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## Identification of paleo Arctic winter sea ice limits and the marginal ice zone: Optimised biomarker-based reconstructions of late Quaternary Arctic sea ice



Simon T. Belt<sup>a,\*</sup>, Patricia Cabedo-Sanz<sup>a</sup>, Lukas Smik<sup>a</sup>, Alba Navarro-Rodriguez<sup>a</sup>, Sarah M.P. Berben<sup>b,1</sup>, Jochen Knies<sup>c,d</sup>, Katrine Husum<sup>e</sup>

<sup>a</sup> Biogeochemistry Research Centre, School of Geography, Earth and Environmental Sciences, Plymouth University, Plymouth, PL4 8AA, UK

<sup>b</sup> Department of Geology, UiT – The Arctic University of Norway, N-9037 Tromsø, Norway

<sup>c</sup> Geological Survey of Norway, N-7491 Trondheim, Norway

<sup>d</sup> CACE – Centre for Arctic Gas Hydrate, Environment and Climate; Department of Geology, University of Tromsø, N-9037 Tromsø, Norway

<sup>e</sup> Norwegian Polar Institute, Fram Centre, NO-9296 Tromsø, Norway

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### ABSTRACT

Analysis of >100 surface sediments from across the Barents Sea has shown that the relative abundances of the mono-unsaturated sea ice diatom-derived biomarker IP<sub>25</sub> and a tri-unsaturated highly branched isoprenoid (HBI) lipid (HBI III) are characteristic of the overlying surface oceanographic conditions, most notably, the location of the seasonal sea ice edge. Thus, while IP<sub>25</sub> is generally limited to locations experiencing seasonal sea ice, with higher abundances found for locations with longer periods of ice cover, HBI III is found in sediments from all sampling locations, but is significantly enhanced in sediments within the vicinity of the retreating sea ice edge or marginal ice zone (MIZ). The response of HBI III to this well-defined sea ice scenario also appears to be more selective than that of the more generic phytoplankton biomarker, brassicasterol. The potential for the combined analysis of IP<sub>25</sub> and HBI III to provide more detailed assessments of past sea ice conditions than IP<sub>25</sub> alone has been investigated by quantifying both biomarkers in three marine downcore records from locations with contrasting modern sea ice settings. For sediment cores from the western Barents Sea (intermittent seasonal sea ice) and the northern Norwegian Sea (ice-free), high IP25 and low HBI III during the Younger Dryas (ca. 12.9-11.9 cal. kyr BP) is consistent with extensive sea cover, with relatively short periods of icefree conditions resulting from late summer retreat. Towards the end of the YD (ca. 11.9-11.5 cal.kyr BP), a general amelioration of conditions resulted in a near winter maximum ice edge scenario for both locations, although this was somewhat variable, and the eventual transition to predominantly ice-free conditions was later for the western Barents Sea site (ca. 9.9 cal. kyr BP) compared to NW Norway (ca. 11.5 cal. kyr BP). For both locations, coeval elevated HBI III (but absent IP<sub>25</sub>) potentially provides further evidence for increased Atlantic Water inflow during the early Holocene, but this interpretation requires further investigation. In contrast, IP25 and HBI III data obtained from a core from the northern Barents Sea demonstrate that seasonal sea ice prevailed throughout the Holocene, but with a gradual shift from winter ice edge conditions during the early Holocene to more sustained ice cover in the Neoglacial; a directional shift that has undergone a reverse in the last ca. 150 yr according to observational records. Our combined surface and downcore datasets suggest that combined analysis of IP25 and HBI III can provide information on temporal variations in the position of the maximum (winter) Arctic sea ice extent, together with insights into sea ice seasonality by characterisation of the MIZ. Combining IP<sub>25</sub> with HBI III in the form of the previously proposed PIP<sub>25</sub> index yields similar outcomes to those obtained using brassicasterol as the phytoplankton marker. Importantly, however, some problems associated with use of a variable balance factor employed in the PIP<sub>25</sub> calculation, are potentially alleviated using HBI III.

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E-mail address: sbelt@plymouth.ac.uk (S.T. Belt).

<sup>\*</sup> Corresponding author.

Current address: Department of Earth Science and the Bjerknes Centre for Climate Research, University of Bergen, N-5007 Bergen, Norway.

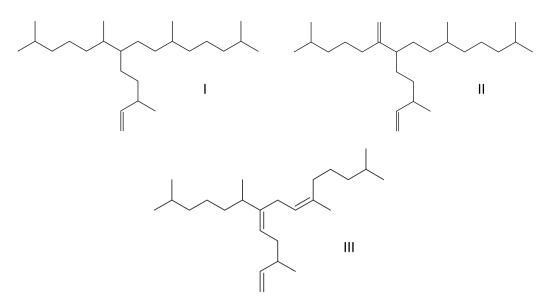


Fig. 1. Structures of C<sub>25</sub> highly branched isoprenoid (HBI) alkenes described in the text. (I) IP<sub>25</sub>; (II) C<sub>25:2</sub>; (III) HBI III (C<sub>25:3</sub>).

