

# Radiogenic Hf isotopic compositions of continental eolian dust from Asia, its variability and its implications for seawater Hf

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## Abstract

The inorganic silicate fraction extracted from bulk pelagic sediments from the North Pacific Ocean is eolian dust. It monitors the composition of continental crust exposed to erosion in Asia.  $^{176}\text{Lu}/^{177}\text{Hf}$  ratios of modern dust are subchondritic between 0.011 and 0.016 but slightly elevated with respect to immature sediments. Modern dust samples display a large range in Hf isotopic composition (IC),  $-4.70 < \varepsilon_{\text{Hf}} < +16.45$ , which encompasses that observed for the time series of DSDP cores 885/886 and piston core LL44-GPC3 extending back to the late Cretaceous. Hafnium and neodymium isotopic results are consistent with a dominantly binary mixture of dust contributed from island arc volcanic material and dust from central Asia. The Hf–Nd isotopic correlation for all modern dust samples,  $\varepsilon_{\text{Hf}} = 0.78\varepsilon_{\text{Nd}} + 5.66$  ( $n = 22$ ,  $R^2 = 0.79$ ), is flatter than those reported so far for terrestrial reservoirs. Moreover, the variability in  $\varepsilon_{\text{Hf}}$  of Asian dust exceeds that predicted on the basis of corresponding  $\varepsilon_{\text{Nd}}$  values ( $-4.7 < \varepsilon_{\text{Hf}} < +2.5$ ;  $-10.9 < \varepsilon_{\text{Nd}} < -10.1$ ). This is attributed to: (1) the fixing of an important unradiogenic fraction of Hf in zircons, balanced by radiogenic Hf that is mobile in the erosional cycle, (2) the elevated Lu/Hf ratio in chemical sediments which, given time, results in a Hf signature that is radiogenic compared with Hf expected from its corresponding Nd isotopic components, and (3) the possibility that diagenetic resetting of marine sediments may incorporate a significant radiogenic Hf component into diagenetically grown minerals such as illite. Together, these processes may explain the variability and more radiogenic character of Hf isotopes when compared to the Nd isotopic signatures of Asian dust. The Hf–Nd isotope time series of eolian dust are consistent with the results of modern dust except two samples that have extremely radiogenic Hf for their Nd ( $\varepsilon_{\text{Hf}} = +8.6$  and  $+10.3$ ,  $\varepsilon_{\text{Nd}} = -9.5$  and  $-9.8$ ). These data may point to a source contribution of dust unresolved by Nd and Pb isotopes. The Hf IC of eolian dust input to the oceans may be more variable and more radiogenic than previously anticipated. The Hf signature of Pacific seawater, however, has varied little over the past 20 Myr, especially across the drastic increase of eolian dust flux from Asia around 3.5 Ma. Therefore, continental contributions to seawater Hf appear to be riverine rather than eolian. Current predictions regarding the relative proportions of source components to seawater Hf must account for the presence of a variable and radiogenic continental component. Data on the IC and flux of river-dissolved Hf to the oceans are

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urgently required to better estimate contributions to seawater Hf. This then would permit the use of Hf isotopes as a monitor of past changes in erosion. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The isotopic compositions (ICs) of Nd, Pb and, most recently, Hf in ferromanganese crusts are widely used to constrain the history of continental erosion and ocean circulation. Hafnium isotopes have become particularly promising as an ocean tracer because the mean oceanic residence time of Hf appears to be longer than that of Nd [1–4] but shorter than the global seawater mixing time of circa 1500 yr [5]. The degree of variation in the Hf IC of continental source materials can be expected to be more pronounced than that of Nd since the time-integrated effects of igneous processes are estimated to be about twice that of Nd [6]. However, recent refinements point to a factor of ca. 1.4 [7]. Lu/Hf ratios are variable in sedimentary rocks because of selective retention of Hf in highly resistant zircon grains [1,8], while little erosional and sedimentary fractionation is documented for the Sm–Nd system (e.g. [9]). It also appears plausible that radiogenic Hf may enter seawater through mid-ocean ridge (MOR) hydrothermal activity [1,2], while rare earth elements (REE) are effectively scavenged from vents [10, 11].

Sediments recycled multiple times such as eolian dust from central Asia are characterized by  $\epsilon_{\text{Hf}}$  values that are more variable and radiogenic than expected from their corresponding, virtually constant  $\epsilon_{\text{Nd}}$  [12]. Based on this observation it was concluded that the Hf IC of the continental flux to oceans is probably more radiogenic than expected and might not be estimated reliably by using a linear  $\epsilon_{\text{Hf}}-\epsilon_{\text{Nd}}$  relationship [12].

For the central Pacific Ocean, Hf isotope profiles are now available for three ferromanganese crusts, CD29-2 and D11-1 [3], and VA13/2 [4], complementing time series of Nd and Pb isotopes from the same crusts [13–15].  $\epsilon_{\text{Hf}}$  data show little temporal variation during the past 20 Myr

( $+6 < \epsilon_{\text{Hf}} < +8$ ). This is surprising given the large variability in potential sources (riverine, eolian and MOR hydrothermal) and the lithologic and geochemical diversity (volcanic island arcs, sediments and basement rocks) and evolution of surrounding landmasses such as progressive buildup of the Himalayan chain and associated desertification of central Asia. The Hf isotopic time series of the Pacific ferromanganese crusts were interpreted [3] to indicate a comparatively long seawater residence time of Hf in central Pacific deep water, longer than that of Nd and Pb. Therefore, Hf may record a well mixed, basin-wide signal. In contrast, modern ferromanganese nodules [16] and crusts [2,4] in different geographic locations show heterogeneous Hf ICs, suggesting a residence time of Hf in seawater that is shorter than the turnover time of the deep oceans. This suggests that provincial inputs of Hf (large rivers, eolian dust plumes) would be resolvable. Therefore, variations in response to migration of the crust growth site beneath zones of different ocean currents and input patterns should be recorded in Hf isotopic time series of ancient seawater.

Considerable uncertainty in how to interpret isotopic records of seawater Hf primarily stems from the poor knowledge of source characteristics and fluxes for Hf isotopes. The continental erosional component has remained essentially unknown. Erosional products, in addition to the chemical weathering of island arc volcanic (IAV) rocks, enter the oceans through rivers as suspended or dissolved loads, or as eolian dust, transported by strong winds over large distances. Hafnium isotopes in the terrestrial system, to a first approximation, behave fairly coherently with Nd isotopes [7]. However, as with Nd isotopes [17], considerable fractionation has been observed between turbidite sand and corresponding muds for Hf [7] – sedimentary sorting appears to

be an important process that may well generate specific source characteristics for very fine-grained particles in the erosional cycle.

This contribution reports the first comprehensive set of data on the Hf IC and abundances of Lu and Hf of eolian dust extracted from Pacific pelagic sediments. These data provide a record of the mean Lu–Hf isotope characteristics of large areas exposed to erosion in central Asia since the Oligocene. Particular emphasis was placed on sample dissolution procedures in order to constrain Hf isotope characteristics of different host minerals for assessing possible effects of incongruent chemical weathering. A geographic distribution pattern downwind of the central Asian dust source and two time series of dust deposition are used to characterize the extent to which Hf, Nd and Pb isotopes are correlated in dust. These data also provide a first order estimate of the IC and flux of dust-bound Hf to seawater, which may help to constrain the Hf IC for the erosional component from continents.

