Palaeoproductivity changes and upwelling variability in the Galicia Mud Patch during the last 5000 years: geochemical and microfloral evidence

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Abstract: The Holocene palaeoclimatic history of the Galician continental shelf has been investigated through the analyses of diatom remains, other siliceous compounds, biogenic silica (BSi) and metals content in a multiproxy approach to a gravity core recovered from the Galicia Mud Patch, NW Iberian Peninsula, covering the last 5000 years. Downcore changes in diatom assemblages composition and abundance reflect changes in diatom production related to long-/short-term variations in climate, regional oceanography, upwelling strength and river influx off the coast of NW Spain and Portugal. Palaeoclimatic variability was related to the relative strengths and position of the Azores High and Iceland Low pressure cells. Metals and microflora fluctuations are interpreted as changes in the riverine influence and upwelling intensity paced by oceanographic, atmospheric and climatic changes. Lack of diatoms between 4700–3300 and 1800–1200 cal. yr BP could be linked to early diagenetic processes taking place in the sediment after burial. Biogenic barium (Ba_{excess}), metals and diatom assemblages, show a general increase of marine productivity for the last 1200 cal. yr BP. Between 800 and 500 cal. yr BP high production of the microflora is triggered by influx of river-derived nutrients under conditions of SW winds and storms resulting from a NAO negative-like phase. The biosiliceous and geochemical signatures of sediments from the last 500 cal. yr BP indicate conditions of enhanced upwelling and increased phytoplanktonic production associated with the intensification of northerly winds. Upwelling strengthening in this area, attributed to recent global warming, could provoke an increase in phytoplankton biomass with consequent biological, climatological and socioeconomical impacts. The imprint of anthropic activities has been recorded by the increasing Pb/Al ratios for the last 400 cal. yr BP.

Key words: Metals, geochemistry, diatom assemblages, late Holocene, palaeoproductivity, upwelling, palaeoclimate, NW Iberian Peninsula, Galicia Mud Patch, palaeoceanography.

Background, study site and objectives

Palaeoenvironmental reconstruction allows an understanding of the processes that drive climate and ocean changes and affect biological systems. In recent years, increasing interest has been shown in the study of Holocene climate variations. The Galician-Portuguese area is, together with the Peruvian, Californian and northwestern African systems, one of the major coastal upwelling regions of the world ocean (Wooster *et al*., 1976). The position of both pressure systems, the Iceland Low and the Azores High, determines the intensity and direction of the coastal winds leading to a marked seasonal cycle and, therefore, a seasonally controlled hydrography (Wooster *et al*., 1976). Moreover, on a millennial–centennial scale, atmospheric conditions, that is the position,

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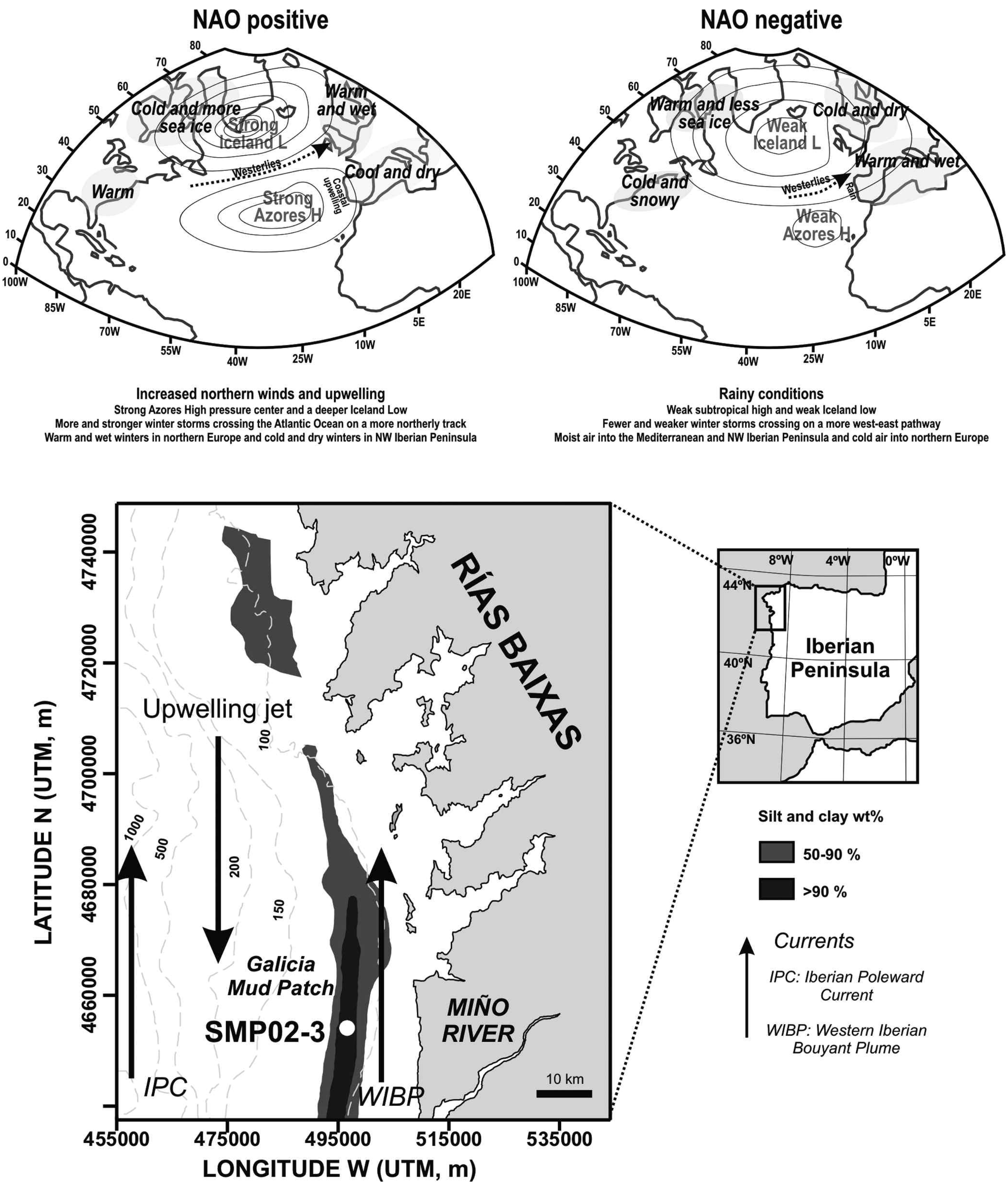

Figure 1 Schematic illustration showing the North Atlantic Oscillation (NAO) regime and the atmospheric situation. Base map of the study area showing the core site (SMP02-3) and the geographical distribution of the sediments containing more than 50% of mud (modified from Dias *et al*., 2002a)

strength and the atmospheric sea level pressure difference between both pressure systems (NAO index), control the patterns of precipitation and upwelling in the area (Figure 1).

