Sedimentological and Geochemical characterisation of Galicia-Minho shelf

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1.INTRODUCTION

The UAlg team contribution to the framework of the OMEX II-II project lies in the knowledge improvement about the sedimentary cover of the Minho/Galicia margin and the diagenetic processes affecting the Galicia margin sediments. Furthermore, the team is trying to better understand the time scale of the long and complex processes of organic carbon immobilisation.

In order to better understand the evolution of this margin and the actuating processes we are analysing, amongst others.

- the grain-size and composition of the sediments
- sediment patterns
- foram. analyses
- geochemical elemental analyses
- clay mineralogy
- hydrolisable amino acids
- total carbon
- inorganic as well as organic carbon
- nitrogen and sedimentation rates based on amino acid geochronology

Furthermore, using information from coresawe pretend to identify logical composition and oriented aggregates for determination of principal clay minerals.

2. THE UALG TEAM (by last name alphabetical order)

- Fátima Araújo (ITN)
- Teresa Barbosa (ITN)
- Tomasz Boski (UAlg)
- Cristina Carapito (UAveiro)
- J. M. Alveirinho Dias (UAlg OMEX Coordinator)
- Carla Garcia (UAlg - supported by OMEX project)
- Virgínia Martins (UAveiro)
- Paulo Pedro (UAlg - supported by OMEX project)

3.CRUISE PARTICIPATION

During the past year (July 1998-June 1999) the University of Algarve OMEX team has participated in four cruises:

1) NO *Côtes de la Manche* – Mission *GAMINEX* (8 July to 18 July 1998),
2) RV *Pelagia* – Mission *PE121-64* (29 July to 17 August 1998),
3) RV *Meteor* – Mission *M43/2* (28 December1998 to 14 January 1999) and
4) RV *Pelagia* – Mission (_).

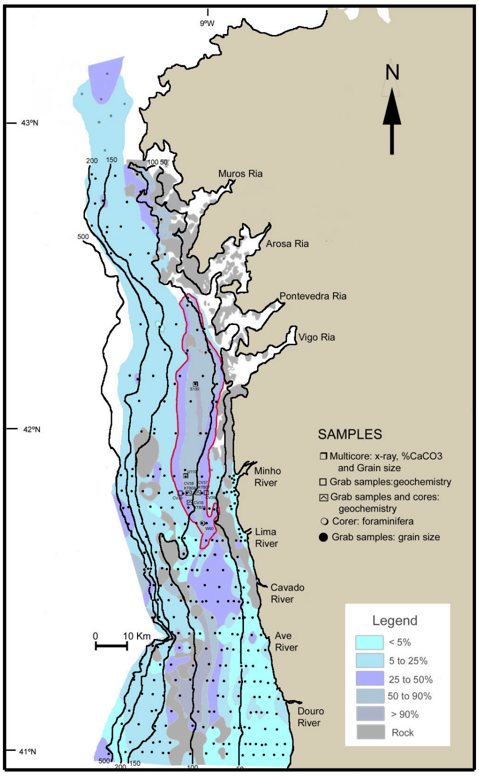

Fig. 1 - Sample location

4.SEDIMENTARY COVER

4.1. SAMPLES

The sample data set is composed mainly of grab samples or surface sediments from box-cores, but we also obtained piston cores (*PE121*, *GAMINEX*, PE138), Kasten cores (*CD110*, *M43/2*), and multicores (*CD110*). For the characterisation of the Minho/Galicia shelf sedimentary cover, grab samples or surface sediments from box-cores were used. Grain size analysis on the available cores has now begun.

4.2. METHODS

The grain size analysis of the sediments is being carried out using the pipette method for the fines and sieves for the coarser grain fractions.

For the core sediments the grain size analyses are being performed in a Malvern Mastersizer apparatus.

4.3. PRELIMINARY RESULTS

Many studies have already been performed with a focus on the sediments and evolution of the northern Portuguese shelf.

Research on the Galicia shelf has been, so far, limited. Studies of the Portuguese shelf have revealed the existence at the middle shelf, of a small mud patch off Minho River, known as the Minho mud patch, at a depth of 100 m.

The data collected during the OMEX cruises on the Galicia shelf have shown that the Minho mud patch actually forms the southern end of the major Galicia mud patch.

Mapping of the Galicia mud patch allowed us to define its morphology more accurately and localise it in both (Minho and Galicia) middle shelves at a depth of around 100 m. The mud patch is approximately 280 km long and 70 km wide at its maximum limits.

Grain size studies show an increasing percentage of fine-grained sediments (silts and clays) towards the centre of the mud patch. While fine-grained sediments constitute 25% of sediments at the periphery, this percentage increases to more than 90% at the centre. There appears to be a strong association between this deposit and the Galicia low *Rias*.

The available data on the thickness of surface sediment formations, most likely composed of post-glacial sediments, indicates a thickness of 10-15 m in the centre and 3 m at the extremities of the mud patch.

