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EARLY DIAGENESIS OF ORGANIC MATTER IN THE SEDIMENTS OF THE CENTRAL BASIN OF TIKEHAU LAGOON-REEF (TUAMOTU ARCHIPELAGO - FRENCH POLYNESIA)

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ABSTRACT

Pore waters from the sediment of a lagoon have been analysed for nutrients, major elements and some trace elements (Fe and Mn).
Using a simple diagenetic model for the organic matter mineralisation we show that the phytobenthos has a global stoichiometry close to the Redfield's formula. Owing to the oligotrophic environment, the burial is very limited and the organic carbon concentration in the sediment is close to 0.5 mg/g. Therefore, $SO_4^=$, which is the main electron acceptor, is only partially reduced in soluble sulfide.
Equilibrium calculations show that pore water is very close to the saturation with respect to aragonite. Hypothesis of authigenic mineral formation within the sediment (amorphous FeS and struvite) cannot be rejected.

INTRODUCTION

Knowledge of the global biogeochemical equilibrium (or non equilibrium) of an aquatic ecosystem can be obtained if the different fluxes of matter and energy are taken into account at every level of the trophic chain.
Autotrophic production represents the first link of this chain and its yield is directly correlated with the amount of dissolved nutrients : soluble mineral carbon, nitrogen, phosphorus and silica. The mineralisation of dead organic material buried in the sediment releases in pore water usually high concentrations of nutrients which diffuse into the water column (Lerman 1979, Berner 1980 and others.). Thus, the sediment acts as a reservoir of dissolved species readily available for the autotrophic benthic community. The aim of this paper is an attempt to model the early stages of organic matter oxidation within sediments and interstitial pore waters.

THE TIKEHAU LAGOON-REEF

The Tikehau lagoon-reef is located in the Pacific Ocean, about 200 km N.E. from Tahiti (French Polynesia) and belongs to the Tuamotu Archipelago. The reef is circular shaped and 75 km in diameter. The average depth of the lagoon is 25 m and the maximum depth, in the central basin, reaches 40 m (Lenhardt 1987). Sampling was made at the deepest part of the lagoon (D.S. site) where light and dissolved oxygen are still present at the Sediment-Water Interface (SWI). Sediment cores exhibit a roughly constant appearance of fine to very fine grained coral sand. The porosity in the upper 30 cm is 70 % for the sediments of the central basin.

SAMPLING AND ANALYTICAL METHODS

i) Pore water sampling :

We used an in situ sampling method previously described by Hesslein (1976).
The "peepers" (in situ sampler) are allowed to equilibrate with the sediment pore water for 19 days. pH, alkalinity and nutrients were analysed within a few hours after retrieval. Pore water samples from a second peeper, close to the first one within a few meters, was acidified on board and analysed a week later in the Paris laboratory for trace elements (Fe and Mn) and nutrients. Concentrations of nutrients in the two different peepers were very similar. The results are presented in a companion paper (Charpy-Roubaud et al. 1988).

ii) Analytical Methods

pH measurments were performed on a submicro sample (500 µl) using Hansson's calibration method described by Almgren et al. (1975). Accuracy is +/- 0.005 pH unit. Then, H^+ concentration is expressed on the sea water ionic medium scale (Mole/kg SW) with a 35 ‰ salinity . The alkalinity was obtained by potentiometric titration using Gran's method (Stumm & Morgan 1981) and the accuracy is +/- 0.5 % . Potassium was analysed by AAS and trace elements by FLAAS (+/- 3 % and +/- 10 % respectively). Calcium and magnesium were analysed by EDTA titration (+/- .5 %). Ionic chromatography was used for major anions analysis ($SO_4^=$) and Cl^- was determined by argentimetry. Precision is respectively +/- 2 % and +/- .5 % . Standard colorimetric methods were used for nutrient (SiO_2, NH_4^+ and PO_4 - Soluble Reactive Phosphate) analysis adapted for submicro samples (MERCK Spectroquant Techniques). NO_3^- and NO_2^- were below the detection limit (<1 µM). Precision is +/- 3 % .

RESULTS

Analytical results are summarized in table 1 and concentration profiles of main species of interest are presented on figure 1. The open squares represent experimental values whereas crosses show calculated values which will be discussed later.
Some general trends can be derived from the observed profiles before to any attempt at quantitative model. The nutrient concentrations in pore water are much higher than in the overlying water. But these concentrations are quite low if compared with other studies dealing with marine coastal sediments (Goldhaber et al.1977, Nissenbaum et

al.1972). The same trend is observed for H_2S, the maximum concentration of this species reaches 251 µM while concentrations in the mM range are quite commonly observed (Murray et al.1978, Gaillard et al.1988, *Boudreau & Canfield 1988*). These global low concentrations suggest several hypothesis :

* The amount of organic material which flows through the water column is small with respect to the global oligotrophic trend of the ecosystem.

