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INFLUENCE OF THE AEROBIC BACTERIAL RESPIRATION ON THE  
EARLY DISSOLUTION OF CARBONATES IN COASTAL SEDIMENTS.

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ABSTRACT

The influence of benthic bacterial activity on early diagenesis of marine coastal carbonates has been investigated by the determination of the vertical distribution of dissolved and particulate carbon in the sediments of the Bay of Calvi. In carbonate rich sediments, one observes an increase of both total dissolved inorganic carbon ( $\Sigma C$ ) and of total alkalinity ( $A_T$ ) indicating the dissolution of carbonate mainly in the ten first centimeters. The 1:1 relation between  $\Delta \Sigma C$  and  $\Delta A_T$  suggests that the dissolution is directly associated with the production of carbonic acid by bacterial degradation of organic matter.

In order to prove the role of bacterial respiration in the carbonate dissolution process, a biological reactor simulating the aerobic degradation of organic matter in marine sediments has been used. This reactor allowed us to confirm that the dissolution of the carbonates was strictly controlled by the  $CO_2$  produced during the bacterial respiration.

The evolution of the composition of solid carbonate with depth indicates that the high-magnesium calcites are dissolved preferentially. In the case of deposits mainly composed of Lithothamnium, the amount of carbonate dissolved during this early diagenetic process has been estimated to be 75% of the initial carbonate deposited.

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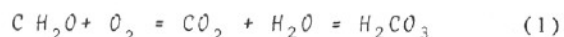
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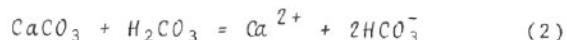
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## 1. INTRODUCTION

The persistence and the accumulation of biogenic carbonates in shallow marine sediments is mainly related to the existence of a lysocline in the deepest parts of the oceans (3000 - 5000 meters). Below this lysocline the water is undersaturated with respect to calcium carbonate and this mineral dissolves rapidly during sedimentation or after deposition at the sediment-water interface. In the coastal zone where numerous organisms produce carbonate skeletons, the water masses are largely oversaturated with respect to  $\text{CaCO}_3$  and the skeletons are thus very well preserved as long as they are in contact with the water column. However, after deposition and burial they are placed in a very different environment which may be very corrosive, due to the production of carbonic acid by bacterial respiration. The coastal sediments are indeed generally rich in organic matter which undergoes an intense bacterial degradation. Under aerobic conditions, the oxidation of organic matter may be represented by the following simplified stoichiometry:



and in the presence of calcium carbonate:



However, this reaction is only possible if undersaturation with respect to  $\text{CaCO}_3$  is realized in the interstitial waters of the sediments and if no other biological or chemical process tends to create adverse conditions. For instance, the release of ammonium during the degradation of organic matter consumes protons and the resulting increase of pH is on the contrary favorable for the precipitation of  $\text{CaCO}_3$ . Although the possible dissolution of calcium carbonate in the upper parts of the sediments due to the bacterial activity is often mentioned in the literature, its actual importance is poorly known.

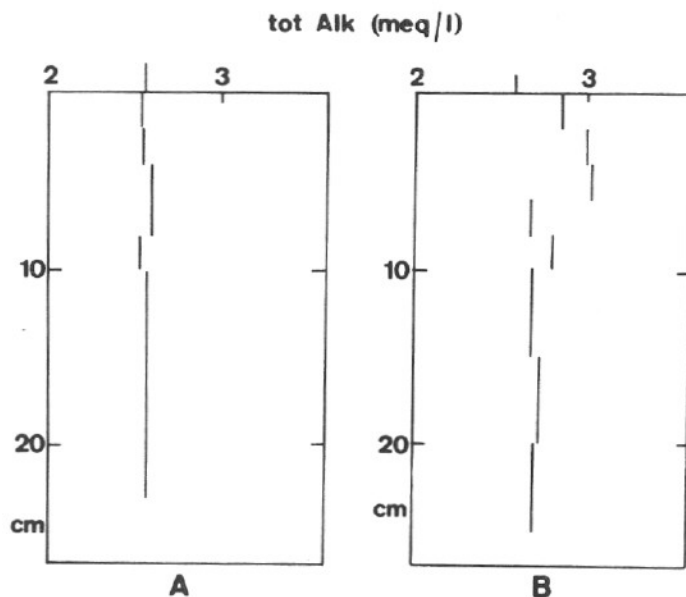


Fig. 1: Vertical profile of alkalinity in the pore waters of A): a sandy sediment with a very low calcium carbonate content, B): a sediment containing 60% of  $\text{CaCO}_3$ .

