



## Coupled transport-reaction pathways and distribution patterns between siliciclastic-carbonate sediments at the Ria de Vigo

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### Abstract

This paper examines the linkages between the space-distribution of grain sizes and the relative percentage of the amount of mineral species that result from the mixing process of siliciclastic and carbonate sediments at the Ria de Vigo (NW of Spain).

The space-distribution of minerals was initially determined, starting from a detailed mineralogical study based on XRD-Rietveld analysis of the superficial sediments. Correlations between the maps obtained for grain sizes, average fractions of either siliciclastic or carbonates, as well as for individual-minerals, were further stabilised. From this analysis, spatially organized patterns were found between carbonates and several minerals involved in the siliciclastic fraction. In particular, a coupled behaviour is observed between plagioclases and carbonates, in terms of their relative percentage amounts and the grain size distribution.

In order to explain these results a conceptual model is proposed, based on the interplay between chemical processes at the seawater–sediment interface and hydrodynamical factors. This model suggests the existence of chemical control mechanisms that, by selective processes of dissolution-crystallization, constrain the mixed environment's long-term evolution, inducing the formation of self-organized sedimentary patterns.

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### 1. Introduction

The general trends for sedimentation in mixed siliciclastic-carbonate systems are usually considered

to be the result of the interplay between the hydrodynamic factors affecting a particular environment and the sediment-forming minerals. Consequently, the space-distributions tend to reflect the energy of the environment and the average mineral grain sizes are usually considered to be the driving variable in the dispersal process. However, together with dynamic

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factors, the mixing of siliciclastic and carbonate sediments involve a great variety of sedimentological, biological and chemical processes that take place at the sediment–water interface. In many cases, these processes are also grain-selective and can, therefore, play an important role in the end-term distribution of minerals within the sedimentary pattern. If, in the depositional models, mechanical variables are considered as the only factors determining the final grain size distribution, the real influence of these other processes could be substantially underestimated.

In recent years, there has been a notable change in the perception of sedimentary systems. Current studies of systems focus on their complexity, which emerges from the interaction of the system's components and is well defined within the general framework of dissipative structures (Nicolis and Prigogine, 1989). The concept of self-organization is often used to characterize the evolutionary behaviour of such systems when it results in the formation of spatial, temporal and/or functional macroscopic patterns (De Boer, 2001; Phillips, 2000).

In sedimentary systems, self-organization was first applied to describe how, during the early diagenesis, diffusion and precipitation interact to form periodic bands. However, the scope of this concept has now been extended to the formation of sedimentary patterns at the macroscopic level, with self-organization being applied to describe sedimentary organization on the basin scale (Ortoleva, 1994; Werner and Fink, 1993).

In a similar way, the formalism of non-linear geochemical cycles (Lasaga, 1983a,b) involves the use of self-organization models to characterize the distribution pathways of sedimentary patterns arising from mechano-chemical feedbacks. In such cases, the rate of dissolution and precipitation processes are critical factors determining the cycling of elements between reservoirs (Nagy, 1995). A common feature in all these systems is that self-organization results from the iterative application of small-scale rules, which produce through time the formation of large-scale patterns. Hence, in a mixed sedimentary environment, the sediment distribution can be considered to be the morphological expression of a stationary agreement between the multiple variables involved. This approach makes possible a better understanding of the physical meaning connected to grain size distributions. In addition, the study of this kind of process in real

environments is of crucial importance to interpret past environments correctly as, in many cases, granulometry and mineralogy provide the only available data that may give information about the interactions between products, processes and mechanisms. This is particularly valid for describing aspects such as the source and rate of sediment production, the relative stability of the materials involved and/or the transport mechanisms (Weltje, 1997).

In this study, the mixing processes that take place between siliciclastic and carbonate sediments at the Ria de Vigo and Baiona bay are analysed. Surficial samples, placed at the sediment–water interface, were employed in this study.

It is well known that the term sediment–water interface has a precise meaning in ocean studies, because of its influence on a number of geochemically important processes, including the dissolution of  $\text{CaCO}_3$  (Schink and Guinasso, 1977). As an interface, it is the locus where the reactions between the sediment bed and the underlying water column proceed more rapidly and the authigenesis is more intense (Boudreau, 2001). The associated region, known as the Halmyrolytic Zone (Berner, 1971), or the Benthic Boundary Layer, is a well-defined geochemical scenario that constitutes an open system of about 0.5 mm to 1cm thick (the Diffusive Boundary Layer) around the sediment bed. More precisely, it has been defined as “the portion of sediment and water column that are affected directly in their properties and processes by the presence of the sediment–water interface” (Boudreau and Jorgensen, 2001).

It is beyond the scope of this paper to analyse in detail the processes taking place at the sediment–seawater interface. The reader is referred to texts devoted specifically to that subject (i.e. Berner, 1981; Boudreau and Jorgensen, 2001; Lasaga and Holland, 1976). Here, the mineral distributions in sediments, after a long period of residence at the seawater interface, provide the source of the experimental data. Consequently, a different procedure is followed in real time studies using an inverse approach: an analysis of the distribution of several properties of the sediment is undertaken in order to retrieve the pathways of the mixing process. These are used as a proxy of their evolution during the period of residence at the seawater interface.

A common procedure in the study of the behaviour of the constituents during estuarine mixing is the identification of source and sink functions, with an implicit assumption that the estuary is a steady-state system and that the temporal and spatial distribution will tend towards this end-member (Burton, 1988). In our case, this procedure has also been followed by using, as experimental data, a detailed characterization of the space-distribution of minerals involved in both, siliciclastic and carbonate fractions. Furthermore, it is implicitly assumed that, in terms of percentage content, the spatial distribution is ultimately determined by hydrodynamic factors. However, it can also reflect the interaction of mechanical and geochemical processes taking place during residence time at the sediment–water interface.

## 2. Materials and methods

Surficial sediment samples were collected at 80 stations from the Ria de Vigo and Baiona bay (Fig. 1)

using Van Veen and Shipek grab samplers. Dry sieving and settling tube analyses were employed in the determination of grain size distributions. The mineralogical study was based on the powder X-ray diffraction (XRD) analysis of sediment samples. Diffraction patterns were obtained using a Siemens D-5000 diffractometer with ( $\text{CuK}\alpha$ ) radiation and graphite monochromator. Spectra were taken between  $2\theta=2\text{--}69.65^\circ$ , with  $\text{step}=0.05^\circ$  and 10 s counting time/step.

For the quantitative phase analysis, the Rietveld method was used (Rietveld, 1967, 1969). This procedure allows the deconvolution of a XRD diagram, formed by multiple mineral phases, by each individual component being fitted to a structural model (Mumme et al., 1996). An important advantage is that errors due to peak overlapping are minimized in comparison to procedures based on the determination of the integrated intensities. The Fullprof code (Rodríguez-Carvajal et al., 1987) was employed in all calculations. The relative mineral contents (wt.%) were determined from the scale