## 2. Samples and analytical techniques

Sample selection for Lu–Hf isotopic analysis was aimed at constraining the geographic distribution and the temporal evolution of the Hf ICs of dust deposited in the central North Pacific Ocean guided by published Nd isotope data [18–20]. Samples from the North-West Pacific margin essentially consist of a binary mixture of dust from central Asia and IAV material mixed in various proportions. Modern dust deposited in the central North Pacific is predominantly Asian dust [18,19,21]. Lu–Hf concentrations and Hf isotopic time series were obtained for two sediment cores, the composite record of Ocean Drilling Program (ODP) Site 885/886 [22–25] and the well studied large-diameter piston core LL44-GPC3 (hereafter named GPC3 [26–31]). Sample localities are shown in Fig. 1.

The eolian inorganic silicate fraction, termed dust, was extracted from the bulk sediments following procedures outlined in detail by Snoeckx et al. [24]. This extraction procedure comprised the following steps. Fe–Mn oxi-hydroxides and

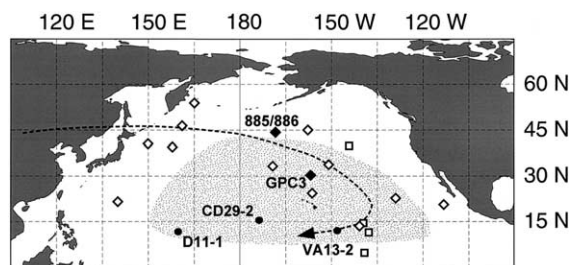


Fig. 1. Map of the North Pacific Ocean and adjacent continents showing sample locations and the predominant track of dust transport from central Asia (dashed arrow, after Merrill [43]). The central North Pacific dust province [19,44] is stippled. Modern dust samples analyzed in this study are shown in open diamonds, sites of GPC3 and composite stratigraphy 885/886 time series are indicated by black diamonds. Bulk pelagic red clays [2,16,7] are shown in open squares; samples Rama BC15R and Rama BC20 [2] are from the immediate vicinity of GPC3, hence not shown separately. Black dots show ferromanganese crusts (labeled) for which Hf isotopic time series are available.

zeolites, including any hydrogenetic and hydrothermal deposits, were removed by a hot sodium dithionite–sodium citrate solution buffered with sodium bicarbonate. Biogenic silica (opal) was removed using sodium hydroxide. The residue was dried. It provided the starting material for samples analyzed here (100 mg dry sample splits) as well as for published work [18,19,22,26] to which our data can be related. It is important to note that this established extraction procedure for obtaining the eolian inorganic silicate fraction of bulk pelagic sediments does not guarantee that elements not structurally bound in dust are quantitatively removed. Therefore, the dust samples were first leached in a 1 M ammonium acetate solution, in order to remove contamination from exchangeable sites of clays or adsorbed onto the sample surface. While this leachate fraction amounted to several percent for Nd and Sr [22], it was always below 1% of the total for Hf. This extra cleaning step has thus been aborted for subsequent samples (Table 1). Chemical cleaning using a stronger acid treatment was considered inappropriate because strong acids are capable of leaching lattice-bound cations from clays. It is possible that the ammonium acetate cleaning procedure was too weak to remove Hf adsorbed to the dust particle surfaces. The Hf IC obtained

Table 1  
Lu–Hf and Nd isotope data for modern and time series samples of eolian silicate dust extracted from sediments of the North Pacific Ocean

Sample	Coordinates	Core depth (cm)	Water depth (m)	Dissolution procedure <sup>a</sup>	Strat. Age (Ma)	Lu (ppm)	Hf (ppm)	<sup>176</sup> Lu/ <sup>177</sup> Hf	<sup>176</sup> Hf/ <sup>177</sup> Hf	± 2 S.E.M. abs. <sup>b</sup>	ε <sub>Hf</sub>	± 2 S.E.M. abs. <sup>b</sup>	ε <sub>Nd</sub>	± 2 S.E.M. abs. <sup>b</sup>
<b>North Pacific margin province</b>														
RP2OC72-01GC	21°18'N; 139°59'E	0–3	4699	WB, WS	0.1	0.3911	3.926	0.0141	0.282883	± 8	+3.93 ± 0.28	± 0.28	−2.98	± 0.20 [19]
RP2OC72-01GC	21°18'N; 139°59'E	0–3	4699	WB, WS	0.1	0.4012	3.741	0.0152	0.282927	± 10	+5.47 ± 0.36	± 0.36	−2.98	± 0.20 [19]
RP2OC72-01GC	21°18'N; 139°59'E	0–3	4699	S, B	0.1	0.4015	3.858	0.0147	0.282868	± 9	+3.39 ± 0.32	± 0.32	−2.98	± 0.20 [19]
RC14-105	39°24'N; 157°18'E	34–35	5630	WB, WS	0.1	0.5153	6.420	0.0114	0.282814	± 6	+1.47 ± 0.22	± 0.22	+0.88	± 0.20 [18]
RC14-105	39°24'N; 157°18'E	34–35	5630	WB, WS	0.1	0.5195	6.466	0.0114	0.282798	± 6	+0.90 ± 0.20	± 0.20	+0.88	± 0.20 [18]
RC14-105	39°24'N; 157°18'E	34–35	5630	WB, WS	0.1	0.5170	6.408	0.0114	0.282808	± 7	+1.26 ± 0.26	± 0.26	+0.88	± 0.20 [18]
V20-122	46°18'N; 161°24'E	26–28	5563	WB, WS	0.1	0.3526	3.997	0.0125	0.282856	± 8	+2.95 ± 0.28	± 0.28	−0.49	± 0.20 [18]
V20-122	46°18'N; 161°24'E	26–28	5563	WB, WS	0.1	0.3586	4.009	0.0127	0.282868	± 9	+3.40 ± 0.32	± 0.32	−0.49	± 0.20 [18]
V20-122	46°18'N; 161°24'E	26–28	5563	WB, WS	0.1	0.3628	4.062	0.0127	0.282863	± 8	+3.22 ± 0.30	± 0.30	−0.49	± 0.20 [18]
V20-122	46°18'N; 161°24'E	26–28	5563	RB	0.1	0.0012	0.055	0.0032	nm		nm			
V20-122	46°18'N; 161°24'E	26–28	5563	RB	0.1	0.0015	0.101	0.0021	nm		nm			
V20-122	46°18'N; 161°24'E	26–28	5563	RB	0.1	0.0009	0.059	0.0021	nm		nm			
Vinogra-dov1917GGC	53°42'N; 165°01'E	4–7	3960	WB, WS	0.1	0.3122	3.442	0.0128	0.283083	± 10	+11.01 ± 0.36	± 0.36	+3.76	± 0.50 [19]
Vinogra-dov1917GGC	53°42'N; 165°01'E	4–7	3960	WB, WS	0.1	0.3357	2.669	0.0178	0.283139	± 8	+12.99 ± 0.28	± 0.28	+3.76	± 0.50 [19]
Vinogra-dov1917GGC	53°42'N; 165°01'E	4–7	3960	S, B	0.1	0.3407	2.879	0.0168	0.283237	± 11	+16.45 ± 0.40	± 0.40	+3.76	± 0.50 [19]
TT49-18AC	41°01'N; 150°01'E	0–3	5185	WB, WS	0.1	0.3556	3.772	0.0134	0.282867	± 8	+3.35 ± 0.30	± 0.30	−5.19	± 0.20 [19]
Y70-1-12MG1	45°04'N; 157°25'W	0–3	5372	WB, WS	0.1	0.3806	4.099	0.0132	0.282742	± 10	−1.06 ± 0.36	± 0.36	−8.41	± 0.20 [19]
Y74-2-31MG2	20°15'N; 113°57'W	0–3	3590	WB, WS	0.1	0.3208	4.509	0.0101	0.282765	± 11	−0.25 ± 0.40	± 0.40	−6.30	± 0.10 [19]
<b>North Pacific central province</b>														
RP2OC72-04GC	24°50'N; 156°12'E	0–3	5262	WB, WS	0.1	0.3879	4.054	0.0136	0.282705	± 11	−2.37 ± 0.40	± 0.40	−10.10	± 0.20 [19]
RP2OC72-04GC	24°50'N; 156°12'E	0–3	5262	WB, WS	0.1	0.3483	4.163	0.0119	0.282842	± 9	+2.48 ± 0.32	± 0.32	−10.10	± 0.20 [19]
RP2OC72-04GC	24°50'N; 156°12'E	0–3	5262	S, B	0.1	0.3357	4.317	0.0110	0.282802	± 10	+1.06 ± 0.34	± 0.34	−10.10	± 0.20 [19]
Y74-2-35MG3	22°35'N; 129°20'W	0–3	4647	WB, WS	0.1	0.3584	4.236	0.0120	0.282661	± 8	−3.93 ± 0.30	± 0.30	−10.90	± 0.40 [19]
Y74-3-69MG4	33°26'N; 151°01'W	0–3	5524	WB, WS	0.1	0.3845	4.528	0.0120	0.282639	± 7	−4.70 ± 0.24	± 0.24	−10.77	± 0.40 [19]
Scan-10PG	13°52'N; 140°10'W	5–7	4864	WB, WS	0.1	0.3255	4.399	0.0105	0.282724	± 7	−1.70 ± 0.26	± 0.26	−10.24	± 0.10 [19]
KK75-PCOD.03	33°22'N; 169°05'E	0–4	5736	WB, WS	0.1	0.3747	4.157	0.0128	0.282654	± 11	−4.17 ± 0.40	± 0.40	−10.48	± 0.20 [19]
<b>Downcore 885/886</b>														
A-2H-5	44.7°N; 168.3°W	1360	5710	WB, WS	2.4 [23]	0.4137	5.535	0.0106	0.283015	± 8	+8.58 ± 0.28	± 0.28	−9.54	± 0.14 [22]
A-3H-1	44.7°N; 168.3°W	2000	5710	WB, WS	3.2 [23]	0.4084	6.083	0.0095	0.283064	± 8	+10.32 ± 0.30	± 0.30	−9.83	± 0.12 [22]
A-4H-6	44.7°N; 168.3°W	3687	5710	WB, WS	5.9 [23]	0.4068	6.533	0.0088	0.282764	± 8	−0.28 ± 0.28	± 0.28	−10.16	± 0.12 [22]
A-5H-5	44.7°N; 168.3°W	4723	5710	WB, WS	7.4 [23]	0.3687	5.633	0.0093	0.282663	± 8	−3.87 ± 0.28	± 0.28	−10.01	± 0.14 [22]
A-6H-4	44.7°N; 168.3°W	5517	5710	WB, WS	11.1 [23]	0.3050	5.989	0.0072	0.282750	± 7	−0.79 ± 0.26	± 0.26	−9.03	± 0.10 [22]

