Isotopic tracing (Sr, Nd, U and Hf) of continental and marine aerosols in an 18th century section of the Dye-3 ice core (Greenland)

M. Lupker [a,b,*], S.M. Aciego [a], B. Bourdon [a], J. Schwander [c], T.F. Stocker [c]

[a] Institute of Isotope Geochemistry and Mineral Resources, ETH Zurich, CH-8092 Zurich, Switzerland
[b] Centre de Recherches Pétrographiques et Géochimiques, UPR2300, CNRS, BP20, Vandoeuvre-les-Nancy, France
[c] Climate and Environmental Physics, Physics Institute, University of Bern, Switzerland

ARTICLE INFO

ABSTRACT

Determining the sources and pathways of atmospheric mineral dust and marine aerosols remains a difficult problem. In order to address this problem, the radiogenic isotopic composition of the dust and soluble ice components of Greenland ice has been determined and used as a source tracer for mineral dust and marine aerosols. Sr and Nd isotopic composition was measured, with a yearly to seasonal resolution, on both the bulk dust and soluble fractions of a section of the Dye-3 (1988) ice core from Greenland in the age range of 1786–1793 A.D. Hf isotopic composition was also measured for three of the dust samples as a complementary tracer of dust origin, the first direct measurement of Hf in paleo-atmospheric dust. Measured Nd and Sr isotopic composition of the dust corrected for carbonate contributions are compared to literature potential source area (PSA) data (<5 μm size fraction) and shows variability of the potential source area on short time scales. Half of the samples show similar Sr and Nd compositions as previous work from Greenland ice cores, indicating Asia as one potential source to the Greenland dust load with contributions from the Taklimakan, Gobi desert and the Ordos Plateau. However, the remaining samples, with less radiogenic Sr compositions, suggest another dust source mixing with the Asian dust. Hf isotopic compositions exclude volcanic aerosols as the other main mixing source and we propose the Sahara as being this additional dust source to Greenland based on the limited data set from this region. The radiogenic isotopes within the soluble fraction are found to be of marine origin with $^{87}Sr/^{86}Sr$ values and $^{234}U/^{238}U$ activity ratios close to seawater. ε_{Nd} variations are significant (>6 ε units) and are decoupled from dust composition, indicating that the Nd composition of seawater is preserved in the ice. The ε_{Nd} of the ice suggests variable mixing of aerosols from Arctic sea salts with another, more radiogenic, source during transport.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Among the different indicators of past climate in ice cores, the changes in insoluble airborne mineral particles, hereafter termed dust, records differences in atmospheric conditions through time. Mineral dust is a major component of the overall atmospheric aerosol loading with an estimated burden of 8 to 36 Tg and emissions of 1200 to 1800 Tg yr^{-1} (Zender et al., 2003). Atmospheric aerosols are established direct climatic forcing factors (IPCC AR4, 2007) both on long and short terms: by reflecting short wave radiation and by affecting cloud physical properties and lifetimes. In both cases aerosols are thought to act as a negative feedback within the climate system as increased aerosol optical thickness results in a decrease of net surface solar radiation (Haywood and Boucher, 2000) and high aerosol concentrations result in the nucleation of smaller cloud particles that reflect more solar radiation, extending cloud lifetime by decreasing precipitation efficiency (Lohmann and Feichter, 2005). By supplying nutrients to the marine environment, mineral dust also promotes oceanic productivity thereby affecting the global carbon cycle by transferring carbon from the atmospheric to the geologic reservoir such as sediments (Martin, 1991). The variability of Northern Hemisphere dust sources and transport pathways through time remains poorly known. The main dust sources i.e. potential source areas (PSAs) are situated in arid areas at tropical latitudes, e.g. the Sahara and Arabia, and at higher latitudes due to continentality and orography effects, e.g. the Northern Tibet and Inner Mongolian deserts, and have been found to emit dust for long-range transport (Uno et al., 2009).

One powerful tool for determining dust origin is the isotopic composition of the dust, and the combination of Sr and Nd ratios has been found to be an excellent "fingerprint" in most cases (Grousset and Biscaye, 2005 and references therein). Pettke et al. (2002) have also applied hafnium isotopes to dust provenance in Asia indicating that Hf is a potential dust source tracer. However, little information is available on the Hf isotopic composition PSAs around the globe.
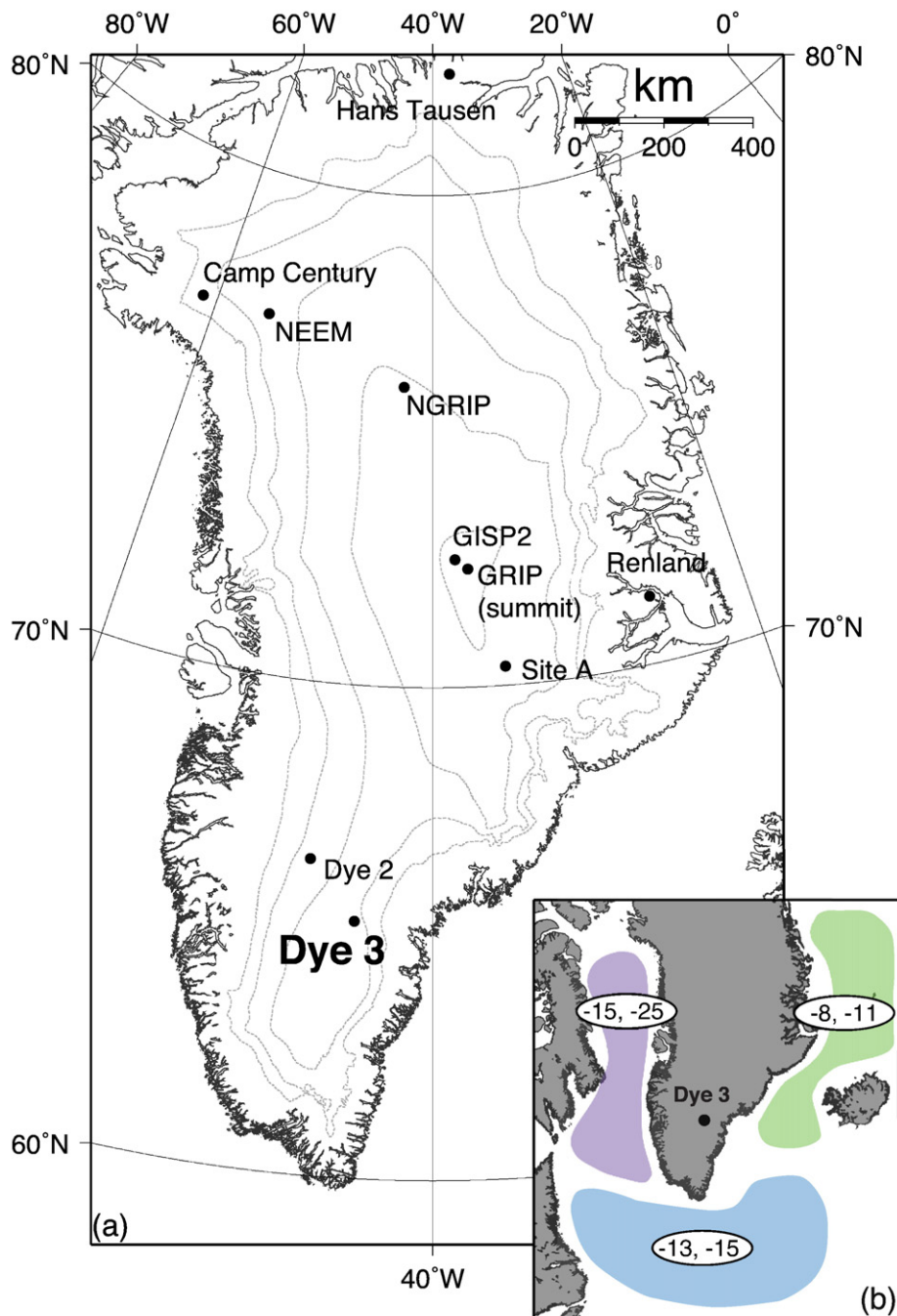
Fig. 1. Map of the Greenland ice sheet, (a) major ice drilling and sampling sites and Dye-3 ice core drilling location. (b) Range of ε_{Nd} values of the water masses around the Greenland ice sheet with West the Labrador Sea and Baffin Bay, South the Northern Atlantic and East the Danemark strait, Fram strait and Icelandic Sea. Nd data from Andersson et al. (2008); Lacan and Jeandel (2004a,c 2005a,b).

Pioneering studies on the dust origin in Greenland ice cores (Fig. 1) compared ice core dust to the long-range transportable fraction of the source area dust. Isotopic signals, and especially Sr isotopic ratios are found to be size-fraction dependent (Dasch, 1969), and this has been verified on aerosols (Kanayama et al., 2005) and Asian PSA samples (Chen et al., 2007). The constraints imposed by the long distance transport thus requires the analysis of consistent size fractions between source and sink dust, which is the smaller size fraction (<5 μm) of PSA samples that matches dust size fractions found in Greenland (Steffensen, 1997). The combination of mineralogical studies (i.e. kaolinite to chlorite ratios) and isotopic measurements (Sr, Nd and Pb) on the dust silicate fraction extracted from the GISP2 and GRIP ice cores suggested that Asia was the main source of

Greenland dust at Summit during glacial periods (Biscaye et al., 1997; Svensson et al., 2000; Burton et al., 2007). Based on similar arguments, an Asian origin for the dust was also found in Holocene ice core sections across the interior of the Greenland ice sheet (Bory et al., 2003b) and in contemporaneous snow pits from the NGRIP site (Bory et al., 2002; Bory et al., 2003a). However, due to analytical limitations, dust isotopic measurements and mineralogy were carried out on long core sections integrating several years to decades of dust deposition history. In this context, distinguishing characteristics of multiple source areas may be smoothed out by these long sampling intervals. By comparing the isotopic characteristics of extracted dust from ice cores with the fine fraction of different Asian source areas, previous workers (Svensson et al., 2000; Bory et al., 2003a,b) have suggested

that the Gobi and Taklimakan deserts are the best candidates for the dust load in Greenland.

