

# SEDIMENT GEOCHEMISTRY OF A MEROMICTIC COASTAL LAGOON, "ES CIBOLLAR" (MAJORCA, SPAIN)

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## ABSTRACT

The concentrations of major and nutrient elements, (Al, Fe, Si, K, Ti, Ca, Mg, Mn, P, carbonate carbon, organic carbon, and N) in the sediments of a small, meromictic coastal lagoon (Es Cibollar, Majorca Island) were measured along a vertical profile in two core samples collected respectively two and eight months after a mixing event. The geochemical composition was studied through a multivariate statistical approach in order to identify the probable main mineral phases as well as the main processes controlling sediment composition in the lagoon. The results showed the presence of three main mineral fractions: the carbonate phase (magnesium calcite) was the most abundant component (>70 % in dry weight) and presented little vertical variation, whereas the organic fraction and the clay fraction varied markedly with depth. Samples collected after two and eight months of anoxia only presented clear differences for phosphorus, which was associated with iron after two months of anoxia and with organic carbon after eight months. A principal component analysis of the bulk analysis data extracted two principal components that explained respectively 58.2% and 23.7% of total variance. The first factor with high positive loadings for Al, Fe, Ti, K and Si and high negative loadings for Ca, Mg and carbonate is considered to be associated with the relative contribution of allochthonous and autochthonous matter. The second factor with positive loadings for organic carbon, N, P and Mn has been interpreted as the balance between organic matter accumulation and decomposition.

Key words: sediment composition, bulk analysis, principal components, anoxia, decomposition

## RESUMEN

*Se han determinado las concentraciones de los elementos mayoritarios y nutrientes (Al, Fe, Si, K, Ti, Ca, Mg, Mn, P, carbono en forma de carbonato, carbono orgánico y nitrógeno total) a lo largo de un perfil vertical de sedimento de una laguna costera meromictica (Es Cibollar, Mallorca). Los cilindros de sedimento se recogieron tras dos y ocho meses respectivamente de un corto episodio de mezcla total. Para poder identificar las principales fases minerales y los procesos que controlan la composición del sedimento en la laguna se ha estudiado la composición geoquímica mediante un análisis estadístico multivariante. Los resultados muestran la presencia de tres fracciones mayoritarias: la fase carbonatada (calcita magnésica) es la más abundante (70 % del peso seco) presentando una variación vertical muy pequeña, mientras que la fracción orgánica y la fracción arcillosa varían acusadamente en profundidad. Las muestras recogidas tras dos y ocho meses de anoxia solo se diferencian claramente en la concentración de fósforo, que aparece asociado a hierro tras dos meses de anoxia y asociado al carbono orgánico tras ocho meses de anoxia. El análisis de componentes principales efectuado sobre la composición elemental extrae dos componentes principales que explican respectivamente el 58.2% y el 23.7 de la varianza total. El primer factor, que está positivamente relacionado con Al, Fe, Ti, K y Si y negativamente relacionado con Ca, Mg y carbono en forma de carbonato, se considera asociado a la contribución relativa de materiales alóctonos y autóctonos. El segundo factor; determinado por carbono orgánico, nitrógeno total, P y Mn se interpreta como el balance entre acumulación y descomposición de la materia orgánica.*

Palabras clave: composición del sedimento, componentes principales, anoxia, descomposición.

## INTRODUCTION

The study of the chemical composition of lake sediments helps to elucidate the many processes occurring within the total lake system including its groundwater drainage basin. Sediments are the depositional site of mineral and organic matter

transported from the catchment area, as well as matter that forms and settles from within the water body. But sediments also play an active role in regulating cycles of nutrient elements and trace metals, this role depending on chemical and mineral composition, biological activity and redox conditions, which in turn, are closely rela-

ted. Thus, lake sediments integrate the natural weathering processes of the catchment area, the biotic and abiotic transformations in the lake itself and the human activities that affect the water body (Forstner, 1989).

Multivariate statistical treatment of bulk analysis data has been widely used to study trace metal characterization (Belmans et al., 1993) and behaviour (Van Alsenoy et al., 1993; Voutsinou-Taliadouri & Varnavas, 1995) and also to study changes in sediment composition over time (Principi et al., 1994). However, to interpret geochemical data from bulk techniques, two important aspects must be considered: firstly, bulk analyses do not take into account that sediments are a complex mixture of discrete mineral phases and organic compounds (Jones & Bowser, 1978); secondly, the constant sum effect due to the expression of data as part of a whole (percentage or part per million) can produce misleading results when correlations between elements are calculated (Aitchinson, 1986; Rollinson, 1993).

Aitchinson (1986) proposes that compositional data should be expressed as the covariance of log-ratios of the variables rather than the raw percentages, in order to avoid the problems associated with the constant sum effect. From the covariance matrix, associations between elements that coexist in a same mineral can be observed, and mineral phases can be identified (Aitchinson, 1986; Rollinson, 1993).

The geochemical composition of the sediments of Es Cibollar, a small meromictic coastal lagoon was studied within a wider project performed on the Albufera of Majorca/Alcudia Bay system. The aims of the study presented here were:

- 1) to assess the main relationships between the geochemical variables in a meromictic coastal system and their modifications after a long period of anoxia.

- 2) to identify the main processes that control the sediment composition in this lagoon, through a multivariate statistical approach.

## MATERIAL AND METHODS

### Study area

The Es Cibollar lagoon is a pond located in the northeast of the Albufera of Alcudia (Majorca island), a marsh area with several ponds connected through an extense system of channels (Martinez-Taberner et al., 1990). It was formed by dredging of a shallower pond about 30 years ago. The lagoon has a dual connection with the sea, either through another lagoon and directly through a canal. The surface area is 0.04 Km<sup>2</sup>, the volume about 130·10<sup>3</sup> m<sup>3</sup>, the mean depth is 3.3 m and the maximum depth 8.25 m. Previous studies (Moyà et al., 1987) showed that it remains stratified throughout the year because of a strong salinity gradient due to seawater input by depth. In very dry and hot summers, the pycnocline disappears because evaporation causes a substantial increase in the salinity of surface water. Nevertheless, the mixing period is short and the water column become stratified rapidly.

