

Hafnium isotopes in Arctic Ocean water

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Abstract

The first isotopic compositions of dissolved hafnium in seawater from across the Arctic Ocean are reported. Most samples from the four sub-basins of the Arctic Ocean have values within error of an average of $\epsilon_{\text{Hf}} = +0.8$. Combined Hf–Nd isotope compositions do not fall on the well-established positive correlation for mantle and crustal rocks. Instead, Arctic waters have Hf that is more radiogenic than that typically found in rocks with similar Nd isotope compositions, a feature previously found in ferromanganese crusts and waters from the Pacific Ocean. Arctic seawater samples generally fall on the lower part of the ferromanganese crust array, reflecting influences of inputs from Arctic rivers and interactions of shelf waters with underlying sediments. Arctic rivers have much higher Hf concentrations (7–30 pM) than Arctic seawater (0.36–4.2 pM). Water from the Mackenzie River has the least radiogenic Hf, with $\epsilon_{\text{Hf}} = -7.1 \pm 1.7$, and plots furthest away from the ferromanganese crust array, while waters from the Ob, Yenisey, and Lena Rivers have values that are indistinguishable from most Arctic waters. In the Amundsen, Makarov, and Canada basins, Hf concentrations are highest at the surface and lowest in the deeper waters, reflecting the influences of riverine inputs and of waters that have flowed over the extensive Siberian continental shelves and have Nd and Hf characteristics that reflect water–sediment interactions. This is in contrast to the relatively low near surface Hf concentrations reported for locations elsewhere. The Pacific water layer in the Canada Basin exhibits the highest value of $\epsilon_{\text{Hf}} = +6.8 \pm 1.8$, reflecting the Hf isotopic composition of waters entering the Arctic from the Pacific Ocean. Mixing relationships indicate that a substantial fraction of the Hf in the Mackenzie River is lost during estuarine mixing; the behaviour of Hf from other rivers is less constrained.

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1. INTRODUCTION

The isotopic compositions of hafnium and neodymium exhibit large variations in inputs to the oceans and have been widely used to document changes in oceanographic circulation patterns resulting from tectonic and climatic factors (see Frank, 2002; Goldstein and Hemming, 2003). The decay of ^{176}Lu ($t_{1/2} = 3.71 \times 10^{10}$ a) produces ^{176}Hf ,

and thus there are wide variations in $^{176}\text{Hf}/^{177}\text{Hf}$ within crustal rocks as a function of age and Lu/Hf fractionation. Analogously, the decay of ^{147}Sm to ^{143}Nd ($t_{1/2} = 1.06 \times 10^{11}$ a) produces variations in $^{143}\text{Nd}/^{144}\text{Nd}$. Fractionations in Lu/Hf and Sm/Nd are generally well-correlated in common melting and differentiation processes, so that $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios (typically reported as ϵ_{Hf} and ϵ_{Nd} , which represent parts in 10^4 deviations from the CHUR standard; see Table 1) show a strong positive correlation for most crustal and mantle-derived rocks (Fig. 1; Patchett et al., 1981; Vervoort et al., 1999). The variability in Hf isotope composition in terrestrial rocks is

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Table 1
Arctic seawater and river data.

Ocean basin profile/river location	Depth [m]	Salinity	Potential temp. (°C)	$\delta^{18}\text{O}$	Silicate (mM)	Hf (pM) ^a	$^{176}\text{Hf}/^{177}\text{Hf}$	$\epsilon_{\text{Hf}}^{\text{b,c}}$	$\epsilon_{\text{Nd}}^{\text{d,c}}$	Nd (pM) ^a	Hf/Nd
Nansen Basin, Leg II, Station 11, 4039 m 84°16.87'N 33°39.81'E 18-July-2001	8	33.98	-1.59	0.08	2.2	0.36	0.282827	2.0 ± 2.4	-10.9 ± 0.2	17.8	0.021
Nansen Basin, Leg II, Station 10, 4025 m 83°46.93'N 31°57.10'E 18-July-2001	100	34.43	-1.67	0.10	2.5	0.45	0.282691	-2.9 ± 2.7	-11.2 ± 0.2	17.0	0.026
	300	34.93	1.94	0.30	4.4	0.48	0.282720	-1.8 ± 2.4	-11.6 ± 0.2	16.1	0.030
	1000	34.91	-0.25	0.20	5.3	0.52	0.282781	0.3 ± 3.0	-10.7 ± 0.4	14.1	0.037
Amundsen Basin, Leg V, Station Drift 2, 4379 m 88°54.29'N -02°13.57'E 2-Aug-2001	8	31.45	-1.58	-3.08	3.5	2.39	0.282759	-0.5 ± 1.3	-11.0 ± 0.2	34.2	0.070
	75	33.81	-1.81	-1.20	2.5	1.00	0.282758	-0.5 ± 1.9	-8.4 ± 0.3	26.6	0.038
	300	34.87	1.45	0.20	3.8	0.49	0.282812	1.4 ± 2.4	-10.5 ± 0.3	17.3	0.028
	1000	34.89	-0.23	0.20	5.6	0.50	0.282760	-0.4 ± 2.4	-10.8 ± 0.2	16.3	0.031
Amundsen Basin, Leg V, Station Drift 8, 4386 m 88°16.75'N -04°50.32'E 16-Aug-2001	3000	34.94	-0.95	0.25	7.5	0.56	0.282765	-0.2 ± 2.4	-10.6 ± 0.2	18.2	0.031
Makarov Basin, Leg II Station Mak, 3985 m 87°54.97'N 154°22.50'E 26-July-2001	8	31.23	-1.60	-3.60	2.9	2.53	0.282769	-0.1 ± 1.3	-11.1 ± 0.2	46.0	0.052
	100	33.62	-1.71	-0.40	4.5	0.80	0.282717	-1.9 ± 0.8	-8.6 ± 0.2	31.6	0.025
	300	34.84	0.92	0.20	5.6	0.57	0.282822	1.8 ± 2.6	-10.3 ± 0.2	16.9	0.034
	1000	34.89	-0.18	0.20	5.9	0.59	0.282732	-1.4 ± 2.4	-9.9 ± 0.2	13.8	0.039
Canada Basin, Station 1, 50 m 71°37'96"N 154°56'49"W 22-Aug-2000	5	29.31	4.57							79.0	
	25	30.44	4.58	-1.75	7.1	4.17	0.282855	2.9 ± 1.3	-5.8 ± 0.2	72.7	0.057
Canada Basin, Station 2, 170 m 71°50'10"N 153°59'56"W 22-Aug-2000	5	27.46	-0.89	-2.95	3.1	0.97	0.282795	0.8 ± 1.8	-6.8 ± 0.2	42.1	0.023
	125	33.39	-1.64	-1.40	33.3	1.53	0.282865	3.3 ± 0.5	-4.8 ± 0.2	43.6	0.035
Canada Basin, Station 3, 3850 m 75°13'N 149°54'W 22-Aug-2000	5	25.90	-1.16	-3.80	2.3	0.86	-	-	-	27.7	0.033
	50	31.24	-0.074	-2.45	4.8	0.74	-	-	-	31.5	0.023
	150	32.92	-1.53	-1.55	29.0	0.84	-	-	-	29.7	0.028
	400	34.80	0.52	0.20	4.8	0.62	-	-	-	19.3	0.032
	2000	34.94	-0.41	0.25	6.5	0.59	-	-	-	15.2	0.039
	3000	34.96	-0.33	0.25	7.5	0.58	-	-	-	15.3	0.038
Canada Basin, Station 4, 3894 m 73°50'N 152°55'W 24-Aug-2000	35	30.71	-0.37	-2.65	3.3	0.81	0.282780	0.3 ± 1.8	-6.6 ± 0.2	27.8	0.029
Canada Basin, Station 5, 1200 m 73°15'N 155°06'W 26-Aug-2000	5	26.56	-0.44	-3.65	1.8	0.75	0.282793	0.8 ± 1.9	-7.7 ± 0.2	27.7	0.027
	125	32.86	-1.54	-1.75	19.9	0.92	0.282965	6.8 ± 1.8	-6.1 ± 0.2	22.6	0.040
Mackenzie River, 2003				-19.00	38.8	7.61	0.282571	-7.1 ± 1.7	-12.9 ± 0.3	111	0.069
Ob River, 2003				-15.30	54.9	30.19	0.282813	1.5 ± 1.3	-6.1 ± 0.3	2152	0.014
Yenisey River, 2003				-18.80	58.5	15.15	0.282856	3.0 ± 1.3	-5.2 ± 0.3	154	0.098
Lena River, 2003				-20.60	52.8	29.57	0.282849	2.7 ± 1.3	-14.2 ± 0.3	826	0.036

All data are for filtered waters.

^a Hf concentrations errors are 5%; those of Nd, 10%.

^b $\epsilon_{\text{Hf}} = [(^{176}\text{Hf}/^{177}\text{Hf})_{\text{sample}} - (^{176}\text{Hf}/^{177}\text{Hf})_{\text{CHUR}}] / (^{176}\text{Hf}/^{177}\text{Hf})_{\text{CHUR}} \cdot 10^4$.

^c Including external reproducibility.

^d $\epsilon_{\text{Nd}} = [(^{143}\text{Nd}/^{144}\text{Nd})_{\text{sample}} / (^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}} - 1] \cdot 10^4$; where $(^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}} = 0.512638$.

