Chemical diagenesis in coastal marine sediments

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ABSTRACT

The chemical composition of interstitial waters from an organic-rich sediment (Villefranche Bay, Mediterranean Sea, France) is presented. Pore water analyses were carried out using *in situ* equilibration devices (peepers). We report major ion and nutrient profiles at various seasons. Interstitial waters are enriched in ΣCO_2, ΣH_2S, alkalinity and nutrients but are depleted in calcium and sulphate.

Using a consistent set of data, we investigated the carbonate system in these pore fluids. Special care was taken in determining pH for computing chemical equilibria on the ionic medium scale and on the infinite dilution scale using the specific interaction approach. These calculations show that calcite and aragonite are saturated through the entire length of the core.

A stoichiometric model of organic matter oxidation coupled with sulphate reduction and precipitation of authigenic minerals is proposed in explanation of the observed distribution of elements. This model suggests that, during the first steps of early diagenesis in these sediments, $CaCO_3$ and FeS are precipitating from the pore waters.

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RÉSUMÉ

Diagenèse chimique dans les sédiments marins côtiers

Nous présentons la composition chimique des eaux interstitielles des sédiments riches en matières organiques de la baie de Villefranche-sur-Mer, Mer Méditerranée. Les échantillons d'eau interstitielle ont été obtenus grâce à des regards à sédiment (peepers) qui se sont équilibrés *in situ*. Nous présentons les profils des ions majeurs, ainsi que ceux des sels nutritifs à différentes saisons. Les eaux interstitielles sont enrichies en ΣCO_2, ΣH_2S, alcalinité et sels nutritifs, mais sont appauvries en calcium et sulfates.

Nous avons étudié le système des carbonates dans ces fluides interstitiels en utilisant un ensemble cohérent de données. Nous avons, pour ce faire, déterminé le pH avec un soin particulier afin de pouvoir calculer les équilibres chimiques sur deux échelles : celle du milieu ionique et celle de la dilution infinie en utilisant le modèle de l'interaction spécifique pour paramétriser les écarts à l'idéalité. Ces calculs montrent que la calcite et l'aragonite sont sursaturés sur l'ensemble de la colonne sédimentaire.

Nous proposons un modèle stœchiométrique de l'oxydation de la matière organique couplée à la réduction des sulfates et la précipitation de minéraux authigènes pour expliquer les profils que nous avons observés. Ce modèle nous permet de prédire les quantités de $CaCO_3$ et de FeS qui précipitent lors des premières étapes de la diagenèse de ces sédiments.

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INTRODUCTION

Interstitial water chemistry provides an insight into early diagenetic processes occurring in marine sediments. Variations in the composition of pore fluids can be utilized to evaluate the influence of diagenesis on the distribution of elements and quantify their fluxes at the sediment-water interface. In coastal waters, where organic-rich debris accumulates at the sediment-water interface, chemical diagenesis of organic matter leads to high dissolved inorganic carbon concentrations in pore waters. The objective of this paper is to examine the carbonate system in such organic-rich and carbonate-rich coastal marine sediments.

Oxidative mineralization of soft tissue is responsible for important changes in interstitial water composition (Sholkovitz, 1973; Goldhaber et al., 1977; Murray et al., 1978; Martens and Klump, 1980; Elderfield et al., 1981; Klump and Martens, 1981; and others). The principal electron acceptor driving the oxidation of organic matter in these types of sediment is sulphate (Berner, 1964; Berner, 1980). This biogeochemical process, mediated by bacteria, produces the release of nutrients, the increase of ΣCO_2 and the depletion of sulphate in the pore fluids. Pore water chemistry can be used to investigate the equilibrium conditions governing the precipitation of authigenic phases and to compute geochemical mass balances depicting early diagenesis.

In this paper we discuss the chemical diagenesis of major ions from coastal marine sediments of Villefranche Bay (Mediterranean Sea) in terms of chemical equilibria and stoichiometric modelling. In order to obtain a further insight into the carbonate system, we process a consistent set of data using two approaches for computing equilibrium: the ionic medium scale (Sillen, 1967) and the specific interaction developed by Pitzer (1973) and applied to geochemical systems by Harvie and Weare (1980) and Harvie et al. (1984). In addition, we propose a stoichiometric model including authigenic mineral precipitation in order to delineate the geochemical mass balance of organic matter oxidation with concomitant sulphate reduction.

ENVIRONMENTAL SETTING

The Villefranche Bay is located close to Nice on the French Riviera. The area has been previously described by Gaillard et al. (1986). Briefly, we report here the main characteristics of the sediments. Around the sampling site FR, the sediments consist of grey mud with a few sea-shells and decomposing plant debris. Sedimentation rates have been measured by Rapin (1980) using the ^{210}Pb dating technique giving an average of 1 mm/year. The water depth is 18-20 m. Coastal sediment transport, although minimal in this area of the bay, depends strongly on wind direction. During the final experiment, in October 1984, violent winds from the open sea induced an off-onshore motion of an approximatively 10 cm thick layer of sediments in the area, according to scuba-divers. This phenomenon perturbed our sampling, but we assumed that it did not drastically modify the underlying diagenetic features.

METHODS

Field work was carried out from a small boat operated by the CEROV, University Pierre-et-Marie-Curie, Paris-VI.

Interstitial water and sediment sampling

All the samples were obtained using "peepers": close interval samplers similar to Hesslein's (1976) original model (Carignan et al., 1985). Two different sets of peepers were prepared according to the scale resolution and the number of analyses required. The first set consisted of peepers with 71 sampling compartments, 1 cm deep, spaced at 1 cm intervals, of 3.5 ml volume. The second set provided more sampling volume — 10 ml — but a 3 cm resolution, and was used in order to obtain more precise analytical determinations. These peepers were tested versus squeezing in Swedish coastal marine sediments and proved to be reliable for Alk_t, Ca, and trace metal determinations (unpublished results).

Prior to use, the peepers were flushed overnight with N_2 gas in order to remove all dissolved oxygen from the deionized water (Milli-Q RM, Millipore Inc.) filling the compartments. We used a chemically and biologically inert membrane-Versapor 200, pore size 0.2 μm Gelman Sciences, Inc. The membranes were acid-cleaned and washed several times with deionized water (Milli-Q) in order to remove all contaminants and acid. The peepers were assembled using nylon screws in order to avoid metal contamination. Peepers were inserted vertically inside the sediment by scuba-divers.

Aften an equilibration time of at least 20 days, the peepers were retrieved and sampled, within minutes of retrieval, either on the small boat or in the laboratory. In the latter case, precautions were taken to avoid air exposure by keeping the peepers secure in N_2-flushed plastic containers.

We sampled interstitial waters by piercing the membrane with syringes equipped with stainless steel needles for major ion analyses or with cleaned pipette tips for trace components. The different aliquots were stored in various containers according to the analysis specification. Clean Falcon RM tubes were used to recover aliquots for pH, major ions and alkalinity measurements. The tubes were pre-acidified with Merck HCl Suprapur for trace metals and nutrient analyses. Plastic syringes and [18 G-1″] needles were utilized for collecting interstitial waters for ΣH_2S. After flushing out any possible air bubbles, the syringes were sealed by inserting the needle tip into a rubber stopper. These samples were then stored in a glass jar flushed with N_2 and stored at 4°C, and analysed within 8 hours. For ΣCO_2 determination, interstitial waters were injected, using

syringes with [20 G-1″], into venoject Terumo RM tubes. The samples were preserved in these airtight tubes by previously placing a CO_2-free aqueous solution of $HgCl_2$ in order to prevent further microbial activity during storage.

The sediment samples used for porosity determination and organic carbon analysis were collected using a plexiglàss corer operated by a scuba-diver.

