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 $\sum CO_2$, $\sum H_2S$, 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.


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 $\sum CO_2$, $\sum H_2S$, 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 paramétrer 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 stoichiométrique 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.

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 carbonaterich 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 $\Sigma$CO$_2$ 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 approximately 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, 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.

After 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 $\Sigma$H$_2$S. 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 $\Sigma$CO$_2$ determination, interstitial waters were injected, using
CHEMICAL DIAGENESIS IN COASTAL MARINE SEDIMENTS

Porosity was determined on the sediment cores by a scuba-diver. Analytical method

Pore water samples were determined by syringes with [20 G-1'], into venoject Terumo RM
tubes. The samples were preserved in these airtight tubes by previously placing a CO2-free aqueous solution of HgCl2 in order to prevent further microbial activity during storage.

The sediment samples used for porosity determination and organic carbon analysis were collected using a plexiglass 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 pH1 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 pH1 is related to the total H+ concentration:

\[ [H^+] = [H^+]_1 + [HSO_4^-] \]

\[ pH_1 = -\log([H^+]) \]

where \( [\cdot] \) 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 \( +/-0.1^\circ C \) and the pH was then corrected for in situ temperature; reproducibility was \( +/-0.003 \) pH units on Tris buffer. Total alkalinity - Alk, 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 Na2SO4 were added relative to seawater composition). The equivalent volume was computed by means of Gran's function F2. Reproducibility was 0.7% on IAPSO standard seawater used as reference for titrant molarity. \( \Sigma H_2S \) was determined on 1 ml by means of a computerized titration developed from the manual method described by Boule`gue et al. (1979) and Dyrssen et al. (1985). Reproducibility was better than 0.5% for concentrations ranging from 0.25-10.0 mM, millimoles per kg of seawater. Only \( \Sigma H_2S \) was determined with the HgCl2 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 AgNO3 titration using Gran’s function to compute \( V_{eq} \). The overall reproducibility was better than 0.4%. Cl- and SO42- were determined by ion chromatography using a Dionex 2000, or Vydac 213. Reproducibility on weight diluted samples was 2.5% for Cl- and 5% for SO42-. 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. Ca2+ and Mg2+ 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. \( \Sigma CO_3 \) was determined by gas chromatography on a Poropak Q.18 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. 1a).

![Figure 1](Image)

**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.
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 1b. 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 CaCO₃, 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).

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**Figure 2**

Distributions of pH (determined on the NBS Scale), ΣCO₂, Alk, ΣH₂S, Ca and SO₄ 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.
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 groundwater 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 chlorinity profiles, as this yielded a better precision than chloride performed by IC, using the following relation:

\[
\text{(Conc)}_z = \frac{(\text{Conc})_z \cdot (\text{Cl}_z)}{(\text{Cl}_z)}
\]

where:

- \((\text{Conc})_z\) = normalized species concentration at depth \(z\).
- \((\text{Conc})_z\) = measured species concentration at depth \(z\).
- \(\text{Cl}_z\) = chlorinity at the top of the core.
- \(\text{Cl}_z\) = 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. Mg²⁺ 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.

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Figure 3
Distribution of pH, (determined on the Hanssen Scale), Alk, ΣH₂S, SO₄, Ca, Mg, ΣCO₃, CI, Mn, ΣPO₄, 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):

\[
\text{CH}_3\text{O}_{106}\text{NH}_3\text{H}_3\text{PO}_4 + 53\text{SO}_4^{2-} \\
\rightarrow 106\text{HCO}_3^- + 16\text{NH}_3 + 53\text{H}_2\text{S} + \text{H}_3\text{PO}_4^-. 
\]

Consequently, sulphate concentrations decrease from 31 mM to 11 mM downcore. This mineralization process produces a total alkalinity variation of 27 meq/kg and a \( \Sigma\text{CO}_2 \) variation of 24 mM. Because of the contribution of \( \text{HS}^- \) and \( \text{NH}_3 \) to total alkalinity, in the pH range of these interstitial waters, one generally has \( \text{Alk}_R > \Sigma\text{CO}_2 \). When considering solely the previous stoichiometric equation, one should obtain a \( \Sigma\text{H}_2\text{S} \) increase of approximately the same magnitude. Instead we observed a total sulphide variation of 5.5 mM which suggests sulphidic mineral phase formation and/or \( \text{H}_2\text{S} \) 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 to 8.1 mM, certainly as a consequence of carbonate phase formation.

The determined value of 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 \( \mu \)M 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) fulfill 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 interstitial 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 \( \text{H}^+ \).

