

Hafnium isotope fractionation during continental weathering: Implications for the generation of the seawater Nd-Hf isotope relationships

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[1] To investigate the mechanisms of the offset of seawater radiogenic Nd-Hf isotope compositions from those of the upper continental crust rocks, combined Nd-Hf isotope compositions of desert and loess samples from northern China (which integrate a wide range of lithologies and ages of continental rocks) are presented in this study. The results show significant and systematic fractionation of Hf isotopes between fine-grained detritals/leachates (<5 μm) and coarser fractions (<75 μm) of the same samples. A small but systematic difference of Nd isotope compositions between leachates and detrital silicates is also revealed. Overall, the leaching data either plot along or slightly above the Nd-Hf seawater array, providing strong direct support that the seawater Nd-Hf isotope relationship is predominantly generated by weathering of upper continental crust. Our study supports the application of dissolved Hf isotopes as a proxy for different modes of weathering regimes rather than for continental source provenances. **Citation:** Chen, T.-Y., G. Li, M. Frank, and H.-F. Ling (2013), Hafnium isotope fractionation during continental weathering: Implications for the generation of the seawater Nd-Hf isotope relationships, *Geophys. Res. Lett.*, 40, 916–920, doi:10.1002/grl.50217.

1. Introduction

[2] Since the finding of a strong Hf-rare earth element (REE) fractionation in the Earth's sedimentary system in the 1980s [Patchett *et al.*, 1984; White *et al.*, 1986], a number of studies have contributed to the understanding of Hf isotope geochemistry during sediment transport and oceanic cycling [cf. van de Fliert *et al.*, 2007; Vervoort *et al.*, 2011]. With more radiogenic Hf isotopes for a given Nd isotope composition, seawater and ferromanganese crusts show a unique correlation (seawater array, Figure 1), which is oblique to the terrestrial array in $\epsilon_{\text{Nd}}-\epsilon_{\text{Hf}}$ space [Albarède *et al.*, 1998]. Despite earlier studies proposing that contributions of radiogenic Hf from hydrothermal sources may be important for the seawater budget of Hf [White *et al.*, 1986; Godfrey *et al.*, 1997; Bau and Koschinsky, 2006], recent dissolved seawater Hf isotope

and concentration data have not favored such a scenario [Rickli *et al.*, 2009; Firdaus *et al.*, 2011; Stichel *et al.*, 2012]. However, an unambiguous conclusion has not been achieved due to the fact that hydrothermal contributions of Hf have so far not been measured, and also because there are still no isotopic measurements of truly dissolved versus colloidal Hf isotopes in seawater [e.g., Bau and Koschinsky, 2006]. In addition, Hf isotope data on rivers that directly supply the world's oceans are very scarce. Available data on rivers such as the Hudson ($\epsilon_{\text{Hf}} > +30$ [Godfrey *et al.*, 2009]) and Moselle basin rivers ($\epsilon_{\text{Hf}} < -3$ [Bayon *et al.*, 2006]) are actually not consistent with the seawater array (Figure 1), whereas a recent study of four Swiss rivers [Rickli *et al.*, 2013] suggested that the Hf-Nd isotope compositions of the rivers are broadly consistent with the seawater array, but also that the lithologies and even runoff may exert a large influence. It is still possible, however, that the drainage areas of all these rivers are too small to realistically represent the mean upper continental crust (UCC) trend. In this study, we aim to obtain a broader picture of the UCC weathering signal and clarify whether UCC weathering can produce combined Hf-Nd isotope signatures that are consistent with the seawater array.