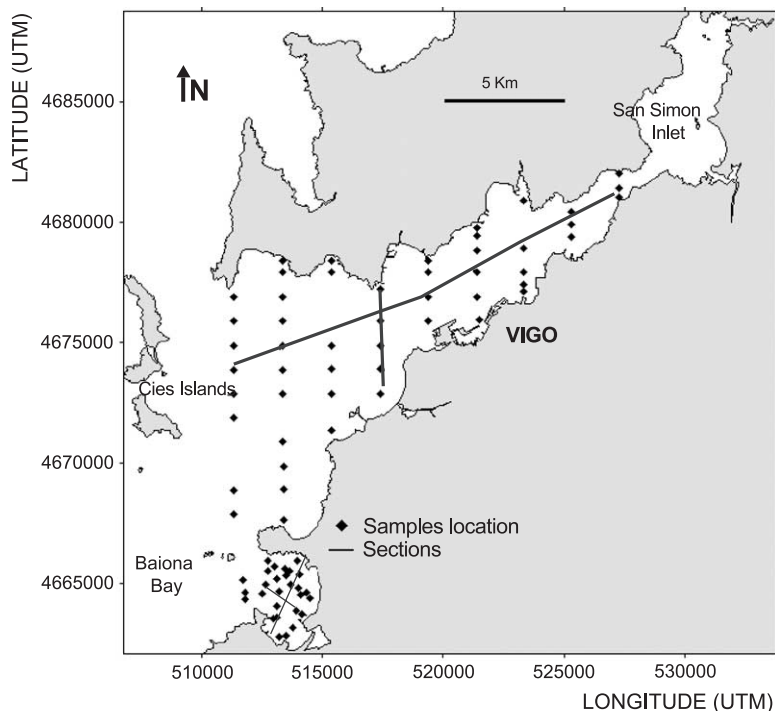


Fig. 1. Map of the study area showing the locations for sampling and sections.

factors, according to the expression (Hill and Howard, 1987):

$$W_j = S_j(ZMV)_j / \sum_{i=1}^n S_i(ZMV)_i \quad (1)$$

where  $W$  is the relative weight percentage of each phase  $j$  in a mixture of  $n$  phases,  $S$  is the scale factor,  $Z$  is the number of formula units per unit cell,  $M$  is the mass of the formula units (in atomic mass units) and  $V$  is the unit cell volume (in  $\text{\AA}^3$ ). The reliability of the measurements was in the range of 0.2–1 wt.%, as estimated by the standard deviation of the scale factors resulting from the refinements.

Additionally, SEM and EDX analysis were performed to determine morphological and compositional aspects of selected mineral grains.

### 3. Results and discussion

From the mineralogical analysis, specific content maps (wt.%) have been produced for each of the

mineral phases present in the samples of both the carbonate and siliciclastic components. These have been further used to compare the spatial distribution of each mineral taken individually, the general pattern of each fraction (siliciclastic and carbonated) and the average grain size obtained by dry sieving.

A comparison of the map showing the average grain size distribution for the complete set of minerals involved in the sediments (Fig. 2) with those relating to the distribution, either terrigenous or carbonates (Fig. 3A and B, respectively) clearly suggests that the spatial distribution of both fractions is governed by dynamic factors resulting in spatial patterns that reflect the energy of the medium. However, by comparing the percentage amount from the maps of each individual mineral (Figs. 4 and 5), with the average fractions and the grain size maps, three aspects are observed: the existence of a specific behaviour in the space-distribution of each mineral; a non-independent behaviour between the wt.% distribution of certain pairs of minerals; and the fact that this coupled variation can be correlated in a direct or inverse way with the grain size distribution.

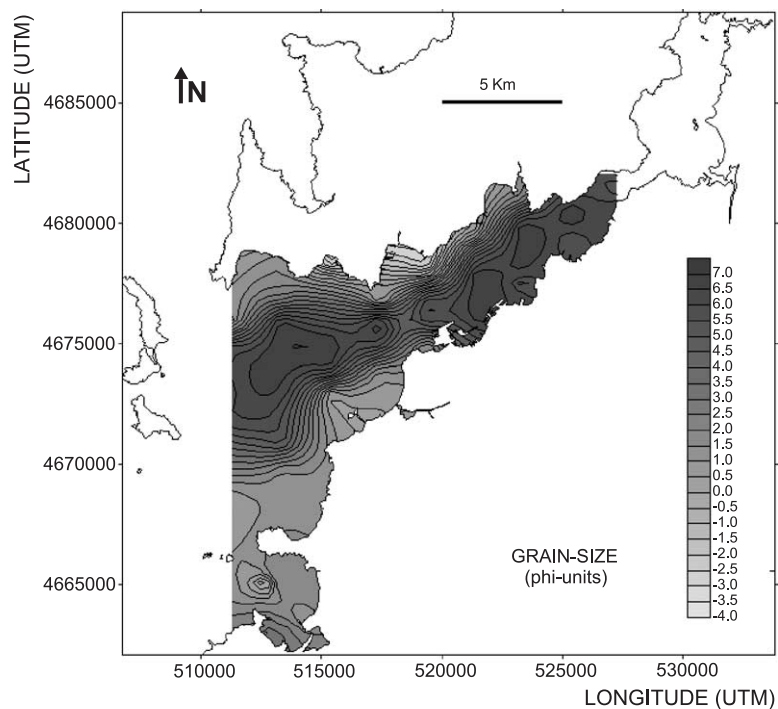


Fig. 2. Average grain size spatial distribution of the studied area.

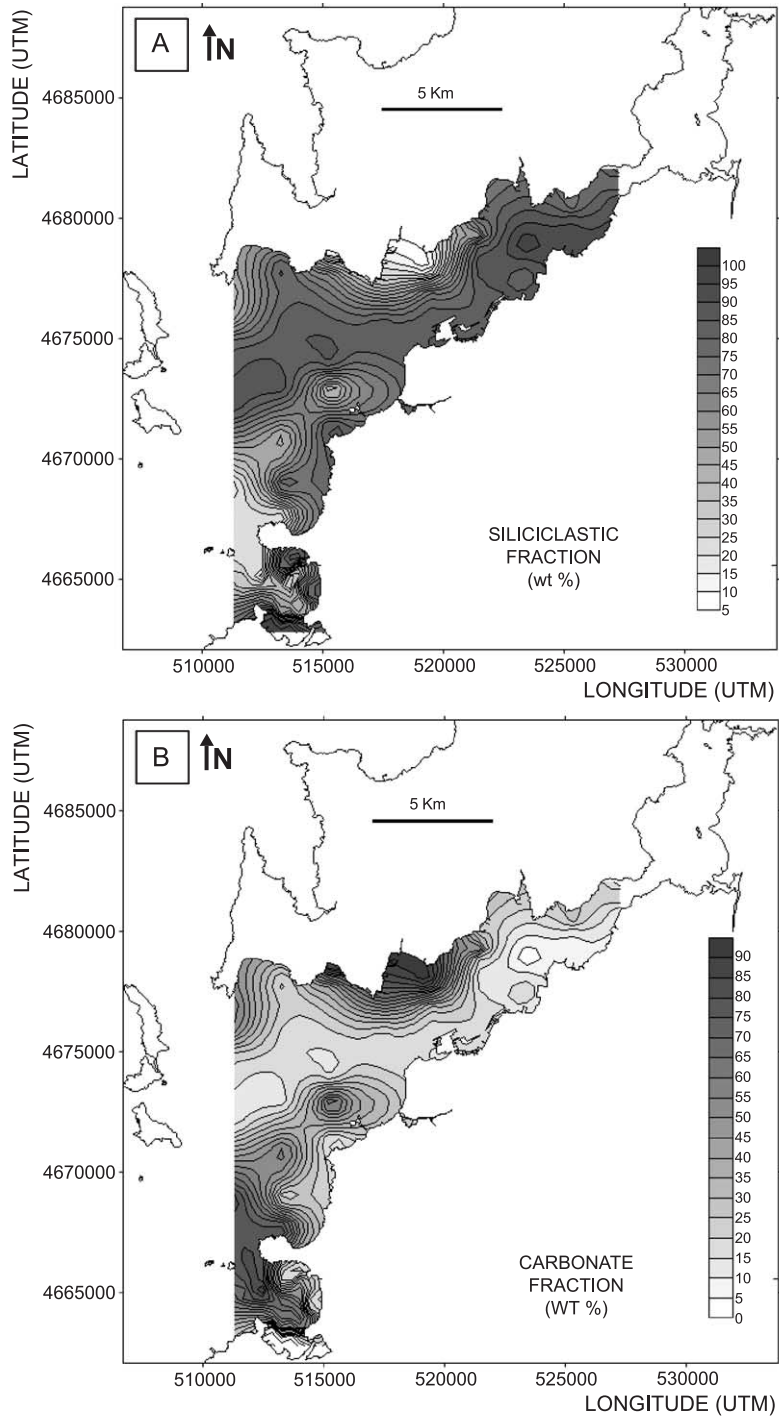


Fig. 3. The average patterns, showing the spatial distribution of (A) the siliciclastic fraction and (B) the carbonate fraction.