Upwelling events mainly occur from April to October (Fraga, 1981), when the Azores anticyclone moves northwards and the N–NNE winds along the coast exert a southwards surface stress that causes Ekman transport offshore (Blanton *et al*., 1984; Álvarez-Salgado *et al*., 1993). Upwelling forces the nutrient-rich Eastern North Atlantic Central Water (ENACW) towards the coast during most of spring and summer (Fraga, 1981). In contrast, in winter the Iceland Low strengthens and centres over the northern North Atlantic. As a result, downwelling-favourable southerly winds prevail along the coast (Wooster *et al*., 1976; Fraga, 1981) and lead to the development of the downwelling regime (Vitorino *et al.*, 2002a,b) and a persistent poleward flow (Iberian Poleward Current, IPC) along the continental slope (Peliz *et al.*, 2003). Moreover, the Western Iberian Buoyant Plume (WIBP), a fresher surface-water lens flowing northwards, is also well developed during this season (Peliz *et al.*, 2002) because of high river runoff related to high rainfall. In this way, the Galician-Portuguese region off the Iberian Peninsula is a suitable area to assess climatic conditions and productivity implications.

These hydrodynamic and oceanographic features affect the primary production of this region. Primary production in these upwelling areas is high because of the influx of nutrients in spring and summer to the surface waters controlling phytoplankton activity, and especially that of diatoms, which increases drastically (Abrantes and Moita, 1999). However, during winter, supply of nutrients may come from the riverine runoff of the Atlantic Rivers draining hinterland. Diatom assemblages have been used as qualitative indicators of primary production, changes in palaeo-upwelling intensity, as well as other environmental variables such as temperature and salinity. In the studied area, different diatom groups are linked with the various surface and subsurface water masses, freshwater inputs and hydrological fronts generated by the upwelling processes (Abrantes and Moita, 1999).

Depositional systems of continental shelves are natural archives of data on changes in past environmental conditions. A high number of palaeoenvironmental tracers can be extracted from their sediments. The sediment cover of the narrow shelf west of Galicia is composed mostly of thin Pleistocene–Holocene units (López-Jamar *et al.*, 1992). The morphology and extent of this shelf sedimentary environment is controlled by storm surges, supply of sediments, currents and a structural control (Dias *et al.*, 2002a,b; Jouanneau *et al.*, 2002). The present sea-floor surface sediments are dominantly silty clay with some areas of muddy sand sediments and gravels at the ría mouths near the coast (Dias *et al.*, 2002a; Jouanneau *et al.*, 2002). Large quantities of suspended fine sediment to the shelf are supplied by the main river systems (Miño-Douro), and other small rivers and streams along the coast, forming the Galicia Mud Patch. Therefore, sedimentation on this margin is highly influenced by terrigenous inputs from rivers draining the hinterland. The nature of sediments that accumulate in the Galician continental shelf results from the combination of several main mechanisms: (i) the supply of terrestrial material from the main river-systems draining the area; (ii) the dispersal of the material through the current systems and hydrographic conditions; (iii) the rate of primary production in the surface waters and the subsequent accumulation of biogenic material (organic, calcareous and siliceous) in the sediment; and (iv) the dissolution processes throughout the water column, at the sediment–water interface and within the sediment.

In this way, Galician shelf sediments contain geochemical, faunal and floral tracers of terrestrial input, primary productivity, physico-chemical conditions of the surface waters and terrestrial vegetation (González-Álvarez and Francés, 2005; González-Álvarez *et al.*, 2005; Martins *et al.*, 2005, 2006a,b, 2007), which show that this area is highly sensitive to climatic fluctuations. Little information about the history of the marine palaeoproductivity and palaeoclimatology exists in this area, only some studies restricted to the Rías Baixas (Diz *et al.*, 2002; Desprat *et al.*, 2003; Álvarez *et al.*, 2005; Muñoz-Sobrino *et al.*, 2007). The understanding of upwelling variability and the ecological consequences during the late Holocene remain poorly studied.

In this paper we present a 4700 yr record of the climatic changes in the western Galician continental shelf. This sediment record provides the opportunity for high-resolution reconstruction of past marine environmental conditions in this temperate zone. We analysed the core sediment samples on the basis of a multivariable study based on sedimentological data, bulk sediment composition, biogenic silica content, diatoms and concentration of several metals.

The general objectives of this work are to identify the variations in siliceous production and to assess the intensity of upwelling and productivity off the Galician coast during the last 5000 years. We also investigate how oceanographic and biological processes (eg, upwelling, surface water dynamics, nutrient input, primary productivity) in the euphotic zone control the production, export and burial of some palaeoenvironmental proxies (eg, the biosiliceous compounds and metals). We also examine the production-recording potential of the diatom assemblages in the context of seasonal changes of biological productivity associated with the upwelling cycles. The results obtained are discussed in relation to previous research in the study area. We focus on the timing and the magnitude of the main production events during the late Holocene and their relation to global climatic events and regional correlations.

Data acquisition and methods

Core location and sampling

The material used in this work was obtained from a 260 cm long gravity core SMP02-3 (42°02.207′N, 9°02.363′W), retrieved from a water depth of 121 m in the core of the Galicia Mud Patch offshore Galician coast during a cruise onboard *R/V Mytilus* in October 2002 (Figure 1).

The core was stored at 4°C until it was longitudinally split into two equal parts (diameter 9 cm). The core was visually described, logged, photographed, x-rayed and subsampled at constant intervals. The working-halves of the gravity core were cut into 1 cm thick slices. Each slice was then separated into subsamples and stored in plastic bags for different analyses. One half was subject to various sedimentological studies and the other half was used for micropalaeontological fossils identification and biosiliceous material counts, bulk component analyses and metal determinations. Samples for siliceous microfossil analysis were collected at the same depth intervals as sediment subsamples used for geochemical determinations.

Chronological control

AMS ^{14}C dating of foraminiferal tests (~10 mg carbonate) recovered from several levels of the core were performed at the Geochron Laboratories (Massachusetts, USA) and at the AMS facility of the Aarhus University (Denmark) (Figure 2).

Ages are given in calibrated years before present (cal. yr BP) to facilitate comparison of the present results with other records of different origins. The raw ^{14}C ages were corrected from the global reservoir effect (apparent surface-water age δR=376±46) and, therefore reported as cal. yr BP with the Calib 5.0.1 software (Stuiver and Reimer, 1993, modified version 2002; http://calib.qub.ac.uk/calib/) using the Marine04 calibration data set for radiocarbon ages younger than 26 000 ^{14}C years (Hughen *et al.*, 2004). A calibrated age range within 2σ confidence limits (95% probability) was obtained (Figure 2). The dates used in figures and discussion represent the intercept of the radiocarbon age with the calibration curve. No local-reservoir effect was applied ($\Delta R = 0$) as shown by Abrantes *et al.* (2005).

Bulk biogenic component analyses

Sediment composition was analysed on bulk sediment and ground subsamples. One portion of each 1 cm slice was used for the bulk geochemical analysis with a sampling interval of 6 cm. $CaCO_3$, organic carbon and nitrogen are standard parameters measured on cores taken for marine studies. These tracers were measured on LECO carbon element analysers. Total carbon (TC) content and total nitrogen (TN) were measured with the CN-2000 analyser using samples that had not been ashed prior to analysis. The total inorganic carbon (TIC) was obtained by acid digestion of a portion of the sediment in a LECO CC-100 connected to the CN analyser.

