

## BIODIVERSITY COLLAPSE AND RED ALGAL BLOOM IN THE NEOPROTEROZOIC SNOWBALL EARTH AFTERMATH

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The present results show that the eukaryotes suffered losses of diversity in the aftermath of the Marinoan glaciation. Eukaryotic steroidal biomarkers distribution, never observed before in any sediments, can be ascribed to only red algae. The proliferation of red algae is explained by a dim light water resulting from a massive terrestrial input. Molecular study provide arguments on the formation of platform carbonates and the evolution of multicellular life after the deglaciation. Both topics are hotly debated.

The Araras Group was deposited at the southeastern margin of the Amazon craton. It rests unmetamorphosed and undeformed, atop diamictites of the Puga Formation and is covered by siliciclastics of the Alto Paraguay Group (Nogueira et al., 2003). The whole carbonate succession is about 700 m thick and comprises, at the base, a transgressive post-glacial cap carbonate formed by stromatolitic dolostones of the Mirassol d'Oeste Formation (~20 m thick) and the base of the overlying Guia Formation limestones (~50 m thick). Given their isotopic and stratigraphic record they have been correlated to the post-Marinoan carbonate successions. Bitumen occurs at the top of the Mirassol d'Oeste dolostones and into the Guia limestones. Here we have focused on the lowermost level rich in organic matter of the post-glacial carbonates, which is located in the Mirassol dolostones, 20 m above the diamictite-carbonate contact. In there, bitumen is associated to peloidal microbial doloboundstone and peloidal dolopackstone with megaripple bedding. Sampled rocks are finely streak due to the alternation of dolostone and bitumen-rich layers (filling-in fenestral, intercrystalline and moldic porosities). Bitumen is also found along bedding-parallel stylolite planes formed probably during burial. These features imply an early capture of bitumen into the rock porosity, before compaction.

The bitumens are totally soluble in dichloromethane. Maturity parameters indicate that they were derived from a source bed which had reached the maximum of oil generation. Bitumens yield up to 230 mg/g of saturated hydrocarbons and up to 110 mg/g of aromatic hydrocarbons. The presence of dibenzothiophenes ( $m/z$  184, 198, 212) could account for the interaction of reactive sulphur ( $H_2S$  and  $H_2S_n$ ) with organic matter under the action of

sulphate-reducing bacteria (Orr and Sinninghe Damsté, 1991). The evidence that sulphate-reducing bacteria flourished in the sediment strongly support the microbially-mediated model proposed for dolomite formation in cap dolostones (Vasconcelos and McKenzie, 1997). The identification of aryl isoprenoids suggests the presence of green sulphur photosynthetic bacteria (Summons and Powell, 1987; Koopmans et al., 1997; Brocks et al., 2005). These bacteria were likely associated to the sulphate-reducing bacteria in a microbial consortium. The main distinctive feature of the analyzed bitumen is their sterane signature. In Mirassol d'Oeste dolostones only the C<sub>27</sub> steranes are detected which could be ascribed to red algae. The 13β(H),14α(H)-tricyclic terpanes with 19-32 carbon atoms dominate the terpanes distribution while hopanes are in trace levels or absent

The biomolecular study combined with available geochemical and isotopic data enabled us to suggest a post-Marinoan world, in which the identified organisms likely composed a post-glacial ecosystem marked by a drastic decline in marine algal diversity, and the thriving of a consortium of opportunist microbial organisms which contributed to the precipitation of the carbonates. This scenario helps to explain sedimentary and isotopic “anomalous” features and the ubiquitous carbonate deposits that cap the Neoproterozoic glacial rocks.

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## RE-INTERPRETING THE CHLORIN SIGNAL IN SEDIMENTS TO DECIPHER PAST CHANGES IN THE MARINE CARBON CYCLE

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Finding an explanation for the occurrence of the glacial/interglacial CO<sub>2</sub> cycles is still one of the main challenges faced by the paleoceanographic community. The oceans, as they hold 50 times more carbon than the atmosphere, are one of the key elements of the puzzle. Marine biota plays a central role in the sequestration of atmospheric carbon dioxide by the oceans by extracting organic carbon from the surface and transferring it to the deep sea. This is the process of export production and is one of the fundamental parameters of the biological carbon pump. A reliable tool for reconstructing past export productivity is needed to determine the efficiency of the biological pump through time since it plays a key role in the global carbon cycle. Unfortunately, none of the proxies used so far are by themselves reliable indicators of export production. In here we re-evaluate the use of total chlorophyll derivatives for the purpose of reconstructing global glacial-interglacial differences in marine export production.

The concentrations or mass accumulation rates in sediments of phytoplanktonic biomarkers have often been used to reconstruct past primary productivity of individual plant functional types or general phytoplanktonic production. A few studies have attempted the reconstruction of changes in primary productivity using total chlorins mass accumulation rates in sediments (e.g. Summerhayes et al., 1995; Harris et al., 1996). However, chlorin mass accumulation rates in sediments is the result of both phytoplankton primary productivity and the transfer efficiency of chlorins mediated by a range of degradation processes occurring in the water column and in the water-sediment interface. One of the main questions to resolve is to determine which are the degradation processes controlling chlorin fluxes signal in different sedimentary regimes.

To address this question we have compiled a suite of 60 deep sea sediment cores and measured chlorin mass accumulation rates in two main intervals, the late Holocene and the Last Glacial Maximum (Figure 1). The aim is to provide a large scale overview and reconstruct regional patterns in the changes of mass accumulation rates of chlorins in different sedimentary and productivity regimes. By comparing surface sediment chlorin data with satellite observations on marine primary productivity and information from the water column

on oxygen content and particle fluxes we are developing a transfer function for primary export production. However, it is unlikely that information on absolute export values can be obtained with enough confidence. Therefore a key element of the approach is to rely on the relative changes between two climatic relevant periods as a way to infer changes in the marine carbon cycle.