* A large part of the organic matter is oxidized in the water column and does not reach the SWI.

* The organic matter which reaches the SWI is only partially *oxidized. Therefore, the remainder is* fairly resistant to subsequent oxidation.

Within a few millimeters below the SWI, oxygen is relayed by $SO_4^=$ as the main electron acceptor together with Fe and Mn oxides.
After reaching a maximum concentration, profiles of NH_4^+, H_2S, Fe and Mn exhibit a drastic decrease in concentration with depth in the sediment core.

DISCUSSION

i) General assumptions :

As previously stated, light and dissolved oxygen are present at 40 m depth in the central basin. Since neither nitrate nor nitrite were detected in the overlying water, then we can write the first step of the mineralisation as :

$$(CH_2O)_x(NH_3)_y(H_3PO_4)_t + x\ O_2 \Longrightarrow x\ CO_2 + y\ NH_3 + t\ H_3PO_4 + x \cdot H_2O$$

This reaction takes into account the occurence of dissolved ammonia just above the SWI.

A large amount of the dissolved silica is probably linked to the biogenic material (benthic diatoms) in this environment. Then we can associate the dissolution reaction of opal frustules :

$$v\ SiO_2 + 2\ v\ H_2O \Longrightarrow v\ H_4SiO_4$$

If it is assumed that the oxygen is consumed with depth within the first few millimeters of sediment, a change in dissolved O_2 of a given value $DelO_2$ would produce :

$DelC_t = DelO_2$, $DelSi_t = DelO_2*(v/x)$,

$DelN_t = DelO_2*(y/x)$, $DelP_t = DelO_2*(t/x)$

and $DelAlk = DelO_2*(y-t/x)$

where :

$C_t = [H_2CO_3] + [HCO_3^-] + [CO_3^=]$

$Si_t = [H_4SiO_4] + [H_3SiO_4^-]$

$N_t = [NH_4^+] + [NH_3]$

$P_t = [H_2PO_4^-] + [HPO_4^=]$ (other ionic species are neglected in the observed pH range)

The dissociation constants for carbonic and boric acids are taken from Hansson (1973). Others are from Sillen and Martell (1971).

The total alkalinity (Alk)is defined by :

$$Alk = [HCO_3^-] + 2[CO_3^=] + [BO_3H_2^-] + [H_3SiO_4^-] + [NH_3] + [HPO_4^=] + [OH^-] - [H^+] \quad (1)$$

and can be rewritten as a function of C_t, N_t, Si_t, P_t and H^+.

Then as oxygen concentration declines with depth,pH and the complete pore water composition can be recalculated.
The basic assumptions of the model are the following:
Dissolved oxygen is consumed according to global first order reactions and advection is neglected. Then, if steady state is supposed to occur we can write :

$$D_{ox}(d^2C_{ox}/dz^2) - k_{ox}C_{ox} = 0 \quad (2)$$

Where :

z = distance from the SWI (positive downward)
k_{ox} = first order kinetic constant for oxygen reduction

Diffusion coefficient D_{ox} was set at $15.10^{-6} cm^2/s$. This value is lower than expected in the true diffusive boundary layer where $D_{ox} = 20.10^{-6} cm^2/s$. (Revsbech et al. 1986). In situ measurements which take in account tortuosity and possible adsorption were made by the same workers and are in the range 13.9 to 14.3 cm^2/s. They also infer a maximum penetration depth of 0.8 mm for near shore sediments. On the other hand, Reimers & Smith (1986) report penetration depths in the range 16 to 18 mm. We chose a "medium" depth of 4 mm. This choice is somewhat arguable but is not critical.

Integration of equation (2) lead to an exponential decrease of oxygen :

$$C_{ox} = C^{\circ}_{ox} exp-[(k/D_{ox})^{1/2} z]$$

The initial value C°_{ox} was set at 4 ppm. No direct measurements are available from the D.S. site. Usual concentrations in lagoon surface water range from 3 to 6 ppm according to the light input. A 4 ppm value is quite reasonable if we consider the small light flux which reaches the SWI.
We take only in account the diffusion of oxygen as the main transport process through the SWI. This can be justified if we compare this diffusive flux to the amount of oxygen carried by advection.

