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What do IP_{25} and related biomarkers really reveal about sea ice change?

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Abstract

Significant changes to Arctic and Antarctic sea ice in recent decades has prompted the development and application of novel approaches to the reconstruction of past sea ice conditions over much longer timeframes. One such approach is based on the variable distribution of certain source-specific highly branched isoprenoid (HBI) lipid biomarkers in well-dated marine sediment records. Thus, IP_{25} and $IPSO_{25}$ have emerged as useful proxy measures of seasonal sea ice in the Arctic and Antarctic, respectively. An overview of the salient features of IP_{25}, $IPSO_{25}$ and related biomarkers is presented, together with aspects that are currently less well understood and potentially provide direction for future research.

Arctic and Antarctic sea ice extent, thickness, and other characteristics, have undergone dramatic changes over recent decades, attracting considerable interest from scientists, the public and the media. Contextualisation of such changes, however, requires a greater understanding of how sea ice has changed in the past, and how sea ice variability can be understood within a broader climatic framework. In practice, this is not particularly straightforward to achieve.

One of the main approaches to past sea ice reconstruction has been the application of so-called proxy methods to well-dated marine sediment cores. A number of sea ice proxies exist, each possessing different merits and limitations (de Vernal et al., 2013), but understanding these can itself be quite challenging. Sea ice proxies with a biological origin are the most common, and are based, generally, on microorganisms such as diatoms (microalgae) or other biota that reside within the sea ice itself or in the immediate neighbouring open ocean – a region often referred to as the Marginal Ice Zone (MIZ). Strictly sea ice-associated diatoms are frequently quite low in abundance compared to their open-water counterparts, and are often susceptible to degradation in the water column or sediments, so their contribution can be under-estimated (Leventer, 2013).

Interestingly, some diatoms biosynthesise unusual highly branched isoprenoid (HBI) lipids or biomarkers that are *well-preserved* in marine sediments, and can be readily detected using modern analytical instrumentation (e.g. gas chromatography–mass spectrometry), even at low concentration. A key attribute of some HBIs is their apparent *source-selectivity*. Thus, one mono-unsaturated HBI termed IP_{25} ("Ice Proxy with 25 carbon atoms"; Fig. 1) appears to be made selectively by certain Arctic sea ice diatoms (Belt et al., 2007, Brown et al., 2014), so its sedimentary occurrence provides proxy evidence for past sea ice occurrence. Despite their relatively low

percentage in total sea ice diatom assemblages, IP_{25}-producing species are common across the Arctic; a further important feature. Consistent with this, IP_{25} is a common constituent of surface sediments from all regions of the Arctic underlying seasonal sea ice cover (>500 surface sediments have so far been analysed; Fig. 1), yet is mainly absent from lower latitude locations which are ice-free, year-round. Currently, this binary signature of IP_{25} is probably its most reliable feature (Belt, 2018). On the other hand, its sea ice origin and source-selectivity do not ipso facto make IP_{25} a 'better' sea ice proxy than other 'less direct' methods (Belt, 2018).

Of course, other than its presence/absence, there may be other characteristics of Arctic sea ice that sedimentary IP_{25} might provide insights into, yet only relationships between sedimentary IP_{25} and sea ice extent or concentration have so far been explored. Further, those factors that control IP_{25} production, its transit from sea ice to sediments, and its long-term stability in sediments, are still not well understood, and all of the above are in need of future investigation. In the meantime, directional changes in IP_{25} concentration in palaeo (i.e. downcore) marine sedimentary records are normally interpreted in terms of corresponding fluctuations in sea ice *extent*, an interpretation based on various empirical surface sediment calibrations and comparisons of sedimentary IP_{25} content with documented sea ice records (Massé et al., 2008; Belt, 2018).

The significance of IP_{25} absence in Arctic sediments is more challenging to understand. Currently, two end-member scenarios have been offered – ice-free conditions and permanent/extensive sea ice cover. Both are logical if the production of IP_{25} by certain Arctic sea ice diatoms during the spring algal bloom period is accepted, yet there have been no dedicated studies aimed at confirming these end-members. These, and additional scenarios, should be considered and investigated

further as part of future proxy development studies. In the meantime, absent IP_{25} may simply result from: (i) sea ice with insufficient diatom content (for which there are a number of reasons) or the 'wrong' diatoms; (ii) removal from the water column through grazing of sea ice algae by primary consumers; (iii) degradation in the water column/sediments (Belt, 2018).

Following a few (mainly) Holocene studies (Belt and Müller, 2013), there are now more than 60 published palaeo sea ice reconstructions based on IP_{25}, and some longer timeframe investigations have appeared in the last few years, including those spanning recent glacial/interglacial cycles, the Mid-Pleistocene Transition, the Pliocene/Pleistocene boundary, and the late Miocene (Fig. 1; for a compendium up to mid-2018, see Belt, 2018). Such studies provide some insights into the likely long-term sedimentary stability of IP_{25} and the potential for carrying out future sea ice reconstructions over even longer timeframes.