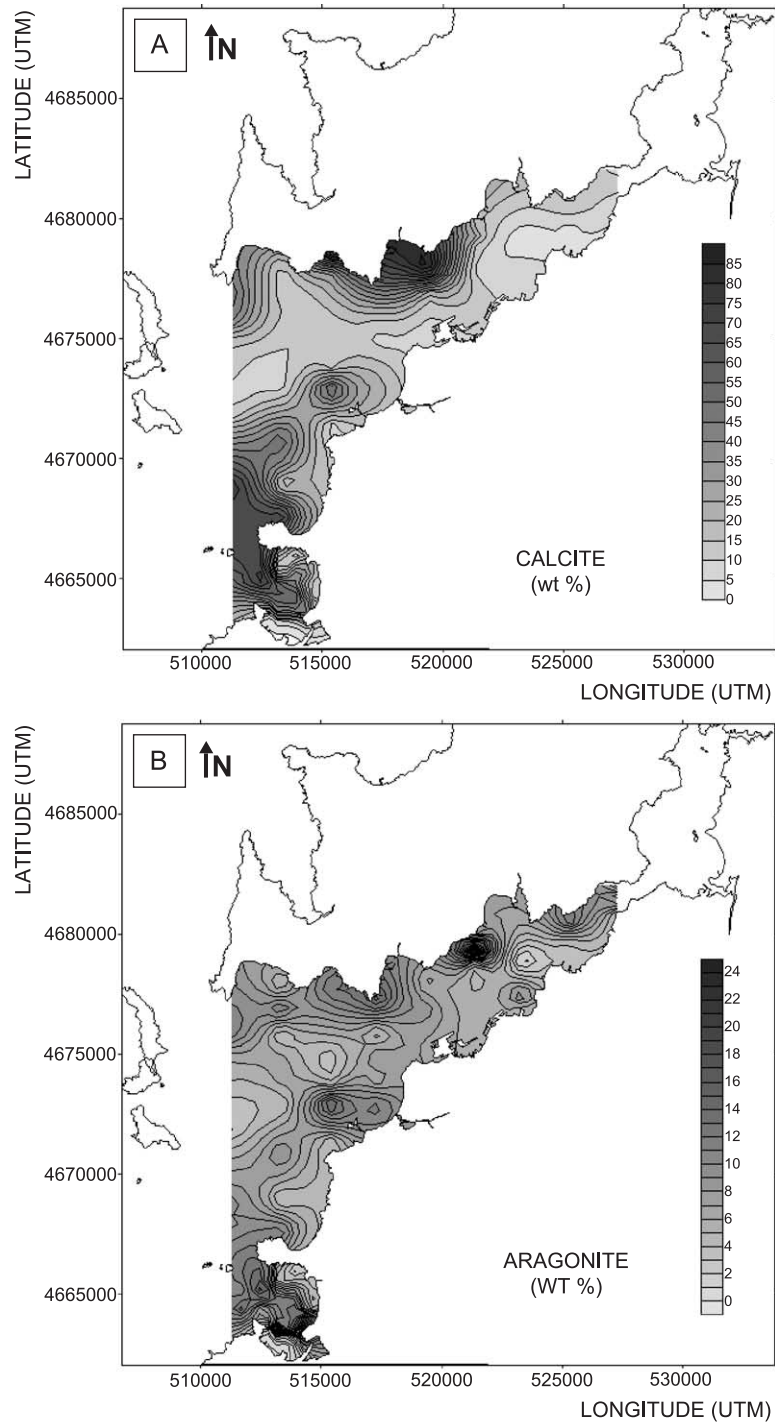


Fig. 4. Specific content maps (wt.%) of minerals involved in the carbonate fraction (A) calcite and (B) aragonite.

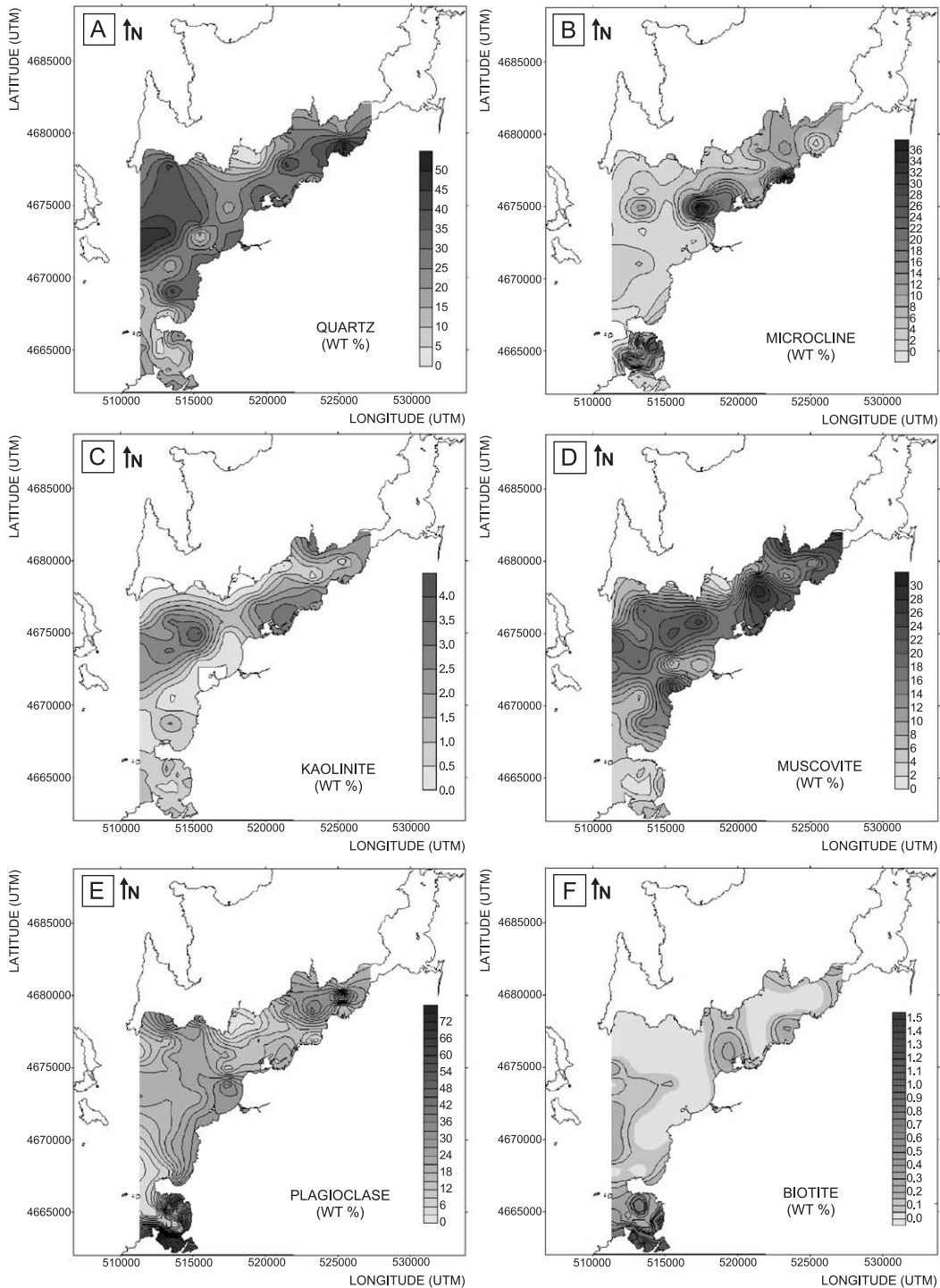


Fig. 5. Specific content maps (wt.%) of minerals involved in the siliciclastic fraction: (A) quartz, (B) microcline, (C) kaolinite, (D) muscovite, (E) plagioclase and (F) biotite.

