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An Arctic Ocean paleosalinity proxy from δ^2H of palmitic acid provides evidence for deglacial Mackenzie River flood events

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A B S T R A C T

The hydrogen isotopic composition ($^2H/^1H$, or δ^2H) of palmitic acid (PA) was measured in surface sediments from the Laptev and Kara Seas in the Russian Arctic to evaluate its use as a paleohydrographic proxy. δ^2H_{PA} values in surface sediments varied by 118‰ over a 21 ppt range in mean annual surface salinity, and the two properties were highly correlated ($R^2 = 0.8$, $p < 0.001$) according to the relationship $\delta^2H_{PA} = 4.22$ (±0.60)*S - 338 (±15). In contrast, δ^2H values of vascular plant wax *n*-alkanes (nC_{27}, nC_{29}, nC_{31}) did not change systematically with salinity. These differing lipid δ^2H trends support the interpretation of PA as derived primarily from marine microalgae at these sites. Both the range and absolute values of δ^2H_{PA} compared favorably to those predicted from published Arctic Ocean salinity and water isotope data and the expected response of δ^2H_{PA} to salinity in cultured phytoplankton. Some 64–74% of the observed sedimentary δ^2H_{PA} increase is estimated to have resulted from increasing δ^2H_{water} values, with the remainder resulting from decreased ^2H-discrimination during lipid biosynthesis at higher salinities. The large signal and high sensitivity of δ^2H_{PA} to surface salinity changes in the Russian Arctic was exploited to test the hypothesis that floodwaters emanated from the Mackenzie River during the late deglacial period. Measurements of δ^2H_{PA} were performed in a sediment core from the continental slope off the Mackenzie River in the Canadian Arctic. In samples from the top Bølling/Allerød-Younger Dryas period, reconstructed surface salinities (and δ^2H_{PA} values) off the Mackenzie River declined from 20 (−253‰) to 16 (−269‰) before rebounding to 24 (−236‰) in the early Holocene, close to the modern value of ~25. A large salinity depression in the Canadian Arctic just prior to the start of the Younger Dryas would support the hypothesis of a northern routing of flood-waters from glacial Lake Agassiz via the Mackenzie River as a trigger for the Younger Dryas event.

1. Introduction: background and approach

The Arctic Ocean plays a key role in the climate system, owing to the strong feedback between sea ice and air temperature (i.e., the ice-albedo feedback) and the export of buoyant, low-salinity water to North Atlantic Ocean regions where deep convection drives the global thermohaline circulation (Serreze and Barry, 2011; Stocker, 2014; Thomas and Dieckmann, 2010). It is noteworthy, then, that Arctic sea ice cover has been declining rapidly over the last 30 years as the Arctic Ocean has warmed at twice the rate of the planet as a whole (Comiso et al., 2017; Ding et al., 2017). At the same time, large portions of the Arctic Ocean have been freshening as a result of increased river runoff, enhanced precipitation, and both oceanic and atmospheric circulation changes (Mauritzen, 2012). Discharge from rivers in the Russian Arctic, for instance, increased some 20% between 1987 and 2007 (Shiklomanov and Lammers, 2009). Freshening in the Eastern Arctic, however, has been countered since the 1990s by the inflow of surface waters from the Atlantic with a higher salinity than in earlier decades (Holliday et al., 2008). While anthropogenic climate change has likely been a primary driver of

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these changes, natural variations internal to the climate system have also played a role, with as much as half the decline in summer sea ice concentrations since 1979 attributed to natural processes (Ding et al., 2017). Diminished sea ice cover in the Arctic, regardless of cause, creates positive buoyancy anomalies that weaken the Atlantic Meridional Overturning Circulation (AMOC) in models (Sevellec et al., 2017), a process that may already be underway (Smeed et al., 2014).

What is clear from these and other studies is that (1) Arctic climate is highly variable year-to-year, (2) climatic trends in the Arctic can last for decades, only to reverse without warning, (3) both natural and anthropogenic processes play important roles in these changes, and (4) a short instrumental record prevents firm conclusions from being drawn regarding the attribution of Arctic climate changes to specific forcing. One way to augment this short instrumental record is to develop Arctic paleoclimate proxy records with high temporal and spatial resolution. Attempts to do this have been hampered, however, by a dearth of well-dated, high accumulation-rate sediment cores from the Arctic Ocean, due in part to low primary production rates in seasonally or permanently ice-covered surface waters with limited insolation (Sakshaug, 2004; Wassmann, 2011). Furthermore, several proxies common to low- and mid-latitude paleoceanography have limitations in the Arctic Ocean (discussed below and by Stein, 2008).

Despite these difficulties, multiple studies based on sedimentological, geochemical and micropaleontological proxies have documented significant natural variations in Arctic sea ice concentration (e.g. Belt et al., 2015; Cronin et al., 2013; de Vernal et al., 2013; Fahl and Stein, 2012; Müller et al., 2009; Nørgaard-Pedersen et al., 2003; Stein et al., 2017; Xiao et al., 2015), river runoff (e.g. Fahl and Stein, 2007; Hörner et al., 2016; Polyakova and Stein, 2004; Spielhagen et al., 2005; Stein, 2000; Stein et al., 2004), and surface-water salinity (e.g. Spielhagen and Erlenkeuser, 1994; Stein et al., 1994; Volkmann and Mensch, 2001) during the late Quaternary. Each of the proxies used in these studies has shortcomings, though, and virtually all Arctic paleoceanographic proxies are indirect and qualitative indicators of surface-water characteristics.