A systematic shift towards less radiogenic $^{87}Sr/^{86}Sr$ in Greenland dust compared to PSA isotopic compositions is attributed to mixing with circum-pacific volcanic ash or aerosols that may contribute up to 25% of the dust load (Biscaye et al., 1997). High-resolution (2 month to annual) snow-pit dust samples, allowed Bory et al. (2002) and Bory et al. (2003a) to detect a seasonal variability in dust origin, which the authors attributed to a dominant Taklimakan source in spring and to an Inner Mongolian source in autumn. The seasonal to annual variation in dust source regions over Asia could be linked to changes in the arctic oscillation and the position of the westerly jet (Han et al., 2008), emphasizing the need for precise and high-resolution dust source tracing. The contribution of other PSA mineral dust in Greenland has not yet been shown. A Saharan contribution was not detected (Biscaye et al., 1997) but no fine fraction Sr and Nd isotopic data are available for this region, which accounts for nearly half of the total atmospheric dust load (Tanaka and Chiba, 2006). North America is also a potential candidate for exporting dust to Greenland. Donarummo et al. (2003) proposed that the central U.S. plains are important dust sources for Greenland during severe droughts and identified a possible dust transport event to Greenland. Palynological evidence also points toward North America as a potential source area (Rousseau et al., 2006).

The dissolved component of ice core has also received much attention within the last decade. Various dissolved major element sea salts (SS) and non-sea salts (nSS) have been recognized in polar ice and can be used for paleoclimatic reconstructions (e.g. Laj et al., 1997; Wolff et al., 2003; Fisher et al., 2007). Sea salt, one of the major contributors to the dissolved species in polar ice, is formed from bubble bursting over open seawater and sea ice covered with highly saline brine and frost flowers. This last mechanism is thought to be dominant, at least for coastal sites, which could explain the higher SS concentrations observed during winter and glacial periods (Wagenbach et al., 1998; Fisher et al., 2007) making SS in ice cores a potential proxy for sea-ice production in high latitudes (Wolff et al., 2003). The relative contribution of the different sources and origin of SS to the ice remains unknown and the use of other tracers, such as radiogenic isotopes, could improve our understanding of the recorded dissolved signal.

In this study we used high precision isotopic measurements along with ultra clean preparation procedures to investigate the feasibility of a seasonal to yearly dust record on a Greenland ice core to capture dust origin variations on small ice samples. To avoid ambiguity between various source areas and detect contributions of other aerosols, such as

volcanic ash, to the Greenland dust load we introduced Hf isotopic compositions of samples as a complementary tracer to Sr and Nd to determine dust origin. In addition to dust analysis, we also focused on the composition of the dust-free soluble fraction of the ice core to investigate whether the isotopic compositions of Sr, Nd and U of the filtered ice are tracers of marine aerosols origin and test whether they could be valuable tools for further climate reconstructions.

2. Samples and methods

Available samples used in this work are part of the 183 m shallow ice core drilled at the Dye-3 site (65″11′N, 43″49′W) in 1988 on the Greenland ice sheet (Fig. 1). The high accumulation rate of the Dye-3 site (0.55 m ice equivalent/year) is responsible for low dust concentrations in the ice core of 0.1 to 0.2 mg/kg for Holocene ice (Hammer et al., 1985). The low dust to ice ratio allows us to measure the isotopic composition of both dust and soluble fractions at high temporal resolution despite the overall low elemental concentrations.

The samples were 10.2 cm diameter ice core sections from 128 m to 132 m depth from which 1 m (130–131 m) was not available. The studied section was dated by correlating hydrogen peroxide composition to the hydrogen peroxide composition of the well-dated 1986 Dye-3 core (Sigg, 1990). The 128–132 m section covers the years 1786–1793 A.D., each sample covering on average one year of precipitation. The exact time span covered by each sample was not determined, but age–depth correlation shows that in this section, one year precipitation is recorded as 57 cm of ice (consistent with the local accumulation rate). We cannot exclude that our largest sample (130A) covering 60 cm of ice records more than a year of precipitation, but recording two full winters/summers is unlikely as this would need more than a meter of ice core.

Samples (with size ranging from 1.3 to 2.9 kg ice, see Table 1) were handled and decontaminated under HEPA laminar flow benches by removing the outer ice layers with acid cleaned PFA chisels. The core sections were subsequently melted while buffered to neutral pH with ultra-pure ammonia and EDTA and the liquid immediately filtered through two pre-cleaned 0.2 μm and 30 μm filters. The 30 μm filter was used to prevent mixing of any non-mineral aerosol with the filtered dust fraction. The dust fraction was directly dissolved off the 0.2 μm filters for elemental separation. The liquid fraction was evaporated under nitrogen flow and infrared light before being re-dissolved for subsequent chemistry. Elemental separation of Sr, Nd, Hf and U was performed by a sequential ion exchange chromatography procedure described in Aciego et al. (2009). Elemental concentrations

Table 1
Dust and ice isotopic composition and concentrations. Isotopic measurements were corrected for mass fractionation and normalized: Sr isotopic ratios were normalized to $^{88}Sr/^{86}Sr = 8.375209$; Nd isotopic ratios were normalized to $^{146}Nd/^{144}Nd = 0.7219$; U isotopic ratios were normalized to $^{238}U/^{235}U = 137.88$; Hf isotopic ratios were normalized to $^{179}Hf/^{177}Hf = 0.7325$.

Sample	Depth (m)	Size (g)		$\delta^{18}O$ (‰) V-SMOW	Sr (ppt)	Nd (ppt)	Hf (ppt)	U (ppt)	$^{87}Sr/^{86}Sr$ $\pm 2\sigma\,10^{-6}$	$^{143}Nd/^{144}Nd$ $\pm 2\sigma\,10^{-6}$	ε_{Nd} 2σ	$^{176}Hf/^{177}Hf$ $\pm 2\sigma\,10^{-6}$	ε_{Hf} 2σ	$[^{234}U/^{238}U]$ 2σ
129A	128.3–128.6	1298	Dust		n.d.	n.d.	n.d.	0.03	0.712416 (337)	0.512290 (96)	−6.8 (1.9)	n.d.	n.d.	0.92 (0.05)
	128.3–128.6	1298	Ice	−30.6	n.d.	n.d.	n.d.	0.14	0.709975 (15)	0.512163 (55)	−9.2 (1.1)	n.d.	n.d.	1.11 (0.03)
129B	128.6–129.0	2594	Dust		n.d.	n.d.	n.d.	0.04	0.717700 (42)	0.511932 (69)	−13.7 (1.4)	n.d.	n.d.	0.88 (0.05)
	128.6–129.0	2594	Ice	−27.7	n.d.	n.d.	n.d.	0.17	0.710359 (10)	0.512339 (131)	−5.8 (2.6)	n.d.	n.d.	1.12 (0.02)
130A	129.0–129.6	2886	Dust		5.9	1	0.2	0.14	0.716440 (22)	0.512186 (37)	−8.8 (0.7)	0.282867 (70)	3.4 (2.5)	0.98 (0.03)
	129.0–129.6	2886	Ice	−26.1	29	0.9	0.1	0.24	0.710114 (18)	0.512187 (55)	−8.8 (1.1)	n.d.	n.d.	1.12 (0.02)
			Ice						0.710123 (11)					
130B	129.6–130.0	2221	Dust		n.d.	n.d.	n.d.	0.03	0.717021 (118)	0.511929 (94)	−13.8 (1.8)	n.d.	n.d.	0.98 (0.05)
	129.6–130.0	2221	Ice	−28.2	n.d.	n.d.	n.d.	0.17	0.710008 (11)	0.511991 (112)	−12.6 (2.2)	n.d.	n.d.	1.1 (0.02)
132A	131.0–131.5	2854	Dust		6.3	0.9	0.3	0.16	0.720226 (25)	0.511982 (44)	−12.8 (0.9)	0.282646 (75)	−4.4 (2.7)	0.99 (0.02)
	131.0–131.5	2854	Ice	−27.6	31.7	1.2	0.1	0.23	0.710524 (19)	0.512051 (30)	−11.4 (0.6)	n.d.	n.d.	1.12 (0.01)
			Ice						0.710522 (22)					
132B	131.5–132.0	2986	Dust		1.9	0.3	0.2	0.05	0.717407 (27)	0.511818 (191)	−16 (3.7)	0.282562 (146)	−7.3 (5.2)	0.92 (0.05)
	131.5–132.0	2986	Ice	−25.4	14.3	0.5	0.1	0.11	0.710343 (17)	0.512140 (54)	−9.7 (1.1)	n.d.	n.d.	1.11 (0.03)
			Ice						0.710352 (19)					

were determined by subtracting a spiked aliquot from the samples and analyzed the exact same way.

Blank levels were measured regularly and yielded less than 54 pg (Sr), 3 pg (Nd and U) and 6 pg (Hf) for the dust fraction and 220 pg (Sr) and 20 pg (Nd and U) for the liquid fraction accounting for less than 1% of the sample size. All measurements were carried out at the IGMR, ETH Zurich. Sr and Nd isotopic composition were determined on a TRITON TIMS and the NBS987 standard was measured at $^{87}Sr/^{86}Sr = 0.71026 \pm 0.000027$ (2σ SD. $n = 20$) on 1–10 ng samples. JNdi-1 was measured at $^{143}Nd/^{144}Nd = 0.512106 \pm 0.000051$, $n = 10$, 0.5–5 ng samples. Hf and U were measured on a Nu-Instrument MC-ICPMS and JMC475 was measured at $^{176}Hf/^{177}Hf = 0.282135 \pm 0.000028$, $n = 21$ with 10–50 ppb solutions corresponding to 3 to 12 ng of Hf. Spiked uranium samples were bracketed with SRM960 for mass bias and ion counter efficiency corrections, (2σ SD) reproducibility of our external standard (AThO) was better than 1% for concentrations of 2 ppb, or 1 ng per measurement with a measured value of $^{234}U/^{238}U$ activity of 1.001 ± 0.013, $n = 91$. For a complete description of the methods, see Aciego et al. (2009).

3. Results

The Sr, Nd and Hf concentrations and isotopic composition of the Dye-3 dust and ice samples are summarized in Table 1. Six ice core sections have been analyzed for ice and dust isotopic composition and elemental concentrations have been determined on 3 sections (130A, 132A and 132B). Hf isotopic compositions have been measured on dust samples only, because the concentration in the soluble fraction was expected to be too low (0.1 ppt). Valid Hf isotopic measurements were obtained only for half of the samples (130A, 132A and 132B). The complete down-section isotopic compositions for Sr, Nd, U and O are shown in Fig. 2.

