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Zircon effect alone insufficient to generate seawater Nd-Hf isotope relationships

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[1] Many studies have suggested that continental weathering inputs have controlled the dissolved oceanic budget of hafnium (Hf). However, whether the offset of seawater Nd-Hf isotope compositions from the terrestrial array can be fully generated by incongruent weathering of continental rocks (the zircon effect) is still not well constrained. In recent years, an increasing amount of combined U-Pb ages and Hf-isotopic compositions of riverine detrital zircons have been published. Here a new model of the Nd-Hf isotopic compositions of the weathered zircon-free part of the upper continental crust is presented, which is based on published Hf isotope compositions and formation ages of modern riverine detrital zircons combined with Nd isotopic compositions of rocks from the upper continental crust. Our model results indicate that the Nd-Hf isotopic composition of the weathered zircon-free part of the upper continental crust is not consistent with the seawater isotopic compositions. This suggests that the elevated seawater Hf isotope compositions for given Nd isotope compositions cannot be fully explained by incongruent zircon weathering of the continents, which is also supported by a recent study demonstrating incongruent weathering of other minerals than zircon.

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1. Introduction

[2] It has been well recognized that the element pair Lu-Hf behaves similar to Sm-Nd during most magmatic processes within the Earth's lithosphere. Thus, Hf and Nd isotopic compositions of most terrestrial rocks display a broad correlation, termed the terrestrial array ($\varepsilon_{Hf} = 1.35\varepsilon_{Nd} + 2.82$ [*Vervoort et al.*, 1999]). (Radiogenic Nd and Hf isotope compositions are expressed in ε units, which are

