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Hydrocarbon geochemistry in coral reef pore waters, French Polynesia

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ABSTRACT: Origin and transformation processes of the organic matter in coral reef pore waters were studied using non-aromatic hydrocarbons as biomarkers. A significant enrichment in hydrocarbons was observed in the deeper borehole sections. Their origin appeared to be related to intensive microbial activity inducing early diagenetic transformations of the organic matter. The detection of 17α,21ß hopanes indicated that the organic matter, probably entrapped in the deep carbonate structure, has undergone maturation processes. Its occurrence near the top part of the reefs implies an ascending movement of pore waters as proposed by the "endo-upwelling" model.

1 INTRODUCTION

The organic geochemical composition of pore solutions in atoll and fringing-reef bodies can be considered as the result of water-rock interaction between the organic matter trapped in reef-constituting carbonate grains and pore waters. These waters can be either marine or fresh, the latter being commonly localized in the top part of the reef and forming the "Gybhen-Herzberg" lens.

If very little, or nothing, is known about the organic geochemical composition of the waters themselves, the preliminary studies of the organic matter associated with the reef rocks suggest that its composition results from the diagenesis, probably under bacterial control, of the organic constituents entrapped in the skeletal carbonate grains (Trichet et al., 1984; Poupet, 1989).

A new insight is being brought to the understanding of the composition of pore waters, and more generally to all the geochemistry of atoll-reef bodies, by the "endo-upwelling" concept and model (Rougerie and Wauthy, 1986). This model implies that marine deep waters (ca. 400 to 600 m) can penetrate the reef in the contact zone between the carbonate body and the underlying volcano, then ascend through the reef, driven by a low-temperature geothermal "forcing" associated with evaporation acting in the same direction in the top part of the reef. Recent studies strongly suggest the actuality of this process (Rougerie et al., 1991; Bernat et al., 1991).

In order to investigate the organic biogeochemistry of coral reef pore waters in French Polynesia, we have undertaken a study of the organic matter by the biomarker approach. We present here data on the hydrocarbon composition of pore waters collected in the Tikehau atoll.

2 EXPERIMENTAL

Pore waters were sampled in boreholes drilled on the reef plate conglomerate and on a lagoonal pinnacle. The samples were filtered on 0.7μm glass fibre filters and their lipid content was solvent extracted. Hydrocarbons were isolated by silica gel chromatography and analyzed on gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS).

3 RESULTS AND DISCUSSION

3.1 Hydrocarbon concentrations

The non-aromatic hydrocarbon (HNA) series detected in our samples included GC resolved compounds, mainly normal alkanes (n-alkanes), branched alkanes and some minor saturated cyclic alkanes, as well as broad unresolved complex mixtures (UCM) appearing as a hump in the gas chromatogrammes. The latter are constituted by naphthenic compounds and represented the major fraction of the HNA. The quantitative variability of the n-alkanes showed similar trends in each borehole.

Generally, in boreholes on the reef flat n-alkanes concentrations was enhanced, starting from the near-surface level. significantly in the sub-surface level. Then, a progressively increasing trend was observed as a function of sampling depth (Table 1). In the borehole B3 drilled on a lagoon pinnacle the increasing trend of n-alkanes concentrations was enhanced, starting from the near surface level. Similar features were observed for the non-aromatic hydrocarbon concentrations.

Table 1. Hydrocarbon concentrations in coral reef pore waters

	n-alkanes (ng/l)	HNA (ng/l)
B1-2		
1m	111.98	1177.12
4.5m	73.90	223.74
9m	86.95	719.08
10m	120.01	777.61
20m	177.20	1233.33
B4-5		
4m	318.53	1123.32
11m	141.97	833.30
20m	179.17	1080.12
27m	285.23	1156.68
33m	356.28	1965.32
B3		
4m	315.45	708.37
10m	2021.55	6627.21
17m	3071.52	8621.71

B1-2, B4-5: boreholes in the reef plat conglomerate (Tikehau atoll)
B3: borehole in a pinnacle (Tikehau atoll lagoon)

These profiles evidenced the presence of organic matter inputs near the top of the boreholes which is logically linked to the intensive algal-coral activity occurring in this environment. The transfer of the organic material within the carbonate framework is accompanied by microbial degradation which is mostly responsible for the decrease of hydrocarbon concentrations in pore waters sampled at the subsurface level. The recycling of the organic matter within the top meters of the carbonates is a rather rapid process which partly accounts for the enrichment of pore waters in nutrients relative to the surrounding marine and lagoonal waters (Rougerie et al., 1991).

The subsequent increase of hydrocarbon concentrations in the deeper sections can not be easily interpreted as resulting directly from a downward transport of biological organic material produced near the surface. This process should rather lead to a progressive decrease of concentrations due to microbial degradation. The hydrocarbon enrichment of pore waters in the deeper section of boreholes concerned both n-alkanes and unresolved complex mixtures (UCM). The latter are commonly related to complex cyclic, multi-branched microbial degradation products. Hence, its increase with depth could effectively reflect such degradation processes. Nevertheless the increase of n-alkanes concentrations, which are more labile compounds than UCM, can not reflect such mechanisms. It rather indicates important reworking and diagenesis of the organic matter contained initially in pore waters or derived from organic matter entrapped in the carbonate skeleton.