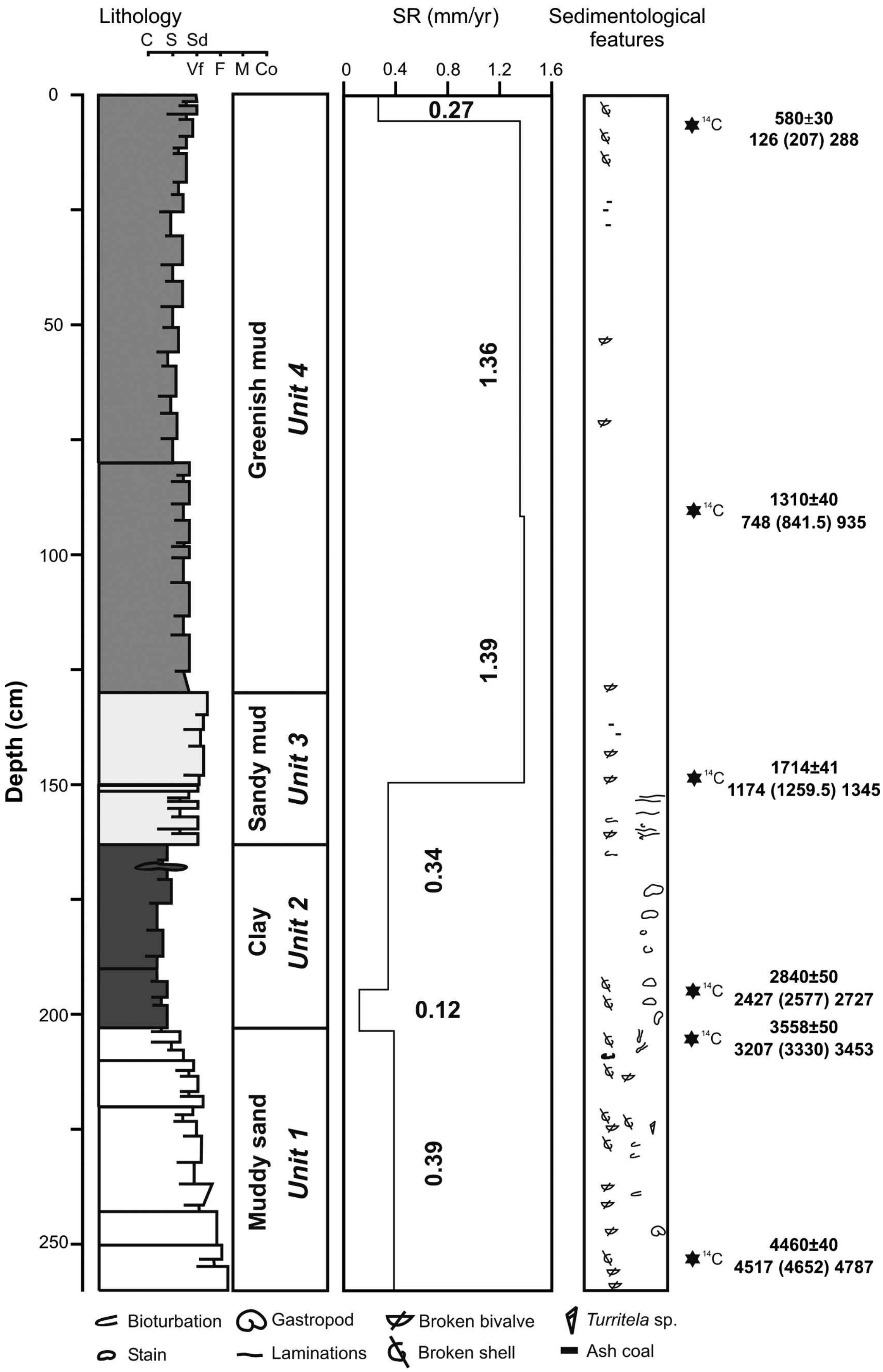

Figure 2 Sedimentary logs of the core. Distribution of depositional facies are also shown. ^{14}C AMS raw ages (yr BP) and the result of the calibration (cal. yr BP, in brackets) are also presented. C, clay; S, silt; Sd, sand; VF, very fine sand; F, fine sand; M, medium sand; Co, coarse sand

Organic carbon (TOC) was calculated as TC minus TIC. Calcium carbonate ($CaCO_3$) concentration was calculated multiplying the total inorganic carbon (TIC) content by the factor 8.33, supposing that all the inorganic carbon is calcium carbonate.

The extraction of amorphous silica particles was made following a soda-hydrolysis technique based on Mortlock and Froelich (1989). Standard deviation for this method is ±0.2, indicating good reproducibility (Bernárdez *et al*., 2005). The resulting

Table 1 Comparison of the analytical results of the certified reference material PACS-2 (NRCC, Canada) with the measured data

PACS-2	Al (mg/g)	Fe (mg/g)	Mn (mg/g)	Cu (µg/g)	Pb (µg/g)
Measured value	67.6±3.9	41.6±2.0	0.48±0.04	318±47	186± 11

extract was determined for the dissolved silicate concentration on the basis of molybdate-blue spectrophotometry at 812 nm (Hansen and Grashoff, 1983) by means of a continuous flow analyser AutoAnalyser Technicon II. Data are expressed as weight of Si (eg, biogenic silicon) and opal content was calculated as 2.14×Si. This conversion does not account for the bound-water content (2–15% depending on the type and age of the material; Mortlock and Froelich, 1989) of the opal, which is difficult to predict.

All the results are given in weight percent of dry, salt-free sediment. The proportion of non-organic, non-opaline and non-calcareous constituents is regarded as the siliciclastic or terrigenous sediment fraction and it is calculated as the residual from 100% of the calcium carbonate, total nitrogen and organic carbon and opal sum.

Analytical procedures for metal determinations: Ba, Cu, Mn, Pb, Al, Fe

For chemical analyses of the metal contents, the dry bulk and homogenized samples were subjected to total acid digestion. Approximately 40–50 mg of sediment was weighed directly into Teflon® pressure vessels. The samples underwent an acid digestion using a mixture of concentrated HNO_3, and HF using 6 ml HNO_3 (65%) and 2 ml HF (48%) in a Milestone MLS 1200 Mega microwave oven following the Environmental Protection Agency (EPA) 3052 guideline (EPA, 1996) for siliceous-type matrices. Handling and analysis of samples were carried out in a clean laboratory (ISO class 7–8) and plastic labware employed for sampling, storage and sample treatment was previously acid-cleaned (HNO_3 10%) for at least 48 h and washed throughout with Milli-Q water.

Fe, Al, Mn and Ba were determined using a flame atomic absorption spectrometry (FAAS) technique with a Varian 220FS apparatus. The concentrations of Cu and Pb were measured by means of electrothermal atomic absorption spectrometry (GF-AAS) using a Varian 220 apparatus equipped with Zeeman background correction. The accuracy of the analytical procedure was tested by repeated analyses of certified reference materials (CRMs), PACS-2 from the National Research Council of Canada (Table 1), except Ba. In this case, accuracy was determined analysing a control sample with a known concentration of Ba and checking the reproducibility. RSD for Ba is 5.72%. The results obtained agree well with the certified values. Relative Standard Deviations (RSDs) were typically lower than 10% except for Cu (14.8%) (Table 1).

