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Maleimides in recent sediments - New insights into chlorophyll degradation and palaeoenvironmental reconstructions

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Chlorophylls and bacteriochlorophylls are the most abundant photosynthetic pigments on Earth. These compounds and their transformation products (chlorins, porphyrins, maleimides) can be preserved in limnic and marine sedimentary deposits and crude oils and serve as valuable proxies for palaeoenvironmental reconstructions. Among these degradation products, maleimides (1H-pyrrole-2,5-diones), oxidation products of the tetrapyrrole pigments, have been hardly studied so far in recent sediments and most studies being focused on ancient deposits (e.g., Grice et al., 1996).

In this study, both "free" (i.e. naturally-occurring) maleimides and maleimides formed by chromic acid oxidation of sedimentary pigments were analysed in recent sediments from the eutrophic Swiss lake Rotsee and the Black Sea to identify maleimide sources, to investigate chlorin degradation processes and the role of oxygen in maleimide formation. In the solvent extract of these recent deposits, free Me,H, Me,Me, and Me,Et-maleimides were observed, the latter largely dominating the distributions. In addition, trace amounts of Me,i-Bu maleimide were detected in the Rotsee and some of the Black Sea sediments. Following chromic acid oxidation, a more complex distribution was obtained, additionally comprising Me,n-Pr and Me,n-Bu and some maleimides with unknown structures, but their possible mode of formation, origin(s) and significance is currently under study.

The large predominance of the Me,Et homologue in all distributions is to be expected since this compound can be formed from most of the tetrapyrrole pigments, including notably chlorophyll-a derivatives from primary producers living in the oxic part of the water column, as well as from bacteriochlorophylls from sulfur photosynthetic bacteria. In contrast, the origin of Me,H and Me,Me maleimides is more intriguing, these compounds possibly arising from unknown chlorin precursors. Me,n-Pr and Me,i-Bu, originating specifically from bacteriochlorophylls c, d and e from Chlorobiaceae, are mainly present among the maleimides formed by chromic acid oxidation, and represent specific indicators of photic zone anoxia, including Unit 3 of Black Sea, indicating at least temporary development of an anoxic zone extending into the photic zone during the limnic phase.

Oxygen was found to be crucial for maleimide formation within the water column of these systems, but probably other electron acceptors are also responsible for the decomposition of chlorins during diagenesis.

We propose a novel maleimide based degradation index for the qualitative estimation of the degree of OM degradation similar to the chlorin index (Schubert et al., 2005), which is possibly applicable for longer timescales.

References

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