Earth and Planetary Science Letters ••• (••••) •••–•••

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Transport and transformation of riverine neodymium isotope and rare earth element signatures in high latitude estuaries: A case study from the Laptev Sea

Georgi Laukert [a,*], Martin Frank [a], Dorothea Bauch [a], Ed C. Hathorne [a], Marcus Gutjahr [a], Markus Janout [b], Jens Hölemann [b]

[a] GEOMAR Helmholtz Centre for Ocean Research Kiel, Wischhofstr. 1-3, 24148 Kiel, Germany
[b] Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research, Am Handelshafen 12, 27570 Bremerhaven, Germany

A R T I C L E   I N F O

Article history:
Received 3 February 2017
Received in revised form 7 August 2017
Accepted 8 August 2017
Available online xxxx
Editor: D. Vance

Keywords:
Nd isotopes
rare earth elements
stable oxygen isotopes
seawater–particle interactions
estuarine processes
sea ice

A B S T R A C T

Marine neodymium (Nd) isotope and rare earth element (REE) compositions are valuable tracers for present and past ocean circulation and continental inputs. Yet their supply via high latitude estuaries is largely unknown. Here we present a comprehensive dissolved Nd isotope (expressed as ε_{Nd} values) and REE data set together with seawater stable oxygen isotope ($\delta^{18}O$) compositions of samples from the Laptev Sea recovered in two Arctic summers and one winter.

The Laptev Sea is a shallow Siberian Shelf sea characterized by extensive river-runoff, sea-ice production and ice transport into the Arctic Ocean. The large variability in ε_{Nd} (-6 to -17), REE concentrations (16 to 600 pmol/kg for Nd) and REE patterns is controlled by freshwater supply from distinct riverine sources and open ocean Arctic Atlantic Water. Strikingly and contrary to expectations, except for cerium no evidence for significant release of REEs from particulate phases is found, which is attributed to low amounts of suspended particulate matter and high dissolved organic carbon concentrations present in the contributing rivers. Essentially all shelf waters are depleted in light (L)REEs, while the distribution of the heavy REEs shows a deficiency at the surface and a pronounced excess in the bottom layer. This distribution is consistent with REE removal through coagulation of riverine nanoparticles and colloids starting at salinities near 10 and resulting in a drop of all REE concentrations by ~30%. With increasing salinity preferential LREE removal is observable reaching ~75% for Nd at a salinity of 34. Although the delayed onset of dissolved REE removal contrasts with most previous observations from other estuarine environments, it agrees remarkably well with results from recent experiments simulating estuarine mixing of seawater with organic-rich river waters. In addition, melting and formation of sea ice leads to further REE depletion at the surface and strong REE enrichment near the shelf bottom as a function of ice melting and brine transfer, respectively. The ice-related processes significantly affect the distribution of dissolved REEs in high-latitude estuaries and likely also similarly contribute to the redistribution of other dissolved seawater constituents.

1. Introduction

The radiogenic neodymium (Nd) isotopes (the $^{143}Nd/^{144}Nd$ ratio, expressed as $\varepsilon_{Nd} = [(^{143}Nd/^{144}Nd)_{sample}/(^{143}Nd/^{144}Nd)^{CHUR} - 1] \times 10^4$ with CHUR = 0.512638 referring to the 'CHondritic Uniform Reservoir', Jacobsen and Wasserburg, 1980) have been widely used to trace modern and past ocean circulation (cf. Frank, 2002; van de Flierdt and Frank, 2010). In addition to Nd isotopes, the complete set of dissolved rare earth elements (REEs, here including yttrium) has been shown to provide constraints on the composition of the source areas, on the time that passed since last contact of a water mass with weathering inputs, as well as on particle adsorption and desorption processes (e.g. Haley et al., 2014; Molina-Kescher et al., 2014; Rousseau et al., 2015). The Nd isotope and REE distribution in the open Arctic Ocean reflects the lateral advection of water masses and their mixing (Andersson et al., 2008; Laukert et al., 2017a; Porcelli et al., 2009) but fluxes and behavior of these tracers in Arctic estuarine regions, such as the freshwater-dominated Siberian Shelf seas, are largely unknown. This has so far prevented the utilization of the full potential of Nd

* Corresponding author.
E-mail address: glaukert@geomar.de (G. Laukert).