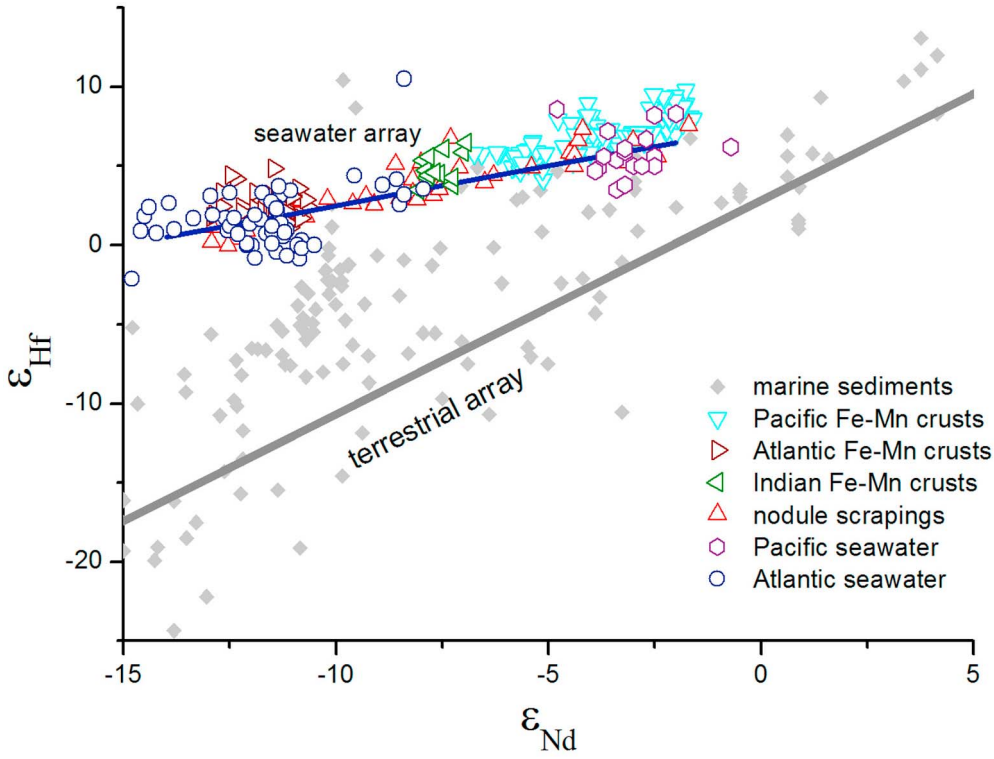

Figure 1. Global Nd-Hf isotopic compositions of marine detrital sediments, hydrogenetic Fe-Mn crusts and nodules [*van de Flierdt et al.*, 2004, and references therein], and dissolved seawater samples [*Rickli et al.*, 2009a, 2010; *Zimmermann et al.*, 2009b]. The scatter of the data of marine sediments results from sorting effects and incongruent dissolution of heterogeneous continental materials during the processes of weathering and subsequent material transport [*Carpentier et al.*, 2009]. The terrestrial array ($\varepsilon_{Hf} = 1.35\varepsilon_{Nd} + 2.82$ [*Vervoort et al.*, 1999]) is derived from unweathered igneous rocks. The modern seawater array presented [*Albarède et al.*, 1998] is constrained by Nd-Hf isotopic compositions of surface scrapings of Mn nodules, excluding a few diagenetic samples.

defined as the deviation of the respective isotopic ratio ($^{176}Hf/^{177}Hf$, $^{143}Nd/^{144}Nd$) from the chondritic uniform reservoir (CHUR) in parts per 10000. The ε_{Nd} for CHUR (chondritic uniform reservoir) is presently 0.512638 [*Jacobsen and Wasserburg*, 1980]. The ε_{Hf} for CHUR is 0.282769 [*Nowell et al.*, 1998]). Studies on hydrogenetic Fe-Mn crusts and seawater samples have revealed that seawater Nd-Hf isotopic compositions also display a well-defined correlation, which is, however, clearly offset from the terrestrial array (Figure 1) [*Patchett et al.*, 1984; *White et al.*, 1986; *Godfrey et al.*, 1997; *Albarède et al.*, 1998; *Piotrowski et al.*, 2000; *David et al.*, 2001; *van de Flierdt et al.*, 2002, 2004; *Rickli et al.*, 2009a; *Zimmermann et al.*, 2009a, 2009b]. The seawater array is constrained by combined Hf and Nd isotope compositions of Pacific, Indian and Atlantic Fe-Mn nodule surface scrapings and defines a fit with a shallower slope than the terrestrial array: $\varepsilon_{Hf} = 0.5\varepsilon_{Nd} + 7.5$ (Figure 1) [*Albarède et al.*, 1998]. This offset has existed since at least the early Cenozoic as documented by the Nd-Hf isotopic record of past seawater extracted from hydrogenetic Fe-Mn crusts [*van de Flierdt et al.*, 2004] and has been explained as a result of incongruent weathering of upper continental crust (UCC) possibly combined with radiogenic hydrothermal Hf inputs [e.g., *White et al.*, 1986; *Bau and Koschinsky*, 2006]. Zircons contain large amounts of Hf, which is a chemical twin of Zr, but do not incorporate significant amounts of Lu. As a consequence of the resulting very low Lu/Hf and the radioactive decay of ^{176}Lu to ^{176}Hf, over time this results in highly unradiogenic Hf isotope compositions of zircons compared with other minerals [*White et al.*, 1986; *David et al.*, 2001]. During weathering processes, the unradiogenic Hf in the zircons is retained due to their extreme resistance to weathering. Hence, Hf released to the aqueous system from weathering of rocks is expected to be more radiogenic than that of the bulk rocks. This has been termed the "zircon effect" [*White et al.*, 1986]. The Sm-Nd isotopic system is not affected by such a process since Sm/Nd ratios of zircons and bulk rock are similar [e.g.,

Bayon et al., 2006]. This explanation is readily understandable qualitatively. But can the seawater array be fully generated by the zircon effect alone? Recent studies suggested that incongruent release of radiogenic Hf originating from the weathering of labile minerals with high Lu/Hf may also play an important role [*Bayon et al.*, 2009]. The quantitative significance of the zircon effect for the marine Hf budget is thus still not well understood. For example, if the zircon effect would form enough radiogenic Hf to generate the observed seawater Hf isotope compositions, incongruent weathering of other minerals, even if it existed, may be quantitatively negligible. So far, only one study has dealt with the zircon effect quantitatively using an isotopic mass balance model based on data of average UCC and the results suggested that it is possible to generate the seawater array by the zircon effect through weathering of UCC with ~65–70% of the total crustal Hf retained in zircons [*van de Flierdt et al.*, 2007]. In recent years, a large number of combined U-Pb ages and Hf isotopic compositions of riverine detrital zircons have been published. Here, these data combined with Nd isotope compositions of rocks from the continental crust are used in a new model to assess the importance of the zircon effect for the seawater budget of Hf from a new perspective.