Sediment was sampled in winter (December 1992), two months after a short mixing event that allowed to a oxygenation of the sediment, and summer (July 1993), after eight months of permanent anoxia.

### Methods

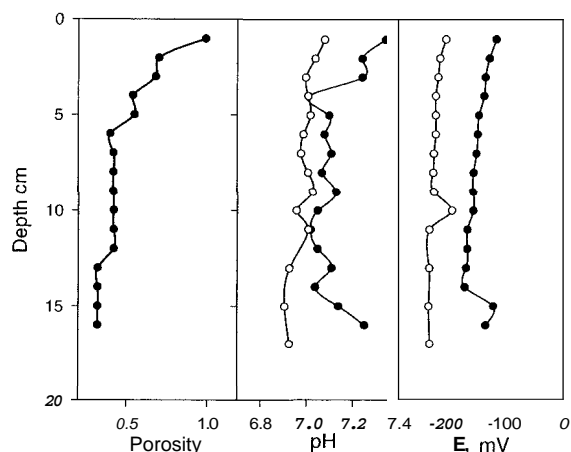
The cores obtained with a modified Eckman-grab were immediately sliced into 1 cm sections and pH and E<sub>h</sub> were measured. Redox potentials were read with a platinum electrode with a calomel electrode as reference. The electrodes were allowed to equilibrate for approximately 5 minutes at each depth. Potentials are reported relative to a standard H<sub>2</sub>/H<sup>+</sup>. pH was measured with a Ross electrode (Orion). The 1cm-sections were centrifuged (15 min, 4500 rpm) and the precipitate was dried at 110°C and, after homogenization it was divided into three aliquots. One was used to determine major components of the solid phase through X-ray fluorescence analysis (Musikas & Vantighem, 1977). Another was used to determine total carbon and nitrogen with

a Carlo-Erba analyzer, and the last was acidified with HCl to remove carbonates and then analyzed for organic carbon. Following Jones & Bowser (1978) and Principi et al. (1994) the analyses were performed without separating granulometric classes or chemical fractions. Statistical treatment of data was performed with the SPSS program.

## RESULTS AND DISCUSSION

### pH and E<sub>s</sub>

The sediments of the Cibollar lagoon were extremely fluid on their surface, with a porosity near 1 at the first centimeter (Fig. 1). In both seasons, E<sub>s</sub> was negative up to the surface; in winter, E<sub>s</sub> decreased sharply (around 30 mV) in the top 5 cm and below this depth its diminution was less pronounced (around 20 mV in 10 cm). In summer, E<sub>s</sub> showed a vertical profile fairly homogeneous, around -200 mV (Fig. 1). pH presented a significant decrease from 0 to 4 cm in winter (Fig. 1), stabilizing around 7.1 below this depth. In summer it was rather homogeneous, with values near 7.0, along the vertical profile.



**Figure 1.** Vertical profiles for porosity, pH and E<sub>s</sub> in the sediments of Es Cibollar lagoon. Full circles: December data; empty circles: July data. *Perfil vertical de porosidad, pH y E<sub>s</sub> en el sedimento de la laguna de Es Cibollar. Círculos negros: datos de Diciembre. Círculos blancos: datos de Julio.*

The values of E<sub>s</sub> and pH observed at Cibollar lagoon are characteristic of anoxic and highly reducing sediments, suggesting sulphate reduction as the main respiratory process in July. The pH of this kind of sediments is affected by a complex set of reactions remaining with rather narrow limits of 6.9-7.2 (Striebel et al., 1991). The pore water composition of the Cibollar lagoon also agrees with sulphate-reduction occurring as main decomposition pathway in summer (Lopez et al., in press).

### Geochemical Composition

The elemental composition of sediments of the Es Cibollar lagoon is presented in Table 1 and figures 2 and 3. Table 1 gives mean concentrations, standard deviations and coefficient of variation of the elements analyzed in the cores collected in December (C1), and July (C2) separately and for the whole set of data. Figures 2 and 3 show the vertical variation of major elements on both cores.

Calcium and carbonate were the most abundant components of the sediment, their sum accounting for more than 73% of dry weight. These components showed little variation with depth (Fig. 3) and differences between cores were also very small, although values in C2 were always slightly higher except at 12/13 cm. Magnesium (Fig. 2) was the second cation in abundance, presenting a pattern of variation very close to those of calcium and carbonate.

Aluminium, iron, titanium, silicon and potassium presented low concentrations, as it could be expected from the calcareous nature of the sediments. These elements showed more vertical variation (CV around 25%), with a clear increase in their concentrations with depth from 10 cm. Differences between cores were less apparent, but, as a whole, concentrations were lower in C2 (Fig. 2).

The concentrations of organic carbon (C<sub>org</sub>) and total nitrogen (N<sub>tot</sub>) were moderate, with a maximum of 3.10% for C<sub>org</sub> and 0.50% for N<sub>tot</sub>. These values were lower than those reported for other anoxic coastal systems (Bonanni et al., 1992) and for eutrophic lake sediments (Principi

**Table 1.** Mean, standard deviation and coefficient of variation ( $SD/*100Mean$ ) of the analyzed elements in **both** cores separately and in the whole data set. *Media, desviación estandar y coeficiente de variación ( $SD/100Media$ ) de los elementos analizados en cores separados y para el total de los datos obtenidos.*