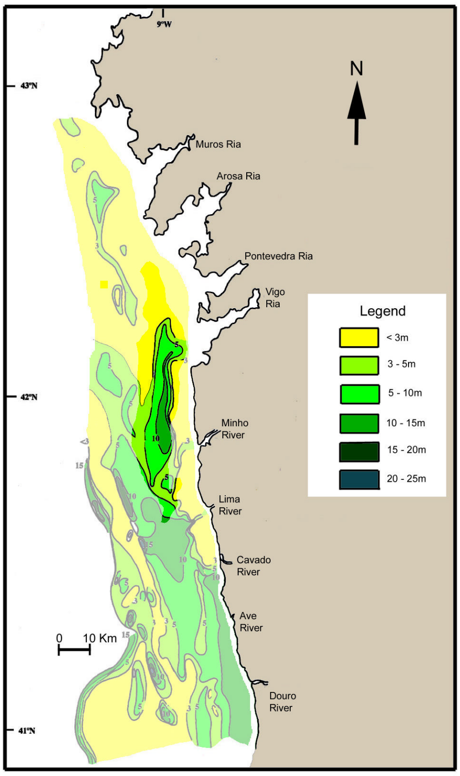

Fig. 2 -Map of isopacs

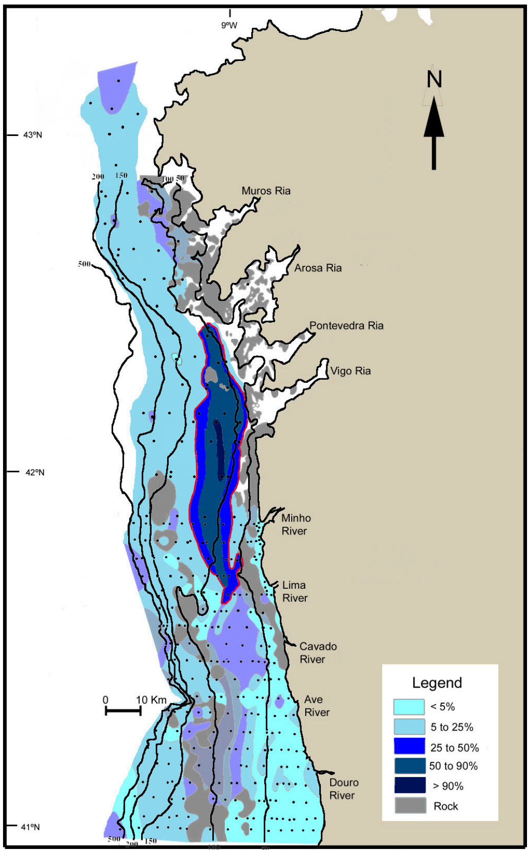

Fig. 3 - The Galicia-Minho Mud Patch

5. BENTHIC FORAMINIFERA

5.1. SAMPLES

The micropaleontological study of benthic foraminifera was carried out in the sedimentary fraction >63 µm of 19 samples from the core *PE109-13*, obtained at a depth of 2000 m in the continental slope of Galicia (there are more 36 samples to study from this core), and of 31 samples from core W90 (*CD110*) on the Minho-Galiza mud deposit.

5.2. METHODS

Almost 300 benthic foraminifera shells were identified and counted in each sample of *PE109-13*. We obtained the spatial distribution of 210 species of outer neritic to bathyal benthic foraminifera, along the core.

The analysis of the data of relative abundance of the main species (≥5%, at least in one sample), allowed us to observe changes in the composition of paleothanatocoenoses of benthic foraminifera along the core, possibly reflecting changes in the paleoenvironmental conditions (table 1).
In the core W90 a total of 111 species were identified.

5.3. PRELIMINARY RESULTS

Table I shows that in *PE109-13* some species such as *Cassidulina laevigata*, *Nonionella iridea* and *Epistominella vitrea* are cyclically the most abundant members of the paleothanatocoenoses along the core.
Uvigerina peregrina, *Cibicidoides kullenbergi*, *Trifarina angulosa* (Lutze and Coulbourne, 1984), *Epistominella exigua* (Murray, 1991) have been encountered in large numbers in the bathyal faunas under the influence of NADW water masses. A large number of individuals of *Cassidulina laevigata* (including the variety *carinata*) and *Globocassidulina subglobosa* have been related by several authors to the presence or the influence of Mediterranean water masses on the European continental shelves and slopes (Murray, 1991).
A small number of predators and a large crop of individuals from the genera *Bulimina*, *Bolivina* and *Uvigerina* (Phleger and Soutar, 1973), represented in this study by the species *Uvigerina peregrina*, *Bolivina ordinaria*, *Bolivina pseudoplicata* and *Bulimina inflata*, is found in areas with a periodically high content of organic detritus in the sediment. Here, due to the surface productivity of phytoplankton resulting from the annual upwelling events, there is a low oxygen content in sediments beneath the surface and interstitial waters.
The assemblages of *Cassidulina laevigata* (like *C. carinata*) and of *Epistominella exigua*, as well as the large number of individuals of *Trifarina angulosa* are also correlated with a high flux of oceanic organic matter due to a high productivity in the surface waters (Gupta, 1997) and low oxygen levels, but not with periodical anoxia in the sediments. *Stainforthia fusiformis* can also live in sediments rich in organic matter and support periodical anoxia (Alve, 1990). This opportunistic species is not necessarily associated with the organic matter produced in the ocean because it can live in some zones with anthropogenic pollution.
The presence of *Trifarina angulosa* has been associated with strong bottom currents (Mackensen *et al.*, 1985). The abundance of *Cibicidoides kullenbergi* may reflect periods with lower organic carbon in the sediments (Lutze and Coulbourne, 1984). Epistominella vitrea is more frequent in shallower waters of the continental shelf and slope (Murray, 1991). *Nonionella iridea* and *Eponides tumidulus*

