Neodymium isotopes trace marine provenance of Arctic sea ice


Supplementary Information

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Neodymium Isotope Systematics in the Arctic Ocean

The isotopic composition of neodymium (Nd) is commonly expressed as $\varepsilon_{\text{Nd}} = \left( \frac{^{143}\text{Nd} / ^{144}\text{Nd}_{\text{sample}}}{^{143}\text{Nd} / ^{144}\text{Nd}_{\text{CHUR}}} - 1 \right) \times 10^4$, with CHUR = 0.512638 (Jacobsen and Wasserburg 1980). In rocks, $\varepsilon_{\text{Nd}}$ ranges from −56 to +11 on the global scale (Lacan et al., 2012; van de Flierdt et al., 2016). This variability is caused by the fractionation between Nd and samarium (Sm) during magmatic processes and the decay of $^{147}\text{Sm}$ to $^{143}\text{Nd}$, which together result in more radiogenic (i.e. more positive) $\varepsilon_{\text{Nd}}$ signatures in young mantle-derived rocks compared to old continental rocks. Water masses acquire these distinct rock signatures mainly at the land-ocean interface after their introduction through weathered continental material via rivers, groundwater and coastal erosion. Tracing of the seawater (i.e. dissolved) signatures and the water masses they are carried by is enabled by the quasi-conservative behaviour of Nd in the open ocean (Frank, 2002; Goldstein and Hemming, 2003) and its intermediate average oceanic residence time of several hundred years (Tachikawa et al., 2003; Ar sulphur, 2009; Rempfer et al., 2011; Pöppelmeier et al., 2020).

In the Arctic Ocean, seawater $\varepsilon_{\text{Nd}}$ signatures have been attributed primarily to terrestrial inputs and water mass circulation and mixing, whereas $\varepsilon_{\text{Nd}}$ changes associated with seawater-particle interactions have been shown to be restricted to certain shelf regions (Andersson et al., 2008; Porcelli et al., 2009; Charette et al., 2016; Laukert et al., 2017a, 2017b, 2017c, 2019; Paffrath et al., 2021a, 2021b). The main Nd sources of the Arctic Ocean and their $\varepsilon_{\text{Nd}}$ are shown in Fig. S-1. The Atlantic-derived waters dominate the Nd budget with $\varepsilon_{\text{Nd}}$ signatures around −13 at the Iceland-Scotland Ridge and the Denmark Strait (Laukert et al., 2017a and references therein). Pacific-derived waters entering the Arctic Ocean through the Bering Strait have more radiogenic $\varepsilon_{\text{Nd}}$ signatures around −3 to −2, which are slightly modified in the Chukchi Sea resulting in $\varepsilon_{\text{Nd}}$ signatures of −5.5 entering the open Arctic Ocean (Charette et al., 2016).
Freshwater introduced by the various Arctic rivers has a wide range in \( \varepsilon_{\text{Nd}} \) compositions from \(-17\) to \(-5\) (Porcelli et al., 2009; Zimmermann et al., 2009; Persson et al., 2011; Laukert et al., 2017a, 2017b). Significantly less radiogenic signatures (\(<-17\)) are only introduced through discharge from Greenland and the Canadian Arctic Archipelago (Filippova et al., 2017; Laukert et al., 2018; Grenier et al., 2022). The sea ice cover prevents aeolian Nd to reach the entire Arctic Ocean in winter and year-round in the central Arctic Ocean. Instead, atmospheric Nd is likely trapped in snow deposited on sea ice and released only during the melt season.

All published \( \varepsilon_{\text{Nd}} \) data for surface seawater are shown in Figure S-1 in addition to major external Nd sources. Despite considerable mixing, laterally and vertically separated contributions from the Lena and Yenisei/Ob rivers were recently identified in the central Arctic Ocean and considered as different source clusters of the Transpolar Drift (Paffrath et al., 2021a). Similar provenance tracer characteristics have been observed in the northern Laptev Sea (Laukert et al., 2017b), suggesting that the Laptev Sea is the main source region for freshwater, nutrients, and trace elements transported via the Transpolar Drift. Depending on the wind fields, the Lena plume is transported either northward or eastward (Janout et al., 2020), resulting in spatiotemporal variability in the distribution of source tracers within the Transpolar Drift.

