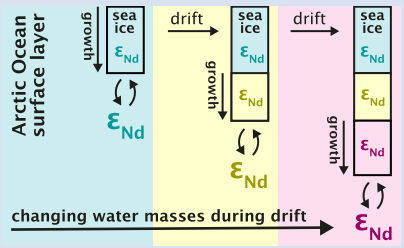
Geochemical Perspectives Letters

Neodymium isotopes trace marine provenance of Arctic sea ice

G. Laukert[1,2,3*], I. Peeken[4], D. Bauch[5], T. Krumpen[4], E.C. Hathorne[1], K. Werner[4,6], M. Gutjahr[1], M. Frank[1]

https://doi.org/10.7185/geochemlet.2220

Abstract



Radiogenic neodymium (Nd) isotopes (ε_{Nd}) have the potential to serve as a geochemical tracer of the marine origin of Arctic sea ice. This capability results from pronounced ε_{Nd} differences between the distinct marine and riverine sources, which feed the surface waters from which the ice forms. The first dissolved Nd isotope and rare earth element (REE) concentration data obtained from Arctic sea ice collected across the Fram Strait during RV *Polarstern* cruise PS85 in 2014 confirm the incorporation and preservation of the parental surface seawater ε_{Nd} signatures despite efficient REE rejection. The large ε_{Nd} variability between ice floes and within sea ice cores (−32 to −10) reflects changes in water mass distribution during ice growth and drift from the central Arctic Ocean to Fram Strait. In addition to the parental seawater composition, our new approach facilitates the reconstruction of the transfer of matter between the atmosphere, the sea ice and the ocean. In conjunction with satellite-derived drift trajectories, we enable a more accurate assessment of sea ice origin and spatiotemporal evolution, benefiting studies of sea ice biology, biodiversity, and biogeochemistry.

Received 6 January 2022 | Accepted 5 May 2022 | Published 10 June 2022

Introduction

The ongoing decrease in the age, thickness and extent of Arctic sea ice cover is projected to strongly impact climate, weather, ecosystems, matter fluxes and human activities in the near future (IPCC, 2022). The transition from a perennial ice cover with major sea ice transport systems to a seasonally ice-free ocean with isolated ice fields and floes of different origin is already impacting the distribution of gaseous, dissolved, and particulate matter, with far reaching consequences for Arctic ecosystems and biogeochemical cycles (*e.g.*, Krumpen *et al.*, 2019). Accurate knowledge of sea ice origin and drift is therefore required to understand the changing role of the marine cryosphere in regulating matter fluxes and ecological processes.

Satellite-based sea ice motion products are currently the only available resource for reconstructing sea ice origin and drift trajectories (Krumpen *et al.*, 2021). However, these mainly provide information about ice and atmospheric conditions, while the water mass distribution during ice growth and drift remains unexplored. Biological and biogeochemical processes in sea ice are, however, tightly linked to the parental seawater composition. Geochemical provenance tracers have the potential to reveal this composition as well as biogeochemical atmosphere-ice-ocean exchange during drift, thus ideally complementing satellite-based observations.

Radiogenic neodymium (Nd) isotopes (expressed as $\varepsilon_{Nd} = (^{143}Nd/^{144}Nd)_{sample}/(^{143}Nd/^{144}Nd)_{CHUR} - 1\} \times 10^4$, with CHUR = 0.512638; Jacobsen and Wasserburg, 1980) are a powerful tracer of water mass mixing and ocean circulation (Frank, 2002), but their application as a tracer of the water masses from which sea ice forms is novel. This potential results from the incorporation of small amounts of Nd from the ocean surface layer into sea ice during sea ice growth (Laukert *et al.*, 2017c). Due to salt-proportional rejection, the concentrations of Nd and other rare earth elements (REEs) in sea ice drop below those of seawater. This makes precise and accurate ε_{Nd} analysis difficult but can be compensated for by larger sample volume.