	C1			C2			GLOBAL		
	Mean	S.D	C.V	Mean	S.D.	C.V.	Mean	S.D.	C.V.
Al mmol.g <sup>-1</sup>	0.48	0.17	34.86	0.42	0.17	39.69	0.45	0.17	37.65
Fe mmol.g <sup>-1</sup>	0.14	0.03	21.89	0.13	0.03	25.35	0.13	0.03	23.87
Ti μmol.g <sup>-1</sup>	15.59	4.28	27.47	13.35	4.66	34.87	14.54	4.60	31.64
Si mmol.g <sup>-1</sup>	1.97	0.28	14.00	1.88	0.29	15.41	1.93	0.29	14.82
Ca mmol.g <sup>-1</sup>	7.02	0.23	3.25	7.25	0.31	4.22	7.13	0.29	4.08
Mg mmol.g <sup>-1</sup>	0.69	0.05	7.97	0.12	0.05	6.71	0.70	0.05	7.71
P μmol.g <sup>-1</sup>	24.92	12.21	49.00	15.72	3.33	21.18	20.59	10.26	49.83
K μmol.g <sup>-1</sup>	127.8	37.2	29.1	109.1	39.6	36.3	119.0	39.5	33.2
Mn μmol.g <sup>-1</sup>	4.70	2.25	47.95	3.79	1.08	28.56	4.27	1.85	43.46
C.CO <sub>3</sub> mmol.g <sup>-1</sup>	7.55	0.41	5.48	7.96	0.44	5.47	7.75	0.47	6.01
C.Corg mmol.g <sup>-1</sup>	2.16	0.41	19.11	1.78	0.44	24.79	1.98	0.47	23.65
N.Ntot mmol.g <sup>-1</sup>	0.21	0.06	30.89	0.20	0.08	39.96	0.21	0.07	35.36

et al., 1994). Both elements decreased with depth (Fig. 3),  $N_{tot}$  being more variable than  $C_{org}$ . At surface,  $C_{org}$  and  $N_{tot}$  were higher in C2, but below 2 cm  $C_{org}$  was clearly lower in C2 and  $N_{tot}$  presented similar concentrations in both cores.

Phosphorus was the most variable element, mainly in C1 where the vertical profile was similar to that of aluminum, with a notable increase below 10 cm. In C2, phosphorus varied with depth as  $C_{org}$  and  $N_{tot}$  decreasing from the surface. The mean concentration of phosphorus was of the same order as those reported for other Mediterranean lagoons (Bonanni et al., 1992).

Finally, manganese presented a coefficient of variation of the same order as aluminum (about 28%), but its vertical profile was very different from the other components, with the maximum concentrations being found between 6 and 12 cm.

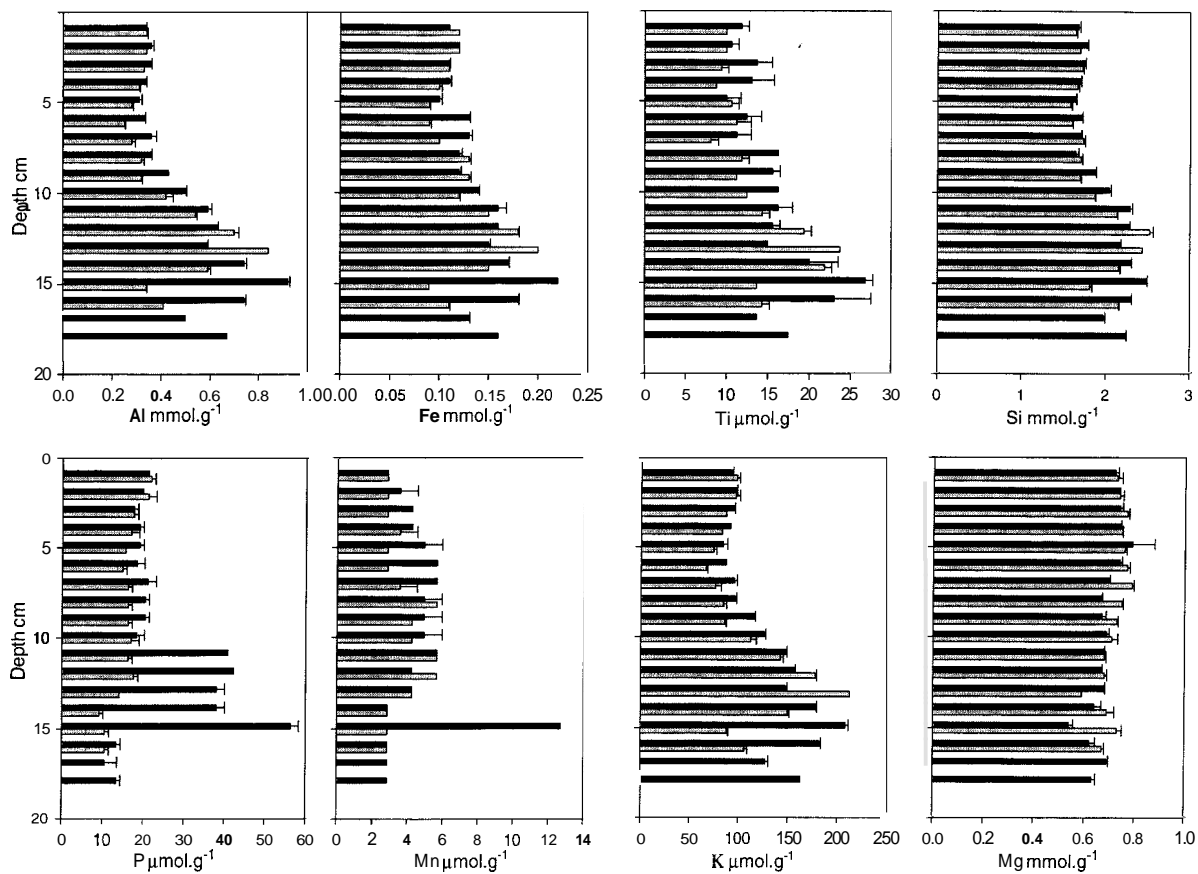
### Relationships Between Geochemical Variables

In order to identify the main relationships between the elements studied, compositional data are expressed as a variation matrix, in which log-ratio variances are calculated for every variable