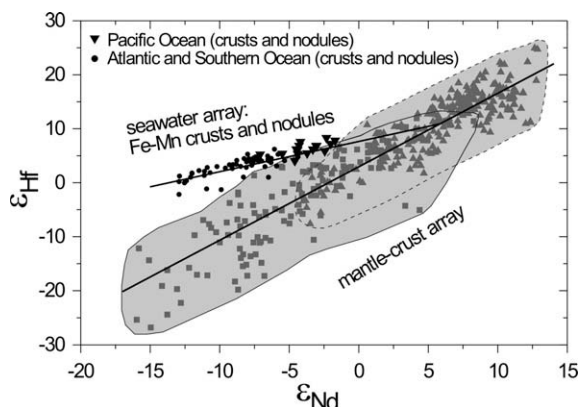


Fig. 1. Data for continental crust and mantle rocks fall on a broad positive correlation between ϵ_{Hf} and ϵ_{Nd} , reflecting correlated fractionations between Lu/Hf and Sm/Nd. Data for marine ferromanganese deposits, Fe–Mn crusts and Mn nodules, all of which are expected to reflect the compositions of overlying seawater, fall on a separate array. This suggests that marine Hf isotope signatures are not dominated by runoff of Hf with bulk crust isotope compositions, but rather are biased towards compositions that have more radiogenic Hf. (Crust and mantle data from compilation by Vervoort et al. (1999), Fe–Mn data from Albarède et al. (1998), David et al. (2001) and van der Fliert (2004b)). (From Zimmermann et al., 2009.)

twice as large as that of Nd, ranging from the most unradiogenic values of $\epsilon_{\text{Hf}} = -50$ in Archean rocks (Vervoort and Patchett, 1996), to values as high as +25 in MORB (Patchett and Tatsumoto, 1980a; Salters and Hart, 1991; Salters and White, 1998). Modern pelagic sediments exhibit ϵ_{Hf} values that lie in the range of -30 to $+4$ (Vervoort et al., 1999; van de Fliert et al., 2007). In general, there is a correlation between the age of a continental terrain and the isotopic composition of Nd it supplies to the ocean (see review by Goldstein and Hemming (2003)). In seawater, the isotopic composition of Nd varies both between and within ocean basins due to inputs of Nd derived from weathering of rocks of different ages, and these variations are maintained because the average oceanic residence time of Nd in the oceans of ~ 500 – 1000 years (Piegras and Wasserburg, 1987; Tachikawa et al., 2003; Lacan and Jeandel, 2005) is shorter than the global ocean circulation time of 1500 years (Broecker and Peng, 1982). The resulting variations between different water masses have proven useful as fingerprints for studying global circulation patterns.

In contrast to Nd, there is only a limited number of Hf seawater concentration data available (Godfrey et al., 1996; McKelvey and Oriens, 1998; Firdaus et al., 2008; Zimmermann et al., 2009). These studies showed open ocean Hf concentrations ranging from 0.3 pM in surface waters up to 1 pM at water depths of several kilometers. Due to analytical difficulties associated with measuring very small quantities of Hf, records of seawater Hf isotope compositions generally have been sought through measurements of ferromanganese (FeMn) crusts that have been shown to take up seawater Nd, and presumably Hf, during formation (White et al., 1986; Godfrey et al., 1997; Albarède

et al., 1998; Lee et al., 1999; Piotrowski et al., 2000; David et al., 2001; van de Fliert et al., 2002, 2004a). Zimmermann et al. (2009) reported the first direct measurements of the Hf isotope composition of seawater from the Pacific, which indicate that FeMn crust Hf isotope compositions do indeed reflect seawater Hf isotope compositions, which has recently been corroborated by the first Hf isotope data for Atlantic seawater (Rickli et al., 2009). Estimates of the oceanic residence time of Hf were somewhat longer than for Nd but still shorter than the global ocean circulation time (Godfrey et al., 1996; McKelvey and Oriens, 1998; White et al., 1986) whereas more recent estimates based on dissolved seawater data suggest a residence time that may even be shorter than that of Nd (Zimmermann et al., 2009; Rickli et al., 2009). This suggests that seawater Hf isotopes could be a powerful tracer for past water masses, ocean circulation, and changes in element provenance of the weathering inputs.

The ϵ_{Hf} and ϵ_{Nd} measurements from FeMn crusts and Mn nodules fall along an array that is offset from the terrestrial Hf–Nd isotope array towards higher ϵ_{Hf} for a given ϵ_{Nd} (Fig. 1; Albarède et al., 1998). This offset has been explained as a result of the so-called zircon effect (Patchett et al., 1984; White et al., 1986). Zircons concentrate Hf, and with very low Lu/Hf ratios maintain unradiogenic ϵ_{Hf} values relative to their host rocks. Preferential dissolution of more easily weathered mineral phases with higher Lu/Hf ratios results in riverine, and so ultimately seawater, Hf isotope compositions that are more radiogenic than those of the Hf source rocks (Albarède et al., 1998; Bayon et al., 2006). In contrast, there are numerous published seawater and river data for Nd, and the large variability in the Nd isotope compositions of rocks exposed in the watersheds appears to be reflected in river compositions (e.g. Goldstein et al., 1984; Goldstein and Jacobsen, 1987, 1988). Seawater Hf, like Nd, is probably dominated by riverine inputs while it has been argued that other sources of seawater Hf, such as aeolian dust and hydrothermal inputs, seem to be of minor importance (Piotrowski et al., 2000; van de Fliert et al., 2002, 2004a,b). This is supported by recent data for riverine Hf (Bayon et al., 2006). However, it has been suggested that the ocean Hf budget may indeed be affected by hydrothermal inputs (White et al., 1986; Godfrey et al., 1997; Bau and Koschinsky, 2006) contributing to elevated ϵ_{Hf} values in Fe–Mn-crusts and Mn nodules (Godfrey et al., 1997), as well as in seawater.

In this study, the first measurements of the isotopic composition of Hf in Arctic seawater are presented. Using data for samples from across the Arctic Ocean, as well as from the four largest rivers draining into the Arctic Ocean, the variations of Hf concentrations and isotopic compositions across the Arctic are documented. Along with data for Nd and O isotopes and Si concentrations, the Hf and Nd isotope signals of input waters from rivers and surrounding ocean basins are shown to be modified by estuarine and shelf–water interaction processes. The Hf concentration results were first reported in abstract form in Zimmermann et al. (2002) and the isotope data in Zimmermann et al. (2003).

2. METHODS

2.1. Sampling

Water samples were collected from across the Arctic Ocean and in vertical profiles through the water column in order to sample the various water masses. The Arctic Ocean water column is strongly stratified (see Aagaard et al., 1985; Carmack, 1990; Jones et al., 1991). In general, the uppermost 10–30 m is occupied by the Polar Mixed Layer, which has temperatures near the freezing point and low salinities. Below this surface water mass the Cold Halocline Layer extends over approximately 100 m, and is formed by the supply of river water and inflowing low salinity water through Bering Strait (Rudels et al., 1996). It is underlain by the relatively warm (>0 °C) and saline Atlantic Layer down to a water depth of ~ 750 m (Rudels et al., 2004). Further below in the water column there is a weak thermocline of the Upper Polar Deep Water down to ~ 1700 m depth, below which a cold, more saline deep layer (Jones, 2001; Rudels et al., 2004) is found that is warmer and saltier in the Canadian Basin (CBDW) than in the Eurasian Basin (EBDW).

Locations of the sampling stations are provided in Table 1 and Fig. 2, and include all the major Arctic sub-basins. Water samples from depth profiles in the Nansen, Amundsen and Makarov Basins were collected from the Swedish icebreaker *I/B Oden* during June to August 2001 (see Björk et al., 2002); sampling is described in Andersson et al. (2008). The profiles from the Amundsen and Nansen Basins are each composites of two nearby casts. Water samples from the Canada Basin were collected from the *USCG Polar Star* during August 2000, according to the sampling procedures described by Trimble et al. (2004). Stations 1 and 2 are located on the shelf, while Station 5 is on the slope of the Canadian Basin. Station 4 is located just off the shelf, while Station 3 is located further away from the slope in the deep basin.

In brief, samples were collected using Niskin bottles (Canada Basin) and Go-Flo samplers (other samples) mounted on a rosette equipped with a conductivity-temperature-depth (CTD) instrument. In the Amundsen Basin, waters from a depth of 8 m were also periodically collected from a purpose-built continuous inflow port beneath the *I/B Oden* that fed directly into the water-processing laboratory. Upon collection, water was transferred to laboratory-cleaned polyethylene bottles. Within a few hours after collection, the samples were filtered using a peristaltic pump through pre-cleaned 142 mm diameter membrane filters of either 0.45 μm (Canada Basin samples) or 0.22 μm (other samples). The samples were acidified to $\text{pH} \leq 2$ with ultra pure HCl (Seastar[®]) and stored in acid-washed polyethylene containers. Due to the low dissolved Hf concentrations in seawater, 60 L were required per sample for the determination of Hf isotope compositions, and separate 2 L samples were used for Hf concentration measurements.

River water samples of the four major Arctic rivers (Mackenzie, Ob, Yenisey, Lena) were collected in 2003 during the sampling for the PARTNERS project (sampling details are provided in <http://ecosystems.mbl.edu/partners/>).

Samples were taken from the rivers during ice-free, high-discharge summer conditions. There was a delay of 5–15 days between recovery and filtration and acidification (to $\text{pH} \sim 2$) of the river samples, and so the possibility of minor losses of Hf due to adsorption to bottle walls or to particles before filtration and acidification cannot be definitively discounted. For the analyses of river water, 1 L was sufficient for the concentration measurements and 8 L (20 L for the Mackenzie) for the determinations of Hf isotopic compositions.

2.2. Hafnium concentration and isotope measurements

The chemical and analytical procedures used here were described by Zimmermann et al. (2009). For Hf concentration determinations, a spike enriched in ^{178}Hf was added to 2 L sample aliquots. Hafnium was preconcentrated by Fe coprecipitation using aqueous ammonia following procedures typically used to concentrate Nd, and was then separated from Fe and interfering elements using a modified version of the cation column chemistry of Patchett and Tatsumoto (1980b). Samples were measured by MC-ICPMS. Mass fractionation of Hf was monitored with an added W standard (Nist 3163) and sample-standard bracketing allowed corrections for ion counter gain. For the determination of the external precision of the measurements, five 2 L aliquots of the same 20 L bottle were separately processed and measured on the MC-ICPMS. The 1σ standard deviation of the five concentration measurements was 2.5% of the average concentration. A 5% 2σ error has therefore been assigned to all Hf concentration measurements.