Interestingly, IP_{25} has not been reported in the Antarctic, probably due to the absence of the necessary source diatoms. However, a structurally similar lipid with two double bonds in its structure has been identified in Antarctic sea ice diatoms and sediments (Fig. 1). Recently termed $IPSO_{25}$ ("Ice Proxy for the Southern Ocean with 25 carbon atoms"; Belt et al., 2016) when detected in the Antarctic, this biomarker is less developed as a sea ice proxy than IP_{25}, and only a few $IPSO_{25}$-based palaeo sea ice reconstructions have been reported (Fig. 1; for a summary, see Belt, 2018).

Although relatively few in number, studies of IP_{25} and $IPSO_{25}$ in their native sea ice have, nonetheless, provided some valuable insights. Thus, production of IP_{25} by Arctic sea ice diatoms during the spring bloom prior to ice melt provides a further refinement to its sedimentary signature – namely, a proxy measure of *seasonal* sea ice. Time series studies have not been carried out on $IPSO_{25}$, so its sedimentary

fingerprint is less certain. However, a recent source identification and analysis of its distribution in near-coastal Antarctic sediments led to the conclusion that $IPSO_{25}$ may be a better proxy of the *type* of sea ice in which it is produced (platelet ice in this case) rather than other parameters such as sea ice *extent* or *seasonality* (Belt et al., 2016). Interestingly, since $IPSO_{25}$ (although not generally known by this name in the Arctic) is co-produced with IP_{25} in the Arctic, with their respective concentrations normally very well correlated, it follows that the *same biomarker* ($IPSO_{25}$) might actually possess quite diverse proxy signatures between the Arctic and the Antarctic. However, studies aimed at developing $IPSO_{25}$ as an Antarctic sea ice proxy are still in their infancy and future investigations will need to carefully factor in the potentially different controls over its production, transport and stability in sediments.

Analysis of some other biomarkers can potentially improve the quality or detail of palaeo sea ice reconstructions based on IP_{25} or $IPSO_{25}$ alone. Again, such approaches are currently far more developed in the Arctic than in the Antarctic. First, for sedimentary intervals of absent IP_{25}, the identification of relatively high or low concentrations of biomarkers derived from open water biota (generally phytoplankton) can be useful for distinguishing between the possible two end-member scenarios of ice-free conditions and permanent ice cover, respectively (Müller et al., 2009; Belt, 2018). Further, by combining the relative sedimentary abundances of IP_{25} and open-water biomarkers in the form of the so-called Phytoplankton-IP_{25} (PIP_{25}) index (Müller et al., 2011), some semi-quantitative descriptions of sea ice conditions have been proposed, including numerical estimates of spring sea ice *concentration*, in some cases. However, the success (or otherwise) of the PIP_{25} approach is dependent on a number of factors, including the

region of study, the open-water biomarker selected, and the timeframe of the sediment sequence.

Recently, a further HBI biomarker (often referred to as HBI III; Fig. 1) has been proposed as a potentially suitable open-water counterpart to both IP_{25} and $IPSO_{25}$, not least because it is found in both the Arctic and the Antarctic, and its production is also believed to be source-specific (i.e. by certain open-water diatoms only), an attribute not shared by many other phytoplankton biomarkers, which can sometimes also have a terrestrial and even sea ice origin. Further, in the albeit relatively few studies carried out so far on HBI III, highest concentrations were found in samples taken from regions of the MIZ, a signature that has helped refine interpretations of sea ice conditions based on IP_{25} and $IPSO_{25}$ in some palaeo records (Fig. 1; Belt, 2018). However, the extent to which HBI III represents the optimal open-water biomarker, more generally, requires further investigation, especially under in situ conditions (i.e. water column studies). In fact, its probable production by a relatively small number of diatoms, and its potentially higher susceptibility towards degradation due to its chemical structure, may be limiting factors in some instances.

The more general challenge of identifying the most suitable lipids for sea ice and open biomarker conditions may potentially be addressed through the application of multi-variate statistical methods to suites of biomarkers. Such approaches compare biomarker compositional data with known oceanographic conditions and, importantly, identification of the components (and their % composition) that best define certain boundary sea ice conditions is achieved without pre-selection or bias. Multi-variate methods based on so-called ‘decision trees’ also provide visually intuitive output, and performance metrics provide error estimates not available using

other (simpler) approaches. As such, the use of multi-variate analyses applied to a suite of HBIs (IP_{25}, $IPSO_{25}$, HBI III and others) measured in the same samples may also help provide (semi-)quantitative estimates of seasonal sea ice concentrations, as shown by two recent pilot studies in the Barents Sea (Köseoğlu et al., 2018a,b). Such approaches may also provide the opportunity to combine and compare biomarker data with other composition-based sea ice proxies (e.g., diatoms, dinocysts, ice-rafted debris, etc.) in the future.

Finally, it should be noted that for all combinative biomarker methods (decision trees, PIP_{25}, etc.), accurate quantification is especially important (Belt, 2018). More generally, following an initial inter-laboratory study of IP_{25} and other HBIs (Belt et al., 2014), it has been recommended that all aspects of HBI identification and quantification (i.e. GC retention indices, mass spectral data, methods for calculating GC responses factors, etc.) are reported as routine (Belt, 2018). Standardisation of analytical methods and their reporting, together with on-going inter-laboratory calibrations, would certainly help inform identification of the most reliable datasets, including those to be used for comparison or combining purposes.

