 2003; Bayon et al., 2004; Martin and Scher, 2004; Piotrowski et al., 2005; Vance et al., 2004).

Due to the very low concentrations of Hf in seawater (Godfrey et al., 1996; McKelvey and Orians, 1998) and associated analytical difficulties in measuring Hf isotope compositions, our overall understanding about fractionation processes and internal cycling of Hf in the ocean is not as well developed as it is for Nd. However, recent studies by Zimmermann et al. (2004, 2005) and Bayon et al. (2006) have taken advantage of the advancement of MC-ICP-MS (multiple collector inductively coupled plasma mass spectrometry) techniques to measure the Hf isotope composition of seawater and river waters. The results from these studies indicate that ferromanganese crusts and nodules reliably reflect the Hf isotopic composition of seawater. This is an important confirmation because global Nd–Hf isotope systematics for most mantle and crustal rocks show a tight positive correlation called the “terrestrial array” (Vervoort et al., 1999), whereas ferromanganese crusts and nodules form a “seawater array”, oblique to the terrestrial array with higher Hf isotope ratios for a given Nd isotope composition (Albarède et al., 1998).

Based on ferromanganese crust studies, it has been suggested that the Hf isotopic composition of seawater can serve as a tracer for enhanced physical weathering resulting from glaciation because of the significant fractionation of Lu and Hf within the sedimentary system (Patchett et al., 1984; Piotrowski et al., 2000; van de Flierdt et al., 2002, 2004a). A recent study by Bau and Koschinsky (2006) questions this interpretation on the basis of an “elemental perspective” on Nd–Hf systematics in the ocean and proposes the contrasting view that seawater Hf is dominated by hydrothermal

inputs due to efficient scavenging of dissolved riverine Hf in the estuaries.

Here we revisit the discussion on the origin of elevated Hf isotopes in seawater (e.g., Patchett et al., 1984; White et al., 1986; Godfrey et al., 1997; Albarède et al., 1998; Piotrowski et al., 2000; van de Flierdt et al., 2002; Bau and Koschinsky, 2006) by taking an “isotopic perspective” on global Nd–Hf systematics. We highlight the problem by presenting new data for detrital Nd–Hf isotope compositions from Antarctica and compare them to existing Southern Ocean Nd–Hf isotope data from ferromanganese nodules. The circum-Antarctic Nd–Hf trends faithfully follow the global systematics. As developed below, the global isotope mass balance implies that while hydrothermal contributions of Hf to the ocean are possible, continental contributions are absolutely required to explain the observed variation and distribution of Hf isotope ratios in global seawater.

## 2. Antarctic and Southern Ocean Nd–Hf isotope systematics

Constraining southern high latitude Nd–Hf systematics is important for several reasons. Firstly, the Southern Ocean plays a crucial role in the present-day global ocean current system (as part of the “global ocean conveyor belt”; Broecker, 1991). The connections among all three major ocean basins provided by the ACC not only permit efficient global water-mass exchange, but also control the transport of heat and other properties that influence climate (e.g., Schmitz, 1995; Rintoul et al., 2001). Secondly, the Southern Ocean offers the possibility to study input and transfer pathways of dissolved and particulate tracers from the glaciated Antarctic continent. Understanding the composition of dissolved and detrital erosional inputs from Antarctica to the Southern Ocean is important due to the potential rapid dispersal and export of these trace metal signatures to the rest of the world’s ocean. Thirdly, among the global data that forms the terrestrial array (Vervoort et al., 1999), Hf isotope data on sediments derived directly from Proterozoic and Archean basement are sparse. Most of the basement of East Antarctica is of Proterozoic and Archean age and therefore new data from these areas will fill a significant gap in the coverage of global Nd–Hf isotope systematics.