2. Data Collection and Modeling Approach

[3] Combined U-Pb dating and Hf-isotope analysis of individual detrital zircons from modern river sediments have made it possible to effectively unravel both the evolutionary history of the zircons and the corresponding zircon-free parts (ZFPs). The zircons have been collected following a well-defined method for representative sampling and for studying the evolution of the upper crust in continental blocks around the world. For example, these samples were typically collected at or near the mouth of each river and usually as many grains as possible (>50) were measured to recover the full age spectra of the drainage basin sampled by the river [*Bodet and Schaerer*, 2000]. Since the ZFPs corresponding to riverine detrital zircons have been weathered and largely removed with the zircon grains left behind in the river sediments, these data allow retrieving information of continental weathering on a global scale.

[4] We compiled data of combined U-Pb ages and present-day Lu-Hf isotopic compositions of riverine detrital zircons from the world's 15 rivers (see Data Set S1).[1] The zircons were collected from different drainage basins that cover a large part of the Earth's continental terranes, such as central Africa [*Batumike et al.*, 2009; *Iizuka et al.*, 2010], North China [*Yang et al.*, 2009; *Iizuka et al.*, 2010], the Korean Peninsula [*Wu et al.*, 2007], South China [*Xu et al.*, 2007], SE Asia [*Bodet and Schaerer*, 2000; *van Hoang et al.*, 2009], North America [*Wang et al.*, 2009; *Iizuka et al.*, 2010], and South America [*Iizuka et al.*, 2010]. In the above studies, U-Pb isotope compositions of zircon samples were measured with laser ablation inductively coupled plasma mass spectrometer (LA-ICP-MS) and corrected by measuring standard zircon references at the same analytical process. Two sigma errors of these measurements are mostly less than 5 Ma, which is precise enough for our model calculations. Lu-Hf isotope analyses were performed using a laser ablation system attached to a MC-ICP-MS Plasma. On average, about 180 single zircon grain data are available for each river. For calculating ε_{Hf}, all the $^{176}Hf/^{177}Hf$ collected were normalized to $^{176}Hf/^{177}Hf_{CHUR} = 0.282769$ [*Nowell et al.*, 1998]. From these data, we can readily obtain the modern ε_{Nd}-ε_{Hf} composition of the ZFP corresponding to each zircon grain through the following procedure: The initial $(^{176}Hf/^{177}Hf)_t$ values of each zircon grain, at the time of crystallization constrained by the zircon U-Pb age, can be directly calculated from the measured $(^{176}Lu/^{177}Hf)_{zircon}$ and $(^{176}Hf/^{177}Hf)_{zircon}$ data. The initial Hf isotopic composition of the defined ZFP and bulk rock corresponding to each zircon grain equals $(^{176}Hf/^{177}Hf)_t$ of the zircon grain given that they all crystallized from the same magma. Under the assumption that the riverine detrital zircons are from the typical UCC rock with present-day $(^{176}Lu/^{177}Hf)_{bulk} = 0.0078$, $Lu_{bulk} = 0.32$ ppm and $Hf_{bulk} = 5.8$ ppm [e.g., *van de Flierdt et al.*, 2007] of which a certain percentage of the Hf partitioned into the zircons ($Hf_{zirccon}$), the present-day $^{176}Lu/^{177}Hf$ values for the corresponding ZFP [denoted as $(^{176}Lu/^{177}Hf)_{ZFP}$] can be calculated. From the above initial $(^{176}Hf/^{177}Hf)_t$ values of the ZFP and bulk rock, present-day $(^{176}Lu/^{177}Hf)_{ZFP}$ and $(^{176}Lu/^{177}Hf)_{bulk}$ values corresponding to each zircon grain, the present-day $(^{176}Hf/^{177}Hf)_{ZFP}$ and $(^{176}Hf/^{177}Hf)_{bulk}$ can be extracted. On the other hand, from the resultant present-day $(^{176}Hf/^{177}Hf)_{bulk}$ values and the well correlated crustal Nd-Hf isotopic array [*Vervoort et al.*, 1999], the present-day

[1] Auxiliary materials are available at ftp://ftp.agu.org/apend/gc/2010gc003363.