The pH 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 \( [\text{H}^+] \), 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 \( \text{HSO}_4^- \) concentrations should decrease with decreasing \( \text{SO}_4^{2-} \) concentrations. As the electrode is only sensitive to \( \text{H}^+ \), 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 completely 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 \( \text{SO}_4^{2-} \) reduction because of the protonation equilibrium:

\[
\text{SO}_4^{2-} + \text{H}^+ \rightleftharpoons \text{HSO}_4^- .
\]

Hence we transformed total \( \text{H}^+ \) concentrations into free \( \text{H}^+ \) concentrations by subtracting the \( \text{HSO}_4^- \) contribution in the pH value of the 35 salinity standard. This gives the following relation:

\[
[H^+]_T = [H^+]_0/(1 + K_{\text{su}} S_u) 
\]

where:

- \( S_u \) is the total \( \text{SO}_4 \) concentration, and
- \( K_{\text{su}} = [\text{HSO}_4^-]/([H^+].[\text{SO}_4^{2-}]) \).

**Computing Alk, \( \Sigma\text{CO}_2 \), and \( \Sigma\text{CO}_2 \) from Alk, and pH**

The titrated alkalinity corresponds to all bases titrated at the end point of the \( \text{CO}_2 \) system (Dickson, 1981; Morel, 1983). Therefore, in anoxic interstitial waters one has:

\[
\text{Alk}_t = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] \\
+ [\text{HPO}_4^{2-}] + [\text{HS}^-].
\]

This is a simplified expression for total alkalinity. The contributions of numerous species such as \( \text{H}_3\text{SiO}_4^- \) and...
These constants were determined on the pH, Hansson's scale. Therefore the values had to be corrected by adding log(1+Ks. Su). Ks and Su were calculated from the interstitial water chlorinities. Consequently the carbonate and total dissolved CO2 are given by the following equations:

\[
\text{Alk}_c = \text{Alk}_t - \left[ \text{B} + \text{K}_1 \cdot [\text{H}^+] \right] - \left[ \text{H}_2\text{SO}_4 / (1 + \text{K}_p \cdot [\text{H}^+]) \right] \cdot \left[ \text{H}_2\text{S} / (1 + \text{K}_s \cdot \text{Su}) \right] = \left[ \text{HCO}_3^- \right] / (1 + \text{K}_1 \cdot [\text{H}^+] ) + \left[ \text{CO}_2^- \right] / (1 + \text{K}_2 \cdot [\text{H}^+] )\]

In order to compute the in situ carbonate alkalinity on the ion activity product range from 7.13 to 10.50 \times 10^{-9} \text{ mol/kg} \text{H}_2\text{O} (\text{molal units; Millero, 1982). Pitzer calculations require knowledge of } \text{H}_2^+ \text{ obtained as previously presented. The results of the calculation are presented in Table 2 and Figure 4. The ion activity products range from 7.13 to 10.50 \times 10^{-9} \text{ mol/kg} \text{H}_2\text{O} (\text{molal units; Millero, 1982). Pitzer calculations require knowledge of } \text{H}_2^+ \text{ obtained as previously presented. The results of the calculation are presented in Table 2 and Figure 4.}

**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 chloride. In Figure 4 showing an evident supersaturation relative to calcite (K_\text{sp} = 3.54 \times 10^{-9}) and aragonite (K_\text{sp} = 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, because reliable H_2^+ 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_\text{sp} is not made truly possible. The sole determination of K_\text{sp} to our knowledge, on the Hansson scale has been presented by Almgren (1975). From his solubility measurements on Globigerina ooze, he found a relation leading to a K_\text{sp} of 9.0 \times 10^{-7} \text{ at } T = 18.3^\circ \text{C.}

The author emphasizes that these measures were not precise but performed in order to define the variation.
of \( K' \) 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 \( K' \) for calcite and aragonite as a function of temperature and salinity yielding values varying respectively, for these interstitial waters, from 4.38 \( \times 10^{-7} \) to 4.86 \( \times 10^{-7} \) from 4.76 \( \times 10^{-7} \) to 7.49 \( \times 10^{-7} \).

Although the pH scales are not compatible, the difference between the constants of Almgren 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 \( pK' \) 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 \( \Omega_{\text{aragonite}} > 1.7 \), we obtain high saturation states: 1.34 < \( \Omega_{\text{aragonite}} < 1.93 \).