Analytical method

pH was determined, immediately after sampling, on two different scales: the infinite dilution scale and the Hansson pH_t scale (Hansson, 1973). An Ingold microcombination electrode and a Metrhom pH meter (model 605) were calibrated, using NBS standard buffers and the Tris buffer in artificial seawater. The quantity pH_t is related to the total H^+ concentration:

$$[H^+]_t = [H^+]_f + [HSO_4^-]$$
$$pH_t = -\log([H^+]_t)$$

where t is the total and f the free ion concentration.

The electrodes were soaked in Tris buffer at 35 salinity seawater for 12 hours prior to use. Measurements were made at room temperature following the procedure described by Almgren et al. (1975). The temperature of the buffer and samples were recorded with a accuracy of $+/-0.1°C$ and the pH was then corrected for in situ temperature; reproducibility was $+/-0.003$ pH units on Tris buffer. Total alkalinity $-Alk_t-$ was determined on 1 ml pore water, diluted with 10 ml of Milli-Q water, by titration with HCl at the desired ionic strength (NaCl and Na_2SO_4 were added relative to seawater composition). The equivalent volume was computed by means of Gran's function F_2. Reproducibility was 0.7% on IAPSO standard seawater used as reference for titrant molarity. ΣH_2S was determined on 1 ml by means of a computerized titration developed from the manual method described by Boulègue et al. (1979) and Dyrssen et al. (1985). Reproducibility was better than 0.5% for concentrations ranging from 0.25-10.0 mM_w-millimoles per kg of seawater. Only ΣH_2S was determined with the $HgCl_2$ titration owing to lack of reproducibility observed for the other sulphur species. These three determinations were performed as soon as possible after interstitial water recovery.

Chlorinity was determined on weighed 1.4 ml samples of pore water by $AgNO_3$ titration using Gran's function to compute V_{eq}. The overall reproducibility was better than 0.4%. Cl^- and SO_4^{2-} were determined by ionic chromatography using a Dionex 2000$_1$ or Vydac 213. Reproducibility on weight diluted samples was 2.5% for Cl^- and 5% for SO_4^{2-}. Br^- was analyzed after weight dilution on 0.5 ml by ion chromatography using a Whatman Partisil 10-SAX column (Stetzenbach and Thompson, 1983) and UV detection. Ca^{2+} and Mg^{2+} were determined by flame atomic absorption on a Perkin Elmer 403 with a reproducibility of 4 and 2% respectively, or by titration with EDTA using Merck's procedures. Reproducibility was 0.7% for $Mg + Ca + Sr$ and $< 1\%$ for $Ca + Sr$. ΣCO_2 was determined by gas chromatography on a Poropak Q 1.8 m long column using thermal-conductivity detection and helium as carrier gas. The content of the venoject tubes, after equilibration to atmospheric pressure with He, is acidified with 0.1 ml HCl 6N, and a gas headspace analysis is performed. Reproducibility is 5%. Nutrients were analyzed by Technicon on acidified samples. Reproducibility is 2%. Manganese was determined by flameless atomic absorption using an Hitachi (180-70) equipped with a polarized Zeeman background correction device. Reproducibility is 5%.

Porosity was determined on the sediment cores by weight loss after oven drying at 90°C. Organic carbon was determined by oxidation via sulphochromic acid and back titration of the excess by the Mohr reagent.

RESULTS AND DISCUSSION

In this section we report the chemical diagenesis of the Villefranche Bay sediments, and interpret the interstitial water data in terms of equilibrium state calculations and stoichiometric equations related to organic matter oxidation with authigenic mineral formation.

The porosity decreases gradually with depth from 0.85 to an average value of 0.68 at 30 cm depth (Fig. 1 a).
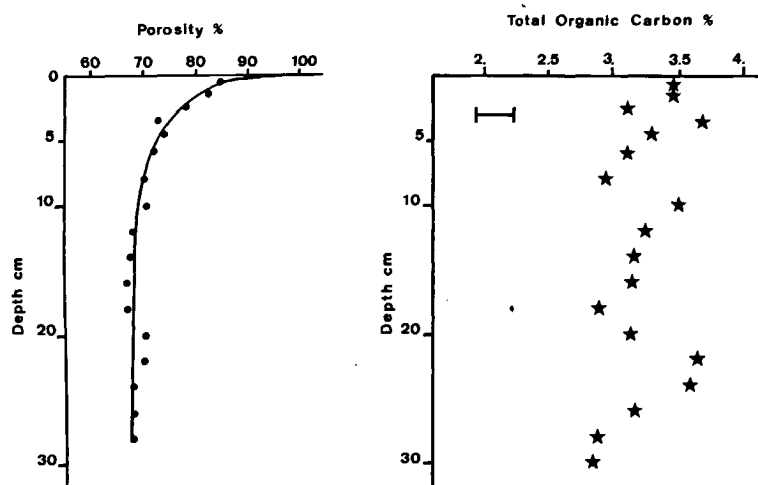

Figure 1
a) Porosity versus depth. The solid line represents the smoothed variations of porosity with depth;
b) organic carbon content versus depth. The horizontal bar represents the reproducibility of the determination.
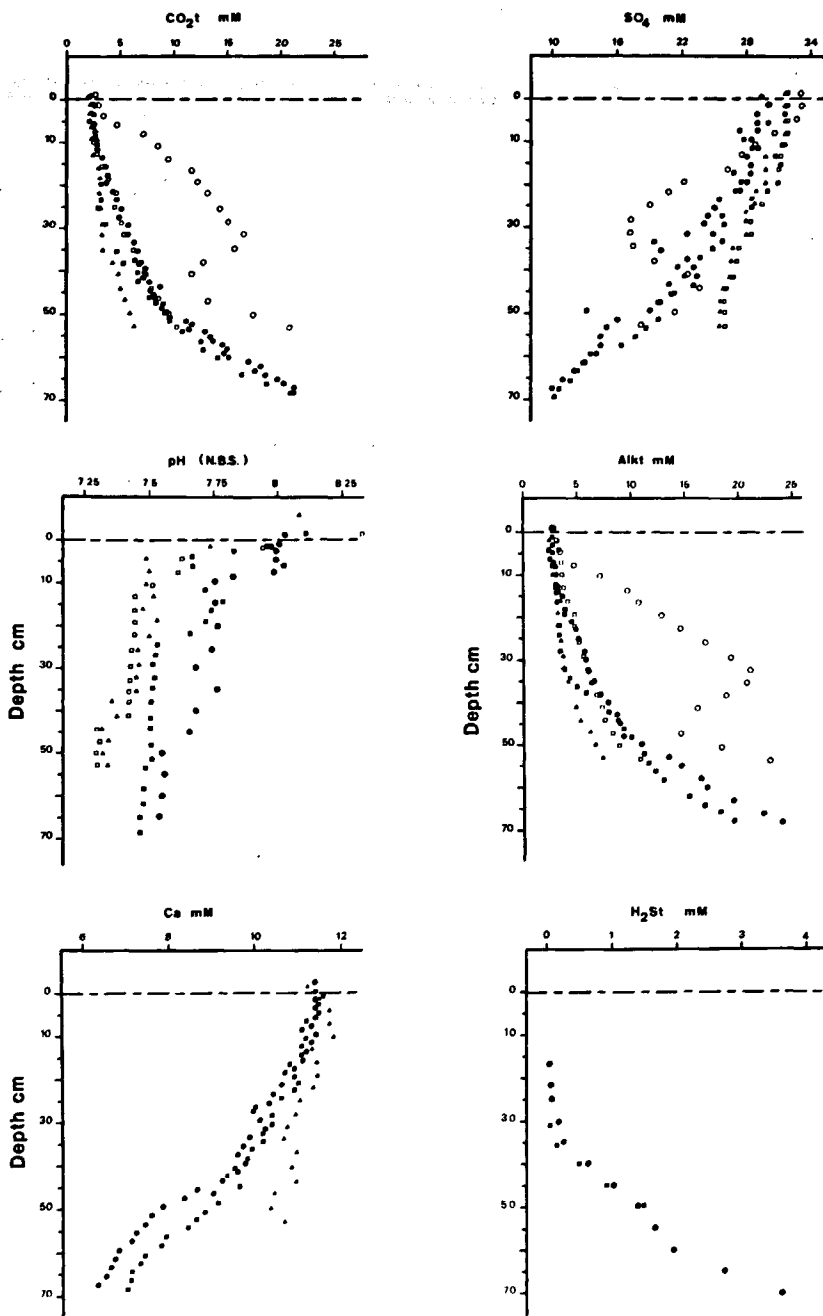
Figure 2