3.1. Dust fraction

The $^{87}Sr/^{86}Sr$ and ε_{Nd} composition for the dust fraction compared to PSA isotopic characteristics (Fig. 3) shows the distinct compositions of the Dye-3 dust content. Three distinct groups can be identified: (1) samples 129A and 130A are characterized by the least radiogenic Sr (0.712416, 0.71644) and most radiogenic Nd isotopic composition (-6.8, -8.8 ε_{Nd}).

(2) 129B, 130B and 132B exhibit lower ε_{Nd} values (-13.7, -13.8, -16) with intermediate Sr compositions (0.717700, 0.717021, 0.717407). (3) 132A is the most radiogenic Sr sample (0.720226) with intermediate ε_{Nd} values (-12.8). Hf isotopic compositions of dust correlates with ε_{Nd} values, generally following the zircon-free sediments array defined by Bayon et al. (2009). Concentrations of Sr (2–6 ppt), Nd (0.3–1 ppt) and Hf (0.2–0.3 ppt) do not show particular patterns: while Sr and Nd are lower for the deepest sample Hf concentrations remain constant. Sr/Nd ratios are between 5.9 and 7 whereas Nd/Hf ratios show more variability (1.5–5). The dust uranium isotopic composition varies by as much as 10% ($^{234}U/^{238}U$ activity ratios of 0.83 to 0.98). Concentrations of uranium in the dust fraction vary by a factor of ten, but Sr/U ratios only vary between 36 and 42.

3.2. Soluble fraction

The isotopic composition of the soluble fraction is characterized by small variations in $^{87}Sr/^{86}Sr$ (less than 0.0006) with an almost constant value of 0.7102205 but significant variations in ε_{Nd} (6.8 ε units) (Figs. 2, 3). Concentrations of Sr and Nd vary by a factor of two (15–30 ppt and 0.5–1.2 ppt respectively). The Sr concentrations are 5 to 7 times higher in the water than in the dust fraction whereas Nd and Hf are respectively similar and lower. Sr/Nd and Nd/Hf ratios are constant, respectively 30 and 10. Uranium isotopic compositions of the soluble fraction are almost equivalent within the measurement uncertainties: $^{234}U/^{238}U$ activity ratios vary between 1.10 and 1.12. Similarly, the concentrations of uranium in the ice are relatively constant, varying by a factor of two. While different from the dust ratios, the Sr/U ratios for the liquid fraction also show little variability between 123 and 140. Oxygen isotope data show large variations of about 5‰, the expected range for seasonal variability at high latitudes.

4. Discussion

4.1. Dust origin

The isotopic results of Sr and Nd isotopic composition in the dust extracted from the Dye-3 ice core demonstrate the variability in
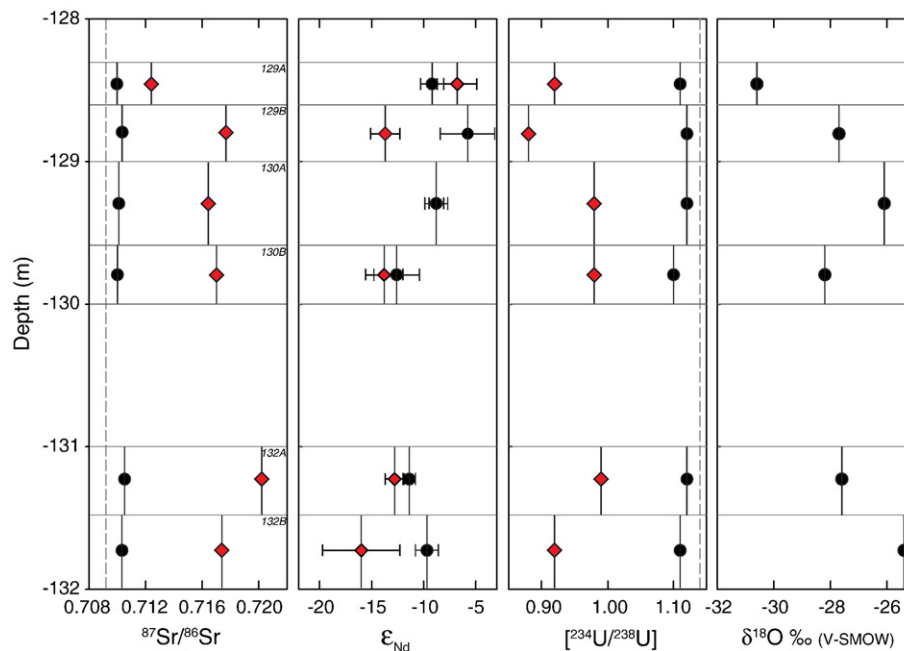

Fig. 2. Strontium, neodymium, and uranium isotopic compositions of dust (diamonds) and ice (circles) of the analyzed Dye-3 ice core shown as a depth profile of core sections, oxygen isotopic composition of ice also plotted. Vertical error bars denote depth integration of the analyzed sample. The (constant) isotopic composition of seawater is indicated for Sr and U by dashed lines. 2σ errors are smaller than symbols for all except Nd, where error bars are drawn.
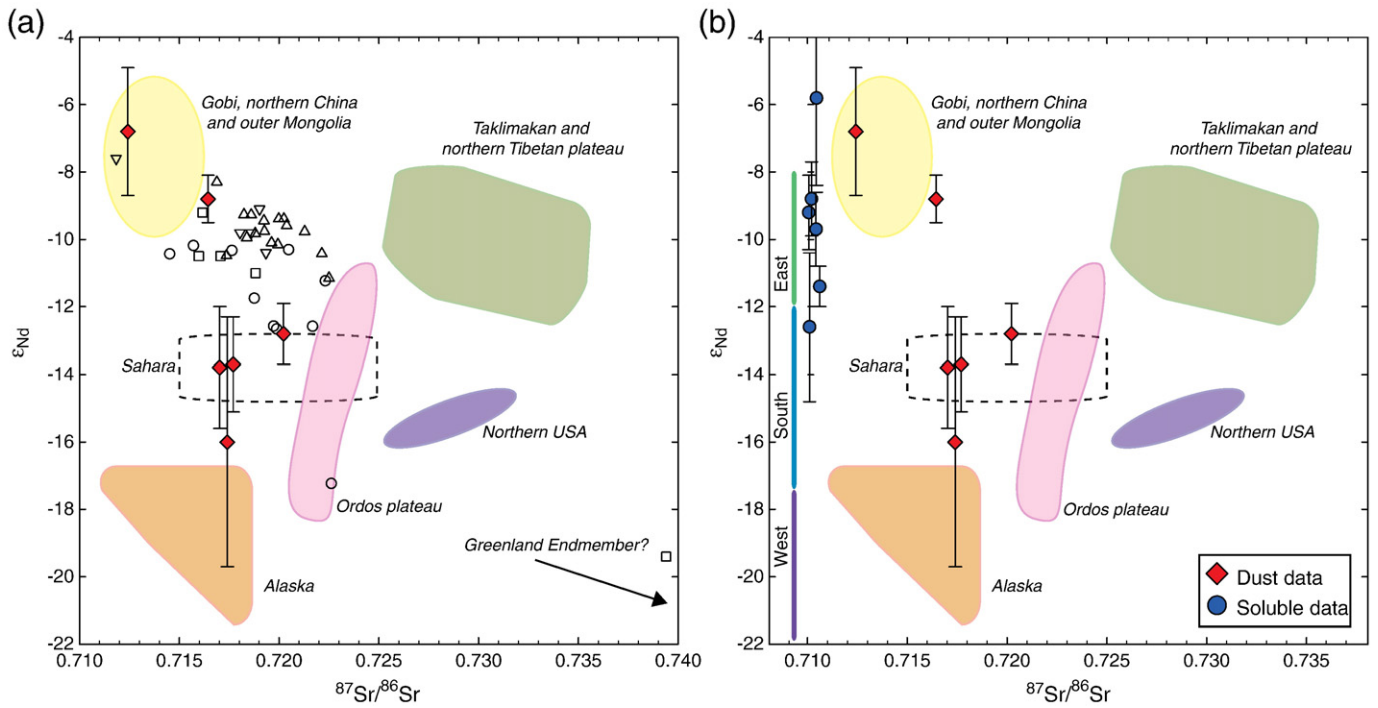
Fig. 3. (a) Strontium and neodymium isotopic composition of Dye-3 dust samples plotted (large diamonds) in context of literature derived potential source areas (PSAs) isotopic compositions (Biscaye et al., 1997; Kanayama et al., 2002; Chen et al., 2007). Also plotted (empty symbols) are the previously published ice core dust data from: *inverted triangles*: Biscaye et al., 1997 (GISP2); *triangles*: Svensson et al., 2000 (GRIP); *circles*: Bory et al., 2002 (NGRIP snow), and *squares*: Bory et al., 2003a (Hans Tausen, NGRIP, Renland, Site A, Dye-3 snow), errors for literature data are 0.5–1.0 ε_{Nd}. (b) Strontium and neodymium isotopic composition of Dye-3 ice samples (large circles) in context of literature seawater values for region around Greenland; waters off the West, South and East coasts indicated (Arsouze et al., 2007). 2σ errors for $^{87}Sr/^{86}Sr$ are smaller than the size of the symbols, individual errors in ε_{Nd} are plotted for the new data.

source area contribution as previously proposed by Bory et al. (2003a). Intrinsic variability in the isotopic composition from a single source area alone cannot explain the observed variations of the measured dust samples if the currently available PSA isotopic data is representative of the different source areas. The radiogenic isotopic data show a weak correlation with oxygen isotopes (correlation coefficients: $r_{O-Sr} = 0.59$, $r_{O-Nd} = 0.58$) with the most negative $\delta^{18}O$ (129A, $-30.6‰$ — V-SMOW) corresponding to the least radiogenic Sr (0.712416) and most radiogenic Nd ($-6.8\,\varepsilon_{Nd}$) values in dust (Fig. 4). If $\delta^{18}O$ is taken as a temperature or precipitation proxy, this suggests that for our samples, the local climatic conditions are linked to long-range dust transport and deposition. Asian sources such as the Gobi desert, northern China, Mongolia and the Ordos plateau are likely candidates for the analyzed dust. However, our dust data is systematically shifted towards less radiogenic $^{87}Sr/^{86}Sr$ values relative to these source areas. Three possibilities can be proposed for this shift: (1) the contribution of Sr of carbonates in the dust fraction, (2) mixing with some volcanic end member with low $^{87}Sr/^{86}Sr$ values or (3) mixing with other source areas.