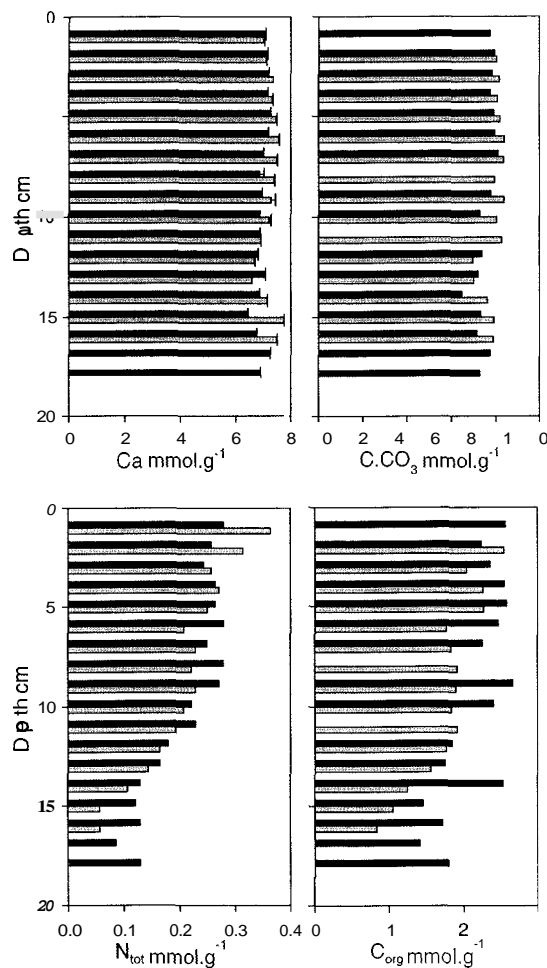
divided by every other variable (Table 2) and as a centred log-ratio covariance matrix (i.e. the covariance of each pair of elements expressed as natural logarithms of concentration of each element divided by the geometric mean of all components) (Table 3). High values in the variation matrix identify the pairs of elements that show the greatest variability. In the covariance matrix, high positive values can be interpreted to mean that the elements coexist in the same mineral phase, whereas large negative values tend to confirm the variability indicated in the variation matrix (Rollinson, 1993).

Data from Tables 2 and 3 allow us to distinguish four main groups of elements, that may be identified as different mineral phases.

The first group is formed by aluminium, potassium and titanium with very low variances and high positive covariances between them in both cores. The mean molar ratio K/Al was 0.26, a value similar to that reported by Belmans et al. (1993) for alumino-silicate particles, so this phase may be identified as clay materials. Silicon was also related to this phase, showing moderate positive values of covariances with clay elements and moderate values of variance, which indicate that silicon was present in the Es Cibollar sediments not only as clay materials but also as other mineral phases (quartz or diatom detritus). The molar ratio Si/Al varied with depth and between cores (Fig. 4), with a minimum value (2.7) close to that of alumino-silicates (Belmans et al., 1993)



**Figure 2.** Mean concentrations and standard deviation of the major elements along the vertical profile of sediment in Es Cibollar lagoon. Black bars: December data (C1); Grey bars: July data (C2). *Concentración media y desviación estándar de los elementos mayoritarios a lo largo de un perfil vertical en el sedimento de Es Cibollar. Barras negras: datos de Diciembre (C1); Barras grises: datos de Julio (C2).*



**Figure 3.** Mean concentrations and standard deviation of calcium, organic carbon, carbonate carbon and nitrogen along the vertical profile of sediment in Es Cibollar lagoon. Values of organic carbon, carbonate carbon and nitrogen are from single data. Black bars: December data (C1); Grey bars: July data (C2). *Concentración media y desviación standard de calcio, carbono orgánico, carbono en forma de carbonato y nitrógeno a lo largo de un perfil vertical en el sedimento de Es Cibollar. Los valores de carbono orgánico, carbono en forma de carbonato y nitrógeno son valores individuales. Barras negras: datos de Diciembre (C1); Barras grises: datos de Julio (C2).*

at 15/13 cm and a maximum (6.5 in C2, 5.3 in C1) at 6 cm.

The second group is formed by  $C_{org}$  and  $N_{tot}$ . They presented high positive covariance, and very high negative values with the other elements, especially those associated to the clay

fraction. The variance of the  $C_{org}/N_{tot}$  ratio was relatively high (although it was lower than the ratios with the other elements), reflecting the increase of the  $C_{org}/N_{tot}$  ratio observed with depth (Fig. 4).

The third group is formed by calcium, carbonate and magnesium and may be associated with the carbonate phase. These elements were constant in their vertical profiles, so covariances were small. Nevertheless, the most positive values were observed between calcium and carbonate and between carbonate and magnesium, which also presented extremely low values of their ratio variances. The molar ratios  $Ca/CO_3$  and  $Mg/CO_3$  (0.9 and 0.1 respectively) agree with magnesian calcite deposits, which are characteristic of brackish and saline sediments (Stumm & Morgan, 1981). The three components presented high negative covariances with clay elements, what indicates that calcium and magnesium were practically excluded from clay material.

The fourth association of elements can be distinguished only in C1. It is formed by phosphorus, iron and aluminium with high positive covariances and high negative values with carbonate elements. This group may be associated with the iron oxyhydroxide phase, because association between phosphorus and metals appeared only in C1 (two months after a complete mixing that allowed oxygenation of sediments) and was not observed in C2, collected after eight months of permanent anoxia (Fig. 5a). Iron oxyhydroxides have a strong capacity to adsorb phosphate (Lijklema, 1980; Brinkman, 1993), but under anoxic conditions redissolution of iron hydroxides makes the sediment ineffective for phosphorus trapping (Span et al., 1992; Lazzareti et al., 1992): phosphorus is released to the porewater and later to the water column, whereas iron remains in the sediment because of the precipitation of FeS. The high concentrations of phosphate in porewater observed in July (250  $\mu\text{mols.l}^{-1}$  in July, 50  $\mu\text{mols.l}^{-1}$  in December) also agree with both, the decrease of phosphorus in the solid phase (see Table 1) and the change in the association of phosphorus with the other elements. In C2, sedi-

