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The C_{20} highly branched isoprenoid biomarker – A new diatom-sourced proxy for summer trophic conditions?

Francesco Muschitiello [a,*], August Andersson [b], Barbara Wohlfarth [a], Rienk H. Smittenberg [a]

[a] Department of Geological Sciences, Stockholm University, SE-10691 Stockholm, Sweden
[b] Department of Applied Environmental Science, Stockholm University, SE-10691 Stockholm, Sweden

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ABSTRACT

The exact biological source of the C_{20} highly branched isoprenoid (HBI) present in sediments from aquatic systems is unclear. We therefore examined the relationship between the distribution of fossil diatoms and the concentration of the C_{20} HBI in a Late Glacial sedimentary record from the Hässeldala Port paleolake in southern Sweden. Using Bayesian multiple linear regression analysis, we show that its concentration is linked primarily to the production of the diatom taxon *Gomphonema acuminatum*, which accounts for the largest proportion of the temporal variability in the biomarker. By analogy with modern observations, we argue that an increasing amount of *G. acuminatum* biomass in our sedimentary record reflects increasing oligotrophy in the paleolake during the summer growing season, especially at times defined by subdued hydrologic flow. Our conclusions are corroborated by the $\delta^{13}C$ composition of the C_{20} HBI biomarker, which points to a negative photosynthetic fractionation between atmospheric CO_2 and the pool of dissolved inorganic carbon during diatom bloom, a distinct phenomenon at times of inhibited hydrological flow. Accordingly, we suggest that the C_{20} HBI biomarker can be effectively used to reconstruct the trophic state of the paleolake at Hässeldala Port, while its stable isotope composition can provide physicochemical information about the lake conditions during the dry summer season.

Moreover, we note that the major hydrological shifts recorded in the *G. acuminatum*-C_{20} HBI stratigraphy do not coincide with the pollen zone boundaries. We thus infer that aquatic and terrestrial environmental responses to climate change are substantially decoupled through the hydrological system, which highlights the necessity for multi-proxy investigations to decipher past climate events.

1. Introduction

To understand past climate-environment interaction, it is important to first accurately determine the characteristic input sources that denote a biological proxy that can serve as climate indicator. For instance, the presence of specific compounds can be related to precursor organisms, thereby providing information on the prevailing environmental and climatic conditions within definite biological systems and ecological niches (e.g. Didyk et al., 1978; Meyers and Ishiwatari, 1993; Auel et al., 2002).

Within aquatic environments, one compound that lacks precise identification of its biological source is the C_{20} highly branched isoprenoid (HBI), a hydrocarbon found in sediments and biota from different parts of the globe (Bayona et al., 1983; Rowland and Robson, 1990; Atahan et al., 2007; Aichner et al., 2010; McKirdy et al., 2010). The first firm structural identification was established by Yon et al. (1982), who acknowledged that the compound could be a potentially useful biomarker for paleo-environmental reconstruction. Its occurrence in freshwater environments was later associated with *Ulva enteromorpha f. prolifera*, a cosmopolitan green alga, in combination with epiphytic diatoms (Robson and Rowland, 1986). More recently, it was found to be abundant in an extract from periphyton organic matter (OM) in estuarine samples (Jaffé et al., 2001). It was detected in samples of macrophytic algae (i.e. *Chara* spp.) and a freshwater planktic origin was suggested, such as blue-green algae, diatoms, cyanobacterial mats and desmids, which colonize macrophyte communities. On the other hand, Sinninghe Damsté et al. (2005) invoked a distinct diatom origin for the C_{20} HBI, justified by its structural resemblance to two types of diatom biomarkers, C_{25} and C_{30} HBIs. However, the specific source of the C_{20} HBI alkane in freshwater diatoms was still unclear.

Coupling diatom and quantitative biomarker analysis provides an opportunity to link the putative biological input to specific molecular records, ultimately improving understanding of the dynamics that control paleo-ecosystems. More importantly, the approach could help identify the potential season of the maximum

* Corresponding author.
E-mail address: francesco.muschitiello@geo.su.se (F. Muschitiello).

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of the diatom bloom associated with the source proxy. This could in turn direct interpretation of molecular paleo-hydrologic proxies towards an explicit seasonal time window, providing useful information about past hydrologic change on local to regional scales.

To investigate the C_{20} HBI marker as a paleo-proxy, we have examined the biological relationship between isolated fossil diatoms and the abundance of the C_{20} HBI from the same sedimentary record, a Late Glacial sequence from the Hässeldala Port paleolake in southern Sweden.

2. Site information and background

Hässeldala Port is an infilled lake basin in Blekinge, southeastern Sweden (56°16′N; 15°03′E; 65 m above sea level; Fig. 1). The basin contains a sedimentary sequence that covers the period between the Late Bølling and Early Holocene pollen zone (ca. 14500–9500 cal yr BP; Wohlfarth et al., 2006). The sediments have been extensively studied using a variety of biological and geochemical proxies. The pollen stratigraphy and lithostratigraphy were established by Wohlfarth et al. (2006). The tephro-chronological framework of the site was established by Davies et al. (2003, 2004), whereas more recently, sediment geochemistry and fossil leaf stomata records have been investigated (Kylander et al., 2013; Steinthorsdottir et al., 2013). Temperature reconstructions based on midge and beetle stratigraphy were also produced (Whitehouse et al., unpublished results), while the diatom proxy records used here were recently presented by Ampel et al. (2015).