Here we present new Hf and Nd isotope data from marine core top sediments from all around Antarctica, with most sampling sites being located south of the Antarctic Divergence (~65° S; Deacon, 1937; Orsi et al., 1995) marking the southern edge of the Antarctic Circumpolar Current (Fig. 1; details on the samples and

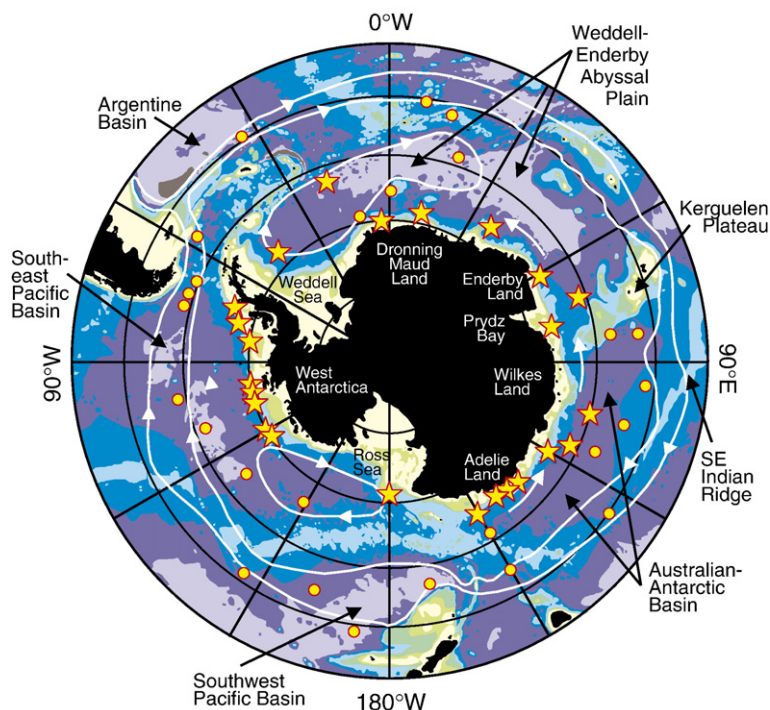


Fig. 1. Map of sample locations. Circum-Antarctic area south of 40° S with locations of investigated glacio-marine core-top sediments (yellow stars) and previously published ferromanganese nodules (yellow circles; van de Flierdt et al., 2006). White lines with arrows indicate the main eastward flow in the Antarctic Circumpolar Current (ACC) associated with the Subtropical Front and the Subpolar Front, the Weddell Gyre, and the Ross Gyre. White arrows in the Indian Ocean sector reflect westward flowing currents south of the ACC.

methods are given in the supplementary material in the Appendix). Due to the variety of basement lithologies and ages exposed around Antarctica, the detrital sediment data cover a large part of the terrestrial array, with  $\varepsilon_{\text{Hf}}$  ranging from  $-30.0$  to  $+3.9$  and  $\varepsilon_{\text{Nd}}$  ranging from  $-21.3$  to  $+0.9$  (Fig. 2). With two exceptions (RC17-56 and ELT 50-13; see supplementary material, Table 1 in the Appendix), all data follow the terrestrial array, describing a slope on Fig. 2 that is very similar to the global dataset. Details of the data, such as the outliers RC17-56 and ELT 50-13, as well as the relationship of the core top Nd isotope analyses to Antarctic geology are discussed elsewhere (van de Flierdt et al., in preparation; Roy et al., under revision). Here we will use the new data to compare them to existing Southern Ocean seawater values as derived from ferromanganese nodules (Fig. 2; Albarède et al., 1997; David et al., 2001; Frank et al., 2002; van de Flierdt et al., 2006) to make the point that circum-Antarctic Nd–Hf systematics follow the well-established global systematic trends. Importantly, the data add significantly to the sparse global dataset for very low  $\varepsilon_{\text{Nd}}$  and  $\varepsilon_{\text{Hf}}$  samples. As the explanation for the contrasting terrestrial and seawater arrays is still under

debate (e.g., Patchett et al., 1984; White et al., 1986; Godfrey et al., 1997; Albarède et al., 1998; Piotrowski et al., 2000; van de Flierdt et al., 2002; Bau and Koschinsky, 2006), we will focus on revisiting this discussion on global Nd–Hf isotope systematics in the low-temperature environment in the remainder of our paper.