**Table 2.** Variation matrix where Al-Fe etc., means the variance of natural logarithm of the ratio AlFe, etc. A: variances in core C1; B: variances in core C2; C: variances for the whole data set. *Matriz de varianzas en la que Fe-Al etc., indica la varianza del logaritmo natural de la relación AlFe, etc. A: varianzas del core C1; B: varianzas en el core C2; C: varianzas de todo el conjunto de datos.*

A	Fe	Ti	Si	Ca	Mg	P	K	Mn	C.CO <sub>3</sub>	C.C <sub>org</sub>	N.Ntot
Al	0.0237	0.0255	0.0382	0.1195	0.1559	0.1451	0.0117	0.2071	0.1411	0.2371	0.4020
Fe		0.0177	0.0135	0.0527	0.0755	0.1221	0.0284	0.1114	0.0602	0.1313	0.2477
Ti			0.0268	0.0757	0.1068	0.1700	0.0246	0.1431	0.0930	0.1628	0.2917
Si				0.0252	0.0440	0.1643	0.0227	0.1229	0.0339	0.0976	0.2238
Ca					0.0038	0.2243	0.0914	0.0906	0.0027	0.0403	0.1286
Mg						0.2431	0.1272	0.0827	0.0048	0.0281	0.1010
P							0.1801	0.1767	0.2266	0.2609	0.3321
K								0.2056	0.1147	0.2069	0.3713
Mn									0.0711	0.0710	0.0841
C.CO <sub>3</sub>										0.1207	0.2190
C.C <sub>org</sub>											0.0531
B	Fe	Ti	Si	Ca	Mg	P	K	Mn	C.CO <sub>3</sub>	C.C <sub>org</sub>	N.Ntot
Al	0.0267	0.0205	0.0445	0.1435	0.1659	0.2092	0.0014	0.1231	0.1611	0.2650	0.5144
Fe		0.0382	0.0208	0.0744	0.0853	0.1038	0.0193	0.0573	0.0824	0.1443	0.3395
Ti			0.0410	0.1203	0.1447	0.2257	0.0226	0.1301	0.1339	0.2688	0.5432
Si				0.0315	0.0435	0.0989	0.0364	0.0665	0.0385	0.1438	0.3739
Ca					0.0023	0.0608	0.1263	0.0882	0.0016	0.0901	0.2842
Mg						0.0482	0.1463	0.0895	0.0022	0.0715	0.2467
P							0.1815	0.0958	0.0460	0.0199	0.1138
K								0.1132	0.1421	0.2380	0.4725
Mn									0.0869	0.1141	0.3007
C.CO <sub>3</sub>										0.0771	0.2407
C.C <sub>org</sub>											0.0558
C	Fe	Ti	Si	Ca	Mg	P	K	Mn	C.CO <sub>3</sub>	C.C <sub>org</sub>	N.Ntot
Al	0.0260	0.0233	0.0441	0.1395	0.1706	0.1879	0.0069	0.1664	0.1606	0.2517	0.4564
Fe		0.0289	0.0175	0.0670	0.0852	0.1334	0.0255	0.0856	0.0761	0.1412	0.2910
Ti			0.0377	0.1074	0.1369	0.2066	0.0236	0.1371	0.1231	0.2150	0.4125
Si				0.0297	0.0459	0.1613	0.0331	0.0970	0.0382	0.1273	0.2947
Ca					0.0032	0.1895	0.1181	0.0940	0.0023	0.0790	0.2048
Mg						0.1966	0.1480	0.0908	0.0036	0.0652	0.1733
P							0.1915	0.1494	0.1837	0.1506	0.2522
K								0.1611	0.1403	0.2223	0.4212
Mn									0.8130	0.1016	0.1891
C.CO <sub>3</sub>										0.1262	0.2403
C.C <sub>org</sub>											0.0579

ment phosphorus was clearly associated with C<sub>org</sub> (Fig. 5b) showing high negative covariance with clay elements. In both cores iron was also associated with the clay elements with which it presented high covariance values. The molar ratio

Fe/Al was around 0.30, slightly higher than that reported for aluminosilicates (Belmans et al., 1993), what also indicate the existence of iron phases other than clay minerals. The vertical profile of Fe/Al ratio showed a clear increase of the

**Table 3.** Centred log-ratio covariance matrix (see text for explanation). **A:** Covariances in core C1; **B:** covariances in core C2; **C:** covariances for the whole data set. *Matriz de covarianzas centradas de la relación logarítmica (ver texto para la explicación). A: Covarianzas en el core C1; B: covarianzas en el core C2; C: covarianzas para todo el conjunto de los datos.*

<b>A</b>	<b>K</b>	<b>Ti</b>	<b>P</b>	<b>Mn</b>	<b>Fe</b>	<b>Si</b>	<b>Ca</b>	<b>Mg</b>	<b>CO<sub>3</sub></b>	<b>C<sub>org</sub></b>	<b>Ntot</b>
Al	0.0910	0.0740	0.0852	0.0251	0.0636	0.0447	-0.0080	-0.0242	-0.0155	-0.0458	-0.0887
K		0.0622	0.0544	0.0091	0.0488	0.0406	-0.0054	-0.0201	-0.0143	-0.0425	-0.0848
Ti			0.0501	0.0330	0.0448	0.0288	-0.0067	-0.0201	-0.0112	-0.0275	-0.0523
P				0.0970	0.0641	0.0305	-0.0108	-0.0177	-0.0103	-0.0076	0.0008
Mn					0.0344	0.0058	-0.0075	-0.0132	0.0039	-0.0072	0.0300
Fe						0.0245	-0.0059	-0.0149	-0.0076	-0.0245	-0.0404
Si							-0.0026	-0.0094	-0.0197	-0.0197	-0.0390
Ca								0.0022	0.0009	0.0017	0.0018
Mg									0.0032	0.0118	0.0195
CO <sub>3</sub>										0.0030	0.0138
C <sub>org</sub>											0.0678