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

---

**Table 2**

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

<table>
<thead>
<tr>
<th>Ionic medium &quot;free&quot; scale</th>
<th>Specific interaction model</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{pH}_c )</td>
<td>Alk, meq.kg(^{-1})</td>
</tr>
<tr>
<td>--------------------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>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</td>
<td></td>
</tr>
<tr>
<td>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</td>
<td></td>
</tr>
<tr>
<td>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</td>
<td></td>
</tr>
<tr>
<td>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</td>
<td></td>
</tr>
<tr>
<td>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</td>
<td></td>
</tr>
<tr>
<td>6 7.690 3.368 0.112 - - - - - - - - -</td>
<td></td>
</tr>
<tr>
<td>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</td>
<td></td>
</tr>
<tr>
<td>8 7.616 3.600 0.108 10.50 1.052 10.8 57.1 27.5 0.207 0.229 0.121 7.50</td>
<td></td>
</tr>
<tr>
<td>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</td>
<td></td>
</tr>
<tr>
<td>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</td>
<td></td>
</tr>
<tr>
<td>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</td>
<td></td>
</tr>
<tr>
<td>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</td>
<td></td>
</tr>
<tr>
<td>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</td>
<td></td>
</tr>
<tr>
<td>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</td>
<td></td>
</tr>
<tr>
<td>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</td>
<td></td>
</tr>
<tr>
<td>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</td>
<td></td>
</tr>
<tr>
<td>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</td>
<td></td>
</tr>
<tr>
<td>18 7.121 14.426 0.131 - - - - - - - - -</td>
<td></td>
</tr>
<tr>
<td>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</td>
<td></td>
</tr>
<tr>
<td>20 7.073 16.835 0.138 8.59 1.185 8.89 53.9 35.5 0.219 0.235 0.127 8.78</td>
<td></td>
</tr>
<tr>
<td>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</td>
<td></td>
</tr>
<tr>
<td>22 7.008 19.370 0.137 8.43 1.153 8.74 53.3 34.9 0.222 0.226 0.128 8.67</td>
<td></td>
</tr>
<tr>
<td>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</td>
<td></td>
</tr>
<tr>
<td>24 7.004 22.456 0.157 8.39 1.317 8.70 54.4 39.8 0.224 0.227 0.128 9.93</td>
<td></td>
</tr>
<tr>
<td>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</td>
<td></td>
</tr>
</tbody>
</table>

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**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.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Stoichiometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Sulfate reduction to ( \text{H}_2\text{S} ):</td>
<td>(2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow 2\text{HCO}_3^- + \text{H}_2\text{S})</td>
</tr>
<tr>
<td>(2) Sulfate reduction and pyrite (FeS(_2)) precipitation:</td>
<td>(15\text{CH}_2\text{O} + 8\text{SO}_4^{2-} + \text{H}^+ + 4\text{FeOOH} \rightarrow 15\text{HCO}_3^- + 4\text{FeS}_2 + 10\text{H}_2\text{O})</td>
</tr>
<tr>
<td>(3) Sulfate reduction and FeS precipitation:</td>
<td>(9\text{CH}_2\text{O} + 4\text{SO}_4^{2-} + 4\text{FeOOH} \rightarrow 4\text{FeS} + 9\text{HCO}_3^- + \text{H}^+ + 6\text{H}_2\text{O})</td>
</tr>
<tr>
<td>(4) CaCO(_3) precipitation:</td>
<td>(\text{Ca}^{2+} + \text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{H}^+)</td>
</tr>
</tbody>
</table>

Global stoichiometric relationship if pyrite precipitation
\[
(15 + 2\alpha)\text{CH}_2\text{O} + (8 + \alpha)\text{SO}_4^{2-} + \beta\text{Ca}^{2+} + 4\text{FeOOH} \rightarrow (15 + 2\alpha - \beta)\text{HCO}_3^- + \beta\text{CaCO}_3 + 4\text{FeS}_2 + (\beta - 1)\text{H}^+ + 10\text{H}_2\text{O} + \alpha\text{H}_2\text{S} \\
\Delta \Sigma \text{CO}_2 = \left[\frac{15 + 2\alpha - \beta}{8 + \alpha}\right] \Delta \text{SO}_4^{2-} \quad \text{and} \quad \Delta \Sigma \text{H}_2\text{S} = \left[\frac{\alpha}{8 + \alpha}\right] \Delta \text{SO}_4^{2-}
\]