The measured redox potential indicates that all cores were under oxidizing conditions over the entire depth investigated ( $E_h > 200$  mV). Figure 1 shows as an example two typical vertical profiles of alkalinity. There is a clear correlation between the observation of an increase in the alkalinity in the pore waters and the presence of calcium carbonate in the sediments. The first profile corresponding to sandy material with a very low carbonate (less than 5%) content shows a constant alkalinity in the pore waters equal to that of the overlying water. The second one is typical of a carbonate rich sediment: the alkalinity increases in the first few centimeters, reaching a maximum at a depth around 5 cm and then decreasing to reach finally a constant value at depths below 10 to 20 cm. This maximum strongly suggests that carbonate is dissolving in the first few centimeters. If this dissolution is simply related to

We will first present the field observations, showing that calcium carbonate is dissolving in the carbonate rich sediments of the Gulf of Calvi (Corsica-France). We will further confirm by in-vitro experiments that the carbonic acid produced by bacterial activity is almost totally used to dissolve the calcium carbonate initially present in the sediments. These observations are restricted to the aerobic conditions which prevail in most of the carbonate sediments of the Gulf of Calvi.

It must be pointed out that under anaerobic conditions, very different, if not opposite, processes may occur. They will not be discussed here.

## 2. ANALYSIS OF THE SEDIMENTS OF THE GULF OF CALVI

The sediments of the Gulf of Calvi are mainly composed of a mixture of detrital quartz of terrestrial origin and biogenic carbonate (Burhenne, 1981). The strong currents and periodic storms prevent the accumulation of fine material and organic rich sediments in this shallow Gulf (0 - 80 meters). Thus the superficial sediments are roughly represented by carbonate free coarse sands along the coastal line which grade into almost pure biogenic carbonate deposits at greater depths. The carbonate particles are mixtures of calcite, aragonite and magnesium calcites containing up to 20 moles %  $\text{MgCO}_3$ . Ten cores of 20 to 70 cm long, covering various types of sediments of the Gulf, were collected with a gravity corer and were processed immediately after sampling. This included cutting the core in slices of 2 to 5 cm, squeezing of the slices under nitrogen and immediate measurement of Eh and pH. The alkalinity of the interstitial water was measured later in the laboratory, with great precision following the Gran method (Almgreen and Fonselius, 1976).

On the other hand, the solid fraction was analyzed for total carbonate content (%  $\text{CO}_2$  by gazometry),  $\text{CaCO}_3$  and  $\text{MgCO}_3$  (by complexometry after attack with acetic acid), and organic matter. The granulometric distribution was investigated for a few selected cores.

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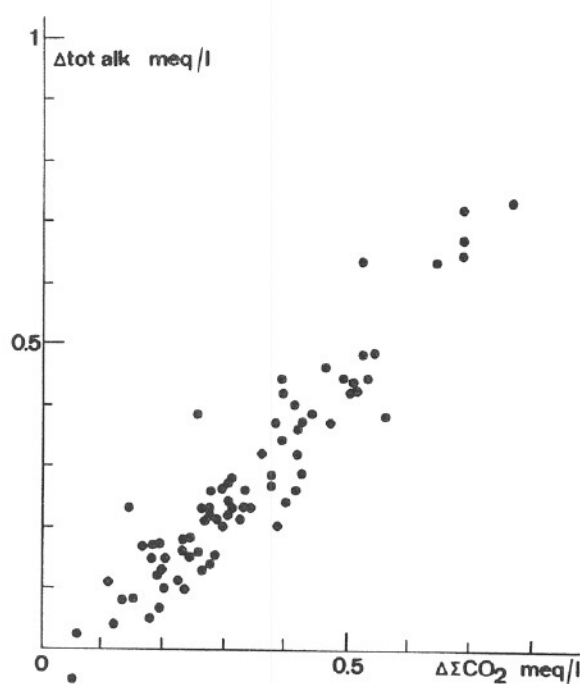
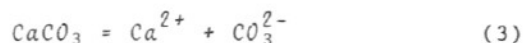