### 3. Discussion

#### 3.1. Circum-Antarctic data in the context of global Nd–Hf isotope systematics

Neodymium and Hf isotopes in nearly all terrestrial bulk rock samples form a linear positive correlation, the terrestrial array (Vervoort et al., 1999, and references therein; Fig. 2). All data analyzed so far to characterize seawater, which are ferromanganese crust and nodule proxy data, plot off this trend and form the seawater array (Albarède et al., 1998). Authigenic and detrital Nd and Hf data from the circum-Antarctic realm (Roy et al., under revision; van de Flierdt et al., 2006; this study) match these global patterns (Fig. 2). Although authigenic ferromanganese precipitates are proxies for

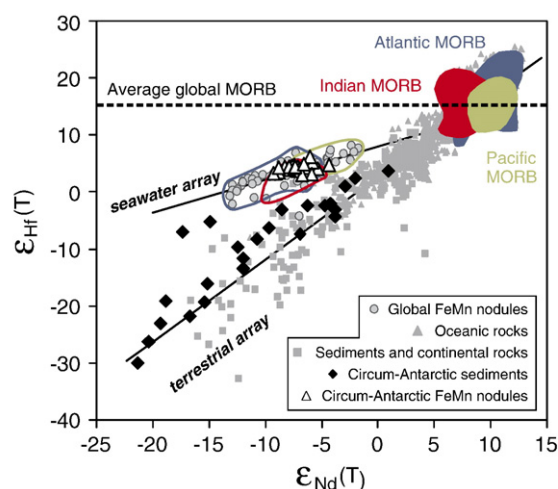


Fig. 2. Observed global Nd–Hf isotope systematics. Silicate rocks (gray triangles: oceanic rocks; gray squares: sediments and continental rocks) form the terrestrial array, and ferromanganese crusts and nodules (gray circles) define the seawater array. Black diamonds and hollow triangles highlight circum-Antarctic sediments and ferromanganese nodules respectively. MORB compositions for the Indian Ocean (red), the Pacific Ocean (green), and the Atlantic Ocean (blue) are highlighted in order to show the potential composition of hydrothermal Hf. The black stippled line shows the average Hf isotopic composition of global MORB ( $\epsilon_{\text{Hf}} \sim +15$ ), which is significantly more radiogenic than any data point observed in the seawater array. Ferromanganese crusts and nodules from the three different ocean basins are circled in the same colors as MORB, revealing that there exists a clear provinciality among the different ocean basins, although MORB data for all three ocean basins are overlapping. Both of these observations are in contrast to the hypothesis that most Hf in the ocean is of hydrothermal origin. A full list of references for the background dataset and the different MORB compilations can be obtained from the authors upon request (see also PETDB database and GEOROC database). Date of compilation: December 2005.

seawater composition, the first results for Hf isotopes on 0.45  $\mu\text{m}$  filtered seawater samples from the Arctic and North Pacific Ocean agree with published ferromanganese crust data (Zimmermann et al., 2004, 2005).

The reason for the offset of the seawater array from the terrestrial array has been explained by incongruent weathering, whereby zircon is a major host of unradiogenic Hf and is much more resistant to chemical weathering than most terrestrial minerals (e.g., Patchett et al., 1984; Piotrowski et al., 2000; van de Flierdt et al., 2002, 2004a; Bayon et al., 2006). However, an alternative interpretation is that most of the Hf in seawater is of hydrothermal origin (White et al., 1986; Godfrey et al., 1997; Bau and Koschinsky, 2006). For example, Bau and Koschinsky (2006) argue that a hydrothermal pathway for colloid-bound dissolved MORB-derived Hf to the ocean exists, but that there is no important riverine pathway for colloidal or dissolved continent-derived Hf because of estuarine scavenging.

These authors conclude that Hf isotopes as recorded by ferromanganese crusts do not reflect truly dissolved Hf in the ocean but argue that Hf isotopes in crusts are controlled by the origin and pathway of hydrous Fe oxide colloids in the oceans, which carry a significant fraction of hydrothermal Hf but no continental Hf. In the following discussion we will make the point from an isotopic perspective that hydrothermal Hf cannot be the predominant source of Hf in ferromanganese precipitates, and to the extent that they represent the dissolved or colloidal Hf load of seawater, hydrothermal sources cannot be dominant. Furthermore, we show that extraction of Hf from the non-zircon fraction of upper continental crust, contributed to the dissolved seawater pool by incongruent weathering, can readily explain the isotopic offset of the seawater array from the terrestrial array without any hydrothermal input.

