GLOBAL CALIBRATION OF SEDIMENTARY CHLORINS AS QUANTITATIVE PROXIES OF PRIMARY PRODUCTIVITY AND NUTRIENT AVAILABILITY

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Elucidation of the role of the marine carbon cycle in the glacial-interglacial cycles of CO_2 is vital to our understanding of the key feedbacks operating in the present-day Earth system. Primary productivity is the driving factor in the marine carbon cycle and many efforts have been made to estimate it in the past (Kohfeld et al.,2005). However, most proxies availables provide partial insights on past ocean carbon fluxes. For instance, total organic carbon might be biased by terrigenous organic matter, and carbonate proxies by dissolution. Another commmon strategy to estimate export productivity is to analyse long chain C_{37} alkenones. However, export fluxes of these biomarkers are not representative of the overall phytoplaknton community, just the Haptophyceae algae. An alternative approach is to measure phytoplankton nutrient availability using nitrogen isotopes in bulk sediments or foraminifera, but it is constrained by diagenetic processes (Altabet and Francois,1994; Tyler et al.,2010).

Primary productivity can also be estimated by measuring chlorophyllic pigments and since 1997, global chlorophyll-a concentration on the ocean surface has been measured by satellite. In here, we take a global approach to constrain the use of total sedimentary chlorins, derivatives of chlorophyll-a, as a quantative proxy for both primary export productivity and phytoplankton nutrient availability. In contrast to other available proxies, chlorins are directly produced by primary producers. Moreover, as chlorins have 4 nitrogen atoms, they can provide information on phytoplankton nutrient availability by measuring chlorin nitrogen isotopes. Hence, we can obtain complementary information on carbon cycle processes at the ocean surface from the same proxy, which simplifies the interpretation of palaeorecords.

The aim of the study is to relate sedimentary chlorin concentration from a global suite of 123 surface marine sediments with satellite chlorophyll-a estimates, to constrain the chlorins proxies to estimate past primary export productivity. In addition, alkenones concentration in sediments have also been measured for comparison to assess their relative merits. To assess chlorin nitrogen isotopes as a proxy for phytoplankton nutrient availability, $\delta^{15}N$ of individual pigments have been measured in selected samples as well as $\delta^{15}N$ in bulk.

We have found that indeed there is a correlation between satellite chlorophyll estimates and chlorins in sediments (Fig. 1). However, such correlation is non linear and strongly dependent on the oceanic basin. Thus, sediments from the North Atlantic show no correlation with satellite chlorophyll, whereas, those from Southern Ocean and equatorial locations do. In these sites, primary productivity is the chief driving factor in determining sedimentary chlorins concentration. In the other locations we are now in the process of identifying the biogeochemical processes that control export flux of chlorins to sediments. The ultimate aim is identifying the biogeochemical conditions, and thresholds, which would allow inferring quantitatively surface export chlorophyll in the past. Alkenone concentrations also relate to primary productivity, but they are constrained by different processes in different regions.
In parallel, we are also calibrating the use of $\delta^{15}N$ to estimate phytoplankton nutrient availability. Initial data show that isotopic differences between pigments for some sediments

suggest that best estimates would be derived from weighted average signals of specific pigments. Moreover, the results show that the $\delta^{15}N$ approach, albeit time consuming does provide more accurate estimates of nutrient utilization by phytoplankton, and hence primary productivity. In conclusion, our study shows that from a sediment sample, three complementary measurements can be derived from biomarkers that provide, in specific cases, a unique way to constrain past export marine productivity.

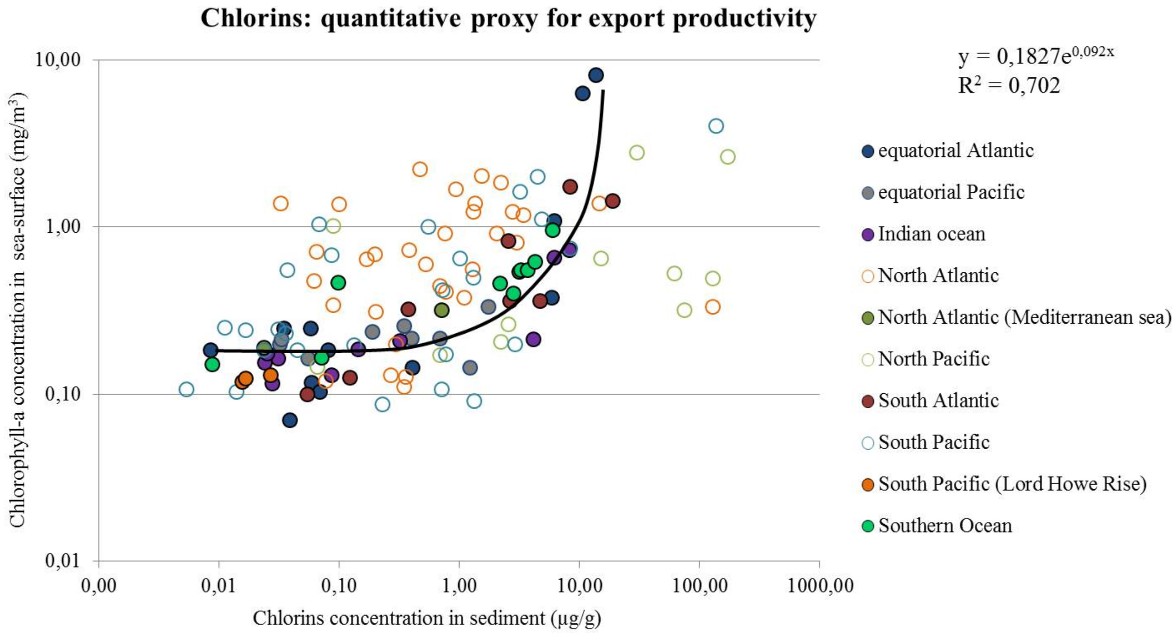

Figure.1 *Correlation between marine sedimentary chlorin concentrations and surface ocean satellite chlororophyll-a contents. The equation has been calculated taken into account the filled circles.*

References

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