Fig. 2: Increase of alkalinity as a function of increase of total inorganic carbon in the pore waters of the sediments of the Gulf of Calvi. The equation of the regression line is  $Alk = 1.04 \Sigma C - 0.0074$ .

### 3. LABORATORY EXPERIMENTS

It is not easy to interpret quantitatively the processes occurring in the first few centimeters of the sediments by considering only the vertical distribution of chemical parameters in the sedimentary column. Especially in the upper part of the sediments, uncontrolled natural processes and perturbations during coring may be critical for the quantitative interpretation of the data very critical. We have therefore simulated the influence of the bacterial respiration on the behaviour of carbonate minerals present in the sediment with the aid of laboratory experiments.

the fact that the pore water becomes undersaturated with respect to the carbonate minerals present, then the chemical dissolution represented by:



implies that the amount of the increase in alkalinity must be twice that of the increase in total dissolved inorganic carbon  $\Sigma \text{CO}_2$ . On the contrary, if the dissolution is related to the production of carbonic acid by bacterial degradation of the organic matter, then equations (1) and (2) hold instead and the increase of alkalinity is exactly equal to the increase of the total dissolved inorganic carbon.  $\Sigma \text{CO}_2$  can be easily calculated from the measured alkalinity and pH by taking into account the contribution of the boron alkalinity and the dissociation constants of carbonic acid in sea-water. The values used here are those selected by Morse et al (1980).

We have represented in figure 2 the results of these calculations performed for all the cores where an increase of alkalinity in the pore waters was observed with respect to the alkalinity of the overlying sea-water. This figure represents the increase of alkalinity as a function of the increase of total inorganic carbon in the pore waters. The slope of the regression line between these two parameters is equal to 1.04, indicating that the dissolution of  $\text{CaCO}_3$  is well described by reaction (2) and that the amount of carbonate dissolved is entirely due to the utilization of carbonic acid. However, the intercept of the regression line at zero increase of alkalinity is approximately equal to 0.1 meq of  $\Sigma \text{CO}_2$ . In other words, there may be an input of 0.1 mM/l of  $\text{H}_2\text{CO}_3$  by bacterial respiration before any carbonate mineral present in the sediments starts to dissolve. This may correspond to the amount of carbonic acid used to bring the initial overlying water to the undersaturation conditions required to dissolve the carbonate phases present in the sediments.

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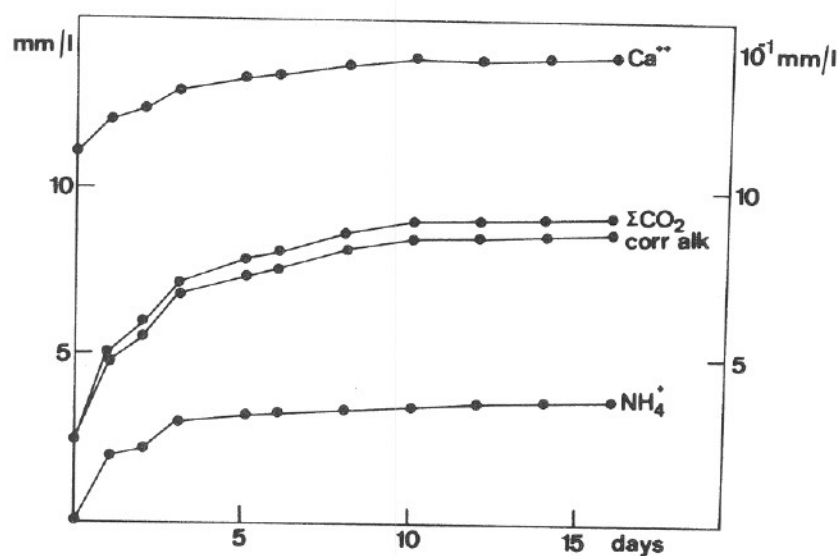


Fig. 3: Evolution with time of the concentration of  $\text{NH}_4^+$  alkalinity, total inorganic carbon C and  $\text{Ca}^{++}$  during the respiration of organic matter in the reactor.