For isotope measurements, Hf was separated from 20 L sample aliquots by Fe coprecipitation. For each sample, Hf from three 20 L aliquots was combined. A combination of the modified cation column by Patchett and Tatsumoto (1980b) and the 2-column chemistry described by Lee et al. (1999) was used to further separate and purify Hf. Neodymium was separated from the REE split from the cation column and purified following the method described by Cohen et al. (1988). The total procedural blank for the Hf isotopic composition was ~ 80 pg, corresponding to 1–2% of each sample, which is negligible given the limited range in natural Hf isotopic compositions and the other sources of error. Yields for the precipitation and chemical separation procedure were $\sim 80\%$. Each column separation step, as well as the coprecipitation of Hf from the seawater, resulted in a loss of $\sim 5\%$ of the sample.

Hf and Nd isotope ratios were measured on a Nu Instruments MC-ICPMS at ETH Zurich. The measured $^{176}\text{Hf}/^{177}\text{Hf}$ was corrected for instrumental mass bias to a $^{179}\text{Hf}/^{177}\text{Hf}$ ratio of 0.7325. The JMC 475 standard was measured after each sample. All $^{176}\text{Hf}/^{177}\text{Hf}$ results were normalized to 0.282160 for JMC 475 (Nowell et al., 1998). The errors for the results of $^{176}\text{Hf}/^{177}\text{Hf}$ measurements represent the 2σ standard deviation of repetitive Hf standard measurements (JMC 475) with similar concentrations to the sample solution. In those cases where the within-run error (2σ standard error of the mean) was larger than the 2σ error of the external reproducibility, this error was used. Despite the large volumes of water used, the precision

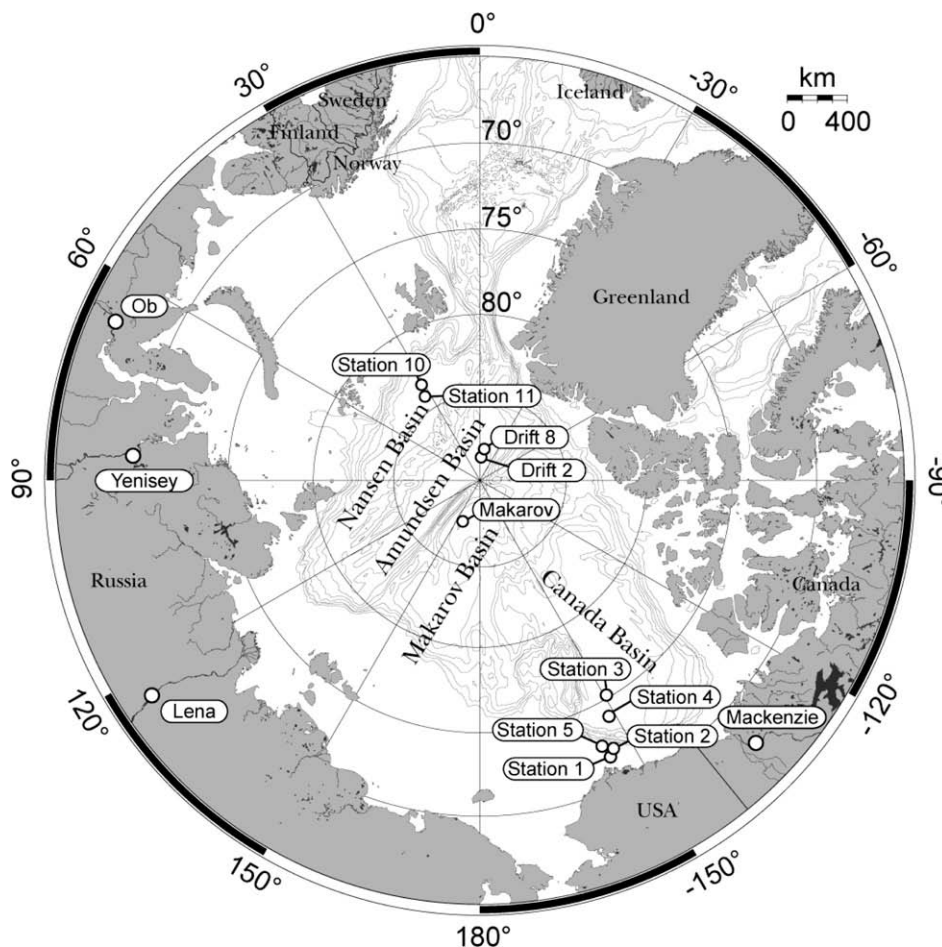


Fig. 2. The five sampling locations of the AWS 2000 cruise in the Canada Basin are shown, along with the full profiles collected during the AO-01 expedition in 2001 to the Nansen, Makarov, and Amundsen Basins. Samples were also collected from the four Arctic rivers shown. The bathymetric map is taken from the International Bathymetric Chart of the Arctic Ocean (IBCAO); <http://www.ngdc.noaa.gov/bathymetry/arctic/arctic.html>.

of the measurements was limited by the small total sample size of only 3–7 ng of Hf.

For Nd isotopic composition measurements, the instrumental mass bias was eliminated by correction to a $^{146}\text{Nd}/^{144}\text{Nd}$ ratio of 0.7219. The measured and mass bias-corrected $^{143}\text{Nd}/^{144}\text{Nd}$ was normalized to 0.511833, the averaged $^{143}\text{Nd}/^{144}\text{Nd}$ of an in-house Nd standard, which has been cross-calibrated to the commonly used La Jolla standard (van de Flierdt et al., 2004b). Due to the higher Nd concentrations compared to Hf in Arctic seawater, at least 40 ng total Nd were available for all isotopic ratio measurements, resulting in higher precision and a better external reproducibility of 0.19–0.38 ϵ units (2σ standard deviation) for repeated standard measurements during individual measuring sessions. The errors of the Nd concentration measurements via ICP-MS, based on sample-standard comparison, were <10%.

3. RESULTS

Background data for the samples, including salinity, potential temperature, O isotopes and silicate concentrations,

are provided in Table 1, with potential temperature and salinity profiles plotted in Fig. 3. The Hf concentrations, C_{Hf} , and isotopic compositions, ϵ_{Hf} , are listed in Table 1 along with data for Nd concentrations, C_{Nd} , and ϵ_{Nd} . The characteristics of Nd isotopes for these locations (though not always from the same depths) and from nearby profiles obtained during the same cruises and determined by TIMS were reported previously (Andersson et al., 2008, Porcelli et al., 2009). The Hf concentration profiles of Arctic seawater (Fig. 4) show distinct variations with depth and between basins, with a total range of 0.37–4.2 pmol/kg. The Hf isotope variations in Arctic seawater (Fig. 5) vary over the range of $\epsilon_{\text{Hf}} = -2.9$ to +6.8, but there are only limited clearly resolvable variations; the average ϵ_{Hf} of +0.76 provides a benchmark for these variations in the discussions below.

3.1. Nansen Basin

The salinity and potential temperature profiles of the Nansen Basin show a rather weakly developed Cold Halocline Layer, with lower salinity water on top of warm

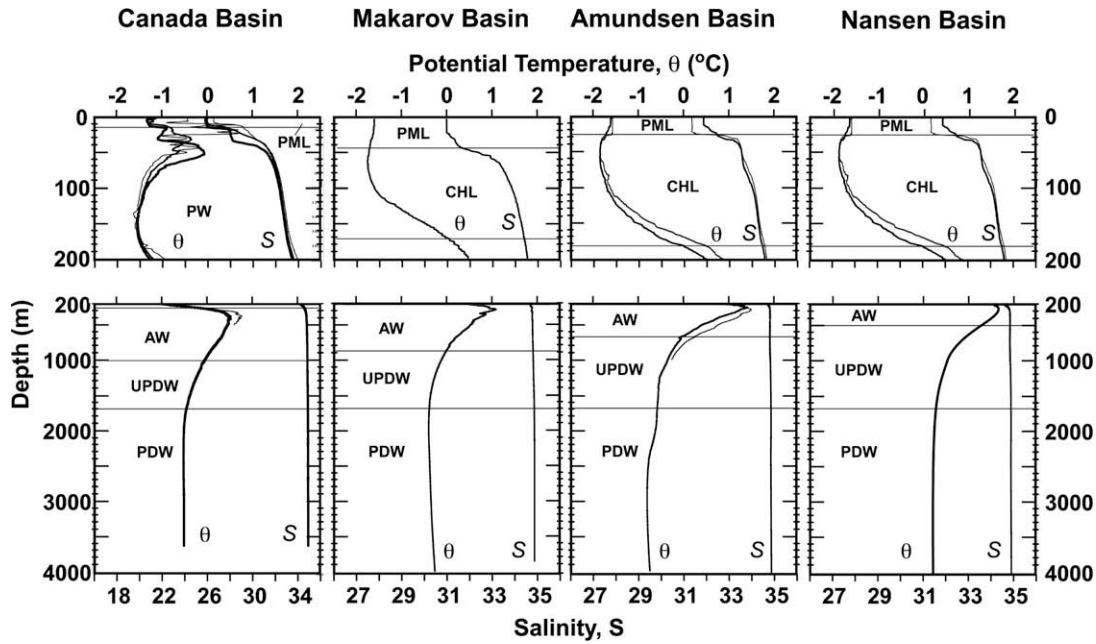


Fig. 3. The salinity and potential temperature structure for the deep profiles sampled in each basin in the upper 300 m (upper panel) and throughout the water column (lower panel) are shown here (from Andersson et al., 2008 and Porcelli et al., 2009). The lowered salinities at the surface constitute the polar mixed layer. The cold halocline layer (CHL) is clearly seen in the Eurasian basins, with relatively constant low temperatures as salinity increases with depth. In the Canada Basin, relatively warm Pacific Water intrudes at a depth of around 60 m. The relatively warm Atlantic Layer below a depth of ~140–200 m is represented by the prominent temperature maximum, and is underlain by Upper Polar Deep water to 1700 m, and the quite uniform Polar Deep Water (PDW) at greater depths. (From Andersson et al., 2008; Porcelli et al., 2009.)