In the Arctic Ocean, the ε_{Nd} signature of surface waters reflects contributions from water masses and major rivers and ranges between −17 and −5.5 (see Fig. S-1 and description of marine ε_{Nd} systematics in the Supplementary Information; Andersson *et al.*, 2008; Porcelli *et al.*, 2009; Laukert *et al.*, 2017a, 2017b, 2017c, 2019; Paffrath *et al.*, 2021). Significantly less radiogenic ε_{Nd} signatures (<−17) are only introduced *via* discharge from Greenland and the Canadian Arctic Archipelago (Filippova *et al.*, 2017; Laukert *et al.*, 2018; Grenier *et al.*, 2022). Four ice floes sampled in the central Arctic Ocean in 2012 had ε_{Nd} compositions similar to their parental waters (Laukert *et al.*, 2017c), pointing to the incorporation of seawater ε_{Nd} signatures during sea ice growth. However, these samples

1. GEOMAR Helmholtz Centre for Ocean Research, Kiel, Germany
2. Department of Oceanography, Dalhousie University, Halifax, Canada
3. Woods Hole Oceanographic Institution, Woods Hole, USA
4. Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research, Bremerhaven, Germany
5. Christian-Albrecht University of Kiel, Kiel, Germany
6. University of Rostock, Rostock, Germany
* Corresponding author (email: georgi.laukert@dal.ca)

were unfiltered and direct contributions from particulate phases could not be excluded.

To further explore the suitability of Nd isotopes for tracing the marine origin of sea ice, we determined dissolved Nd isotopes along with salinity, temperature, stable oxygen isotopes and the complete set of REEs in different sea ice cores collected from ice floes in Fram Strait during cruise PS85 of RV *Polarstern* in 2014. Comparison with snow cover and surface seawater properties as well as ice drift trajectories reconstructed with IceTrack (Krumpen *et al.*, 2019) allows us to significantly expand our knowledge of the mechanisms controlling ε_{Nd} in the marine cryosphere.

Tracer Data and Satellite-Based Sea Ice Origin

The tracer data were determined in sea ice and snow samples collected from nine sea ice floes of different sizes, ages, and origins across Fram Strait as well as in nearby surface seawater (Fig. 1; see Supplementary Information for methodology and data). Based on visual inspection, the ice cores and the filters used for filtration of the melted sea ice samples were free of ice rafted detrital material. The dissolved ε_{Nd} of the sea ice ranges between −31.6 and −10.1, while less variability is observed in snow and surface seawater (average $\varepsilon_{Nd} = -14.7 \pm 1.0$ and -11.1 ± 0.7, respectively; 1 s.d., $n = 7$). The least radiogenic ε_{Nd} compositions were determined in the lowermost ice core intervals at stations 419, 454 and 472 and correspond to highest Nd concentrations ([Nd]) and the lowest heavy (H) to light (L) REE ratios normalised to PAAS (Post Archaean Australian Shale $\times 10^6$; see Supplementary Information) (Fig. 1). A low HREE/LREE ratio generally indicates exchange with freshly weathered rock material and is characteristic of freshwater that has been recently discharged to the ocean (*e.g.*, Laukert *et al.*, 2017a). [Nd] and HREE/LREE in our sea ice correlate well with ε_{Nd} ($R^2 = 0.75$ and 0.86, respectively; Fig. 2a,b). A correlation is also observed between HREE/LREE and ε_{Nd} ($R^2 = 0.7$) for surface seawater despite the smaller range in ε_{Nd} compositions. In contrast, no significant correlations between any of these parameters exist for the snow samples. On average, REE patterns from sea ice are similar in the dissolved (<0.45 µm) and truly dissolved (<3 and 30 kDa) size fractions, exhibiting LREE depletion and negative Ce anomalies, whereas REE patterns in snow are much flatter, consistent with the origin of REEs from atmospheric aerosols (Figs. S-2, S-3). The truly dissolved REE concentrations of sea ice average ~85 % of the dissolved REEs, except at station 481 where only ~55 % of the dissolved REEs were present in the truly dissolved pool. In snow, the truly dissolved concentrations average 50–60 % of the dissolved REEs. The dissolved [REE] in sea ice on average correspond to only 10–30 % of the dissolved [REE] of Arctic surface seawater.