are species that have been registered in the colder bottom waters of the North Sea (Alve and Murray, 1995), as well as the Arctic and Antarctic Oceans (Murray, 1991).
A cluster analyses of relative abundance of the most important species/genres (>10%) and their distribution along the core W90 allowed to highlight the fluctuations of three groups of benthic foraminifers:

ASSEMBLAGE 1 is mainly related to the temporal variability of continental organic matter flux, which has undergone more decomposition and is therefore poor in nutrients. River runoff (mainly during the winter season) and low saltiness on the continental shelf cause this. It is composed of opportunistic species characterised by rapid exploitation of ephemeral resources, rapid maturation and prolific reproduction. For example ***Stainforthia fusiformis***, ***Nonionella miocenica*** (including the var. *stella)* had significant peaks of abundance at 9-10 cm, 30 cm, 40 cm, 50 cm, 60 cm, 75 cm.. The concentration of the first two populations with ***Buliminella tenuata,*** that prefer bathyal waters, may be a result of the species choice of microhabitats within the sediments.

ASSEMBLAGE 2 is related mainly to the influx of marine organic matter during the spring bloom of phytoplankton and upwelling events (food supply) to the bottom. This marine organic matter is less decomposed and therefore richer in nutrients.
Assemblage 2.1: is composed of ***Bolivina gr. dilatata, B. ordinaria, Bolivina spp., Fursenkoina loeblichi*** which have significant peaks of abundance at 8-9 cm, 25 cm, 35 cm, 45 cm, 55 cm, 65 cm.
Assemblage 2.2: is composed of ***Cassidulina carinata, Bolivina spathulata, Bulimina spp.*** which have significant peaks of abundance at 3-4 cm, 7-8 cm, 10-11 cm, 17-18 cm.
The dominance of 2.1 or 2.2 assemblages may reflect a greater or a lesser amount of oxygen depletion.

Table 1- Distribution of the more abundant species along the core in the studied samples.

Depth in the core	**The most abundant species**	**Others species with abundance 5%**
At 0 cm and at 10 cm	*Cassidulina laevigata* (12%-14%)	*Epistominella exigua* (8%-11%) *Cassidulina minuta* (6%-7%) *Eponides tumidulus* (6%) *Cibicidoides kullenbergi* (5%-6%) *Bulimina inflata* (3%-6%) *Gavelinopsis lobatula* (4%-5%) *Trifarina angulosa* (4%-5%)
At 20 cm, 30 cm, 40 cm, 50 cm and at 60 cm	*Eponides tumidulus* (12%-18%)	*Gavelinopsis lobatula* (5%-12%) *Cassidulina laevigata* (4%-11%) *Cassidulina minuta* (7%-11%) *Globocassidulina subglobosa* (5%-6%) *Nonionella iridea* (3%-9%) *Bolivina ordinaria* (3%-7 %) *Epistominella exigua* (0%-9%) *Stainforthia fusiformis* (3%-5%) *Bolivina pseudoplicata* (2%-5%) *Epistominella vitrea* (2%-5%)
At 70 cm, 80 cm, 88 cm and at 150 cm	*Cassidulina laevigata* (14%-21%)	*Cassidulina minuta* (3%-15%) *Stainforthia fusiformis* (3%-9%) *Eponides tumidulus* (3%-8%) *Nonionella iridea* (4%-8%) *Bolivina pseudoplicata* (5%-7%) *Bolivina ordinaria* (5%-6%) *Epistominella exigua* (4%-6%) *Gavelinopsis lobatula* (2%-5%) *Stainforthia sp.* (0,3%-8%)
At 200 cm	*Nonionella iridea* (27%)	*Stainforthia sp* (12%) *Cassidulina laevigata* (8%) *Stainforthia fusiformis* (7%)
At 250 and at 300 cm	*Cassidulina laevigata* (31%-32%)	*Nonionella iridea* (7%-8%) *Globocassidulina subglobosa* (3%-7%) *Stainforthia fusiformis* (5%-6%) *Trifarina angulosa* (5%-6%) *Epistominella vitrea* (3%-5%)

At 350 cm	*Nonionella iridea* (19%)	*Bulimina inflata* (17%) *Stainforthia fusiformis* (11%) *Cassidulina laevigata* (9%) *Stainforthia spp.* (5%) *Epistominella vitrea* (5%)
At 400 cm	*Epistominella vitrea* (39%)	*Cassidulina laevigata* (14%) *Bolivina pseudoplicata* (5%) *Nonionella iridea* (5%)
At 450 cm	*Cassidulina laevigata* (14%)	*Nonionella iridea* (12%) *Trifarina angulosa* (8%) *Stainforthia fusiformis* (5%) *Epistominella vitrea* (5%) *Bolivina pseudoplicata* (5%)
At 500 cm	*Epistominella vitrea* (15%)	*Cassidulina laevigata* (13%) *Nonionella iridea* (8%) *Stainforthia fusiformis* (7%) *Trifarina angulosa* (7%) *Eponides tumidulus* (5%) *Stainforthia spp.* (5%)
At 540 cm	*Cassidulina laevigata* (11%)	*Nonionella iridea* (9%) *Uvigerina pegreina* (8%) *Trifarina angulosa* (8%) *Stainforthia fusiformis* (7%) *Epistominella exigua* (7%)

