# Arctic Sea Ice Reconstruction for the Past 500 Years Using Palaeo-Based Proxies

## A case study of $PIP_{25}$ Biomarker

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## Abstract

**To deduce paleoclimatic changes attributable to variability in the sea ice, a long-term record of sea-ice is required, beyond the time period covered by direct instrumental monitoring. A recent proxy for Arctic Ocean sea-ice has been developed based on the analysis of an isomer of C25, also known as $IP_{25}$ (Ice Proxy with 25 carbon atoms). In addition, other phytoplankton- derived biomarkers such as brassicasterol (Phytoplankton marker - $IP_{25}$ index; $PIP_{25}$) are employed to confirm sea ice change deductions for the past 500 years.**


## Introduction

There has been dramatic decline in the thickness and extent of sea-ice in the Arctic Ocean over past three decades, reflected by distortions in:

- Climatic conditions
- Permafrost thawing
- Coastal erosion

The relationship between global climate and sea ice is such that even minute changes in sea ice can prompt drastic climate changes (Figure 1). Therefore, in order to anticipate any future climatic conditions, past fluctuations in sea ice cover have to be examined.

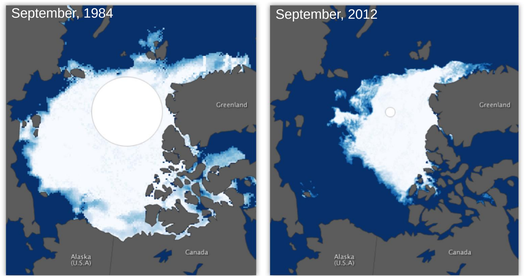


**Figure 1: Arctic sea ice decline**
**(*Source: http://earthobservatory.nasa.gov/IOTD/view.php?id=79256*)**

A recent proxy for Arctic Sea reconstruction has been developed based on the analysis of highly branched isoprenoid (HBI) lipid biomarkers that are characteristic of Arctic marine and freshwater organisms (Figure 2) (Brown *et al.*, 2014). $IP_{25}$ is associated with diatoms present underneath the first year sea ice cover (Belt & Simon, 2012). During freezing, $Na^+$, $K^+$, $Ca^+$, $Mg^+$, $Cl^-$, $SO_4^{2-}$, and $CO_3^{2-}$ ions are removed from the crystalline structure, leading to brine production and formation of macro and microscopic channels into which algae and other microorganisms can discharge.

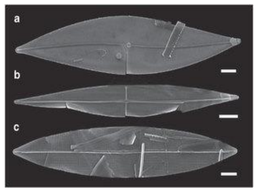


**Figure 2: SEM of $IP_{25}$ -producing diatoms**
***(a) Pleurosigma stuxbergii var. rhomboides***
***(b) Haslea crucigeroides (and/or Haslea spicula)***
***(c) Haslea kjellmanii***

The melting of sea ice starts releasing these diatoms into the underlying water and depositing them in seabed sediments. Therefore, it has been expected that the presence of $IP_{25}$ biomarker indicates the presence of sea ice cover and reduced $IP_{25}$ concentration suggests the lack of seasonal sea ice or a perennial sea ice cover. Additional use of the Phytoplankton-derived biomarkers such as brassicasterol validates the reconstructions based on $IP_{25}$ signals.

***The decreased $IP_{25}$ flux and elevated $PIP_{25}$ indicates ice-free conditions, whereas the absence of both biomarkers suggests permanent ice cover. On the other hand, the presence of both biomarkers reflects the seasonal sea ice cover*** (Muller *et al., 2011)*.

## Methods and Materials

The push core 99LSSL-001F analyzed in the following procedure was retrieved from the Coronation Gulf (68.095 ºN, 114.186 ºW) in the low Arctic region (Figure 3).

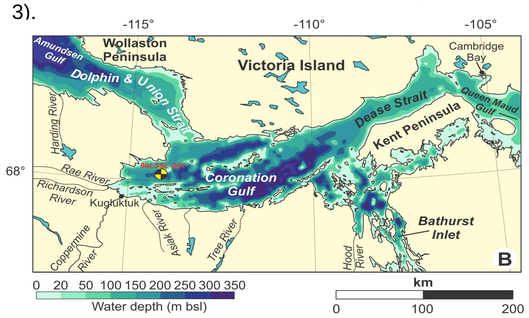


**Figure 3: Coronation Gulf**

### Sediment Extraction

- 1g of each sample spiked with 10 $\mu$L of internal standards (9 octylheptdec-8-ene and cholesterol-d6).
- Addition of DCM/Methanol in 2:1.
- Ultrasonication and centrifugation to separate the supernatant.