<b>B</b>	<b>K</b>	<b>Ti</b>	<b>P</b>	<b>Mn</b>	<b>Fe</b>	<b>Si</b>	<b>Ca</b>	<b>Mg</b>	<b>CO<sub>3</sub></b>	<b>C<sub>org</sub></b>	<b>Ntot</b>
Al	0.1159	0.1057	0.0774	0.0502	0.0373	-0.0129	-0.0232	-0.0181	-0.0206	-0.0309	-0.0659
K		0.0959	0.0726	0.0458	0.0339	-0.0124	-0.0215	-0.0167	-0.0145	-0.0252	-0.0523
Ti			0.0625	0.0434	0.0248	-0.0092	-0.0206	-0.0143	-0.0381	-0.0437	-0.0900
Fe				0.0292	0.0387	-0.0097	-0.0139	-0.0114	0.0019	-0.0017	-0.0064
Si					0.0161	-0.0045	-0.0093	-0.0074	-0.0132	-0.0209	-0.0424
Mn						-0.0058	-0.0049	-0.0042	0.0175	0.0241	0.0257
Ca							0.0023	0.0019	-0.0032	-0.0026	-0.0049
Mg								0.0033	0.0052	0.0091	0.0168
CO <sub>3</sub>									0.0026	0.0050	0.0109
P										0.0595	0.1133
C <sub>org</sub>											0.1528

<b>C</b>	<b>K</b>	<b>Ti</b>	<b>P</b>	<b>Mn</b>	<b>Fe</b>	<b>Si</b>	<b>Ca</b>	<b>Mg</b>	<b>CO<sub>3</sub></b>	<b>C<sub>org</sub></b>	<b>Ntot</b>
Al	0.1064	0.0931	0.0718	0.0477	0.0097	-0.0112	-0.0248	-0.0182	0.0496	-0.0294	-0.0726
K		0.0834	0.0624	0.0438	0.0058	-0.0098	-0.0227	-0.0173	0.0382	-0.0238	-0.0640
Ti			0.0559	0.0366	0.0117	-0.0091	-0.0218	-0.0143	0.0256	-0.0259	-0.0644
Fe				0.0270	0.0202	-0.0091	-0.0152	-0.0103	0.0433	-0.0081	-0.0218
Si					0.0029	-0.0038	-0.0097	-0.0073	0.0142	-0.0175	-0.0384
Mn						-0.0047	-0.0015	0.0007	0.0359	0.0260	0.0482
Ca							0.0026	0.0017	-0.0101	-0.0020	-0.0019
Mg								0.0038	-0.0113	0.0078	0.0168
CO <sub>3</sub>									-0.0089	0.0010	0.0107
P										0.0441	0.0595
C <sub>org</sub>											0.1102

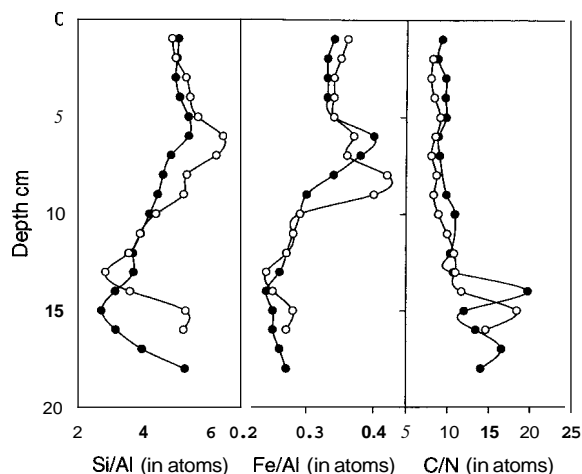
quotient towards surface with a maximum at 6/8 cm (Fig. 4), indicating a preferential accumulation of iron at this point.

Finally, manganese presented high variances of the ratios with all the other components, indicating that it was not clearly associated with any other phase in the sediments.

### Processes Controlling Sediment Composition

Principal component analysis was used to identify the main factors that control chemical composition of the Es Cibollar sediments. Following Aitchinson (1986), principal component analysis was performed on the centred log-ratio data.





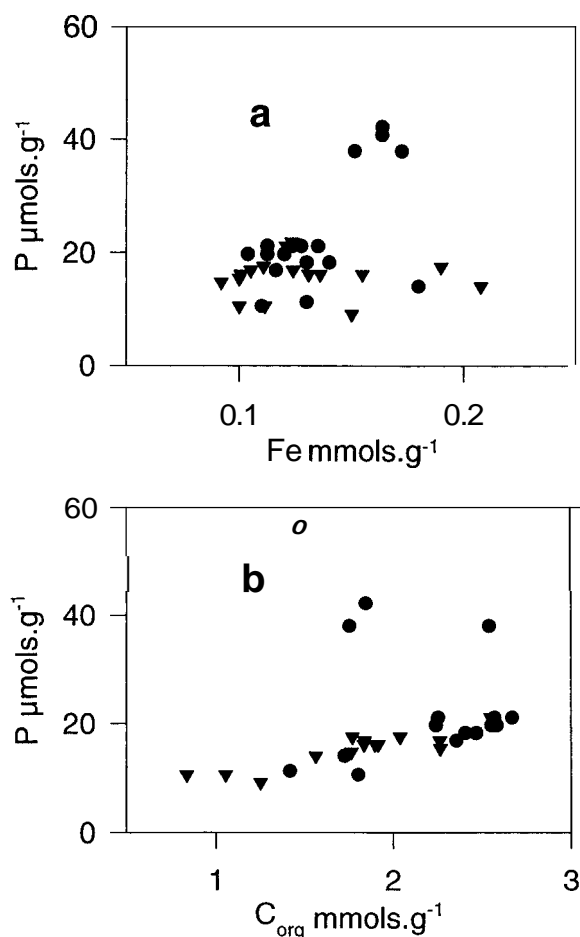
**Figure 4.** Vertical variation of the atomic ratio Si/Al, Fe/Al and organic carbon/nitrogen. Full circles: December data; empty circles: July data. *Variación vertical de los cocientes atómicos Si/Al, Fe/Al y carbono orgánico/nitrógeno. Círculos negros: datos de Diciembre. Círculos blancos: datos de Julio*

Because of the small number of samples in each core (14/16), factor analysis was conducted on the whole set of data.