[3] The Chinese continent was formed through multiple stages of collision and aggregation of many continental blocks [e.g., Ren, 1996]. Thus, it provides an opportunity to constrain the averaged Nd-Hf isotope signatures of the exchangeable component of upper continental crustal rocks. The dust samples of our study recovered from deserts and other arid areas that distributed over an area extending 600 km from north to south and 4000 km from east to west in northern China are ideal for investigating continental Hf isotope fractionation. The extent of the Chinese deserts and arid areas have been tectonically controlled by the major orogenic belts in East Asia and have been associated with Asian aridification over the late Cenozoic [Chen *et al.*, 2007; Chen and Li, 2011]. Despite that the exact source areas of Chinese deserts and loess deposits are still a matter of debate, these eolian materials always integrate a large range of lithologies (including recycled sedimentary rocks) exposed at the Earth's surface. Dust particles are commonly coated with Fe-Mn oxyhydroxides (the so-called desert varnish [e.g., Bayon *et al.*, 2004]) and trace metal evidence indicated that the desert varnish components are largely formed through natural aqueous leaching of the dust materials [Thiagarajan and Lee, 2004]. Therefore, leaching experiments conducted on these dust samples are assumed to be representative of the Nd-Hf isotopic composition of the labile component of UCC rocks ultimately released by chemical weathering, which provides valuable information on the formation mechanism of the seawater Nd-Hf isotopic array.

All Supporting Information may be found in the online version of this article.

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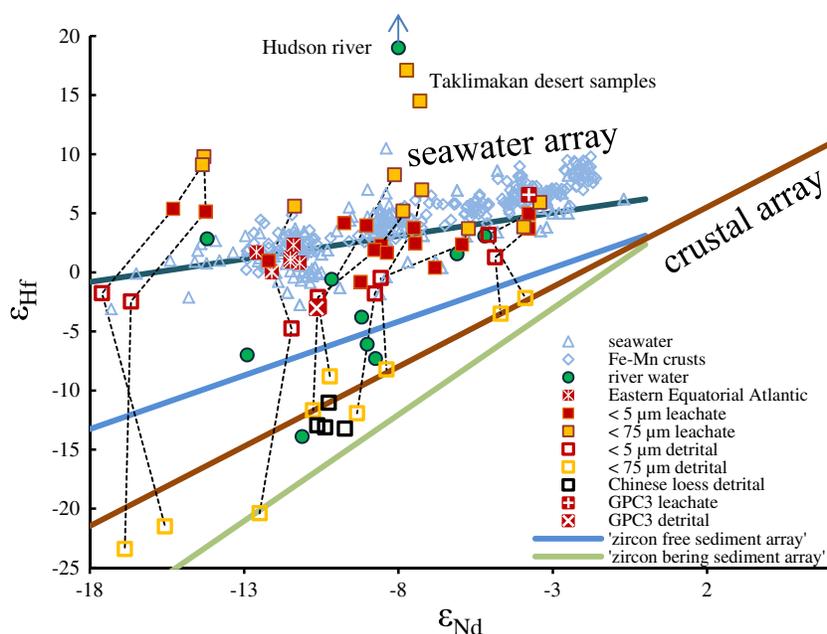


Figure 1. Combined hafnium-neodymium isotope compositions of dust leachates and detrital fractions (<5 and <75 μm), compared with seawater and river water signatures [van de Flierdt et al., 2004, and references therein; Bayon et al., 2006; Godfrey et al., 2009; Zimmermann et al., 2009; Stichel et al., 2012, and references therein]. The seawater array reflects the Nd-Hf isotopes of ferromanganese precipitates and dissolved seawater, while crustal array reflects the isotopic trend of upper continental rocks [Vervoort et al., 1999], e.g., see also the data of <75 μm detrital fractions and bulk Chinese loess [Vervoort et al., 2011]. The dashed lines link the leachates and detrital fraction of the same samples. For comparison, the zircon free and zircon rich sediment arrays (defined by regression of the marine fine-grained and coarse-grained sediment data, respectively [Bayon et al., 2009]). 2σ errors of the data presented in this study are similar to the size of the symbols.

2. Materials and Methods

[4] The desert and loess samples of this study were collected through the efforts of the Institute of Surficial Geochemistry at Nanjing University, and have been described in detail elsewhere (Chen et al., [2007], Li et al., [2009]; see Supporting Information Figure S1 and Table S1).

[5] Before leaching, a decarbonation step was carried out using excess 0.5 M acetic acid for 8 hours. This is expected to remove the detrital and secondary carbonates while leaving the labile Fe-Mn oxyhydroxide fraction of the silicate grains untouched. Then a dilute reducing and complexing solution consisting of 0.005 M hydroxylamine hydrochloride, 1.5% acetic acid, and 0.03 M EDTA-2Na, buffered to pH about 4 with superpure NaOH was used to extract the mobile component of the dust for about 2 h [Chen et al., 2012]. After complete removal of Fe-Mn oxides, the silicate residues, of which paired leachate data (<75 and <5 μm size fractions) have been obtained, were totally dissolved in steel jacketed autoclaves at ~ 180 – 200°C for 4 days. Subsequent purification and measurement of the Nd and Hf isotopes followed Chen et al. [2012] (see Table S1 for more details).