### 3.2. Hafnium isotopes from ocean and river waters

As pointed out by Bau and Koschinsky (2006) all data available for “dissolved Hf” in natural waters may in fact be dominated by “colloidal Hf” and may be different from the pool of “truly dissolved” Hf. To better understand the elemental cycling of Hf in the ocean, analyses of ultrafiltered seawater and river water samples are clearly needed. However, if truly dissolved Hf in the ocean is really negligible, a potential isotopic difference between truly dissolved and colloidal Hf should not affect the applicability of Hf isotopes as a paleo-proxy reflecting seawater Hf, as the colloidal signature would simply dominate the entire low temperature environment. Recently, Zimmermann et al. (2004, 2005) obtained the first results for Hf isotopes on 0.45  $\mu\text{m}$  filtered seawater samples from the Arctic and North Pacific Ocean. The reported  $\epsilon_{\text{Hf}}$  values for Pacific seawater at various depths between +3.5 and +8.6, are in good agreement with previously published ferromanganese crust data ( $\epsilon_{\text{Hf}} = +3.7$  to +9.0; Godfrey et al., 1997; David et al., 2001; van de Flierdt et al., 2004a). The first river water analyses by Bayon et al. (2006) report Hf isotopic compositions on 0.2  $\mu\text{m}$  filtered samples from five rivers in eastern France, four of which drain Variscian age (ca. 330 Ma, reflecting the crystallization age and not the crustal residence age) granites and gneisses, and display  $\epsilon_{\text{Hf}}$  values between −7.3 and −0.6. Suspended particles from the same water samples exhibit much lower  $\epsilon_{\text{Hf}}$  values from −14.6 to −10.8 (Bayon et al., 2006). These data, taken together with leaching experiments on granites yielding very radiogenic first leachates (0.5 M  $\text{HNO}_3$ ,  $\epsilon_{\text{Hf}}$  up to +250; Bayon et al., 2006) provided the first direct



evidence that granite weathering can lead to the preferential release of radiogenic Hf in the dissolved load of rivers compared to the bulk sediments, most

likely by the preferential dissolution of easily leachable phases with very high Lu/Hf ratios such as apatite (Lu/Hf: 1–5; Barfod et al., 2003; Soederlund et al., 2004). Based on these data, Bayon et al. (2006) calculated a first estimate of the isotopic composition of Hf released during silicate weathering in the North Atlantic, which matches the seawater composition (as derived from ferromanganese crusts) and therefore suggests that riverine supply dominates the dissolved Hf in the North Atlantic.

### 3.3. Mid-ocean ridge basalts and hydrothermal Hf in the ocean

Here we show that isotopic mass balance constraints from ferromanganese crusts preclude a predominantly hydrothermal source for dissolved or colloidal Hf in the ocean. The isotopic composition of hydrothermal Hf can