A number of cores have been collected over the years and the present work refers to Core #5 collected in 2011, the new template core for Hässeldala Port (Steinthorsdottir et al., 2013; Ampel et al., 2015). The sequence is underpinned by a solid age-depth model, which has been lately updated (Steinthorsdottir et al., 2014).

3. Material and methods

3.1. Sampling, diatom analysis and lipid extraction

The core was contiguously sub-sampled every 1 cm into 96 sections. A number (34) of samples (ca. 1 cm^3) were prepared for diatom analysis (Ampel et al., 2015). Diatoms were analysed according to standard procedures. Samples were cleaned from dissolved carbonate and clay particles, and diatom valves were assigned under 1000× magnification on the basis of taxonomic identifications from Krammer and Lange-Beralot (1997, 1999, 2004a,b). A minimum of 400 valves was identified in samples with a large number of fossil diatoms. Diatom abundance is expressed as a proportion (%) relative to the total number of assigned valves (Ampel et al., 2015). A diatom stratigraphy with four diatom assemblage zones (DAZs) was generated on the basis of the dendrogram produced by constrained incremental sum of squares using the TGView1.7.16 software (Grimm, 1991). For a detailed description of the diatom stratigraphy, the reader is referred to Ampel et al. (2015).

A number (54) of samples (ca. 8 cm^3) were also prepared for biomarker analysis (26 corresponded to diatom-analysed levels and 28 were obtained from adjacent samples). Each sample was freeze dried, weighed and extracted (3×) via sonication with dichloromethane:MeOH (9:1 v/v) for 20 min, and subsequent centrifugation. The supernatants were combined and the aliphatic hydrocarbon fraction isolated using a silica gel column (5% deactivated) and elution with hexane. To obtain the alkanes, the fraction was purified over 10% $AgNO_3$–SiO_2 silica gel, again using hexane as eluent. Solvent was removed under a stream of pure N_2 between the various steps in the procedure.

3.2. Biomarker assignment, quantification and stable isotope analysis

The alkane fraction was analysed using gas chromatography–mass spectrometry (GC–MS) with a Shimadzu GCMS-QP2010 Ultra system, equipped with an AOC-20i auto sampler and a split-splitless injector operated in splitless mode. Components were separated using a Zebron ZB-5HT Inferno column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The GC oven program was: 60–180 °C at 20 °C/min and then to 320 °C (held 30 min) at 4 °C/min. He was the carrier gas (continuous 1 ml/min). The ion source of the MS operating system was at 200 °C and the ionization energy was 70 eV. The C_{20} HBI and C_{18} to C_{33} *n*-alkanes were assigned on the basis of mass spectra from the literature and retention times

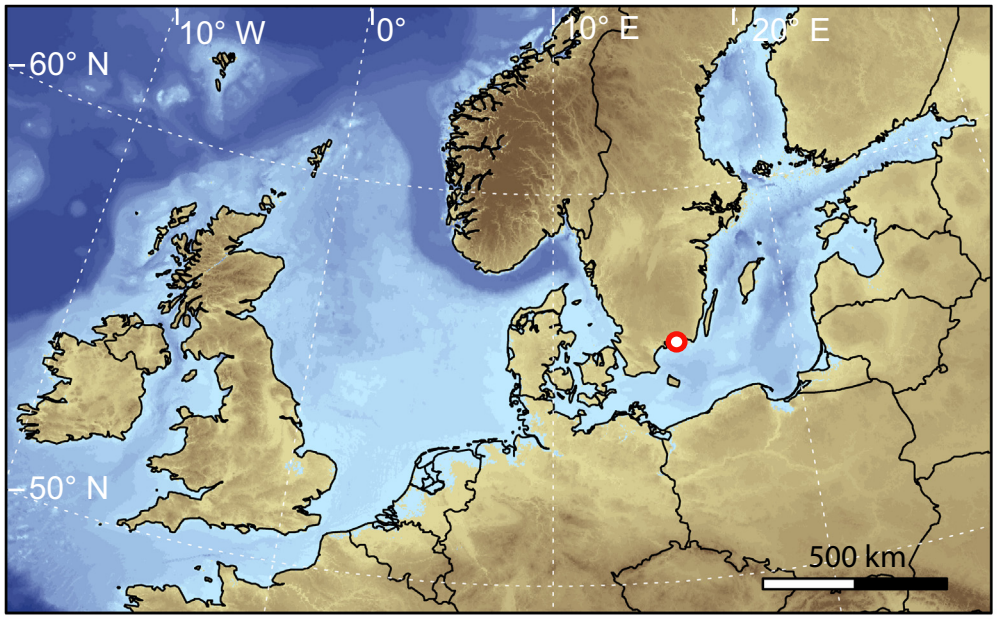

Fig. 1. Map showing location of Hässeldala Port in southern Sweden.