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Restricted utility of the pristane/phytane ratio as a palaeoenvironmental indicator

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The acyclic C_{19} and C_{20} isoprenoid hydrocarbons, pristane (Pr) and phytane (Ph), respectively, have been widely assumed to be diagenetic products of the phytyl side chain of chlorophyll[1–3], although alternative sources of precursors have been suggested. The ratio of these two compounds is usually interpreted to be an indicator of the oxicity of the environment of deposition[3,4]. Recent advances in organic geochemistry in combination with geological constraints lead us to suggest that the Pr/Ph ratio cannot be used as an indicator for oxygen levels. However, in hypersaline environments of deposition the rationale behind a low Pr/Ph ratio is easier to understand, and in these environments application of the Pr/Ph ratio can be expected to be successful.

As early as 1969 Brooks *et al.*[2] suggested that variations in the Pr/Ph ratio may reflect variations in the degree of oxidation during early diagenesis of chlorophyll. In extension of this, Didyk *et al.*[4] proposed a direct relationship of the Pr/Ph ratio with the oxicity of the environment of deposition, but they also emphasized that other lines of evidence, such as chlorin contents, should be considered in order to assess properly the depositional environment. A Pr/Ph ratio of less than unity, according to these authors, would indicate an anoxic and thus reducing environment, and *vice versa* for a ratio greater than unity. With strict adherence to these guidelines, but without paying attention to the limitations, this invoked application of the ratio as an environmental indicator has had an enormous impact on the organic geochemical literature, because both isoprenoid compounds are almost ubiquitously present in the geosphere. Many organic geochemists and petroleum geochemists use this parameter, partly because of its easy measurement by simple gas chromatography of the hydrocarbon fraction of sediment extracts or crude oils.

The rationale of the Pr/Ph ratio as an environmental indicator is that in an anoxic environment reducing diagenetic pathways prevail over oxidative pathways. The isoprenoid alcohol, phytol, assumed to be liberated from chlorophyll at an early stage of diagenesis by hydrolysis, is taken as starting point for a series of defunctionalization reactions[1–4]. While under reducing conditions phytol may ultimately be transformed to phytane, it is hypothesized that under oxic conditions pristane is generated from phytol via decarboxylation of an intermediate carboxylic acid.

The recent suggestion that archaebacterial lipids (for example, from methanogens or halophiles) could be another source for these isoprenoids[5,6] in combination with a possible origin of pristane from tocopherols[7], has greatly weakened the rationale for the use of the Pr/Ph ratio. In addition, pristane and pristenes have also been detected in zooplankton[8,9], although such an origin of sedimentary pristane has never really been considered to be a major source. Furthermore, an analytical problem of precise determination of Pr/Ph ratios arises from the recent identification of an unusually branched alkane (2, 6, 10-trimethyl-7-(3-methylbutyl)-dodecane) in sediments, which coelutes with pristane on most capillary columns[10]; this raises doubt about the validity of Pr/Ph ratios previously published in the literature.

Geological constraints are rarely considered. Invariably ignored is the geological fact that all fine-grained nearshore, shelf and hemipelagic sediments are anoxic below a surface oxic layer, the thickness of which depends on several factors, the most important one being the rate of sedimentation[11]. Stepwise extraction techniques, applied to decipher the mode of occurrence of lipids in organic-matter-rich sediments from the eastern Mediterranean, covering a time span from 1.10^3 to 2.10^5 years BP, revealed that most of the phytol encountered (>95%) was present in an esterified form and in abundant quantities[12,13], while alleged phytol transformation products (for example, phytadienes, dihydrophytol, phytanic acid, phytane, pristane[4]) were absent or present in very low concentrations. When phytol is eventually degraded in these sediments, this process will take place under reducing conditions, giving rise to low Pr/Ph ratios following the scheme of Didyk *et al.*[4]. Hence, this ratio would not be expected to reflect the oxicity of the environment of deposition, but would be merely the result of reactions taking place well after reducing conditions have been established.

Gravity-driven mass transport is another geological phenomenon which can lead to a misinterpretation of the Pr/Ph ratio. Turbidites, enriched in organic matter, have been found interbedded in pelagic sediments at several locations[14,15]. Progressive subsurface oxidation fronts greatly alter the labile organic matter in these turbidites[14]. Assuming that most of the phytol is still esterified to chlorophyll, such a post-depositional oxidation effect would result in elevated Pr/Ph ratios, which, however, do not reflect the original environment of deposition of these organic-matter-rich sediments. It has also been suggested that microenvironments, which do not reflect the redox conditions of the sediment as a whole, may be active sites where pristane and phytane are formed via microbially mediated reactions[6].