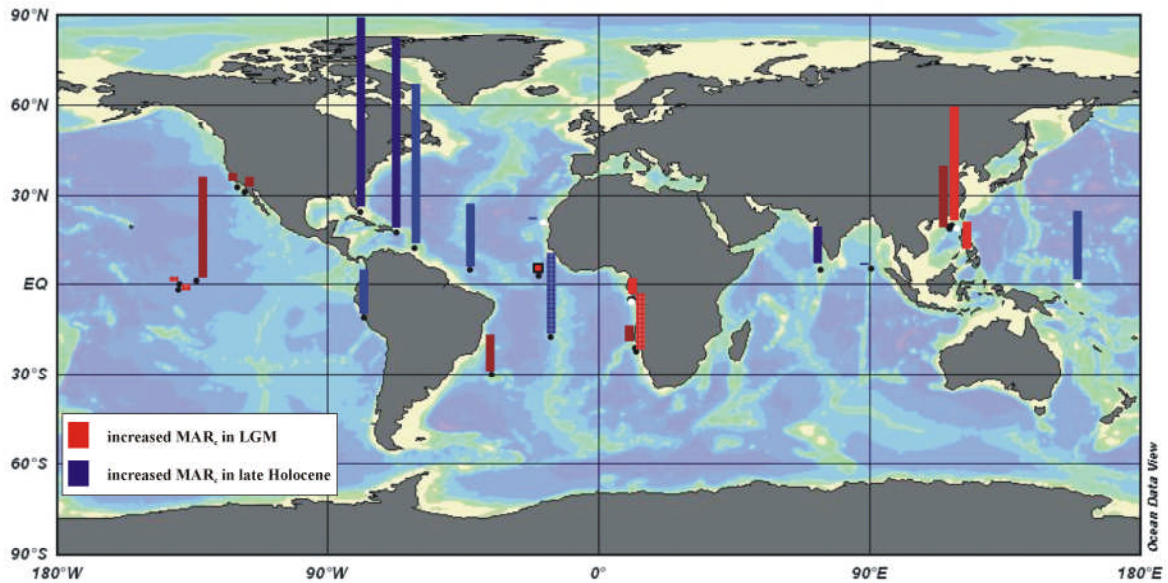


Figure 1. Preliminary results of the relative change on chlorin mass accumulation rates ( $MAR_C$ ) between Last Glacial Maximum (LGM) and late Holocene. Colors bars indicate whether the chlorin mass accumulation rate increased (red) or decreased (blue) during LGM compared to late Holocene.

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**NOVEL HIGHLY BRANCHED ISOPRENOID BIOMARKERS AS INDICATORS OF  
SEA-ICE DIATOMS: IMPLICATIONS FOR HISTORICAL SEA-ICE RECORDS  
AND FUTURE PREDICTIONS**

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Polar oceans are important contributors to the Earth's climate systems. In particular, sea-ice influences the exchanges of heat and moisture between polar oceans and atmosphere, and its high albedo means that it reflects much of incoming solar radiation. In addition, when melting, the outflow of low-salinity surface water impacts on the global deep oceanic circulation, which can influence the climate to a large extent. Therefore, increasing our knowledge about how changes in past sea-ice extent contributes to our understanding of the actual changes in climate is critical if we aim to succeed in predicting future changes (Thomas and Dieckmann, 2003).

Direct global estimates of sea-ice cover derived from remote sensing observations are now routine but have only been possible since the 1970's (Stroeve *et al.*, 2005). Previously, analysis of data derived from early ship records have been carried out, providing an observed sea ice record for the 20<sup>th</sup> century and earlier. Such records have been based on archive materials including lighthouse diaries, ships logs, travellers journals and newspaper reports. However, only the most recent direct estimations of sea-ice cover are believed to be reliable and therefore, longer time scales studies are only possible using proxy data sources.

In the current project, we are investigating the potential to use chemical biomarkers of sea-ice associated diatoms to serve as a proxy of sea-ice cover in the Arctic (Belt *et al.*, 2007). To date, our investigations have revealed that a restricted number of diatoms biosynthesise a class of secondary metabolite chemicals termed highly branched isoprenoids (HBIs). These chemicals are ubiquitous to marine sediments, but only one structural form of the HBIs exists in Arctic sea-ice. In turn, this chemical (a C<sub>25</sub> HBI mono-unsaturated alkene – IP<sub>25</sub>) can almost certainly be associated with some *Haslea* spp. which are known to occur in Arctic sea-ice. Indeed, we have identified three such species in our work and now have them in culture.

In order for the HBI biomarker to be useful as a historical indicator of past sea-ice, its behaviour in sediments also needs to be understood. Therefore, we have obtained sediment cores from the East-West Canadian Arctic (ArcticNet 2005) and analysed them for their biomarker content. We have detected the same HBI mono-unsaturated HBI alkene found in sea-ice in sediments collected from Lancaster Sound, Barrow Strait, Victoria Strait, the Amundsen Gulf, Franklin Bay and the North Icelandic Shelf. This has been achieved using extremely small sample sizes and with rapid turnaround times (< 1 g sediment; > 10 samples per day). The HBI biomarker has been readily detected in sediments covering the entire Holocene. These data, together with analyses from sediments obtained from the North Icelandic shelf (MD99-2275) will be discussed.

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