Table 1 (Continued).

Sample	Coordinates	Core depth (cm)	Water depth (m)	Dissolution procedure <sup>a</sup>	Strat. Age (Ma)	Lu (ppm)	Hf (ppm)	<sup>176</sup> Lu/ <sup>177</sup> Hf	<sup>176</sup> Hf/ <sup>177</sup> Hf	$\pm 2$ S.E.M. abs. <sup>b</sup>	$\epsilon_{\text{Hf}}$	$\pm 2$ S.E.M. abs. <sup>b</sup>	$\epsilon_{\text{Nd}}$	$\pm 2$ S.E.M. abs. <sup>b</sup>
<b>Dowcore LL44-GPC3</b>														
55704	30.3°N; 157.8°W	320	5705	WB, WS	1.5 [27]	0.3587	4.729	0.0107	0.282683	$\pm 6$	-3.17	$\pm 0.20$	-10.65	$\pm 0.12$ [26]
55705	30.3°N; 157.8°W	380	5705	WB, WS	2.0 [27]	0.3536	4.879	0.0103	0.282694	$\pm 7$	-2.62	$\pm 0.36$	-10.81	$\pm 0.12$ [26]
55707	30.3°N; 157.8°W	460	5705	WB, WS	2.9 [27]	0.3427	4.981	0.0097	0.282723	$\pm 7$	-1.75	$\pm 0.24$	-10.26	$\pm 0.16$ [26]
55710	30.3°N; 157.8°W	540	5705	WB, WS	5.0 [27]	0.3470	4.690	0.0105	0.282682	$\pm 10$	-3.18	$\pm 0.42$	-10.16	$\pm 0.12$ [26]
55712	30.3°N; 157.8°W	600	5705	WB, WS	6.8 [27]	0.3391	4.543	0.0106	0.282696	$\pm 7$	-2.69	$\pm 0.24$	-9.87	$\pm 0.12$ [26]
55713	30.3°N; 157.8°W	630	5705	WB, WS	7.4 [27]	0.3338	4.823	0.0098	0.282725	$\pm 5$	-1.68	$\pm 0.18$	-9.91	$\pm 0.16$ [26]
55730	30.3°N; 157.8°W	1150	5705	WB, WS	35.7 [27]	0.1643	6.983	0.0033	0.282844	$\pm 6$	+2.55	$\pm 0.20$	-9.15	$\pm 0.16$ [26]
55738	30.3°N; 157.8°W	1330	5705	WB, WS	43.6 [27]	0.0876	3.243	0.0038	0.282908	$\pm 7$	+4.79	$\pm 0.26$	-6.67	$\pm 0.18$ [26]
55747	30.3°N; 157.8°W	1490	5705	WB, WS	49.8 [27]	0.0778	2.842	0.0039	0.282936	$\pm 6$	+5.80	$\pm 0.20$	-6.85	$\pm 0.16$ [26]
55762	30.3°N; 157.8°W	1900	5705	WB, WS	64.5 [27]	0.1131	2.215	0.0072	0.282875	$\pm 27$	+3.64	$\pm 0.94$	-7.06	$\pm 0.16$ [26]
55767	30.3°N; 157.8°W	2320	5705	WB, WS	70.4 [27]	0.1636	3.380	0.0069	0.282707	$\pm 8$	-2.30	$\pm 0.28$	-10.20	$\pm 0.28$ [26]

nm = not measured.

<sup>a</sup> Describes the type of sample dissolution procedure (see text): S = surface cleaned; WS = without surface cleaning; B = bomb fraction included; WB = without bomb fraction; RB = residue from beaker dissolution bombed and processed as an isolated ID sample.