Diffusion flux of oxygen can be calculated with the expression :

$$F_D = P.D_{ox}.C^{\circ}_{ox}.(k_{ox}/D_{ox}$$

while advection flux is calculated with the expression :

$$F_A = P.V.C^{\circ}_{ox}$$

where P is the porosity (0.7) for both expressions and V is the advection rate (0.2 $cm.yr^{-1}$) of sediment and water.
Using a calculated value of $k_{ox} = 1.77*10^5\ yr^{-1}$ we get a ratio :

$F_D / F_A = 10^4$

This shows that mainly diffusion drives oxygen penetration into the pore water.
The thermal stability of the water column excludes convextion as an efficient transport mode of dissolved oxygen. On the other hand, bioturbation can enhance greatly the advection of oxygen by mixing continuously the top of the sediment with the overlying water. If bioturbation was an efficient process of oxygen transfert at this site of the lagoon, the sediment anoxia would not appear as close from the SWI as it does.

This part of the model is only used to calculate the water composition within the first 4 mm of the sediment core. Below this point sulphate replaces oxygen downwards. Then the organic matter oxidation can be written :

$$(CH_2O)_x(NH_3)_y(H_3PO_4)_t + x/2\ SO_4^{=} + x\ H^+ \Longrightarrow x\ CO_2$$
$$+\ y\ NH_3 + t\ H_3PO_4 + x/2\ H_2S + x\ H_2O$$

associated with the dissolution of biogenic silica :

$$v\ SiO_2 + 2\ v\ H_2O \Longrightarrow v\ H_4SiO_4$$

Equation (1) is only modified by including HS^- in the total alkalinity.

For an incremental variation of $SO_4^{=}$, the other variables are changed as follow :

$DelC_t = 2DelSO_4^{=}$, $DelSi_t = 2DelSO_4^{=}(v/x)$,

$DelN_t = 2DelSO_4^{=}(y/x)$, $DelP_t = 2DelSO_4^{=}(t/x)$,

$DelAlk = 2DelSO_4^{=}(y+x-t/x)$ and $DelS_t = DelSO_4^{=}$

with $S_t = [H_2S] + [HS^-]$

Assuming steady state and constant porosity of the sediment the differential equations which describe both evolution of oxidizable (and non diffusive) organic matter and sulphate concentration are written :

$$-v(dG/dz) - k'G = 0 \qquad (3)$$

$$D_s(d^2C_s/dz^2) - V(dC_s/dz) - k'C_s = 0 \qquad (4)$$

where :

V = advection rate of sediment and water

D_s = apparent diffusion coefficient of sulphate corrected for tortuosity and adsorption.

k' = first order kinetic constant for bacterial sulphate reduction.

C_s = dissolved suphate concentration (M/kg) undergoing bacterial reduction.

G = concentration of oxidizable organic carbon.

Details of this classical diagenetic model are described by Berner (1980)

ii) Calculated profiles and experimental values :

Fitting calculated profiles to experimental values requires the adjustment of the "Redfield parameters" (Redfield et al.1966) and the other variables of the differential equations set.

Usually, marine sediments of continental margins are rich enough in organic matter to reduce a large amount of the available sulphate (Berner 1980, Gaillard et al 1988). Then a decreasing profile of $SO_4^{=}$ vs depth is observed. This does not happen here and the sulphate concentration is quite constant in pore water.
Integration of equation (3) and (4) and solving the H^+ polynomial equation (1) allow us to derive the theoritical profiles shown on figure 1. The best fit is obtained when we set the reduced sulphate concentration at 0.45 % of the total. This emphasizes the very low content of reactive organic matter present.
The adjustment of Redfield parameters gives a stoichiometric formula for the phytobenthos :

$$(CH_2O)_{106}(NH_3)_{20}(H_3PO_4)_{0.8}$$

One mole of this organic matter is associated with the dissolution of 80 moles of silica. If all the dissolved silica is assumed to be from biogenic origin this gives a C/Si ratio of 1.32 (atoms) or 0.57 (grams). We have to keep in mind that the model uses a single first order kinetic constant for sulphate reduction and, implicitely, for silica dissolution.
As the mineralisation of the "hard parts" (here, diatoms frustules) is probably much slower than the mineralisation of the soft tissues, then the silica linked with the organic matter is probably greater than the value obtained by the model. Therefore, the C/Si ratio in the organic matter is probably smaller but we did not find in the litterature any experimental values of this ratio.
The slight depletion in phosphorus, if compared with the classical ratio C/P or N/P has been observed in carbonate-rich sediment where P may be adsorbed on calcitic or aragonitic debris (Stumm & Morgan 1981, Gaillard et al 1986).