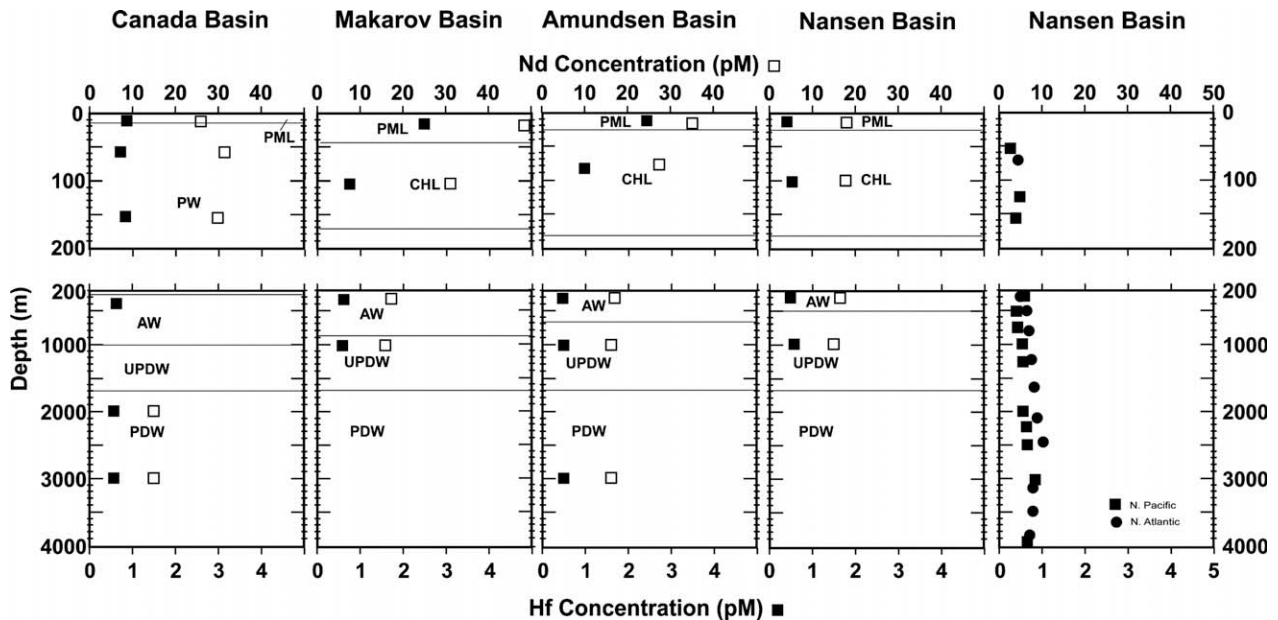


Fig. 4. Measured Hf and Nd concentration profiles in the four Arctic sub-basins, along with reported Hf concentration profiles from the N. Pacific (McKelvey and Orians, 1998) and the N. Atlantic (Godfrey et al., 1996). While the surface water of the Nansen Basin has the lowest Hf concentration in a profile that is similar to those of the Pacific and Atlantic, surface water in the Canada Basin profile (Station 3) is somewhat enriched in Hf (and greatly enriched at other Canada Basin locations; Table 1), and Hf concentrations strongly decrease with depth in the Amundsen and Makarov Basins. As noted previously, Nd concentrations decrease with depth in the Amundsen, Makarov, and Canada Basins (Porcelli et al., 2009), in contrast to profiles from the Nansen Basin (Andersson et al., 2008) and from outside the Arctic.

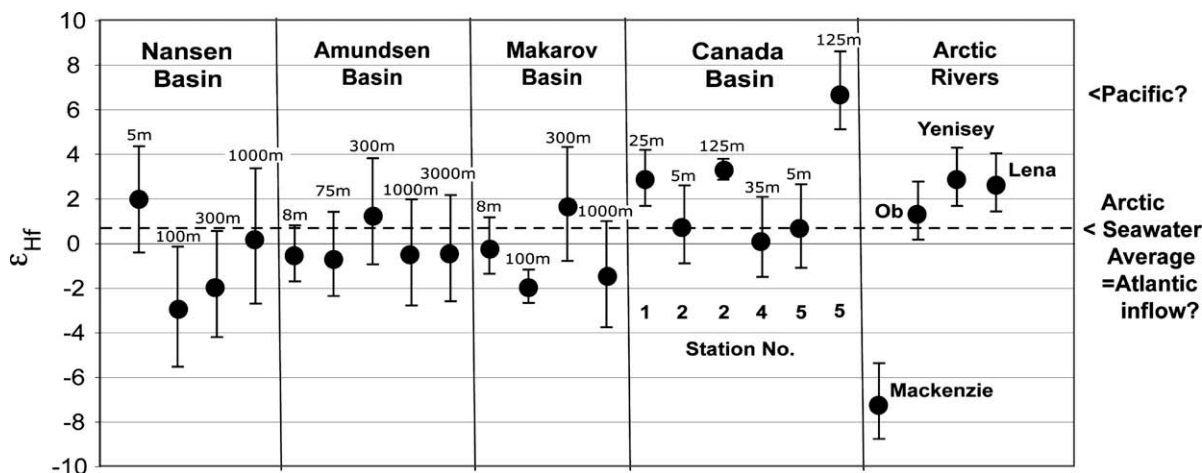


Fig. 5. Measured Hf isotope compositions for Arctic seawater. Most of the samples are within error of the Arctic seawater average of 0.76. Exceptions include lower values found at 100 m in the Nansen and Makarov Basins, and higher values in the Canada Basin. River values that are somewhat higher are found in the Siberian rivers, while the Mackenzie River exhibits the lowest ϵ_{Hf} value. For reference, the value for the Pacific inflow, estimated from measurements in the Pacific by Zimmermann et al. (2009), and for the Atlantic, estimated to be similar to that of average Arctic deep water (0.6) and so about the same as the overall average for Arctic seawater, are shown.

Atlantic Water. The Upper Polar Deep Water then extends down to about 1700 m depth, where it meets the Eurasian Basin Deep Water (Fig. 3).

Concentrations of Hf in the Nansen Basin are in the range 0.36–0.52 pM and increase monotonically with depth, in a pattern similar to that observed in the N. Pacific (McKelvey and Oriens, 1998) and N. Atlantic (Godfrey et al., 1996). The concentration of Nd (Fig. 4) is highest in the 8 m (18 pM) waters and decreases to 16 pM at 300 m. These values are in agreement with those values reported previously for the same samples (Andersson et al., 2008). The concentration of the sample from 1000 m water depth from station 10 (14 pM) is somewhat low compared to the previously published values for sample from station 11 at 1000 m (18.2 pM) and at greater depths (17.0–17.1 pM; Andersson et al., 2008). The Hf/Nd ratios range from 0.021 to 0.037 and increase with depth as Hf concentrations increase and Nd concentrations decrease.

The Hf isotope compositions of all the Nansen Basin waters (Fig. 5) are within error of one another, with $\epsilon_{\text{Hf}} = -2.9 \pm 2.7$ to 0.3 ± 3.0 . The measured Nd isotope compositions fall within a narrow range of -11.6 ± 0.2 to -10.7 ± 0.4 , in accord with the range of values reported previously for this section of -11.1 ± 0.4 to -10.8 ± 0.4 (Andersson et al., 2008). In particular, values of -10.9 ± 0.2 for 8 m and -10.7 ± 0.4 for 100 m reported here are within error of -11.1 ± 0.4 reported for both of these samples measured by TIMS (Andersson et al., 2008).

3.2. Amundsen and Makarov Basins

The salinity and potential temperature profiles for the Amundsen and Makarov Basins are shown in Fig. 3. The Polar mixed layer extends to a depth of ~ 25 m, and is underlain by somewhat colder waters centred at about 50 m in the upper halocline. The underlying warmer Atlantic water is found in the depth range of ~ 170 –800 m.

In contrast to the pattern seen in the Nansen basin, as well as in the N. Pacific and N. Atlantic, it is in the surface water (8 m) of the Amundsen Basin that the highest Hf concentration of 2.4 pM Hf is found (Fig. 4). Within the halocline at 75 m, the concentration drops to 1.0 pM, and at greater depths it is substantially lower, with 0.49–0.56 pM Hf (Fig. 4). The Nd concentrations show a similar pattern, with 34 pM at 8 m, 27 pM at 75 m and 16 to 18 pM at greater depths. The resultant Hf/Nd ratios are generally in the range of 0.028–0.038, although the surface water has 0.070, reflecting the observation that Hf in surface water is proportionally more enriched relative to deep waters than is Nd. The Hf isotope compositions of all the Amundsen Basin waters are within error of one another, with $\epsilon_{\text{Hf}} = -0.5 \pm 1.3$ to 1.4 ± 2.4 . The measured Nd isotope compositions generally fall within a narrow range of $\epsilon_{\text{Nd}} = -10.5 \pm 0.3$ to -11.0 ± 0.2 , with a higher value of $\epsilon_{\text{Nd}} = -8.4 \pm 0.3$ at 75 m, in accord with the range of values reported previously for a nearby profile (Porcelli et al., 2009).