<sup>b</sup> Two standard error of the mean on the last digits quoted.

here, however, do not correlate with the mean grain size of the dust [21] as would be expected for an important contribution of radiogenic Hf adsorbed to the sample surface (radiogenic Hf from hydrogenetic or hydrothermal components dissolved during extraction and adsorbed on the silicate fraction of the dust). Therefore, extraneous Hf adsorbed onto the dust sample surface appears not to pose a problem here. Note that all dust samples were extracted according to the same procedure, hence relative differences in Hf ICs are considered to be robust.

Various dissolution techniques have been explored in order to better characterize the carrier phases of Lu and Hf in the dust. Dry sample splits were dissolved in Savillex screw-top beakers (HF:HNO<sub>3</sub> ~ 9:1) at 110°C for 5 days, repeatedly stirred in an ultrasonic bath. This yielded non-reproducible  $\epsilon_{\text{Hf}}$  values in some cases, indicating that such splits are inhomogeneous with respect to their Hf IC or that refractory minerals (mainly zircon) were only partially attacked during conventional beaker dissolution of the dust. In order to evaluate the importance of such refractory minerals for the Hf in dust, dry splits of a few samples were dissolved in various ways. (a) Savillex screw-top beaker-only dissolutions as above, (b) Savillex screw-top beakers, centrifuged, supernatant solution pipetted off and any residue digested in steel-jacketed bombs at 180°C for 5 days. Both fractions mixed together. (c) Some residues of beaker dissolutions were spiked and subsequently exposed to steel-jacketed bomb digestion to determine Lu and Hf abundances (Hf concentrations of these samples were too low for high-precision Hf IC analysis).

Isotope dilution (ID) measurements of Lu and Hf were made on aliquots from 6 N HCl–1 N HF sample solutions and subsequently spiked with a mixed <sup>176</sup>Lu–<sup>178</sup>Hf spike (which was checked bi-monthly against Lu and Hf standard solutions). Spike–sample equilibration was ensured by the following procedure. The ID fraction was dried and then dissolved in 500  $\mu$ l 6 N HCl on the hotplate to equilibrate Lu. This was then dried and dissolved in 4 N HF and left overnight before centrifugation and loading the Hf fraction on the first column. The Lu fraction was taken from the

insoluble residue (chiefly fluorides) centrifuged off the Hf ID loading for the first column. Chemical separation for Hf ID and Hf IC samples followed the procedure described in Lee et al. [3]. Nd and Pb fractions of some GPC3 duplicate samples presented in Pettke et al. [26] were taken from the insoluble residue centrifuged off the first Hf IC column loading. Purification of Lu was by cation exchange chemistry on AG50W-X8 in HCl milieu calibrated to collect a heavy REE fraction with a single elution procedure. Total procedure Hf blanks were always below 38 pg and therefore negligible.

Multiple collector inductively coupled plasma mass spectrometric measurements were made on the Plasma 54 (P54) of VG Instruments at the University of Michigan [32,33]. Replicate analyses of the Hf standard JMC475 bracketing and in between the Hf samples gave  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282157 \pm 11$  ( $n = 28$ ), identical to the long-term laboratory mean [3]. This corresponds to an external reproducibility of  $\pm 0.4\epsilon_{\text{Hf}}$  at the  $2\sigma$  level. All Hf ICs are expressed as  $\epsilon$ -values relative to CHUR  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282772$  [34]; all literature  $\epsilon_{\text{Hf}}$  values cited below have been recalculated accordingly.

### 3. Results

Hafnium ICs and abundances of Lu and Hf are presented in Table 1. Modern dust samples display a range in Hf IC of  $-4.70 < \epsilon_{\text{Hf}} < +16.45$ , which encompasses that observed for the time series of Site 885/886 and GPC3.

Evaluation of the data obtained from dry sample splits processed individually as screw-top beaker-only dissolutions resulted in different Hf ICs for some samples (RP2OC72-01GC, Vinogradov1917GG, RP2OC72-01GC) while others were reproducible within the  $2\sigma$  uncertainty. This contrasts with the reproducibility obtained for Nd, Pb and Sr isotopes on individually processed dry sample splits [22,26] and suggests that such splits may not always be identical with respect to their Hf IC. Dry sample splits processed with various dissolution techniques (i.e. with or without a bomb-dissolution step) also reveal different Hf

ICs in some cases. ID Lu and Hf concentrations of the isolated bomb fractions of one triplicate sample (V20-122) accounted for up to 0.4 and 2.5% of the total sample Lu and Hf abundances. The bomb-only fraction (i.e. the beaker residue bombed subsequently) is characterized by  $^{176}\text{Lu}/^{177}\text{Hf}$  ratios around 0.003, which is typical for zircon. It is, therefore, concluded that some (sub-?) micrometer-sized zircons may be transported by wind for distances of several thousand kilometers [12], possibly as mineral inclusions in clays (former mica) or volcanic ash shards. This is consistent with evidence from excess  $^4\text{He}$  in sediments from the Ontong Java Plateau interpreted to be hosted in zircon [35].

Screw-top beaker-only dissolutions gave reproducible  $\epsilon_{\text{Hf}}$  values for triplicate analyses of two samples (RC14-105 and V20-122) and possibly represent the fraction of the dust with little or no contribution of zircon-hosted Hf. These data also demonstrate the reproducibility of the analytical procedure. If the variability in Hf IC between dry sample splits processed in different ways as described above is indeed caused by a variable contribution of Hf from zircon, it would suggest that dust contains several distinct populations of zircons each with its characteristic Hf IC. For samples from the North-West Pacific margin province, these zircon populations could correspond to zircon from young IAV rocks and zircon from central Asian dust. Multiple zircon populations may also be invoked to explain the heterogeneity in Hf isotopes for the triplicate analysis of a sample from the central North Pacific (RP2OC72-04GC;  $\epsilon_{\text{Nd}} = -10.1$ ). Asian dust originates from sediments of the former Tethyan ocean recycled multiple times as implied by the uniform Nd and Pb ICs, the mean age of the K-bearing clay minerals in the sediments ( $\sim 200$  Ma) [22], and paleogeographic considerations [36]. Multiply recycled sediments are likely to contain various populations of zircon (IAV rocks and mixed populations from continental Asia) each possibly characterized by a distinct Hf IC (note that a few micrograms of zircon could make up to several percent of the total Hf content in a bulk dust sample).

On the basis of the above considerations, and

with the aim of assessing the geochemical cycle of Hf in erosion, weathering and ultimately in seawater, it was decided to process further samples with the screw-top beaker-only dissolution method. This way, most of the subordinate Hf fraction of the dust fixed in zircons (up to a few percent of the total according to our data in Table 1) is avoided, the fraction of Hf that is excluded from the hydro-geological cycle. The data presented below may therefore help to constrain the geochemistry of the ‘mobile’ Hf fraction (i.e. the ‘non-zircon component’ as termed by White et al. [1]).

#### 4. Implications

Hafnium ICs for modern dust vary between  $\epsilon_{\text{Hf}} = -4.5$  and  $+16.2$ , with corresponding  $\epsilon_{\text{Nd}}$  values between  $-10.9$  and  $+3.8$ . Discussion of the data is now done in two groups, modern samples (i.e. depositional age younger than  $\sim 0.1$  Ma) and samples from Tertiary time series.