Global stoichiometric relationship if FeS precipitation
\[
(9 + 2\alpha)\text{CH}_2\text{O} + (4 + \alpha)\text{SO}_4^{2-} + \beta\text{Ca}^{2+} + 4\text{FeOOH} \rightarrow (9 + 2\alpha - \beta)\text{HCO}_3^- + \beta\text{CaCO}_3 + 4\text{FeS} + (\beta - 1)\text{H}^+ + 6\text{H}_2\text{O} + \alpha\text{H}_2\text{S} \\
\Delta \Sigma \text{CO}_2 = \left[\frac{9 + 2\alpha - \beta}{4 + \alpha}\right] \Delta \text{SO}_4^{2-} \quad \text{and} \quad \Delta \Sigma \text{H}_2\text{S} = \left[\frac{\alpha}{4 + \alpha}\right] \Delta \text{SO}_4^{2-}
\]

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 \(K_{sp}\) of calcite changes, but not the thermodynamic \(K_s\). 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\(_2\)O);
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 \(\Sigma\text{H}_2\text{S}\) 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\(^2\)NO\(_3\) ... (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 FeS₂). It may be observed that, according to the mineral proposed we obtain different relationships between ΣCO₂ produced during organic matter oxidation and concomitant sulphate reduction:
\[ \frac{d\Sigma CO_2}{dSO_4^-} = 15/8 \] in the case of pyrite formation,
\[ \frac{d\Sigma CO_2}{dSO_4^-} = 9/4 \] in the case of FeS.

These ratios are different from 2.0, as expected from the reaction:
\[ 2CH_3O + SO_4^- + 2HCO_3^- + H_2S. \]

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 seawater at 25°C for SO₄²⁻ and HCO₃⁻ and estimates from Li and Gregory (1974) for Ca²⁺ 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 ΣH₂S were assumed equal and were estimated from Cl⁻ tracer diffusion coefficient variations from seawater to infinite dilution.

<table>
<thead>
<tr>
<th>Stoichiometric ratios</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>[ \frac{d(\Sigma CO_2)}{dSO_4^-} ]</td>
<td>[ \frac{\Delta CO_2}{\Delta SO_4^-} ]</td>
</tr>
<tr>
<td>[ \frac{d(\Sigma H_2S)}{dSO_4^-} ]</td>
<td>[ \frac{\Delta H_2S}{\Delta SO_4^-} ]</td>
</tr>
<tr>
<td>[ \frac{dCa^{2+}}{dSO_4^-} ]</td>
<td>[ \frac{\Delta Ca^{2+}}{\Delta SO_4^-} ]</td>
</tr>
</tbody>
</table>

Diffusion coefficients

\[ D_{SO_4^-} = 102 \times 10^{-7}, \quad D_{SO_4^-} = 82 \times 10^{-7}, \]
\[ D_{SO_4^-} = 140 \times 10^{-7}, \quad D_{SO_4^-} = 81 \times 10^{-7}. \]

We have defined the complete set of equations and can therefore estimate the coefficients related to the proportion of ΣH₂S remaining in solution and the proportion of calcite precipitated. From the slopes of the linear relationships for ΣCO₂ versus SO₄²⁻ and ΣH₂S versus SO₄²⁻ shown in Figure 6, we obtain:

\[ [d\Sigma CO_2/dSO_4^-] _{calc} = -1.54 +/- 0.06 \]
\[ [d\Sigma H_2S/dSO_4^-] _{calc} = -0.40 +/- 0.02. \]

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:

\[ [d\Sigma CO_2/dSO_4^-] _{calc} = -1.916 +/- 0.075 \]
\[ [d\Sigma H_2S/dSO_4^-] _{calc} = -0.683 +/- 0.034. \]

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 \[ dCa^{2+}/dSO_4^- \] determined from linear regression analysis on the data is:

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

hence the real stoichiometric ratio is 0.143 because in seawater Ca²⁺ and SO₄²⁻ 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 ΣH₂S concentrations are high enough to precipitate FeS instead of FeS₂. But generally in marine sediments the proportion of FeS₂ 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...
not describe the possibility of FeS₂ formation from the reaction:

\[
\text{FeS} + S^\circ \rightarrow \text{FeS}_2,
\]

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, \textit{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 \textit{et al.}, 1988).

\section*{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 \(\Sigma \text{CO}_2\) content in pore fluids is increased, leading to the precipitation of a calcareous phase as suggested by Ca depletion 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 (SO₄⁻) is strongly depleted but leads to similar results as a more sophisticated treatment. The determination of pH on the Mₜ 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 \(d\Sigma \text{CO}_2/d\text{SO}_4\) 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.

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