The dust samples from different PSA used for comparison with the Greenland dust fraction have been analyzed after removal of carbonates by acetic acid leaching in order to keep only the silicate fraction. For the samples analyzed in this study leaching was not performed in order to keep the uranium signal pristine. In this case, the Sr carbonate contribution can be estimated and corrected for using the Sr/Nd ratio of the different dust components. The presence of carbonates was attested both in Asian dust (Schi et al., 2005; Sullivan et al., 2007) and Greenland ice trapped dust (Biscaye et al., 1997; Svensson et al., 2000) but in low concentrations (Laj et al., 1997). The mean Sr/Nd ratio found in leached Greenland dust samples is 3.4 (± 1) (Svensson et al. (2000) and Bory et al. (2002)). In this study the Sr/Nd ratios range between 5.9 and 7 (mean 6.4) indicating that the contribution of Sr-rich carbonates to the overall Sr budget must be taken into account.
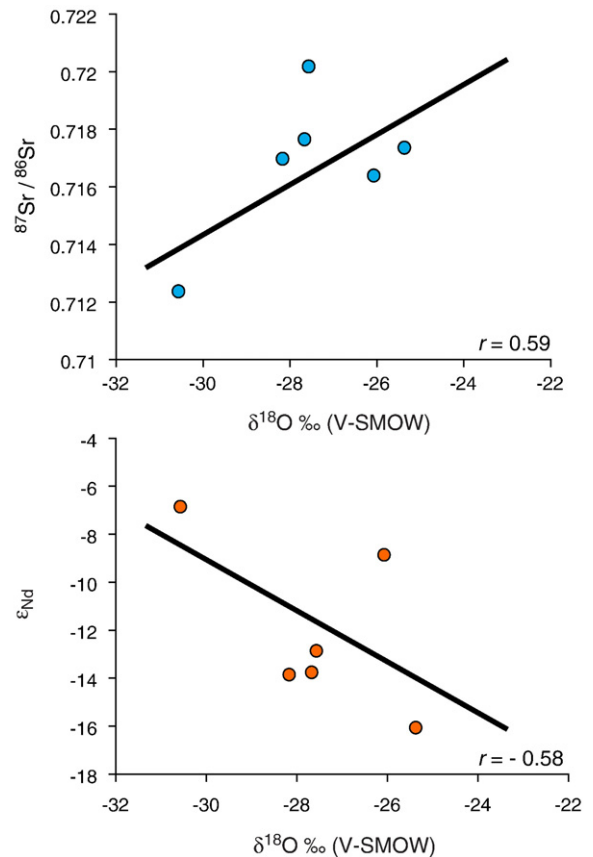

Fig. 4. Strontium and neodymium isotopic composition plotted against oxygen isotopic composition of the ice showing a correlation between temperature or moisture source ($\delta^{18}O$) and dust composition.

In order to estimate the carbonate fraction, the Sr/Nd ratio of the carbonate in the dust fraction must be known. There is no literature data documenting the Sr and Nd concentrations of carbonates in size fractions under 5 μm, but typical Sr/Nd ratios in bulk Asian loess carbonates leachates range from 20 to 75 and these variations are primarily controlled by variations in Sr concentration (Honda et al., 2004). A simple mass balance calculation yields that the contribution of carbonates to the overall Sr budget is smaller than 10%. This is in agreement with Asian aerosol composition studies that found carbonate contents ranging from 2.6 to 12.2% (Derbyshire et al., 1998; Wang et al., 2005). The uranium activity ratios smaller than 1 are typical of a continental weathering environment and exclude significant marine contamination of the dust fraction (Vigier et al., 2001; Dosseto et al., 2008). Leaching experiments on Asian loess samples show $^{87}Sr/^{86}Sr$ values ranging from 0.71073 to 0.71281 for the leachates (Yokoo et al., 2004) and allow us to constrain the possible carbonate contribution to the Sr isotopic compositions. By correcting for 10% of carbonate-derived Sr, with a value of $^{87}Sr/^{86}Sr$ of 0.71 that would maximize our correction, the dust isotopic composition of our samples is shifted towards higher $^{87}Sr/^{86}Sr$ ratios. The corrected $^{87}Sr/^{86}Sr$ ratios for our samples would be 0.71268 for the least radiogenic sample (129A) and 0.72136 for the most radiogenic sample (132A). No correction has been made to the Nd isotopic ratios as the contribution of Nd from carbonates to the overall dust is small and any correction attempt would lie within experimental errors. The possible carbonate correction is able to explain part of the offset between PSA samples and the dust extracted from the Dye-3 ice core, but it is not sufficient to account for the full difference. This offset is in agreement with other literature data, where an offset between PSAs composition and dust samples remains even after carbonate leaching (Biscaye et al., 1997; Svensson et al., 2000; Bory et al., 2003b).

Mixing of volcanic aerosols is a plausible hypothesis to explain the observed shift toward less radiogenic Sr isotopic ratios. Northern hemisphere volcanic activity is a potential source for mineral aerosols in the atmosphere that may reach as far as Greenland (Clausen et al., 1997). No major volcanic activity is known for the studied interval, although the 133–134 m sections of the core recorded the Laki eruption that occurred in Iceland in 1783–1784. Volcanic aerosols are characterized by less radiogenic $^{87}Sr/^{86}Sr$ and more radiogenic ε_{Nd} values and mixing with volcanic dust sources should lead to a shift towards more radiogenic Nd and less radiogenic Sr values. Our Sr and Nd data do not exclude this hypothesis but based on the Hf measurements no significant contribution of a volcanic end member was detected in our samples.

The ε_{Hf} and ε_{Nd} data measured for 132A and 132B is less radiogenic than the Asian dust component found in Pettke et al. (2002) (Fig. 5),

and only limited mixing between Asian dust and a volcanic end member is possible. Sample 130A plots toward more radiogenic Hf and Nd values than average Asian dust, but not directly on a binary mixing line between Asian dust and a volcanic end member, which makes an interpretation in terms of volcanic contribution more difficult. Nevertheless 130A still closely agrees with a purely Asian dust end member (as defined by Pettke et al. (2002): $-10.8 > \varepsilon_{Nd} > -9.0$ and $-4.7 > \varepsilon_{Hf} > 2.5$). The overall shift towards more radiogenic ε_{Hf} values compared to the terrestrial $\varepsilon_{Hf}/\varepsilon_{Nd}$ array of the dust samples is thought to be due to sorting effects during transport. Zircons are enriched in Hf and have a low ε_{Hf} value compared to the average continental crust (van de Flierdt et al., 2007; Bayon et al., 2009) and will be mainly concentrated in coarse-grained sediments (Patchett et al., 1984). The high density of zircons compared to average minerals makes it prone to segregation during surface processes. Mobilization of zircons is not favored during atmospheric transport: for identical grain sizes and according to Stocke's law, settling velocities of zircons ($d = 4.85 \, g\,cm^{-3}$) will be approximatively 1.8 times higher than average continental crust minerals ($d = 2.7 \, g\,cm^{-3}$). This implies that eolian deposits should exhibit more radiogenic Hf isotopic ratios for a given ε_{Nd} value during long-range transport to Greenland. This "zircon effect" was observed in Saharan dust samples, where concomitant low Hf concentrations and high variability in ε_{Hf} was measured (Rickli et al., 2010). But even taking into account this potential sorting effect, measured Hf isotopic ratios are still too low to be explained by mixing of Asian and volcanic dust (Fig. 5).

Based on these isotopic characteristics, the influence of other source areas should be examined. According to model studies, the Saharan and Arabian regions contribute up to 75% of the total atmospheric dust load (Tanaka and Chiba, 2006 and references therein). No isotopic data of PSA size fractions smaller than 5 μm are available for these regions, but the comparison of Sr and Nd dust compositions to <30 μm size fractions of Sahara aerosols sampled off the Atlantic coast (Fig. 3, see data of Grousset et al., 1998) shows that a Saharan dust contribution to Greenland is a very probable explanation for the offset between Greenland ice core dust and Asian PSAs. The Sr and Nd isotopic compositions of modern Saharan aerosols ($^{87}Sr/^{86}Sr$: 0.715–0.725, ε_{Nd}: -12.8 to -14.6; Grousset et al., 1998) can explain the offset toward less radiogenic $^{87}Sr/^{86}Sr$ values and are compatible with ε_{Nd} of samples 129B, 130B, 132A and 132B (Table 1).

An equally compelling argument for a Saharan dust contribution to Greenland is found in the Hf isotopes. Recent work by Rickli et al. (2010) presented the first direct measurements of Hf isotopes in airborne dust collected off the coast of western Africa from a Saharan dust storm (Fig. 4). The unradiogenic Hf and Nd values found in the two of the three samples in the Dye-3 ice core compare very favorably with the unradiogenic Hf and Nd values of the Saharan dust; both sets of data plot on the more unradiogenic side of the Asian dust end member.

Evidence for material transported from North America to Greenland has also been found (Donarummo et al., 2003; Rousseau et al., 2006) but the contribution of North America to the global dust load is small: 0.1% (Tanaka and Chiba, 2006). Isotopic data is only available for limited parts of the source area and does not explain the measured variations in Greenland dust. Furthermore, the most proximal North American dust source to Greenland, northeast Canada, exhibits very unradiogenic crustal signatures for Nd ratios (Jeandel et al., 2007), which would be partially inherited by the dust phase. But this source cannot be an important contribution to the dust samples we have analyzed as this would lead to a general shift towards less radiogenic ε_{Nd} values (Fig. 3) for the Greenland dust samples.