3. Results

[6] The Hf and Nd isotope data of dust leachates and detrital fractions are shown in Table S1 and Figure 1.

[7] There is virtually no difference between the Nd isotope composition of coarse- and fine-grained dust leachates (Figure 2a). In addition, the total dissolution data of the fine- and coarse-grained silicate fraction further reveal that their Nd isotope compositions are also distributed very close to

the 1:1 line (Figure 2b). Interestingly, a small but detectable and systematic difference between the Nd isotope compositions of the leachates and detrital silicate fractions (about 1.4 epsilon units) is remarkable (Figure 2c).

[8] With the exception of Taklimakan leachates, which have highly radiogenic Hf isotope signatures (ϵ_{Hf} : +14.5, +17.0), most of the ϵ_{Hf} values of the leachates are in the range of -0.8 to $+9.9$, while their corresponding ϵ_{Nd} signatures vary from -15.4 to -3.4 . The most striking feature of the leaching data is that they all fall along or slightly above the seawater array (Figure 1). Also, the hafnium isotope compositions are more radiogenic in leachates of the coarser size fraction (<75 μm) than the corresponding finer grain size leachates (<5 μm) (Figures 1 and 2d).

[9] As expected, the detrital silicates of the <75 μm size fraction has Nd and Hf isotope signatures consistent with the crustal array in ϵ_{Hf} - ϵ_{Nd} space, while the <5 μm fraction is more radiogenic in its Hf isotope composition (Figures 1 and 2e). Moreover, the leachate Hf isotope data of the fine and coarse size groups deviate notably from such a 1:1 line (Figure 2d). Also, the Hf isotope compositions of the leachates are fractionated significantly from those of the silicates (Figure 2f).

4. UCC Weathering Could Fully Produce the Seawater Array

[10] Interestingly, the leachate of a typical Asian dust sample GPC3 recovered from the North Pacific (Table S1) [Pettker et al., 2002] shows ϵ_{Nd} and ϵ_{Hf} signatures of -3.8 and $+6.6$, respectively (Figure 1), which are entirely consistent with central North Pacific deep water compositions [Amakawa et al., 2009]. Thus, the Nd-Hf isotopic signal of