**Sample Collection and Preparation**

Sampling of sea ice, snow and seawater was carried out during the PS85 cruise with the RV *Polarstern* in the Fram Strait in June and July 2014. At each ice station, a designated coring site was assigned and, if present, the snow was sampled prior to the drilling of the sea ice cores. Several ice cores free of ice rafted detrital material based on visual inspection were taken at each station, one of which was used for high-resolution temperature and salinity profiles and another one for tracer analysis. Nitrile gloves were used during sampling and cores were drilled with a Kovacs 9 cm diameter corer (Kovacs Enterprise, Roseburg, USA). The temperature of the ice was directly measured on the floe by drilling into the ice and determining the temperature every 5 cm with a Testo 720 RTD thermometer. Thereafter the core was sectioned in 10 cm pieces and weighted to calculate the brine volume. After melting the salinity was determined with a WTW salinity probe. The ice cores were immediately transferred into plastic bags (LDPE tube films by Rische and Herfurth) and stored at \(-20^\circ\)C. Snow was collected with an acid-cleaned plastic shovel and stored at \(-20^\circ\)C in acid-cleaned plastic bags. A SBE32 rosette water sampler equipped with 24 Niskin-type sample bottles (12 L) was used for collection of the seawater samples, which were directly filtered through AcroPakTM500 Capsules with Supor Membrane (pore size, 0.8/0.2\(\mu\)m) filter cartridges, collected in 20 L acid-cleaned LDPE-containers and stored on board.

The frozen sea ice samples were transported to GEOMAR and processed in the clean room laboratory (MK-Versuchsanlagen, class 100 hoods) immediately after removal from the freezer. All mechanical work on the ice cores was carried out on a clean plastic table covered with acid-cleaned Teflon foil. To remove contaminants from the surfaces of the sea ice samples, the ice cores were rinsed with deionised water (18.2 M\(\Omega\) cm, Milli-Q system) at a temperature of \(-20^\circ\)C for about 15 seconds. Subsequently, the top surface of the ice cores was scraped off with a custom-made titanium grade 1 chisel. The cores were then split into several pieces with a titanium grade 1 hammer and put into acid-cleaned LDPE-buckets with closed plastic lids for melting. No release of brine water was observed throughout the sample processing period. The ice melted within \(-12\) h or less, and the meltwater samples were filtered through Merck Millipore\({}^\circledR\) 0.45 \(\mu\)m cellulose acetate filters immediately after the last piece of ice melted. The meltwater was then transferred to acid-cleaned LDPE cubitainers. The snow samples were treated similarly to the sea-ice samples, except that they were not rinsed with deionised water (this was not necessary given that the plastic bags in which the snow was stored were acid-cleaned). After sub-sampling of sea ice and snow meltwater for salinity and stable oxygen isotope analysis as well as REE ultrafiltration, the filtered sea ice, snow and seawater samples were acidified to pH \(\approx 2.2\) with ultra-pure concentrated hydrochloric acid and at least 48 h for equilibration were given before another aliquot was separated into an acid-cleaned LDPE-bottle for REE concentration and other analyses.
Ultrafiltration of the sea ice and snow meltwater for REE analysis was performed immediately after initial filtration through Merck Millipore 0.45 µm cellulose acetate filters. Amicon® Ultra-15 centrifugal filter units with a volume of 15 mL and either 3000 or 30,000 Nominal Molecular Weight Limit (i.e. 3 or 30 kDa) were used. The tubes were first acid-cleaned and deionised water (18.2 MΩ cm, Milli-Q system) was filtered twice before the actual sample was filtered and collected. Filtration was carried out at 3500 rpm for 20 minutes. The samples were then acidified to a pH of ~2.2 with ultra-pure concentrated hydrochloric acid before further processing.

**Laboratory Analyses**

**Radiogenic neodymium isotopes**

The entire pre-concentration, purification and measurement techniques reported here strictly followed approved GEOTRACES protocols and were confirmed through participation in the international GEOTRACES inter-calibration study (van de Flierdt et al., 2012). To each seawater, sea ice and snow sample trace metal clean FeCl₃ solution was added (~200 mg Fe/mL) and the samples were left for equilibration for 24 h before trace metal clean ammonia solution (25%, Merck Suprapur®) was added to raise the pH to 7.5–8.0. After 48 h, the co-precipitated trace elements settled to the bottom of the cubitainers together with FeOOH and the supernatant water was syphoned off. The precipitates were centrifuged and rinsed three times with deionised water (MilliQ, 18.2 MΩcm) in 50 mL centrifuge tubes to remove major ions, transferred into 60 mL PFA vials with 6 M HCl and then evaporated to dryness. To remove organic components, the samples were treated with aqua regia at 120 °C for 24 h. After evaporation to dryness, the samples were dissolved in 6 M HCl and the sample in solution was washed with pre-cleaned di-ethyl ether to remove 99% of the Fe (Stichel et al., 2012), dried down and dissolved in 1 M HCl for column chemistry. The REEs were separated from matrix elements through cation exchange chromatography (BIORAD®, AG50W-X8 resin, 200–400 µm mesh-size, 1.4 mL resin bed) with a slightly modified separation scheme of Stichel et al. (2012), where instead of a mixture of HCl and HF acids only HCl was used as a reagent. Nd was further purified from the other REEs for isotope measurements using Eichrom® LN-Spec resin (2 mL, 50–100 µm) following previously established procedures (Pin and Zalduegui, 1997; Le Fèvre and Pin, 2005). To destroy residual traces of the resin and organic compounds the samples were finally treated with concentrated quartz-distilled HNO₃ before Nd isotope measurements.