It is known from previous work [18–20] that modern eolian dust in the North Pacific Ocean is primarily composed of a binary mixture between IAV material and Asian dust. Comparison of our results for modern dust with a model binary Hf–Nd mixing line between Asian dust and IAV rocks (crosses on Fig. 2) reveals that most samples fall on this mixing model.  $\epsilon_{\text{Hf}}$  values have a weak negative correlation with Hf concentration and have a weak positive correlation with  $^{176}\text{Lu}/^{177}\text{Hf}$  ratios (not shown). These observations confirm that the principal source components for eolian dust deposited in the North Pacific Ocean are Asian dust and IAV material. Three samples deviate significantly from this binary mixing model, however. Samples RC14-105 and V20-122 from the northwestern Pacific are significantly less radiogenic in  $\epsilon_{\text{Hf}}$ , sample RP2OC72-04GC is more radiogenic than expected from their corresponding  $\epsilon_{\text{Nd}}$  values. Calculation of a Hf–Nd isotopic correlation for all analyses ( $n=22$ ) of modern dust samples, regardless of the outliers, results in  $\epsilon_{\text{Hf}} = 0.78\epsilon_{\text{Nd}} + 5.66$  ( $R^2 = 0.79$ ; solid line in Fig. 2) that is flatter than the Hf–Nd isotopic correlations published so far for terrestrial rocks [6,7,37].

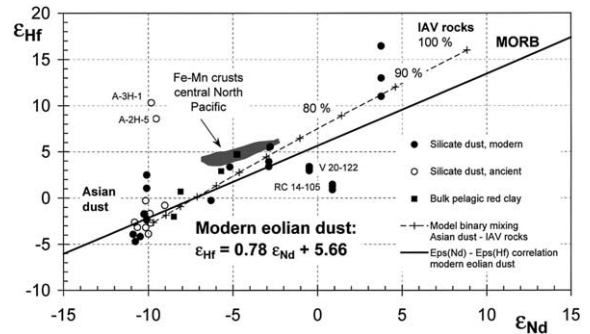


Fig. 2.  $\epsilon_{\text{Hf}}-\epsilon_{\text{Nd}}$  correlation plot for modern (filled circles) and ancient (1.5–11.1 Ma; open circles) eolian dust, and bulk pelagic red clays (filled square) shown in relation to a model binary mixing trend between IAV rocks [42,45] and the central Asian dust (this work) end-member components (end-members and 10% mixing increments marked with crosses, respectively, tied with a thin dashed line). The gray field corresponds to hydrogenous ferromanganese crusts and nodules from the North Pacific deep ocean. The correlation (thick solid line) for modern dust samples is flatter than all terrestrial rock correlations defined so far, it approaches that defined for ferromanganese crusts and nodules [16]. See text for discussion.

Preliminary Hf isotopic time series of Asian dust deposited during the past 11 Myr at two different locations, the composite Site 885/886 and GPC3, conform well to the data obtained for modern samples. Exceptions are two samples from Site 885/886 (A-2H-5 and A-3H-1; Fig. 2), the Hf ICs of which are far too radiogenic for their corresponding  $\epsilon_{\text{Nd}}$  and Pb [22,26] isotope values. This bimodal distribution in  $\epsilon_{\text{Hf}}$  may point to the presence of two source contributions that cannot be distinguished on the basis of Nd and Pb isotopes alone. The presence of a source component of continental dust with such unusual Hf–Nd isotopic signatures itself is intriguing. Moreover, closer inspection of the Hf IC of the Asian dust end-member component ( $-10.8 < \epsilon_{\text{Nd}} < -9.0$  and  $-4.7 < \epsilon_{\text{Hf}} < +2.5$ ) reveals a variability in  $\epsilon_{\text{Hf}}$  (Fig. 3) that exceeds that predicted on the basis of the Hf–Nd isotope correlations shown in Fig. 2.

Source rocks for Asian dust are dominated by Mesozoic Tethyan sediments that underwent diagenesis and/or cooling at  $\sim 200$  Ma (as detailed in [22]). During diagenesis, equilibration of radiogenic isotope systems occurred between continen-

tal detrital material and a hydrogenetic and/or a hydrothermal source component, and this mixture was then incorporated as initial isotopic signature into diagenetically grown minerals such as the abundant illite [25,30]. It is conceivable that a radiogenic contribution of Hf originating from MOR activity (that is not paralleled by a Nd or Pb contribution) might account for the apparent excess of radiogenic Hf for some of the Asian dust samples. Alternatively, this may be a mass-balance problem; hydrogenetic deposits are more strongly enriched in Hf compared to Nd or Pb [2], and an easily soluble contribution of radiogenic Hf from hydrogenetic deposits during diagenetic re-equilibration of the sedimentary pile could be responsible. Finally, it is not known how efficiently Hf, Nd and Pb redistribute during diagenesis; there could be a process that fractionates Hf from Nd and Pb. Whatever the reasons, the observation remains that Asian dust is more radiogenic and more variable in  $\epsilon_{\text{Hf}}$  than expected from its Nd IC. Most  $\epsilon_{\text{Hf}}$  values cluster between  $-0.3$  and  $-4.7$  (hence we chose as best estimate  $\epsilon_{\text{Hf}} = -2.6$  for the Asian dust end-member component to calculate the binary mixing trend shown in Fig. 2). For the same samples,  $^{176}\text{Lu}/^{177}\text{Hf}$  ratios are uniform between 0.009 and

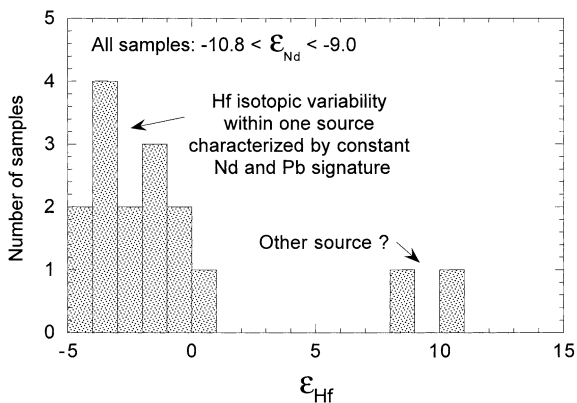


Fig. 3. Distribution of  $\epsilon_{\text{Hf}}$  values of pure central Asian dust from the central North Pacific province, including the past 11 Myr of the time series 885/886 and GPC3 [22,26]. Bimodal Hf isotopic variability is demonstrated for multiply recycled sediments characterized by uniform Nd and Pb ICs [18,19,22,26,44]. How common such radiogenic Hf signatures are for unradiogenic Nd ('other source') remains uncertain to date.

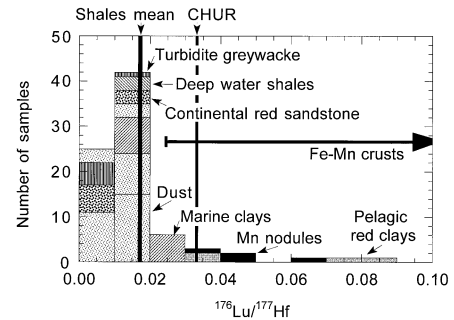


Fig. 4. Lu/Hf ratios expressed as  $^{176}\text{Lu}/^{177}\text{Hf}$  for terrestrial sediment types (this work and [1,7,8]) and CHUR [34] show that central Asian dust closely corresponds to shales. Clastic sediments typically show sub-chondritic, sediments containing a hydrogenetic component tend to have super-chondritic  $^{176}\text{Lu}/^{177}\text{Hf}$  ratios.