The excess/biogenic Ba concentration (Ba_{excess} or Ba_{bio}) was calculated following the Equation (1) (normative method). Ba/Al aluminosilicate ratio is required to assess the biogenic barium, in particular in sediments with high detrital background (Reitz *et al.*, 2004). This ratio is presumed to be representative of the terrigenous input and serves as a correction factor for subtracting Ba associated with terrigenous inputs (Gingele and Dahmke, 1994). After detrital barium is accounted for, the remainder is attributed to biogenic barite and linked to the productivity in surface waters (Gingele and Dahmke, 1994; Dymond and Collier, 1996; Gingele *et al.*, 1999).

Table 2 Bulk Ba (Ba_{total}), biogenic (Ba_{excess}) and Al concentrations

Depth (cm)	Age cal. yr BP	Al (mg/g)	Ba_{total} (mg/g)	Ba_{excess} [a]
0	19	65.47	2.74	2.49
6	214	65.54	2.92	2.68
12	259	79.54	2.70	2.41
18	303	80.42	2.74	2.44
24	347	79.33	2.62	2.33
30	391	84.44	2.61	2.29
36	436	85.14	2.61	2.30
42	480	85.65	2.61	2.30
48	524	118.76	3.99	3.55
54	569	94.46	2.81	2.46
60	613	104.39	3.35	2.97
66	657	115.76	3.71	3.29
72	701	90.89	2.95	2.61
78	746	102.97	3.24	2.86
84	790	98.59	2.93	2.56
90	834	87.20	2.81	2.49
96	878	69.58	2.00	1.75
102	921	58.75	1.61	1.40
108	964	64.85	1.75	1.51
114	1007	66.36	1.54	1.29
120	1051	67.04	2.40	2.15
126	1094	55.85	2.05	1.85
132	1137	56.03	1.89	1.68
138	1180	49.60	1.62	1.43
144	1223	61.26	2.22	2.00
150	1289	61.15	2.18	1.95
156	1464	69.02	2.71	2.46
162	1640	78.91	2.79	2.50
168	1816	89.20	3.20	2.87
174	1991	91.00	2.94	2.60
180	2167	65.42	2.03	1.79
186	2343	67.99	2.36	2.10
192	2518	85.53	2.56	2.24
204	3356	77.38	2.26	1.97
210	3511	54.78	1.57	1.37
216	3667	61.61	1.39	1.16
222	3823	59.81	1.24	1.02
228	3978	37.70	0.34	0.20
234	4134	34.30	0.69	0.56
240	4289	33.85	0.15	0.02
246	4445	33.22	0.00	−0.12
252	4600	36.52	0.00	−0.14
258	4756	36.73	0.00	−0.14

[a] Reitz *et al.* (2004) new global average 0.0037.

A normative approach for conservative elements such as Al is commonly used to assess the detrital barium background:

$$Ba_{excess}=Ba_{total}-Ba_{terr}=Ba_{total}-(Al\times Ba/Al_{det}) \quad (1)$$

Ba should be affected by early diagenesis (McManus *et al.*, 1994, 1998; Paytan *et al.*, 1996; Schenau *et al.*, 2001), but in this work we will designate the biogenic barium as barium excess (Ba_{excess}) since we consider that the diagenetic remobilization is discarded and the terrigenous component was excluded by normalization to Al (Schenau *et al*., 2001). The Ba/Al_{det} ratio can be estimated independently and is constant in time and source. Owing to the impossibility of determining a regional ratio, we simply use the global average crustal ratio (0.0037, Reitz *et al*., 2004; Table 2).

Siliceous microfossils preparation: diatom counting and relative species percentages

The sediment samples for diatom identification were prepared by a standard method devised by Abrantes (1988). Suspension volume and volume used to mount the glass slides were known. A 500 µl of slurry (after mixing the solution for homogenization) was pipetting across 18 mm × 18 mm circular cover slips. Cover slips were placed in a circular Petri dish (diameter 47 mm) and were left to dry at room temperature. When evaporation was complete and cover slips dry, they were removed and fixed onto permanently labelled smear slides using the high refractive mounting medium Permount™ (Fisher Scientific).

Light microscopes (LEICA DMLB and Zeiss) with phase contrast optics and a magnification up to 1000× were used for quantification and diatom identification. Several non-overlapping transverses across the cover slips were examined depending on the diatom concentration. For each sample, at least 300 diatom valves were counted to ensure proper assessment of diatom abundance and composition. Although 300 valves is generally regarded as the optimum number needed for quantitative interpretations, the scarcity of preserved diatoms within the sedimentary record in several levels of the core prevented this in all but a few samples. However, in micropalaeontological studies based on the interpretation of the proportional distribution of the dominant taxa (>3%) counts of around 100 specimens are sufficient (Fatela and Taborda, 2002). The counting procedure and definition of diatom counts and total number estimates followed those of Schrader and Gersonde (1978). Specimens representing more than one-half of the valve were counted as one and for pennate diatoms, such as *Thalassionema* spp., each pole was counted as one-half specimen. Remaining fragments were not counted as one specimen. Diatoms were identified to the lowest taxonomic level possible, based principally on the keys of Hustedt (1930, 1959), Hartley (1996), Hasle and Syvertsen (1996) and Witkowski *et al*. (2000). Each individual was identified to the species level, otherwise they were assigned to a genus on the basis of Round *et al*. (1990). Data concerning the ecology of the diatom taxa were compiled from previous references in addition to several specific bibliographies, and species were divided into freshwater, benthic and marine planktonic species.

Number of diatom fragments, silicoflagellates, sponge spicules, phytoliths, crysophycean cysts and radiolaria per gram of sediment were also assessed, as well as palynomorphs abundance (data in Bernárdez *et al*., 2008). For evaluation of the state of preservation of diatom valves, the preservation index defined by Abrantes (1988) was calculated.

Palaeoenvironmental proxies

Chronostratigraphical features

Lithological characteristics of the core and the age model based on the ^{14}C AMS planktonic foraminiferal dates are shown in Figure 2. The record spans from 4700 cal. yr BP to present, assuming that sample 0–1 cm corresponds to 0 cal. yr BP. Sedimentation rate was quite variable over the age range studied, ranging between 0.12 and 1.39 mm/yr (Figure 2), but it sharply increases during the last 1200 years (0–150 cm). This abrupt increase coincides with a change in sedimentary units (Figure 2).

Table 3 Content of opal, TOC, calcium carbonate and terrigenous.

