Quaternary Science Reviews 79 (2013) 9–25

Contents lists available at SciVerse ScienceDirect

Quaternary Science Reviews

journal homepage: www.elsevier.com/locate/quascirev

The Arctic sea ice biomarker IP_{25}: a review of current understanding, recommendations for future research and applications in palaeo sea ice reconstructions

Simon T. Belt [a,*], Juliane Müller [b]

[a] Biogeochemistry Research Centre, School of Geography, Earth and Environmental Sciences, Plymouth University, Plymouth PL4 8AA, UK
[b] Alfred Wegener Institute for Polar and Marine Research, 27568 Bremerhaven, Germany

ARTICLE INFO

Article history:
Received 18 June 2012
Received in revised form
29 November 2012
Accepted 4 December 2012
Available online 17 January 2013

Keywords:
Sea ice
Arctic
Proxy
IP_{25}
Biomarker
Palaeoclimate

ABSTRACT

In recent years, a novel proxy for the past occurrence of Arctic sea ice has been proposed that is based on the variable marine sedimentary abundance of an organic geochemical lipid derived from sea ice diatoms in the spring. This lipid, termed IP_{25} (Ice Proxy with 25 carbon atoms), is a highly branched isoprenoid mono-unsaturated alkene that appears to be sufficiently stable in sediments to permit meaningful palaeo sea ice reconstructions to be carried out over short- to long-term timescales. Since the first proposed use of IP_{25} as a proxy for palaeo sea ice by Belt et al. (2007), a number of laboratories have measured this biomarker in Arctic sediments and it is anticipated that research activity in this area will increase further in the future. The content of this review is divided into a number of sections. Firstly, we describe the scientific basis for the IP_{25} proxy and its initial discovery in Arctic sea ice, sedimenting particles and sediments. Secondly, we summarise the relatively few studies that have, to date, concentrated on examining the factors that influence the production and fate of IP_{25} and we identify some areas of future research that need to be addressed in order to improve our understanding of IP_{25} data obtained from sedimentary analyses. What is clear at this stage, however, it that the presence of IP_{25} in Arctic marine sediments appears to represent a proxy measure of past seasonal sea ice rather than permanent or multi-year ice conditions. Thirdly, we highlight the importance of rigorous analytical identification and quantification of IP_{25}, especially if measurements of this biomarker are going to be used for quantitative sea ice reconstructions, rather than qualitative analyses alone (presence/absence). Fourthly, we review some recent attempts to make the interpretations of IP_{25} biomarker data more detailed and quantitative by combining sedimentary abundances with those of phytoplankton- and other sea ice-derived biomarkers. Thus, the bases for the so-called PIP_{25} and DIP_{25} indices are described, together with an overview of potential limitations, concluding that investigations into the use of these indices needs further research before their full potential can be realised. In the final section, we provide a summary of IP_{25}-based palaeo sea ice reconstruction case studies performed to date. These case studies cover different Arctic regions and timescales spanning decades to tens of thousands of years.

1. Introduction

The purpose of this paper is to provide a review of current knowledge regarding the Arctic sea ice proxy biomarker IP_{25}. In the first section of the paper, we describe the scientific basis behind, and the subsequent discovery of, IP_{25}, while in the second section, we provide an overview of areas that we have identified as needing further attention before the full potential of the IP_{25} proxy can be realized. In the third section, we describe how sedimentary IP_{25} abundances may be coupled with those of other biomarkers to potentially obtain either quantitative or more detailed information about past sea ice conditions and, finally, we summarise how the analysis of IP_{25} and other biomarkers in Arctic marine sediments has been used as the basis for several palaeo sea ice reconstruction studies in recent years. In this respect, some comparisons are also made with other proxy data, although the emphasis in this review is placed on the analysis of IP_{25} and other biomarkers.

* Corresponding author. Tel.: +44 1752 584799.
E-mail address: sbelt@plymouth.ac.uk (S.T. Belt).

0277-3791/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.quascirev.2012.12.001

1.1. Background to biomarkers and applications in palaeoclimatology

Molecular biomarkers are chemical signatures or fingerprints of the biota from which they are produced (e.g. Peters et al., 2005; Killops and Killops, 2009). They occur across all taxonomic levels and can be classified into general classes (e.g. lipids), smaller groupings (e.g. fatty acids, sterols) or individual representatives of these (e.g. cholesterol is a specific and commonly occurring example of a sterol). In addition, biomarkers may be either primary or secondary metabolites and their occurrence can either represent general indicators of origin (e.g. long-chain *n*-alkanes from terrestrial plants) or be of a more source-specific nature (e.g. alkenones from unicellular eukaryotic haptophytes – coccolithophores). In recent decades, an increasing appreciation of the structures and sources of individual and groups of such chemicals has resulted in several biomarker-based applications in palaeoclimatology across the geosphere (for a recent review, see Eglinton and Eglinton, 2008) and the development of these methods has been further aided by an understanding of the environmental factors that influence the production and distributions of individual chemicals. For example, the influence of temperature on the distribution of alkenones from the coccolithophore *Emiliana Huxleyi* (Brassell et al., 1986) and glycerol dialkyl glycerol tetraethers (GDGTs) from Archaea (Schouten et al., 2002; Kim et al., 2008) have provided the basis for the $U^{K'}_{37}$ and TEX_{86} indices, used commonly for reconstructing past sea surface temperatures. A further attribute of the alkenones and the GDGTs is their source-specific nature, which enables their occurrence and distributions to be interpreted with greater certainty. Indeed, it is through an understanding of source specificity and the influences of environmental factors on biomarker distributions that molecular biomarker-based proxies are developed, so studies on both of these aspects remain key research areas for organic geochemists/palaeoclimatologists.