Distributions of pH (determined on the NBS Scale), ΣCO_2, Alk_t, ΣH_2S, Ca and SO_4 in the interstitial waters of Villefranche Bay sediments situated in the vicinity of the sampling site. Open circles, June 1982; open squares, August 1982; filled triangles, July 1983; filled circles, December 1983; filled squares, January 1984. The dashed line symbolizes the sediment-water interface.

The profile does not demonstrate perturbations and shows relatively low values of porosity for a coastal sediment (*i. e.* Murray *et al.*, 1978).

The total organic carbon distribution vs depth is shown in Figure 1 b. This distribution does not yield a well-defined pattern with depth. The profile reflects patchiness due to rather large amounts of vegetation in the sediment. The mean carbonate content of the core, reported as $CaCO_3$, is 45.3% with a standard deviation of 1.43%. X-Ray diffraction patterns confirm that carbonates are the main minerals of these sediments.

Interstitial water results

Interstitial water results are presented in Figure 2 for some of the analyses performed before October 1984. For the October 1984 sampling period pore water results are presented in Table 1 and profiles in Figure 3.

All these profiles emphasize significant variations in pore water concentration for all the elements. The general trend for each element is the same, but with different magnitude, and is reproducible. The results imply that these sediments are relatively well irrigated, particularly in the top 20 cm, by benthic faunal activity. Enhancing the transport of dissolved substances across the sediment-water interface, this process explains the shapes of the different profiles. Moreover increased benthic activity in summer might result in an increase of these exchanges and consequently produce a decrease in the gradient during summer compared to winter. Figure 2 presents a survey of interstitial water composition at different seasons. The range of concentration variations are, in general, similar to those observed previously with near-shore organic-rich sediments (Sholkovitz, 1973; Murray *et al.*, 1978; Elderfield *et al.*, 1981).

Chloride and bromide show a pronounced minimum (around 8‰) close to 25 cm downcore. This pattern may be due to:

1) an incomplete peeper equilibration – the waters filling the peeper compartment did not reach complete equilibrium with interstitial waters for these species;

2) interstitial water dilution by groundwaters originating in the karstic system surrounding the Villefranche Bay.

This lack of complete equilibration or dilution introduces perturbations in the profiles affecting the concentrations by not more than 10%. Apparently these variations are more pronounced on inactive and/or major anions such as Br^- and Cl^- and also affect the Mg profile. They are, however, small compared to those observed with other elements subject to diagenetic processes. Subsequently, for the purpose of this work, we normalized non-reactive species used in computing chemical equilibrium or stoichiometric relationships with respect to chlorinity profiles, as this yielded a better precision than chloride performed by IC, using the following relation:

$$(Conc)_n = (Conc)_z \cdot (Cl_t / Cl_z)$$

where:

$(Conc)_n$ = normalized species concentration at depth z.
$(Conc)_z$ = measured species concentration at depth z.
Cl_t = chlorinity at the top of the core.
Cl_z = measured chlorinity at depth z.

Normalizing data in this manner constitutes an approximate means of decoupling geochemical diagenetic processes from dilution effects and allows us to consider diagenetic changes free from interferences. Such corrections may not be valid if interstitial waters reflect equilibrium with a solid phase, but as will be demonstrated later, these corrections do not modify our conclusions. When surface concentrations are small compared to downcore variations, no normalization was performed because these species were not influenced by the changing water balance. But, as will be clear later, this treatment is mandatory in order to deal with species which can be removed from solution by precipitation or exchange: e.g. Mg^{2+} during chemical diagenesis.

When performing the normalization on the magnesium profile, we observe a corrected pattern reflecting reduced Mg concentration variations of only 7% compared to 12%. However, even after normalization and taking into account the analysis accuracy, the Mg concentrations decrease slightly with depth, suggesting a removal. On the other hand, normalized bromide profiles give concentration variations which are constant within the range of analytical error, indicating that dilution is the sole process contributing to these changes.

These results suggest that a carbonate phase is precipitating out of these pore fluids, since calcium is depleted with depth. Although in deep-sea sediments, carbonate is believed to be dissolving close to the sediment-water interface due to organic matter oxidation, we observe in these coastal marine sediments that, at lower depth, Ca decreases. Hence the carbonate system in these sediments should be studied in detail in order to assess and quantify the importance of the mineralization processes.

The major objectives were to compute chemical equilibrium with the carbonate phases and define with reliability the geochemical mass balances of early diagenesis in these sediments. Therefore, we refer in the main to the more complete data set-October 1984 – and consider all preliminary results as complementary in the discussion.

Table 1
Interstitial water data from Villefranche Bay.