0.014, hence tend to be lower than those of the Pacific margin province, and do not correlate with  $\epsilon_{\text{Hf}}$  values. Therefore, radiogenic ingrowth of  $^{176}\text{Hf}$  since the dust source became a closed system for Lu–Hf cannot account for the observed variability in  $\epsilon_{\text{Hf}}$ .

Comparison of the few bulk central North Pacific sediment data (pelagic red clays) from the literature [1,2,8] with eolian dust from Asia suggests that modern bulk deep sea sediments are indistinguishable from the dust data in the  $\epsilon_{\text{Hf}}-\epsilon_{\text{Nd}}$  array and plot between the Pacific seawater as inferred from ferromanganese crusts and Asian dust end-member components (Fig. 2). This provides confirmation that eolian dust supplies a major component of the Hf–Nd inventory of central North Pacific deep sea sediments.

Abundances of Lu and Hf of modern dust vary between 0.34 and 0.42, and 3.4 and 6.5 ppm, respectively, and the corresponding  $^{176}\text{Lu}/^{177}\text{Hf}$  ratios are sub-chondritic between 0.011 and 0.016 (Fig. 4). This compares well with the mean values for shales ([Lu] = 0.59 ppm, [Hf] = 4 ppm,  $^{176}\text{Lu}/^{177}\text{Hf}$  = 0.016 [8]). Coarse-grained detrital sediments tend to have lower while hydrogenetic sediments have higher Lu/Hf ratios than dust. This may be the combined result of a depletion of zircon in clay-rich sediments relative to immature sandstones (the 'zircon effect', [1,8]), and it is consistent with the observed increase of the REE/Hf ratio with increasing degree of chemical weather-



ing in sediments of the past 1.9 Gyr [8]. This observation points to an increase of the  $^{176}\text{Lu}/^{177}\text{Hf}$  ratios with progressive maturing of the dust source, suggesting incongruent chemical weathering as a possible process responsible for the fractionation of Lu from Hf. Elemental fractionation to such an extent is not observed for the Sm/Nd system (e.g. [9]). As a consequence, multiple recycling episodes of sediments with a hydrogenetic component favor growth of authigenic or diagenetic minerals which may incorporate an initial Hf IC that is more radiogenic than that expected on the basis of the corresponding Nd IC (by analogy with what would be expected for Neogene bulk pelagic sediments of the central North Pacific Ocean). This feature will be enhanced for sediments that had enough time to evolve to more radiogenic Hf (several tens of millions of years) before isotopic resetting occurred in response to sedimentary reworking or diagenesis. Eolian dust from central Asia may be an excellent example for such a source component. Asian dust is derived from sediments of the paleo-Tethys, and these may well contain a significant hydrogenetic or hydrothermal component that is more radiogenic in Hf isotopes than detrital continental material. During diagenesis, this radiogenic component was fixed by illite growth. Therefore, silicate sediments in the Asian source terrain may have Hf IC that is variable and more radiogenic than expected from its Nd isotopic signature.

It is evident from ferromanganese crusts that fairly uniform yet radiogenic Hf has dominated central Pacific seawater for the past 20 Myr. Modern Pacific [3,4] and Indian [38] ferromanganese crusts fall on the radiogenic end of a trend of roughly  $\epsilon_{\text{Hf}} = 0.5\epsilon_{\text{Nd}} + 7.5$  described by ferromanganese nodules from the Atlantic and Pacific Oceans [16,38]. This suggests that the radiogenic Hf in the Pacific Ocean is not an exception but rather that radiogenic Hf is a global feature of seawater. For the source of this radiogenic Hf three scenarios appear plausible. (1) The sources of Nd and Hf in seawater are decoupled, e.g. much of the Nd originates from a dissolved continental ‘basement’ component while Hf is dominated by chemical weathering of IAV rocks or from MOR hydrothermal activity. (2) The sources

of seawater Nd and Hf are not decoupled. In this case, the source would be characterized by a Hf IC that is more radiogenic than that predicted on the basis of its corresponding Nd signature. (3) Incongruent chemical weathering of sources uniform with respect to their Hf–Nd isotope systematics could leave behind unradiogenic Hf bound in weathering-resistant zircons (the ‘non-zircon component’ of White et al. [1]), unless such zircon is made available for chemical attack through mechanical erosion, e.g. during glaciations of large cratonic blocks [39].

Assessing the relative likelihood of these three scenarios is strongly hampered by the lack of knowledge of input fluxes from continents to oceans. It may well be that the dominance of radiogenic Hf in seawater may result from a very low flux of continental Hf rather than a particularly high flux from IAV rocks [1]. Alternatively, a hitherto unknown source component characterized by radiogenic Hf for its corresponding Nd IC might be important. It may be the class of (multiply recycled) mature sediments such as Asian dust. We speculate that such a radiogenic crustal component may play a key role in rendering central North Pacific seawater Hf as radiogenic as observed, in addition to incongruent chemical weathering of crustal rocks. If ridge vents contributed a significant proportion of radiogenic Hf to seawater, the similarities between dust and nodule/crust data would be a coincidence (Fig. 2).

The Pliocene period encompasses an order of magnitude increase in dust flux to the North Pacific Ocean at 3.6 Ma (e.g. [23]), hence allows us to test the hypothesis that dust-bound Hf consists an important source for deep water Hf in the Pacific. The three time series of Pacific seawater Hf signatures are inconclusive with respect to the Hf isotopic evolution of Pacific deep water since the Pliocene. One crust, CD29-2 [3], has remained essentially constant across this time interval, while the two crusts, D11-1 [3] and VA13-2 [4], record a decrease in  $\epsilon_{\text{Hf}}$  of 1.3 and 2.3 units, respectively. If this decrease in  $\epsilon_{\text{Hf}}$  indeed results from the increase in dust flux to the central Pacific Ocean, it is difficult to explain why such an increase is not observed for crust CD29-2. Nevertheless, we favor

the interpretation that dust-bound Hf has significantly affected North Pacific seawater starting circa 3.5 Ma. Clearly, the conclusion that dust-bound Hf may have been significant as a source for seawater Hf (this work and [4]) and seawater Nd [26] only holds for situations like the past few million years in the central North Pacific for which the dust flux has been extremely high. Sources and input fluxes vary widely for the various oceans, hence the mass balance between input fluxes will be different and ultimately govern the importance of a dust-bound contribution to seawater Hf and Nd. For example, dust-bound Hf (and Nd [26]) is likely to have had little, if any, effect on the seawater budget of the North Pacific prior to the Pliocene. This contrasts with the conclusion of David et al. [4] who argued that eolian supply of Hf to the Pacific Ocean has been a long-term important feature. It is likely that the continental source components that have been brought to the Pacific have changed significantly through time – from a predominantly riverine input to a combined riverine–eolian input since the middle Pliocene. Such a change in transport mechanism of Hf to the Pacific Ocean would be consistent with the observation [4] that the data of the Hf isotopic time series plot along the present-day array for Fe–Mn crusts and Mn nodules [16], and with the evolution of Asian paleoclimate [36].