Depth (cm)	Age (cal. yr BP)	TOC (%)	$CaCO_3$ (%)	Opal (%)	Terrigenous (%)
0	19	1.72	3.92	1.43	92.94
6	214	1.54	3.58	1.38	93.50
12	259	1.70	3.75	1.33	93.23
18	303	1.61	3.79	1.37	93.24
24	347	1.49	3.87	1.49	93.15
30	391	1.52	3.62	1.43	93.43
36	436	1.62	3.29	1.51	93.58
42	480	1.70	3.00	1.44	93.86
48	524	1.62	3.00	1.58	93.80
54	569	1.64	3.21	1.42	93.73
60	613	1.76	2.78	1.48	93.98
66	657	1.86	2.58	1.40	94.16
72	701	2.03	3.28	1.64	93.05
78	746	1.95	3.87	1.85	92.33
84	790	2.13	3.29	1.76	92.83
90	834	1.65	4.58	1.76	92.01
96	878	1.66	4.78	1.67	91.89
102	921	1.58	5.33	1.78	91.31
108	964	1.72	5.21	1.78	91.30
114	1007	1.81	5.41	1.79	90.99
120	1051	1.72	5.33	1.58	91.38
126	1094	1.49	6.21	1.67	90.64
132	1137	1.37	5.83	1.59	91.22
138	1180	1.09	7.16	1.60	90.14
144	1223	1.19	7.30	1.56	89.95
150	1289	1.18	7.41	1.59	89.82
156	1464	1.08	5.66	1.54	91.73
162	1640	1.18	3.12	1.18	94.52
168	1816	1.11	2.25	1.29	95.35
174	1991	1.11	1.79	1.35	95.75
180	2167	1.18	2.25	1.36	95.21
186	2343	1.32	2.37	1.62	94.70
192	2518	1.35	2.62	1.45	94.58
204	3356	1.45	5.25	1.42	91.89
210	3511	1.37	7.25	1.75	89.63
216	3667	1.30	8.66	1.70	88.34
222	3823	1.27	10.08	1.79	86.86
228	3978	1.11	10.95	1.91	86.03
234	4134	1.09	12.50	1.92	84.50
240	4289	0.92	12.20	2.06	84.82
246	4445	1.05	10.70	1.95	86.31
252	4600	0.94	18.91	1.89	78.26
258	4756	0.81	14.41	2.07	82.71

Bulk biogenic components

Sediments are predominately siliciclastic with the terrigenous fraction clearly dominating. The biogenic fraction represents a low proportion, consisting of calcareous remains of gastropods, bivalves and foraminifers, and siliceous microfossils. Visual core description, colour variation, and x-ray data do not show significant evidence of sediment disturbance, only some bioturbation at specific levels.

Concentrations of biogenic silica (BSi) reveal consistently high values at the bottom of the core compared with those obtained in the upper muddy sequence. Opal content falls in the range between 1.18 and 2.07 wt.%, accounting on average for the 1.61 dry weight percent of the core sediment. Biogenic silica, as well as TOC constitutes a small source of biogenic components to the sediments, $CaCO_3$ being the major component of the marine-derived biogenic sediments. TOC and BSi show a similar profile, displaying a strong peak around 700 cal. yr BP (Table 3).

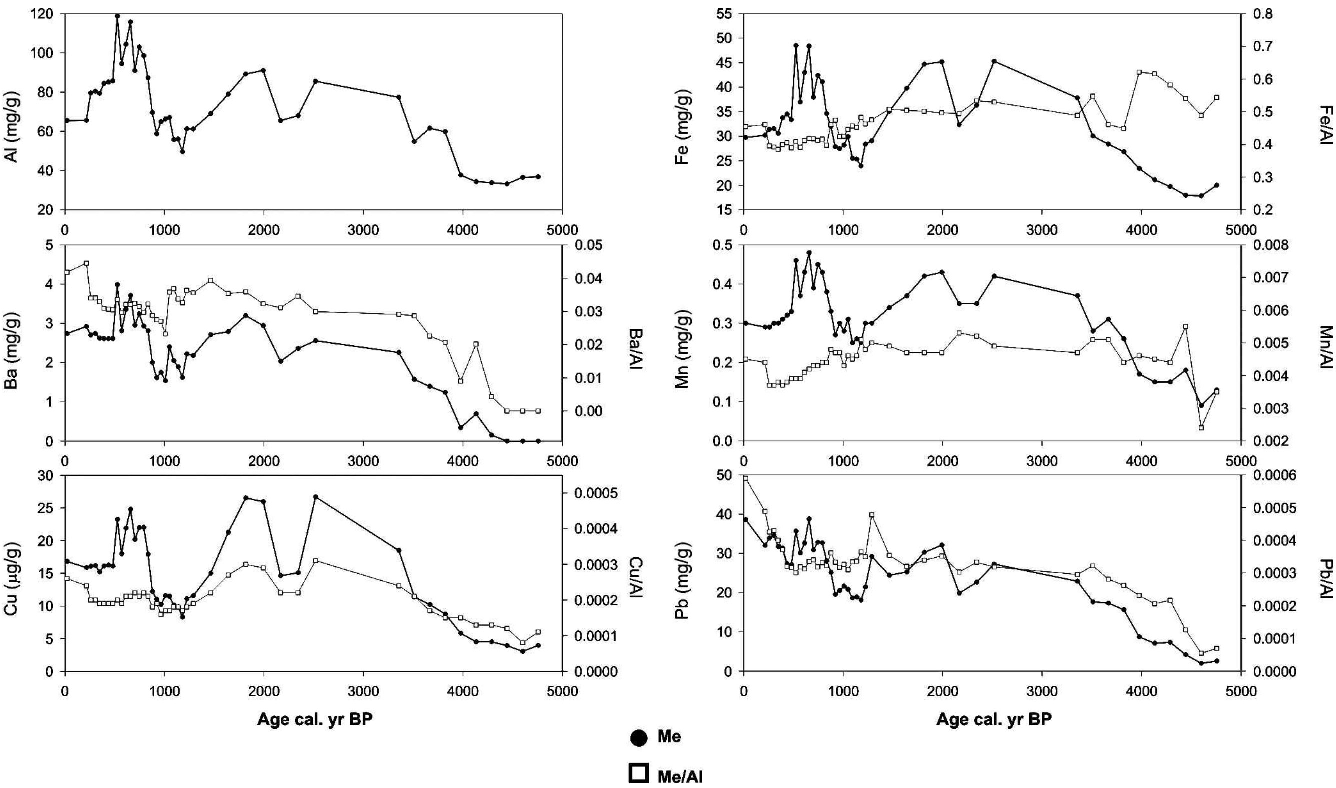

Figure 3 Profiles of the chemical elements analysed in the core. Total concentration (solid circles) is shown on the left axis and metal/Al normalization (open squares) is shown on the right axis

Metals content

The major components of the core sediments are Si, which represents 227 mg/g as a mean value (85–364 mg/g), and Al (33–119 mg/g, averaging 71 mg/g) (Bernárdez *et al*., 2008). Low Al values are found between 4700 and 4000 cal. yr BP. An increasing trend is recorded towards the top of the core peaking around 2000 cal. yr BP. Maximum values occur between 800 and 500 cal. yr BP.

Fe (ranging from 18 to 49 mg/g) is also an important contributor to the sediment. Good linear correlation between Fe and Al (Bernárdez *et al*., 2008) implies that Fe/Al downcore variability is reduced, except for a small peak in the lower Unit 1 around 4200–3900 cal. yr BP (Figure 3).