6. AMINOACIDS

6.1. SAMPLES

To this date, we have been able to collect material from three cruises although the analysed material is essentially from the *Pelagia PE121* cruise (table II). The sample data set is composed of material of different origin, mainly box-cores, but also piston cores (*PE138*), one Kasten core (*CD110*), and 2 multi-cores (*CD110*). Box-core sample tubes and multi-cores were sliced in 1-cm intervals from the top and frozen to minus 20 degrees Celsius immediately after recovery where possible.

The material presently being analysed is essentially distributed among three transects from the shelf to the abyssal plain in the Galicia margin: The La Coruña transect, the Cape Finisterre transect and the Vigo transect.

Table II – Details of coring data set being analysed.

Name	*Cruise*	*Type*	*Date*	*Latitude*	*Longitude*	*Depth (m)*
W90K	*CD110*	Kasten	1997	41º21´38	08º59´53	87
S300M	*CD110*	Multi.	1997	42º09´39	09º18´05	210
S90M	*CD110*	Multi	1997	42º09´06	08º57´19	91
04	*PE121*	Box	1998	42º38´00	10º01´00	2570
05	*PE121*	Box	1998	42º38´00	09º29´00	200
06	*PE121*	Box	1998	44º00´00	10º00´00	4200
07	*PE121*	Box	1998	43º56´50	09º57´45	4940
08	*PE121*	Box	1998	43º43´12	09º42´59	2109
11	*PE121*	Box	1998	42º00´22	09º43´45	2061

6.2. METHODS

6.2.1. AMINO ACIDS

The 500 mg aliquots of homogenised and freeze dried sediment from 1-cm thick slices were submitted to 6N HCl (3 ml) hydrolysis in vacuum vials flushed with nitrogen, placed in an aluminium heating block and maintained at a temperature of 110º C for 24 hours. Three amino acid standards, α-aminopimelic acid, o–methylthreonine and hydroxylysine were added as recovery standards for acidic, neutral and basic amino acids.

The subsequent HPLC analyses of amino acids were carried out on the fluorescent derivatives with (OPA) orthophtaldialdehyde (Lindroth and Mopper, 1979). The OPA solution was prepared by dissolving 135 mg of OPA in 5 ml of HPLC grade methanol adding 100 µl of 2-mercaptoethanol and making up the volume to 25 ml with borate buffer. Due to its high instability, this solution was prepared prior to every series of HPLC runs and stored in a refrigerator to avoid exposure to light. The derivatisation reaction was carried out in constant agitation during 120 seconds on a sample of 1 ml (standard) solution with 400 µl of OPA and borate buffer added to make up 10 ml volume. Six minutes after the beginning of the derivatisation reaction, the analyte was injected through an Anotop filter into the instrument loop. Gradient elution was carried out in 7 steps during 25 min in a reverse phase column (Superspher 60 RP –select B from Merck).

6.2.2. TOTAL ORGANIC CARBON, TOTAL CARBON AND NITROGEN

For the total carbon analysis and total nitrogen analyses, 20 mg aliquots of each sample were packed in tin capsules and compressed to remove air. Organic carbon was determined in silver crucibles after hydrochloric acid digestion of the carbonates. The analysis was performed in a GC Carlo Erba C/N gas phase elemental analyser coupled with a thermic conductivity detector.

6.2.3. GRAIN-SIZE

The grain size analyses of the mineral fraction were carried out after the elimination of carbonate in the samples with 10% HCl. The analyses were performed in a Malvern Mastersizer apparatus. 1 g of Calgon per litre of distilled water was added to avoid flocculation of clay minerals.

6.2.4. MINERALOGY AND CLAY MINERAL SPECIES

The XRD analysis was carried out following two procedures: on un-oriented powder mounts for overall mineralogical composition and oriented aggregates for determination of the principal clay mineral species.

Three distinct series of oriented aggregates were prepared before being submitted to a diffractometric analysis. The first series was analysed in a routine comprising three diffractometer runs: air dried or normal (N), solvated with ethylene glycol vapours (EG) and heated to 500°C (500). The two following series were necessary because routine investigation (N---EG--500) did not allow a direct identification of several of the clay components. The second series was analysed after Li-saturation (Green - Kelly test), recording three X-ray patterns: air dried or normal (Li-N); heated to 300°C (Li-300-; and glycerolated Li-300Gl) aggregates.