Among the three possible scenarios, carbonate contribution to the isotopic signal, volcanic contribution to the dust load and contribution of additional dust sources, mixing of Asian-derived dust with a Saharan dust source is the best explanation for the observed dust composition in the Greenland Dye-3 ice core.
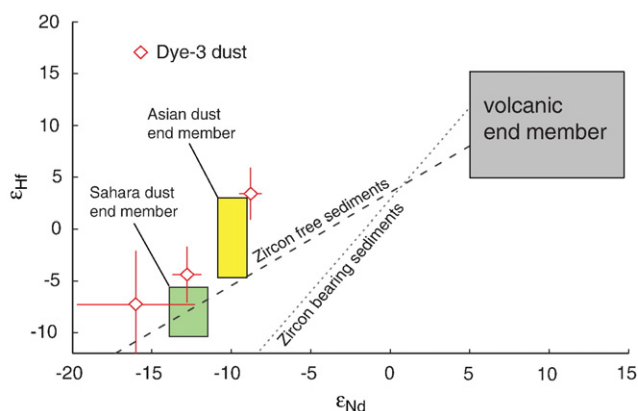

Fig. 5. Neodymium and hafnium isotopic compositions of the analyzed Dye-3 dust. Asian dust end member and modern dust array from Pettke et al., 2002. Asian loess from Aciego et al., 2009 falls in the Asian dust end member field. 2σ errors for both ε_{Nd} and ε_{Hf} are shown for each sample. Saharan dust end member from Rickli et al. (2010).

No direct evidence for Saharan dust export to Greenland has been presented until now, but Saharan dust has been found to reach Europe (e.g. Schwikowski et al., 1995; Vanderstraeten et al., 2008), Asia (Tanaka et al., 2005) and America via trans-Atlantic (e.g. Chiapello et al., 2005) and trans-Pacific transport (McKendry et al., 2007) which supports the role played by the Sahara as a long-range dust source. While northward meridional transport to Europe and westward transport to Central America of dust is an unlikely to contribute significantly to deposition over Greenland (Barkan et al., 2005; Chiapello et al., 2005) eastward zonal transport over Asia is a potential long-range pathway to Greenland. It has to be noted that the analysis presented here only cover a very short time span (4 yr) and that extrapolation to longer time series is hazardous. Trans-Pacific transport of African dust has been documented only for one event (McKendry et al., 2007) and its frequency is unknown. Nevertheless the presence of at least 3 samples that point towards a Saharan contribution to the Greenland dust load in a four year time series indicates that this transport pathway could be active on a yearly basis even if further confirmations on longer time scales are needed. It is also improbable that Saharan dust was the main contributor to the Greenland dust load in the past, as this would have been detected in other, lower resolution ice core studies (Biscaye et al., 1997; Svensson et al., 2000; Burton et al., 2007). However regarding the short time series, we do not claim this frequency to be a climatological mean and further confirmations on longer time scales are needed.

4.2. Origin of soluble component in ice

The origin of radiogenic species in the soluble fraction of ice cores has not yet been studied and could be of great interest in interpreting the dissolved chemical species signal of ice cores. Dissolved species in polar ice are primarily inherited from sea salts that are formed over sea ice and the open ocean (Fitzgerald, 1991; Wagenbach et al., 1998; Rankin et al., 2000, 2002). Tracing the sources of these dissolved elements would be a complementary proxy for atmospheric and marine processes in the polar environment: such as SS production, marine aerosol transport and sea-ice extent (Wolff et al., 2003).

Our measurements on the dust-free soluble fraction show variability in ε_{Nd} whereas the $^{87}Sr/^{86}Sr$ and $^{234}U/^{238}U$ values are homogeneous. Little is known about the origin and composition of dissolved Sr, Nd, and U in precipitation (Martinez-Aguirre et al., 1991; Herut et al., 1993; Stevenson and Pan, 1996; Negrel and Roy, 1998; Nakano et al., 2006). For ice cores, either prior attempts have not been made to separate the dust fraction or the water has not been buffered to avoid carbonate dissolution during melting (e.g. Biscaye et al., 1997; Bory et al., 2002, 2003a,b; Burton et al., 2007; Gabrielli et al., 2009).

The contributions of Sr, Nd, and U to the dust-free ice have two possible sources: (1) leaching from the dust fraction during dust mobilization, long-range transport or ice processing and (2) oceanic derived Sr and Nd carried by marine aerosols. Assessing the isotopic compositions and concentrations of these elements should provide some insight into the dominant source.

The $^{87}Sr/^{86}Sr$ ratios are close to the present day seawater value 0.70916, which has been relatively constant over the last 400 ka (Palmer and Edmond, 1988; Henderson et al., 1994) and does not show large variations from sample to sample. The measured $^{234}U/^{238}U$ activity ratios of the water fraction support a seawater origin of the soluble fraction: activity ratios of 1.10–1.12 compare well to seawater activity ratios, which have been constant at 1.14 for the last 500–800 ka (Henderson, 2002). Furthermore, the Nd isotopic composition falls within the range of expected values for surface seawater around Greenland (Stordal and Wasserburg, 1986; Piepgras and Wasserburg, 1987; Lacan and Jeandel, 2004a,b,c, 2005a,b; Andersson et al., 2008; Porcelli et al., 2009; Rickli et al., 2009) (see Fig. 3). Therefore, the

radiogenic isotope record generally supports a marine origin for the dissolved species.

However, the small offset between the seawater values of Sr and U and our measured values in the soluble fraction of the ice core must be explained. Leaching of the dust phase during transport and precipitation processes when "dusty" air masses mix with moist oceanic air cannot be excluded. Furthermore, leaching of dust during melting and filtering of the ice core is an issue even if great care was taken to avoid this effect (Aciego et al., 2009). Sr isotopic composition of the ice correlates with Sr isotopic composition of the dust (Fig. 6) but using a simple two component mixing model (Fig. 7), with the dust as one end member and seawater as the other, one can quantify the amount of leaching or dissolution that has taken place for these samples. The parameter that controls the shape of the mixing hyperbola in a $^{87}Sr/^{86}Sr$ versus $^{234}U/^{238}U$ diagram is:

$$r = (Sr_{sea} / U_{sea}) / (Sr_{dust} / U_{dust}). \qquad (1)$$

Given the high Sr/U in seawater (close to 3000), lower values in the continental crust, and our measured values of Sr/U in dust of 35 and in ice of 125, values of $r > 1$ seem likely. The isotopic compositions of the ice samples are plotted in Fig. 7 showing only a slight difference from the seawater values, but the uncertainties in the $^{234}U/^{238}U$ make it impossible to determine r better than $0.25 < r < 2.5$. Even with this large uncertainty, the amount of dissolution necessary to shift the strontium and uranium isotopic compositions is 10–15% of the total mass. In order to rule out the possibility of carbonate dissolution, we also show the range in carbonate values for possible Asian dust sources based on leaching experiments. The Asian loess leaching experiments of Yokoo et al. (2004) distinguish between water soluble,
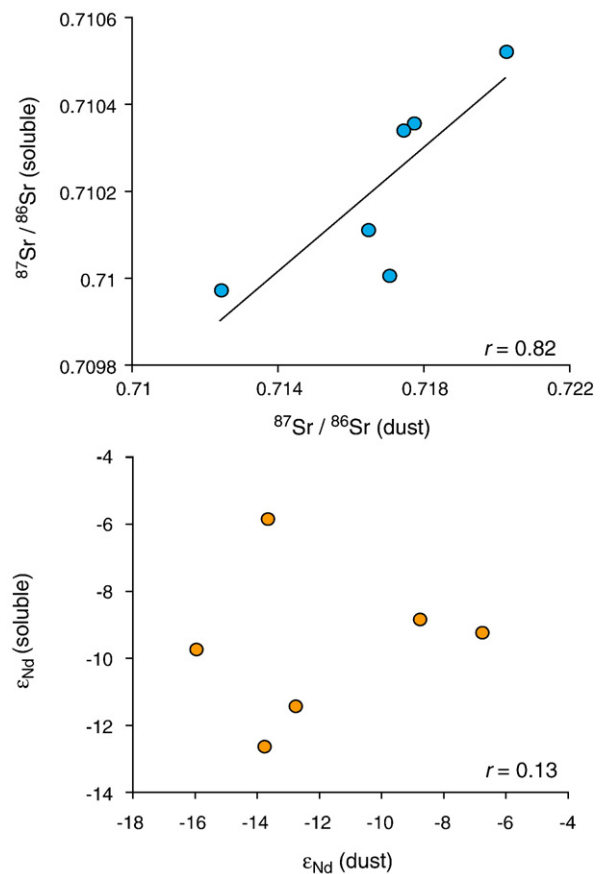