Nc	pH_t	Alk_t (mM_w)	SO_4^{2-} (mM_w)	ΣH_2S (mM_w)	Cl^- (mM_w)	Br^- (μM_w)	Ca^{2+} (mM_w)	Mg^{2+} (mM_w)	ΣCO_2 (mM_w)	Mn^{2+} (nM_w)	ΣPO_4 (μM_w)	Cl $(\%)$
1	7.731	2.591	30.9	–	595	918	11.15	57.96	2.380	966	1.56	21.30
2	7.724	2.595	31.6	–	594	918	10.72	57.91	2.480	812	1.22	21.29
3	7.672	2.601	29.7	–	589	915	10.82	57.96	2.490	938	2.06	21.28
4	7.608	2.809	28.7	–	590	908	10.50	57.30	2.300	980	0.47	21.12
5	7.614	3.033	28.5	–	579	905	10.70	56.55	2.460	1700	0.53	21.05
6	7.584	3.400	27.6	–	575	908	–	–	–	520	0.92	20.80
7	7.577	3.578	27.3	–	573	901	10.38	54.88	2.560	325	1.30	20.76
8	7.510	3.628	27.2	–	576	901	10.42	54.99	2.680	333	1.83	20.54
9	7.456	4.220	26.0	–	568	901	10.07	53.45	2.660	312	3.12	20.24
10	7.414	4.977	24.8	0.125	554	900	9.83	52.12	2.880	231	6.36	19.64
11	7.404	6.292	23.7	0.287	547	880	9.67	51.68	3.940	158	8.35	19.75
12	7.295	7.141	23.3	0.487	550	879	9.73	51.30	4.840	144	10.30	19.80
13	7.267	8.530	23.0	0.742	548	870	9.65	51.24	5.630	135	11.40	20.00
14	7.263	9.589	21.9	0.982	541	878	9.48	51.27	6.970	134	12.50	19.89
15	7.172	11.710	21.2	1.182	547	871	9.50	52.58	8.020	117	13.70	19.77
16	7.132	13.130	21.0	1.475	550	867	9.17	52.54	9.330	100	15.60	19.70
17	7.071	14.516	20.4	1.715	549	863	9.12	52.06	10.430	99	17.40	19.79
18	7.015	15.976	18.9	2.035	548	875	–	–	12.100	96	17.90	19.93
19	7.015	17.420	18.9	2.435	554	876	9.27	51.92	14.900	76	19.20	19.88
20	6.967	18.755	17.3	2.595	570	885	8.58	51.97	17.000	70	20.20	20.06
21	6.959	20.465	16.1	2.945	560	889	8.47	51.50	19.000	66	21.80	19.90
22	6.902	22.061	14.6	3.808	556	897	8.43	51.48	20.800	74	24.30	19.99
23	6.915	23.320	14.4	4.158	567	901	8.24	51.20	22.900	74	26.30	20.07
24	6.898	25.560	12.2	4.710	575	900	8.39	52.47	25.300	85	28.30	20.27
25	6.871	29.694	10.9	5.550	576	903	8.09	53.36	26.200	69	30.60	20.71
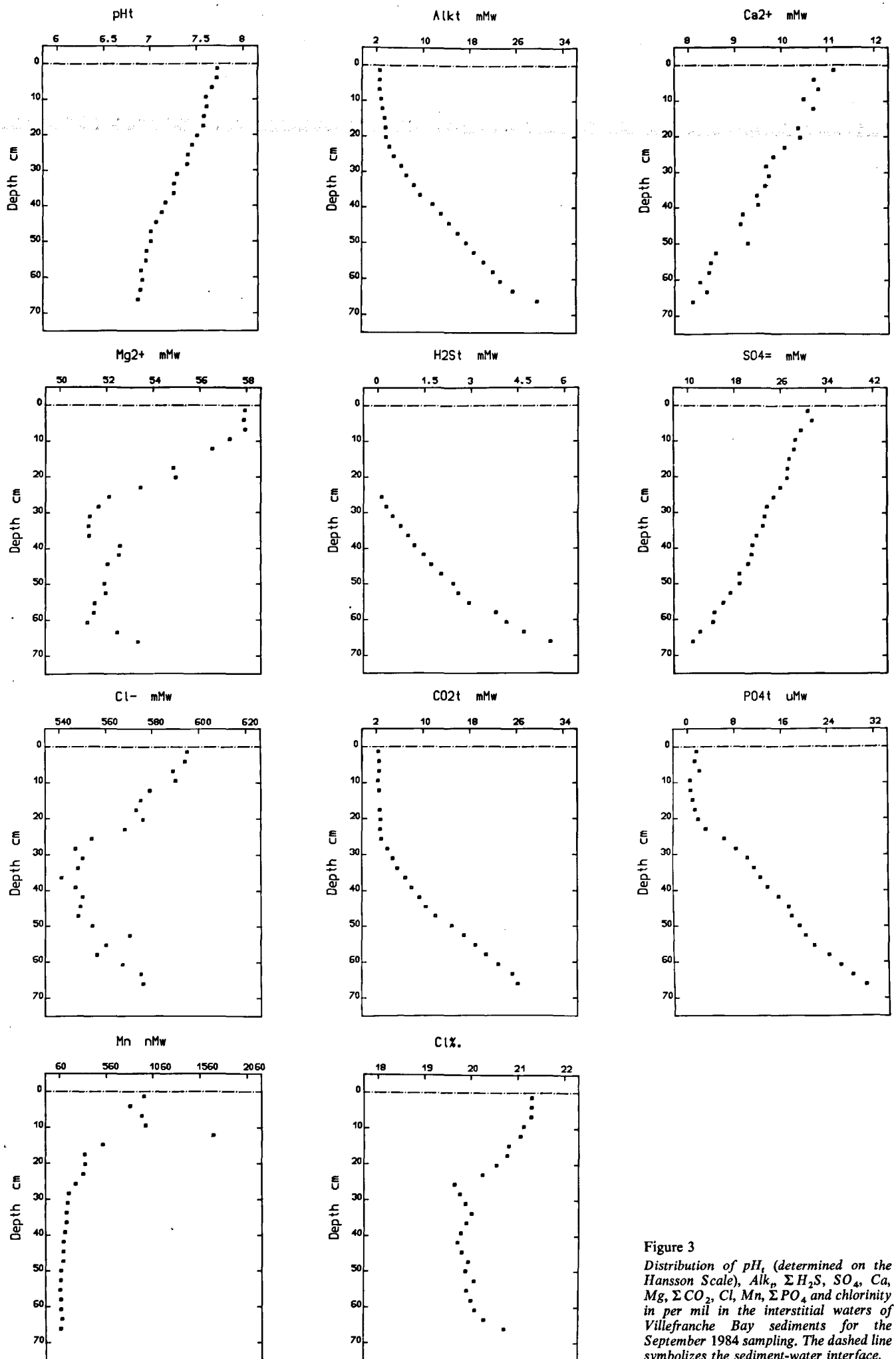
Figure 3

Distribution of pH$_t$ (determined on the Hansson Scale), Alk$_t$, ΣH_2S, SO_4, Ca, Mg, ΣCO_2, Cl, Mn, ΣPO_4 and chlorinity in per mil in the interstitial waters of Villefranche Bay sediments for the September 1984 sampling. The dashed line symbolizes the sediment-water interface.

Sulphate is the major electron acceptor driving organic matter oxidation in anaerobic marine sediments after O_2 utilization in the top few millimetres. The data suggest that below 20 cm the pore water chemical composition varies according to the main reaction: organic matter oxidation by bacterial sulphate reduction as described by Richards (1965):

$$CH_2O_{106}NH_{3\ 16}H_3PO_4 + 53\ SO_4^{2-}$$
$$\rightarrow\ 106\ HCO_3^- + 16\ NH_3 + 53\ H_2S + H_3PO_4.$$
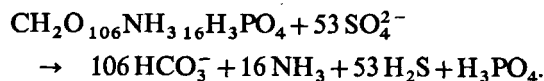
Consequently, sulphate concentrations decrease from 31 mM_w to 11 mM_w downcore. This mineralization process produces a total alkalinity variation of 27 meq./kg and a ΣCO_2 variation of 24 mM_w. Because of the contribution of HS^- and NH_3 to total alkalinity, in the pH range of these interstitial waters, one generally has $Alk_t > \Sigma CO_2$. When considering solely the previous stoichiometric equation, one should obtain a ΣH_2S increase of approximatly the same magnitude. Instead we observed a total sulphide variation of 5.5 mM_w which suggests sulphidic mineral phase formation and/or H_2S diffusion towards overlying waters.

The release of inorganic carbon dissolved in interstitial waters affects the carbonate system in the sediment, as is shown by the obvious depletion of calcium with depth. In October 1984, calcium dropped from 11 mM_w to 8.1 mM_w, certainly as a consequence of carbonate phase formation.

pH_t decreases significantly from 7.73 beneath the sediment water interface to 6.87 at 70 cm depth, indicating a pore water acidification process due to the oxidation of organic matter and concomitant sulphate reduction.

Dissolved Mn^{2+} concentrations are homogeneous at the core top, increase strongly to reach a maximum value of 1.7 μM at 10 cm depth and subsequently decrease to reach an asymptotic value of 70 nM. Phosphate demonstrates a general increase with depth reflecting organic matter decomposition (Froelich et al., 1979; Berner, 1980; Elderfield et al., 1981).

Chemical equilibrium in interstitial waters

In attempting to perform equilibrium calculations in a complex electrolyte mixture such as sea water, one must adopt a reference scale that is thermodynamically well defined. The infinite dilution activity scale and the ionic medium scale (Sillen, 1967) fulfil the necessary requirements. In this work we have applied both approaches in comparing the results.

