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Biomarker-derived phytoplankton community for summer monsoon reconstruction in the western South China Sea over the past 450 ka



Li Li ^{a,*}, Qianyu Li ^{a,b,**}, Juan He ^a, Hui Wang ^a, Yanming Ruan ^a, Jianru Li ^a

^a State Key Laboratory of Marine Geology, Tongji University, Shanghai 200092, China

^b School of Earth and Environmental Sciences, University of Adelaide, SA 5005, Australia

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ABSTRACT

Marine algal-derived lipid biomarkers (alkenones, brassicasterol, dinosterol, and long-chain diol/keto-ol representing haptophytes, diatoms, dinoflagellates, and eustigmatophytes, respectively) were used to evaluate the phytoplankton productivity and community structure changes in core MD05-2901 from the western South China Sea, which features distinct summer upwelling induced by southwest Asian monsoon. The results revealed substantial differences in the distribution patterns between the four major marine primary producers. Diatom and dinoflagellate biomarkers displayed slightly higher abundances, mostly in interglacials especially after MIS 8, while alkenones exhibited lower values in MIS 12 and MIS 1, with higher values in between especially in the middle of MIS 7, but eustigmatophytes increased in most glaciations, indicating complex responses of different phytoplanktons to paleoclimatic and paleoenvironmental changes over the past 450 ka. The sum of the four phytoplanktons shows subtle glacial–interglacial patterns, probably reflecting the combined hydrological dynamics driven by enhanced summer monsoon during summer/interglacials and enhanced winter monsoon during winter/glacials in the region. The biomarker-based community structure showed relative high contribution from diatoms and dinoflagellates during interglacials, high contribution in the middle part of the section centered at ~210 ka from the coccolithophorids, but varying levels from the eustigmatophytes with high percentages in most glacials. Diatoms show strong nutrient sensitivity and positive relation with other paleo-proxies, and their enrichments during interglacials can be attributed to enhanced nutrient level induced by the East Asian summer monsoon, which could have been coupled with the influence of the global ice volume, the summer insolation and the Southern Hemisphere latent heat.

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1. Introduction

Phytoplankton productivity is crucial in controlling the partitioning of carbon between the ocean and atmosphere, thus playing an important role in the global carbon cycle and climate change (Falkowski et al., 1998). For a better understanding of paleoclimatic change, therefore, to evaluate and reconstruct paleoproductivity history wisely becomes extremely important. Numerous proxies, including organic carbon, calcium carbonate, biogenetic opal, foraminiferal population and trace elements have been used for this purpose with insightful results. However, the mixture of terrestrial and marine TOC input, variable contribution from different groups

of silica-producing plankton in opal content, complex food webs in foraminifera, terrestrial introduction and some geochemical alteration on trace elements made their interpretations quite complicated and sometimes unconvincing. The molecular biomarkers, due to their specificity and preservation virtue, have become an attracting and promising approach in tracing the contribution of different planktonic groups for productivity reconstructions (e.g., Volkman et al., 1998).

The South China Sea (SCS) is the largest marginal sea in the western Pacific, and its biogeochemical processes are linked to the atmospheric forcing and surface hydrography (Wang and Li, 2009). Despite the largely oligotrophic nature of the SCS, high productivity generally occurs in estuaries and coastal zones as well as regions featured by seasonal upwelling. For the SCS paleoproductivity, different reported patterns reflect the complex situation in different regions of this marginal sea basin. In the northern SCS, enhanced glacial productivity has been determined using different proxies, such as the TOC and chlorin records for the total

* Corresponding author. Tel.: +86 21 65982215; fax: +86 21 65988808.

** Corresponding author at: State Key Laboratory of Marine Geology, Tongji University, Shanghai 200092, China. Tel.: +86 21 65987968; fax: +86 21 65988808.

E-mail addresses: lilitju@tongji.edu.cn (L. Li), qli01@tongji.edu.cn (Q. Li).

productivity, opal for the diatom productivity, alkenones for the haptophytes productivity, and multi-biomarkers for the phytoplankton productivity (Huang et al., 1997; Kienast et al., 2001; Higginson et al., 2003; He et al., 2013; Li et al., 2014a). However, the reported levels of paleoproductivity are different between the southern and western SCS. In the southern SCS, for example, benthic foraminiferal assemblages indicated higher productivity during the last glacial maximum (Kuhnt et al., 1999), while the abundance of siliceous microfossils (radiolarians, diatoms and sponge spicules) indicated enhanced productivity during interglacials since the mid-Pleistocene climate revolution (Wang and Andrea, 2002; Wang and Li, 2003). Meanwhile, elemental analyses implied calcareous plankton increased during interglacials but siliceous plankton increased during glacials in the southern SCS (Wei et al., 2003a). Although similar studies in the eastern SCS are few, relatively low carbonate and opal combined with high TOC have been reported as characterizing the glacial stages there (Shiau et al., 2008). More specifically, alkenone records revealed a general decreasing trend in coccolithophore productivity since MIS 5 without any apparent glacial and interglacial patterns from various SCS localities (Pelejero et al., 1999; Kienast et al., 2001; Shiau et al., 2008; He et al., 2013; Li et al., 2014a), while a maximum biological growth in the mid Holocene in the southern SCS has also been reported (Chen et al., 2008). Therefore, new approaches are needed to address the controversial issues by different proxies in order to better understand the marine productivity dynamics as related to climate change, and multi-algal biomarkers appear to be a suitable means for achieving this purpose (He et al., 2013).