The surface water (8 m) of the Makarov Basin also has the highest Hf concentration, with 2.5 pM Hf. At 100 m, within the halocline, the concentration drops to 0.80 pM, and at greater depths is substantially lower, with 0.57–0.59 pM Hf (Fig. 4). Again, Nd concentrations show a similar pattern, with 46 pM at 8 m, 32 pM at 100 m, and 14 to 17 pM at greater depths. The data reported by Porcelli et al. (2009) of 49 pM Nd for the sample from 8 m depth and 15 pM from 1000 m are comparable. The Hf/Nd ratios are generally in the range of 0.025–0.039, although the surface water has 0.052, again indicating that the enrichment in Hf in the surface water relative to deeper waters is greater than that of Nd. The Hf isotope compositions of the Makarov Basin waters are within error of one another, with $\epsilon_{\text{Hf}} = -1.9 \pm 0.8$ to 1.8 ± 2.6 , and generally within error of the Arctic average of 0.76, except for the sample from 100 m, which appears to be marginally lower. The

measured Nd isotope compositions are more variable than in the Amundsen Basin, with the lowest value of $\epsilon_{\text{Nd}} = -11.1 \pm 0.2$ at 8 m, a higher value of $\epsilon_{\text{Nd}} = -8.6 \pm 0.2$ at 100 m, and lower values again of $\epsilon_{\text{Nd}} = -10.3 \pm 0.2$ at 300 m, and $\epsilon_{\text{Nd}} = 89.9 \pm 0.2$ at 1000 m. Porcelli et al. (2009) reported values by TIMS of $\epsilon_{\text{Nd}} = -10.7 \pm 0.4$ for the sample from 8 m and -10.5 ± 0.4 for the sample from 1000 m, within error of the values reported here by MC-ICPMS, but did not report a measurement for 100 m. Interestingly, the data suggest that the sample from 100 m has somewhat more radiogenic Nd but less radiogenic Hf than both overlying and underlying waters.

3.3. Canada Basin

The salinity and temperature structure of the Canada Basin at station 3 is shown in Fig. 3. The halocline extends to ~ 300 m, with relatively warm Pacific waters that have been modified by interaction with the shelf centred at ~ 50 m. The underlying warm Atlantic water layer is clearly marked by a prominent temperature maximum, with a peak at ~ 400 m. Deeper waters with potential temperatures less than 0°C are found below ~ 1000 m.

The Hf concentration data for the deep basin profile at Station 3 is shown in Fig. 4. The concentrations at this station fall in a limited range; the highest values were found at 5 m (0.86 pM) and 150 m (0.84 pM), with a slightly lower value in the halocline of 0.74 pM at 50 m, where warmer Pacific summer water is present. Waters of 400 m and below fall in the range 0.58–0.62 pM. Data is only available for waters within the upper 125 m at the other stations. At Stations 2 to 5, similar values of 0.75 to 0.97 pM were found at shallow depths in the Polar Mixed Layer, without any correlation with distance from shore. In the Pacific Water layer, higher values were found nearer shore in the shallowest profiles at Station 1 (4.2 pM at 25 m) and at Station 2 (1.5 pM at 125 m), while further away from the coast values similar to those found in Station 3 were found at Station 4 (with 0.81 pM at 35 m) and at Station 5 (0.92 pM at 125 m).

The Nd isotope concentrations for Station 3 follow a pattern that is similar to those found for the Amundsen and Makarov Profiles, with the highest concentrations in the upper section of the water column. The 5 m and 25 m sample from Station 1 have the highest Nd concentrations (79 and 73 pM, respectively) reported for the Arctic, and those from Station 2 also have higher concentrations (42–44 pM) than previously reported (Porcelli et al., 2009) for the Canada basin. Concentrations previously reported for Station 3 follow a similar pattern to that shown here (but did not include measurements for 150 m and 2000 m), although the value found here for 50 m (32 pM) is 19% higher. The value for Station 5, 5 m of 28 pM Nd is comparable to the value reported by Porcelli et al. (2009) of 32 pM. The Hf/Nd ratio generally varies between 0.023 and 0.039, though the sample with the highest Hf concentration from 25 m at station 1 has a value of 0.057.

The largest variations in Hf isotope compositions were found in the Canada Basin (Fig. 5). Data for three samples (Station 2, 5 m; Station 4, 35 m; Station 5, 5 m) have similar

values of $\epsilon_{\text{Hf}} = 0.3 \pm 1.8$ to 0.8 ± 1.9 , which are within error of the Arctic Ocean average of 0.76. A somewhat higher value (but still within error of the others) of 2.9 ± 1.3 was found at Station 1, 25 m, and clearly higher values were found at the same depth of 125 m in both Station 2 (3.3 ± 0.5) and Station 5 (6.6 ± 1.8). The last two samples also have amongst the highest silicate concentrations (along with Station 3, 150 m, for which there are no Hf isotope data) of 20–33 μM , compared to a range of 1.8 to 7.5 μM for the other samples, as well as the lowest potential temperatures of $< -1.5^\circ\text{C}$. Nd isotope compositions have previously been reported for Stations 3, 4, and 5 (Porcelli et al., 2009), with $\epsilon_{\text{Nd}} = -6.4 \pm 0.4$ to -11.8 ± 0.4 . The only sample that was analyzed both in that study and here was for Station 5, 5 m, where the value here of $\epsilon_{\text{Nd}} = -7.7 \pm 0.2$ is within error of the Porcelli et al. (2009) TIMS value of $\epsilon_{\text{Nd}} = -8.0 \pm 0.4$. The values found here for Station 1 and 2, of $\epsilon_{\text{Nd}} = -4.8 \pm 0.2$ to -6.8 ± 0.2 , include the highest values reported for the Arctic to date. The values for station 4 (35 m) and 5 m at station 5 are consistent with previously reported values (Porcelli et al., 2009). The deepest water at Station 5 measured here, from 125 m, has a value of $\epsilon_{\text{Nd}} = -6.1 \pm 0.2$ (corresponding to the highest measured ϵ_{Hf} value), while a deeper water sample from 400 m was earlier found to have less radiogenic Nd, with $\epsilon_{\text{Nd}} = -9.1 \pm 0.4$ (Porcelli et al., 2009).

3.4. Arctic rivers

Overall, rivers entering the Arctic have Hf concentrations that vary by a factor of 4, between 7.6 and 30 pM, and are substantially higher than seawater. The Nd concentrations are also substantially higher than those in Arctic seawater, with a range of Hf/Nd = 0.014–0.098. The Ob has the highest concentration of Hf of 30 pM, as well as of Nd (2200 pM), resulting in the lowest Hf/Nd ratio, which reflects the much greater enrichment of Nd than of Hf compared to the other rivers. The Lena River has a similar Hf concentration of 30 pM that is in good agreement with the value of 25 pM previously determined by Godfrey et al. (1996). The sample from the Mackenzie River has the lowest concentrations of both Hf (7.6 pM), and Nd (110 pM). The highest Hf/Nd ratio was found for the Yenisey River.

There are few other published data on dissolved riverine Hf concentrations. Godfrey et al. (1996), Picouet et al. (2002), and Gaillardet et al. (2005) generally found a range of 0.32–39 pM for a selection of rivers, with an unusually high value of 110 pM for the relatively minor Beaton River in Canada (Gaillardet et al., 2005). In particular, Godfrey et al. (1996) reported several other values for Siberian rivers; 20 pM for the Kolyma and 19 pM for the Aldan. Higher values of 60–200 pM were reported for small rivers and tributaries in Venezuela (Tosiani et al., 2004). The present values for the Ob and Lena are similar to some other major rivers, including the Rio Negro (Godfrey et al., 1996), Congo, Zaire, and Kasai (Gaillardet et al., 2005), but higher than the Solimoes and Orinoco (Godfrey et al., 1996). The rivers in the present study have Hf/Nd molar ratios that overlap the narrower range exhibited in the seawater

values (Table 1), and are substantially lower than the upper continental crust value of 0.18 (Rudnick and Gao, 2003), reflecting either the greater mobility or preferential release of Nd by chemical weathering. The relatively wide range of values is a function of the larger range in concentrations of Nd than that of Hf.

The riverine Hf isotopic ratios also cover a substantial range. The Mackenzie has the lowest value, with $\epsilon_{\text{Hf}} = -7.1 \pm 1.7$. The samples from the Siberian rivers have higher values that are indistinguishable from one another and fall in the range of 1.5 ± 1.3 to 3.0 ± 1.3 . The Mackenzie River also has a low value of $\epsilon_{\text{Nd}} = -12.9 \pm 0.3$, consistent with the considerable proportion of Canadian Shield rocks exposed in the drainage basin (Millot et al., 2003). The Lena River was also found to be dominated by Nd eroded from older terrains, with $\epsilon_{\text{Nd}} = -14.2 \pm 0.3$ and yet has a higher ϵ_{Hf} value, so that there is no clear overall correlation between Hf and Nd isotopes in the rivers.

4. DISCUSSION

4.1. Hafnium concentrations in the Arctic

The Hf concentrations in the profiles from the Amundsen, Makarov, and Canada Basins seawater generally decrease with depth. A similar feature was previously observed for Nd (Porcelli et al., 2009). This is in sharp contrast to Nd and Hf concentration measurements from the North Atlantic near Iceland and the NW Pacific (McKelvey and Orians, 1998; Zimmermann et al., 2009). Godfrey et al. (1996) generally found similar results in the Northeastern Atlantic except for in one station on the shelf with a total water depth of only 250 m. There, the highest Hf concentrations were measured in the uppermost part of the water column, with surface water concentrations of 1.9 and 2.4 pM, similar to those of Arctic surface waters. Overall, it appears that the higher Hf concentrations in the upper waters of the Arctic are due to inputs within the Arctic Basin, carried by waters that are also responsible for the salinity and temperature stratifications. This does not extend to the Nansen basin, which has both Hf and Nd (Andersson et al., 2008) profiles that decrease with depth.