Mn content shows high downcore variability (0.09–0.48 mg/g). Higher amounts are found at 790–524 cal. yr BP and around 2000 cal. yr BP (Figure 3). Mn/Al ratio displays relatively stable values between 0.004 and 0.005, except at the bottom of the core where ratios oscillate around 0.003. As observed for the Fe/Al ratio, the Mn/Al ratio shows a progressive decrease from 1200 cal. yr BP to 200 cal. yr BP (Figure 3).

Pb is one of the minor components of the core sediments. This metal is detected in the range of 2–39 µg/g. Pb displays very low values in the lower part of the core, increasing progressively up to 3300 cal. yr BP. From 1200 cal. yr BP to present, Pb content progressively increases to reach the maximum value in recent times (Figure 3). The Pb/Al ratio follows the same trend as that found for Pb content in the lower part of the core, and around 3330 cal. yr BP values stabilize around 0.0003. From 400 cal. yr BP to present this ratio progressively increases, reaching the maximum value at present (Figure 3).

Cu levels in the core vary from 3 to 27 µg/g, peaking around 1800–1990 cal. yr BP and 790–520 cal. yr BP. From 1200 to 800 cal. yr BP, very low and stable values are found (Figure 3). Cu/Al distribution presents low variability. Only a small peak on the Cu/Al ratio is recorded around 2000 cal. yr BP and also at the top of the core (Figure 3).

Barium in marine sediments occurs as biogenic barite or is associated with aluminosilicates. The Ba/Al detrital ratio is the crucial factor in the Ba_{bio} calculated from Ba_{total}. We have decided to use the most recent global average crustal ratio (0.0037, Reitz *et al*., 2004; Table 2). The amount of biogenic barium in the sediment ranges from 3.9 mg/g to almost nothing. Ba_{excess} exhibits a distinct profile, with two major peaks around 1800 cal. yr BP and 834–524 cal. yr BP (Table 2, Figure 4). In fact, values increase progressively from the bottom of the core towards the top. Total Ba content follows the same trend, although values are slightly higher, between 0.12 and 0.44 mg/g (Table 2, Figure 3). Total Ba versus Al follows the same trend to that found for total barium from the bottom of the core up to 1200 cal. yr BP. During the last 1200 years the Ba/Al ratio slightly increases, reaching the highest values during last 200 years (Figure 3).

Diatoms

The frequency of the major species amounts to an average around 80% of the total species percent throughout the core, including mainly species of the genera *Chaetoceros*, *Leptocylindrus*, *Paralia* and *Thalassionema*. *Chaetoceros* resting spores (R.S.) (mostly *Chaetoceros affinis*), are the main component of the diatom assemblage, ranging from 20% up to 70% for the last 500 cal. yr BP. Their percentage progressively increases from the bottom to the top of the core. *Chaetoceros cinctus* R.S. has the same profile as found for *C. affinis* R.S. but relative percentages are very low (0–3%). *Chaetoceros diadema* R.S. represents also a high contribution of the total *Chaetoceros* spores. The downcore pattern of this species shows high abundances (~6%) around 1000–700 cal. yr BP (Figure 4). *Leptocylindrus danicus* R.S. represents 8–30% of the assemblage. Higher percentages around 30% are found at 3300, 2200 and 1200 cal. yr BP. From this age to the top of the record values become stable (around 18%) (Figure 4). *Paralia sulcata* relative abundance varies from 5 to 43%, although a high amount of this species is observed at around 1200–960 cal

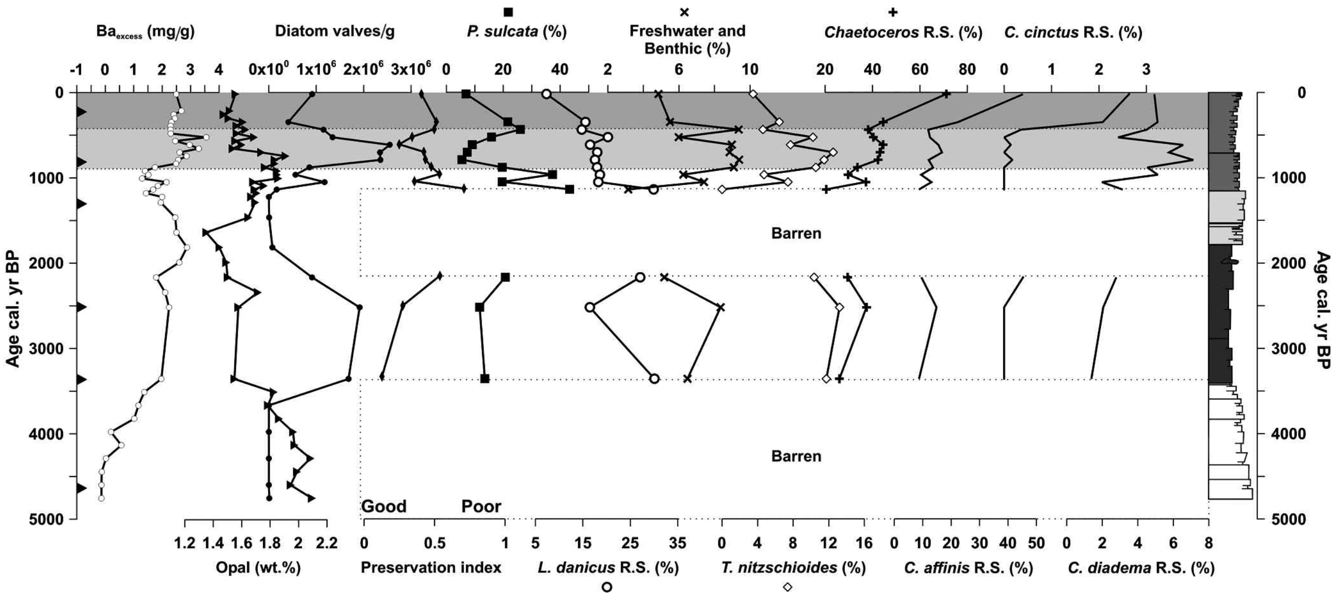

Figure 4 Compilation of diatoms and geochemical proxies in the sediment core SMP02-3. Grey areas indicate climatic events discussed in the text. Lithostratigraphic units and AMS ^{14}C datings (solid triangles) are also displayed

yr BP and around 400 cal. yr BP. The degree of preservation of the assemblage calculated from the margin dissolution of this species follows the same pattern to that found for *P. sulcata*. Higher abundances are found when preservation is poor (Figure 4). *Thalassionema nitzschioides* relative abundance varies between 2 and 6%. Higher values (averaging 11.7%) are found from 3300 to 2200 cal. yr BP. A strong peak, with values up to 10% between 878 and 524 cal. yr BP, is also recorded (Figure 4).

Discussion

Knowledge of the seasonal diatom succession and its record in the sediments of the Galician shelf is limited. There are only a few studies regarding diatom water column assemblages of the Portuguese-Galician shelf (Bode and Varela, 1998; Abrantes and Moita, 1999; Bode *et al*., 2002). Interpretation of the diatom assemblages in the core is mainly based on the ecological characteristics of the species described in Abrantes (1988) and Bao *et al*. (1997).