The activity coefficients, for the infinite dilution scale, were calculated using the specific ion interaction model proposed by Pitzer (1973) and applied to natural waters, in an updated version, by Harvie et al. (1984). For the ionic medium scale we used the apparent constants for protolytic equilibria in sea water given in Johansson's thesis (1981).

The master variable for acid-base equilibrium calculations is pH: consequently special care is called for when making pH measurements.

pH determination

When studying acid-base equilibria, different pH scales can be used. NBS (National Bureau of Standards) buffers have been widely used in previous intersial water studies (Goldhaber et al., 1977; Froelich et al., 1979; Murray et al., 1980; Emerson et al., 1980; and others). However the pH thus measured is not the real thermodynamic pH (Hansson, 1972; Johanson, 1981; Dickson, 1984; Harvie et al., 1984) but an operationally defined quantity. The pH defined on the Hansson scale is adequate for Pitzer's calculations because it directly provides the concentration of H^+.

The pH_t measurements (Fig. 3) exhibit a sharp decrease from the value of 7.731 at the core top down to 6.871 at about 70 cm depth. This trend was previously observed with pH determinations performed according to the NBS specification (Fig. 2). This increase in $[H^+]_t$ might be related to the oxidation of organic matter via various electron acceptors present in the environment. In this case sulphate reduction appears to be the most important process. The question is: is this acidification inherent to the definition of the pH scale, such HSO_4^- concentrations should decrease with decreasing SO_4^{2-} concentrations. As the electrode is only sensitive to H^+, a decrease in pH with depth is indeed observed, corresponding to the oxidation of organic matter and related chemical changes. This shows that the Hansson procedure would not be completly appropriate for interstitial water studies because of ionic medium variations of composition.

Hence the major drawback is related to the sulphate decrease with depth resulting from organic matter oxidation and simultaneous SO_4^{2-} reduction because of the protonation equilibrium:

$$SO_4^{2-} + H^+ \rightleftarrows HSO_4^-.$$
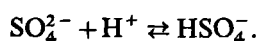
Hence we transformed total H^+ concentrations into free H^+ concentrations by subtracting the HSO_4^- contribution in the pH_t value of the 35 salinity standard. This gives the following relation:

$$[H^+]_f = [H^+]_t/(1 + K_{Su} Su_t)$$

where:
Su_t is the total SO_4 concentration, and

$$K_{Su} = [HSO_4^-]/([H^+] \cdot [SO_4^{2-}]).$$

Computing Alk_c, $[CO_3^=]$, and ΣCO_2 from Alk_t and pH

The titrated alkalinity corresponds to all bases titrated at the end point of the CO_2 system (Dickson, 1981; Morel, 1983). Therefore, in anoxic interstitial waters one has:

$$Alk_t = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-]$$
$$+ [HPO_4^{2-}] + [HS^-].$$

This is a simplified expression for total alkalinity. The contributions of numerous species such as $H_3SiO_4^-$ and

NH_3 were omitted because they were negligible, $<1°/_{oo}$ (Johasson and Wedborg, 1982). It should also be pointed out that since Alk_t reproducibility was $7°/_{oo}$, consequently $1°/_{oo}$ contributions are meaningless.

In order to compute the carbonate alkalinity,

$$Alk_c = [HCO_3^-] + 2[CO_3^{2-}],$$

one has to deduct the borate, sulphide and phosphate contribution. Total borate was not determined on the pore water samples, therefore we calculated its $B(OH)_4^-$ concentration using the total borate (ΣB)-chlorinity relationship established by Uppström (1974):

$$\Sigma B/Cl = 0.0000215.$$

Hence, assuming that PO_4^{3-} and $H_2PO_4^-$ are negligible in this pH range, one obtains:

$$Alk_c = Alk_t - [\Sigma B/(1 + K_b \cdot [H^+])]$$
$$- [\Sigma H_2S/(1 + K_s \cdot [H^+])] - [\Sigma PO_4/(1 + K_p \cdot [H^+])].$$

In order to calculate the in situ carbonate alkalinity on the ionic medium "free" we determined the necessary constants using the temperature salinity equations published in Johansson and Wedborg (1982). We calculated the salinity variations with depth using the salinity chlorinity ratio of standard sea water:

$$S = Cl . 1.80655.$$

These constants were determined on the pH_t Hansson's scale. Therefore the values had to be corrected by adding $\log(1 + K_{Su} \cdot Su_t)$. K_{Su} and Su_t were calculated from the interstitial water chlorinities.

Consequently the carbonate and total dissolved CO_2 are given by the following equations:

$$[CO_3^{2-}] = Alk_c/(2 + K_2 \cdot [H^+]).$$
$$\Sigma CO_2 = Alk_c [1 + K_1 \cdot [H^+]]$$
$$- (1/(2 + K_2 \cdot [H^+]))(2 . K_1 \cdot [H^+] + 1)];$$

with:

$$K_1 = [H_2CO_3]/([H^+] \cdot [HCO_3^-])$$
$$K_2 = [HCO_3^-]/([H^+] \cdot [CO_3^{2-}]).$$

All the constants were calculated for in situ temperature and in situ chlorinity variations.

Interstitial water: carbonate saturation

In this subsection we evaluate the in situ results in terms of interstitial water saturation state. In order to delineate saturation states, one must rely on an ionic model for sea water. In the subsequent pages the cases of calcite and carbonate solid solutions will be discussed. The ion concentration products (ICP) have been determined using the constant ionic medium "free" scale. The ion activity products (IAP) were calculated by means of the specific interaction approach.
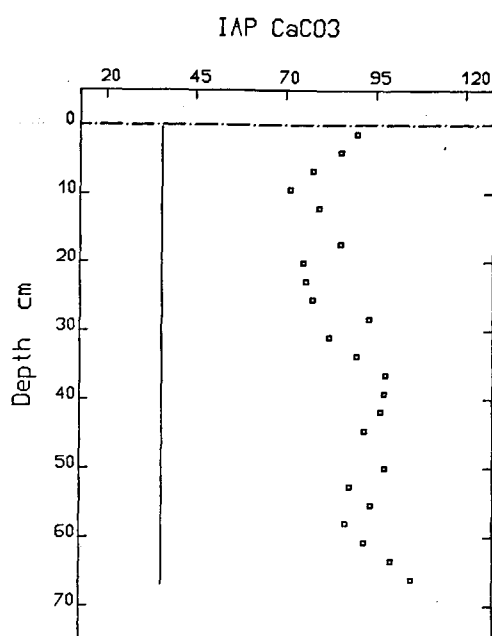

IAP CaCO3

Figure 4

Variations of the calcite ion activity product IAP with depth in interstitial waters of Villefranche Bay sediments. The solid line represents the thermodynamic Ksp of calcite at the in situ temperature.

Specific interaction model

For the specific interaction model, involving the parameterization of deviations from ideality, all the major ion concentrations must be known for computing the total ionic strength and the interactions between ions. Na^+ and K^+ concentrations were not measured, hence we determined their concentrations using their ratio to chlorinity in standard sea water. A correction factor q was used to convert the total concentration from mole/kg sea water to mole/kg H_2O (molal units; Millero, 1982). Pitzer calculations require knowledge of H_f^+ obtained as previously presented. The results of the calculation are presented in Table 2 and Figure 4. The ionic activity products range from 7.13 to 10.50×10^{-9} (Fig. 4) showing an evident supersaturation relative to calcite $(K_s = 3.54 \times 10^{-9})$ and aragonite $(K_s = 5.45 \times 10^{-9})$.

Ionic medium scale

On this scale, care should be taken regarding the choice of a consistent set of apparent equilibrium constants related to the pH definition used. As discussed earlier, we utilized the pH_f because reliable H_f^+ concentration would be determined from Emv measurements. The results of these calculations are presented in Table 2 and plotted on Figure 5.