In order to focus upon these observations the study was developed in several directions. Initially, minerals that could be geochemically associated were considered (i.e. by the presence of a common cation) and, subsequently, two additional situations were studied. The distribution behaviour was analysed along cross-sections of the area following the gradient lines. The variation of the percentage contents and grain size should then be maxima and, therefore, representative of the long-term mixing throughout the entire basin. This procedure was applied to estimate the possible coupling between two minerals competing for  $\text{Ca}^{2+}$ , as occurs for the calcium plagioclases and the carbonates.

In a second separate analysis, profiles were plotted through accumulated distance, following specific isolines of the average maps. Thus, the variations of the wt.% of each mineral, along these isolines, were normalized to a constant wt.% value of the average fraction (either siliciclastic or carbonate). In such cases, correlated fluctuations in wt.% for individual minerals can, for short periods of time, give information on the local chemical interactions between them. These must be considered as “temporary” fluctuations that are not recorded permanently but that reflect perturbations in the relative mineral stability, as a result of fluxes across the sediment–water interface. This kind of analysis can highlight the relative importance of reactivity at the seawater interface, as compared to the characteristic time response of the whole sedimentary system (Van Cappellen et al., 1993). In our case, this procedure has been applied to estimate the distribution relationships between the different calcium carbonate polymorphs (calcite and aragonite), magnesium calcites (HMC, LMC) and biotite, as the main modifying source of the Mg/Ca relation in seawater.

A conceptual model, based on the previous assumptions, has been developed to explain the observed sediment distributions and is discussed in the following sections.

### 3.1. Long-term chemical constraints during siliciclastic-carbonate mixing: the coupling between carbonates and Ca-plagioclases as a mechanism leading to selective dispersal patterns

Fig. 6A,B shows plagioclase vs. calcium carbonate content profiles along length and cross-sections of the

Ria de Vigo and Baiona bay (see Fig. 1). The average grain size values ( $\phi$  units,  $\Phi$ ) along the studied sections are shown in the upper part of these figures. In all cases, the percentage amount of each mineral (plagioclase and calcium carbonate) follows opposite trends. Both curves are virtually mirror images of each other. When they are compared with the average grain size curve it can be observed that the plagioclase content curve matches the grain size curve in the same trend and the calcium carbonate matches the opposite trend.

The possibility that this behaviour results from any analytical coupling during data treatment was discarded, as the results shown in both curves stem from different techniques (quantitative analysis from XRD-Rietveld and the average grain size distribution from dry sieving, respectively) and were applied to physically different samples.

In addition, this characteristic pathway is not followed by other minerals, such as microcline, even though their hydrodynamic properties are similar to that of the plagioclases (see microcline content profiles in Fig. 6A,B).

A possible explanation of these features can be found by assuming a competitive scheme during the dissolution of those minerals that release  $\text{Ca}^{2+}$  to seawater. In fact, during high productivity periods (i.e. upwelling periods), the formation of carbonate organisms can act as a sink. Hence, as a result of biomineralization processes, it can give rise to a decrease in the relative  $\text{Ca}^{2+}$  content in seawater, close to the sediment–water interface and below its stationary concentration values. The dissolution of Ca-bearing minerals involved in surficial sediments has to take place to allow a return to the steady state. These minerals, mainly carbonates and Ca-feldspars, may act as sources. This assumption implies the existence of a competitive dissolution process between bioclastic carbonates and plagioclases, as a function of the factors influencing their relative solubility. The contribution of Ca-plagioclases to the total Ca dissolved in water in granitic areas has been reported by Koh et al. (2002). Based on the strontium isotope composition of the water, these authors demonstrate that the carbonate minerals do not supply the total Ca-content. Therefore, Ca enrichment is likely to be controlled by another mechanism, possibly stemming from the differences in solubility between anorthite and albite.