From the study of the record archived in core SMP02-3, different sediment conditions are inferred for the last 5000 years. Two periods barren of diatoms have been identified (4700–3300 and 1700–1200 cal. yr BP), intercalated between periods where diatoms are present (Figure 4). Diatom-barren sequences in the Galician shelf record may reflect lower production, combined with more intense dissolution of diatom frustules. We suggest that the low diatom abundances observed in some samples result from severe dissolution, indicating a diagenetic control. Fe and Mn contents are indicative of early stages of diagenesis (Froelich *et al*., 1979) especially in organic matter-rich environments. Normalization of these chemical elements to Al (Hanson *et al*., 1993) reports the separation of metal concentrations into natural (marine-derived and terrestrial-derived) and other fractions (eg, anthropogenic). In this way, variations in the Fe/Al and Mn/Al ratios in our record point to different reducing/oxidizing conditions within the sediment. Both periods barren of diatoms (Figure 3) record the highest values of the Fe/Al and Mn/Al ratios, therefore they are representative of an oxic environment promoted by coarser sediments, which favours the biogenic silica dissolution. Profile of relative abundance of *P. sulcata* shows that even heavily silicified forms disappear from the sedimentary record (Figure 4). This species has been related to enhanced upwelling conditions (Abrantes, 1988, 1991; Bárcena and Abrantes, 1998) and linked to vertically mixed water column and high surface water salinity (McQuoid and Nordberd, 2003 and references therein). In our record, higher abundances of *P. sulcata* coincide with high values of the preservation index. Therefore, as reported by Bao *et al*. (1997) in the Galician shelf surface sediments, abundance of this species is mostly related to preservation conditions.

On the contrary, the anoxic–suboxic conditions that lead to the reduction of Mn and Fe are indicated by low values of Fe/Al and Mn/Al ratios. The remobilization of Fe and Mn and the increase of the reduced species in solution occur when dissolved oxygen is consumed in pore-waters after organic matter remineralization. In our record, during the last 1200 cal. yr BP sediment grain size is finer and a high influx of organic matter occurs (Table 3), therefore, anoxic conditions in the sediment are well established. Most of the diatom assemblages remain in this suboxic–anoxic environment, getting preserved. Similar geochemical patterns have been already observed in a nearby core (Martins *et al*., 2006b, 2007), pointing to depressed levels of oxygen and early diagenetic changes in muddy sediments between 2200–1200 cal. yr BP and 500–0 cal. yr BP. However, imprecision in their age model impedes the correlation of both records.

Despite the preservation effects on the diatom assemblage, we consider that downcore variations in diatom abundance are the result of changes in primary production. Clear trends are observed when looking at the individual species data.

The high input of allocthonous diatoms (benthic and freshwater groups) at 800–500 cal. yr BP to the shelf leads to the maximum abundance of the diatom valves. A strong peak in the relative percentage of *T. nitzschioides* and *C. diadema* occurs at this age. *T. nitzschioides* responses to a weakened upwelling and/or high fluvial input discharge (Pokras and Molfino, 1986; van Iperen *et al*., 1987; Abrantes, 1988; Bao *et al*., 1997). In this way, *T. nitzschioides* is present in significant percentages where runoff influence is detected by the presence of freshwater, benthic species and other riverine input tracers (Bernárdez *et al*., 2008). The downcore profile of *C. diadema* also follows the same pattern, reaching the highest abundances (~6%) at 1000–700 cal. yr BP (Figure 4). Although ecological preferences of *C. diadema* R.S. are not extensively investigated, a few studies report the appearance of this species during spring blooms (Tiselius and Kuylenstierna, 1996; McQuoid and Nordberg, 2006) and high nutrient concentrations (Rebolledo *et al*., 2005). In our case, the clear relationship between the percentage of the freshwater assemblage and *C. diadema* R.S. suggests high influx of river-derived nutrients to the shelf.

It has been assumed that upwelling is the main mechanism for enhancing primary production off Galicia. However, influence of river runoff during winter has not been properly assessed. Prego and Bao (1997) indicated that upwelling is the main forcing controlling the silicate concentrations in the Galician continental waters during summer, but they also pointed to the possible influence on productivity of silicate derived from freshwater inputs during winter. deCastro *et al*. (2006) also suggested that high freshwater discharge fertilizing the area can induce a phytoplankton bloom in the Galician shelf. This is in apparent contradiction to Bode *et al*. (2002), who have suggested that relatively low numbers of diatoms in Galician waters occur under high runoff.

Ba_{excess} is commonly used as a tool for the reconstruction of palaeoproductivity, although some authors have discussed its validity (eg, Anderson and Winckler, 2005). In core SMP02-3, high correlation between Ba and Al in bulk sediment reveals that the barium comes from several different sources and some of the barium is associated with terrigenous aluminosilicate materials. The non-terrigenous barium follows the same profile to that found for other palaeoproductivity indicators, such as TOC and opal (Table 3, Figure 4). Maximum values of Ba_{excess} (Figure 4) coincide with strong humid periods reported by Bernárdez *et al*. (2008): around 2000 cal. yr BP during the 'Roman Warm Period' (RWP) and at 800–500 cal. yr BP. During the RWP we cannot evaluate the primary production and the oceanographic conditions since it is one of the periods barren of diatoms. However, we can conclude that at 800–500 cal. yr BP primary production is enhanced.

Downcore values of total Cu are within the range reported for the recent sediments deposited in the western Galician shelf (Araújo *et al*., 2002; Corredeira *et al*., 2005). Two strong peaks are observed around 2000 cal. yr BP and at 800–500 cal. yr BP, paralleling the pattern found for total Ba (Figure 3). These Cu peaks are related to strong input of detrital materials from continental soils and weathered rocks, since when normalizing to Al values the Cu/Al profile becomes stable, except for maximum values found at 2000 cal. yr BP. Cu is an essential micronutrient for ,phytoplankton being part of the biogeochemical cycles (Sunda *et al*., 1981). A strong biological uptake for Cu is observed in the Galician shelf waters (Santos-Echeandía *et al*., 2005) since Cu concentrations in the suspended particulate matter are in the range of dissolved values. Peak in Cu/Al around 2000 cal. yr BP and in recent sediments could be linked to more biological activity and diatom productivity in surface waters that can raise its content in the sediments.

Chaetoceros R.S. are heavily silicified and characteristic of turbulent waters rich in nutrients of upwelling areas (Abrantes, 1988; Pitcher, 1990; Abrantes and Moita, 1999; Romero and Hebbeln, 2003). Under present-day conditions in the western Iberian shelf, *Chaetoceros* spp. proliferate in spring and summer when upwelling is well developed (Abrantes and Moita, 1999). As one of the main contributors to diatom community in our record (Figure 4), it is suggested that the presence of these spores is linked to more frequent upwelling events and high nutrient input. There are important amounts of different spore morphotypes of the diatom genus *Chaetoceros*. One of these high nutrient input indicators is *C. cinctus*. It is absent from the record, but appears during the last 500 cal. yr BP, reflecting the upwelling intensification. *C. affinis* presents the same pattern, a species also related to the coastal upwelling phenomena off Chile (Romero and Hebbeln, 2003).