The stable oxygen isotope signatures ($\delta^{18}O$) of the sea ice range from −5.8 to −0.7 ‰ at an average salinity of 3.6 ± 0.8 (1 s.d., $n = 29$). Melting of sea ice is evidenced by near zero salinities only for the upper 50 cm of station 481 and the uppermost 10 cm of stations 461 and 472 (Fig. S-4). The snow samples have more negative $\delta^{18}O$ values reaching ~−23 ‰ and salinities approaching zero, consistent with atmospheric deposition. Neither salinity nor $\delta^{18}O$ in sea ice or snow correlate with [Nd], HREE/LREE or ε_{Nd} (Fig. 2c,d). Surface seawater $\delta^{18}O$ values are not available for our samples but likely range between −2.8 and +0.3 ‰ (Laukert *et al.*, 2017a).

Tracking of sea ice drift based on satellite data (see Supplementary Information) reveals that the ice floes of stations 419 and 426 originated from the nearby Norske Øer Ice Barrier (NØIB), a fast ice field that forms along East Greenland's coast and was sampled directly at station 408 (Fig. 1). The common origin of this ice is confirmed by similar temperature and salinity profiles, except at station 408 where near-freezing temperatures reflect direct sampling from the NØIB (Fig. S-4). According to IceTrack, all other ice floes originated from ice fields of the central Arctic Ocean transported *via* the Transpolar Drift (Fig. S-5). Exactly where and when the individual ice floes were formed along the drift route cannot be determined from IceTrack alone. However, the different ice thicknesses of these floes indicate that they must have formed at different times and places along the route.

Reconstructing Marine Provenance of Sea Ice and Atmosphere-Ice-Ocean Exchange

Our data show that the dissolved ε_{Nd} signature of surface seawater is incorporated into sea ice during growth and preserved during transport despite rejection of up to ~90 % of the seawater REEs. Most upper ice core intervals have an ε_{Nd} signature between −15 and −10 and a salinity normalised [Nd] of ~1 pmol, which is within the compositional range of surface seawater in the central Arctic Ocean (Fig. 3a) and hence in agreement with ice growth along the drift route reconstructed for the pack ice floes (Fig. S-5). We use the ratio of [Nd] and salinity ([Nd]/S) to correct for salt-proportional rejection of Nd, which enables direct comparison between sea ice and seawater (Laukert *et al.*, 2017c). The least radiogenic ε_{Nd} signatures reported to date for waters circulating in the vicinity of Greenland (~−24; Laukert *et al.*, 2018) are more positive than the values determined in the lower ice core intervals at stations 419, 454, and 472 (reaching ~−32). However, despite the lack of published seawater data with similarly low signatures, these likely were introduced from Greenland through erosion and weathering of metamorphic rocks with even lower ε_{Nd} reaching values of ~−42 (Laukert *et al.*, 2017a and references therein). Dissolved ε_{Nd} signatures of Canadian rivers draining the same lithologies in a similar glacial environment are as low as those in our ice cores and, due to the very high [Nd] and despite estuarine REE removal, likely extend well beyond coastal areas once introduced into the surface ocean (Grenier *et al.*, 2022). Similarly unradiogenic ε_{Nd} signatures are therefore expected for surface waters near Greenland that were incorporated into sea ice at the end of the Transpolar Drift at stations 419, 454, and 472. Alternatively, the partial dissolution of small labile particulate phases originating from Greenland and incorporated during sea ice formation and drift or during sample processing may explain the very negative signatures. However, the ice core intervals with these signatures have [Nd]/S and HREE/LREE/S values for a given ε_{Nd} similar to Greenland coastal waters or sea ice expected to form from them (Fig. 3; the slight offset between actual and expected HREE/LREE/S values in sea ice reflects a process discussed below), which strongly suggests that these signals reflect direct incorporation of Greenland meltwater. Besides, a contribution of Greenland-sourced particles to the sea ice signal would not change our interpretation, given that their distribution in surface waters will not be significantly different from that of Greenland-sourced meltwater.

At station 419, despite the proximity to the Greenland coast, surface seawater ε_{Nd} signatures were around −11 and thus differed markedly from the sea ice ε_{Nd} of −27.6. The ice floes from stations 454 and 472 originated from the central Arctic Ocean and have similar ice core lengths and ε_{Nd} distributions.