6.3. PRELIMINARY RESULTS

6.3.1. AMINO ACIDS

The THAA contents were already determined on 4 box-cores from the *Pelagia PE121* cruise on the La Coruña Transect and Cape Finisterre Transect (fig. 4). Among the 12 quantified amino acids the most abundant ones are aspartic acid, glycine, serine, alanine and glutamic acid, representing between 60 to 80 % of the total (Table III). The content of aspartic acid, (quantitatively the most important) has a mean value of 107 µg/g dw followed by glycine with 102 µg/g dw. All analysed samples considered THAA ranged between 891µg/g dw and 228 µg/g dw.

A clearly decreasing trend in concentration of individual amino acids with depth was observed in the core *PE121-07* but was less clear in the other sites. Site *PE121-08* - situated on the continental slope - shows the highest yields in THAA and is the most homogenous in terms of depth variations of concentration of individual amino acids, probably due to bioturbation.

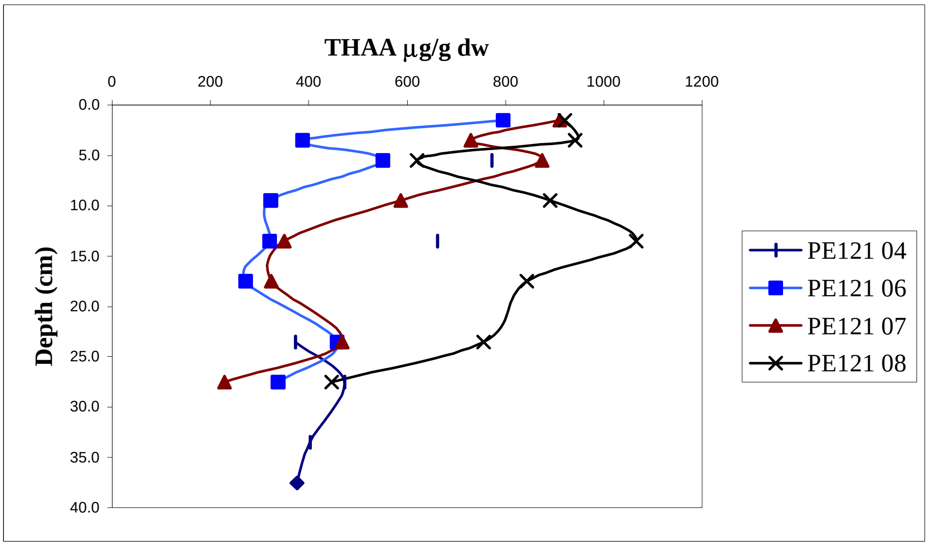

Fig. 4 – THAA variation of analysed sediment cores with depth.

6.3.2. TOTAL CARBON, TOTAL ORGANIC CARBON AND NITROGEN

The total nitrogen contents range from 0,75 to 0,02 % dw, decreasing from the shelf to the abyssal plain (fig. 5). Total organic carbon contents are between 3,20% and 0,20 % dw, with a decrease in depth on each analysed core (Fig. 6). The total carbon contents are between 7,0 and 4,0 % dw, with exception for one of the cores *PE121-05* with a total carbon content of around 1,4 – 1,20 %.

6.3.3. GRAIN SIZE

Grain size analysis of the carbonate free fraction of the sediments shows a predominance of fine silts and clays (median grain size 10 µm) in all sites except for *PE121-05* situated on the shelf, with median grain size of 120 µm (fig. 7). In the sites *PE121-04* and *PE121-08* a polymodal distribution of the grain sizes frequencies in the deepest samples may indicate their turbiditic character.

6.3.4. MINERALOGY AND CLAY MINERALS

After biogenic calcite, clay minerals (with a clear predominance of illite) are the second quantitatively most important group (32 % average). Diffraction patterns of illite reveal very frequent poor crystalinity (broadening of 001 peak and multiples) and opening of the sheets. In terms of decreasing abundance it is followed by kaolinite, smectites, interstratifieds and chlorites (averages respectively 19, 18, 15 and 9%). Smectites are represented exclusively by montmorillonite of which <35% is swelling component, as determined by Li saturation test.

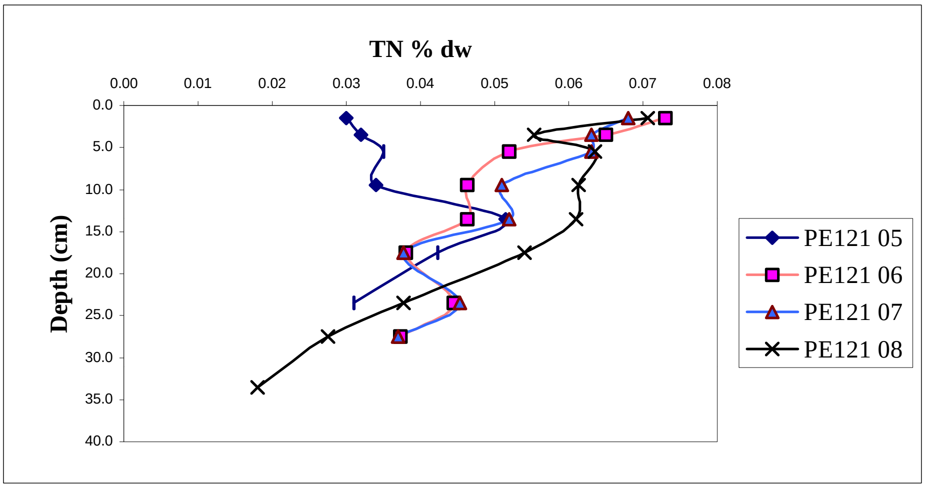

Fig. 5 – Total nitrogen variation with depth on analysed sediment cores.