The $^{143}$Nd/$^{144}$Nd ratios were measured on a Neptune Plus MC-ICP-MS (40 cycles at 4 s, 10¹² Ω resistors assigned to masses 143 and 146) and were double-corrected for instrumental mass bias to $^{146}$Nd/$^{144}$Nd = 0.7219 and to $^{142}$Nd/$^{144}$Nd = 1.141876, provided that the $^{142}$Ce beam intensity was sufficiently low (Vance and Thirwall, 2002), monitored via ensuring a raw measured $^{140}$Ce/$^{144}$Nd < 1 (i.e. Ce/Nd < 0.3) for each sample and standard solution. Isobaric interferences between $^{144}$Sm and $^{144}$Nd were corrected by measuring the abundance of the interference free isotope $^{147}$Sm and by calculating the potential $^{144}$Sm contribution on mass 144 from the natural abundance of Sm. The $^{143}$Nd/$^{144}$Nd ratios of all samples were normalised to the accepted JNd1 standard value of 0.512115 (Tanaka et al., 2000). The external reproducibility of the Nd isotope measurements as estimated by repeated measurements of the JNd1 standard at concentrations matched to fit those of the samples (between 0.2 and 3 ng, n = 4) ranged between 0.5 and 3.6 $\epsilon$Nd units (2 s.d.). Some of the snow and sea ice samples had a low Nd yield likely due to loss during column chemistry. The procedural laboratory blanks (n = 3) had <10 pg, which corresponds to <6 % of the lowest Nd concentration used for the isotope measurements. Blank corrections were not applied, and blank contributions are provided in % in Tables S-2 and S-3.
 Rare earth element concentrations

The REE concentrations were determined for filtered and ultrafiltered samples using an online pre-concentration (OP) ICP-MS technique at GEOMAR by directly coupling a “seaFAST” system (Elemental Scientific Inc., Nebraska, USA) to an ICP-MS (Agilent 7500ce) (Hathorne et al., 2012). The method of Hathorne et al. (2012) was further improved by using an 8 mL sample loop and by preparation of calibration standards with a mixed REE solution of a seawater-like composition in a natural seawater matrix (Osborne et al., 2015). Repeated measurements of GEOTRACES intercalibration sample BATS 2000m (van de Flierdt et al., 2012) and the diluted (500×) reference material SLRS-4 were used to monitor the external reproducibility, which based on BATS 2000m was better than ~6 %, ~7 % and ~11 % for the LREEs, MREEs and HREEs, respectively, and based on SLRS-4 was better than ~8 %, ~18 % and ~34 %, respectively. We diluted SLRS-4 to monitor the accuracy and precision of measurements of snow and sea ice samples with similarly low REE concentrations. The measured REE of SLRS-4 and BATS 2000m agree well with literature values (Table S-8). The procedural laboratory blanks (n = 3, filtered and ultrafiltered) had similar REE concentrations on average corresponding to less than 5 % of sea ice and snow samples analysed, except for Ce which was on average ~7 % (Table S-8).

Stable oxygen isotopes and sample salinity

Oxygen isotope compositions were analysed at the Stable Isotope Laboratory of the College of Earth, Ocean, and Atmospheric Sciences at Oregon State University (Corvallis, USA) applying a CO2-water isotope equilibration technique (Epstein and Mayeda, 1953) on at least two subsamples on a DeltaPlusXL instrument. The external reproducibility for the δ18O measurements was ±0.04 ‰ or better and the measured 18O/16O ratio is provided as a deviation from Vienna Standard Mean Ocean Water in the δ-notation (Craig, 1961). Sample salinity was determined with an AutoSal 8400A salinometer at GEOMAR with a precision of ±0.003 and an accuracy better than ±0.005.