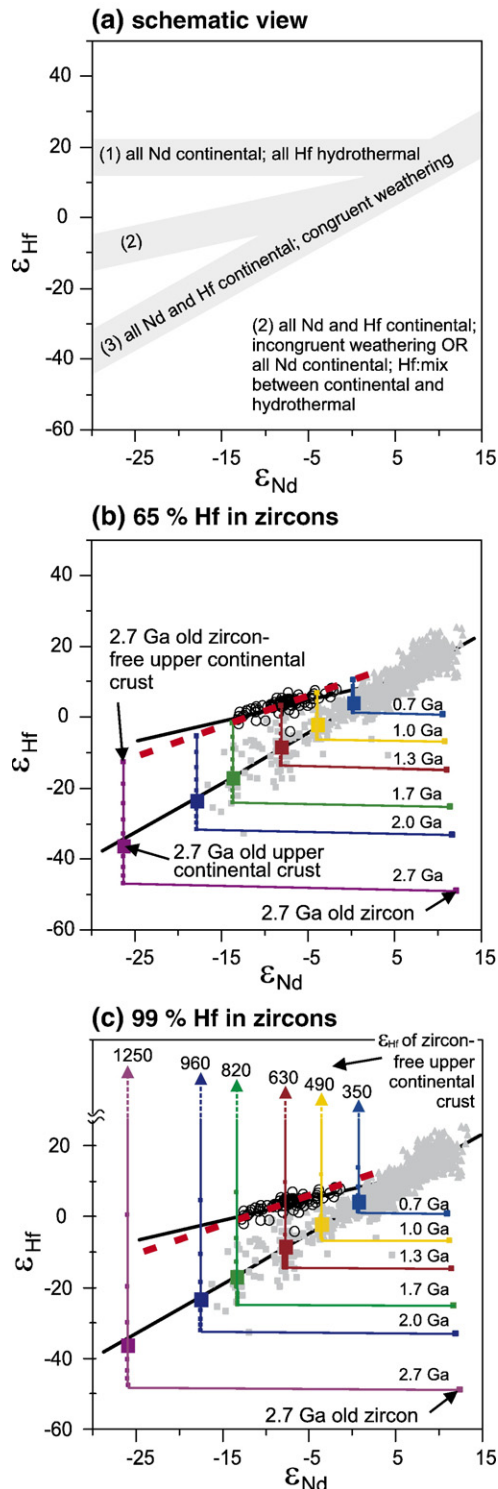


Fig. 3. Schematic and modeled Nd–Hf isotope systematics. Different scenarios for creating the seawater array using a simple mass balance between the Sm–Nd and Lu–Hf isotope systems in zircons on the one hand, and a zircon-free upper continental crust residue on the other hand. (a) Schematic trends of hypothetical seawater values in the Nd–Hf isotope correlation diagram for different end member scenarios. (1) If all Nd were continental in origin, and all Hf were hydrothermal, the seawater isotopic composition should plot along a horizontal line with the Hf isotopic composition of MORB. (3) On the contrary, if Nd and Hf are both continental in origin, and the continental crust is weathered and eroded congruently, the seawater isotopic composition should plot along the terrestrial array. What is observed in nature is scenario (2), in between the two extremes. The trend labeled (2) can be generated either by mixing hydrothermal and continental end members (~50:50 by Hf mass) or by Hf solely derived from continental weathering with fractionation of REE and Hf (incongruent weathering). (b) and (c) Model results for a simple mass balance between a zircon-component and a zircon-free upper continental crust. The colored lines are calculated mixing curves between zircons and zircon-free upper continental crust of different ages (2.7 Ga to 0.7 Ga). The large squares are calculated upper continental crust (UCC) compositions, which match the terrestrial array very well. The small squares represent 10% steps on the mixing lines. In case (b) the calculation was carried out under the assumption that 65% of the Hf in the UCC is sequestered in zircons, and that none of this Hf is available for weathering. A line similar to the seawater array can be derived by weathering the non-zircon fraction of the UCC (35%). In case (c) the assumption has been made that nearly all of the Hf contained in the continental crust is hosted in zircons (99%). In this case, some zircon weathering has to be included to create the seawater array as indicated by the intercept of the modeled lines with the seawater array at ~25% zircon contribution (red stippled line). In summary, as long as 65–70% or more of the Hf in the UCC is sequestered in zircons, the seawater array can be created by incongruent weathering from continental crust only. If less than 65–70% Hf is hosted in zircons, some radiogenic Hf contributions are required, which could be hydrothermal. However, even in this case we would consider island-arc weathering as the most plausible source of radiogenic Hf, as argued in van de Flierdt et al. (2004a).