In summary, the development and application of certain source-specific HBI lipid biomarkers as proxies for Arctic and Antarctic sea ice have received increasing attention over the last decade, with a steady year-on-year growth in research publications based on IP_{25}, in particular. Future studies aimed at unravelling the source-to-sink characteristics of these lipid biomarker proxies might enable some further important nuances and limitations to be identified, which would improve their overall value to those researchers using them for past climate reconstruction

purposes in the polar regions. In this respect, an open question still remains - What do IP_{25} and related biomarkers really reveal about sea ice change?

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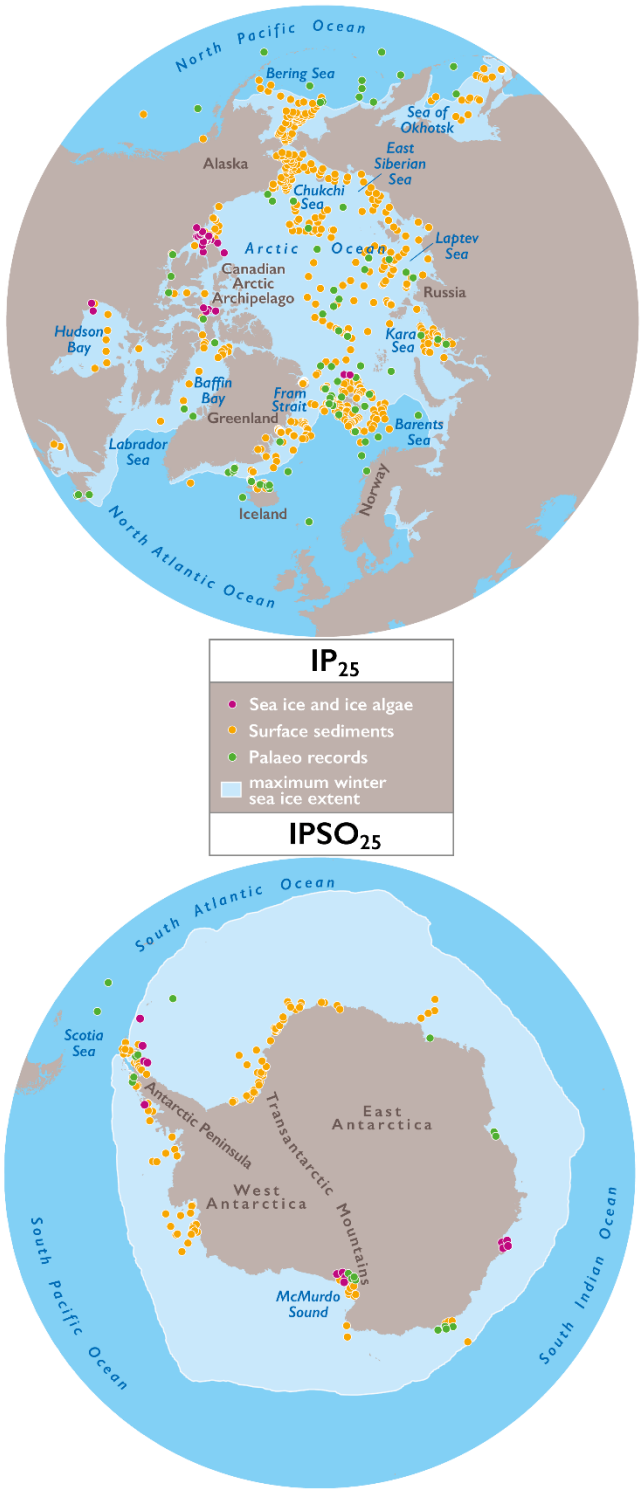
Figure legend.

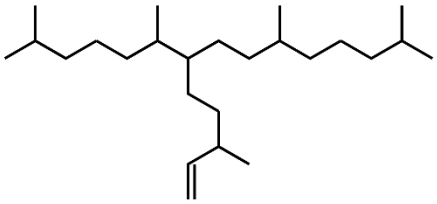
Figure 1. Summary maps showing where studies based on IP_{25} and $IPSO_{25}$ have been carried out in the Arctic and Antarctic, respectively. The structures of different source-specific HBIs, together with their currently proposed primary proxy signatures, are also shown. Adapted from Belt, 2018.

Figure 1.



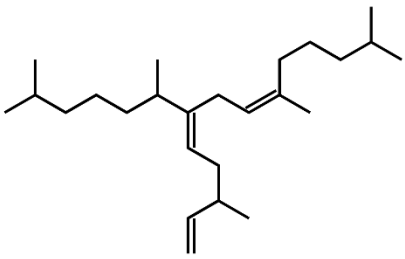
IP_{25}

Seasonal Arctic sea ice



HBI III

Open waters and enhanced in the Marginal Ice Zone (Arctic and Antarctic)



$IPSO_{25}$

Seasonal Arctic and Antarctic sea ice (possible inference of Antarctic platelet ice)