High concentrations of other trace elements have been found in the upper water column of the Arctic. High concentrations of Ba in the Polar Mixed Layer have been documented across the Arctic (Falkner et al., 1994; Guay and Falkner, 1997; Taylor et al., 2003). Although Ba concentrations in the surface water can be reduced by biological activity, high surface concentrations were generated by strong riverine contributions (Guay and Falkner, 1998). The highest river water Ba concentrations were measured for the Mackenzie River and the riverine signal can be found beyond the estuary in the Beaufort Sea. Although the Eurasian rivers have lower Ba concentrations than the Mackenzie, a distinct Ba signal originating from river water can be observed across the Eurasian shelf seas as well (Taylor et al., 2003). Similarly, ^{228}Ra concentrations are elevated in surface waters from the Nansen Basin to the

Central Arctic and are associated with decreased salinities. Unlike Ba, the elevated ^{228}Ra concentrations appear to reflect intensive exchange with shelf sediments (Rutgers Van der Loeff et al., 1995, 2003; Smith et al., 2003). The highest concentrations of these metals also occur in the Polar Mixed Layer, and have been interpreted to result from large riverine inputs, but could also be the result of water–sediment interactions on the shelf (Moore, 1981). Overall, inputs from rivers as well as from shelves are important for a variety of constituents across the Arctic. The sources of Hf in shallow waters of the Arctic can be further constrained using Hf isotope systematics, as discussed below.

4.2. General Hf–Nd isotope relationships in the Arctic

The ϵ_{Nd} and ϵ_{Hf} ratios for the Arctic waters are plotted against each other in Fig. 6, and fall entirely above the broad positive correlation between ϵ_{Nd} and ϵ_{Hf} defined by crustal and mantle rocks, and so, like ferromanganese deposits, have relatively radiogenic Hf compared to rocks with similar Nd isotope ratios. Since the Arctic seawater samples generally have similar Hf isotope ratios (Fig. 5) but a range of Nd isotope compositions, together they form a broadly horizontal array. For comparison, also shown are the published data for ferromanganese crusts (from Fig. 1), which scatter around a best-fit line shown in Fig. 6. The Arctic seawater samples fall within the field of data defined by these deposits, although most of them are below the best-fit line of the ferromanganese crust array. As the data for ferromanganese crusts from the Atlantic and Pacific only represent the waters from those basins (Zimmermann et al., 2009; Rickli et al., 2009), this suggests that Arctic seawaters contain somewhat less radiogenic Hf than other locations with similar Nd isotope ratios. However, it is likely that the seawater Hf–Nd isotope correlation so far defined by ferromanganese crusts is actually more diffuse globally due to variations in the separation of Hf isotope signals during weathering, decoupling of Hf and Nd during estuarine transport, and inputs from shelf sediments. Also, it is possible that ferromanganese crust samples, which generally incorporate material from over at least 10^4 years, provide seawater records in which shorter-term variations have been masked. Therefore, firm conclusions comparing different ocean basins cannot easily be made, especially without more high precision seawater data. Nonetheless, some scatter in the data presented here is due to additional processes that are important in the Arctic, including substantial additions of river waters to shallow waters over wide areas of the Arctic, and contributions of trace elements from underlying shelf sediments (see below).

Contributions of waters from the Siberian rivers can be found across the Eurasian Basin (e.g. Anderson et al., 2004; Porcelli et al., 2009), and have ϵ_{Nd} and ϵ_{Hf} ratios that fall around the ferromanganese crust array. The Mackenzie River falls significantly below the array, and is thus closest to the mantle–crust array, suggesting that a greater proportion of unradiogenic Hf in weathering rocks is released into solution from within this watershed. This might be expected to result in a relationship between Hf isotopes and Hf/Nd ratios amongst different rivers. However, because there is

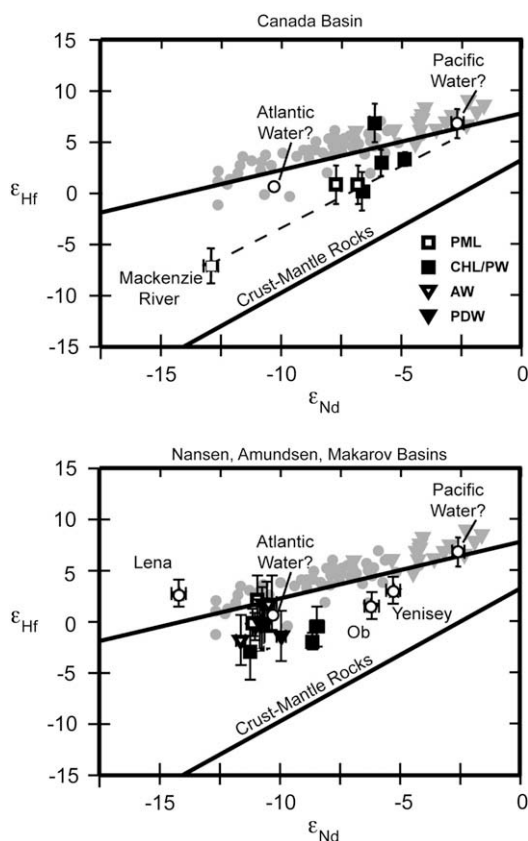


Fig. 6. The ϵ_{Hf} and ϵ_{Nd} data for the Arctic samples are shown here along with the published data for ferromanganese crusts from Fig. 1 (in grey). All the Arctic seawater samples plot above the crust-mantle correlation towards more radiogenic Hf, and around the array for ferromanganese crusts. The composition of Pacific seawater is shown (Zimmermann et al., 2009), although there are no direct measurements of Pacific water flowing into the Arctic. The composition of inflowing Atlantic water that is shown is based upon ϵ_{Nd} values from Andersson et al. (2008) and the average Hf isotope composition of Arctic deep water. In the Canada Basin (upper panel), the Mackenzie River falls substantially below the array, and the PML waters and possibly also PW samples appear to be the result of mixing between such river water and Pacific seawater. In the other Arctic Ocean basins (lower panel), the Siberian river samples fall around the ferromanganese array. Many of the seawater samples fall on the lower part of the array, especially shallower depth samples, but still generally remain within the range of published ferromanganese crust data.

a lack of correlation between displacement from the array, Hf isotope composition, Hf/Nd ratio, or Hf concentration (Table 1), no simple inferences can be made from the data here regarding the proportional release of Hf between the different watersheds. Further, since these are major rivers that drain vast watersheds of highly diverse rocks, it is not possible to determine the cause for this difference without considerably more data.

Another source of trace element constituents in Arctic waters is the continental shelves, which underlie 50% of the Arctic Ocean (Jacobsson, 2002). It has been previously inferred that interactions between waters and underlying sediments release Nd in shelf environments (Lacan and Jeandel, 2005), including the Arctic (Andersson et al.,

2008, Porcelli et al., 2009). Shelf sediments may release Nd, and presumably also Hf, during diagenesis followed by diffusion through porewaters or resuspension of sediments, but may also occur via so called boundary exchange that does not result in increased concentrations of Nd (and Hf) (see Lacan and Jeandel, 2005). This may involve constituents from within detrital material as well as trace elements scavenged from the water column by adsorption or incorporation into flocs during initial sedimentation.

The differing contributions from the various sources to each of the Arctic samples are discussed in greater detail below.

4.3. River inputs to Hafnium in the Nansen, Amundsen, and Makarov Basins

The waters in the Nansen, Amundsen, and Makarov Basins are largely derived from inflows from the Atlantic Ocean, with inputs from the Siberian rivers. Shelf-water interactions may add or remove constituents in the waters, and melting of ice can change elemental concentrations. The proportions of river water and ice melt in the freshwater component of the seawater samples can be determined from the salinity and O isotope compositions (Ostlund and Hut, 1984; Melling and Moore, 1995; Ekwurzel et al., 2001), since O in ice is only slightly isotopically fractionated from seawater and is thus distinctive from O in the Siberian river waters. These isotopic compositions are compared in Fig. 7, and all of the seawater samples fall on mixing between deeper waters of the Arctic (with $S > 34.8$ and $\delta^{18}\text{O} = 0.2$) and Siberian river waters (with $S = 0$ and $\delta^{18}\text{O} = -15.3$ to -20.6), indicating that there are no significant inputs from ice melt. In fact, the waters from 8 m depth appear to have even slightly lower $\delta^{18}\text{O}$ values than expected for mixing between The Lena/Yenisey and Arctic seawater, although the reason for this cannot be readily evaluated without further data.

Andersson et al. (2008) established that waters flowing into the Arctic from the Atlantic generally have a concentration of 15.5 pM and value of $\epsilon_{\text{Nd}} = -10.8$, and identified the deep water samples of this study from the Nansen basin as most similar to Atlantic inflow waters, based upon Nd isotopes and concentrations. Unfortunately, the Hf isotopic composition of this sample of $\epsilon_{\text{Hf}} = 2.0 \pm 2.4$ is not sufficiently precise to closely constrain the Atlantic composition. However, waters from >100 m in the Nansen, Amundsen, and Makarov Basins are isotopically indistinguishable and have an average of $\epsilon_{\text{Hf}} = 0.6$ and an average concentration of 0.55 pM. If this is the Hf isotopic composition as the average for Atlantic inflow water, then the Atlantic inflow falls close to, but slightly below, the $\epsilon_{\text{Nd}} - \epsilon_{\text{Hf}}$ ferromanganese best-fit line (Fig. 6).