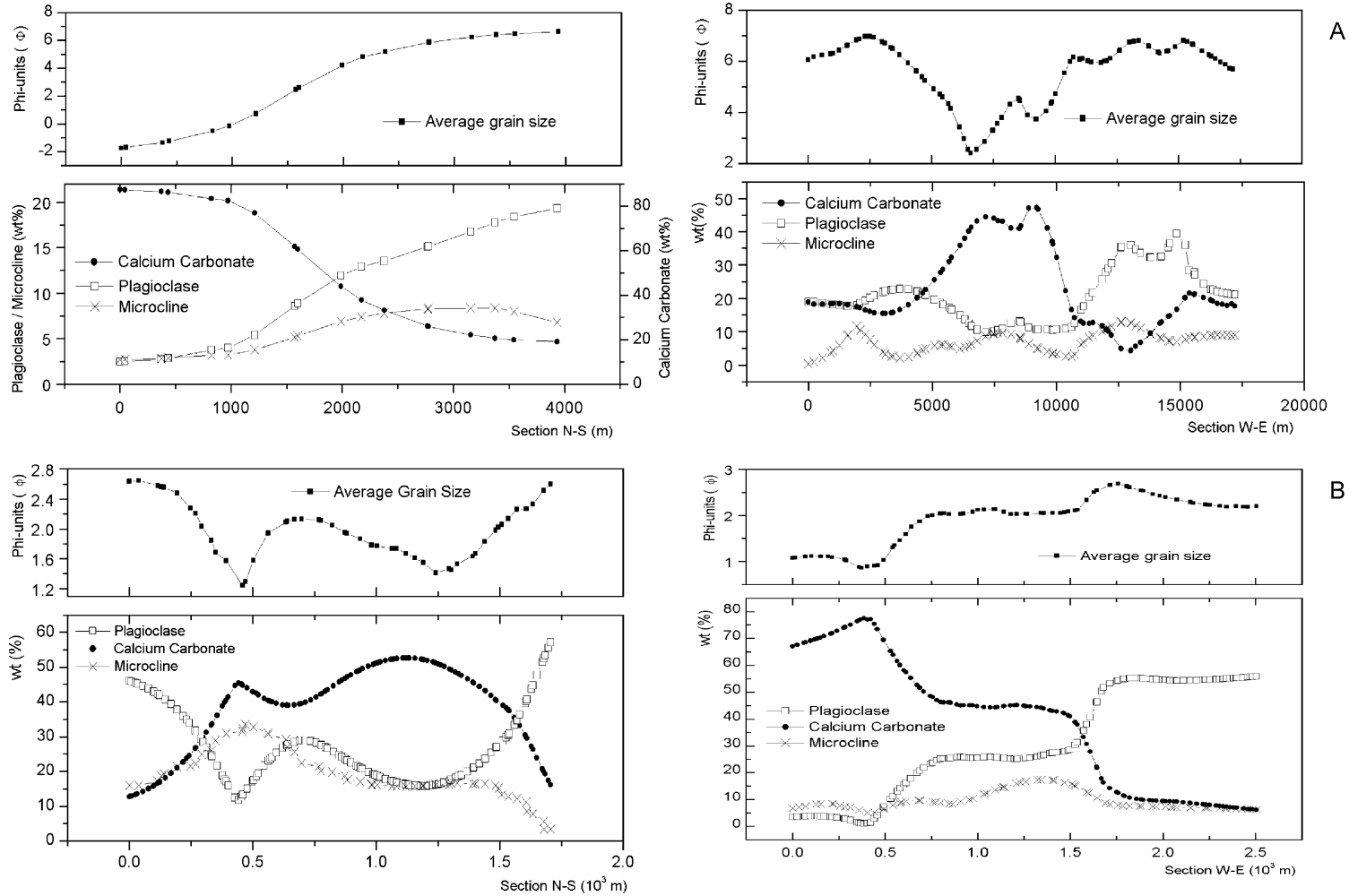


Fig. 6. Average grain size distribution in phi units ( $\phi = -\log_2$  (grain diameter in mm)) and content profile lines for the relative plagioclase, microcline and calcium carbonate amounts (wt.%) through length and cross-sections in (A) Ria de Vigo, (B) Baiona Bay.

In the most general sense, the dissolution rate of a mineral depends on three factors: the rate constant ( $K$ ), the specific surface area of the crystals ( $S=A_{\text{Crystal}}/V_{\text{SeaWater}}$ ), and the saturation ratio ( $\Omega=IAP/K_{\text{ps}}$ ), according to the following expression (Lasaga, 1983a,b):

$$R_d = KS(1 - \Omega)^n \quad (2)$$

where  $n$  is the “reaction order”.

Temperature and pH are the main controlling factors of the rate constant ( $K$ ). Moreover, for plagioclases, several additional factors must be taken into account, such as compositional and crystallographic heterogeneities. The  $K$ -values for plagioclases in the near neutral pH region, ranges from  $10^{-9}$  mol  $\text{m}^{-2}$   $\text{s}^{-1}$  for anorthite, to  $10^{-12}$  mol  $\text{m}^{-2}$   $\text{s}^{-1}$ , as the stoichiometry approaches a more albitic term (Blum and Stillings, 1995). For calcite, the  $K$ -value is in the order of  $10^{-6}$  mol  $\text{m}^{-2}$   $\text{s}^{-1}$  (Chou and Wollast, 1989).

The term  $n$  in the Eq. (2) denotes the reaction order and is connected with the dissolution subprocess, either surface-reaction or diffusion-controlled dissolution, which in turn depends on the saturation state. The average reaction order ( $n$ ) for biogenic calcite dissolution in the ocean is around 4.5 (Keir, 1980).

Many studies about calcite dissolution in seawater, based on field and laboratory measurements, show that the dissolution reactions are rather complex for applying first order reaction kinetics and, therefore, a non-linear law must be applied to describe this process (Berger, 1967; Berner and Morse, 1974). In particular, this is the case for the sediment–water interface in shallow marine environments. This region is usually considered as the locus in the oceans where carbonate dissolution can take place above the Calcite Compensation Depth (CCD) (Schink and Guinasso, 1977; Boudreau, 2001) and is thermodynamically characterized by low undersaturation levels, around the equilibrium value (Adler et al., 2001). These conditions are usually induced by a reduction in pH to nearly neutral values at the Diffusive Boundary Layer (Jorgensen and Revsbech, 1985), coupled with aerobic oxidation of the organic matter into  $\text{CO}_2$ , which may promote the dissolution of carbonates (Van Cappellen et al., 1993).

For Ca-plagioclases, the reported experimental values suggest first order kinetics. However, small

variations are found in the literature. For example, during anorthite dissolution at 25 °C,  $n$  varies within the range of 0.95–1.1 (Sverdrup, 1990).

The dissolution rate value ( $R_d$ ) of carbonates and plagioclases depends on grain size. For carbonates, assuming cubic-shaped crystals, an inverse variation with grain diameter ( $R_d \approx 1/t$ ) has been defined (Keir, 1980). For plagioclases the size-dependence is more complicated and less reproducible, as they are heavily influenced by the presence of defects, twin domains and compositional heterogeneities. The experimental results of Murphy and Drever (1993) suggest that the dissolution rate is nearly constant, irrespective of grain size. However, other studies reporting the grain size dependence for plagioclases show that the dissolution rate is even lower as grain size decreases (Holdren and Speyer, 1987). This is explained by assuming that the number of preferred sites favouring the dissolution process (mainly crystal defects and exsolution domains) drops below a critical value as crystal-size decreases, the dissolution rate being a function of the density of dislocations (Holdren and Berner, 1979).

In order to obtain an average estimation of the competitive behaviour between plagioclases and carbonates during the dissolution process  $R_d$ -values for calcite ( $R_{d-\text{Cc}}$ ) are plotted in Fig. 7A, as a function of both undersaturation (in the range from 0.6 to 1) and grain size. Two plane surfaces have been included in Fig. 7A as well as the surface showing calcite  $R_d$ -values. The upper one ( $R_{d-\text{An}}$ ) represents anorthite dissolution rate, and the lower surface ( $R_{d-\text{Ab}}$ ) corresponds to the values for the albite dissolution rate. In both cases constant supersaturation degrees were used,  $\Omega=0.001$  and  $\Omega=0.01$  for anorthite and albite, respectively, as average values for their respective saturation states in seawater (Ramseyer et al., 1992). The most unfavourable situation (i.e. dissolution rate independent of grain size) was considered.

Following the arrows in Fig. 7A, an intersection line between both calcite and anorthite surfaces can be seen. Preferential dissolution of Ca-plagioclases will take place in the region of coarse grain sizes and for calcite undersaturation from  $\Omega \approx 0.70$  to 1. This range corresponds to values close to the equilibrium, as observed at the sediment–water interface (Diffusive Boundary Layer) in shallow marine waters (Adler et