While there has been recent development of a semi-quantitative method with which to reconstruct sea ice distributions from the sedimentary concentration of a C_{25} highly branched isoprenoid (C_{25} HBI monoene, IP_{25}; Belt et al., 2007, 2015; Müller et al., 2011; Xiao et al., 2015), there remains a need for additional (semi-) quantitative proxies of surface water salinity and river runoff that can be widely applied throughout the Arctic. One outstanding question in Quaternary paleoclimatology that could be addressed with salinity reconstructions in the Arctic concerns the origin, magnitude, and timing of freshwater discharge that occurred during the brief return to glacial conditions some 13-12 ka BP known as the Younger Dryas. Toward that end, we report the results of hydrogen isotope ($^2H/^1H$) measurements in lipid biomarkers from phytoplankton and terrestrial vascular plants in two surface-sediment transects along salinity gradients in the Kara and Laptev Seas.

The hydrography of these marginal seas is influenced by the inflow of warm, saline Atlantic water and the supply of freshwater from large rivers. The Atlantic water enters the Arctic Ocean through Fram Strait and the Barents Sea before continuing east towards the central and northern Kara and Laptev seas (Fig. 1). Freshwater discharge into the Kara and Laptev seas comes predominantly from the Yenisey, Ob, and Lena Rivers. With a combined discharge exceeded only by the Amazon, these rivers drain about 60% of the Eurasian Arctic landmass (Peterson et al., 2002) and transport large fluxes of suspended organic and inorganic particulate material to the Arctic continental shelf (e.g. Fahl and Stein, 2007; Stein et al., 2004; Stein and MacDonald, 2004).

The large flux of runoff into the Kara and Laptev Seas results in large surface salinity gradients (from 11 to 32) across the studied transects (Table 1 and Fig. 1). Over that range, one would expect the δ^2H values of phytoplankton lipids (such as palmitic acid, an unsaturated C_{16} fatty acid) to increase by several permil per ppt due to the combined effects of (1) highly ^2H-depleted freshwater emanating from the Yenisey, Ob and Lena Rivers, and (2) decreasing $^2H/^1H$ fractionation during lipid synthesis at higher salinity (Heinzelmann et al., 2015; M'boule et al., 2014; Maloney et al., 2016; Sachs et al., 2016; Schouten et al., 2006; Weiss et al., 2017). Although palmitic acid (PA) is produced by most organisms — marine and terrestrial, autotrophic and heterotrophic — multiple lines of evidence are presented that support marine phytoplankton as its primary source to Arctic Ocean sediments. We describe the empirical relationship between δ^2H_{PA} and SSS in this region, and demonstrate this relationship's utility by reconstructing salinity during the late deglacial period in two locations: the Canadian Arctic off the Mackenzie River (Beaufort Sea) and the Russian Arctic off the Lena River (Laptev Sea).

During the transition out of the last ice age, the decay of the large circum-Arctic ice sheets resulted in the discharge of large amounts of meltwater that likely depressed surface salinities in the Arctic Ocean. One such salinity depression likely occurred during the Younger Dryas event (Keigwin et al., 2018), which is thought to have been caused by meltwater-derived freshening of the North Atlantic Ocean that disrupted the AMOC (Broecker, 2006; Broecker et al., 1989; Emiliani et al., 1978; Johnson and McClure, 1976; Keigwin et al., 2018; Murton et al., 2010; Rooth, 1982; Teller, 1990; Teller et al., 2005). The exact source of this meltwater pulse, along with its magnitude and timing, has been the subject of great debate. Catastrophic drainage of glacial Lake Agassiz seems a widely-accepted candidate, but the route those flood-waters may have traveled to the sea — e.g., the Mississippi, St. Lawrence, and/or Mackenzie River (Fig. 2B) — has been difficult to confirm (see Sec. 4.3.1 for additional details). Here we use δ^2H_{PA} measurements in late deglacial sediments from the continental slope off the Mackenzie River to reconstruct salinity and evaluate whether floodwaters can be detected there, and compare these results to those from a second core, across the basin, on the continental slope off the Lena River.

2. Materials and methods

2.1. Field sampling

Surface sediments along two transects from the Laptev and Kara seas towards the central Arctic Ocean were used to establish a new lipid δ^2H approach for quantitatively reconstructing Arctic surface salinity. This method was then applied to a small set of late deglacial samples from two sediment cores.

2.1.1. Surface sediments

The sites included in the two surface sediment transects of the Kara and Laptev Seas are shown in Fig. 1. Samples from the Laptev Sea shelf-slope transect were taken during the *Polarstern* Expedition ARK XI/1 (1995) and the *Ivan Kireyev* Expedition Transdrift I (1993). Samples from the Yenisey-Kara Sea -North Pole transect were recovered during the *Akademik Boris Petrov* expeditions BP99, BP00 and BP01 in 1999, 2000, and 2001, respectively, and during the *Polarstern* Expedition ARK XXVI/3 in 2011 (for references to the cruise reports see Stein et al., 2004; Xiao et al., 2015). Sampling was carried out with a giant box corer and/or a multicorer. All samples were stored at $-30\,^\circ C$ until further treatment. Surface (0 m) salinity data to pair with these samples were obtained from $1^\circ \times 1^\circ$ objectively analyzed fields from the World Ocean Atlas 2013 (https://www.nodc.noaa.gov/OC5/woa13/woa13data.html; Zweng