While most of the other waters are within error of the average Hf isotope composition (Fig. 5), the water from the Cold Halocline Layer at 100 m depth in the Makarov Basin is lower, with $\epsilon_{\text{Hf}} = -1.9 \pm 0.8$. The 100 m sample from the Nansen Basin is also marginally lower, with $\epsilon_{\text{Hf}} = -2.9 \pm 2.7$. The ϵ_{Hf} values of these samples are also lower than the measured Siberian rivers, but an additional mixing endmember with a suitable composition on this side

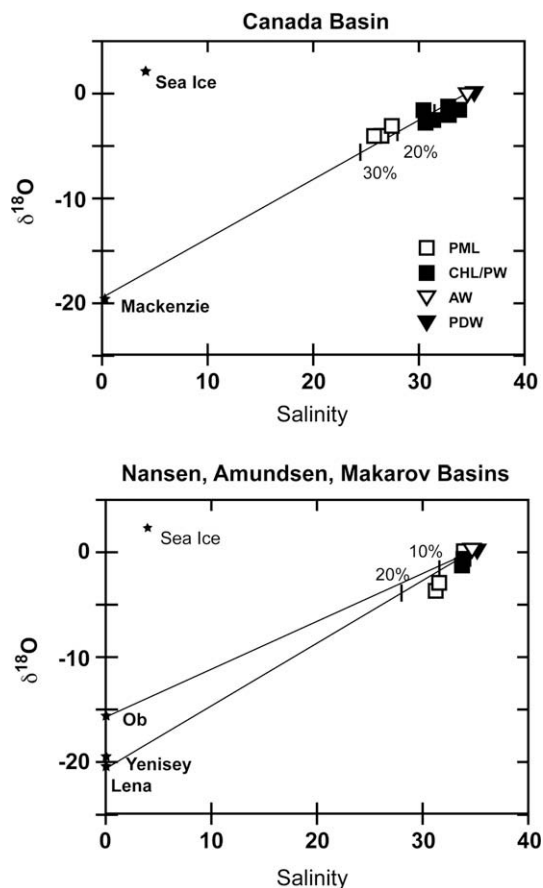


Fig. 7. The relationship between $\delta^{18}\text{O}$ and salinity indicate that melting of sea ice (Ostlund and Hut, 1984; Melling and Moore, 1995) is not a significant contributor to the freshwater component in seawater samples with reduced salinities. Rather, addition of up to $\sim 25\%$ river water in the Canada Basin, and of up to $\sim 12\%$ in the other basins, can explain the salinity and O isotope variations.

of the Arctic Ocean has not been identified. Possibilities include Hf released from underlying sediments where the waters forming the halocline passed over the shelf, or waters from other rivers that have not been measured but have lower ϵ_{Hf} values, such as observed for the Mackenzie River.

The highest Hf concentrations are found in the shallowest waters from the Amundsen and Makarov Basins (with 2.4 – 2.5 pM), which are accompanied by moderately elevated values in the underlying waters at 75 – 100 m (with 0.8 – 1.0 pM). These increased concentrations, which are associated with lowered salinities, are consistent with additions from the Siberian rivers (Fig. 8). While the Hf isotope compositions are also consistent with such mixing, the similar Hf isotope compositions in the river and seawater samples make it impossible to distinguish contributions from the different Hf sources at each location. The Siberian rivers also appear to have contributed Nd to these waters (Porcelli et al., 2009). In contrast, the shallowest water from the Nansen Basin does not show elevated Nd concentrations (Andersson et al., 2008) and has the lowest measured Hf concentration, consistent with the absence of low salinities due to river water contributions at this station.

4.4. River and shelf inputs to Hf in the Canada Basin

The contribution of Mackenzie River waters to the shallow waters in the area of the Canada Basin of this study has been clearly documented previously (e.g. Guay and Falkner, 1998; Macdonald et al., 2002) and has also been demonstrated from the same samples analyzed here using U (Andersen et al., 2006) and Nd (Porcelli et al., 2009). The proportions of river water and ice melt to the freshwater component of the Canada Basin samples are determined from the salinity and O isotope compositions in Fig. 7, where all of the samples from depths ≤ 50 m fall on mixing lines between underlying waters from the Pacific (McLaughlin et al., 1996) and isotopically distinct Mackenzie River waters, indicating that there are no significant inputs from ice melt (Ostlund and Hut, 1984; Ekwurzel et al., 2001). This had been observed previously for the same profiles by Andersen et al. (2006). The data for waters from 5 m are consistent with riverine contributions of 20–30%, while waters from 25–50 m require 10–15%. This establishes that the waters sampled at these stations are dominantly mixtures of Mackenzie River water and Pacific inflow water.

Freshwater from the Mackenzie has a distinctly low value of $\epsilon_{\text{Hf}} = -7.1 \pm 1.7$ and a Hf concentration much higher than found in the seawater samples of 7.61 pM, and thus could have a significant effect on seawater compositions. There are no direct measurements of Hf in Pacific water entering the Arctic Ocean. Zimmermann et al. (2009) reported that water from a depth of 10 m in the northwest Pacific ($50^{\circ}00'N$ $167^{\circ}00'E$ and so just south of the western margin of the Bering Sea) has $\epsilon_{\text{Hf}} = 6.7 \pm 1.4$ and $\epsilon_{\text{Nd}} = -2.7 \pm 0.5$ while water from 600 m depth in the same profile had $\epsilon_{\text{Hf}} = 5.0 \pm 1.4$ and $\epsilon_{\text{Nd}} = -3.7 \pm 0.5$. Concentrations in the top 600 m of this profile were in the range of 0.20–0.35 pM, so that average values of ~ 0.3 pM and up to $\epsilon_{\text{Hf}} = 6.7$ may be reasonable estimates for Pacific waters entering the Chukchi Sea. Overall, Pacific waters appear to have relatively high ϵ_{Nd} values, with surface waters in the N. Pacific up to $\epsilon_{\text{Nd}} \sim -2$ (Piepgras and Jacobsen, 1988; Amakawa et al., 2004; Zimmermann et al., 2009). Waters that have crossed the Chukchi Sea have somewhat lower ϵ_{Nd} values of ~ -5.5 and higher Nd concentrations due to water–shelf interactions (Dahlqvist et al., 2007; Porcelli et al., in press). There are no direct measurements of Hf in the Chukchi Sea as yet to determine if Hf seawater compositions are also modified.

Contributions to the Hf budget of Polar Mixed Layer waters are evaluated in Fig. 8. In a plot of salinities and Hf concentrations, a mixing line between Pacific seawater and Mackenzie River water predicts much higher Hf concentrations for waters with salinities like those found in PML waters. However, if 50% of the Hf in the river water was lost, presumably during estuarine mixing, then the Hf concentrations can be matched with mixtures determined by sample salinities. Therefore, substantial losses of riverine Hf seem inescapable. The Hf isotopic composition of mixtures can be seen in a plot of ϵ_{Hf} against the inverse of Hf concentration (Fig. 8). The PML water samples do not fall on the mixing line between Pacific water and Mackenzie River water (after 50% loss); rather, they have higher

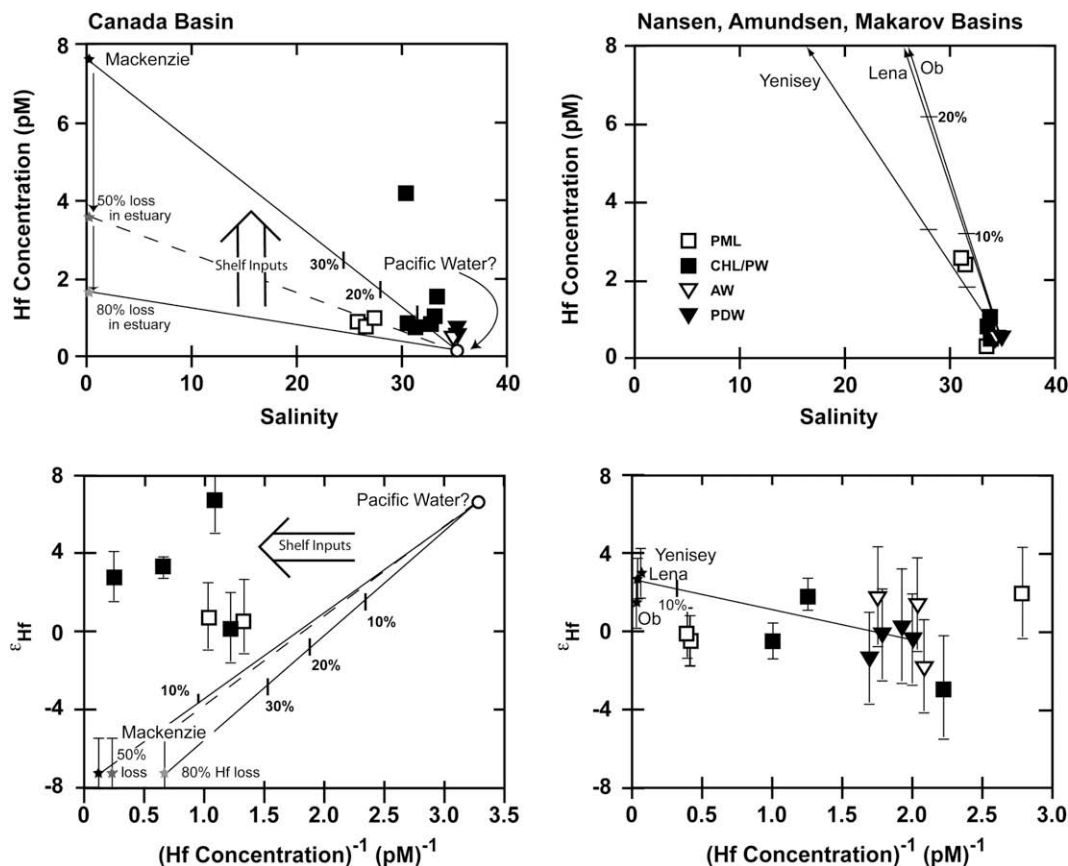


Fig. 8. Using combined Hf concentration and salinity data, and combined Hf concentration and ϵ_{Hf} data, mixing relationships can be assessed. In the Canada Basin, the salinities and Hf concentrations (top left panel) of samples from the Polar Mixed Layer fall on a mixing line between Pacific water and Mackenzie River water after 50% of the riverine Hf has been lost, presumably during estuarine mixing. However, the relationships between ϵ_{Hf} and Hf concentrations (bottom left panel) require additional Hf, likely from release from underlying shelf sediments, and so the samples must contain somewhat less Mackenzie River water, which may therefore have been depleted in Hf by e.g. 80%. Samples from the Pacific Water layer have Hf concentrations that extend above any mixing line with the Mackenzie River, and so have even greater additions of shelf-derived Hf. This is consistent with the ϵ_{Hf} data as well. Waters from the other Arctic basins have Hf concentrations and salinities (top right panel) as well as ϵ_{Hf} values (bottom right panel) that are consistent with mixing of deeper waters with Siberian river waters, without substantial loss of Hf during estuarine mixing. There is no evidence for addition of shelf-derived Hf to the waters, although such additions, or a combination of such additions and Hf depletion in the river waters through estuarine losses, cannot be discounted.