http://dx.doi.org/10.1016/j.epsl.2017.08.010

Please cite this article in press as: Laukert, G., et al. Transport and transformation of riverine neodymium isotope and rare earth element signatures in high latitude estuaries: A case study from the Laptev Sea. Earth Planet. Sci. Lett. (2017), http://dx.doi.org/10.1016/j.epsl.2017.08.010

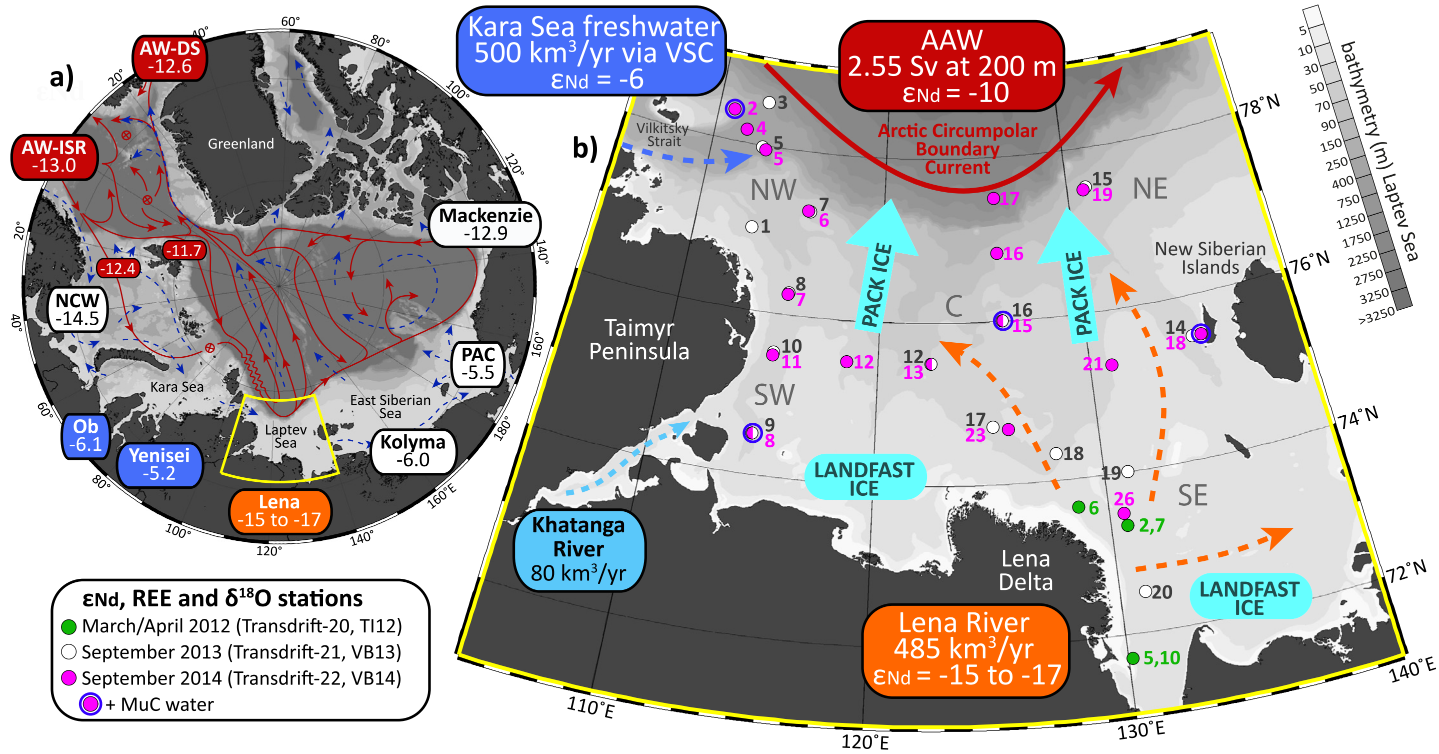

Fig. 1. a) Bathymetric map (IBCAO, Jakobsson et al., 2012) of the Arctic Mediterranean (i.e. Nordic Seas and Arctic Ocean) with circulation scheme of the upper layers (dashed blue lines) and subsurface Atlantic and intermediate layers (solid red lines) (modified after Rudels et al., 2012). REE sources with known ε_{Nd} values and [Nd] are Atlantic-derived waters entering through the Iceland–Scotland Ridge (AW-ISR) and the Denmark Strait (AW-DS), Norwegian Coastal Water (NCW), Pacific-derived water (PAC) and the major Arctic rivers Ob, Yenisei, Lena, Kolyma and Mackenzie (Laukert et al., 2017a and references therein). The area shown in b) is highlighted in yellow. b) Laptev Sea region with the Arctic Boundary Current (estimated mean volume transport at 104°E is from Aksenov et al., 2011, and given in Sv, i.e. in 10^6 m^3/s) and potential freshwater pathways (mean annual freshwater transport for the Khatanga and Lena rivers is taken from R-Arctic-NET: http://www.r-arcticnet.sr.unh.edu/, and for Kara Sea freshwater provided by Janout et al., 2015). Known REE sources are shown together with their ε_{Nd} values. Arctic Atlantic Water (AAW) is modified AW at ∼200 m depth. Stations of this study are shown as color-coded symbols along with station numbers. Figures were produced using Ocean Data View (Schlitzer, 2017) and modified manually. (For interpretation of the colors in this figure, the reader is referred to the web version of this article.)

isotopes and REEs to determine water mass sources and mixing in the entire Arctic Ocean and to provide information on inputs and ice-related processes in freshwater and sea-ice dominated high latitude shallow marginal seas beyond what is provided by classical hydrographic parameters.

The Laptev Sea is a wide and shallow Siberian Shelf sea characterized by extensive river runoff, strong sea-ice formation and sea-ice transport into the open Arctic Ocean (Fig. 1). The upper water column of the central and southeastern (SE) Laptev Sea is dominated by variable freshwater contributions from the Lena River, whereas the northwestern (NW) Laptev Sea is influenced by freshwaters from the Yenisei and Ob Rivers advected from the Kara Sea via the Vilkitsky Strait Current (VSC; Janout et al., 