From the above discussion it is clear that it is virtually impossible to draw valid conclusions from the Pr/Ph ratio with respect to the oxicity of the environment of deposition, although this does not imply that we refute the observation that sediments deposited under strictly anoxic conditions are often characterized by low Pr/Ph ratios[4]. An alternative explanation for this observation is that pristane reflects the primary production of organic matter (represented by chlorophylls, tocopherols) and that most of the phytane stems from the strictly anaerobic methanogenic bacteria[5,6], which after burial flourish on organic matter well preserved as a result of anoxic conditions during deposition. However, in this respect it should be noted that phytanyl ether lipids are of minor importance in methanogens in comparison with biphytanyl ether lipids[16] which should not produce phytane very easily during diagenesis.

A special case, in which there may be some application of the Pr/Ph ratio as an environmental indicator, seems to be a hypersaline environment of deposition[17,18]. Reported Pr/Ph ratios of hypersaline environments are presented in Table 1. Low values are clearly characteristic, but this criterion alone is, of course, not sufficient to identify such an environment positively. An example of such an exception are the Pr/Ph ratios of the sediments from the Paradox Basin (Table 1). Other biological marker characteristics should therefore be considered[17–20], if possible, supported by geological information.

Hypersaline environments can be zones of high biological productivity, but with a low diversity of organisms[21,22]; of these

Table 1 Pristane/phytane ratios of hypersaline environments

Sample	Location	Age	Pr/Ph	Ref.
	Mediterranean area			
Rocks (3)	Northern Apennines	Miocene	0.1	18
Oils (3)	Sicily	Miocene	0.01–0.1	17, 27
Oil	Prinos, Greece	?	0.3	28
Oils (5)	East Mediterranenan	Tertiary	0.3–0.8	29
Oil	Greece	Miocene	0.25	30
Rocks (20)	East Mediterranean	Tertiary	0.4–0.8	29
Oil	Amposta, Spain	Miocene	0.61	31
Rock	Israel	Cretaceous	0.45	32, 33
Rock	Jordan	Cretaceous	0.47*	34
	Central Europe			
Rocks (3)	Rhine graben	Lower Miocene/Upper Oligocene	0.05–0.14	35
Rocks (17)	Rhine graben	Lower Miocene/Upper Oligocene	0.02–0.7	29
Oils (3)	Rhine graben	Lower Miocene/Upper Oligocene	0.05–0.4	29
Rocks (10)	South Germany	Triassic	0.36–0.53	36
Rock†	Aquitaine, France	Jurassic	1.20	37
Rock‡	Aquitaine, France	Jurassic	0.30	37
Oils(?)	Aquitaine, France	?	0.48–0.90	37
Rock	Scotland	Devonian	0.6	38
Rocks (28)	Germany	Permian + Miocene	<1	39
	China			
Rocks (12)	Jianghan Basin	Oligocene	0.05–0.46	40
Oils (2)	Jianghan Basin	Oligocene	0.08–0.18	41
Oils (2)	Chaidamu Basin	Lower Miocene/Upper Oligocene	0.27–0.30	41
	North America			
Oils (33)	Michigan Basin	Silurian	0.4–0.5	42
Oils (3)	Michigan Basin	Silurian	~0.56	43
Oils (8)	Michigan Basin	Silurian	~0.47	44
Oils (18)	Ontario	Silurian	0.47–0.66	45
Oil	Alberta	Devonian	0.15	46
Rocks (19)	Williston Basin	Triassic	~0.70	47
Oils (7)	South Florida	Cretaceous	0.54–0.73	48,49
Rocks (7)	Paradox Basin	Carboniferous	1.1–1.4	50
Oil	Rozel Point, Utah	Miocene	0.1	17
	Other areas			
Rocks (9)	Guatemala	Cretaceous	0.32–0.75	51
Oils (?)	Guatemala	Cretaceous	~0.6	37, 48
Oils (10)	Australia	Cambrian	0.82–1.10	52

The reported Pr/Ph ratios are maximum values, as a coelution of 2,6,10-trimethyl-7-(3-methylbutyl)-dodecane with pristane would decrease the pristane/phytane ratio. Numbers in parentheses give number of samples tested.

* Sample reanalysed in Delft Laboratory. A hypersaline environment is inferred from characteristic biological markers[17,18] and literature descriptions from adjacent areas of the same age[33].

† Sample with 30% anhydrite and 61% dolomite.

‡ Sample with 70% anhydrite and 28% dolomite.

halophilic bacteria are very important. These bacteria are known to contain complex lipids with a phytanyl moiety[23] in much higher amounts than in methanogenic bacteria, which can explain why sediments from hypersaline environments are characterized by low Pr/Ph ratios. At a certain level of salinity halophilic bacteria will have their prolific growth stage and it is, therefore, postulated that the salinity will be the key control for the Pr/Ph ratio in such environments.