As there is almost no determination of the apparent solubility constant of calcite and aragonite, and since these constants are pH dependent (Mucci, 1983) on this scale, the comparison of these ICP with K_s' are not made truly possible. The sole determination of K_s', to our knowledge, on the Hansson scale has been presented by Almgrem (1975). From his solubility measurements on Globigerina ooze, he found a relation leading to a K_s' of 9.0×10^{-7} at $T = 18.3°C$. However, the author emphasizes that these measures were not precise but performed in order to define the variation

Table 2

Saturation calculation for carbonate precipitation in the sediments of Villefranche Bay.

		Ionic medium "free" scale				Specific interaction model						
Nc	pH_f	Alk_t meq.kg^{-1}	CO_3^{2-} (mM_w)	Ca^{2+} (mM_w)	ICP (10^{-6})	Ca^{2+} (mM)	Mg^{2+} (mM)	CO_3^{2-} (mM)	γ_{Ca}	γ_{Mg}	γ_{CO_3}	IAP (10^{-9})
1	7.837	2.549	0.118	11.15	1.315	11.5	60.2	32.6	0.203	0.227	0.118	8.98
2	7.830	2.551	0.116	10.72	1.247	11.1	60.2	32.1	0.203	0.227	0.118	8.54
3	7.778	2.561	0.104	10.82	1.130	11.2	60.2	28.8	0.204	0.227	0.118	7.76
4	7.714	2.775	0.098	10.50	1.030	10.9	59.6	26.8	0.205	0.228	0.119	7.13
5	7.720	2.999	0.107	10.70	1.145	11.1	58.7	29.3	0.205	0.228	0.119	7.93
6	7.690	3.368	0.112	–	–	–	–	–	–	–	–	–
7	7.683	3.546	0.116	10.38	1.202	10.8	56.9	31.5	0.207	0.229	0.121	8.52
8	7.616	3.600	0.101	10.42	1.052	10.8	57.1	27.5	0.207	0.229	0.122	7.50
9	7.562	4.194	0.104	10.07	1.043	10.5	55.4	28.0	0.208	0.230	0.124	7.58
10	7.520	4.785	0.107	9.83	1.053	10.2	54.0	29.1	0.209	0.230	0.125	7.75
11	7.510	6.011	0.130	9.67	1.261	10.0	53.5	35.1	0.211	0.232	0.126	9.33
12	7.401	6.700	0.114	9.73	1.114	10.1	53.2	30.5	0.212	0.232	0.126	8.23
13	7.373	7.878	0.127	9.65	1.224	10.0	53.1	33.6	0.212	0.232	0.126	8.98
14	7.369	8.734	0.139	9.48	1.317	9.82	53.1	36.8	0.213	0.233	0.127	9.78
15	7.278	10.724	0.139	9.50	1.317	9.84	54.5	36.8	0.214	0.232	0.126	9.76
16	7.238	11.927	0.141	9.17	1.289	9.50	54.4	37.2	0.215	0.232	0.127	9.65
17	7.177	13.162	0.136	9.12	1.236	9.45	53.9	35.6	0.215	0.233	0.127	9.19
18	7.121	14.426	0.131	–	–	–	–	–	–	–	–	–
19	7.121	15.565	0.142	9.27	1.313	9.61	53.8	36.9	0.217	0.233	0.127	9.77
20	7.073	16.835	0.138	8.58	1.185	8.89	53.9	35.5	0.219	0.235	0.127	8.78
21	7.065	18.299	0.147	8.47	1.243	8.78	53.3	37.7	0.221	0.235	0.128	9.36
22	7.008	19.370	0.137	8.43	1.153	8.74	53.3	34.9	0.222	0.236	0.128	8.67
23	7.021	20.357	0.148	8.24	1.223	8.54	53.0	37.7	0.223	0.236	0.128	9.19
24	7.004	22.456	0.157	8.39	1.317	8.70	54.4	39.8	0.224	0.237	0.128	9.93
25	6.977	25.869	0.174	8.09	1.406	8.40	55.4	43.6	0.226	0.237	0.127	10.50

of K'_s with temperature. All the other determinations were performed on the NBS scale and the more recent ones presented by Mucci (1983) provide an estimation of K'_s for calcite and aragonite as a function of temperature and salinity yielding values varying respectively, for these interstitial waters, from 4.38×10^{-7} to 4.86×10^{-7} and from 6.76×10^{-7} to 7.49×10^{-7}.

Although the pH scales are not compatible, the difference between the constants of Almgrem and Mucci is apparently too important to be explained only by these operational definitions.

Conclusions

The interstitial waters from Villefranche Bay sediments are found to be supersaturated with respect to calcite and aragonite regardless of the manner in which the degree of saturation is calculated. In order to determine whether the precision of our analysis was not the consequence of such oversaturation, we computed the range of variations in ICP obtained through an error propagation technique. Basically we sampled at random numbers (on a rectangular distribution) in the error range of the analysis and computed on these sets at least a thousand ICP values for every depth. We assumed that pK_s were known at $+/-0.02$. For each set we obtained the lowest and the highest value at 3 sigma. The results are reported in Figure 5. The 3 sigma limit reaches at its maximum 12% of the mean value. This calculation shows that the precision on the analysis can not account for the departure from calcite equilibrium solubility product of Mucci (1983), even for aragonite.

Supersaturation in anoxic or suboxic sediment pore waters appears to be a common feature (Sholkovitz, 1973; Berner et al., 1978; Emerson et al., 1980; Morse et al., 1985; Sayles, 1985). Our results are comparable with the saturation indexes observed by Morse et al.

(1985) in shallow water sediments from the Bahamas and with Berner's (1966) study of carbonate sediments from Bermuda, Florida Bay, and the Everglades. As for the suite of samples from the Bahamas, where half of the samples have $\Omega_{aragonite} > 1.7$, we obtain high saturation states: $1.34 < \Omega_{aragonite} < 1.93$.

These patterns have been the subject of numerous hypotheses concerning the stoichiometry of the precipitating solid carbonate phase and the relation between
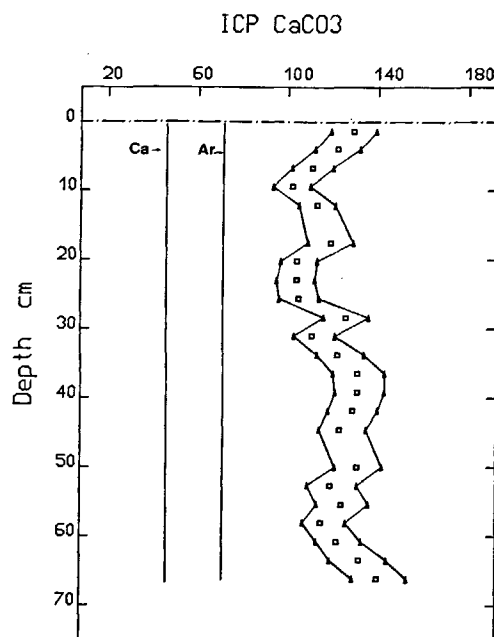
ICP CaCO3

Figure 5

Variations of the calcite ion concentration product ICP with depth in interstitial waters of Villefranche Bay sediments. The two solid lines represent the range obtained by the error analysis performed on the data. For comparison the Mucci 1983 values for calcite (Ca) and for aragonite (Ar) at the in situ temperature and mean salinity are plotted.
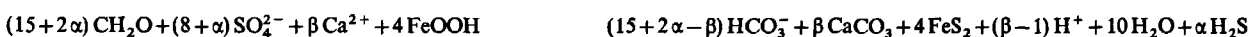
Table 3

Stoichiometry of organic matter oxidation reactions and calcium precipitation during early diagenesis.