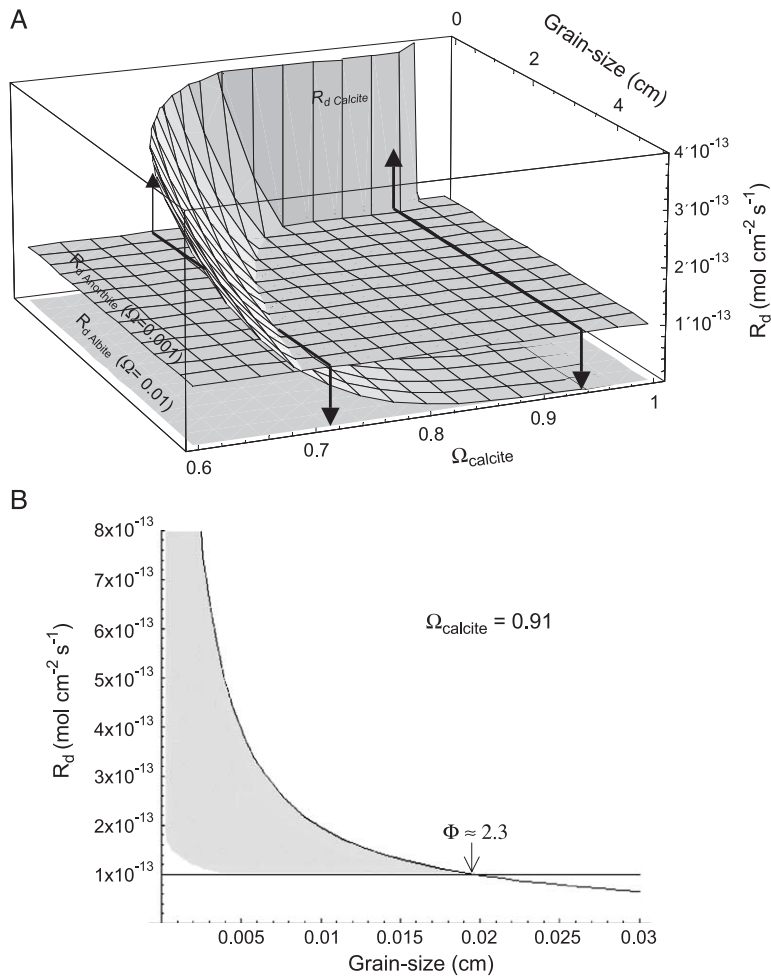


Fig. 7. (A) Surface plot showing the calcite dissolution rate vs. undersaturation and grain size. Dissolution rates for anorthite and albite at selected saturation levels are also shown. (B) Section of surface (A) for  $\Omega_{\text{calcite}}=0.91$ . Here the crossover between  $R_{\text{calcite}}$  and  $R_{\text{anorthite}}$  takes place at grain size values corresponding to  $\Phi \approx 2.3$ .

al., 2001). For small grain sizes the situation is the opposite because calcite dissolution rate increases rapidly as grain size falls below the value of 0.1 cm.

In addition, the dissolution process of Ca-plagioclases usually involves progressive albitization. This simultaneous chemical and structural transformation has an important effect on both the rate constant and saturation state. As a result, the stability of the residual grains increases as the dissolution rate falls to the value represented by the surface  $R_{d-Ab}$  in Fig. 7A.

By following different sections in the Ria de Vigo and Baiona bay (see Fig. 6), the observed profile lines

for calcite-plagioclase indicate that the wt.% of calcite tends to decrease in relation to the wt.% of plagioclase, which is consequently more stable when the average grain size reaches  $\Phi$  values up to (2–4  $\approx$  0.25–0.062 mm) in these areas. The cross-section of Fig. 7A representing such a situation for  $\Omega=0.91$ , is specifically shown in Fig. 7B.

The intersection between the surfaces that represent the calcite and plagioclase dissolution rates in this range of sizes, corresponds to  $\Omega$ -values for calcite placed in a narrow undersaturation interval close to equilibrium ( $\Omega=0.9-1$ ). In this situation both the dissolution of the smaller calcite grains and the

simultaneous growth of carbonates through biomineralization processes may occur. The latter is assumed as biomineralization usually proceeds by heterogeneous nucleation. Hence, the critical supersaturation-threshold required for crystallization is locally reduced. Furthermore, other microscopic factors, such as the clustering degree of dissolution (Gago-Duport et al., 1995) or the involved organic substrates, can play a relevant role in the nucleation kinetics induced by organisms.

Thus, two situations can be considered. In areas of coarse grain sizes with carbonate crystals slightly bigger than the plagioclase ones, plagioclase grains will tend to dissolve more quickly. In areas of fine grain sizes the process will be the opposite. These distribution trends become widespread through time and hydrodynamic transport. In this way, plagioclases are mainly accumulated in areas where the average grain size is small, and the carbonates in areas with higher grain sizes.

It should be stressed that this mechanism is not an in situ type of mixing. Its quantitative extension and efficiency for redistributing both materials in opposite grain sizes will be more favoured as increasing amounts of the materials are removed. Thus, in the case of sporadic, dynamic high-energy events like a storm, a new situation of disequilibrium will arise. As a result, selective dissolution processes will again take place.

Therefore, only after long periods of time can this self-organizing behaviour be reflected in the general distribution pattern of the minerals mutually involved in the dissolution and growth processes.

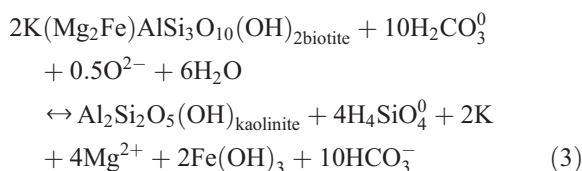
The other siliciclastic minerals follow markedly anisotropic patterns that seem more linked to other factors such as the lithological differences at the source areas, or mechanical grain size selection. This very different behaviour is in agreement with the hypothesis that only the minerals related to carbonate production are involved in the observed coupled behaviour.

To confirm that dissolution processes effectively take place in the surface sediments within the area, the morphology of selected mineral grains was studied by optical microscopy analysis and SEM. EDX microanalyses were also performed on Ca-plagioclase and carbonate grains, at several resolution levels of the SEM and with different grain orientations. An

example of morphological dissolution features is shown in Fig. 8A and B. In Fig. 8A, plagioclase EDX analysis reveals marked differences in the Ca content between the interior regions of the mineral and its surface (from 16 wt.% in the internal region to 1 wt.% at the surface of the mineral). These features are similar to the SEM dissolution morphologies described by Berner and Holdren (1977). They suggest that dissolution starts at point-defects or dislocations and progresses across the compositional inhomogeneities of the crystals (Hochella and Banfield, 1995), following a non-stoichiometric rate (i.e. by an incongruent mechanism). In the case of carbonate grains, dissolution may be enhanced by the action of micro-boring or other microorganisms (Tudhope and Risk, 1985). As an example, the boring of carbonate grain by microtubular organisms is shown in Fig. 8. EDX-analysis shows that they are coated by Al and Si, suggesting the existence of coupled dissolution–recrystallization processes between carbonate and siliciclastic minerals.

### 3.2. Short-term dissolution–crystallization processes: local interactions between carbonates and biotite

It is well known that through chemical weathering, biotite is one of the main sources of Mg to seawater, following the reaction:



Stoichiometric weathering of biotite to kaolinite is expected to release 0.4 mol of magnesium per mole of bicarbonate, playing an important role in processes such as the nucleation and relative stability of carbonate polymorphs.

As the presence of  $\text{Mg}^{2+}$  retards calcite crystallization and kinetically favours the formation of the metastable aragonite polymorph, the  $\text{Mg}^{2+}$  ions fit more easily into the calcite lattice. However, their smaller size compared to  $\text{Ca}^{2+}$  ions implies a higher surface charge and, therefore, the hydration sphere is also larger (Reeder, 1983; Fernández-Díaz et al., 1996). Thus, the solubility of calcite increases as its