Back-tracking of Sea Ice Based on Satellite Data

Pathways, age and source area of sampled sea ice were investigated with the AWI IceTrack system (Kruppen et al., 2020). The low-resolution sea ice drift product OSI-405-c from the Ocean and Sea Ice Satellite Application Facility (OSI SAF; Lavergne, 2016; 62.5 × 62.5 km grid spacing) is used to trace sea ice backward in time until sea-ice concentration at a specific location drops below a predefined threshold (here 50 %) and we assume the ice to be formed. The sea-ice concentration product is based on the 85 GHz Special Sensor Microwave/Imager (SSM/I) and provided by CERSAT (Ezraty et al., 2007; 12.5 km resolution). To assess the accuracy of this Lagrangian tracking approach, Kruppen et al. (2019) reconstructed the pathways of 56 GPS buoys deployed between 2011 and 2016 in the central Arctic Ocean. The displacement between real and virtual tracks is rather small (36 ± 20 km after 200 days). However, the accuracy of the method is lower in Fram Strait, likely due to a general underestimation of drift velocities by low-resolution satellite products in this area (Kruppen et al., 2021) (Fig. 2c). Therefore, in this study, the sampled sea ice in Fram Strait was first manually tracked for a short distance using optical satellite data (MODIS - provided via https://worldview.earthdata.nasa.gov) before tracking was continued with IceTrack.
Supplementary Tables

Table S-1  Sea ice and snow sampling and accompanying information.

Table S-2  Salinity, $\delta^{18}$O and dissolved (<0.45 μm) $\varepsilon_{Nd}$ compositions of sea ice.

Table S-3  Salinity, $\delta^{18}$O and dissolved (<0.45 μm) $\varepsilon_{Nd}$ compositions of snow.

Table S-4  Dissolved (<0.45 μm) and truly dissolved (<30 kDa and 3 kDa) REE concentrations of sea ice.

Table S-5  Dissolved (<0.45 μm) and truly dissolved (<30 kDa and 3 kDa) REE concentrations of snow.

Table S-6  Dissolved (<0.2 μm) $\varepsilon_{Nd}$ compositions and REE concentrations of surface seawater.

Table S-7  High-resolution temperature and salinity profiles of sea ice cores from same stations.

Table S-8  REE concentrations of reference materials SLRS-4 (500× dilution), BATS 2000m and blanks.

Tables S-1 to S-8 are available for download (Excel) from the online version of the article at https://doi.org/10.7185/geochemlet.2220.
Supplementary Figures

Figure S-1  Bathymetric map of the Arctic Ocean (IBCAO; Jakobsson et al., 2012) with major Nd sources and their \( \varepsilon_{\text{Nd}} \) signatures as well as published surface seawater \( \varepsilon_{\text{Nd}} \) data (Andersson et al., 2008; Porcelli et al., 2009; Zimmermann et al., 2009; Persson et al., 2011; Charette et al., 2016; Laukert et al., 2017a, 2017b; Paffrath et al., 2021a). The Transpolar Drift (TPD) and the general circulation pattern of surface (dashed black arrows) and AW (black arrows) waters are shown in addition (modified after Rudels et al., 2012). The known Nd sources are Atlantic-derived waters (AW) entering through the Iceland-Scotland Ridge and the Denmark Strait, Norwegian Coastal Water (NCW), modified Pacific-derived waters (PAC), major Siberian Rivers (Ob, Yenisei, Lena, Kolyma), and the Mackenzie River.
Figure S-2  Averaged rare earth element (REE) concentrations of the different size pools in sea ice (upper figure) and snow (lower figure) samples normalised to Post Archaean Australian Shale (×10⁶; McLennan, 2001).
Figure S-3  Rare earth element (REE) concentrations of all sea ice and snow samples normalised to Post Archaean Australian Shale (×10^6; McLennan, 2001) with the corresponding averages (same colours as in Fig. S-1). For comparison, the reference material SLRS-4 is shown (500× dilution).
Figure S-4  High-resolution temperature and salinity profiles of fast ice (upper figures) and pack ice (lower figures). Temperature was averaged from 5 cm intervals.
Figure S-5  Reconstructed sea ice origin and drift trajectories from short-distance manual tracking (all fast ice stations and dashed lines for pack ice) using optical satellite data (MODIS - provided via https://worldview.earthdata.nasa.gov) and long-distance tracking (solid lines, only pack ice) based on the AWI IceTrack system (Krumpen et al., 2020).
Supplementary Information References