be inferred from the compositions of mid-ocean ridge basalts (MORB). Global MORB shows a range in  $\varepsilon_{\text{Hf}}$  between 0 and +25, and an average value of  $+15.6 \pm 0.5$  ( $2\sigma$  standard error) (Fig. 2; based on 347 Hf isotope ratios listed in the PetDB database (Lehnert et al., 2000) as “spreading center” samples; compilation as of December 2005 omitting samples identified as enriched MORB). This contrasts with ferromanganese crusts and nodules, for which the average Hf isotopic composition is  $\varepsilon_{\text{Hf}} = +3.5$  in the global ocean, and for which the individual ocean basins show distinct and representative Hf isotopic signatures (Atlantic Ocean:  $\varepsilon_{\text{Hf}} = +2.1$ , Indian Ocean:  $\varepsilon_{\text{Hf}} = +2.7$ , Southern Ocean:  $\varepsilon_{\text{Hf}} = +4.2$ , Pacific Ocean:  $\varepsilon_{\text{Hf}} = +6.1$ ; Fig. 2; Godfrey et al., 1997; Albarède et al., 1998; Piotrowski et al., 2000; David et al., 2001; van de Flierdt et al., 2004a, 2006). Therefore, most MORBs are much more radiogenic than authigenic seawater deposits, and the authigenic samples clearly require an unradiogenic source to balance any significant mantle input. At least a 50% contribution from continental crust is required to balance a MORB-like composition and create the seawater array (Fig. 3a). Unless hydrothermal fluids happen to have an Hf isotopic composition very different from MORB (e.g. through addition of sediment components), which is not likely, a significant pathway of continental Hf into the oceans must exist. In fact, mass balance dictates that the more significant the contribution of hydrothermal Hf, the greater the magnitude of continental input that is required to create the observed Hf isotope compositional range of seawater as reflected by ferromanganese crusts. Moreover, there is no reason to expect the observed regional as well as Nd-correlated variation in the Hf isotope composition of seawater if Hf was derived predominantly from hydrothermal sources.

Finally, if hydrothermal Hf were the predominant source of Hf in seawater, one would expect to find a pronounced radiogenic Hf isotope signal in ferromanganese deposits close to active hydrothermal sources. As shown by van de Flierdt et al. (2004b), a time series of the Hf isotopic composition of deep water reflecting an increasing distance to the now extinct Galapagos spreading center neither shows enhanced radiogenic Hf isotope signatures, nor a temporal trend corresponding to the hydrothermal signature revealed by the Pb isotopic composition of the same samples.

### 3.4. Incongruent weathering and the Nd–Hf isotope seawater array

As argued above and shown schematically in Fig. 3a, a minimum fractional contribution of conti-

mental sources to the Hf pool in seawater is on the order of 50%. This minimum case is based on the unrealistic assumption that the seawater array is generated by pure mixing of mantle-derived Hf and congruently weathered continental crust. However, incongruent release of Hf from higher Lu/Hf phases and the well known resistance of zircon (with extremely low Lu/Hf) to chemical weathering is expected to lead to a more radiogenic  $\varepsilon_{\text{Hf}}$  signal in continental weathering products than would be expected from the bulk signatures. In the section below, we show that simple but realistic incongruent weathering scenarios, in which zircons are enriched in the solid residue of weathering, allow for the continental crust to be the sole contributor of Hf to the ocean (Fig. 3b,c).

Zirconium (Zr) is undersaturated in basaltic magmas, but is a crystallizing phase in metaluminous and peraluminous silica-rich melts typical of the continental crust. As a result, Zr behaves as a moderately incompatible trace element in basalts but as a major structural constituent of a crystallizing phase in intermediate to siliceous magmas. Hafnium is a moderately incompatible element similar to Sm in basaltic magmas, but a compatible element in zircons, typically constituting between ~1 and 4 wt.% and averaging ~1.7 wt.% (Hoskin and Schaltegger, 2003). As a result, once zircon becomes saturated in silicate magmas, its crystallization imparts a major fractionation of Zr and Hf from other elements, including the REEs. Both, Zr and Hf, are among the most insoluble elements and zircons are highly resistant to chemical weathering compared to other minerals (e.g., Folk, 1974; Velbel, 1999; Balan et al., 2001a,b). The insolubility of Hf relative to REEs is manifested by very high Nd/Hf ratios in authigenic precipitates, river water, and seawater (between 10–30, c.f. Patchett et al., 1984; Godfrey et al., 1997; Hein et al., 2000 and references therein), compared to average upper continental crust (~3.6, Taylor and McLennan, 1985) and the depleted upper mantle (~4.5; Salters and Stracke, 2004). Therefore, chemical alteration in near surface environments leads to a relative enrichment of Nd (and Lu) over Hf. The simplest explanation for this fractionation is the sequestration of Hf into zircons.