(1) Sulfate reduction to H_2S:

$$2CH_2O + SO_4^{2-} \rightarrow 2HCO_3^- + H_2S \qquad (\alpha)$$

(2) Sulfate reduction and pyrite (FeS_2) precipitation:

$$15CH_2O + 8SO_4^{2-} + H^+ + 4FeOOH \rightarrow 15HCO_3^- + 4FeS_2 + 10H_2O$$

(3) Sulfate reduction and FeS precipitation:

$$9CH_2O + 4SO_4^{2-} + 4FeOOH \rightarrow 4FeS + 9HCO_3^- + H^+ + 6H_2O$$

(4) $CaCO_3$ precipitation:

$$Ca^{2+} + HCO_3^- \rightarrow CaCO_3 + H^+ \qquad (\beta)$$

Global stoichiometric relationship if pyrite precipitation

$$(15+2\alpha)CH_2O + (8+\alpha)SO_4^{2-} + \beta Ca^{2+} + 4FeOOH \qquad (15+2\alpha-\beta)HCO_3^- + \beta CaCO_3 + 4FeS_2 + (\beta-1)H^+ + 10H_2O + \alpha H_2S$$

$$\Delta\Sigma CO_2 = -\left[\frac{15+2\alpha-\beta}{8+\alpha}\right]\Delta SO_4^{2-} \quad \text{and} \quad \Delta\Sigma H_2S = -\left[\frac{\alpha}{8+\alpha}\right]\Delta SO_4^{2-}$$

Global stoichiometric relationship if FeS precipitation

$$(9+2\alpha)CH_2O + (4+\alpha)SO_4^{2-} + \beta Ca^{2+} + 4FeOOH \qquad (9+2\alpha-\beta)HCO_3^- + \beta CaCO_3 + 4FeS + (\beta-1)H^+ + 6H_2O + \alpha H_2S$$
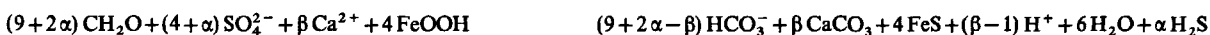
$$\Delta\Sigma CO_2 = -\left[\frac{9+2\alpha-\beta}{4+\alpha}\right]\Delta SO_4^{2-} \quad \text{and} \quad \Delta\Sigma H_2S = -\left[\frac{\alpha}{4+\alpha}\right]\Delta SO_4^{2-}$$

supersaturation and existence of solid solution (Ca, Mg, Mn, $Sr - CO_3$). Moreover according to Berner *et al.* (1978) carbonate supersaturation might be explained in pore waters by the presence of phosphates or organic compound poisoning the surface and inhibiting nucleation. This explanation is certainly more correct: the precipitation of solid solution should decrease IAP, because of the thermodynamics of solid solution formation. In the case of $CaCO_3$, it may be noted that during the equilibrium experiments performed with solid solutions of $Ca - Mg - CO_3$ (Mucci and Morse, 1984), only the K_s' of calcite changes, but not the thermodynamic Ks. Hence in these interstitial waters we interpret the supersaturation as a result of precipitation inhibition or kinetic factors inhibiting the attainment of true and reversible equilibrium.

Stoichiometric model

Stoichiometric models have been used in numerous studies to predict chemical changes during early diagenesis (Sholkovitz, 1973; Berner, 1977; Murray *et al.*, 1978; Emerson *et al.*, 1980; Elderfield *et al.*, 1981; Emerson *et al.*, 1982). In the present section we apply this approach to extend our understanding of early diagenesis in organic-rich coastal marine sediments, our primary aim to develop a set of stoichiometric equations depicting the major geochemical transformations taking place in the sediments. These reactions are, to a certain extent, simplistic, in comparison with the complexity of sedimentary environments, but offer a

practical means of interpreting data. We go on to consider that the driving equations are related to organic matter oxidation *via* bacteria sulphate reducers (Berner, 1980) and mineral formation. Hence, below the top 10 cm of the sedimentary column, we assume that:

1) the average oxidation state of organic matter is zero (CH_2O);

2) bacterial sulphate reduction is the major process of organic matter oxidation;

3) iron oxyhydroxides (FeOOH) are reduced to form Fe^{2+};

4) iron-sulphides are precipitating from the pore fluids as pyrite (FeS_2) or as FeS;

5) a fraction of ΣH_2S produced during two remains in solution because the FeOOH concentration in the solid is the limiting factor, consequently Fe^{2+} concentrations are negligible in the mass balance;

6) pore waters are precipitating $CaCO_3$, because they are supersaturated with respect to calcium carbonate and because Ca^{2+} concentrations are significantly decreasing with depth;

7) after a certain depth, contributions of other possible steps in organic matter oxidation, like $O^2NO_3^-$... (Froelich *et al.*, 1979) are supposed to be quantitatively small enough to be negligible.

Thus we propose, at first, two different stoichiometric models based on the equations presented in Table 3 to depict the geochemical transformations in the sediment. These two models are directly related to the iron-

sulphide mineral phase proposed (FeS or FeS_2). It may be observed that, according to the mineral proposed we obtain different relationships between ΣCO_2 produced during organic matter oxidation and concomitant sulphate reduction:

$$d\Sigma CO_2/dSO_4^{2-} = 15/8 \text{ in the case of pyrite formation,}$$

$$d\Sigma CO_2/dSO_4^{2-} = 9/4 \text{ in the case of FeS.}$$

These ratios are different from 2.0, as expected from the reaction:

$$2\,CH_2O + SO_4^{2-} \rightarrow 2\,HCO_3^- + H_2S.$$
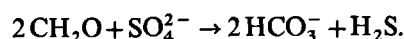
As sediments are not closed systems, species distributions are also affected by diffusion and advection (Berner, 1980). As we had no information on the advective term, we assume that only differential diffusion (*i. e.* the difference in ionic diffusion coefficients) modifies their relative distributions. Hence, in order to find the real values of the stoichiometric coefficients, we must correct these ratios from a differential diffusion term derived from conservation equations such as those proposed by Berner (1977) and subsequently utilized in numerous studies (*e. g.* Emerson *et al.*, 1980; Bender *et al.*, 1985). The appropriate relations and coefficients are presented in Table 4. These relations suppose that the different constituents are not affected by adsorption during early diagenesis of the sediments.

As little is known about *in situ* diffusion coefficients for the chemical species in sediments, we used tracer diffusion coefficients given by Papaud (1982) in sea water at 25°C for SO_4^{2-} and HCO_3^- and estimates from Li and Gergory (1974) for Ca^{2+} and HS^-. We assumed that the porosity and the tortuosity of the sediment will affect these coefficients uniformly and that temperature variations from 25°C to our *in situ* temperature will not modify their ratios. The diffusion coefficient of the sulphur species HS^- and ΣH_2S were assumed equal and were estimated from Cl^- tracer diffusion coefficient variations from seawater to infinite dilution.

Table 4
Stoichiometric relationship with diffusion transport and tracer diffusion coefficients in $cm^2.s^{-1}$ at 25°C.