Fig. 6. Strontium and neodymium isotopic composition of dust and soluble fractions. Sr composition of dust and ice is correlated but Nd isotopic composition of both phases is independent.
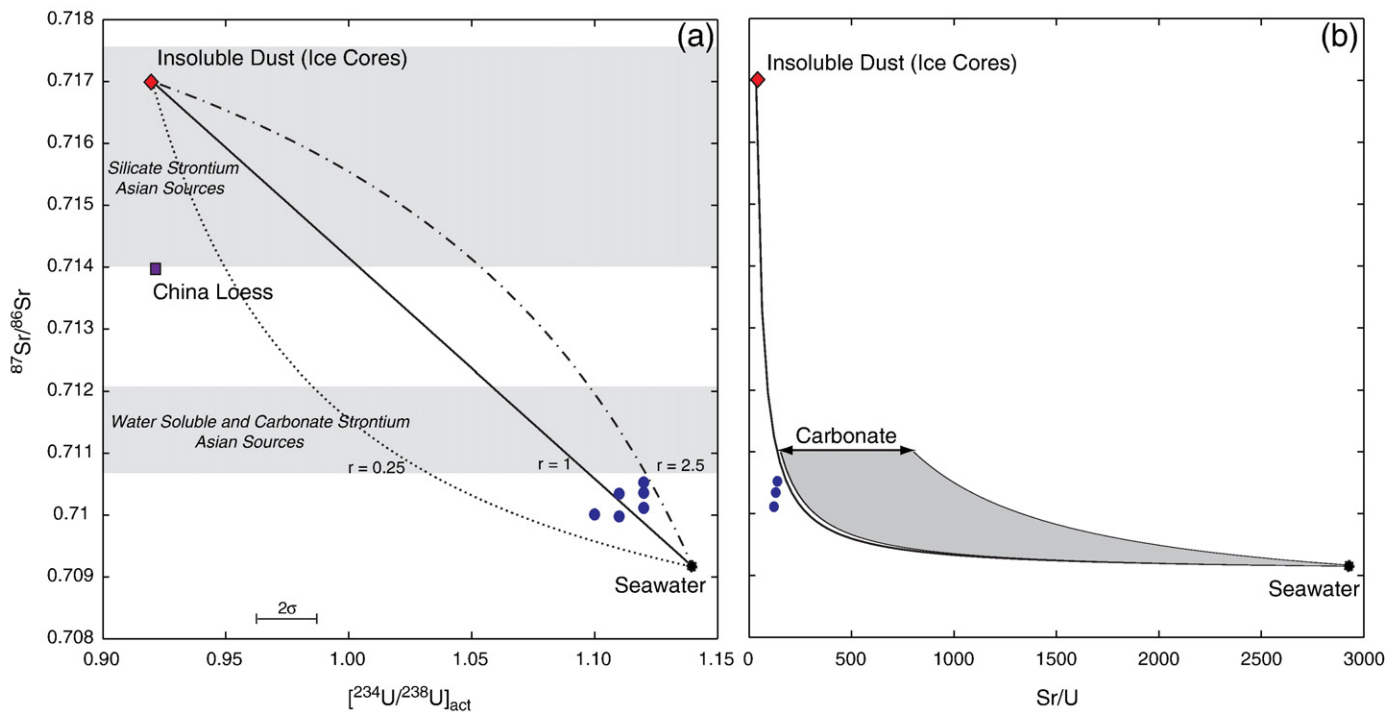
Fig. 7. Strontium and uranium isotopic variations in soluble and insoluble components within the ice core with mixing lines. Diamond denotes average insoluble composition measured in this work, small circles are measurements of the dust-free soluble fractions reported here. Large circle is the average seawater composition (Palmer and Edmond, 1988 and Henderson, 2002). (a) Mixing lines between seawater and insoluble dust are calculated with *r* values of 0.25, 1, and 2.5 indicating the difference in concentration ratios between uranium and strontium in the seawater and dust end members. Also indicated are the ranges in $^{87}Sr/^{86}Sr$ for leaching experiments of possible Asian sources (Yokoo et al., 2004) and the Sr and U isotopic compositions of the Asian loess measured by Aciego et al., 2009. (b) Mixing lines between seawater and carbonate or seawater and dust as a function of Sr/U concentration. $^{87}Sr/^{86}Sr$ of end members as in (a), Sr/U of end members based on measured values in this work, (Sr) from Yokoo et al., 2004, and a range in (U) from 0.5 to 5 ppm. The soluble fraction isotopic composition is compatible with a mixing of seawater and carbonate dissolution (a), but carbonate dissolution is not compatible with the Sr/U ratios measured. The most likely explanation of the isotopic offset between seawater composition and measured soluble fraction being bulk dust dissolution.

carbonate, strong-acid leachable and residual strontium thus providing a possible carbonate end member, and we can calculate the fraction of Sr in the soluble fraction that could be derived from carbonates (50%). A simple mixing model using Sr–U concentration data and the $^{87}Sr/^{86}Sr$ ratios suggests that carbonate dissolution would result in higher Sr/U ratios in the ice (Fig. 7b). Given these constraints, we conclude that dissolution of the bulk dust during transport or filtration is the most likely cause for the small shift in isotopic composition. However the Nd isotopic composition of the dust and soluble fraction are uncorrelated (Fig. 6), which supports the Nd isotopic signature of the ice being unaffected by leaching. We propose that the Nd signal can be used to trace the origin of marine contributions to the dissolved component of the ice core.

Determining the origin of precipitation would be the most obvious utilization of Nd isotopes, but the pathway for marine contributions to ice sheets is likely complex. Models indicate that precipitation on Greenland originates from different oceanic water masses: mainly the Arctic, North Atlantic (Sodemann et al., 2008) and North Pacific (Werner et al., 2001) surface waters. These water masses have contrasting ε_{Nd} due to Nd short oceanic residence time (500–1000 yr) and contrasting lithogenic inputs from the surrounding continents (Lacan and Jeandel, 2005b). The Nd isotopic composition of North Atlantic Deep Waters (NADW) has remained stable over glacial–interglacial periods (Foster et al., 2007) even if changes in ocean circulation likely occurred over these time periods (Hillaire-Marcel et al., 2001; Rasmussen and Thomsen, 2004). Even though Nd isotopic compositions of these northern hemisphere water masses are compatible with the ones measured in this study, it is expected that the Sr, Nd and U concentrations would not be incorporated in the gas phase during evaporation processes. Furthermore, the measured Sr/Nd, Sr/U and Nd/Hf concentration ratios, respectively 30, 130 and 10, are lower than that of seawater (e.g. Piepgras and Wasserburg, 1987; Palmer and Edmond, 1988; Henderson

et al., 1994; Henderson, 2002; Lacan and Jeandel, 2004a,b,c, 2005a; Porcelli et al., 2009; Rickli et al., 2009; Zimmermann et al., 2009), and indicate that the Sr, Nd, Hf and U measured in the ice cannot be directly derived from seawater of the open ocean.

Marine aerosols and sea salts are the more likely source of dissolved radiogenic species to the Greenland ice sheet. Marine aerosols are found to affect snow chemistry even in central Greenland (e.g. Fischer and Wagenbach, 1996) and originate both from open water and sea ice (Wolff et al., 2003). It has been recognized that this latter source is the dominant source for sea-salt aerosols (Rankin et al., 2002) and could generate aerosols with a different chemical composition from that of bulk seawater (Rankin et al., 2000; Kaleschke et al., 2004).

While little is known about the atmospheric cycle of radiogenic isotopes, especially marine aerosols and sea-ice composition, we nevertheless propose an origin for the sea salts measured in the Dye-3 section. With ε_{Nd} values of our samples ranging from −12.6 to −5.8, the contribution of sea salt from the surface waters west of Greenland to our samples is limited, as typical Labrador Sea and Baffin Bay isotopic composition is unradiogenic with values from −25 to −14.5 (Lacan and Jeandel, 2005a,b). North Atlantic does not appear to be the dominant source either as surface waters range from −14.8 to −13.6 ε_{Nd} (Lacan and Jeandel, 2005a). Sea-salt sources to the east of Greenland are more likely contributors to the Dye-3 record: neodymium isotopic composition of surface waters from the Denmark strait with −11.5 to −9.5 ε_{Nd} (Lacan and Jeandel, 2004a) and further north to the Fram strait with waters from −10.7 to −9.8 ε_{Nd} and up to −8 in the Icelandic sea (Lacan and Jeandel, 2004c; Andersson et al., 2008). A more radiogenic end member is however needed to account for values up to −5.8 ε_{Nd}. Even if our data set does not allow us to draw firm conclusions two different sources could provide this radiogenic end member: on both sides of the Denmark strait the Icelandic and Tertiary basalts on the east coast of Greenland (between

68°N and 70°N) with a radiogenic ε_{Nd} signature (Mertz et al., 1991; Bernstein et al., 1998; Lacan and Jeandel, 2004a) could locally enrich oceanic water to higher ε_{Nd} values due to crustal radiogenic inputs (Arsouze et al., 2007).

These areas could act as a marine aerosol source with a radiogenic signature especially when covered by seasonal sea ice. Long-range transport should not be excluded and Fischer (2001) suggests from meteorological re-analysis data that sea-salt deposition onto Greenland is mainly controlled by eastern and northern Pacific cyclonic activity. North Pacific waters have positive ε_{Nd} values (Piepgras and Jacobsen, 1988) and are compatible with the needed radiogenic end member. Unfortunately Nd isotopic composition alone is not able to resolve these two possible additional sea-salt sources to Greenland without further information about sea-ice processes.

5. Conclusions

Previous ice core studies argued for Asia as the primary source of the mineral dust transported to the Greenland ice sheet. However, low concentrations of dust had limited radiogenic isotopic measurements compared to dusty glacial ice, or to large-volume modern snow samples. Previous ice core studies did not show the variability observed in the high-resolution snow-pit studies, likely due to the integration of the signal over hundreds of years. This work demonstrates the feasibility of high-resolution dust isotopic measurements on small sample sizes, including the measurement of hafnium isotopes, on a section (1789–1793 A.D.) of the Dye-3 ice core.

The significance of the resulting ice core dust record is twofold. First, we confirm Asia is the main contributor to the dust content in the sections analyzed from the Dye-3 ice core. Variability within Asian sources is detected, with alternating contributions from the Gobi and Taklimakan deserts and the Ordos plateau, consistent with previous studies. Second, differences in isotopic composition between known PSAs and dust samples suggest the existence of an additional dust source mixing with Asian dust in Greenland. Hf isotopic data show that in our samples volcanic aerosols contribute only to a minor degree, if at all, to the dust load at Dye-3. More importantly, we are able to pinpoint this source based on the limited PSA and dust data sets available and we find that the Sahara is the most likely additional source. These isotopic results are the first pieces of chemical evidence supporting models for Saharan dust transport to the higher latitudes.

There is further potential for investigating paleo-transport pathways by using the dust-free soluble fractions. The ice fraction carries a strong marine signature and the observed Nd isotopic variations are interpreted in terms of sea-salt origin. These interpretations are hindered by our limited knowledge of the behavior of radiogenic isotopes in the atmospheric cycle. Further work aimed to understanding the formation of marine aerosols from sea ice or open ocean, with a special focus on Nd isotopes is needed to draw firm conclusions and fully interpret the dissolved Nd record. Nevertheless we see high potential in dissolved isotopic composition studies in potentially addressed paleo-atmospheric circulation or sea-ice extent questions.

References

Aciego, S.M., Bourdon, B., Lupker, M., Rickli, J., 2009. A new procedure for separating and measuring radiogenic isotopes (U, Th, Pa, Ra, Sr, Nd, Hf) in ice cores. Chem. Geol. 266 (3–4), 203–213. doi:10.1016/j.chemgeo.2009.06.003.

Andersson, P.S., Porcelli, D., Frank, M., Bjork, G., Dahlqvist, R., Gustafsson, R., 2008. Neodymium isotopes in seawater from the Barents Sea and Fram Strait Arctic–Atlantic gateways. Geochim. Cosmochim. Acta 72, 2854–2867.

Arsouze, T., Dutay, J.C., Lacan, F., Jeandel, C., 2007. Modeling the neodymium isotopic composition with a global ocean circulation model. Chem. Geol. 239, 165–177. doi:10.1016/j.chemgeo.2006.12.006.

Barkan, J., Alpert, P., Kutiel, H., Kishcha, P., 2005. Synoptics of dust transportation days from Africa toward Italy and central Europe. J. Geophys. Res. 110. doi:10.1029/2004jd005222.