#### 1. Introduction

Sea ice plays a major role in controlling the energy budget at the Earth's surface by reflecting a significant part (>90%) of incoming radiation due to the so-called albedo effect. Sea ice also acts as a physical barrier to heat and gas exchange between the oceans and the atmosphere, and contributes to ocean circulation through brine release during formation and freshwater discharge during melting (e.g. Dickson et al., 2007 and references therein). It also experiences large seasonal variations and inter-annual variation can also be significant. Variations in sea ice also influence climate change scenarios beyond the polar regions through teleconnections (e.g. Wang et al., 2005). However, despite recognition of the key roles that sea ice plays in global climate, with recent reductions in extent and thickness attracting considerable attention (e.g. Stroeve et al., 2012), long term records of sea ice and variations in its distribution have, until recently, remained relatively scarce, principally due to a combination of the logistical constraints of working in the polar regions and a lack of suitable (proxy) methodologies. Observational records of past sea ice are spatially incomplete and, in any case, rarely extend beyond a few hundred years (Divine and Dick, 2006), while reconstructions based on geological archives are particularly challenging since sea ice leaves no direct legacy signature in marine or terrestrial records; however, a number of proxy methods have been developed to specifically address this. Some of these approaches are based on the responses of pelagic or benthic organisms whose distributions and composition (e.g. stable isotopes) are influenced by sea ice cover (for an overview, see de Vernal et al., 2013 and references therein), while others rely on the identification of material entrained within the sea ice itself (i.e. ice-rafted debris (IRD)) which is deposited in sediments following release from melting ice (Andrews, 2009).

In recent years, the analysis of the biomarker  $IP_{25}$  (structure I; Fig. 1; Belt et al., 2007), a  $C_{25}$  highly branched isoprenoid (HBI) lipid made uniquely by certain Arctic sea ice-dwelling diatoms (Brown et al., 2014), has been suggested to provide a more direct measure of past sea ice when detected in underlying sediments (see Belt and Müller, 2013 for a recent review). Importantly,  $IP_{25}$  has been identified in sediments from a large number of surface sediments from seasonally ice-covered Arctic locations and downcore records spanning timescales from recent decades (Müller et al., 2011; Stoynova et al., 2013; Xiao et al., 2013; Navarro-Rodriguez et al., 2013), the Holocene (Vare et al., 2009; Müller et al., 2012) and even longer (Stein and Fahl, 2013; Knies et al., 2014; Müller and Stein, 2014). A remaining question, however, concerns the extent to which the analysis of IP<sub>25</sub> can provide more detailed or quantitative estimates of paleo sea ice. Initially, Massé et al. (2008) demonstrated that IP<sub>25</sub> abundances in a marine core from the North Icelandic Shelf exhibited a strong relationship to known sea ice conditions in observational records and, in general, changes in sedimentary concentrations of IP<sub>25</sub> are consistent with corresponding variations in sea ice extent (Belt and Müller, 2013). Absolute abundances of IP<sub>25</sub>, however, vary considerably between different Arctic regions with otherwise similar sea ice extent and no strict relationship with sea ice concentration exists. Despite this limitation, the selectivity of sedimentary IP<sub>25</sub> to seasonally ice-covered locations largely remains, making its presence a useful qualitative sea ice proxy, at least. Exceptionally, IP<sub>25</sub> has been identified in a small number of sediments from either ice-free locations or those from near permanent ice cover, although these are likely explained by sediment advection and (at least) partial ice melt, respectively (Navarro-Rodriguez et al., 2013; Xiao et al., 2015).

In order to distinguish between the two extreme scenarios of ice-free conditions and permanent ice cover, more generally, Müller et al. (2009) suggested the parallel measurement of pelagic phytoplankton biomarkers that might be considered indicators of ice-free sea surface conditions. As such, the absence or low abundance of phytoplankton sterol lipids such as brassicasterol may serve to indicate permanent sea ice coverage, while elevated brassicasterol content would suggest predominantly ice-free conditions. The success of this approach in constructing sea ice conditions for the Fram Strait over the last 30 kyr (Müller et al., 2009) led to the subsequent development of the so-called PIP<sub>25</sub> index. whereby concentrations of IP<sub>25</sub> and a phytoplankton biomarker (typically brassicasterol) are combined to provide semi-quantitative estimates of sea ice concentration (Müller et al., 2011). However, although relationships between PIP<sub>25</sub> data and sea ice concentrations are, in general, better than those using IP<sub>25</sub> alone (e.g. Xiao et al., 2015), this is not always the case (Navarro-Rodriguez et al., 2013) and the underlying reasons for such improved correlations are not fully resolved, not least due to the uncertainties in the true inter-relationship between IP<sub>25</sub> and phytoplankton lipids under different sea ice settings, or the strict pelagic origin of brassicasterol in all cases (e.g. Fahl and Stein, 2012; Belt et al., 2013; Xiao et al., 2015).

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