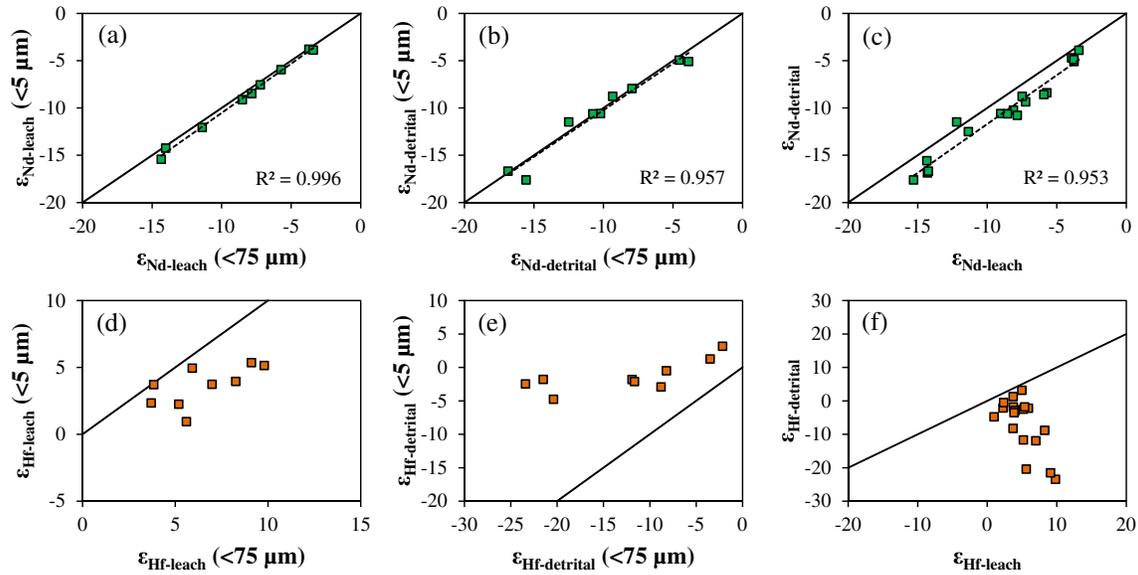


Figure 2. Hafnium and Nd isotope relationships in the dust leachates and corresponding detrital fractions of different grain sizes. (a) ϵ_{Nd} of $<75 \mu\text{m}$ leachates versus $<5 \mu\text{m}$ leachates; (b) ϵ_{Nd} of $<75 \mu\text{m}$ detritals versus $<5 \mu\text{m}$ detritals; (c) ϵ_{Nd} of leachates versus detritals; (d) ϵ_{Hf} of $<75 \mu\text{m}$ leachates versus $<5 \mu\text{m}$ leachates; (e) ϵ_{Hf} of $<75 \mu\text{m}$ detritals versus $<5 \mu\text{m}$ detritals; and (f) ϵ_{Hf} of leachates versus detritals. The solid lines represent 1 to 1 relationships.

the leaching experiments of GPC3 supports that the leaching protocol is robust in extracting the exchangeable component (e.g., Fe-Mn coatings) of the Asian dust (Figure 1).

[11] Supporting evidence for the agreement of the dust leaching signal with seawater array comes from the eastern equatorial Atlantic, which receives high loads of Saharan dust input. The Nd-Hf isotopes of eastern equatorial Atlantic surface waters (5°N – 15°N , Figure 1) were suggested to be dominated by dissolution of Saharan dust [Rickli *et al.*, 2010]. The consistency of leached Nd-Hf isotope trend between the fine-grained dust of this study and the Saharan dust implies that over a wide range of source rock compositions and ages, as well as geographical locations, aquatic Hf isotope fractionation of dust particles can provide Hf isotope signatures radiogenic enough to match the seawater array. Note that the leachates reflect Hf isotope signatures released during weathering of large-scale averaged upper continental crust (in our case represented by the dust materials). Therefore, it is reasonable to assume that Hf isotope signatures released from (large-scale averaged) rivers or shelf sediments are similar to the dust leachates. Our study thus cannot quantitatively distinguish the specific delivery mechanism of Hf-Nd isotopes to the ocean.

[12] For the samples with ϵ_{Nd} signatures below -13 , the Hf isotope compositions of the leachates are more radiogenic than the corresponding value of the seawater array (Figure 1). Because the largest difference between the seawater and crustal arrays (least radiogenic Nd isotope compositions, Figure 1) also indicates the largest degree of incongruent weathering, it is not surprising that actual leaching of Hf isotope signatures from older continental rocks shows more scatter. Given that the least radiogenic Hf isotope signatures of seawater have been found in the Labrador Sea [Rickli *et al.*, 2009], which is surrounded by cold and glacial weathering input, it may be that weathering in such an environment is more congruent [van de Flierdt *et al.*, 2002]. It is also likely that the rocks of northern Canada surrounding the Labrador Sea region had an evolution history different

from the old cratons in North China, resulting in different mineralogical composition and thus a different degree of aquatic Hf isotope fractionation in these two regions.

[13] The leachate data clearly and robustly indicate that no “extra” radiogenic Hf is necessary to produce the observed seawater array. Thus, contributions from hydrothermal Hf sources are probably negligible for the global seawater Hf budget.

5. Implications for Nd and Hf Isotopes as Oceanographic and Provenance Tracers

[14] The exchangeable fractions of continental particles or their preformed coatings either enter seawater via eolian or riverine transport. On the continental shelf, such a preformed leachable component may become the source of “boundary exchange”, a process proposed in previous studies [Lacan and Jeandel, 2005].