2015). Except for areas with frequently opening polynyas (i.e. regions of open water), the Laptev Sea is ice-covered in autumn and winter with mobile pack ice on the deeper shelf and immobile landfast ice in the vast shallower near-shore regions (Bareiss and Görgen, 2005). During these times of the year, brine transfer resulting from sea-ice formation is accompanied by storms and tidal mixing, which erode the stratification and lead to a well-mixed water column by late winter or spring (Janout et al., 2016). The maximum freshwater runoff is reached in May and June and coincides with the onset of sea-ice melting, which induces a strong stratification separating the fresher surface waters from the more saline 'winter waters'. Given that this seasonal variability and the corresponding hydrological features are similar to other high latitude estuarine settings, investigating Nd isotope and REE behavior in the Laptev Sea may have broad implications.

Here we report the first comprehensive dissolved water column Nd isotope and REE data sets for the entire Laptev Sea, which are combined with seawater stable oxygen isotope data obtained from the same samples. In addition, we provide the first winter data obtained from seawater sampled near the Lena Delta. We examine if dissolved Nd isotopes behave conservatively on the Siberian shelves and thus can be applied to trace water mass advection and mixing. We also investigate how formation and melting of sea ice affect the distribution of dissolved Nd isotopes and REEs.

2. Material and methods

The samples presented were obtained during Transdrift expeditions 20–22 in late winter 2012 and the summers of 2013 and 2014 (Fig. 1). In March/April 2012 (Transdrift-20), sampling was conducted with 2 L Niskin-type bottles at three ice camps in the landfast ice area east and northeast of the Lena Delta. During Septembers of 2013 and 2014 (Transdrift-21 and -22, respectively), samples were recovered along with CTD (conductivity, temperature, depth) profiles with a SBE 32 rosette water sampler equipped with 12 Niskin bottles (2.5 L) under ice-free conditions onboard the Russian research vessel RV Viktor Buynitskiy on the entire Laptev Sea shelf and above the shelf slope (down to ∼310 m depth). Most stations of the 2013 expedition were resampled in 2014 (Fig. 1) enabling direct interannual comparison and detection of seasonal variability. Where possible, one surface sample (between 2 and 7 m water depth) and one near-bottom sample (few meters above ground) were collected at each station. The seasonal pycnoline was not sampled, given that this hydrographic transition