### Separation and Purification

- Separation of hydrocarbons and sterols through column chromatography using *n*-hexane and methyl acetate: *n*-hexane (20:80 v/v).

### Quantitation of $IP_{25}$

- Sterols were silylated with 500 $\mu$L of BSTFA
- Analysis using GC-MS.

## Results and Discussion

$IP_{25}$ and brassicasterol were identified based on the distinctive retention time and mass spectra (Figure 4).

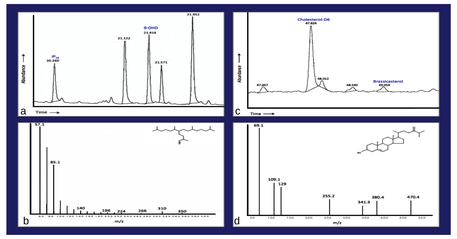


**Figure 4: (a) and (b) TIC and mass spectra of $IP_{25}$ respectively.**
**(c) and (d) TIC and mass spectra of brassicasterol respectively.**

To account for the changing sedimentation rate, concentrations were converted into fluxes using a Linear Age-Depth Model.

A concentration balance factor (c ) was considered for the calculation of $PIP_{25}$ index:

$$PIP_{25} = IP_{25} / ( IP_{25} + (Phytoplankton\ marker \times c))$$

***where c = mean $IP_{25}$ concentration/mean phytoplankton biomarker concentration***

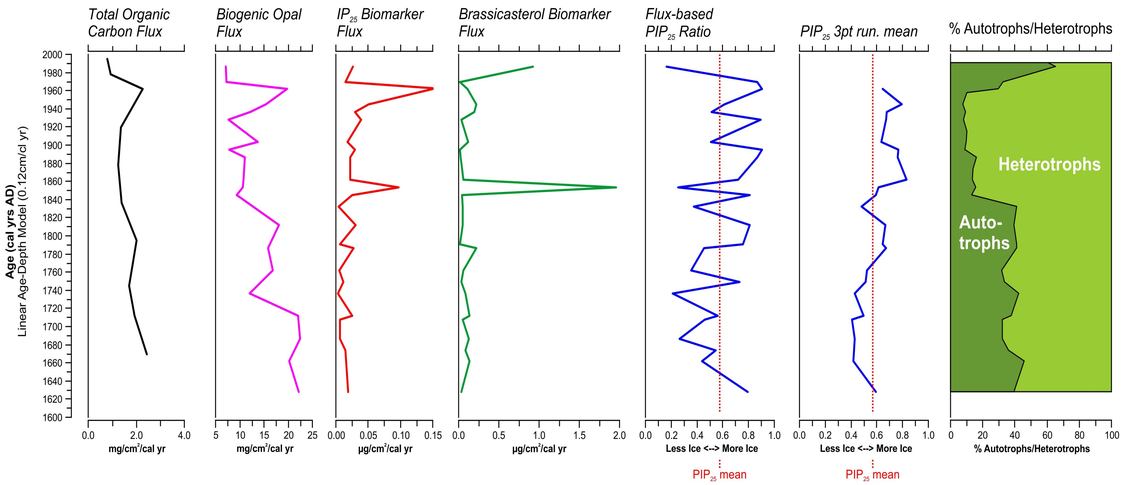


**Figure 5: Biogeochemical and palynological proxies.**

$PIP_{25}$ flux profile suggests marked episodes of very late Holocene sea-ice fluctuations (Figure 5).

- From AD 1630-1840, $PIP_{25}$ suggests high magnitude fluctuations in sea-ice conditions.
- From AD 1840-1960, a longer oscillating sea-ice season is indicated by $PIP_{25}$ ratios.
- From AD 1960-1990, the decreased $PIP_{25}$ implies an extended open water season.

The AD 1630-1840 and AD 1960-1996 broadly shows a good agreement of $PIP_{25}$ ratio with authentic Total Organic Carbon Flux, Biogenic Opal Flux and dinocysts record (% Autotrophs/Heterotrophs) from this core (Figure 5)(Pieńkowski *et al.*, 2011).

## Conclusions

The calculated annual fluxes in $IP_{25}$ , brassicasterol, and $PIP_{25}$ for the core record illustrates annual to decadal variations in the duration of sea-ice season for the past 500 years. The exclusive origin of $IP_{25}$ in Arctic Sea sediments makes it a potential quantitative proxy for sea ice reconstruction. Hence, $PIP_{25}$ fluxes can be successfully used to determine palaeo seasonal sea ice conditions. Ongoing work on this core includes diatom assemblage assay, as well as dinocysts-based quantitative reconstructions to permit a broad inter-comparison between different proxies.


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