[15] Due to the small Sm/Nd fractionation in different minerals [Bayon *et al.*, 2006], the negligible fractionation of Nd isotopes between coarse and fine grain sizes of the detrital material (Figure 2b) is not surprising. Leaching of the dust particles, in contrast, appears to produce small but systematically more radiogenic Nd isotope signatures than the corresponding silicate dust fractions (Figure 2c) although no fractionation is observed between the fine and corresponding coarse grain size leachates (Figure 2a). Given that stable isotope fractionation cannot cause such a difference and that the good correlation in Figure 2c precludes external sources, our preferred explanation is that this pattern reflects the time integrated effect of slightly higher Sm/Nd in the leachable component during past weathering/sedimentary cycles. For example, the typical Middle Rare Earth Element enrichments during aquatic natural leaching of dust [Thiagarajan and Lee, 2004] would lead to a higher Sm/Nd ratio of the mobile component (e.g., preformed Fe-Mn coatings) than that of the silicate residue. Nevertheless, it is possible that the slightly more radiogenic leaching

Nd signal only represents mean state upper continental crust weathering especially in the middle to low latitudes, while recently glacially eroded rocks/till may yield less radiogenic Nd isotope compositions of the leachates than the bulk silicates in a cold climate [Andersson *et al.*, 2001].

[16] Hafnium isotope fractionation during mineral sorting and leaching is significantly larger than that of Nd isotopes. Overall, the Hf isotope fractionation between leachates and corresponding detrital material is larger the older the source rocks are (i.e., less radiogenic Nd isotopes, Figure 1), reflecting the time integrated effect of Hf isotopic differences between different minerals. The Hf isotope signatures of the $<5\ \mu\text{m}$ silicate (Figure 1) are close to the seawater array (though still not radiogenic enough). Interestingly, in marine settings, essentially all detrital sediments fall below the seawater array [Bayon *et al.*, 2009; Vervoort *et al.*, 1999, 2011, Figure 1]. Given that the $<5\ \mu\text{m}$ size samples in this study are already close to the lowest size range observed in natural sediments and are also expected to have experienced maximum heavy mineral loss during weathering and transport (including zircon), we propose that the $<5\ \mu\text{m}$ size fraction reflects the upper limit of Hf isotope fractionation due to zircon loss. Furthermore, the $<5\ \mu\text{m}$ fractions (Figure 1) are close but still systematically more radiogenic in Hf isotope composition than the “zircon-free sediment array” [Bayon *et al.*, 2009]. This implies that the marine fine-grained sediments on average, though clearly depleted in zircons, may not be completely “zircon-free.”

[17] Surprisingly, Hf isotopes are systematically more radiogenic in the leachates of the coarse grain size fraction than of their fine counterparts (Figure 2b). Given that the leachable component is not necessarily the product of current weathering in the arid deserts, one explanation is that the $<5\ \mu\text{m}$ particles may mainly come from a more deeply weathered environment than the large particles ($<75\ \mu\text{m}$). These $<5\ \mu\text{m}$ particles would thus have the potential of receiving somewhat higher contributions from zircon weathering. However, such an explanation is unlikely because Nd isotope compositions of the fine and coarse particles are essentially identical. Therefore, our data imply that incongruent weathering of minerals other than zircon are also important for Hf isotope fractionation during aquatic leaching of UCC rocks and consequently in the formation of Nd-Hf seawater array, which is consistent with recent studies [Bayon *et al.*, 2006, 2009; Rickli *et al.*, 2009; Chen *et al.*, 2011]. Unfortunately, the exact contribution of different minerals to the Hf isotope fractionation is unknown and remains to be studied in detail before an unequivocal explanation for this grain size effect on Hf isotopes can be provided.

[18] Recent direct water mass studies on dissolved Hf isotopes have indicated that Hf isotopes are not a sensitive water mass tracer due to their limited isotopic variability in the oceanic water column [Stichel *et al.*, 2012]. Early studies on Fe-Mn crusts [van de Flierdt *et al.*, 2004] and a recent study on authigenic sediment fractions from the Arctic Ocean [Chen *et al.*, 2012], however, still showed a broad positive correlation between evolution of Hf isotopes and Nd isotopes in seawater, which is also reflected by the well constrained seawater array. As shown in Figure 1, it is evident that there is a large range in the leached Hf isotope compositions from the same rocks which essentially prevents clear identification of source rocks from the dissolved Hf isotope composition of seawater. Consequently dissolved seawater Hf isotope signatures and their records

in authigenic sediment fractions will be most useful in distinguishing different modes of weathering regimes on land or even changes in runoff [Rickli *et al.*, 2013].