It is interesting to note that the  $\epsilon_{\text{Hf}}-\epsilon_{\text{Nd}}$  correlation for IAV rocks is also shallower and shifted towards more radiogenic  $\epsilon_{\text{Hf}}$  values when compared to the MOR basalt correlation [7]. Because IAV rocks are considered by some to be a significant source for seawater Pb and (to a lesser extent) Nd [40,41] it is likely that weathering of IAV material may also contribute a significant fraction of the radiogenic Hf component observed in Pacific deep water as suggested by White and Patchett [42].

## 5. Conclusions

Lu–Hf isotopic data have been presented for the eolian inorganic silicate dust fraction extracted from bulk pelagic sediments from the North Pacific Ocean deposited during the Terti-

ary. Hafnium signatures for the dust are roughly compatible with the binary source component mixing model between IAV material and continental dust from central Asia as derived from Nd and Pb isotopes and bulk dust chemistry. A first order observation is, however, that the Hf IC of Asian dust is variable and more radiogenic than expected on the basis of its corresponding uniform Nd isotopic signature.

The  $\epsilon_{\text{Hf}}$  values of modern dust samples correlate roughly with the corresponding  $\epsilon_{\text{Nd}}$  values ( $\epsilon_{\text{Hf}} = 0.78\epsilon_{\text{Nd}} + 5.66$ ), and this correlation is flatter than correlations for terrestrial reservoirs documented up to date except for ferromanganese crusts and nodules. It is proposed that the characteristics of the central Asian dust source account for this. Source rocks for this dust are Mesozoic Tethyan sediments that underwent diagenesis at  $\sim 200$  Ma [22]. During diagenesis, growth of illite (the dominant mineral in the dust) incorporated Hf representing a mixture of detrital and possibly hydrothermal contributions from the Tethyan Ocean, rendering the initial Hf IC of this material more variable and more radiogenic than if it originated from continental debris alone. Moreover, Lu/Hf ratios tend to increase with progressive chemical weathering of sediments, which may in turn promote accumulation of radiogenic Hf ingrowth in mature sediments before isotopic resetting during growth of authigenic or diagenetic minerals occurs. The above processes would have negligible effect on the Sm–Nd isotopic system. Ancient marine sediments may thus provide a class of rocks that is characterized by more radiogenic Hf for the corresponding Nd signature.

The data presented here suggest that a radiogenic source contribution from Asian dust could have been important for Pacific seawater Hf. If seawater Hf chiefly originated from MOR hydrothermal venting, the similarity of the data for eolian dust, pelagic red clays and ferromanganese crusts and nodules would be a coincidence. Rather, the major source components for Hf in Pacific seawater appear to be weathering of young IAV rocks and mature sediment contributions. The Hf IC of erosional fluxes from continents to the oceans cannot be estimated from linear  $\epsilon_{\text{Hf}}-\epsilon_{\text{Nd}}$  relationships [1], due to the fixation of an

important, unradiogenic and variable fraction of Hf in zircons. It is concluded that the fraction of Hf that is mobile in the erosional cycle has variable and quite radiogenic ICs that may eventually reach the oceans (see also [1]). Direct measurements of the IC and flux of river-dissolved Hf to the oceans and the ocean water ICs, respectively, are key to a more reliable constraint on the significance of Hf isotopic variability in seawater through time. This in turn should provide better constraints on the reliability of Hf isotopic time series as a monitor for past change in erosion.

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### References

- [1] W.M. White, J. Patchett, D. Benothman, Hf isotope ratios of marine-sediments and Mn nodules – evidence for a mantle source of Hf in seawater, *Earth Planet. Sci. Lett.* 79 (1986) 46–54.
- [2] L.V. Godfrey, D.-C. Lee, W.F. Sangrey, A.N. Halliday, V.J.M. Salters, J.R. Hein, W.M. White, The Hf isotopic composition of ferromanganese nodules and crusts and hydrothermal manganese deposits: Implications for seawater Hf, *Earth Planet. Sci. Lett.* 151 (1997) 91–105.
- [3] D.-C. Lee, A.N. Halliday, J.R. Hein, K.W. Burton, J.N. Christensen, D. Gunther, Hafnium isotope stratigraphy of ferromanganese crusts, *Science* 285 (1999) 1052–1054.
- [4] K. David, M. Frank, R.K. O’Nions, N.S. Belshaw, J.W. Arden, The Hf isotope composition of global seawater and the evolution of Hf isotopes in the deep Pacific Ocean from Fe–Mn crusts, *Chem. Geol.* 178 (2001) 23–42.
- [5] W.S. Broecker, T.-H. Peng, *Tracers in the Sea*, Eldigio Press, Columbia University, Palisades, NY, 1982.
- [6] P.J. Patchett, Importance of the Lu–Hf isotopic system in studies of planetary chronology and chemical evolution, *Geochim. Cosmochim. Acta* 47 (1983) 81–91.
- [7] J.D. Vervoort, P.J. Patchett, J. Blichert-Toft, F. Albarede, Relationships between Lu–Hf and Sm–Nd isotopic systems in the global sedimentary system, *Earth Planet. Sci. Lett.* 168 (1999) 79–99.
- [8] P.J. Patchett, W.M. White, H. Feldmann, S. Kielinczuk, A.W. Hofmann, Hafnium rare-earth element fractionation in the sedimentary system and crustal recycling into the Earths mantle, *Earth Planet. Sci. Lett.* 69 (1984) 365–378.
- [9] S.L. Goldstein, R.K. O’Nions, Nd and Sr isotopic relationships in pelagic clays and ferromanganese deposits, *Nature* 292 (1981) 324–327.
- [10] R.M. Owen, A.M. Olivarez, Geochemistry of rare earth elements in Pacific hydrothermal sediments, *Mar. Chem.* 25 (1988) 183–196.
- [11] A.N. Halliday, J.P. Davidson, P. Holden, R. Owen, A.M. Olivarez, Metalliferous sediments and the scavenging residence time of Nd near hydrothermal vents, *Geophys. Res. Lett.* 19 (1992) 761–764.
- [12] T. Pettke, A.N. Halliday, D.C. Lee, D.K. Rea, Extreme variability in Hf isotopic components of eolian dust and its implications for seawater Hf – Abstract, *Mineral. Mag.* 62A (1998) 1165–1166.
- [13] H.F. Ling, K.W. Burton, R.K. Onions, B.S. Kamber, F. vonBlanckenburg, A.J. Gibb, J.R. Hein, Evolution of Nd and Pb isotopes in Central Pacific seawater from ferromanganese crusts, *Earth Planet. Sci. Lett.* 146 (1997) 1–12.
- [14] W. Abouchami, S.L. Goldstein, S.J.G. Galer, A. Eisenhauer, A. Mangini, Secular changes of lead and neodymium in central Pacific seawater recorded by a Fe–Mn crust, *Geochim. Cosmochim. Acta* 61 (1997) 3957–3974.
- [15] J.N. Christensen, A.N. Halliday, L.V. Godfrey, J.R. Hein, D.K. Rea, Climate and ocean dynamics and the lead isotopic records in Pacific ferromanganese crusts, *Science* 277 (1997) 913–918.
- [16] F. Albarede, A. Simonetti, J.D. Vervoort, J. Blichert-Toft, W. Abouchami, A Hf–Nd isotopic correlation in ferromanganese nodules, *Geophys. Res. Lett.* 25 (1998) 3895–3898.
- [17] S.M. McLennan, S.R. Taylor, M.T. McCulloch, J.B. Maynard, Geochemical and Nd–Sr isotopic composition of deep-sea turbidites: Crustal evolution and plate tectonic associations, *Geochim. Cosmochim. Acta* 54 (1990) 2015–2050.
- [18] S. Nakai, A.N. Halliday, D.K. Rea, Provenance of Dust in the Pacific-Ocean, *Earth Planet. Sci. Lett.* 119 (1993) 143–157.
- [19] C.E. Jones, A.N. Halliday, D.K. Rea, R.M. Owen, Neodymium isotopic variations in North Pacific modern silicate sediment and the insignificance of detrital REE contributions to seawater, *Earth Planet. Sci. Lett.* 127 (1994) 55–66.
- [20] E.T. Weber, R.M. Owen, G.R. Dickens, A.N. Halliday, C.E. Jones, D.K. Rea, Quantitative resolution of eolian continental crustal material and volcanic detritus in North Pacific surface sediment, *Paleoceanography* 11 (1996) 115–127.