($^{143}Nd/^{144}Nd)_{ZFP}$ value, which may be considered equal to that of the bulk rock, can be deduced. The detailed calculation procedure is provided in the Data Set S1.

[5] For comparison, we also present results calculated using the single-stage model method for ZFPs corresponding to the riverine detrital zircons. In this model, for calculating initial $(^{176}Hf/^{177}Hf)_t$ values of each zircon grain, its corresponding ZFP, and bulk rock isotope composition, Hf isotope model ages of the zircons instead of their U-Pb ages are used (see Data Set S1). Then the following steps of calculation are the same as the above non-single-stage model. The single-stage model implies that zircons formed when the crustal rocks were extracted from the depleted mantle, which is very similar to the model of *van de Flierdt et al.* [2007], although the latter model did not use specific isotopic data of zircons.

3. Complicating Factors Related to Calculation of the Zircon Effect and Model Tests

[6] Only a small fraction of the zircons can be crystallized from mantle-derived basic magmas because such magmas hardly ever reach saturation with respect to zirconium [e.g., *Zheng et al.*, 2006; *Watson and Harrison*, 1983]. Most zircons in the UCC therefore crystallized from acidic to intermediate magmas formed during remelting of crustal rocks. This is evident from the crystallization ages (U-Pb isotope dating) of most zircon grains. These zircons are usually much younger than the Nd or Hf isotope model ages of their bulk rocks, which represent the ages of first stage juvenile crust formation. It was during the zircon formation stage when those zircons acquired their initial $^{176}Hf/^{177}Hf$ ratios, which were at equilibrium with the intracrust remelting (or multiple-remelting) magmas. Thus, the measured zircon U-Pb ages are used in our calculation and for convenience hereafter we call our model a non-single-stage model, since the UCC is not regarded as a direct product extracted from the mantle. In contrast, the previous quantitative model [*van de Flierdt et al.*, 2007] connotes a premise that all zircons in the UCC were crystallized during the event of crust extraction from the mantle, and thus would have overestimated the actual zircon effect, because a prolonged age for the zircons would yield model results overestimating the unradiogenic Hf isotope composition of the zircons.

[7] Lu/Hf ratios, in fact, vary more significantly than Sm/Nd within the Earth's crust. Assuming the present-day UCC $^{176}Lu/^{177}Hf$ ratios varying from 0.002 to 0.010 [e.g., *Vervoort and Patchett*, 1996; *Bayon et al.*, 2006] and a fixed percentage of Hf (65%) contained in zircons (this percentage will be used below unless other percentages are indicated), our sensitivity test shows that when $^{176}Lu/^{177}Hf$ are varied between 0.0078 and 0.010 by changing Lu or Hf concentrations, the overall distribution of the resultant $(^{176}Hf/^{177}Hf)_{ZFP} - (^{143}Nd/^{144}Nd)_{ZFP}$ (Figure 2) still holds. However, when $^{176}Lu/^{177}Hf$ values approach 0.002, the distribution trend of resultant $(^{176}Hf/^{177}Hf)_{ZFP} - (^{143}Nd/^{144}Nd)_{ZFP}$ moves close to the terrestrial array. Proportionately changing Lu and Hf concentrations of the bulk rocks with fixed $^{176}Lu/^{177}Hf$ ratio does not affect the calculated present-day $(^{176}Hf/^{177}Hf)_{ZFP}$ and $(^{143}Nd/^{144}Nd)_{ZFP}$ values at all. Therefore, the variation of the model results largely depends on the percentages of Hf partitioned into the zircon portion of a rock, which will be further discussed in section 4.