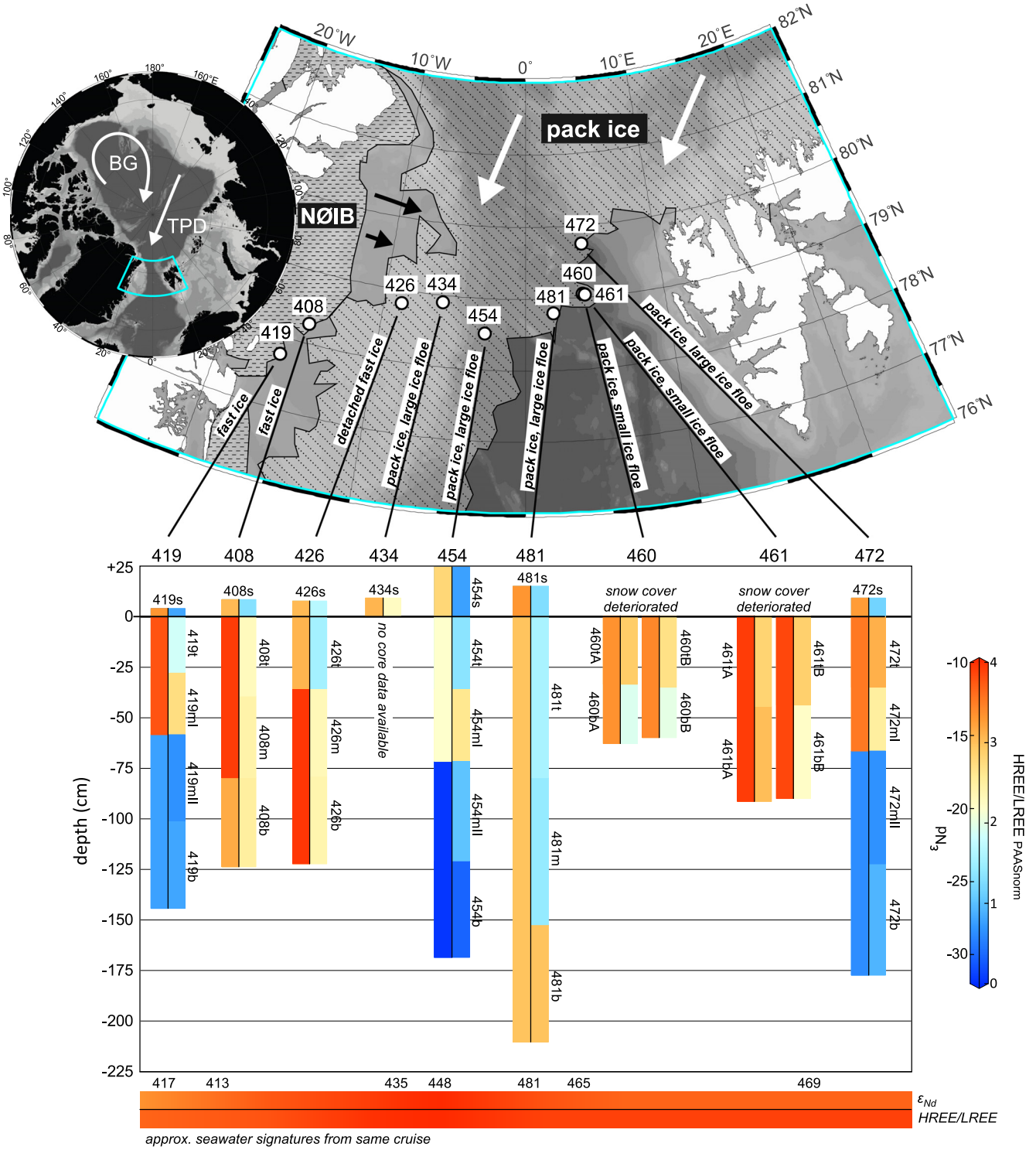


Figure 1 Locations of sea ice stations with approximate distribution of pack ice transported *via* the Transpolar Drift (TPD) and fast ice comprising the Norske Øer Ice Barrier (NØIB) in the Fram Strait in June 2014 obtained from satellite data. In addition, ice transport *via* the Beaufort Gyre (BG) is indicated in the overview map. Below, the ε_{Nd} (left bars) and HREE/LREE (right bars) distributions in snow cover and sea ice cores are shown together with surface seawater signatures of nearby stations (horizontal bar at the bottom).