- [21] D.K. Rea, S.A. Hovan, Grain-size distribution and depositional processes of the mineral component of abyssal sediments – lessons from the North Pacific, *Paleoceanography* 10 (1995) 251–258.
- [22] T. Pettke, A.N. Halliday, C.M. Hall, D.K. Rea, Dust production and deposition in Asia and the north Pacific Ocean over the past 12 Myr, *Earth Planet. Sci. Lett.* 178 (2000) 397–413.
- [23] D.K. Rea, H. Snoeckx, L.H. Joseph, Late Cenozoic eolian deposition in the North Pacific: Asian drying, Tibetan uplift, and cooling of the northern hemisphere, *Paleoceanography* 13 (1998) 215–224.
- [24] H. Snoeckx, D.K. Rea, C.E. Jones, B.L. Ingram, in: D.K. Rea, I.A. Basov, D.W. Scholl, J.F. Allan (Eds.), 14. Eolian and silica deposition in the central north Pacific: results from Sites 885/886, *Proc. ODP Sci. Results* 145, 219–230, 1995.
- [25] E. Arnold, M. Leinen, J. King, in: D.K. Rea, I.A. Basov, D.W. Scholl, J.F. Allan (Eds.), 15. Paleoenvironmental variation based on the mineralogy and rock-magnetic properties of sediment from Sites 885 and 886, *Proc. ODP Sci. Results* 145, 231–245, 1995.
- [26] T. Pettke, A.N. Halliday, D.K. Rea, Cenozoic evolution of Asian climate and sources of Pacific seawater Pb and Nd derived from eolian dust of sediment core LL44-GPC3, *Paleoceanography*, in press.
- [27] F.T. Kyte, M. Leinen, G.R. Heath, L. Zhou, Cenozoic sedimentation history of the central North Pacific: Inferences from the elemental geochemistry of core LL44-GPC3, *Geochim. Cosmochim. Acta* 57 (1993) 1719–1740.
- [28] M. Leinen, The origin of paleochemical signatures in North Pacific pelagic clays: Partitioning experiments, *Geochim. Cosmochim. Acta* 51 (1987) 305–319.
- [29] T.R. Janecek, D.K. Rea, Eolian deposition in the northeast Pacific ocean: Cenozoic history of atmospheric circulation, *Geol. Soc. Am. Bull.* 94 (1983) 730–738.
- [30] B.H. Corliss, C.D. Hollister, A palaeoenvironmental model for Cenozoic sedimentation in the central North Pacific, in: R.A. Scrutton, M. Talwani (Eds.), *The Ocean Floor*, J. Wiley and Sons, 1982, pp. 277–304.
- [31] M. Leinen, G.R. Heath, Sedimentary indicators of atmospheric activity in the northern hemisphere during the Cenozoic, *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 36 (1981) 1–21.
- [32] A.N. Halliday, D.-C. Lee, J.N. Christensen, A.J. Walder, P.A. Freedman, C.E. Jones, C.M. Hall, W. Yi, D. Teagle, Recent developments in inductively coupled plasma magnetic sector multiple collector mass spectrometry, *Int. J. Mass Spectrom. Ion Proc.* 146/147 (1995) 21–33.
- [33] A.N. Halliday, D.C. Lee, J.N. Christensen, M. Rehkamper, W. Yi, X.Z. Luo, C.M. Hall, C.J. Ballentine, T. Pettke, C. Stirling, Applications of multiple collector-ICPMS to cosmochemistry, geochemistry, and paleoceanography, *Geochim. Cosmochim. Acta* 62 (1998) 919–940.
- [34] J. Blichert-Toft, F. Albarede, The Lu–Hf isotope geochemistry of chondrites and the evolution of the mantle-crust system, *Earth Planet. Sci. Lett.* 148 (1997) 243–258.
- [35] D.B. Patterson, K.A. Farley, M.D. Norman, He-4 as a tracer of continental dust: A 1.9 million year record of aeolian flux to the west equatorial Pacific Ocean, *Geochim. Cosmochim. Acta* 63 (1999) 615–625.
- [36] G. Ramstein, F. Fluteau, J. Besse, S. Jousaume, Effect of orogeny, plate motion and land sea distribution on Eurasian climate change over the past 30 million years, *Nature* 386 (1997) 788–795.
- [37] J.D. Vervoort, P.J. Patchett, F. Albarede, J. Blichert-Toft, R. Rudnick, H. Downes, Hf–Nd isotopic evolution of the lower crust, *Earth Planet. Sci. Lett.* 181 (2000) 115–129.
- [38] A.M. Piotrowski, D.C. Lee, J.N. Christensen, K.W. Burton, A.N. Halliday, J.R. Hein, D. Gunther, Changes in erosion and ocean circulation recorded in the Hf isotopic compositions of North Atlantic and Indian Ocean ferromanganese crusts, *Earth Planet. Sci. Lett.* 181 (2000) 315–325.
- [39] T. vandeFliert, M. Frank, D.-C. Lee, A.N. Halliday, Glacial weathering and the hafnium isotope composition of seawater, *Earth Planet. Sci. Lett.* 198 (2002) 167–175.
- [40] D.J. Piepgras, G.J. Wasserburg, Strontium and neodymium isotopes in hot springs on the East Pacific Rise and Guaymas Basin, *Earth Planet. Sci. Lett.* 72 (1985) 341–356.
- [41] F. vonBlanckenburg, R.K. O’Nions, J.R. Hein, Distribution and sources of pre-anthropogenic lead isotopes in deep ocean water from Fe–Mn crusts, *Geochim. Cosmochim. Acta* 60 (1996) 4957–4963.
- [42] W.M. White, J. Patchett, Hf–Nd–Sr isotopes and incompatible element abundances in island arcs – implications for magma origins and crust-mantle evolution, *Earth Planet. Sci. Lett.* 67 (1984) 167–185.
- [43] J.T. Merrill, M. Uematsu, R. Bleck, Meteorological analysis of long range transport of mineral aerosols over the North Pacific, *J. Geophys. Res.* 94 (1989) 8584–8598.
- [44] C.E. Jones, A.N. Halliday, D.K. Rea, R.M. Owen, Eolian inputs of lead to the North Pacific, *Geochim. Cosmochim. Acta* 64 (2000) 1405–1416.
- [45] V.J.M. Salters, S.R. Hart, The mantle sources of ocean ridges, islands and arcs: The Hf-isotope connection, *Earth Planet. Sci. Lett.* 104 (1991) 364–380.