Factor analysis extracted two principal components that explained respectively 58.2% and 23.7% of total variance. Varimax rotated factor loadings are given in Table 4. For purposes of interpretation a “high” loading is defined as greater than 0.75 and a “moderate” loading as 0.40-0.75. These divisions are arbitrary as no single method exists to define a significant loading. However, similar categories have been used by Puckett & Bricker, 1992, Votsinou-Taliadouri & Varnavas (1995) and Evans et al (1996).

The first factor presented high positive loadings with the elements related to the clay fraction and negative loadings with carbonate elements. Total nitrogen also presented a moderate negative loading for this factor. Because of the high values for clay elements, the first component has been considered to be representative of the allochthonous fraction of sediments, since clay minerals primarily reflect source lithologies (Jones & Bowser, 1978). Thus, the negative loadings for carbonate elements can be interpreted as consequence of its autochthonous origin. Calcium car-

bonate precipitation (both biological and chemical) is a common process in coastal systems and the ratio  $\text{Ca}/\text{CO}_3$  and  $\text{Mg}/\text{CO}_3$  (0.92 and 0.09 in mols respectively) agreed with endogenous precipitation of rich-magnesium calcite in saline waters (Stumm & Morgan, 1981). Finally, the moderate negative loading for nitrogen may also be explained in similar terms: the allochthonous organic matter is usually poor in nitrogen because of the high C/N ratio in terrestrial vegetation and the rapid leaching of nitrogen through organic decomposition (Stumm & Morgan,



**Figure 5.** Relationships between phosphorus and iron (a) and organic carbon (b) in the two cores sampled. Circles: December data; triangles: July data. *Relación entre la concentración de fósforo y hierro (a) y fósforo y carbono orgánico (b) en las dos épocas muestreadas. Círculos: datos de Diciembre. Triángulos: datos de Julio.*

1981; Santiago et al., 1994), so sedimentary nitrogen is usually of autochthonous origin, negative loading appearing for the first factor. Nevertheless, organic matter is modified in sediments by decomposing activity so only a moderate loading could be expected.

The second factor was characterized by high loadings for organic elements, carbon and nitrogen, moderate positive loading for phosphorus and manganese and moderate negative loadings for calcium. This second component has been interpreted as representative of the organic matter accumulation/decomposition. High concentrations of organic carbon, nitrogen and phosphorus (from organic origin) may be related to high rates of sedimentation of detritic material rather than to low efficiency of anaerobic respiration. Several authors have established that loss of organic carbon is the same under aerobic and anaerobic conditions (Mackin & Swider, 1989; Canfield 1989, Hansen & Blackburn, 1991). High decomposition rate not only determine lower concentrations of organic elements, but also cause reduced conditions by exhaustion of electron acceptors (oxygen, nitrate and sulfate progressively), which in turn allow desorption of phosphate from oxihydroxide phases and solubilization of manganese (Stum and Morgan, 1981). High positive loading

for carbon, nitrogen, but also phosphate and manganese thus reflected the sum of both processes. More difficult to explain is the negative loading observed for calcium. Organic matter decomposition may cause a redissolution of calcium carbonate through the associated drop in pH and, in this case, positive loadings for carbonate and calcium should appear, which did not occur. On the other hand, an intense sedimentation of organic matter could produce a "solid dilution" of the carbonate phase and, in this case, negative loadings should be expected not only for calcium, but also for carbonate and magnesium. Our interpretation of the behaviour of calcium is that it was related to the input of inland water by horizontal irrigation. Inland water presented a Ca/Mg ratio higher than that of the marine water and it was rich in nitrate (Moyà, com. per.), that may be used as electron-acceptor for respiratory activity. At the depths at which inland water seeps into the lagoon an increase in decomposing activity (by supply of electron-acceptors for respiratory activity) and a relative enrichment of calcium in precipitated calcite (because of the higher Ca/Mg ratio) should appear simultaneously, explaining the negative relationship between calcium and organic elements in the solid phase. However, the importance of horizontal irrigation as factor controlling sediment composition needs further investigation.