concentrations than expected. The only obvious source of Hf is release from underlying sediments of the shelf. Without any constraint on the isotopic composition of this Hf, it is not possible to calculate how much has been added, and whether it involves addition to the Pacific water component prior to mixing, addition to mixtures already containing ~20% river water, or whether an even more complicated history occurred. However, it is clear that the Hf concentration of the river component must be decreased by an even greater fraction in order to accommodate addition from a third component. As an example, if Pacific water and Mackenzie River water (after 80% is removed) is first mixed, this would result in a concentration of 0.54 pM. Measured concentrations in the PML samples are up to 1 pM, so that contributions from the shelf would then have doubled the Hf concentrations. While other component mixture proportions are possible, it is clear that the PML waters are composed of Pacific waters and Mackenzie River water that has been substantially depleted in Hf. For comparison, much of

the Nd concentration variations indicate that about 50% of the riverine Nd is also lost (Porcelli et al., 2009). If 80% of the riverine Hf is lost, then the Hf/Nd ratio of the river, of 0.069, is reduced to 0.028, which is comparable to deeper water ratios of 0.028–0.039 (Table 1), so that variations in ϵ_{Hf} and ϵ_{Nd} due to mixing between Mackenzie water and Atlantic or Pacific waters should be approximately linearly correlated.

Waters from the Pacific water layer in the Canada basin profiles, as identified by low potential temperatures and high silica concentrations, are found in station 2, 125 m (with $\epsilon_{\text{Hf}} = 3.3 \pm 0.5$ and $\epsilon_{\text{Nd}} = -4.8 \pm 0.2$), and station 5, 125 m (with $\epsilon_{\text{Hf}} = 6.8 \pm 1.8$ and $\epsilon_{\text{Nd}} = -6.1 \pm 0.2$), as well as a sample from station 4, 85 m (with $\epsilon_{\text{Nd}} = -6.4 \pm 0.4$ measured by Porcelli et al., 2009). These waters contain a much lower fraction of freshwater than the overlying Polar Mixed Layer waters (Fig. 7). In a plot of salinity against Hf concentration, these samples largely fall above any mixing line between Pacific water and depleted Mackenzie water

that can explain the Polar Mixed Layer waters; several even fall above the mixing line between Pacific water and undepleted river water, with the sample from Station 1 containing the highest seawater Hf concentration measured in this study. Clearly, Hf must be added from a third source, which is most likely the underlying sediments. This is further supported by the relationships between ϵ_{Hf} and Hf concentration (Fig. 8), where it is clear that all samples from the Pacific water layer have higher Hf concentrations than could be explained by mixing between Pacific waters and Mackenzie River water, even without any Hf depletion in the latter. The two samples with the highest concentrations, from Stations 1 and 2, come from only 25 m from the bottom of the shallowest profiles, further suggesting that underlying sediments provided Hf to these waters, possibly locally. The sample with the highest ϵ_{Hf} ratio, from Station 5 at 125 m in the Pacific Water layer, has a value as high as that found in waters collected in the Pacific Ocean, and it is possible that the sediments that have contributed Hf to this water contain Pacific Hf and might be located in the Chukchi Sea. Clearly, interactions with shelf sediments have produced significant Hf isotope variations in these waters.

As discussed above, the samples from the Canada Basin generally fall within the scattered range of values of the ferromanganese crust array (Fig. 6). However, Mackenzie River water falls substantially below the array and contributions of this water to the seawater samples is consistent with their position at the lower side of the array, particularly the PML samples. It is interesting that the Pacific Water samples that have been shown to have Hf derived dominantly from the underlying sediments (Fig. 8) fall very close to the established ferromanganese crust array. It is not clear, however, whether this is due to release of Hf that was previously scavenged from seawater, due to selective decomposition of phases with more radiogenic Hf, or bulk decomposition of sediments that have previously been sorted and so are deficient in minerals such as zircon.

4.5. Shelf contributions to Hf in Arctic deep waters

Deep waters in the Arctic Ocean clearly are derived largely from Atlantic waters, but have slightly higher salinities that require modification of some descending waters on the shelves by ice formation to produce higher salinity water (Swift et al., 1983). Further, since deep waters are warmer than shelf waters at freezing, descending waters need to mix with Atlantic layer water (Aagaard et al., 1985). During these processes, a considerable flux of constituents found in shallow waters can be carried into deep waters (e.g. Anderson et al., 1999). In the Canada basin, deep-water chemistry can be explained by inflows from both the shelf and from the Eurasian basin (Jones et al., 1995). A characteristic feature of the deeper waters of the Arctic, compared to the Atlantic inflow waters, is a general enrichment in Nd concentration. Waters from depths ≥ 1000 m have an average Nd concentration that is approximately 1.2 pM ($\sim 8\%$) greater than that of Atlantic water, most plausibly due to interaction with the shelves, possibly involving remobilization of Nd removed by adsorption

or incorporation into flocculating material in estuarine environments (Andersson et al., 2008; Porcelli et al., 2009).

These observations raise the possibility that similar deep water enrichments may also occur with Hf. However, this is more difficult to document due to the limited data available. Deep-water concentrations measured at 47–50°N in the Atlantic were 0.4–1.1 pM (Godfrey et al., 1996) and similar values of ~ 0.5 –1.0 pM were found at 55°N, 145°W in the Pacific (McKelvey and Orians, 1998). The concentrations found here at depths of ≥ 1000 m of 0.50–0.59 pM fall within these ranges; any change due to shelf interactions can only be made by direct comparison with Atlantic and Pacific waters flowing into the Arctic, for which there is no data available. As discussed above, deep waters from the Nansen Basin have Nd characteristics that are similar to Atlantic inflow water (Andersson et al., 2008). These waters have 0.48–0.52 pM Hf, while in the other basins waters found at depths ≥ 1000 m have 0.56–0.59 pM (with the exception of 1000 m water from the Amundsen Basin with 0.50 pM), suggesting an average enrichment of 0.08 pM. It is interesting to note that the average Hf and Nd enrichments correspond to addition of a component with Hf/Nd = 0.067. This is within the range of measured river values (Table 1) of 0.014–0.088. It also can be compared to the ratio of Hf and Nd removed from estuaries. In the Mackenzie River, if 80% of the Hf and 50% of the Nd is removed, then for this material to have a ratio of Hf/Nd = 0.067, it must be derived from river water with a ratio of 0.04. This value is well within the range of river compositions. This suggests that enrichments on the shelf waters can be due to release of Nd and Hf that had been removed from the water column during estuarine mixing. Data on waters from areas of known deep-water formation is required to assess this further.

Distinctive deep-water Nd isotope signatures in the Amundsen and Canada Basins have also been attributed to the addition of shelf-derived Nd (Porcelli et al., 2009). It is possible that shelf waters display substantial variations along the Siberian coast, reflecting differences in riverine sources, water–sediment interactions, or sediment compositions. In the current dataset, there are no resolvable Hf isotopic differences in the deep waters of the Arctic, and no data available on inflowing Atlantic water for comparison. However, since there is a range of isotopic compositions in river waters flowing into the Arctic, it is likely that there are substantial Hf isotopic variations along the shelves across the region.

Overall, additional data on Hf and Nd compositions of both Arctic rivers and brines contributing to Arctic deep waters, as well as on the Hf and Nd behaviour in Arctic estuaries are required in order to more clearly understand Hf and Nd enrichments in the Arctic Ocean. Higher precision isotope measurements may also allow clearer identification of specific continental Hf sources in the future.

5. CONCLUSIONS

The data presented in this study provide an overall view of the distribution of Hf concentrations and isotope com-

positions in the Arctic Ocean, and expand the global dataset of direct measurements of Hf isotope compositions of seawater started by Zimmermann et al. (2009). All Arctic seawater Hf isotope compositions presented here have more radiogenic Hf than typically found in rocks with similar Nd isotope compositions, a feature found in marine ferromanganese crusts from other ocean basins, and in Pacific and Atlantic seawater (Zimmermann et al., 2009; Rickli et al., 2009). While the Arctic seawater samples are not distinguishable from the broad array defined by Atlantic and Pacific FeMn crusts and seawater, they appear associated with somewhat less radiogenic Hf compositions. Detailed consideration of Hf isotope and Hf concentration variations clearly reflect the additions of river-derived Hf, with the Mackenzie River providing distinctively unradiogenic Hf. Furthermore, all of the rivers measured have much higher Hf concentrations than seawater, and so are responsible for substantially increasing Hf concentrations in Arctic seawaters with significant freshwater contributions. There is also clear evidence of removal of Hf from the Mackenzie, presumably within the estuary. Inputs of Hf from sediments in the shelves to the overlying waters is clearly seen in some samples, and may be responsible for increasing the Hf budget over much of the Arctic, as suggested for Nd isotopes (Porcelli et al., 2009). Future studies and higher precision analyses are required to better understand the specific mechanisms involved and to investigate how their influence changed under different oceanographic or climatic conditions.

Overall, the Hf data for the Arctic Ocean provide an additional tool for constraining the sources of fresh water and trace elements across the ocean basins and provide an understanding that is essential for interpreting the records of past seawater compositions preserved in chemical sediments.

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