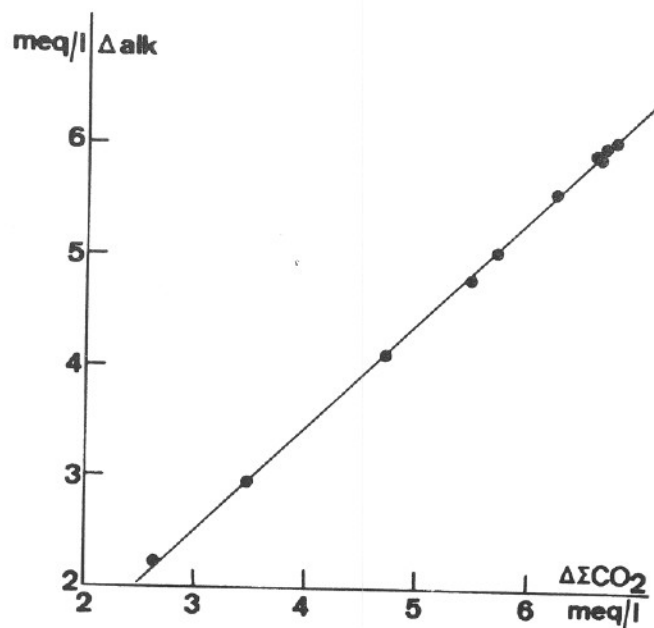


Fig. 4: Increase of alkalinity as a function of increase of total inorganic carbon in the biological reactor. The total alkalinity has been corrected for  $\text{NH}_4^+$ .

The aim of these experiments is to evaluate the efficiency of bacterial respiration under aerobic conditions on the dissolution of carbonates in recent sediments. Therefore a superficial sediment of the Gulf of Calvi containing 60% by weight of carbonates was selected. The X-ray diffraction and the chemical analysis indicate that the carbonate fraction is a mixture containing approximately 65% of magnesium calcite (mean value 11.5 mole %  $\text{MgCO}_3$ ) and 35% of aragonite. One gram of this finely ground sediment was suspended in one liter of Mediterranean surface sea water collected in the Bay of Calvi ( $S = 37.85 \text{ ‰}$ ;  $\Sigma \text{CO}_2 = 2.33 \text{ meq/l}$ ;  $\text{Alk}_T = 2.58 \text{ meq/l}$ ). This water was enriched in organic matter by adding 150 mg of a mixture of gelatine and starch whose C/N ratio is equal to 10. This ratio is similar to the one found in the organic matter of the surficial zone of the marine sediments. This suspension is placed in a respirometer where the oxygen pressure is maintained at 1 atmosphere. The experimental system is closed to prevent the escape to the atmosphere of the  $\text{CO}_2$  produced by bacterial respiration. The amount of organic matter introduced in the system corresponds to 5 mM/l and if the  $\text{H}_2\text{CO}_3$  produced by its bacterial respiration is quantitatively used to react with  $\text{CaCO}_3$ , then according to the stoichiometry of reaction (2), 500mg of  $\text{CaCO}_3$  will dissolve. This corresponds also to the situation where a carbonate rich sediment contains initially 5,2 % by weight of organic carbon or 13% dry weight of organic matter. However, in the experiment, the organic matter is much more reactive and its utilization by bacteria will last only a few days. The mineralization of organic matter has been estimated here by measuring the evolution with time of the concentration of  $\text{NH}_4^+$  in the system. Simultaneously the evolution of total alkalinity, pH and  $\text{Ca}^{++}$  has been followed during the experiment. The results are presented in figure 3. The analysis of the sediment at the end of the experiment confirms that one half of the calcium carbonate initially present in the sediment has been dissolved.