[8] Some of the old zircons in modern riverine sands may have undergone multiple cycles of erosion and sedimentation. In such cases, their corresponding igneous ZFPs were removed through weathering during earlier stages of erosion, which thus did not contribute to the recent seawater Nd-Hf isotope array. We tentatively excluded the oldest zircons until the average Nd isotopic composition of the ZFPs resulting from the model agreed with the average Nd isotopic composition of the riverine sediments (Figure 2b) [*Goldstein et al.*, 1984; *Liu et al.*, 2005; *Colin et al.*, 1999]. Nevertheless, independent from inclusion or exclusion of the old zircons in the model calculations, the overall slopes for the resultant $(^{176}Hf/^{177}Hf)_{ZFP} - (^{143}Nd/^{144}Nd)_{ZFP}$ values (averaged for each river for clarity) are similar and fall below the seawater array (Figures 2a and 2b).

[9] Another concern for the reliability of the model may be the effectiveness of the results to depict the global continental zircon effect. The results could be biased if the collected riverine zircon data of various continental terranes were not proportional to the fluxes of Hf and Nd from these continental areas to the ocean. Nevertheless, the regression lines of calculated $(^{176}Hf/^{177}Hf)_{ZFP}$ and $(^{143}Nd/^{144}Nd)_{ZFP}$ values for different continental terranes are similar (not shown in Figure 2). This implies that Nd-Hf isotopic compositions originating from silicate weathering of different continental areas have a similar correlation slope. Therefore, we suggest that

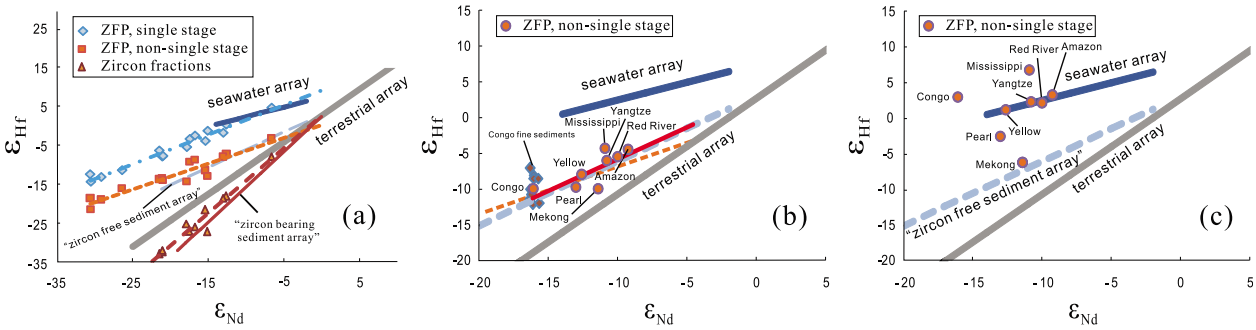

Figure 2. Model results for Nd-Hf isotopic compositions of the zircon-free part of upper continental crust (UCC) under the assumption that (a and b) 65% and (c) 82% of Hf in the UCC stays locked in zircons during weathering. For each river, an average modeled value is shown. The terrestrial array and the seawater array are the same as those in Figure 1. (a) Model results for all 15 rivers, for which zircon ages and Hf isotope data are available. The blue diamonds are the Nd-Hf isotopic compositions of ZFP calculated from the single-stage model, which assumes that all zircons formed when the crustal rocks were extracted from the mantle. The orange squares represent the ZFP calculated from the non-single-stage model in this study, which fall very well on the "zircon-free sediment array" defined by measurements of fine-grained marine sediments [*Bayon et al.*, 2009]. Also shown in Figure 2a are averaged Nd-Hf isotopic compositions of the zircon fractions in each river. The brown dashed regression line of these zircon data is also very similar to the "zircon-bearing sediment array" defined by *Bayon et al.* [2009]. (b) Non-single-stage model results for eight large rivers, for which Nd isotope data of the riverine sediment are available in addition to the zircon data, as well as published Nd-Hf isotope compositions of fine-grained sediment from the Congo River (blue diamonds). Each orange circle represents averaged Nd-Hf isotopic compositions of ZFP calculated for each large river, after excluding the oldest zircons, in order to be consistent with the Nd isotope compositions of the modern riverine sediments. The red regression line also closely matches the zircon-free sediment array (blue dashed line) of *Bayon et al.* [2009]. (c) Non-single-stage model results assuming that 82% of the bulk Hf remains locked in zircons during weathering. Some points match the seawater array well, while other points show a large scatter. We suggest that this case is unlikely (see text for further discussion).

the model indeed reveals a global continental zircon effect.