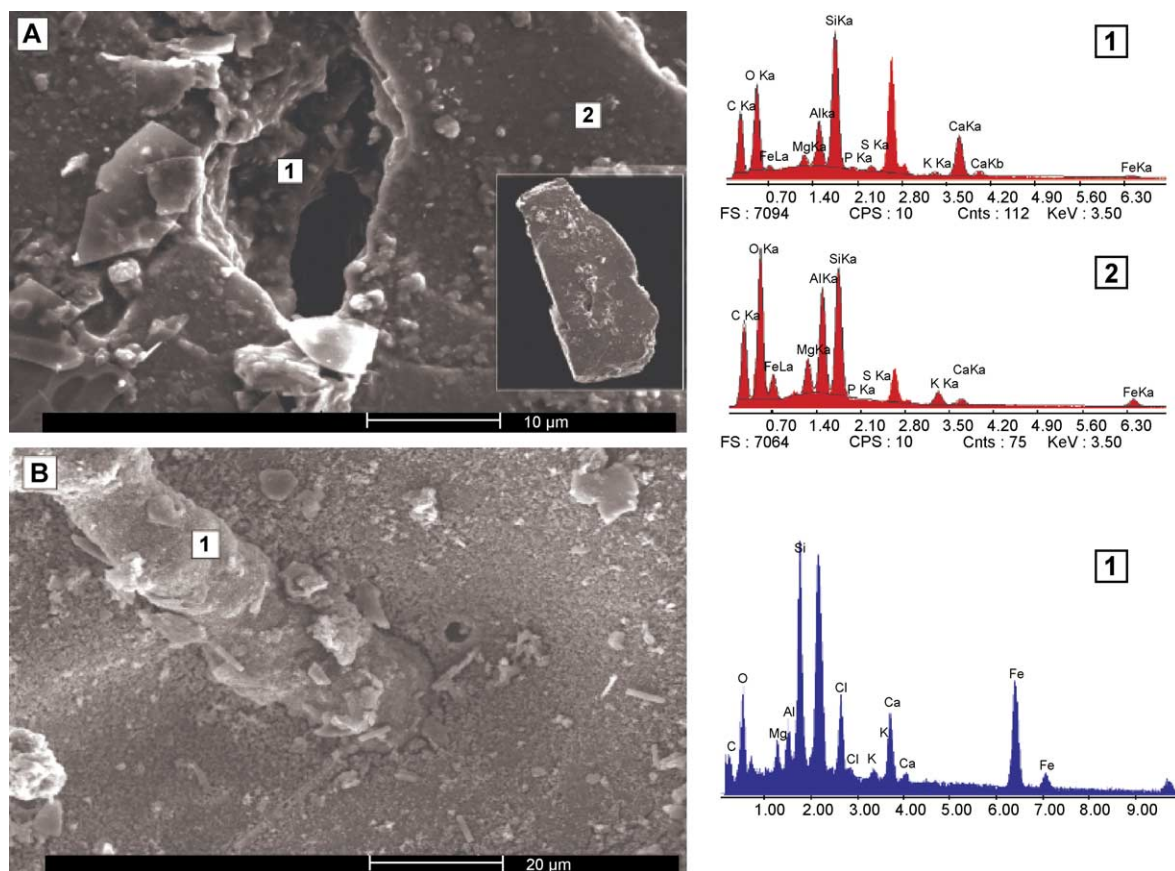


Fig. 8. (A) Dissolution processes in Ca-plagioclase by SEM and EDX analysis indicating a marked compositional difference between the interior region (1) and the mineral surface (2). (B) SEM micrograph showing a carbonate grain dissolution enhanced by micro-boring organisms. Note that EDX analysis show Al–Si content of the microtubular structures.

$Mg^{2+}$  content increases. Calcite with an Mg content of about 12 mol%  $MgCO_3$  has about the same solubility value as aragonite (Morse and Mackenzie, 1990), and is more soluble with a higher Mg-content.

The local variations in percent-amount between biotite, calcite, Mg-calcite and aragonite have been analysed in Baiona Bay. The analyses have been undertaken along the 50% content isoline, denoted in this study as the maximum mixing line or MML (Fig. 9). The MML is associated with 50% content of the average siliciclastic and/or carbonate fractions. This is the locus where the interactions between minerals from both fractions are expected to be maxima.

As can be seen from Fig. 9a–c, the distribution pathways between the carbonate minerals and biotite within the whole studied area tend to follow opposite

trends. In addition, the Mg content of calcite (Fig. 9d) increases as the total calcite content decreases, in close agreement with the higher solubility of magnesium calcite.

In order to determine specific local interactions, the relative wt.% variations between these minerals along the MML were established.

The relationships, outlined in Fig. 9, are clearer in Fig. 10A, which shows the wt.% profiles of biotite, aragonite, calcite, and Mg content in calcite vs. accumulated distance across the MML. The calcite profile behaves in the opposite way to those of aragonite and biotite. The curve showing the Mg content in calcite increases as the total calcite content decreases. From these curves it appears that the local fluctuations of calcite, aragonite and Mg % in calcites

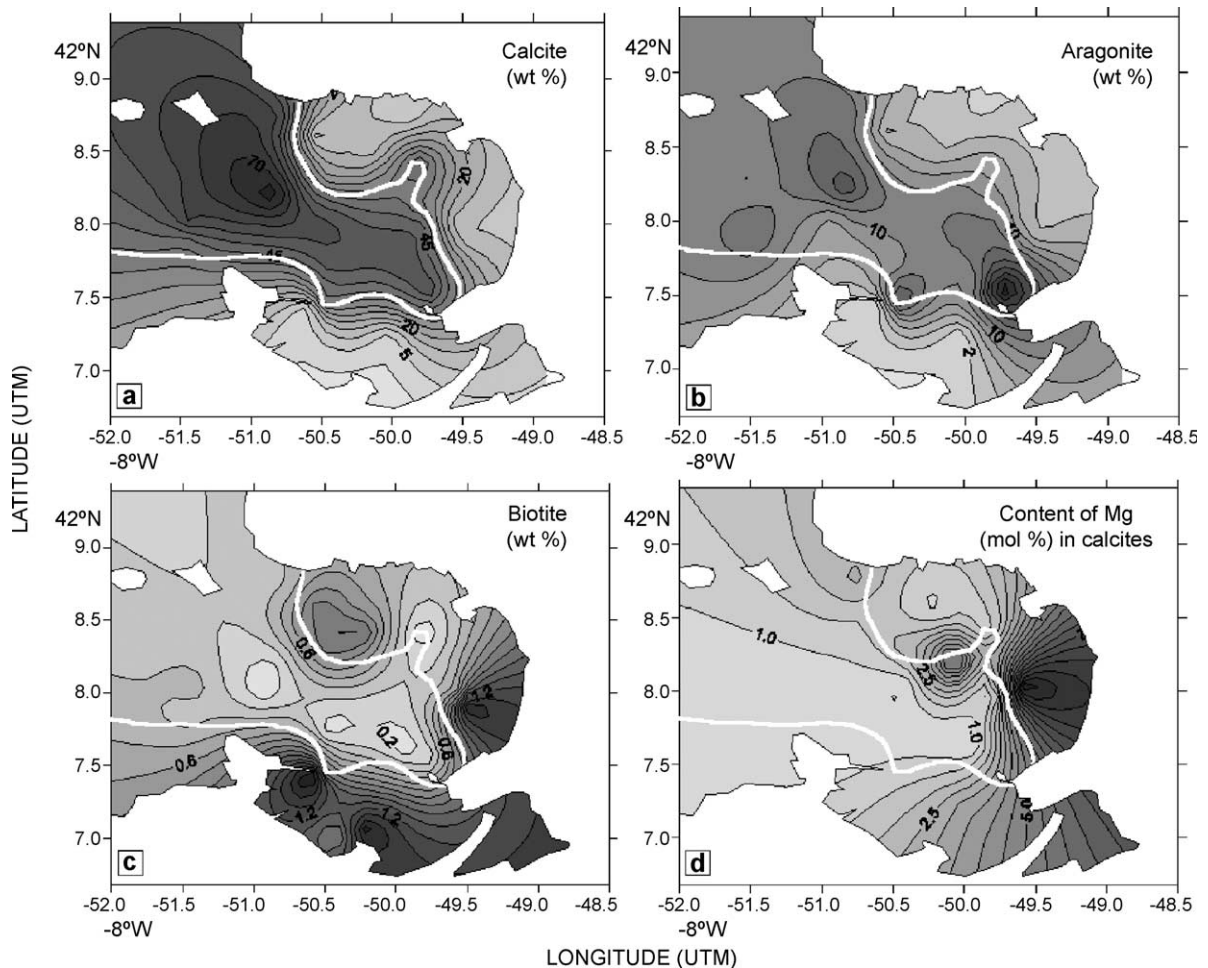


Fig. 9. Specific content maps (wt.%) for calcium carbonate polymorphs, biotite and Mg-content in calcite in Baiona Bay.

along the MML may be related to the variation in the percentage of biotite. Hence, this behaviour can be related to the local variations in the amount of  $\text{Mg}^{2+}$  dissolved in seawater, as the  $\text{Mg}^{2+}/\text{Ca}^{2+}$  ratio is the driving variable for the selective stability between aragonite and calcite.