Using a porosity of 70 %, an apparent diffusion coefficient of $3.17 * 10^6$ cm^2/s (Berner 1980) and a sedimentation rate of 0.2 cm/yr we can calculate the first order kinetic constant and the initial concentration of organic matter in the sediment after total depletion of oxygen. We find respectively :

$k' = 0.071\ yr^{-1}$ and $G° = 43$ mM/kg of dry sediment

(i.e. 0.5 mg of organic carbon per gram of dry sediment)

These results confirm the previous hypothesis concerning a very limited "burial" occuring in the central basin of the lagoon. In addition the low value of k' means that the organic matter which reaches the SWI is fairly resistant to subsequent oxidation.

iii) Experimental and calculated profiles of dissolved iron, sulfide and ammonium :

TABLE 1

ANALYTICAL RESULTS : PORE WATER.FROM CENTRAL BASIN

Depth	pH	Alc.	H2S	Ca	K	Cl	SO4	Fe	Mn	SiO2	NH4	PO4
- 12	8.030	2.405	0	10.05	10.47	558	28.5	-	-	10	7.3	0.10
12	7.450	3.390	80.3	10.06	10.83	562	28.5	2.75	64.1	125	83	5.55
37	7.421	3.398	210.9	9.90	9.70	563	27.5	2.51	36.2	433	123	7.02
62	7.472	3.180	251.0	9.85	10.93	557	26.9	2.53	33.7	543	137	5.68
87	7.408	3.279	217.1	9.92	10.13	565	25.8	0.91	37.3	556	109	5.02
112	7.486	2.986	159.8	9.46	9.60	569	26.9	0.88	35.8	629	99	4.7
137	7.544	3.144	142.3	9.59	11.16	579	24.5	0.67	28.9	632	111	5.8
162	7.517	3.017	95.6	10.10	10.51	576	25.3	0.86	27.5	552	95	5.8
187	7.531	2.581	84.0	10.11	10.64	579	27.3	1.01	25.5	540	72	5.5
212	7.526	2.518	68.6	10.08	10.16	562	28.6	1.11	20.2	502	48	5.5
237	7.536	2.660		10.10	10.30	557	26.2	1.24	17.5	492	52	6.35

Depth is in mm
Alk, Ca, K, Cl, SO_4 are in mM/kg of sw.
H_2S, Fe, SiO_2, NH_4, PO_4 are in µM/kg of sw
Mn is in nM/kg sw
" - " : analysis missing
For standard deviations, see text.