4. Model Results

[10] The present-day ($^{176}Hf/^{177}Hf$) and ($^{143}Nd/^{144}Nd$) values for the ZFPs resulting from our model represent isotopic compositions of the weathered parts of the bulk silicate rocks except zircon, assuming a negligible effect of incongruent weathering and Hf isotope fractionation of other minerals except zircon. This assumption is not necessarily true. Nevertheless it helps to focus on the zircon effect alone during continental weathering.

[11] As pointed out above, the variation of our model results for ZFPs may largely depend on the percentages of Hf partitioned into zircons. In Figure 2a, with ~65% of Hf of UCC distributed in zircons (termed as ~65% zircon effect hereafter), the single-stage model results for ZFPs match the seawater array well. In contrast, the non-single-stage model results show a clear offset of ~5 ε_{Hf} units on average between the ZFPs and the seawater array (Figure 2a). In the following text, unless stated otherwise, all model results mean non-single-stage model results. The offsets increase with decreasing ε_{Nd} values. The ε_{Nd}-ε_{Hf} of zircon fractions have also been presented using the same ε_{Nd} as the corresponding ZFPs. For clarification, each point in Figure 2a represents the average of model results for each river. The regression lines for the overall data and for the averages of individual rivers are essentially consistent. Figure 2b shows averages of model results of 8 major rivers. Interestingly, the regression line for the 8 rivers is still similar to the correlation for all rivers in Figure 2a. Such similarity further demonstrates that the model results are suitable to depict the global zircon effect.

[12] With percentages below 65% of total whole-rock Hf contained in zircons, the ε_{Nd}-ε_{Hf} values for ZFPs resulting from the model are lower than those for 65% of Hf contained in zircons, thus plotting further below the seawater array. If higher percentages of Hf in zircon (>65%) are used for the model calculations, the overall slope of the results for ZFPs will become flatter. And eventually, the overall slope becomes negative with a lot of scatter in the data points when the Hf percentage in the zircons is larger than about 82%. Figure 2c shows

the modeled average values of the 8 major rivers assuming an 82% zircon effect, which seem to plot close to the seawater array. We did not present more results with other percentages of Hf locked in zircon during continental weathering. In these cases, model results of ZFPs are obviously incompatible with seawater array.

5. Discussion

[13] One can immediately deduce from Figures 2a and 2b that the modeled ZFPs and zircon fractions fit very well with the marine fine sediment array ("zircon free sediment array") and zircon rich coarse sand array ("zircon bearing sediment array") [*Bayon et al.*, 2009], respectively. The close agreement between predicted ZFPs of the Congo River and the data of Congo fine-grained sediments is also remarkable (Figure 2b). In the Hf-Nd study of the Congo sediments, *Bayon et al.* [2009] estimated a Hf concentration in zircon-rich sands of ~8.9 ppm and proportions of sand between 30% and 50%. The corresponding zircon free sediments have Hf concentration of ~4 ppm. With these values, a simple calculation yields the estimate that zircon-rich sands represent about 50–70% of the total continental Hf budget, which is in good agreement with the 65% case. Although the robustness of our conclusion does not rely on a specific percentage of Hf locked in zircon during continental weathering, the striking similarity between the modeled results and data of *Bayon et al.* [2009] provides direct support that zircon effect during continental weathering with 65% of all Hf bound in zircons is a reasonable estimate.

[14] Although some of the data points plot close to the seawater array in Figure 2c, for which an 82% zircon effect was applied, the model results for the 8 major rivers as a whole scatter strongly and are not consistent with the oceanic correlation trend. Current research indicates that continental Hf fluxes to the ocean can be expected to be isotopically much more uniform than the corresponding bulk rock compositions [*Rickli et al.*, 2009a, 2010]. For example, dissolved Hf concentrations do not increase along the deep ocean conveyer (i.e., similar concentrations in Pacific and Atlantic deep water) indicating a shorter oceanic residence time of Hf than of Nd, while Hf isotopic compositions are relatively uniform in the deep water [*Rickli et al.*, 2009a]. In the eastern Atlantic, Saharan dust and inputs from the Congo River, which significantly affect Nd isotopes of the surface water, do not have distinctly different Hf isotopic imprints [*Rickli et al.*, 2010]. Therefore, in our opinion percentages of zircon effect much higher than 65% are not very likely and ~65% of Hf locked in zircon is applied as the best estimate for calculation of the global zircon effect during continental weathering.