Stoichiometric ratios
$\left[\dfrac{d(\Sigma CO_2)}{dSO_4^{2-}}\right]_{obs} = \Delta\Sigma CO_2/\Delta SO_4^{2-} \dfrac{D_{SO_4^{2-}}}{D_{HCO_3^-}}$
$\left[\dfrac{d(\Sigma H_2S)}{dSO_4^{2-}}\right]_{obs} = \Delta\Sigma H_2S/\Delta SO_4^{2-} \dfrac{D_{SO_4^{2-}}}{D_{HS^-}}$
$\left[\dfrac{dCa^{2+}}{dSO_4^{2-}}\right]_{obs} = \Delta Ca^{2+}/\Delta SO_4^{2-} \dfrac{D_{SO_4^{2-}}}{D_{Ca^{2+}}}$

Diffusion coefficients
$D_{HCO_3^-} = 102 \times 10^{-7}$, $\quad D_{SO_4^{2-}} = 82 \times 10^{-7}$
$D_{HS^-} = 140 \times 10^{-7}$, $\quad D_{Ca^{2+}} = 81 \times 10^{-7}$

We have defined the complete set of equations and can therefore estimate the coefficients related to the proportion of ΣH_2S remaining in solution and the proportion of calcite precipitated. From the slopes of the linear relationships for ΣCO_2 *versus* SO_4^{2-} and ΣH_2S *versus* SO_4^{2-} shown in Figure 6, we obtain:

$$[d\Sigma CO_2/dSO_4]_{obs} = -1.54 +/-0.06$$

$$[d\Sigma H_2S/dSO_4]_{obs} = -0.40 +/-0.02.$$

These slopes were obtained from the experimental data by regression analysis with error estimates. Then we deduct the corresponding stoichiometric ratios after correction for differential diffusion:

$$[d\Sigma CO_2/dSO_4]_{stoi} = -1.916 +/-0.075$$

$$[d\Sigma H_2S/dSO_4]_{stoi} = -0.683 +/-0.034.$$

Hence, according to the two global stoichiometric models, we propose different values for α and β. In order to check their consistency we must interpret these values in terms of the geochemical mass balance in the sediment *i. e.* verify whether these results are compatible with the concentration variations observed for other elements in these interstitial waters.

From the equations delineating the early diagenesis of these sediments, the only available data to be confirmed are the Ca concentration variations with depth. In the case of pyrite precipitation one has:

$$\alpha = 17.23 +/-0.5$$

$$\beta = 1.13 +/-2.0.$$

Hence, for 1 mole of sulphate reduced during early diagenesis we should observe a precipitation of 0.045 +/-0.08 mole of calcite. In the case of FeS precipitation one has:

$$\alpha = 8.61 +/-0.25$$

$$\beta = 2.06 +/-0.97,$$

consequently for 1 mole of sulphate reduced we should observe a precipitation of 0.163 +/-0.08 mole of calcite. These calculations show that only the formation of FeS is compatible with our results and the errors. As a confirmation the ratio dCa^{2+}/dSO_4^{2-} determined from linear regression analysis on the data is:

$$[dCa^{2+}/dSO_4^{2-}]_{obs} = 0.144 +/-0.008 \,(Fig. 6)$$

hence the real stoichiometric ratio is 0.143 because in seawater Ca^{2+} and SO_4^{2-} have nearly similar tracer diffusion coefficients (Tab. 4). The value obtained lies within the error domain in the case of FeS formation.

This result is consistent with Howarth's (1979) observations, because the observed ΣH_2S concentrations are high enough to precipitate FeS instead of FeS_2. But generally in marine sediments the proportion of FeS_2 is larger than the proportion of FeS, as pyrite is the ultimate authigenic reservoir for most sulphur in sediments (Berner, 1980; Berner, 1984; Lord and Church, 1983; Howarth and Jørgensen, 1984). Our model does
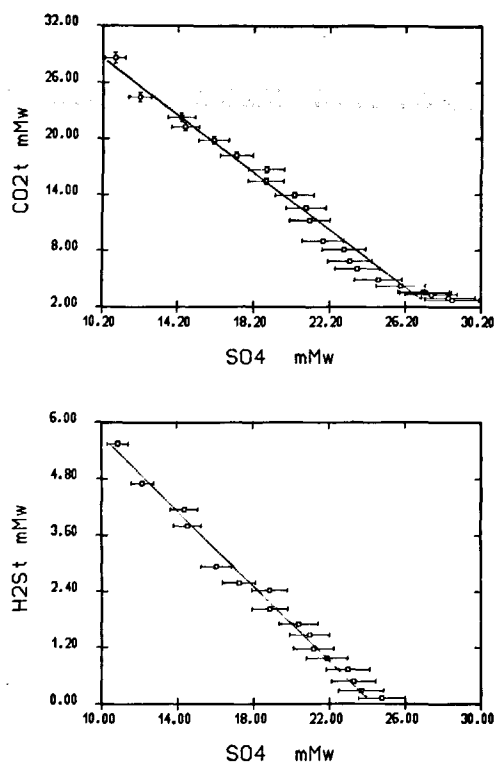
Figure 6

a) Plot of ΣCO_2 versus SO_4. The equation of the linear relationship is $\Sigma CO_2 = 45.4 - 1.536\,SO_4$ with $\rho = 0.945$. *b)* Plot of ΣH_2S versus SO_4. The equation of the linear relationship is $\Sigma H_2S = 9.724 - 0.398\,SO_4$ with $\rho = 0.994$. *c)* Plot of Ca versus SO_4. The equation of the linear relationship is $Ca = 6.344 + 0.144\,SO_4$ with $\rho = 0.960$. The reproducibility of the analysis was used to find the expression linking the two data sets.

not describe the possibility of FeS_2 formation from the reaction:

$$FeS + S^\circ \rightarrow FeS_2,$$
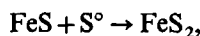
a relatively slow process resulting from the oxidation of HS^- to S°. Hence, our results are debatable with respect to a lack of sediment analysis because the stoichiometric model proposed includes only the reduction of sulphate to sulphide. In order to account for this other step, one needs to depict and study the oxidation of sulphide in these pore waters. Meanwhile we obtain a consistent interpretation of the observed data leading to the first step of iron-sulphide formation in marine coastal sediments.

The stoichiometric model proposed encompasses the variation of the by-products of organic matter mineralization during early diagenesis. This model stresses that authigenic minerals have to be included in order to properly define the stoichiometric ratios. At least, in order to obtain reliable estimates in geochemical mass balances, *in situ* diffusion coefficients are necessary and one need also a consistent model for taking into account cross coupling effects arising from the ionic species migration (Lasaga, 1979; Simonin *et al.*, 1988).

with depth. Although we precisely determined, on a consistent set of samples the carbonate system, we were unable to predict the real composition of the solid phase precipitation. We computed chemical equilibria in these pore waters by means of the ionic medium approach and the specific interaction approach for parametrizing the deviation from ideality. These two calculations emphasize the importance of selecting a consistent thermodynamic frame in order to delineate the carbonate system and strengthen the role of pH determination.

Although the ionic medium scale is convenient for seawater equilibrium calculations it is not satisfactory for pore water investigations as one of its constituents (SO_4^{2-}) is strongly depleted but leads to similar results as a more sophisticated treatment. The determination of pH_f on the M_w scale using Hansson's (1973) procedure is adequate for computing ionic equilibria using the specific interaction approach.

The stoichiometric modelling of early diagenesis in these sediments must include the precipitation of authigenic minerals. These reactions permit prediction, from the variations encountered in the pore water, of the geochemical mass balance resulting from organic matter oxidation. These equations demonstrate that, depending on the sulphur end-product of sulphate reduction, the ratio $d\Sigma CO_2/dSO_4$ changes. From the unfolding of pore water data one can predict that Fe is mainly precipitated in FeS during the first stage of early diagenesis in these marine coastal sediments.

CONCLUSIONS

The distribution of major ions in interstitial waters of Villefranche Bay sediments emphasizes the main process of early diagenesis: the oxidation of organic matter. As a result of this mineralization, the ΣCO_2 content in pore fluids is increased, leading to the precipitation of a calcareous phase as suggested by Ca depletion

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