Patchett et al. (1984) first described strong Hf/REE fractionation in the sedimentary cycle and suggested chemical indestructibility of the mineral zircon, combined with a lesser resistance of minerals such as apatite, as the cause. The Lu/Hf in zircons is ~0.002 (Kinny and Maas, 2003), resulting in nearly negligible increases in the Hf isotope ratios of zircons compared to the estimated Lu/Hf ratio in average upper continental

crust of  $\sim 0.055$  (Taylor and McLennan, 1985). Thus continental Hf is partitioned between a low  $\varepsilon_{\text{Hf}}$  reservoir in zircons and a complementary high  $\varepsilon_{\text{Hf}}$  non-zircon reservoir. Given that zircon is among the most resistant minerals to dissolution, the relative abundance of zircon is increased in sandstones that have experienced an extensive weathering history. It is thus reasonable to conclude that most other REE and Hf phases are more easily affected by chemical weathering. Consequently, there is a high potential for fractionation of Hf from the REE in the sedimentary cycle by means of incongruent weathering.

In Fig. 3b,c we illustrate the case that the seawater array can be explained by incongruent weathering of the upper continental crust using a simple mass balance between the Sm–Nd and Lu–Hf isotope systems in zircons on the one hand, and a zircon-free upper continental crust residue on the other hand. Model parameters are given in Table 2 in the Appendix (supplementary material). The present-day average Nd and Hf isotope ratios of average upper continental crust of any age is estimated by assuming that the crust is derived from a depleted mantle that has linearly evolved from the bulk Earth since the Earth's formation (as used by Goldstein et al., 1984 and others), and where average upper continental crust has a  $^{147}\text{Sm}/^{144}\text{Nd}$  ratio of  $\sim 0.11$  and a  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio of  $\sim 0.0077$ . In order to generate a model Nd–Hf isotope terrestrial array, we calculate the isotope ratios for upper crust of different ages ranging from Archean to Phanerozoic. It can be seen (Fig. 3) that this model line approximates the terrestrial array very well.

We calculate the seawater array as a product of solely continental contributions in two ways. In both calculations, for new crust formed at any point in geological history, we incorporate a significant portion of the Hf into zircons, but only a minor portion of the Lu, and allow both reservoirs to evolve until today. In the first calculation (Fig. 3b) we assume that all Hf locked in zircon remains undisturbed during continental weathering and that only the zircon-free component of the upper continental crust contributes to riverine runoff and ultimately the seawater signal. We find that if  $\sim 65$ – $70\%$  of upper crustal Hf is hosted in zircons, then the zircon-free upper continental crust composition matches very closely the slope and Nd–Hf isotopic compositions of the seawater array (if Hf in zircon averages  $\sim 1.7$  wt.%, as estimated by Hoskin and Schaltegger (2003); this corresponds to  $\sim 58$ – $62\%$  of the Zr in the upper crust being contained in zircons).

It follows that if more than 65–70% of continental Hf is isolated in zircons, the Lu/Hf ratio of the non-zircon