They likely acquired their unradiogenic signatures from coastal waters advected to the area northeast of Greenland *via* the North-East Greenland Coastal Current (Laukert *et al.*, 2017a). The multi-year ice at station 419 thus likely originated from the same area before it attached to the NØIB prior to sampling. In contrast to ε_{Nd}, $\delta^{18}O$ is insensitive to Greenland meltwater incorporation due to indistinguishable $\delta^{18}O$ values in surface waters along the East Greenland coast and Arctic open ocean waters (> ~−3 ‰; Laukert *et al.*, 2017a).

The lower ice core interval at station 481 has some of the highest HREE/LREE of all cores, which argues against incorporation of Greenland meltwater. The ε_{Nd} signature of −15.5 thus can neither be entirely explained by meltwater incorporation nor by infiltration of snow meltwater (ε_{Nd} = −13.7). Instead, it most

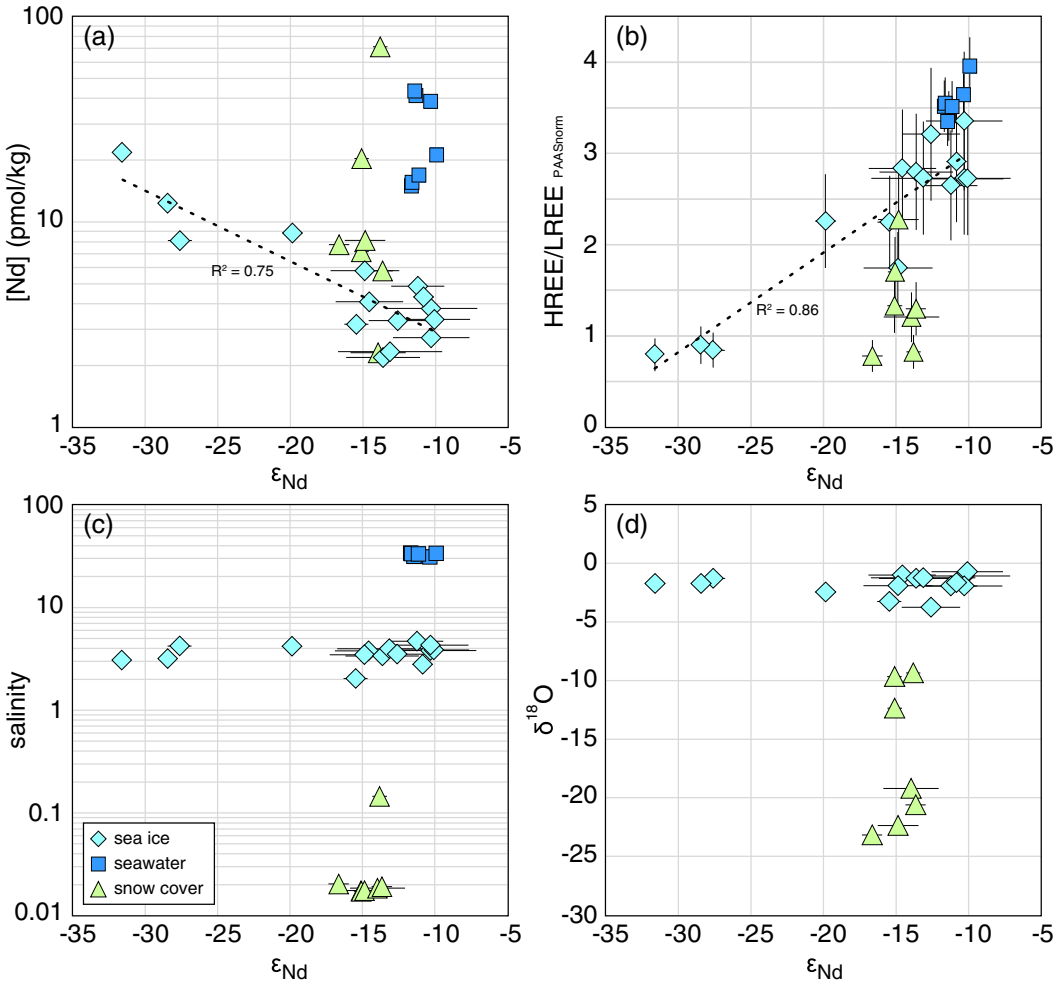


Figure 2 Comparison of ε_{Nd} with **(a)** [Nd], **(b)** HREE/LREE, **(c)** salinity and **(d)** $\delta^{18}O$ for all samples from this study.