In order to test the reliability of these assumptions, an estimation of the total amount of the Mg released by chemical weathering per time and volume unit of water, can be made using the following expression:

$$M_j = K_j S \Delta t \quad (4)$$

where  $M_j$  is the mass released for element  $j$ ,  $K_j$  the rate constant ( $\text{mol m}^{-2} \text{s}^{-1}$ ),  $S$  the specific

surface area ( $\text{m}^2 \text{l}^{-1}$ ) and  $\Delta t$  the time interval (s).  $K$  values from laboratory experiments (Malmström and Banwart, 1997) on the biotite dissolution are in the order of  $10^{-11} \text{Mg mol m}^{-2} \text{s}^{-1}$ .

An estimation from Eq. (4) (an average value of  $[\text{HCO}_3^-] = 2.4 \cdot 10^{-3} \text{mol l}^{-1}$  from Nordstrom seawater is assumed) for an initial biotite concentration of  $1 \text{mol l}^{-1}$  with  $S = 10^{-1} \text{m}^2 \text{l}^{-1}$ , which corresponds to a grain size of  $200 \mu\text{m}$ , yields an Mg-supply of  $0.16 \text{mol l}^{-1}$  per mole of bicarbonate in 10 days.

According to the diagram in Fig. 10B, based on solubility data from Morse and Mackenzie (1990), the above value falls into the region below the

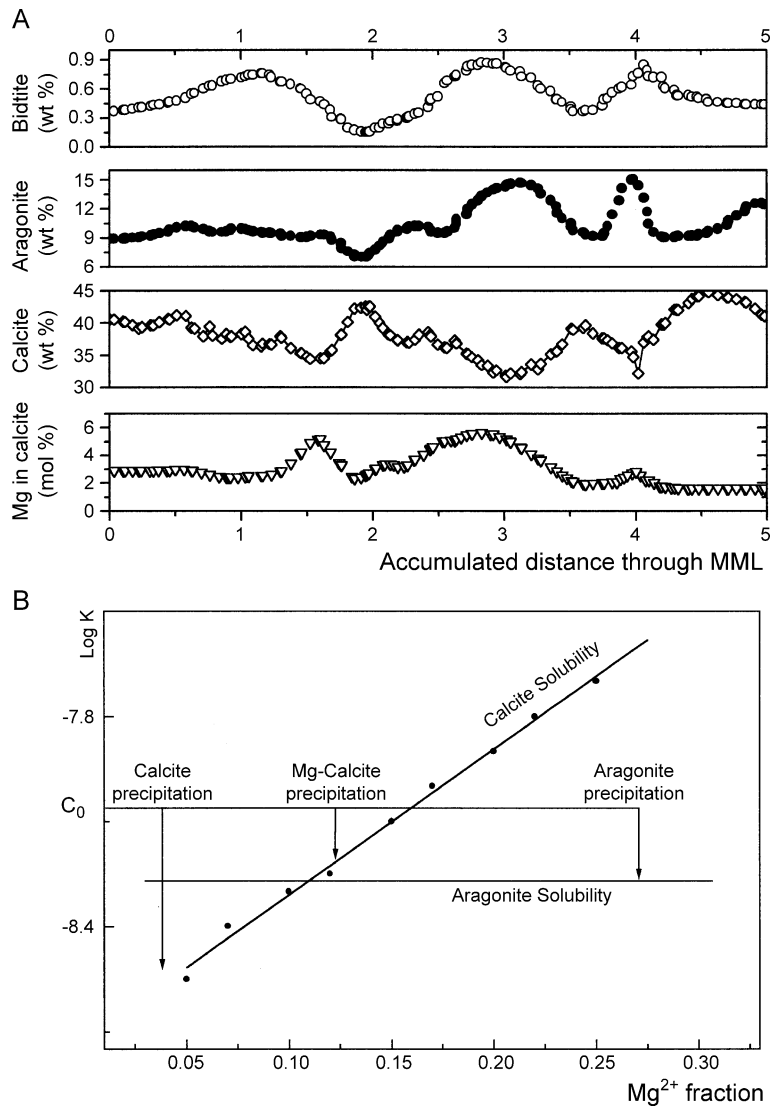


Fig. 10. (A) Content profile lines of biotite, aragonite, calcite and Mg-contents in calcite vs. accumulated distance along the MML. (B) Phase diagram showing the selective precipitation in carbonates as a function of the solubility vs. Mg<sup>2+</sup> content (based in solubility data from Morse and Mackenzie, 1990).

solubility line of Mg-calcite and, as aragonite is the only supersaturated phase, it can precipitate. Furthermore, even if the local Mg content was removed by hydrodynamic factors, the equilibrium value corresponding to the quantity of biotite included in the sediment would be quickly re-established, as, within a short period of time ( $\approx 10$  days), the steady value of the Mg<sup>2+</sup> concentration is reached again (Turner et al., 1995).

This kind of study may help to retrieve information about the chemical interactions between sediment–seawater from the analysis of wt.% amounts of minerals involved in sediments. In our work the procedure was applied to the contents of calcite and aragonite, which in turn, can reflect the distribution of the Mg<sup>2+</sup>/Ca<sup>2+</sup> in seawater induced by a particular siliciclastic mineral involved in Ca–Mg supply.

#### 4. Conclusions

Based on the elaboration of specific maps, showing the distribution of minerals involved in siliciclastic and carbonate fractions, the particular distribution behaviour has been established for every mineral in the studied area. Further comparisons of the grain sizes and the average sedimentary distribution of carbonates and siliciclastic fractions were developed.

Two situations have been analysed. The first is the interaction between plagioclases and carbonates. The long-term tendency of these patterns is shown by a cross-linked wt.-%-content distribution, which is controlled by grain size variations. This behaviour may be considered as invariant for the two studied areas, Baiona Bay and the Ria de Vigo, despite the fact that they are controlled by different hydrodynamic conditions. A conceptual model has been developed suggesting that chemical processes, taking place at the sediment–water interface and overlapping with the hydrodynamical processes, may be responsible for the observed distribution patterns.

Secondly, the fluctuations of the percentage content of calcium carbonate polymorphs and biotite have been analysed across particular isolines from the average maps of siliciclastic and/or carbonate minerals. The results reveal a coupled behaviour between the relative content of aragonite, calcite and Mg-% in calcites, as compared to the biotite content on the same line. This may be connected with the changes in the  $Mg^{2+}/Ca^{2+}$  ratio in seawater due to biotite dissolution.

From this comparative study we can conclude that, even though mechanical factors are responsible for the final sedimentary distribution, chemical factors, affecting grain size and mineral abundance during the mixing process, can induce characteristic distribution patterns.

This present study has been limited to surface sediments. The main reason is that surficial sediments act as an initial condition, prior to sediment burial. Consequently, the reported behaviour can be considered as representative of the initial sediment distribution for the early diagenetic transformations, under the assumption of steady-state diagenesis. Further analysis of the spatial distribution of sediments, at different

depths, is in progress (García, 2001). It is the aim of these forthcoming studies to include the effect of vertical fluxes, which take place during the early diagenetic processes, throughout this initial distribution of sediments and to give, in terms of geochemical facies, a 3D-characterization of the diagenetic sequence in estuarine systems.

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