Bayon, G., Burton, K.W., Soulet, G., Vigier, N., Dennielou, B., Etoubleau, J., Ponzevera, E., German, C.R., Nesbitt, R.W., 2009. Hf and Nd isotopes in marine sediments: constraints on global silicate weathering. Earth Planet. Sci. Lett. 277, 318–326.

Bernstein, S., Kelemen, P.B., Tegner, C., Kurz, M.D., Blusztajn, J., Brooks, C.K., 1998. Post-breakup basaltic magmatism along the East Greenland Tertiary rifted margin. Earth Planet. Sci. Lett. 160, 845–862.

Biscaye, P.E., Grousset, F.E., Revel, M., VanderGaast, S., Zielinski, G.A., Vaars, A., Kukla, G., 1997. Asian provenance of glacial dust (stage 2) in the Greenland ice sheet project 2 ice core, summit, Greenland. J. Geophys. Res. Oceans 102 (C12), 26,765–26,781.

Bory, A.J.M., Biscaye, P.E., Svensson, A., Grousset, F.E., 2002. Seasonal variability in the origin of recent atmospheric mineral dust at north GRIP, Greenland. Earth Planet. Sci. Lett. 196 (3–4), 123–134.

Bory, A.J.M., Biscaye, P.E., Grousset, F.E., 2003a. Two distinct seasonal Asian source regions for mineral dust deposited in Greenland (NorthGRIP). Geophys. Res. Lett. 30. doi:10.1029/2002gl016446.

Bory, A.J.M., Biscaye, P.E., Piotrowski, A.M., Steffensen, J.P., 2003b. Regional variability of ice core dust composition and provenance in Greenland. Geochem. Geophys. Geosyst. 4. doi:10.1029/2003gc000627.

Burton, G.R., Rosman, K.J.R., Candelone, J.P., Burn, L.J., Boutron, C.F., Hong, S.M., 2007. The impact of climatic conditions on Pb and Sr isotopic ratios found in Greenland ice, 7–150 ky BP. Earth Planet. Sci. Lett. 259, 557–566. doi:10.1016/j.epsl.2007.05.015.

Chen, J., Li, G.J., Yang, J.D., Rao, W.B., Lu, H.Y., Balsam, W., Sun, Y.B., Ji, J.F., 2007. Nd and Sr isotopic characteristics of Chinese deserts: implications for the provenances of Asian dust. Geochim. Cosmochim. Acta 71, 3904–3914. doi:10.1016/j.gca.2007.04.033.

Chiapello, I., Moulin, C., Prospero, J.M., 2005. Understanding the long-term variability of African dust transport across the Atlantic as recorded in both Barbados surface concentrations and large-scale Total Ozone Mapping Spectrometer (TOMS) optical thickness. J. Geophys. Res. 110. doi:10.1029/2004jd005132.

Clausen, H., Hammer, C., Hvidberg, C., Dahl-Jensen, D., Steffensen, J., Kipfstuhl, J., Legrand, M., 1997. A comparison of the volcanic records over the past 4000 years from the Greenland Ice Core Project and Dye 3 Greenland ice cores. J. Geophys. Res. 102 (C12), 26,707–26,723.

Dasch, E., 1969. Strontium isotopes in weathering profiles, deep-sea sediments and sedimentary rocks. Geochim. Cosmochim. Acta 33, 1521–1552.

Derbyshire, E., Meng, X.M., Kemp, R.A., 1998. Provenance, transport and characteristics of modern aeolian dust in western Gansu Province, China, and interpretation of the Quaternary loess record. J. Arid Environ. 39, 497–516.

Donarummo, J., Ram, M., Stoermer, E.F., 2003. Possible deposit of soil dust from the 1930's U.S. dust bowl identified in Greenland ice. Geophys. Res. Lett. 30. doi:10.1029/2002gl016641.

Dosseto, A., Bourdon, B., Turner, S.P., 2008. Uranium-series isotopes in river materials: insights into timescales of erosion and sediment transport. Earth Planet. Sci. Lett. 265 (1–2), 1–17.

Fischer, H., 2001. Imprint of large-scale atmospheric transport patterns on sea-salt records in northern Greenland ice cores. J. Geophys. Res. 106. doi:10.1029/2000jd000175.

Fischer, H., Wagenbach, D., 1996. Large-scale spatial trends in recent firn chemistry along an east–west transect through central Greenland. Atmos. Environ. 30, 3227–3238.

Fisher, H., Siggaard-Andersen, M.L., Ruth, U., Röthlisberger, R., Wolff, E., 2007. Glacial/interglacial changes in mineral dust and sea-salt records in polar ice cores: sources, transport, and deposition. Rev. Geophys. 45, RG1002.

Fitzgerald, J.W., 1991. Marine aerosols: a review. Atmos. Environ., A 25, 533–546.

Foster, G.L., Vance, D., Prytulak, J., 2007. No change in the neodymium isotope composition of deep water exported from the North Atlantic on glacial–interglacial time scales. Geology 35 (1), 37–40.

Gabrielli, P., Planchon, F., Barbante, C., Boutron, C.F., Petit, J.R., Bulat, S., Hong, S., Cozzi, G., Cescon, P., 2009. Ultra-low rare earth element content in accreted ice from sub-glacial Lake Vostok, Antarctica. Geochim. Cosmochim. Acta 73, 5959–5974.

Grousset, F.E., Biscaye, P.E., 2005. Tracing dust sources and transport patterns using Sr, Nd and Pb isotopes. Chem. Geol. 222, 149–167. doi:10.1016/j.chemgeo.2005.05.003.

Grousset, F.E., Parra, M., Bory, A., Martinez, P., Bertrand, P., Shimmield, G., Ellam, R.M., 1998. Saharan wind regimes traced by the Sr–Nd isotopic composition of subtropical Atlantic sediments: last Glacial Maximum vs today. Quatern. Sci. Rev. 17, 395–409.

Hammer, C., Clausen, H., Dansgaard, W., Neftel, A., Kristinsdottir, P., Johnson, E., 1985. Continuous imurity analysis along the Dye-3 deep core. Geophysical Monograph, 33. American Geophysical Union, Washington DC (90–94 pp.).

Han, Y.X., Fang, X.M., Kang, S.C., Wang, H.J., Kang, F.Q., 2008. Shifts of dust source regions over central Asia and the Tibetan Plateau: connections with the Arctic oscillation and the westerly jet. Atmos. Environ. 42, 2358–2368.

Haywood, J., Boucher, O., 2000. Estimates of the direct and indirect radiative forcing due to tropospheric aerosols: a review. Rev. Geophys. 38, 513–543.

Henderson, G.M., 2002. Seawater (^{234}U/^{238}U) during the last 800 thousand years. Earth Planet. Sci. Lett. 199, 97–110.

Henderson, G.M., Martel, D.J., O'Nions, R.K., Shackleton, N.J., 1994. Evolution of seawater over the last 400 ka: the absence of glacial/interglacial cycles. Earth Planet. Sci. Lett. 128, 643–651.

Herut, B., Starinsky, A., Katz, A., 1993. Strontium in rainwater from Israel — sources, isotopes and chemistry. Earth Planet. Sci. Lett. 120, 77–84.

Hillaire-Marcel, C., de Vernal, A., Bilodeau, G., Weaver, A.J., 2001. Absence of deep-water formation in the Labrador Sea during the last interglacial period. Nature 410, 1073–1077. doi:10.1038/35074059.

Honda, M., Yabuki, S., Shimizu, H., 2004. Geochemical and isotopic studies of aeolian sediments in China. Sedimentology 51, 211–230. doi:10.1046/j.1365-3091.2003.00618.x.

IPCC AR4, 2007. Climate Change 2007 the Physical Science Basis — Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University press.

Jeandel, C., Arsouze, T., Lacan, F., Téchiné, P., Dutay, J.C., 2007. Isotopic Nd compositions and concentrations of the lithogenic inputs into the ocean: a compilation, with an emphasis on the margins. Chem. Geol. 239, 156–164. doi:10.1016/j.chemgeo.2006.11.013.

Kaleschke, L., Richter, A., Burrows, J., Afe, O., Heygster, G., Notholt, J., Rankin, A.M., Roscoe, H.K., Hollwedel, J., Wagner, T., Jacobi, H.W., 2004. Frost flowers on sea ice as a source of sea salt and their influence on tropospheric halogen chemistry. Geophys. Res. Lett. 31. doi:10.1029/2004gl020655.

Kanayama, S., Yabuki, S., Yanagisawa, F., Motoyama, R., 2002. The chemical and strontium isotope composition of atmospheric aerosols over Japan: the contribution of long-range-transported Asian dust (kosa). Atmos. Environ. 36, 5159–5175.

Kanayama, S., Yabuki, S., Zeng, F.J., Liu, M.Z., Shen, Z.B., Liu, L.C., Yanagisawa, F., Abe, O., 2005. Size-dependent geochemical characteristics of Asian dust — Sr and Nd isotope compositions as tracers for source identification. J. Meteorol. Soc. Jpn. 83A, 107–120.

Lacan, F., Jeandel, C., 2004a. Denmark Strait water circulation traced by heterogeneity in neodymium isotopic compositions. Deep-Sea Res., Part 1, Oceanogr. Res. Pap. 51, 71–82.

Lacan, F., Jeandel, C., 2004b. Subpolar Mode Water formation traced by neodymium isotopic composition. Geophys. Res. Lett. 31.

Lacan, F., Jeandel, C., 2004c. Neodymium isotopic composition and rare earth element concentrations in the deep and intermediate Nordic Seas: constraints on the Iceland Scotland Overflow Water signature. Geochem. Geophys. Geosyst. 5.

Lacan, F., Jeandel, C., 2005b. Acquisition of the neodymium isotopic composition of the North Atlantic Deep Water. Geochem. Geophys. Geosyst. 6.

Lacan, F., Jeandel, C., 2005a. Neodymium isotopes as a new tool for quantifying exchange fluxes at the continent–ocean interface. Earth Planet. Sci. Lett. 3–4, 245–257. doi:10.1016/j.epsl.2005.01.004.

Laj, P., Ghermandi, G., Cecchi, R., Maggi, V., Riontino, C., Hong, S., Candelone, J.-P., Boutron, C., 1997. Distribution of Ca, Fe, K, and S between soluble and insoluble material in the Greenland Ice Core Project ice core. J. Geophys. Res. 102. doi:10.1029/96jc02660.