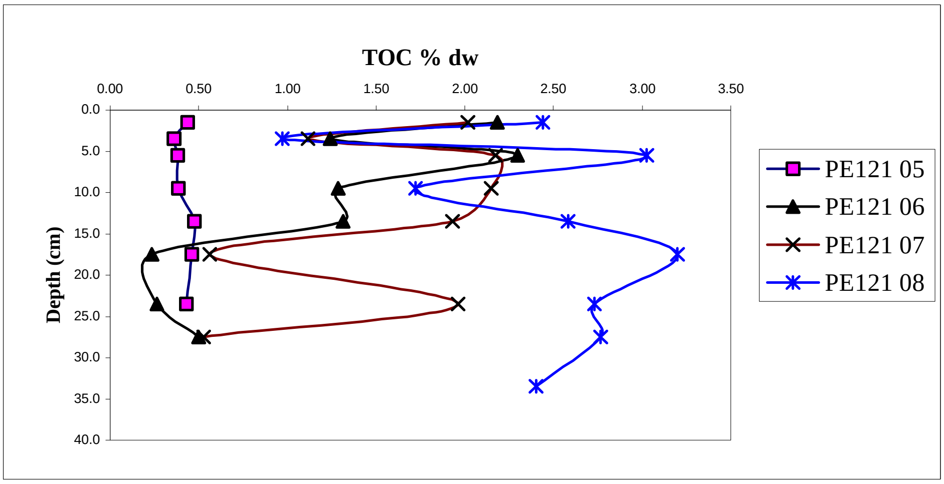

Fig. 6- Total organic carbon (TOC) variation with depth on analysed sediment cores.

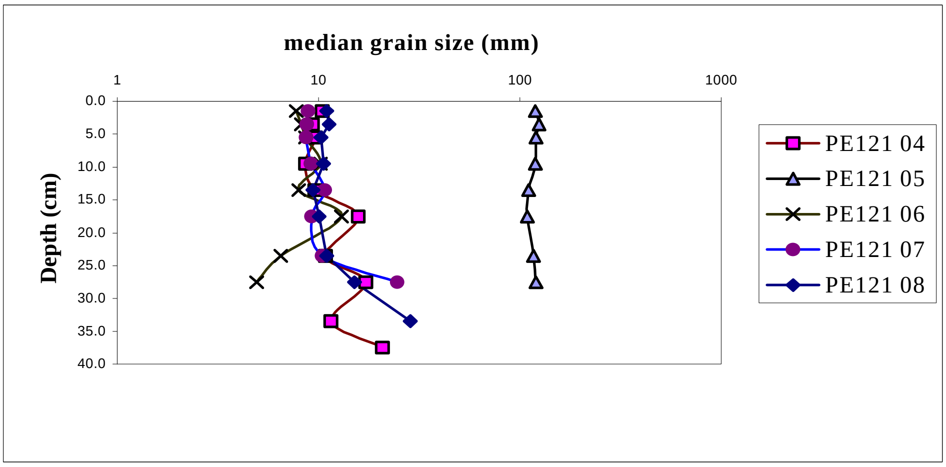

Fig. 7- Median grain size of the carbonate free fraction.

Table III – Individual amino acid concentrations in analysed samples in µg /g sediment dw.(nd – not detected)

Sample	Depth	Asp	Glu	Ser	Gly	Thr	Arg	Ala	Tyr	Val	Phe	Ile	Leu
06B04	5,5	160	86	73	163	43	29	103	6	61	20	nd	28
14B04	13,5	144	72	49	139	33	32	83	5	48	17	10	29
24B04	23,5	104	40	37	72	15	20	42	nd	25	nd	nd	19
28B04	27,5	114	49	70	107	22	31	nd	6	34	16	nd	25
34B04	33,5	105	42	34	70	19	22	45	4	27	14	nd	22
38B04	37,5	40	18	41	84	22	34	59	6	33	17	10	13
02B06	1,5	191	85	81	146	46	44	80	nd	42	27	15	38
04B06	3,5	84	45	32	84	19	24	46	nd	23	10	5	16
06B06	5,5	133	59	43	116	29	34	66	nd	33	16	nd	21
10B06	9,5	70	35	28	69	16	16	45	nd	25	6	nd	12
14B06	13,5	71	37	44	85	15	19	nd	nd	25	8	4	13
18B06	17,5	55	29	19	70	12	16	39	nd	30	nd	nd	nd
24B06	23,5	76	40	42	104	20	27	58	nd	49	14	7	21
28B06	27,5	83	35	29	87	12	24	46	nd	22	nd	nd	nd
02B07	1,5	199	99	90	193	58	56	85	nd	55	26	19	32
04B07	3,5	156	78	61	176	39	41	67	nd	53	21	9	29
06B07	5,5	179	100	67	209	53	52	101	nd	50	27	17	21