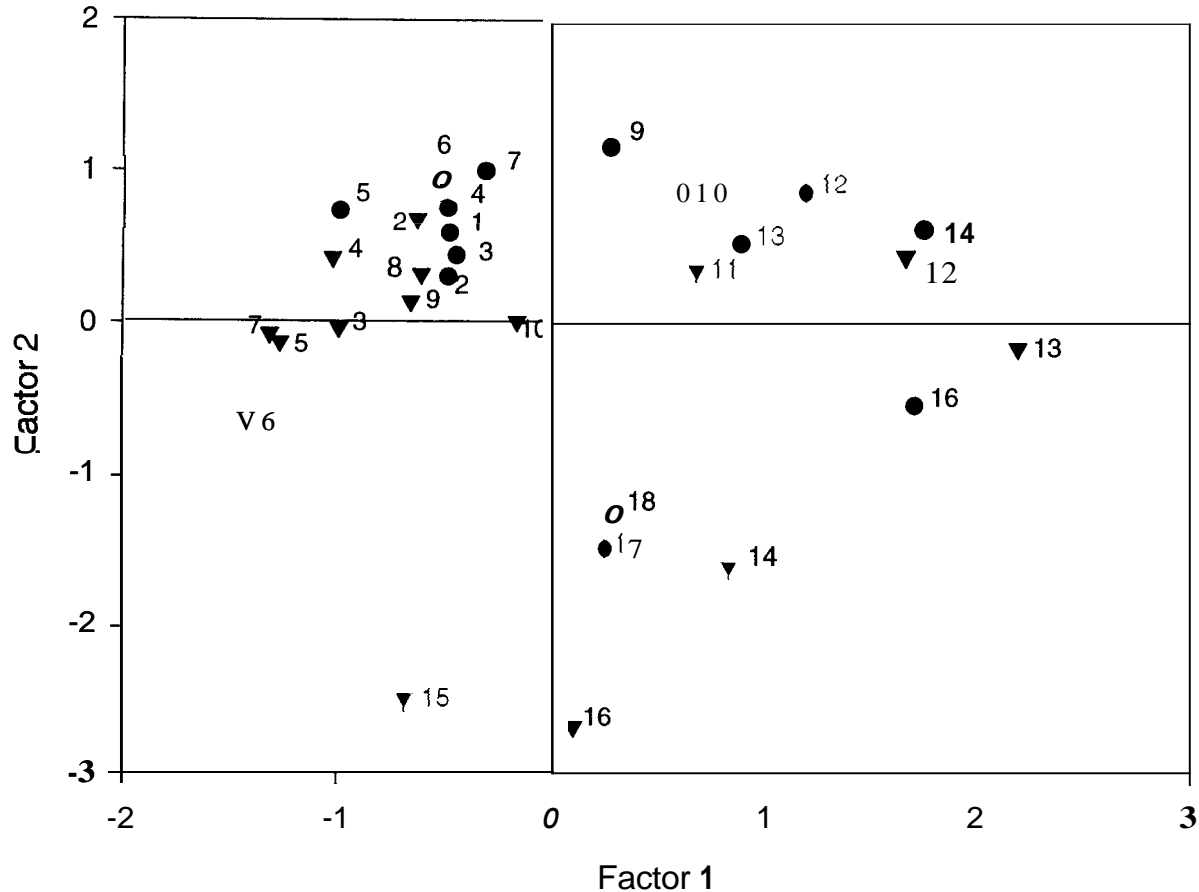
**Table 4.** Varimax rotated factor loadings for the whole data set. Loadings lower than 0.4 have considered to be non-significant and have been omitted. *Matriz rotada según el método varimax de los factores de carga para todo el conjunto de datos. Cargas inferiores a 0.4 se han considerado no significativas y han sido omitidas.*

	Factor 1	Factor 2
Al	0.986	
Fe	0.915	
Ti	0.918	
Si	0.946	
K	0.973	
Mg	-0.932	
CO <sub>3</sub>	-0.857	
Ca	-0.806	-0.511
N <sub>tot</sub>	-0.416	0.855
C <sub>org</sub>		0.893
P		0.748
Mn		0.605

### Vertical Zonation

Another basic goal of principal component analysis is classification of samples, based on the distances calculated for the reduced space defined by the the main components. These score values describe how of each core sample is related to the active process associated with the components. Figure 6 shows the position of the samples studied in the space defined by allochthonous input (Factor 1) and organic matter accumulation/decomposition (Factor 2). From the figure 6, three different layers may be distinguished for Es Cí-bollar sediments.

A: the deepest layer (17 to 18 cm in C1; 14 to 16 cm in C2). It corresponds to the original bed



**Figure 6.** Position of the studied samples in the space defined by the two principal components. Numbers indicated the depth of the sample. Circles: December data; triangles: July data. *Posición de las muestras estudiadas en el espacio definido por las dos componentes principales. Los números indican la profundidad de la muestra. Círculos: datos de Diciembre. Triángulos: datos de Julio.*

of the lagoon, presenting a very different texture with abundance of coarse materials. It was characterized by the low content in organic matter and a high Si/Al ratio caused by the high percentage of quartz sands.

**B:** the clay accumulation layer (9 to 16 cm in C1; 11 to 13 cm in C2). It corresponds to the layer with the highest concentrations of clay elements and with a molar ratio Fe/Al close to that observed in alumino-silicates. Clay elements decreased towards the surface of the layer, whereas organic matter and the Si/Al ratio tended to increase parallelly. A progressive decrease in the allochthonous input of particulate matter since the formation of the lagoon after dredging is con-

sistent with the observed variations. Because of its simultaneous variation with organic matter accumulation, the increase in the Si/Al ratio seems to be due to the accumulation of diatom detritus rather than to an increase in the percentage of quartz sands.

**C:** the endogenous layer (0 to 8 cm in C1; 0 to 10 cm in C2). It corresponds to the most recent sediments and was characterized by the lowest concentrations of clay elements, which also were very homogeneous. A maximum value in the Fe/Al ratio was observed at the transition with layer B. Whereas both cores presented similar features with respect to Factor 1, clear differences appeared between them with respect organic mat-

ter accumulation. In C1, this was higher and tended to increase with depth, but in C2 a maximum was observed at its surface and the minimum values appeared at the middle of the layer (6 cm). The hypothesis of horizontal irrigation as an important factor controlling organic matter decomposition (by providing electron-acceptors for respiratory activity) may also explain these differences. The level of inland groundwater decreases notably in summer (when C2 was collected) because of the increased water demand for agricultural or domestic uses. So, whereas in winter inland water came through horizontal irrigation at the surface of sediments, in summer it arrived only at 6 cm depth causing a maximum decomposing activity at this depth, and, in turn, the minimum in organic matter accumulation observed.

In conclusion, the geochemical composition of the Es Cibollar sediment was mainly related to the relative contribution of allogenic and endogenic settled matter. The marked differences in the vertical profiles of the major constituents, Al, Fe, Si, K, Ca, Mg and carbonate were consistent with changes in the water circulation over time, whereas nutrient elements, such as organic carbon, nitrogen and phosphorus, were dependent on the balance between organic matter accumulation and decomposition. The geochemical data also suggested that the input of inland water by horizontal irrigation and the changes in groundwater level were an important factor that partially determined the vertical distribution of calcium and nutrient elements. Finally, long periods of anoxia only produced a clear modification in the concentration of phosphorus, which changed from iron-phosphorus association after a mixing event to organic carbon/phosphorus association after eight months of permanent anoxia.

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