[15] Figures 2a and 2b clearly show that even with the reasonable ~65% (or any other percentages, not shown in Figure 2) of Hf locked in zircons, Nd-Hf isotope compositions of the model resultant ZFP do not match the seawater array satisfactorily. In other words, even with variable amounts of Hf contained in zircons, the zircon effect alone is not viable to generate the observed seawater array.

6. Implications

[16] Given that the assumption of the single-stage model does not agree with the geological reality of zircon formation (see section 3), we suggest that the apparent agreement between the corresponding model results and the seawater array (Figure 2a) is coincidental. Based on the non-single-stage model results and above discussion, it is clear that zircon effect alone is not sufficient to explain the observed radiogenic Hf isotope composition of seawater (Figure 2b). Additional radiogenic sources for the oceanic dissolved Hf besides zircon effect are needed.

[17] With 65% zircon effect, the non-single-stage model results, i.e., correlations in zircon free parts and zircon fractions (Figures 2a and 2b), corroborate a previous study about Nd-Hf isotopic systematics during weathering of upper continental rocks [*Bayon et al.*, 2009]. We suggest that two reservoirs could be readily generated during weathering of continental crust: a zircon-rich unradiogenic reservoir (e.g., coarse sands) and a zircon-free component (e.g., fine-grained sediments). These two reservoirs are characterized by distinct Hf-Nd correlations that are very similar to the data of *Bayon et al.* [2009].

[18] The weathering processes of the ZFPs may have been incomplete and thus probably incongruent for Hf isotopes, which may have contributed to the offset of Nd-Hf isotopes from the terrestrial array although the magnitude of this contribution is hard to constrain [*Bayon et al.*, 2006, 2009]. It has been proposed that during early stages of weathering, preferential weathering of high Lu/Hf accessory minerals such as apatite, sphene or garnet may significantly contribute to the radiogenic Hf isotope composition of the weathering solutions [*Bayon et al.*, 2006; *Godfrey et al.*, 2007, 2009]. To