3.2 Hydrocarbon composition

The study of the qualitative hydrocarbon composition allowed further deciphering of sources and transformation processes.

In pore waters sampled near the surface, the n-alkane profile in the lower molecular weight range (compounds with 14-20 atom carbons, C14 - C20) was relatively important and characterized by the predominance of odd-carbon numbered components, mainly the n-C17. This distribution revealed significant organic matter inputs derived from biological planktonic activity (Saliot, 1981). In the case of surface lagoonal waters, the n-C17 was the major n-alkane, evidencing the high productivity of this environment. The relative importance of this compound with respect to the entire n-alkane profile decreased with depth in boreholes, which reflected the biodegradation of algal inputs and/or the volatilization of the short chain homologues. Furthermore, in most cases important amounts of bacterial markers were detected in the lower molecular range, namely even-carbon numbered n-alkanes, C16 and C18 (Saliot, 1981).

n-Alkanes from 25 up to 40 carbon atoms generally dominated the whole profile. A slight predominance of odd-carbon numbered components was observed in near surface samples, which indicated only minor inputs deriving from terrestrial higher plants (Simoneit, 1986). In the deeper sections the abundant long chain n-alkanes profiles did not show any predominance. This feature has been frequently found in oil residues and oil products. Moreover, abundant long chain n-alkanes without odd or even predominance constitute an important fraction of many high-wax crude oils in which thermal evolution is denoted by an increase of paraffins (Tissot and Welte, 1984). Marine organic matter from primarily microbial or planktonic residues is believed to yield such paraffinic petroleums. In several cases this profile has also been attributed to intensive microbial reworking of the organic matter.

In many of our samples, and especially in those obtained in the borehole drilled in the lagoonal pinnacle, the n-alkanes profile was depleted in short chain n-alkanes, whereas the compounds with ≥ 25 carbon atoms showed a very smooth, "gaussian", distribution profile (Figure 1). In those cases the concentrations of n-alkanes were the highest ones.

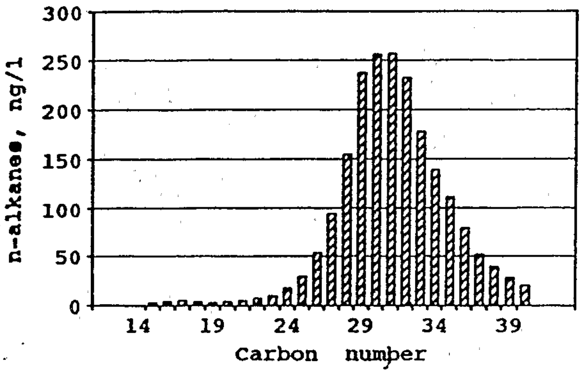

Figure 1. n-alkane distribution in pore waters showing a smooth profile without any predominance.

Similar profiles have been reported in various environments, such as in hydrothermal systems (Simoneit, 1990) and in surface coastal waters (Bouloubassi and Saliot, 1990). A microbial or diagenetic origin has been attributed to this long chain n-alkanes profile. According to Gassmann (1982) these compounds derive from the "bio-conversion" of short chain n-alkanes by microbial activity. The latter was evidenced by the simultaneous presence of an important profile of iso- and anteiso- alkanes in the range C25-C35. Such branched n-alkane profiles were found in our samples, and their relative importance increased with increasing amount of long chain n-alkanes having a "gaussian" distribution. It is interesting to notice that these peculiar distributions were also found in the organic material extracted from phosphate deposits in several Polynesian atolls (Fikri, 1991). This suggested a link between pore waters and phosphate formation as already proposed (Rougerie and Wauthy, 1989; Bernat et al., 1991).

Firth and Eglinton (1974) have shown the intimate existence of organic waxy minerals with inorganic ones. They found smooth long-chain n-alkane profiles in naturally occurring waxy minerals, such as hatchettites, where the absence of odd/even predominance was attributed to maturation processes under mild thermal conditions. These authors have suggested that the organic, hydrocarbon rich, material may have entered the inorganic concretion either during or after the formation of the concretion. In the latter case hydrothermal solutions could have introduced organic material into the concretions, as previously observed (Firth and Eglinton, 1974 and references therein). In both cases a redistribution of the organic material by such solutions was involved.

The gas chromatographic/mass spectrometric analysis provided structural informations on minor hydrocarbon components, namely pentacyclic triterpanes in the hopane series, which constitute very specific molecular markers. The identified compounds had the 17(H)α, 21(H)β configuration which is the thermodynamically stable one, as opposed to the less stable, microbially derived 17(H)β, 21(H)β configuration. The conversion of the latter into the stable configuration takes place during the maturation, frequently thermal, of organic matter over geological time. Hence, the detection of 17(H)α, 21(H)β hopanes pointed out that the organic matter present in the pore waters has undergone maturation processes, probably of thermal nature. This is further confirmed by the detection of hopanes showing a 22S-22R epimerization. The hopane profiles could be confronted with the waxy-like, smooth n-alkanes distibutions, which, as discussed above, have been attributed to mild maturation processes as well. In the studied environment, such processes could have occurred in the deeper framework of the reef carbonates under geothermal forcing.