Since its first attempt in 1997 in the SCS, the use of alkenones for SST reconstructions has dominated the molecular biomarker studies in the region (Huang et al., 1997; Pelejero et al., 1999; Kienast et al., 2001; Steinke et al., 2001; Zhao et al., 2006a; He et al., 2008; Li et al., 2009, 2011), with very few emphasizing the phytoplankton community changes (Hu et al., 2002; He et al., 2013; Li et al., 2014a). Biomarker studies in the western SCS are especially scarce, partly because of its more complex physical, chemical and ecological regimes than other parts of the SCS. In this work, multi-algal lipids in core MD05-2901 (Fig. 1) off southeastern Vietnam over the last 450 ka were analyzed, and the results were used to infer the long-term variability of paleoproductivity and phytoplankton community structure as related to the monsoon evolution in this region.

2. Algal lipids biomarkers for paleoproductivity reconstruction

Algal biomarkers, due to their resistance to degradation and well preservation in sediments, have long been used to assess the sources of the phytoplankton biomass in the ocean (Volkman et al., 1998). Long-chain alkenones constitute the most employed biomarker in paleoceanography because of the widely used thermometer proxy U_{37}^* (Müller et al., 1998). These lipids with the carbon number of 37–40 and double bonds of 2–4 are the specific markers of some coccolith-bearing haptophyte species, i.e., *Emiliania huxleyi* and *Gephyrocapsa oceanica* in the modern ocean (Marlowe et al., 1990). The alkenones can account for 8% of the organic matter in *E. huxleyi* (Prahel et al., 1988) and have been extensively employed as productivity indicators because of their widespread abundances in marine sediments (Table 1).

Sterols are often found in all eukaryotes and in a few bacteria, but specific sterols can serve as indicators for categorizing various organisms (Volkman et al., 1998). Brassicasterol, 24-methylcholesta-5,22-dien-3 β -ol, is the major sterol in some species of diatoms, although some other microalgae, such as haptophytes and

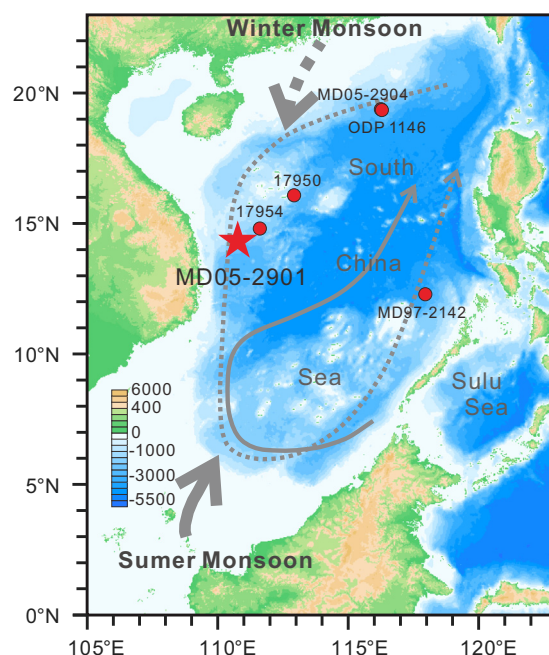


Fig. 1. A schematic map shows the locations of core MD05-2901 (star) and other sites (circles) mentioned in the text. Gray arrows indicate the modern monsoon-driven surface circulation during summer (solid curve) and winter (dashed curve).

cryptophytes, also have the ability of synthesizing this organic matter (Volkman, 1986, 2003). Dinosterol, 4 α ,23,24-trimethyl-5 α -cholest-22E-en-3 β -ol, with a unique methylation position, is mainly confined to dinoflagellates and a few diatoms (Volkman et al., 1998).

Also frequently detected in marine environments are the long-chain alkyl diols homologs with C₂₄–C₃₆ chain lengths, produced likely by the versatile and adaptive Eustigmatophyceae, although other organisms may also biosynthesize these compounds (Versteegh et al., 1997; Sinninghe Damsté et al., 2003). Generally, C₃₀-1,15-diols dominate most oceanic settings among several number of positional isomers and, together with keto-ols, they are often considered as the oxidation products of the corresponding diols in marine sediments. These oxidized matters may have been derived directly from some other sources, such as the eustigmatophyte species *Nannochloropsis gaditana* (Ferreira et al., 2001; Méjanelle et al., 2003). In addition, the long chain 1,14-alkyl diols found in some water and sediments are believed as from the production of diatom *Proboscia* and can be used to indicate the regional hydrological situation (Sinninghe Damsté et al., 2003; Rampen et al., 2014 and references). Other algal biomarkers, such as some unusually highly branched isoprenoid (HBI) alkenes, loliolide/isololiolide, owing to their special producers, are also employed for productivity reconstructions (Repeta, 1989; Hinrichs et al., 1999; Menzel et al., 2003; Rowland and Robson, 1990).

Many studies have shown that algal multi-biomarkers, characteristic of different phytoplankton taxa, are potentially valuable paleoceanographic indicators. In the Sea of Okhotsk, for example, the replacement of the dominant phytoplankton species from coccolithophorid (*E. huxleyi*) during deglaciation to diatoms in the late Holocene was associated with a change in the surface hydrography over the last 30 ka (Seki et al., 2004). In the eastern equatorial Pacific, marine biomarkers provide evidence of algal variability in relationship with climate change and global hydrological variations (Calvo et al., 2011). Multi-biomarkers were also used to support the paleoproductivity reconstruction in the SCS. In the Nansha area, simultaneous variations of C₃₇ alkenones and C₃₀ alkyl diols and the terrigenous long-chain compounds since the last glacial period suggested that the enhanced marine

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