Lohmann, U., Feichter, J., 2005. Global indirect aerosol effects: a review. Atmos. Chem. Phys. 5, 715–737.

Martin, J., 1991. Iron still comes from above. Nature 353.

Martinez-Aguirre, A., Moron, M., Garcia-Leon, M., 1991. Measurements of U-isotopes and Ra-isotopes in rainwater samples. J. Radioanal. Nucl. Chem.-Articles 152 (1), 37–46.

McKendry, I.G., Strawbridge, K.B., O'Neill, N.T., Macdonald, A.M., Liu, P.S.K., Leaitch, W.R., Anlauf, K.G., Jaegle, L., Fairlie, D., Westphale, D.L., 2007. Trans-Pacific transport of Saharan dust to western North America: a case study. J. Geophys. Res. 112. doi:10.1029/2006JD007129.

Mertz, D.F., Devey, C.W., Todt, W., Stoffers, P., Hofmann, A.W., 1991. Sr–Nd–Pb isotope evidence against plume–asthenosphere mixing north of Iceland. Earth Planet. Sci. Lett. 107, 243–255.

Nakano, T., Morohashi, S., Yasuda, H., Sakai, M., Aizawa, S., Shichi, K., Morisawa, T., Takahashi, M., Sanada, M., Matsuura, Y., Sakai, H., Akama, A., Okada, N., 2006. Determination of seasonal and regional variation in the provenance of dissolved cations in rain in Japan based on Sr and Pb isotopes. Atmos. Environ. 40, 7409–7420. doi:10.1016/j.atmosenv.2006.06.049|ISSN 1352-2310.

Negrel, P., Roy, S., 1998. Chemistry of rainwater in the Massif Central (France): a strontium isotope and major element study. Appl. Geochem. 13, 941–952.

Palmer, M., Edmond, J., 1988. The strontium isotope budget of the modern ocean. Earth Planet. Sci. Lett. 92, 11–26.

Patchett, P.J., White, W.M., Feldmann, H., Kielinczuk, S., Hofmann, A.W., 1984. Hafnium/rare earth element fractionation in the sedimentary system and crustal recycling into the Earth's mantle. Earth Planet. Sci. Lett. 69, 365–378.

Pettke, T., Lee, D.C., Halliday, A.N., Rea, D.K., 2002. Radiogenic Hf isotopic compositions of continental eolian dust from Asia, its variability and its implications for seawater Hf. Earth Planet. Sci. Lett. 202, 453–464.

Piepgras, D.J., Jacobsen, S.B., 1988. The isotopic composition of neodymium in the North Pacific. Geochim. Cosmochim. Acta 52, 1373–1381.

Piepgras, D.J., Wasserburg, G.J., 1987. Rare earth element transport in the western North Atlantic inferred from Nd isotopic observations. Geochim. Cosmochim. Acta 51, 1257–1271.

Porcelli, D., Andersson, P.S., Baskaran, M., Frank, M., Bjork, G., Semiletov, I., 2009. The distribution of neodymium isotopes in Arctic Ocean basins. Geochim. Cosmochim. Acta 73, 2645–2659.

Rankin, A.M., Auld, V., Wolff, E.W., 2000. Frost flowers as a source of fractionated sea salt aerosol in the polar regions. Geophys. Res. Lett. 27. doi:10.1029/2000gl011771.

Rankin, A.M., Wolff, E.W., Martin, S., 2002. Frost flowers: implications for tropospheric chemistry and ice core interpretation. J. Geophys. Res. 107. doi:10.1029/2002jd002492.

Rasmussen, T.L., Thomsen, E., 2004. The role of North Atlantic Drift in the millennial timescale glacial climate fluctuations. Palaeogeogr. Palaeoclimatol. Palaeoecol. 210, 101–116. doi:10.1016/j.palaeo.2004.04.005.

Rickli, J., Frank, M., Halliday, A.N., 2009. The hafnium–neodymium isotopic composition of Atlantic seawater. Earth Planet. Sci. Lett. 280, 118–127.

Rickli, J., Frank, M., Baker, A.R., Aciego, S., de Souza, G., Georg, R.B., Halliday, A.N., 2010. Hafnium and neodymium isotopes in surface waters of the eastern Atlantic Ocean: implications for sources and inputs of trace metals to the ocean. Geochim. Cosmochim. Acta 74, 540–557.

Rousseau, D.D., Schevin, P., Duzer, D., Cambon, G., Ferrier, J., Jolly, D., Poulsen, U., 2006. New evidence of long distance pollen transport to southern Greenland in late spring. Rev. Palaeobot. Palynol. 141, 277–286. doi:10.1016/j.revpalbo.2006.05.001.

Schi, Z., Shao, L., Jones, T., Lu, S., 2005. Microscopy and mineralogy of airborne particles collected during severe dust storm episodes dust storm episodes. J. Geophys. Res. 110 (1), D01303. doi:10.1029/2004JD005073.

Schwikowski, M., Seibert, P., Baltensperger, U., Gaggeler, H.W., 1995. A study of an outstanding Saharan dust event at the high-alpine site Jungfraujoch, Switzerland. Atmos. Environ. 29, 1829–1842. doi:10.1016/1352-2310(95)00060-C.

Sigg, A., 1990. Wasserstoffperoxid-Messungen an Eisbohrkernen aus Grönland und der Antarktis und ihre atmosphärische Bedeutung, Ph.D. thesis, Philosophisch naturwissenschaftlichen Fakultat der Universitat Bern.

Sodemann, H., Schwierz, C., Wernli, H., 2008. Interannual variability of Greenland winter precipitation sources: Lagrangian moisture diagnostic and North Atlantic Oscillation influence. J. Geophys. Res. Atmos. 113. doi:10.1029/2007jd008503.

Steffensen, J.P., 1997. The size distribution of microparticles from selected segments of the Greenland Ice Core Project ice core representing different climatic periods. J. Geophys. Res. Oceans 102, 26755–26763.

Stevenson, K., Pan, V., 1996. An assessment of uranium in surface air within the continental US. J. Environ. Radioactiv. 31 (3), 223–235.

Stordal, M.C., Wasserburg, G.J., 1986. Neodymium isotopic study of Baffin Bay water: sources of REE from very old terranes. Earth Planet. Sci. Lett. 77, 259–272.

Sullivan, R.C., Guazzotti, S.A., Sodeman, D.A., Prather, K.A., 2007. Direct observations of the atmospheric processing of Asian mineral dust. Atmos. Chem. Phys. 7, 1213–1236.

Svensson, A., Biscaye, P.E., Grousset, F.E., 2000. Characterization of late glacial continental dust in the Greenland Ice Core Project ice core. J. Geophys. Res. Atmos. 105, 4637–4656.

Tanaka, T.Y., Chiba, M., 2006. A numerical study of the contributions of dust source regions to the global dust budget. Global Planet. Change 52, 88–104. doi:10.1016/j.gloplacha.2006.02.002.

Tanaka, T.Y., Kurosaki, Y., Chiba, M., Matsumura, T., Nagai, T., Yamazaki, A., Uchiyama, A., Tsunematsu, N., Kai, K., 2005. Possible transcontinental dust transport from North Africa and the Middle East to East Asia. Atmos. Environ. 39, 3901–3909. doi:10.1016/j.atmosenv.2005.03.034.

Uno, I., Eguchi, K., Yumimoto, K., Takemura, T., Shimizu, A., Uematsu, M., Liu, Z., Wang, Z., Hara, Y., Suguimoto, N., 2009. Asian dust transported one full circuit around the globe. Nature Geosci. 2, 557–560. doi:10.1038/ngeo583.

van de Flierdt, T., Goldstein, S.L., Hemming, S.R., Roy, M., Frank, M., Halliday, A.N., 2007. Global neodymium–hafnium isotope systematics — revisited. Earth Planet. Sci. Lett. 259, 432–441. doi:10.1016/j.epsl.2007.05.003.

Vanderstraeten, P., Lénelle, Y., Meurrens, A., Carati, D., Brenig, L., Delcloo, A., Offer, Z.Y., Zaady, E., 2008. Dust storm originate from Sahara covering Western Europe: a case study. Atmos. Environ. 42, 5489–5493. doi:10.1016/j.atmosenv.2008.02.063.

Vigier, N., Bourdon, B., Turner, S., Allegre, C.J., 2001. Erosion timescales derived from U-decay series measurements in rivers. Earth Planet. Sci. Lett. 193 (3–4), 549–563.

Wagenbach, D., Ducroz, F., Mulvaney, R., Keck, L., Minikin, A., Legrand, M., Hall, J.S., Wolff, E.W., 1998. Sea-salt aerosol in coastal Antarctic regions. J. Geophys. Res. 103. doi:10.1029/97jd01804.

Wang, Y.Q., Zhang, X.Y., Arimoto, R., Cao, J.J., Shen, Z.X., 2005. Characteristic of carbonate content and carbon and oxygen isotopic composition of northern china soil and dust aerosol and its application to tracing dust sources. Atmos. Environ. 39 (14), 2631–2642. doi:10.1016/j.atmosenv.2005.01.015.

Werner, M., Heimann, M., Hoffmann, G., 2001. Isotopic composition and origin of polar precipitation in present and glacial climate simulations. Tellus B 53, 53–71.

Wolff, E.W., Rankin, A.M., Röthlisberger, R., 2003. An ice core indicator of Antarctic sea ice production? Geophys. Res. Lett. 30. doi:10.1029/2003gl018454.

Yokoo, Y., Nakano, T., Nishikawa, M., Quan, H., 2004. Mineralogical variation of Sr–Nd isotopic and elemental compositions in loess and desert sand from the central Loess Plateau in China as a provenance tracer of wet and dry deposition in the northwestern Pacific. Chem. Geol. 204, 45–62. doi:10.1016/j.chemgeo.2003.11.004.

Zender, C.S., Bian, H.S., Newman, D., 2003. Mineral Dust Entrainment and Deposition (DEAD) model: description and 1990s dust climatology. J. Geophys. Res. Atmos. 108. doi:10.1029/2002jd002775.

Zimmermann, B., Porcelli, D., Frank, M., Rickli, J., Lee, D.-C., Halliday, A.N., 2009. The hafnium isotope composition of Pacific Ocean water. Geochim. Cosmochim. Acta 73, 91–101. doi:10.1016/j.gca.2008.09.033.