Insights into Circum-Arctic sea ice variability from molecular geochemistry

Vera Stoynova [a], Timothy M. Shanahan [a,*], Konrad A. Hughen [b,1], Anne de Vernal [c,2]

[a] Jackson School of Geosciences, The University of Texas at Austin, Austin, TX 78712, USA
[b] Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA
[c] GEOTOP-UQAM-McGill, Montreal, Quebec, Canada H3C 3P8

ARTICLE INFO

ABSTRACT

Geological records of past sea ice, such as those contained in Arctic marine sediments, offer an opportunity to strengthen our understanding of long-term sea ice variability, provided unambiguous paleo-sea ice proxies can be developed. One such recently proposed proxy is IP$_{25}$, a highly branched isoprenoid alkene biosynthesized exclusively by sea-ice dwelling diatoms (*Haslea* spp.), which is well preserved in marine sediments and could be used to reconstruct past changes in spring sea-ice extent. However, little is known about regional-scale controls on IP$_{25}$ production in sea ice, limiting its wider applicability as a paleo-sea-ice proxy. To address this issue we examined the distributions of IP$_{25}$ and the marine productivity biomarkers dinosterol and brassicasterol in a suite of surface sediment samples distributed across the Arctic. We find a statistically significant, logarithmic relationship between IP$_{25}$ and spring sea ice cover in sediment samples from arctic and subarctic sites in the Pacific ($n = 96$, $R^2 = 0.67$, $P < 0.0001$) and the Atlantic $n = 25$, $R^2 = 0.50$, $P < 0.0001$), though the absolute concentrations of IP$_{25}$ are generally higher in the Atlantic (1.6–166.4 µg/g OC) than in the Pacific (0–38.5 µg/g OC) for equivalent sea-ice cover, and there are regional and basin-specific differences in the slope of the IP$_{25}$ − sea ice relationship. Using the P$_D$IP$_{25}$ index, which also includes a biomarker for marine productivity (e.g., dinosterol) the relationship with sea ice cover is improved in all of the study areas ($R^2 = 0.86$ and $R^2 = 0.75$ for Atlantic and Pacific, respectively) and most basin specific differences in the proxy−sea ice relationships are significantly reduced. However, there remain differences in the absolute magnitudes of the P$_D$IP$_{25}$ index for equivalent amounts of sea ice cover between the Atlantic and the Pacific, and with previously published data from Fram Strait. Nevertheless, this work demonstrates that the P$_D$IP$_{25}$ index can provide a valuable tool for sea ice reconstructions at local and regional scales.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Recent satellite observations have revealed dramatic changes in Arctic sea ice over the last few decades, including a 39% reduction of spring sea ice extent and a 38% reduction in perennial sea ice cover (Comiso, 2002; Comiso et al., 2008; Drobot et al., 2008; Kwok and Rothrock, 2009; Maslanik et al., 2011; Stroeve et al., 2011, 2012). A record minimum in sea ice extent in September 2007 was followed by the second and third lowest sea ice extents in 2008 and 2010, and it has been suggested that if these current trends continue, the Arctic could be ice-free in summer within 30 years (Stroeve et al., 2008), with potentially dramatic changes in Arctic climate and biology (ACIA, 2005). However, the instrumental satellite record of sea ice variability spans a relatively short time period (1979-present), and longer instrumental reconstructions based on ship observations are spatially incomplete, making it difficult to assess whether recent changes in sea ice are anomalous in the context of longer term Arctic environmental change.

Geological records of past sea ice, such as those contained in Arctic marine sediments, offer an opportunity to strengthen our understanding of long-term sea ice variability, provided unambiguous paleo-sea ice proxies can be developed. A variety of proxies have been used to qualitatively reconstruct sea ice ranging from ice-rafted debris (IRD) to microfossils (Gersonde and Zielinski, 2000; Gorbarenko et al., 2010; Gregory et al., 2010). However, microfossil (both calcareous and siliceous) species assemblage techniques can be biased by dissolution and a lack of species diversity at high latitude-sites (Thomas and Dieckmann, 2010). Though dinocyst-based reconstructions are less susceptible to dissolution and show excellent spatial correlations with modern sea ice cover (de Vernal et al., 2000, 2005a, 2005b; Mudie et al.,

2001; McKay et al., 2008), as with other biological proxies, dinocysts lack indicator species that are known to be exclusively associated with sea ice.

Recently, a novel molecular sea ice proxy, IP_{25}, (Ice Proxy with 25 carbons) has been proposed (Belt et al., 2007). The IP_{25} index is based on the concentration of a monounsaturated highly branched isoprenoid (HBI) alkene which is believed to be produced exclusively by diatoms living in sea ice (Belt et al., 2007). Studies examining open-water phytoplankton from across the Canadian Arctic show no evidence of IP_{25} (Belt et al., 2007) and the highest IP_{25} abundances in modern sea ice occur 1–3 cm away from the ice–water interface, suggesting that the IP_{25} is produced only within the ice itself (Brown et al., 2011). In surface sediment samples, IP_{25} is only found in association with modern sea ice cover, and generally increases in abundance with increased ice cover duration (Belt et al., 2007; Müller et al., 2011). Furthermore, carbon isotope analysis of IP_{25} in Arctic surface sediments has shown that IP_{25} has an isotopically enriched signature (e.g., $-19.3 \pm 2.3‰$) relative to planktonic or terrigenous organic matter (Belt et al., 2008), consistent with previous observations of significant carbon isotope fractionation during algal growth in sea ice (Schubert and Calvert, 2001). This lends strong support to the hypothesis of IP_{25} as an ice-specific proxy. The identification of IP_{25} in Arctic sediments as old as 30 ka BP and data showing down-core variations in IP_{25} concentrations consistent with other ice proxy data (Massé et al., 2008; Andrews et al., 2009; Müller et al., 2009; Vare et al., 2009, 2010; Belt et al., 2010; Gregory et al., 2010; Axford et al., 2011) suggest that IP_{25} is stable and well preserved in marine sediment records, making it a good candidate for paleo-sea ice reconstructions.