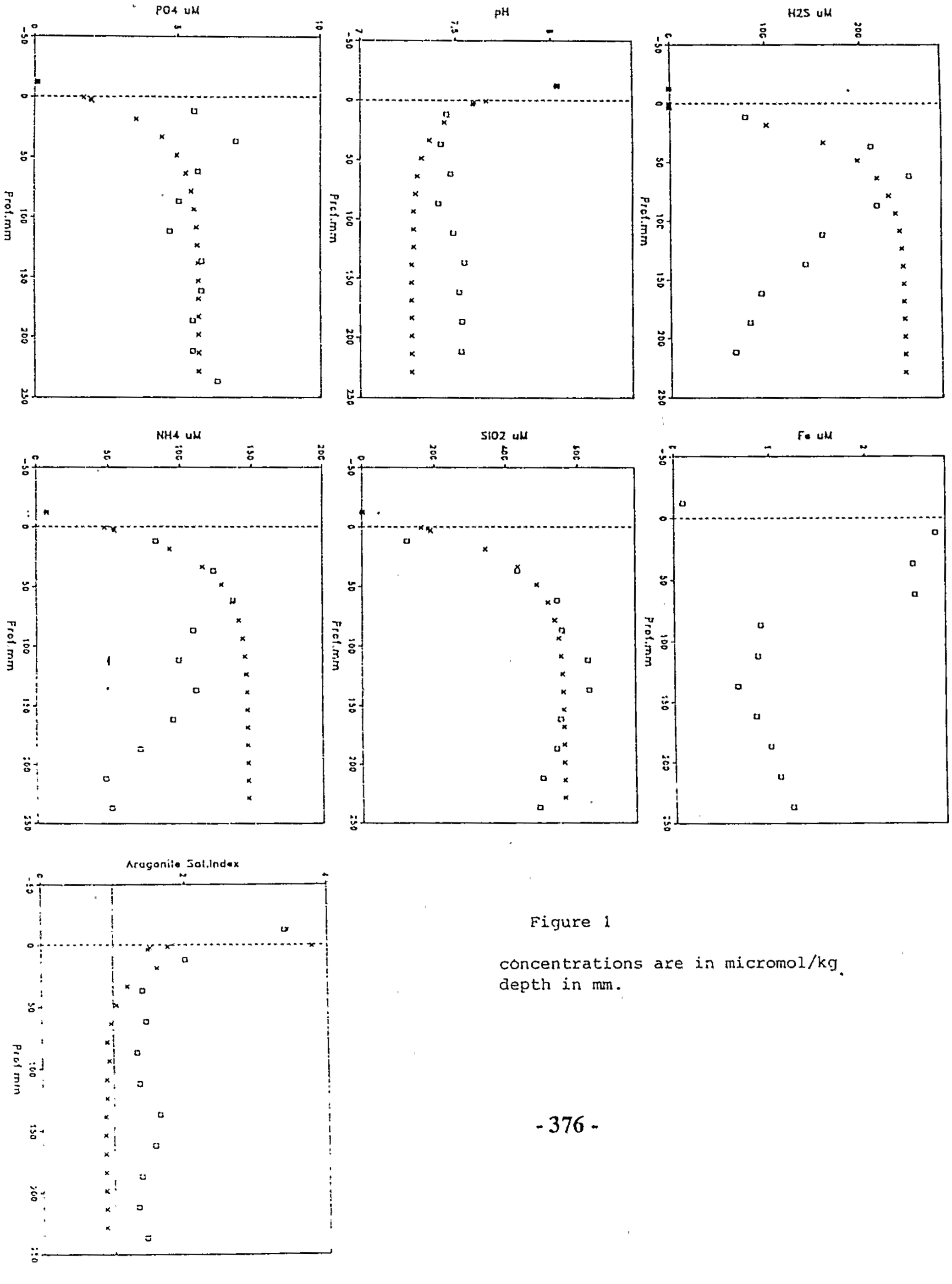

Figure 1

concentrations are in micromol/kg
depth in mm.

* Iron and sulfide :

The pattern of these two profiles strongly suggests the precipitation of amorphous ferrous sulfide (FeS). Calculation of the saturation index with respect to a relatively soluble phase shows that oversaturation happens at the depth where H_2S and dissolved iron are maximum whereas slight undersaturation happens deeper. Because of the poor quality of thermodynamic data concerning both sulfide and Fe(II) species this result must be only considered as a rough estimation. If authigenic mineral is being precipitated this has to be demonstrated by mineralogical investigations. But this occurence cannot be rejected right away.

* Ammonium :

The kind of profile obtained here for ammonium has already been observed for other species like dissolved silica (Reimers & Smith 1986). It can be explained by uptake reactions onto the sediment surfaces. But we cannot exclude any authigenic formation of struvite ($MgNH_4PO_4$). Unfortunately, data for solubility constant in sea water does not exist at all.

iv) Equilibrium between pore water and aragonite :

It's well known that coral sand is mainly composed of aragonitic debris. It is interesting to check if the carbonate phase of the sediment has a tendancy to precipitate or to dissolve.
Using the apparent solubility constant measured by Mucci (1983) together with Hansson's values for the carbonate system, we used our model to calculate a profile of the saturation index of the pore water with respect to aragonite.
Figure (1) shows that oversaturation occurs in the water column and up to a few centimeters inside the sediment while values very close to saturation are obtained below. Small discrepancies must be the reflect of experimental errors both on the calculated carbonate concentration and on the solubility constant of aragonite.

Therefore, aragonite must precipitate in the water column and in the top of the sediment core while equilibrium with this mineral occurs deeper.

CONCLUSIONS

From this simple model applied to a closed system under steady state conditions we are able to derive some geochimical parameters which provide important information on the mineralisation proceses of the organic matter at the SWI.

The main criticisms that we can formulate are the following :

The first step of the mineralisation using oxygen is probably not under steady state conditions owing to large variations in O_2 concentrations between daytime and night. But this affects only the extreme upper part of the sediment and the diffusion looks to be the main process which transfers oxygen from the water column to the SWI. But, obviously <u>in situ</u> oxygen measurments using coulometric microprobe are needed to check the assumptions of what is happening in the top few millimeters of the sediment.

The model fails to predict pH variations. This point remains one of the most difficult geochemical problem. Recently, Boudreau & Canfield (1988) using a much more sophisticated model of pore water profiles also fail to predict the buffering properties of this complex medium.

On the other hand equilibrium calculations show that pore water may be very close to aragonite saturation.

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