fraction would be higher, and combinations of Nd–Hf isotope ratios from that reservoir would plot above the seawater array in Fig. 3. In this case, a less radiogenic source of Hf is needed in order to generate the seawater Nd–Hf array, and the most likely source would be a partial weathering of zircons. As an extreme end member scenario, we consider the case in which 99% of the continental Hf resides in zircon (corresponding to 88.5% of the continental Zr in zircons). In this case, the zircon-free upper continental crust would have a very low Hf concentration ( $\sim 0.057$  ppm, that is, 1% of the bulk upper crust concentration), a correspondingly high  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio (0.74), and an Hf isotope composition far more radiogenic than what is observed in seawater, ranging from  $\varepsilon_{\text{Hf}} = 1250$  for 2.6 Ga old crust to  $\varepsilon_{\text{Hf}} = 65$  for 0.1 Ga old crust (Fig. 3c). At the same time, the  $\varepsilon_{\text{Hf}}$  of zircons would remain close to initial ratios when the zircons formed, reflecting the very low Lu/Hf of zircon. In this limiting “99% case”, in order to generate Hf isotope ratios in seawater, 25% of the Hf in seawater must originate from zircon weathering, and the remainder is derived from the non-zircon rest of the upper crust. Some contribution from zircons is not implausible as detrital zircon grains commonly show evidence of rounding. The proportion of zircon that contributes could be facilitated by glacial action, for example through disruption of mineral lattices by grinding, increasing surface area and leading to increasing propensity to dissolve in low temperature fluids (e.g., Anderson et al., 1997). In particular, erosion will exhume freshly exposed metamict zircons and these may be even more soluble. The slope of the stippled line representing this scenario in Fig. 3c, is almost identical to the result obtained by assuming that 65–70% of the Hf resides in zircons, and that zircons are completely inert to chemical weathering (Fig. 3b).

In summary, simple mass balance constraints based on scenarios in which zircons are preferentially retained in the solid residue of weathering processes provide compelling evidence that the seawater array can be explained by incongruent weathering of continental sources. A more detailed conclusion on whether the seawater array is primarily a result of weathering of the non-zircon fraction only or whether significant zircon weathering is involved are obscured by the uncertainty on the fraction of Zr and Hf in the upper continental crust hosted in zircons. Although this question clearly deserves further scrutiny, it is beyond the scope of this paper. The important result in the context of the discussion on the origin of the seawater array is that the Hf isotopic compositions observed in seawater require a contribution from continental crust, and it is feasible and

very likely, that incongruent weathering is the predominant process creating the seawater array.

We would like to clearly point out here, however, that large uncertainties remain concerning the low temperature Hf cycle. Future seawater measurements, on particles, colloidal samples and truly dissolved samples, as well as process studies across the ocean margins (e.g., estuaries) and around hydrothermal systems will have to be undertaken to achieve a more thorough understanding of the sources, sinks and internal cycling of Hf in the ocean. These objectives should be joined with in depth studies of Lu–Hf isotope systematics in continental weathering environments (e.g., tropical vs. polar climates) combined with careful investigations of Lu–Hf isotope systematics in individual minerals.

#### 4. Conclusions

We presented new Hf and Nd isotope data for bulk sediments from proximal locations around the Antarctic continent. Together with previously published ferromanganese nodule data from the Antarctic Circumpolar Current, the data mimic the global Nd–Hf isotope systematics (e.g., the seawater array and the terrestrial array). In the light of the ongoing discussions on the global relationship between the terrestrial Nd–Hf isotope array and the seawater Nd–Hf isotope array, we revisited the two main hypotheses on the reason why the seawater array is offset from the terrestrial array: (i) incongruent release of Hf from the continents, or (ii) significant hydrothermal contributions to the Hf budget. Simple isotopic mass balance calculations show that it is possible to generate the seawater array with only continental sources, by retention of zircon in the solid residue of weathering and preferential weathering of non-zircon portions of the upper continental crust. Moreover, from an isotopic perspective, a predominantly hydrothermal origin of Hf in the ocean is not possible because the seawater isotopic composition is significantly less radiogenic than hydrothermal sources, and thus requires a minimum fraction of 50% continental Hf. While hydrothermal contributions to seawater Hf are possible, large continental contributions are required. To what extent zircon weathering is involved in creating the modern seawater array remains obscure given that the fraction of Hf (and Zr) that is contained in zircons of the upper continental crust is highly under-constrained and deserves further study. Future studies on Hf isotopes, especially on ultrafiltered seawater samples, across estuaries, on hydrothermal particles, and in different continental weathering regimes are urgently needed to

better understand the Hf cycle in the low temperature environment.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.epsl.2007.05.003](https://doi.org/10.1016/j.epsl.2007.05.003).

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