In order to interpret these results, the concentration of ammonia has been subtracted from the measured total alkalinity to indicate the increase in alkalinity due to the dissolution of carbonates. As shown in figure 4, the increase in alkalinity

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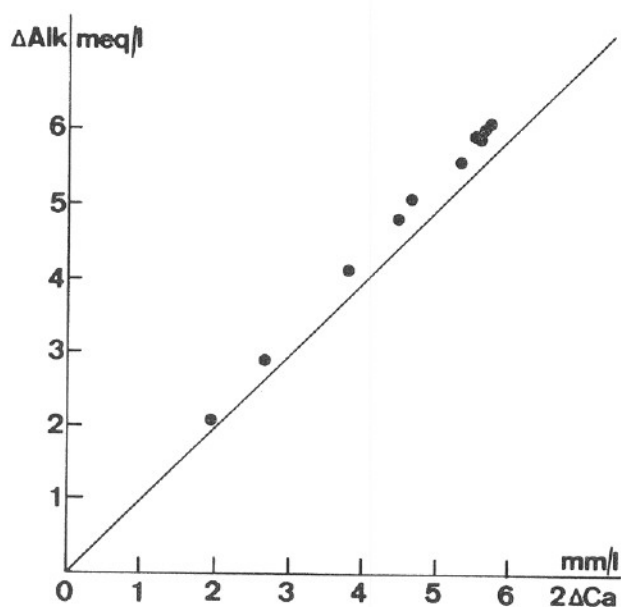


Fig. 5: Increase of total alkalinity corrected for  $\text{NH}_4^+$  as a function of the increase of  $\text{Ca}^{++}$  in the biological reactor.

#### DISCUSSION

The laboratory experiments confirm that the bacterial respiration of organic matter can induce rapid dissolution of a significant amount of carbonate in the sediments. We will try, using some simplified assumptions, to evaluate the importance of this dissolution process in the Gulf of Calvi on the basis of the analysis of the solid fraction of the sediments. We will therefore consider, as an example a core where the carbonate content at the sediment-water interface is higher than 90%. The carbonate is essentially represented by skeletons of *Lithotamnium corallioides*, a high Mg-calcite (15 mole %  $\text{MgCO}_3$ ). This coralline algae is known to be a heterogeneous solid solution (Mackenzie *et al.*, 1983). A microprobe examination\* of fresh *Lithotamnium* specimens present in the bay of Calvi indicates that the skeleton is composed of two distinct phases

\*: This microprobe examination was performed by J. WAUTIER, CAMST, Louvain-la-Neuve.

is then exactly proportional to the increase in total inorganic carbon and the slope of the regression line between the two factors is very close to 1 (slope = 0.96). The intercept of the regression line at zero increase in alkalinity is equal to 0.37 meq/l for  $\text{E CO}_2$ .

One may thus consider that besides a small fraction of carbonic acid utilized to reach an undersaturation state with respect to the carbonates present in the sediment, the  $\text{CO}_2$  produced by the bacteria has been quantitatively used to dissolve these carbonates. The experiment shows also that the dissolution reaction is very fast and the release of  $\text{Ca}^{++}$  and alkalinity to the pore water is simultaneous with the respiration of organic matter.