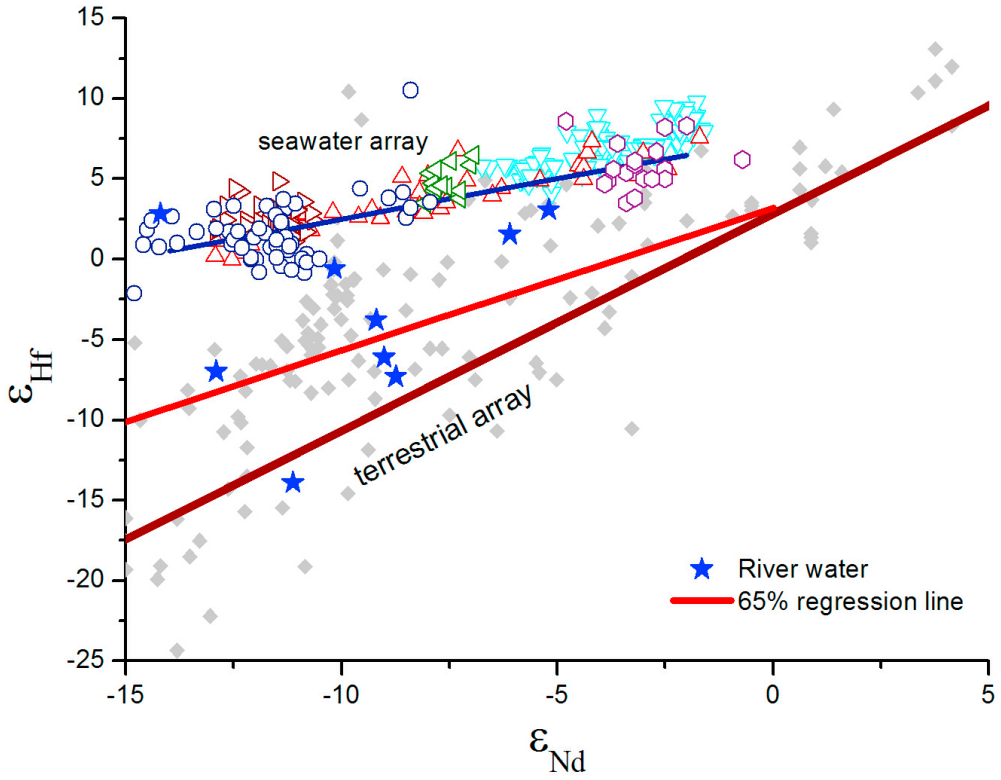

Figure 3. Dissolved Nd-Hf isotopic compositions of river waters (stars) in comparison with those of hydrogenetic Fe-Mn crusts and nodules and seawater. The red 65% regression line is the same as in Figure 2b. Other lines and symbols are the same as in Figure 1. (Data sources for river water: *Zimmermann et al.* [2009a] and *Bayon et al.* [2006]).

constrain this contribution, direct measurements of river water Nd-Hf isotope compositions are of priority. Recently some data of dissolved Nd-Hf isotopic compositions of river waters have been published [*Bayon et al.*, 2006; *Zimmermann et al.*, 2009a]. It appears that Nd-Hf isotopic compositions of most of the river water samples from small European rivers and large circum Arctic rivers do not match the seawater array very well (Figure 3). This is not expected if the dissolved Hf in seawater entirely originated from continental weathering. However, further measurement of dissolved Nd-Hf isotope compositions of river waters are needed before more robust judgments can be made.

[19] The latest study [*Rickli et al.*, 2009b] suggested that recycling of Hf stored in carbonates may be an important radiogenic source for riverine dissolved Hf, with Hf concentrations nearly 1 order of magnitude higher in rivers dominated by carbonate weathering than in rivers draining gneissic regions. However, marine carbonates were directly precipitated from seawater. If the Cenozoic oceanic radiogenic Hf was dominated by weathering of older marine carbonates, this would mean that the oceans prior to the Cenozoic were also highly radiogenic in their Hf isotope composition. As such, the ultimate source for the oceanic radiogenic Hf prior to formation of the carbonates is still an open question.

[20] In addition, inputs from seafloor weathering/submarine hydrothermal fluids [e.g., *Bau and Koschinsky*, 2006; *Godfrey et al.*, 1997] and/or from interaction between seawater and shelf sediments/islands/arcs, which was shown to introduce Nd to seawater [*Lacan and Jeandel*, 2005; *Porcelli et al.*, 2009; *Amakawa et al.*, 2009], could also be potential additional radiogenic sources for the oceanic Hf. For example, If radiogenic sources with Hf isotopic compositions similar to MORB (e.g., +15.6 [*van de Flierdt et al.*, 2007]) have provided additional Hf to the ocean, then about 40% of oceanic Hf from such sources are needed to yield the seawater array with ~65% zircon effect.

7. Summary and Concluding Remarks

[21] Based on riverine detrital zircon data, we quantitatively estimated the influence of the zircon

effect during weathering of upper continental crust on oceanic Hf isotope compositions. Our model results indicate that the zircon effect alone is not sufficient to generate the observed seawater Nd-Hf isotope array, which improves previous quantitative understanding about the zircon effect and provides information for future calculations of the marine Hf budget. In particular, with a 65% zircon effect, the model results agree very well with the zircon-free sediment array and the zircon-bearing sediment array [*Bayon et al.*, 2009]. While previous studies found qualitatively that other specific processes besides the zircon effect may also contribute radiogenic Hf to seawater [*Bayon et al.*, 2006; *Rickli et al.*, 2009b; *Godfrey et al.*, 2009], the model results of this study suggest that, in total, these processes are quantitatively significant in contributing radiogenic Hf to the oceans. The quantitative individual contributions of these processes, however, need to be constrained in future studies.

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