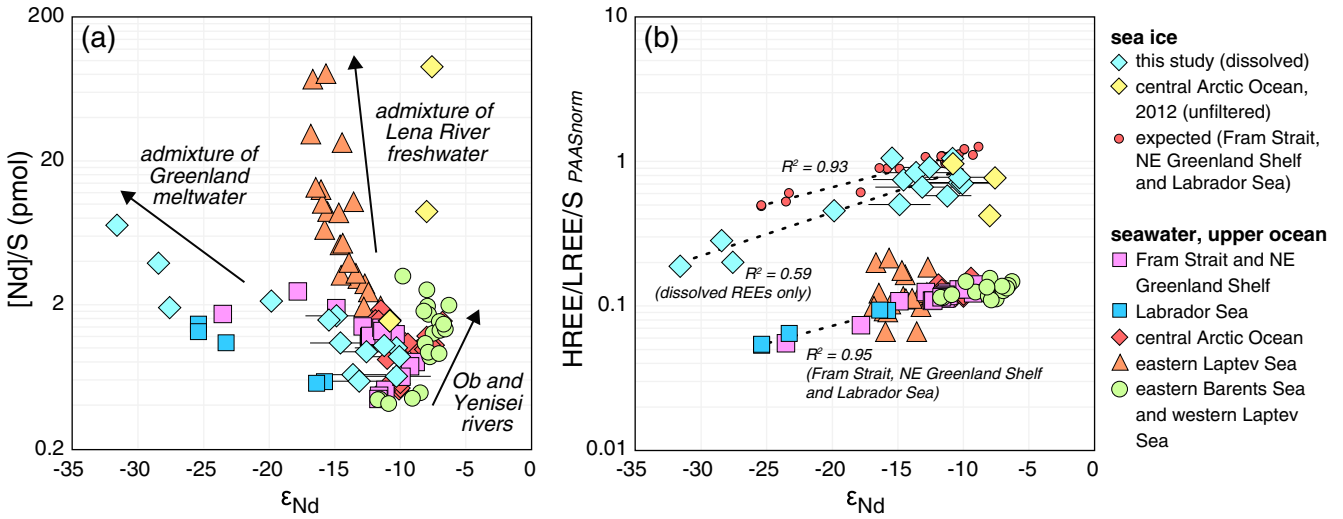


Figure 3 Comparison between ε_{Nd} and **(a)** [Nd]/S and **(b)** HREE/LREE/S for sea ice and seawater samples from this study and from the literature (see main text for references). Expected HREE/LREE/S values for sea ice were calculated by normalising seawater HREE/LREE values with the average salinity of the sea ice samples (3.6) instead of the seawater salinity.

likely reflects the uptake of Nd from Lena River freshwater characterised by an ε_{Nd} of ~−17 to ~−16 (Laukert *et al.*, 2017b). This is supported by a relatively low $\delta^{18}O$ value of −5.8 ‰ in the upper ice core interval and differences in the REE distribution between the different size fraction pools. The incorporation of a higher fraction of colloidal REEs (>30 kDa) at station 481 (~45 %) than at all other stations (~15 %) is consistent with incorporation of river-borne REEs and colloids from the Lena

River (Laukert *et al.*, 2017b). The near zero salinity in the upper ice core interval at this station indicates advanced melting from the previous year, also supporting the formation of this multi-year ice in the Laptev Sea and its long distance transport across the central Arctic Ocean.

The salt-normalised HREE/LREE values in sea ice are slightly lower than expected for a salt-proportional REE rejection with no change in the HREE/LREE ratio (Fig. 3b). The rejection is thus stronger for the HREEs than for the LREEs, which also explains the overall lower HREE/LREE ratios in sea ice compared to surface seawater. Despite the preferential rejection of HREEs, the differences in HREE/LREE between the parental source waters are maintained, as evidenced by a trend towards lower HREE/LREE/S values with decreasing ε_{Nd} in both sea ice and seawater. Lower HREE/LREE ratios were also observed in unfiltered sea ice samples from the central Arctic Ocean and were attributed to the contribution of particulate LREEs or differences in the incorporation of distinct size fraction pools (Laukert *et al.*, 2017c). Our dissolved and truly dissolved REE data allow us to exclude any direct contributions from particulate phases and instead indicate the elemental fractionation of dissolved REEs resulting from differential seawater/brine speciation. Preferential HREE rejection into the water column could also account for the accumulation of dissolved HREEs in bottom waters of the Laptev Sea (Laukert *et al.*, 2017b) but this requires further investigation in future dedicated process studies.