The detection of these organic matter maturity markers in boreholes which do not exceed 50 meters implies that pore waters follow an acsending movement within the porous carbonate structure from the deep sections overlying the volcano up to the top part of the reef as proposed by the endo-upwelling model (Rougerie and Wauthy, 1986). Thus, pore fluids appear to be responsible for the emplacement, leaching and redistribution of organic material within the carbonate framework.

4 CONCLUSIONS

The investigation of the hydrocarbon geochemistry in coral reef pore waters revealed interesting aspects of this environment.

Pore waters appeared as a medium of very intensive microbial activity which induces early diagenetic transformations of the organic matter within the carbonate structure. A significant enrichment of pore waters in hydrocarbons was observed which does not fit well with a downward tranport of organic material produced near the fertile surface of the reefs, since this transport is believed to occur along with an extensive remineralization of the organic matter. These findings were further supported by the analysis of fatty acids in pore waters (Bouloubassi, unpublished data).

Besides the "microbial reactor" character of pore waters and reefs in general, this medium appeared also to support maturation processes of the organic matter, most likely under geothermal forcing. Geothermal warming and induced upward migration of reef pore fluids have been proposed as the driving mechanism of carbonate rock diagenesis, reef building and coral ecosystem growth in the "endo-upwelling" concept and model (Rougerie et al., 1991 and references therein). From the point of view of the organic geochemistry such processes can account for the occurrence of maturated organic matter as well as for its transport towards the top part of the reef. This organic matter is either initially associated with the pore fluids or inherited, by leaching, from organic materials entrapped in carbonate grains. In the latter process pore fluids may also have contributed in the emplacement of the organic material within the carbonates. In all cases pore waters appear as a very important medium in the diagenesis of the organic matter within coral reefs.

Ongoing analyses of aminoacids and determination of the carbon isotope composition of the hydrocarbons will provide us further informations on the precise sources and transformations of the organic matter in those pore waters.

REFERENCES

Bernat M., M. Loubet & A. Baumer 1991. Sur l'origine des phosphates de l'atoll corallien de Nauru. *Oceanol. Acta* 14:325-331.

Bouloubassi I. & A. Saliot 1991. Study of the partitioning of hydrocarbons into dissolved and particulate phases in the Rhone delta; consequences on estimations of hydrocarbon fluxes. *Water Pollution Research Report* 20:231-237.

Fikri A. 1991. *Contribution à l'étude de la géochimie organique des phosphates insulaires; implication dans la phosphatogenèse*. Thèse de Doctorat, Université d'Orléans.

Firth J.N.M. & G. Eglinton 1971. Hatchettite from the South Wales Coalfield. In: H.R.V Gastner & H Wehner (Eds.), *Advances in Organic Geochemistry*, pp.613-628. Pergamon Press, Oxford.

Gassmann G. 1982. Detection of aliphatic hydrocarbons derived by recent "bio-conversion" from fossil fuel oil in North Sea waters. *Mar. Pollut. Bull.* 13:309-315.

Poupet P. 1989. *Géochimie organique et biogéochimie de sédiments de lagon des atolls de Tikehau et Takapoto (Polynésie Française)*. Thèse de Doctorat, Université d'Orléans.

Rougerie, F. & B. Wauthy 1986. Le concept d'endo-upwelling dans le fonctionnement des atolls-oasis. *Oceanol. Acta* 9:133-148.

Rougerie F. & B. Wauthy 1989. Une nouvelle hypothèse sur la genèse des phosphates d'atolls: le rôle du processus d'endo-upwelling. *C.r. Acad. Sci., Paris* 308:1043-1047.

Rougerie F., Ch. Andrié & Ph. Jean-Baptiste 1991. Helium-3 inside atoll barrier reef interstitial water: A clue for geothermal endo-upwelling. *Geophys. Res. Lett.* 18:109-112.

Saliot A. 1981. Natural hydrocarbons in sea water. In: E.K. Duursma & R. Dawson (Eds.), *Marine Organic Chemistry*, pp. 327-374, Elsevier, Amsterdam.

Simoneit B.R.T. 1986. Characterisation of organic constituents in aerosols in relation to their origin and transport: A review. *Intern. J. Environ. Anal. Chem.* 23:207-237.

Simoneit B.R.T. 1990. Petroleum generation, an easy and widespread process in hydrothermal systems: an overview. *Appl. Geochem.* 5:3-15.

Tissot B.P. & D.H. Welte 1984. *Petroleum Formation and Occurrence*. Springer-Verlag, Berlin.

Trichet J., P. Repellin & P. Oustrière 1984. Stratigraphy and subsidence of the Mururoa atoll. *Mar. Geol.* 56:241-257.

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