10B07	9,5	136	64	50	132	33	36	46	nd	35	20	10	25
14B07	13,5	78	40	24	89	15	19	54	nd	17	nd	5	7
18B07	17,5	68	32	43	82	15	13	43	nd	28	nd	nd	nd
24B07	23,5	117	53	46	108	27	24	20	nd	26	17	7	21
28B07	27,5	23	11	25	71	12	16	31	nd	30	nd	nd	10
02B08	1,5	234	119	67	173	70	66	74	nd	50	26	19	23
04B08	3,5	223	122	79	170	80	62	75	nd	48	33	22	27
06B08	5,5	150	75	44	124	49	48	51	7	34	11	8	18
10B08	9,5	228	105	65	164	77	76	71	14	33	18	14	28
14B08	13,5	248	113	79	191	111	95	82	17	56	24	16	33
18B08	17,5	209	101	48	149	76	84	66	15	31	21	14	30
24B08	23,5	189	88	47	142	67	69	59	13	26	18	10	29
28B08	27,5	106	48	25	86	35	38	53	5	14	8	7	20

6.4. FINAL REMARKS

Besides a weak smectite/THAA correlation, no significant statistical relationship between any of the clay minerals and amino-acids was found so far.

The quantity of amorphous material (alofanes) in the studied transects is much more important than in Goban Spur (OMEX I area). Most probably this colloidal matter escaping the X ray quantification is responsible for the trapping of organic components.

Despite the insufficient number of samples analysed so far, it seems that the Galicia Margin receives a much higher sediment supply (OM included) than Goban Spur. High concentrations of organic carbon were obtained, similar to the ones found on the most productive shelf areas and much higher than the ones found in Goban Spur. Such high concentrations could have been originated by spring and summer upwelling and also by river discharges from the *Rias* (predominantly during the winter). The impact of terrigenous material should be much greater than in the Goban Spur area in consequence of the shorter distance to mainland sources. Although burial rates and the refractory characteristics of the organic carbon may account for the differences between the NW Iberian Margin and Goban Spur. Therefore to assess the sediment organic carbon sources, a further analysis on the lignin content (indicator of terrigenous origin) will be carried out in the near future.

7. GEOCHEMISTRY

7.1. SAMPLING

This part of the report is focused on the geochemical study of 13 sediment cores and 9 samples of surface sediments, collected (Fig. 8) on the Portuguese shelf (between 41° 05’ and 41° 52’) during the cruise *CORVET96*, in November 1996 (*R.V. Almeida Carvalho*).

7.2. METHODS

Sample preparation and analytical procedures were accomplished according to a previously reported procedure (Araújo *et al.*, 1998).

Chemical analyses of the sediment cores have been carried out by energy-dispersive X-ray fluorescence spectrometry (EDXRF) for 16 elements (Al, Si, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Y, Zr and Pb). The accuracy and precision of the overall procedure is usually better than 10% (Araújo *et al.*, 1998). REE analyses (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu) have been carried out on 9 surface sediments samples selected from two sites with fine-grained deposits (the Minho and Douro deposits). The samples were ground and passed through a plastic sieve to obtain a

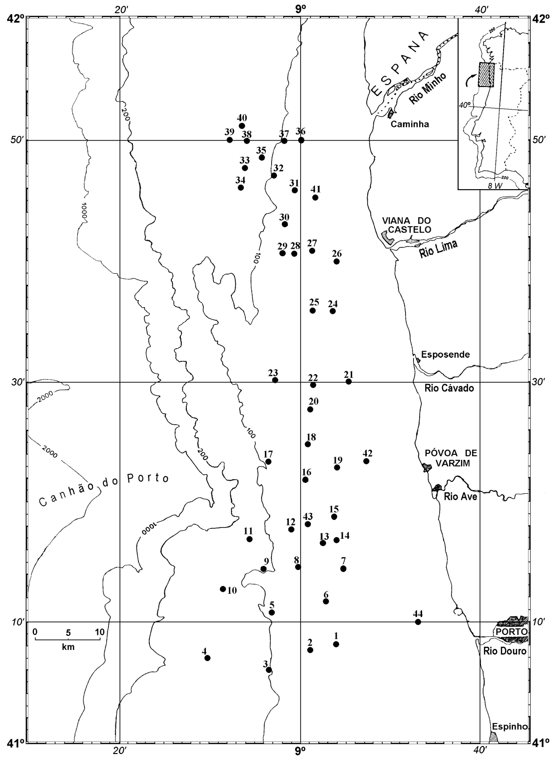

Fig. 8- Sampling locations on the Portuguese shelf

grain size < 64 µm. Fractions between 0.2 and 0.3 g of the dried homogenised sediment were weighed in polyethylene vials for Instrumental Neutron Activation Analyses (INAA). Irradiations were carried out in the core grid of the RPI reactor (Sacavém). The accuracy and precision of the overall procedure is usually better than 5% (Araújo and Gouveia, 1998).