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References

- Albarède, F., A. Simonetti, J. D. Vervoort, J. Blichert-Toft, and W. Abouchami (1998), A Hf-Nd isotopic correlation in ferromanganese nodules, *Geophys. Res. Lett.*, 25(20), 3895–3898.
- Amakawa, H., K. Sasaki, and M. Ebihara (2009), Nd isotopic composition in the central North Pacific, *Geochim. Cosmochim. Acta*, 73(16), 4705–4719.
- Andersson, P. S., R. Dahlqvist, J. Ingri, and O. Gustafsson (2001), The isotopic composition of Nd in a boreal river: A reflection of selective weathering and colloidal transport, *Geochim. Cosmochim. Acta*, 65(4), 521–527.
- Bau, M., and A. Koschinsky (2006), Hafnium and neodymium isotopes in seawater and in ferromanganese crusts: The “element perspective”, *Earth Planet. Sci. Lett.*, 241(3–4), 952–961.
- Bayon, G., C. R. German, K. W. Burton, R. W. Nesbitt, and N. Rogers (2004), Sedimentary Fe–Mn oxyhydroxides as paleoceanographic archives and the role of aeolian flux in regulating oceanic dissolved REE, *Earth Planet. Sci. Lett.*, 224(3–4), 477–492.
- Bayon, G., N. Vigier, K. W. Burton, A. Brenot, J. Carignan, J. Etoubleau, and N. C. Chu (2006), The control of weathering processes on riverine and seawater hafnium isotope ratios, *Geology*, 34(6), 433–436.
- Bayon, G., K. W. Burton, G. Soulet, N. Vigier, B. Dennielou, J. Etoubleau, E. Ponzevera, C. R. German, and R. W. Nesbitt (2009), Hf and Nd isotopes in marine sediments: Constraints on global silicate weathering, *Earth Planet. Sci. Lett.*, 277(3–4), 318–326.
- Chen, J., and G. J. Li (2011), Geochemical studies on the source region of Asian dust, *Sci. China Earth Sci.*, 54(9), 1279–1301.
- Chen, J., G. J. Li, J. D. Yang, W. B. Rao, H. Y. Lu, W. Balsam, Y. B. Sun, and J. F. Ji (2007), Nd and Sr isotopic characteristics of Chinese deserts: Implications for the provenances of Asian dust, *Geochim. Cosmochim. Acta*, 71(15), 3904–3914.
- Chen, T.-Y., H.-F. Ling, M. Frank, K.-D. Zhao, and S.-Y. Jiang (2011), Zircon effect alone insufficient to generate seawater Nd-Hf isotope relationships, *Geochem. Geophys. Geosyst.*, 12(5), Q05003, doi:10.1029/2010gc003363.
- Chen, T.-Y., M. Frank, B. A. Haley, M. Gutjahr, and R. F. Spielhagen (2012), Variations of North Atlantic inflow to the central Arctic Ocean over the last 14 million years inferred from hafnium and neodymium isotopes, *Earth Planet. Sci. Lett.*, 353–354(0), 82–92.
- Firdaus, M. L., T. Minami, K. Norisuye, and Y. Sohrin (2011), Strong elemental fractionation of Zr-Hf and Nb-Ta across the Pacific Ocean, *Nat. Geosci.*, 4(4), 227–230.
- Godfrey, L. V., D. C. Lee, W. F. Sangrey, A. N. Halliday, V. J. M. Salters, J. R. Hein, and W. M. White (1997), The Hf isotopic composition of ferromanganese nodules and crusts and hydrothermal manganese deposits: Implications for seawater Hf, *Earth Planet. Sci. Lett.*, 151(1–2), 91–105.
- Godfrey, L. V., B. Zimmermann, D. C. Lee, R. L. King, J. D. Vervoort, R. M. Sherrell, and A. N. Halliday (2009), Hafnium and neodymium isotope variations in NE Atlantic seawater, *Geochem. Geophys. Geosyst.*, 10, doi:10.1029/2009GC002508.
- Lacan, F., and C. Jeandel (2005), Neodymium isotopes as a new tool for quantifying exchange fluxes at the continent-ocean interface, *Earth Planet. Sci. Lett.*, 232(3–4), 245–257.
- Li, G. J., J. Chen, J. F. Ji, J. D. Yang, and T. M. Conway (2009), Natural and anthropogenic sources of East Asian dust, *Geology*, 37(8), 727–730, doi:10.1130/G30031a.1.
- Patchett, P. J., W. M. White, H. Feldmann, S. Kielinczuk, and A. W. Hofmann (1984), Hafnium Rare-Earth Element Fractionation in the Sedimentary System and Crustal Recycling into the Earths Mantle, *Earth Planet. Sci. Lett.*, 69(2), 365–378.
- Pettke, T., A. N. Halliday, and D. K. Rea (2002), Cenozoic evolution of Asian climate and sources of Pacific seawater Pb and Nd derived from eolian dust of sediment core LL44-GPC3, *Paleoceanography*, 17(3), doi:10.1029/2001PA000673.
- Ren, J. (1996), The continental tectonics of China, *J. Southeast Asian Earth Sci.*, 13(3–5), 197–204.
- Rickli, J., M. Frank, and A. N. Halliday (2009), The hafnium-neodymium isotopic composition of Atlantic seawater, *Earth Planet. Sci. Lett.*, 280(1–4), 118–127.

