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The fate of marine lipids: Biotic vs. abiotic degradation of particulate sterols and alkenones in the Northwestern Mediterranean Sea

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ABSTRACT

Sterol and alkenone compositions in suspended particle and surface sediment samples collected in the Northwestern Mediterranean Sea during the MEDFLUX program were used to evaluate the relative importance of biotic and abiotic degradation processes on marine organic matter. Alkenone concentrations decreased much more rapidly (~500 fold) between 5 and 800 m than Δ^5-sterols (~100-fold) or POC (~100-fold). The diverse functional groups attached to the stable tetracyclic carbon skeleton of Δ^5-sterols appeared to be useful for estimating the relative effects of biotic vs. abiotic (photooxidation and autoxidation) degradation. Products of abiotic degradation predominated over products of biotic degradation in suspended particles in the NW Mediterranean. For alkenones, the $U^{K'}_{37}$ index increased from 0.43 to 0.55 with increasing water depth, and a good correlation between variations of $U^{K'}_{37}$ and concentrations of specific Δ^5-sterol autoxidation products points to selective autoxidation of alkenones in suspended particles. Stereomutated alkenones (with *cis* double bonds) were detected in the surface sediment, allowing us to estimate that stereomutation resulted in a +0.05 increase in $U^{K'}_{37}$. Therefore, abiotic degradation may be another factor effect on alkenone-derived paleothermometry.

1. Introduction

Understanding the biogeochemical cycle of carbon in the ocean requires identifying not only the sources of particulate organic matter (POM) but also those processes responsible for its alteration. Most studies of the alteration of POM have focussed on biotic degradation, but the potential impact of abiotic photooxidation and autoxidation is less well understood owing to the lack of adequate tracers. Nonetheless, photooxidation by photosynthetically active radiation (PAR) and autoxidation [free radical-mediated oxidation via homolytic cleavage of photochemically produced hydroperoxides catalyzed by some metal ions (Pokorny, 1987; Schaich, 1992)] can degrade common marine lipids, including unsaturated fatty acids, the phytyl side-chain of chlorophyll, sterols and alkenones. Chlorophyll-sensitized photooxidation can be important within the euphotic layer, whereas autoxidation may occur throughout the water column and in oxic sediments. Photodegradation and autooxidation may yield diagnostic products (for a review see Rontani, 2008). In the case of alkenones, autoxidation may alter significantly their unsaturation ratio and thus constitute a source of uncertainty during paleotemperature reconstruction (Rontani et al., 2006a, 2007). Unfortunately, tracers allowing direct estimates of autoxidative alterations of alkenones are lacking.

Significant photooxidative and autoxidative alteration of fast sinking organic matter collected by sediment traps at the DYFAMED station (Northwestern Mediterranean Sea) have been documented using newly identified tracers (Marchand et al., 2005; Rontani et al., 2006a). We now hypothesize that effects of abiotic degradation should be amplified in suspended particles due to their slower sinking rates and higher residence time in the water column. To further evaluate the importance of abiotic degradation on marine organic matter, we have now investigated suspended particles in the NW Mediterranean within the framework of the MEDFLUX program (http://www.msrc.sunysb.edu/MedFlux/). Because sterols are excellent biomarkers for tracing diagenetic transformation of organic matter (Mackenzie et al., 1982; Volkman, 1986; Wakeham and Beier, 1991), we used their oxidation products to determine the relative roles of biotic and abiotic degradation. Using our observations of POM degradation derived from sterols, we then examined how abiotic degradation might affect the fate of alkenones, and thus the paleotemperature proxy , UK'37 in the Northwestern Mediterranean.

2. Materials and methods

2.1. Collection of the samples

Suspended particle samples were collected in the Northwestern Mediterranean Sea 52 km off Nice, France at 43°25' N, 07°52'E during MedFlux (R/V *Tethys II*, May, 2006; cruise). MedFlux was a multidisciplinary investigation designed to determine and model