We have also represented in figure 5 the relation between the increase of alkalinity (corrected for  $\text{NH}_4^+$ ) and the increase of  $\text{Ca}^{++}$ . The regression coefficient is very good but the slope of the line is not exactly equal to one. In other words, the observed increase in alkalinity is higher than the corresponding increase in  $\text{Ca}^{++}$ . This may be explained by the fact that high magnesium calcites, which are more soluble, should dissolve first. However, this increase is difficult to measure directly. From a charge balance, one obtains a hypothetical increase of  $\text{Mg}^{++}$  equal to 0.22 mM/l, which would correspond to the dissolution of calcium carbonate containing 7.3 mole %  $\text{MgCO}_3$ . However, besides the Mg calcites, the aragonite present in the sediments is also rather unstable and should also dissolve. The composition of the Mg calcite which was submitted to dissolution was thus probably containing more than 7%  $\text{MgCO}_3$ ).

with modes close to 10 and 20 moles%  $\text{MgCO}_3$  respectively (100 points analyzed). Besides this dominant phase the superficial sediment contains approximately 10% of aragonite as mollusk shell debris. The bottom layer is also very coarse: 95% of the particles are larger than 1 mm.

The vertical distribution of the concentration of carbonates and of their Mg content is given in figure 6. The

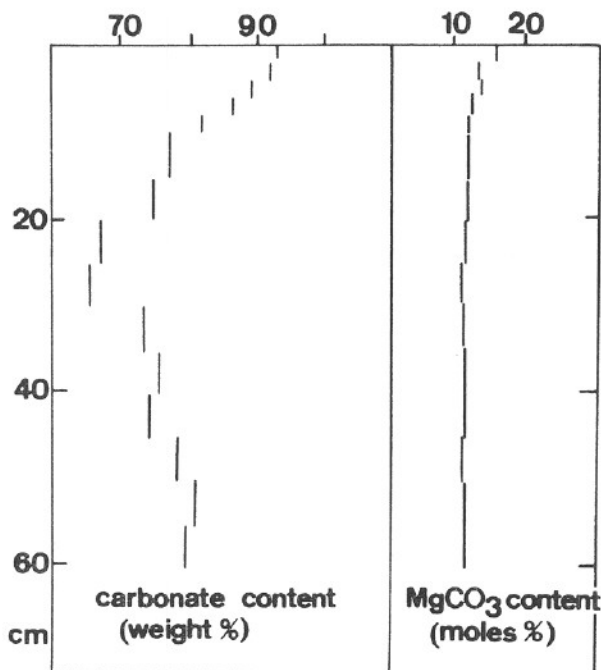


Fig. 6: Vertical distribution and composition of the carbonate phase and of organic matter in a typical sediment of the Gulf of Calvi.

decrease in the carbonate content is rapid in the first 20 cm. In the deeper parts of the sedimentary column the carbonate content tends to reach a rather constant value situated around

75%. The  $\text{MgCO}_3$  matter c

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75%. The magnesium content decreases from 16 to 11 moles%  $\text{MgCO}_3$ . Weight-loss by ignition indicate that the organic matter content remains almost constant.

Let us assume for the sake of simplicity that the sediment is composed of three parts: the organic fraction consumed by the bacteria, the carbonate dissolved due to this bacterial respiration and a small detrital inert fraction. If one assumes that the composition of the material sedimented has remained constant, then it is easy to calculate that a final carbonate content of 75% requires the dissolution of at least 50% of the initial carbonate deposited. The apparently restricted decrease of organic matter is in fact due to the large dissolution of the inorganic phase. A similar extent of the dissolved fraction is obtained by considering the  $\text{MgCO}_3$  content of the carbonate phase, reduced from 16 to 11 moles %. If one takes into account that the mean Mg content results from a mixture of two phases containing respectively 10 and 20 moles %  $\text{MgCO}_3$ , then the composition of the carbonate at depth may be obtained by dissolving the high Mg-calcite phase representing approximately one half of the calcite phase. Furthermore the X-ray diffraction reveals that the aragonite in the deeper layers of the sediment represents 20 % of the carbonate phase instead of 10% in the surface layers. This indicates that aragonite has been less affected by dissolution process than the high Mg calcite phase. Here again the relative increase of aragonite is compatible with a dissolution of one half of the total carbonate phase. These values are of course only rough estimations but they nevertheless suggest that the early dissolution of carbonates due to microbial activity may be very important in coastal sediments. It must be pointed out that the granulometric distribution of the sediments described here above is drastically affected by the dissolution process. At 10 cm depth, the fraction greater than 1 mm has been reduced from 90 to 40%.



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