Conclusions

Our data demonstrate that Nd isotopes are a powerful tracer of the marine provenance of Arctic sea ice and biogeochemical atmosphere-ice-ocean exchange in combination with other source sensitive parameters. Even if exchange between sea ice and seawater immediately before sampling cannot be fully excluded at some stations due to indistinguishable ε_{Nd} signatures, the highly unradiogenic signatures of the Greenland-influenced ice floes suggest that, despite near zero temperatures, ε_{Nd} signatures of sea ice are largely preserved during periods in which the ice does not grow and even during periods of melting. Combined with satellite-derived sea ice motion products, our new approach enables a more accurate assessment of the water mass composition during sea ice growth and drift, which is essential for studies of sea ice formation and marine biology, biodiversity and biogeochemistry.

Author Contributions

GL and IP conceived the study. IP took the sea ice samples. TK reconstructed sea ice trajectories. GL prepared the samples and analysed Nd isotopes together with MG and rare earth elements together with EH. DB overlooked stable oxygen isotope sampling and analysis. All authors were involved in writing the manuscript, data interpretation and discussion.

Acknowledgements

We thank the Captain and Crew of the RV *Polarstern* for their help in collecting and transporting the samples and the chief scientist Ingo Schewe for his support (AWI_PS85_04). We also thank Antje Wildau for collecting the seawater samples and Ulrike Dietrich, Lars Chresten Lund-Hansen, Brian Keith Sorrell and Bibi Ziersen for their help with the sea ice work. Jutta Heinze is acknowledged for laboratory assistance. We acknowledge financial support by the German Federal Ministry of Education and Research (Grant BMBF 03F0776 and 03G0833) and the Ministry of Education and Science of the Russian Federation. GL also acknowledges financial support from the Ocean Frontier Institute through an award from the Canada First Research Excellence Fund. The authors declare no conflicts of interest relevant to this study.

Editor: Gavin Foster

Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2220.

Cite this letter as: Laukert, G., Peeken, I., Bauch, D., Krumpen, T., Hathorne, E.C., Werner, K., Gutjahr, M., Frank, M. (2022) Neodymium isotopes trace marine provenance of Arctic sea ice. *Geochem. Persp. Let.* 22, 10–15. https://doi.org/10.7185/geochemlet.2220

References

Andersson, P.S., Porcelli, D., Frank, M., Bjork, G., Dahlqvist, R., Gustafsson, O. (2008) Neodymium isotopes in seawater from the Barents Sea and Fram Strait Arctic-Atlantic gateways. *Geochimica et Cosmochimica Acta* 72, 2854–2867. https://doi.org/10.1016/j.gca.2008.04.008

Filippova, A., Frank, M., Kienast, M., Rickli, J., Hathorne, E.C., Yashayaev, I.M., Pahnke, K. (2017) Water mass circulation and weathering inputs in the Labrador Sea based on coupled Hf–Nd isotope compositions and rare earth element distributions. *Geochimica et Cosmochimica Acta* 199, 164–184. https://doi.org/10.1016/j.gca.2016.11.024

Frank, M. (2002) Radiogenic isotopes: tracers of past ocean circulation and erosional input. *Reviews of Geophysics* 40, 1–38. https://doi.org/10.1029/2000RG000094

Grenier, M., Brown, K.A., Colombo, M., Belhadj, M., Baconnais, I., Pham, V., Soon, M., Myers, P.G., Jeandel, C., François, R. (2022) Controlling factors and impacts of river-borne neodymium isotope signatures and rare earth element concentrations supplied to the Canadian Arctic Archipelago. *Earth and Planetary Science Letters* 578, 117341. https://doi.org/10.1016/j.epsl.2021.117341

IPCC (2022) *Climate Change 2022: Impacts, Adaptation, and Vulnerability*. Contribution of Working Group II to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change [Pörtner, H.-O., Roberts, D.C., Tignor, M., Poloczanska, E.S., Mintenbeck, K., Alegría, A., Craig, M., Langsdorf, S., Löschke, S., Möller, V., Okem, A., Rama, B. (Eds.)]. Cambridge University Press, in press.