7.3. RESULTS AND DISCUSSION

7.3.1 SEDIMENT CORES

The elemental composition variations of sediments over the studied region as well as the downcore elemental profiles of 13 cores are discussed. The cores were collected at the southern fine sedimentary deposit (KTB 5, KTB 9, KTB 12, KTB 16, KTB 23 and KTB 43), at the northern deposit (KTB 35, KTB 37 and KTB 38), and at a region on the inner shelf showing a dominance of coarser sediments (KTB 26, KTB 28, KTB 30 and KTB 31).

Sediment elemental composition reveals slightly higher percentages of Si in the northern mud patch (max. 30.5%) than in the southern sedimentary deposit (max. 29.3%). Aluminium distribution shows an opposite behaviour being the highest percentages in the cores of the Douro mud patch (up to 7.2%). The major elements (Al, Si, K and Ca) do not show a significant variation on the downcore profile. The Ca distribution shows a general increase towards west in the southern deposit (KTB 5, KTB 9 and KTB 23) also observed in the 3 cores sampled in the northern deposit. The four cores collected in the inner shelf revealed lower values of Al and higher for Si (KTB 26 and KTB 31, the cores located easternmost). The two cores located at the western area (KTB 28 and KTB 30) show the highest percentages of Ca. KTB 30 has a significant variation on the downcore profile being the higher value at 4 cm corresponding to a lower percentage of Al, that may be attributed to the presence of coarser biogenic particles.

The Zr content is higher for samples located at the inner region of the shelf (ex: KTB 37, KTB 26 and KTB 31), probably due to an enrichment in heavy minerals abundant in the region, which tend to have a faster settling.

Table IV – Average elemental composition of the studied cores (in mg/kg, unless otherwise stated)

KTB 5	KTB 9	KTB 12	KTB 16	KTB 23	KTB 26	KTB 28	KTB 30	KTB 31	KTB 35	KTB 37	KTB 38	KTB 43
Mean Values	6.77	6.38	6.17	6.59	5.35	5.33	5.11	5.01	6.29	6.39	5.82	6.46
Al (%)	26.29	26.80	27.57	26.67	30.40	27.37	26.74	30.26	27.93	28.83	27.45	28.12
Si (%)	2.30	2.18	2.15	2.23	1.95	1.82	1.99	1.83	2.19	2.16	2.13	2.21
K (%)	2.68	2.01	2.21	3.47	2.35	3.32	5.79	2.22	2.79	2.09	3.94	2.04
Ca (%)	0.41	0.40	0.41	0.41	0.46	0.33	0.33	0.41	0.39	0.41	0.36	0.43
Ti (%)	67	68	63	69	47	37	39	47	66	54	61	64
Cr	287	280	260	265	215	227	255	261	249	246	223	285
Mn	3.17	2.86	2.70	3.01	2.05	2.40	2.43	2.56	2.91	2.66	2.85	2.84
Fe (%)	32	30	26	30	19	24	22	22	30	26	27	30
Ni	26	26	22	24	21	17	20	20	23	23	21	24
Cu	88	79	77	79	59	66	59	66	75	73	67	80
Zn	174	163	157	162	143	140	134	127	154	153	144	170
Rb	177	144	144	196	214	207	363	161	169	155	194	152
Sr	190	231	247	207	873	324	290	584	240	341	255	270
Zr	41	36	32	38	31	31	32	31	34	37	27	36
Pb												

Elemental profiles of Ti, Fe and Mn are very similar for all samples, with the Fe content increasing slightly at the deep layers for the two mud patches. Elements with similar chemical behaviour such as K and Rb, Ca and Sr exhibit a similar trend for all sampled cores. In fact, Rb can replace K in the K-feldspar; Sr is able to form carbonates like Ca, both mineral present in the discussed samples. Rb and Sr also show similar concentrations for the two mud patches. For the cores sampled at the inner shelf the values of Rb are lower and those of Sr higher.

Trace metal profiles (Ni, Cu, Zn and Pb) exhibit a similar trend for cores within the sedimentary deposits. The concentrations are lower for the inner shelf cores (except for Pb that has similar values), which shows a grain size control of the trace metal distribution.

7.3.2. SURFACE SEDIMENTS

REE concentrations are usually represented using normalisation methods to a chosen reference material to facilitate data comparison. Thus, results on the REE distribution have been normalised using the set of values of the shale abundance (Haskins and Haskins, 1966), applied in many marine geochemistry studies of REE in sediment as well as water (Sholkowitz, 1990).

The shale normalised REE distribution of the selected surface sediments (CV 7, CV 8, CV 9, CV 12, CV 36, CV 37, CV 38, CV 39 and CV 43) showed no significant variations in the REE distribution for the two sedimentary environments. For the studied samples the REE patterns are uniformly flat and similar, and show a negative Eu anomaly throughout the sedimentary deposit.

The $(La/Yb)_n$ ratios were calculated for the nine sediment samples. The five sediment samples collected at the Douro sedimentary deposit present a similar distribution in LREE and HREE, with $(La/Yb)_n$ ranging from 1.15 up to 1.27. The four sediment samples collected at the Minho sedimentary deposit also present similar values, ranging from 1.25 up to 1.35.

Although the REE contents in both deposits can be highly comparable to shales, fine sediments deposited at the northern formation are apparently slightly enriched in LREE.

8. SOME PUBLICATIONS

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