1.2. Highly branched isoprenoid (HBI) alkenes as source-specific biomarkers from diatoms

Highly branched isoprenoid (HBI) alkenes are unusual (structurally) secondary metabolites produced by a relatively small number of marine and freshwater diatoms belonging to the *Haslea*, *Navicula*, *Pleurosigma* and *Rhizosolenia* genera (Volkman et al., 1994; Belt et al., 1996, 2000a, 2001a,b,c; Sinninghe Damsté et al., 1999, 2004). HBIs occur with C_{20}, C_{25} and C_{30} carbon skeletons and are widely distributed in marine sediments worldwide, although the C_{25} alkenes are the most commonly reported (Rowland and Robson, 1990; Belt et al., 2000a). Over the past two decades, the sources and structures of ca 20 individual HBI lipid biomarkers have been reported, mainly following large-scale culturing of individual diatom taxa and subsequent analysis of purified extracts using a combination of mass spectrometric (MS) and nuclear magnetic resonance (NMR) spectrometric methods (e.g. Belt et al., 1996, 2000a, 2001a,b,c; Sinninghe Damsté et al., 1999, 2004). In particular, these investigations have enabled the number, position and stereochemistries of the double bonds to be determined (e.g. Fig. 1). The majority of C_{25} HBIs reported in sediments contain 2–5 double bonds (e.g. Rowland and Robson, 1990; Belt et al., 2000a), although mono- and more poly-unsaturated isomers have also been reported (Dunlop and Jefferies, 1985; Wraige et al., 1997; Xu et al., 2006). Some relationships between the positions of the double bonds and the source diatoms have been identified; for example, HBIs biosynthesized by *Haslea* spp. generally possess a double bond in the C6–C17 or C5–C6 positions (e.g. 2; Fig. 1), while counterparts from *Pleurosigma* spp. usually contain double bonds between C7 and C20 (e.g. 3; Fig. 1). A further difference between HBIs from *Haslea* spp. with those from *Pleurosigma* spp. is that both *E* and *Z* stereoisomers (see C9–C10 positions for 3 and 4; Fig. 1) are usually observed with HBIs from the latter genera. This unusual structural feature is also exhibited by C_{25} and C_{30} HBIs made by *R. setigera* (e.g. Belt et al., 2002). The biosynthesis of HBIs by a limited number of diatom genera has also been demonstrated using molecular phylogeny techniques (Sinninghe Damsté et al., 2004). Despite these advances in source identifications and structural determinations, the functions or role(s) of HBIs in diatoms remains unknown, although the biosynthetic mechanisms responsible for their formation have been established (Massé et al., 2004). What is clear, however, is that the source-specific nature of HBIs makes them potentially useful biomarkers for palaeoenvironment studies.

1.3. Influence of temperature on HBIs and the development of the IP_{25} sea ice diatom proxy

Relatively few studies have investigated the physiological or phenotypic variables that influence or control the distributions of individual HBI alkenes in diatoms and the majority of those

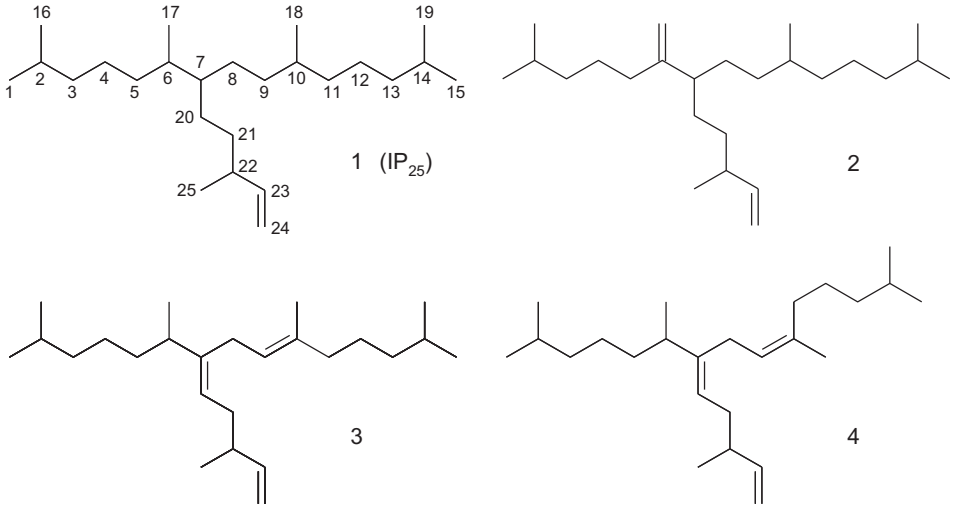

Fig. 1. Structures of C_{25} highly branched isoprenoid alkenes described in the text. (1) IP_{25}; (2) $C_{25:2}$; (3) and (4) HBI trienes.