An increase of the Pr/Ph ratio with depth has been observed in uniform sedimentary sequences[24,25] as well as in non-uniform strata[2,26]. Apparently, maturation has an influence on the Pr/Ph ratio, although this cannot account for the results obtained for the relatively immature sediments from the Paradox Basin. Immature oils and sediment extracts listed in Table 1 are, where reported, characterized by high Ph/*n*-octadecane ratios ($\gg 1$). Due to the generation and release of hydrocarbons during maturation the Ph/*n*-octadecane ratios will decrease and will eventually reach values below unity, while at the same time the Pr/Ph ratio will increase. Again it must be stressed that the above outlined scheme cannot be quantified as it is probably highly dependent on the origin of the organic matter.

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Factors controlling emission of dimethylsulphide from salt marshes

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The emission of biogenic sulphur gases constitutes about half the atmospheric budget for gaseous sulphur[1]. Since dimethylsulphide (DMS) was first implicated as a major component of gaseous sulphur flux[2–4], considerable attention has been given to its emission from various ecosystems. Salt marshes have been identified as one system with a high area-specific sulphur emission[5–13]. Dimethylsulphide and hydrogen sulphide (H_2S) constitute the bulk of the flux from salt marshes, with DMS predominating in vegetated areas of the marsh[6,8–13]. As H_2S is a product of anaerobic decomposition in sediments, it has been assumed that other sulphur gases emitted from salt marshes also originate from decomposition in sediment processes[5]. Our research suggests an alternative explanation for DMS fluxes. We have investigated the distribution of DMS and dimethylsulphoniopropionate (DMSP) in salt marshes and conclude that DMS arises primarily from physiological processes in leaves of higher plants, mainly one species of grass, *Spartina alterniflora*. Furthermore, the emission of DMS from this grass may be influenced by the technique used to measure emission, and emission from sites dominated by *S. alterniflora* cannot be considered to be representative of marsh flora.

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If we assume that DMS and H_2S emission from salt marshes result from processes in the top 2 cm of sediment where plant root biomass and microbial activity are typically greatest[14], it is possible to estimate turnover rates for the dissolved gas pools. The observed flux of H_2S from salt-marsh sediments (150 μmol m^{-2} d^{-1})[9] represents a turnover of only 0.1% per day for typical porewater concentrations of 500 μmol l^{-1} (refs 14, 15). In contrast, DMS emission from sediments with undisturbed plants (1–246 μmol m^{-2} d^{-1})[9] would require turnover rates of 100–30,000% per day for typical porewater concentrations of 50 nmol l^{-1} (ref. 15). This discrepancy suggests that the sources and controlling factors of the two major sulphur gas emissions from salt marshes must differ markedly.

We have investigated the concentration of DMSP in a variety of higher plants inhabiting the intertidal salt marshes of eastern North America. The pool of DMSP is especially high in the tissues of *S. alterniflora* (Table 1). We have not recorded DMSP at concentrations greater than 0.1 μmol per g dry weight in tissues of any other marsh species. Perhaps coincidentally, there are no published reports of measurements of DMS emission from any other marsh species or from marshes lacking *S. alterniflora*. Previously, DMSP has been documented in a wide range of marine algae[16–18] and in two higher plants, *Spartina anglica*[19,20] and *Zostera marina*[18]. In certain species, DMSP seems to be involved in regulating cellular osmotic pressure[21] and may also be important in sulphur storage[20]. DMSP is thought to degrade mainly by an enzymatically catalysed elimination reaction, yielding DMS and acrylic acid[16]. We propose that this reaction is carried out in the leaves of *S. alterniflora* and is the major source of the observed flux of DMS from salt marshes. Similar processes should dominate wherever vegetation contains high concentrations of DMSP: in *S. anglica*[20] and in many intertidal algal genera such as *Ulva*[11]. Degradation of

Table 1 Contents of leaves of major American salt-marsh species

Marsh species	Location	DMSP concentration (μmol per g dry weight)
Spartina alterniflora	MA, DE, SC	80–280
Spartina patens	MA, DE	<0.1
Spartina cynosuroides	DE	<0.1
Distichlis spicata	MA, DE	<0.1
Juncus gerardi	MA	<0.1
Juncus roemerianus	SC	<0.1
Salicornia europeae	MA	<0.1
Phragmites communis	MA	<0.1
Rhizophora mangle	VI	<0.1

Samples were taken during the growing season. Seasonal and geographical variations were minimized by always collecting specimens of *S. alterniflora* with the other plant samples (except in the case of *R. mangle*). The European marsh grass *S. anglica* is reported to contain up to 200 μmol DMSP g^{-1} dry weight[20]. KOH digestion of 13 MeOH extracts of leaves of *S. alterniflora* produced an acrylic acid to DMS ratio of 1.04 (±0.04, s.e.m.), indicating that all the DMS liberated during base digestion arose from DMSP. Rapid extraction of plant tissues in the field precluded production of acrylate and loss of DMS as an artefact. This elimination reaction may occur during the normal course of plant metabolism or as a function of cell death or turnover.

MA, Massachusetts; DE, Delaware; SC, South Carolina; VI, Virgin Islands.