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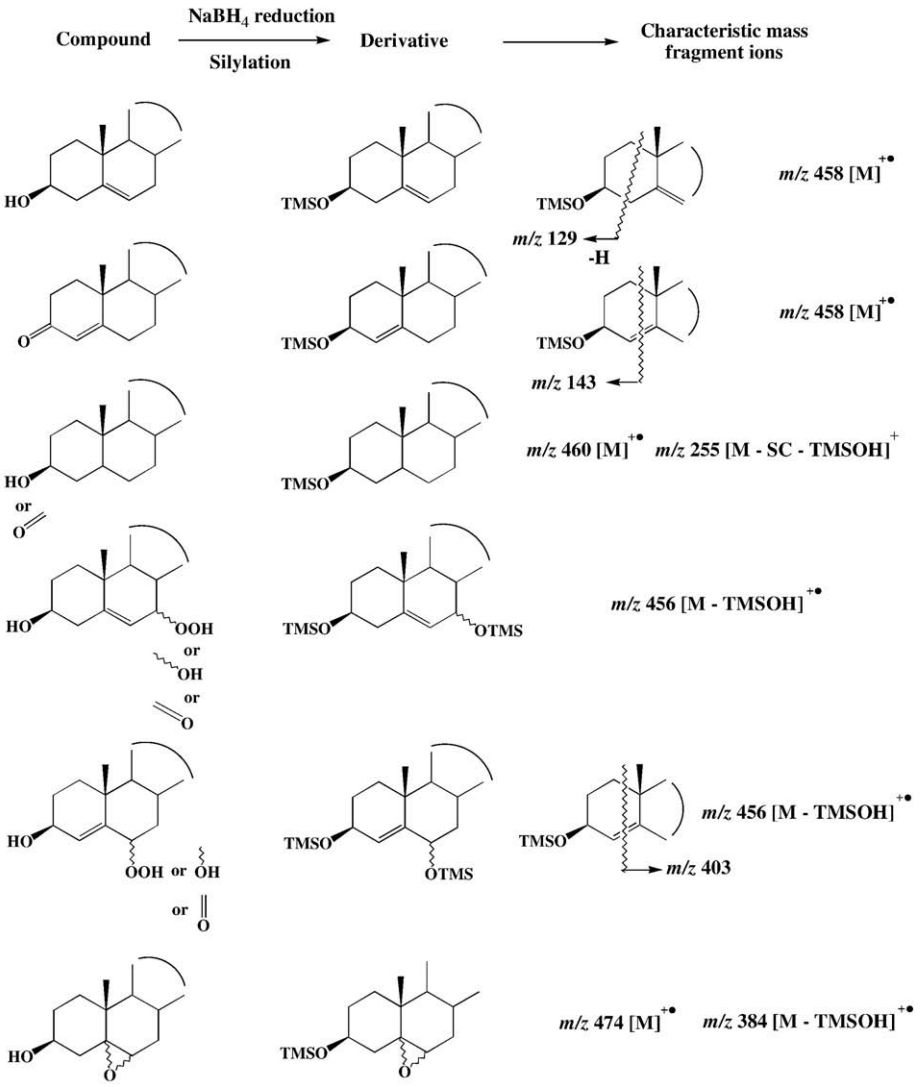

Fig. 1. Mass spectrometric characterization of sterols and their degradation products (the example given is cholesterol).

relationships between organic matter and mineral ballast in particulate matter in the ocean (Lee et al., in press-a, and associated Special MedFlux issue of Deep-Sea Research II). The MedFlux site was located at the French Joint Global Ocean Flux Studies DYFAMED time-series site (Marty 2002, and references therein). Located in the central Ligurian Sea and with a water depth of ~2300 m, the MedFlux/DYFAMED site is thought to be isolated from advection of coastal riverine and resuspended sediments (Durrieu de Madron et al., 1990),

Table 1
Concentration of free Δ^5 sterols and POC in the suspended particulate matter samples investigated

	Depth (m)								
	5	20	40	80	100	125	150	400	800
24-Norcholesta-5,22*E*-dien-3β-ol	4.1	4.2	5.8	2.8	2.5	5.8	2.0	2.5	–
27-Nor-24-methylcholesta-5,22*E*-dien-3-ol	18.1	17.8	9.9	10.0	11.7	8.5	8.7	7.2	4.5
Cholesta-5,22*E*-dien-3β-ol	5.3	5.1	12.6	11.9	11.7	9.6	12.2	10.2	3.3
Cholest-5-en-3β-ol	5.4	6.6	14.1	24.1	27.0	38.5	27.0	31.7	65.0
Cholesta-5,24-dien-3β-ol	27.5	25.6	2.8	3.0	3.2	4.9	2.6	-	–
24-Methylcholesta-5,22*E*-dien-3β-ol	17.8	17.8	31.9	15.9	16.3	11.1	13.3	14.6	11.6
24-Methylcholesta-5,24(28)-dien-3β-ol	7.5	8.2	3.8	5.1	4.1	3.3	3.6	5.2	–
24-Methylcholest-5-en-3β-ol	-	-	1.2	4.1	3.2	–	3.4	3.6	–
24-Ethylcholesta-5,22*E*-dien-3β-ol	4.4	4.3	4.8	6.2	4.3	3.6	7.2	7.2	5.9
24-Ethylcholest-5-en-3β-ol	3.1	3.7	7.2	8.8	8.7	11.5	11.6	12.7	9.7
24-Ethylcholesta-5,24(28)*Z*-dien-3β-ol	2.9	2.6	2.0	2.8	2.5	3.1	3.1	5.1	–
24-*n*-propylcholesta-5,24(28)*E*-dien-3β-ol	1.7	2.0	1.0	1.8	1.5	–	2.4	–	–
24-*n*-propylcholesta-5,24(28)*Z*-dien-3β-ol	2.2	2.5	2.9	3.6	3.3	–	2.9	–	–
Total sterol concentration (μg l^{-1})	3.17	1.57	0.35	0.13	0.10	0.10	0.09	0.04	0.03
POC (μg l^{-1})	126.3	103.5	16.6	9.3	4.8	5.9	4.0	4.0	1.2