- Rickli, J., et al. (2010), Hafnium and neodymium isotopes in surface waters of the eastern Atlantic Ocean: Implications for sources and inputs of trace metals to the ocean, *Geochim. Cosmochim. Acta*, 74(2), 540–557.
- Rickli, J., M. Frank, T. Stichel, R. B. Georg, D. Vance, and A. N. Halliday (2013), Controls on the incongruent release of hafnium during weathering of metamorphic and sedimentary catchments, *Geochim. Cosmochim. Acta*, 101(0), 263–284.
- Stichel, T., M. Frank, J. Rickli, and B. A. Haley (2012), The hafnium and neodymium isotope composition of seawater in the Atlantic sector of the Southern Ocean, *Earth Planet. Sci. Lett.*, 317–318(0), 282–294.
- Thiagarajan, N., and C. T. A. Lee (2004), Trace-element evidence for the origin of desert varnish by direct aqueous atmospheric deposition, *Earth Planet. Sci. Lett.*, 224(1–2), 131–141.
- van de Flierdt, T., M. Frank, D. C. Lee, and A. N. Halliday (2002), Glacial weathering and the hafnium isotope composition of seawater, *Earth Planet. Sci. Lett.*, 198(1–2), 167–175.
- van de Flierdt, T., M. Frank, D. C. Lee, A. N. Halliday, B. C. Reynolds, and J. R. Hein (2004), New constraints on the sources and behavior of neodymium and hafnium in seawater from Pacific Ocean ferromanganese crusts, *Geochim. Cosmochim. Acta*, 68(19), 3827–3843.
- van de Flierdt, T., S. L. Goldstein, S. R. Hemming, M. Roy, M. Frank, and A. N. Halliday (2007), Global neodymium-hafnium isotope systematics - revisited, *Earth Planet. Sci. Lett.*, 259(3–4), 432–441.
- Vervoort, J. D., T. Plank, and J. Prytulak (2011), The Hf-Nd isotopic composition of marine sediments, *Geochim. Cosmochim. Acta*, 75(20), 5903–5926.
- Vervoort, J. D., P. J. Patchett, J. Blichert-Toft, and F. Albarede (1999), Relationships between Lu-Hf and Sm-Nd isotopic systems in the global sedimentary system, *Earth Planet. Sci. Lett.*, 168(1–2), 79–99.
- White, W. M., J. Patchett, and D. Benoitman (1986), Hf Isotope ratios of marine-sediments and Mn Nodules - evidence for a mantle source of Hf in seawater, *Earth Planet. Sci. Lett.*, 79(1–2), 46–54.
- Zimmermann, B., et al. (2009), Hafnium isotopes in Arctic Ocean water, *Geochim. Cosmochim. Acta*, 73(11), 3218–3233.