Jacobsen, S.B., Wasserburg, G.J. (1980) Sm-Nd Isotopic Evolution of Chondrites. *Earth and Planetary Science Letters* 50, 139–155. https://doi.org/10.1016/0012-821X(80)90125-9

Krumpen, T., Belter, H.J., Boetius, A., Damm, E., Haas, C., Hendricks, S., Nicolaus, M., Nöthig, E.-M., Paul, S., Peeken, I., Ricker, R., Stein, R. (2019) Arctic warming interrupts the Transpolar Drift and affects long-range transport of sea ice and ice-rafted matter. *Scientific Reports* 9, 1–9. https://doi.org/10.1038/s41598-019-41456-y

Krumpen, T., von Albedyll, L., Goessling, H.F., Hendricks, S., Juhls, B., Spreen, G., Willmes, S., Belter, H.J., Dethloff, K., Haas, C., Kaleschke, L., Katlein, C., Tian-Kunze, X., Ricker, R., Rostosky, P., Rückert, J., Singha, S., Sokolova, J. (2021) MOSAiC drift expedition from October 2019 to July 2020: sea ice conditions from space and comparison with previous years. *The Cryosphere* 15, 3897–3920. https://doi.org/10.5194/tc-15-3897-2021

Laukert, G., Frank, M., Bauch, D., Hathorne, E.C., Rabe, B., von Appen, W.-J., Wegner, C., Zieringer, M., Kassens, H. (2017a) Ocean circulation and freshwater pathways in the Arctic Mediterranean based on a combined Nd isotope, REE and oxygen isotope section across Fram Strait. *Geochimica et Cosmochimica Acta* 202, 285–309. https://doi.org/10.1016/j.gca.2016.12.028

Laukert, G., Frank, M., Bauch, D., Hathorne, E.C., Gutjahr, M., Janout, M., Hölemann, J. (2017b) Transport and transformation of riverine neodymium isotope and rare earth element signatures in high latitude estuaries: a case study from the Laptev Sea. *Earth and Planetary Science Letters* 477, 205–217. https://doi.org/10.1016/j.epsl.2017.08.010

Laukert, G., Frank, M., Hathorne, E.C., Krumpen, T., Rabe, B., Bauch, D., Werner, K., Peeken, I., Kassens, K. (2017c) Pathways of Siberian freshwater and sea ice in the Arctic Ocean traced with radiogenic neodymium isotopes and rare earth elements. *Polarforschung* 87, 3–13. https://doi.org/10.2312/polarforschung.87.1.3

Laukert, G., Dreyer, J., Frank, M., Hathorne, E.C., Meulenbroek, K. (2018) Greenland-sourced freshwater traced by radiogenic neodymium isotopes and rare earth elements on the North-East Greenland Shelf. *Goldschmidt Abstracts* 2018, 1419. https://goldschmidtabstracts.info/2018/1419.pdf

Laukert, G., Makhotin, M., Petrova, M.V., Frank, M., Hathorne, E.C., Bauch, D., Böning, P., Kassens, H. (2019) Water mass transformation in the Barents Sea inferred from radiogenic neodymium isotopes, rare earth elements and stable oxygen isotopes. *Chemical Geology* 511, 416–430. https://doi.org/10.1016/j.chemgeo.2018.10.002

Paffrath, R., Laukert, G., Bauch, D., Rutgers van der Loeff, M., Pahnke, K. (2021) Separating individual contributions of major Siberian rivers in the Transpolar Drift of the Arctic Ocean. *Scientific Reports* 11, 8216. https://doi.org/10.1038/s41598-021-86948-y

Porcelli, D., Andersson, P.S., Baskaran, M., Frank, M., Bjork, G., Semiletov, I. (2009) The distribution of neodymium isotopes in Arctic Ocean basins. *Geochimica et Cosmochimica Acta* 73, 2645–2659. https://doi.org/10.1016/j.gca.2008.11.046