Müller et al. (2011) compared IP_{25} concentrations in surface sediment samples from Fram Strait against modern spring sea ice concentrations, and showed a statistically significant correlation over this sea ice margin ($n = 38, R^2 = 0.67$), demonstrating the utility of IP_{25} as a qualitative sea ice proxy in marine sediments. However, these relationships were significantly improved ($R^2 = 0.74$) when IP_{25} concentrations were used in combination with a biomarker for marine phytoplankton productivity such as brassicasterol or dinosterol (e.g., the P_BIP_{25} or P_DIP_{25} index). Under changing sea ice conditions (e.g., near the ice edge) or under thick ice factors such as light and nutrient availability can be altered, resulting in changes in IP_{25} production that are unrelated to the duration of ice cover. The PIP_{25} index approach hypothesizes that phytoplankton production will be influenced in a similar way by changes in ice conditions, and that by normalizing IP_{25} concentrations to those of a phytoplankton biomarker, the PIP_{25} index can account for these differences. The improvements in the proxy–sea ice relationships in Fram Strait provide strong support for the validity of this approach.

Despite these promising results, little is known about the broader regional controls on IP_{25} and PIP_{25} and sea ice because of the limited spatial coverage of IP_{25} measurements. For example, can the relationships between IP_{25} (PIP_{25}) and sea ice cover seen in the surface sediment data from Fram Strait be extrapolated to other parts of the Arctic, where sea ice conditions may be different? Can relationships based on modern surface sediments be used to reconstruct temporal changes in sea ice cover from sediment cores? Heterogeneities, both spatial and temporal, could complicate the link between IP_{25} and sea ice, particularly when generating quantitative estimates of paleo-sea ice cover. For example, spatial differences in light or nutrient availability during the seasonal expansion of sea ice could potentially impact IP_{25} concentrations via changes in diatom productivity, independent of changes in total sea ice cover (Mundy et al., 2007; Estrada et al., 2009; Rozanska et al., 2009) and while the PIP_{25} index appears to offer a solution

to this potential problem, the wider applicability of this approach is not known. Additionally, the physical characteristics of sea ice, such as porosity, could also have an impact on IP_{25} formation and distribution through their effects on ice algal growth and productivity (Estrada et al., 2009). Recent work suggests that there may be significant regional variations in the controls on IP_{25} abundance (Caissie et al., 2011; Stoynova et al., 2011; Xiao et al., 2012). The present study expands the existing surface sediment IP_{25} database to locations across the Arctic in order to examine regional differences in the IP_{25} (and PIP_{25}) – sea ice relationships and to further assess the potential use of IP_{25} as a quantitative sea ice proxy.

2. Study area and methods

2.1. Regional setting

The seasonal expansion of sea ice across the Arctic Ocean begins in autumn, forming first over shallow continental shelves where surface water salinities are lowest, and expanding via a combination of freezing and advection of ice from coasts by the wind and ocean currents. Transport and expansion of sea ice across the Arctic Ocean occurs by either the cyclonic Beaufort Gyre over the Canada Basin in the west or the Transpolar Drift in the east. Changes in the strengths of these circulations play an important role in the expansion of sea ice across the Chukchi and East Siberian Seas and out of the Arctic Ocean via the Fram Strait (Carmack, 2000). In the surrounding basins like the Bering Sea and Baffin Bay, sea ice forms as late as November, first along the northern shelves where salinities and temperatures are lowest, after which it expands southward via transport by the northeasterly winds, reaching a maximum extent in March. In contrast, sea ice in Fram strait is derived from a combination of localized expansion of shelf ice and the delivery of older ice from the Arctic Ocean by the Transpolar Drift and the East Greenland Current. Melting and sea ice retreat across the Arctic occurs between the spring and late summer/early fall, depending on latitude and the seasonal increase in temperature. As a consequence, the seasonal extent and duration of ice cover over much of the study area depends on a combination of latitude and regional differences in ocean and atmospheric circulation.

The seasonal expansion of Arctic sea ice plays an important role in ecology of the high latitude oceans and seas via its role in regulating marine primary productivity. This occurs primarily through its regulation of available light, nutrients and water column stratification (Horner, 1980; Hunt et al., 2002; Hill et al., 2005). A critical component of this production comes from algae growing in the sea ice, which contribute between 4 and 25% of net primary productivity in parts of the oceans with seasonally ice cover and >50% in areas with perennial ice (Legendre et al., 1992; Gosselin et al., 1997). Seasonal growth of sea ice algae occurs primarily in association with spring blooms, though it is also strongly influenced by environmental conditions, including light and nutrient availability and ice conditions on local and regional scales (Horner, 1980; Gosselin et al., 1986; Gradinger et al., 1991; Legendre et al., 1992).

2.2. Surface sediment database

The present study uses a suite of archival core top ($n = 121$) surface (0–3 cm) sediment samples obtained from the Oregon State University Marine Geology Repository and the GEOTOP archives, where they have been stored at 5 °C since collection (Fig. 1). The surface sediment samples were taken from box and gravity cores that were collected between 1961 and 2009.