Ecologically, *L. danicus* blooming is related to nutrient depletion, upwelling relaxation and the break of summer stratification after the mixing period (Varela *et al*., 2001; Bárcena *et al*., 2001, 2004). A strong decrease in the abundance of *L. danicus* is recorded at recent times, when high nutrients and enhanced productivity by upwelling intensification are recorded. Ba_{excess} also exhibits high values (~2.5 mg/g) during the last 500 cal. yr BP (Figure 4). However, these values do not reach those found during the humid period. Therefore we can conclude that primary productivity at 800–500 cal. yr BP is triggered by river-derived nutrients, which could be supplied in higher amounts than those derived from upwelled waters.

The intensification of the upwelling in the Galician-Portuguese margin during approximately the last 1000 cal. yr BP is a well known fact (Soares, 1993; Diz *et al*., 2002; González-Álvarez *et al*., 2005; Soares and Dias, 2006; Lebreiro *et al*., 2006; Martins *et al*., 2006a, 2007; Muñoz-Sobrino *et al*., 2007). Meeker and Mayewski (2002) have also pointed that at *c*. AD 1400 the Iceland Low was deeper, and cool and dry conditions were recorded at these latitudes. Moreover, Mayewski *et al*. (2004) indicate that from 600 cal. yr BP to present a bipolar cooling exists and there has been more humidity in the tropics. Our record confirms this interpretation, however high temporal resolution in the upper part of our core allows us to enclose the enhancement of the upwelling regime for the last 500 years.

This upwelling intensification is observed under a well-described NAO negative regime (Bernárdez *et al*., 2008). This apparent contradiction is explained by the seasonality of the oceanographic processes acting in the region. We could define a predominance of a NAO negative-like phase with SW winds and winter storm conditions during the last 1200 cal. yr BP, but this fact does not imply the ceasing of the upwelling regime during summer. This climatic situation could be blurred by prevailing winter conditions, but during the last 500 cal. yr BP, N–NNE winds and, therefore, the upwelling regime, would predominate on a seasonal scale. Combining both climatic situations, the final result is the increase in productivity, but the diatom assemblages permit us to discriminate between both processes.

Other studies show increased upwelling in recent years in many areas around the world and, in particular, in the Canarian-Iberian margin (Bakun, 1990; Anderson *et al*., 2002; Goes *et al*., 2005; Santos *et al*., 2005; McGregor *et al*., 2007) most of them attributed to twentieth-century global warming and atmospheric CO_2 rise. Temporal resolution of our record does not permit us to discriminate enhanced upwelling on a decadal scale, but shows similar patterns to those found by earlier authors on a century–decadal range. This fact also has important implications for diatom productivity since, although dependent on a complex balance of several factors, it is controlled by upwelling. These results imply an increasing in phytoplankton biomass and the response of the ecosystem and the consequent biological, climatological and socioeconomical impacts. Upwelling may continue to strengthen with global warming (McGregor *et al*., 2007), even in our study area, provoking ecosystem and diatom composition changes.

On the other hand, it is important to point out that in recent years a strong increase in Pb content occurred (Figure 3). These values are within the range pointed out by Araújo *et al*. (2002) for surface sediments in the muddy patch. When Pb is normalized with Al, in order to eliminate the natural lithogenic influence, the variability of Pb/Al ratios is lower, but still shows a significant rise in recent times. One of the primary sources of lead into the aquatic domain is atmospheric deposition (Clark, 2001). However, in the Galician shelf the input by rivers flowing onto the shelf could also be an important source. Enrichment factors and isotope ratios seem to indicate that atmospheric Pb pollution started around 3500–3000 years BP, related to human activities

(Martínez-Cortizas *et al*., 2002a), but in the NW Iberian Peninsula atmospheric Pb pollution is only apparent since 2500 years BP (Martínez-Cortizas *et al*., 2002b). A maximum concentration was found during the Roman colonization and also for the last 300 years because of industrial development (Martínez-Cortizas *et al*., 2002b). A small peak in the concentration of this element during the 'Roman Warm Period' is recorded in our core. Moreover, the increase in the Pb/Al ratios occurs approximately during the last 400 cal. yr BP (Figure 3). This result confirms the age model of the core, but we are not able to detect decreased Pb concentrations reflecting the use of unleaded gasoline also observed in other palaeorecords in Galician marine sediments and peat bogs (Cobelo-García and Prego, 2003; Martínez-Cortizas *et al*., 1997). Conversely, the Pb enrichment in the sediments of the core, which provides a high temporal resolution during recent years, is in good agreement with the Pb enrichment resulting from industrial and naval development (Martínez-Cortizas *et al*., 1997, 2002b).

Summary and conclusion

A multidisciplinary study covering sedimentology (texture, organic matter content), geochemistry (major, minor and trace elements), palaeoecolgy (diatoms, biosilica compounds) and isotopic dating (^{14}C) has been carried out on the gravity core SMP02-3 retrieved from the Galician continental shelf (NW Iberian Peninsula). Palaeoproductivity changes in the NW Iberian Peninsula have been inferred from microflora and geochemical distributions of this core. The study of microfossil assemblages and texture, composition and geochemistry of sediments has been proved to yield relevant information on Holocene primary production changes in the NW Iberian Peninsula.

Disappearance of diatoms during some periods of the core has been related to oxygenation conditions and early diagenetic processes occurring during burial. Despite the presumably large influence of biogenic silica preservation conditions in periods 4700–3300 and 1800–1200 cal. yr BP, relative abundances of diatom species are still reliable tracers of oceanographic and indeed climatic conditions. Based on diatom valves abundance and dominance, the assemblage zones present in the core can be divided in subenvironments that have evolved through time. The sediments are characterized by a dominance of diatoms representative of high nutrient environments, accompanied by coastal planktonic, benthic and freshwater species.

The geochemical characterization of the sediment core indicates that sediments deposited at the Galicia Mud Patch come from three different sources: lithogenic, anthropogenic and biogenic. Peaks in metal concentrations are mainly related to terrigenous inputs from the river plumes, especially at 800–500 cal. yr BP.

We have pointed out that the sediment features (biogenic compounds and chemical features) are triggered by climatic and oceanographic conditions in the Galician area, as well as by anthropic activities. The sharp rise in the Pb and Pb/Al concentrations that occurred during the last 400 cal. yr BP is linked to Pb enrichment due to industrialization.

With respect to the timing of coupled marine and terrestrial palaeoenvironmental processes and their effect in the primary production, the record presented here shows that:

(1) high productivity resulting from nutrient enrichment is recorded during the last 1200 cal. yr BP owing to both upwelling intensification and river runoff;
(2) the major wet event occurring at 800–500 cal. yr BP, related to a NAO negative-like regime, SW winds and storms, provokes a high diatom production, the river plumes being the main source of nutrients to the coastal waters off Galicia;
(3) this study indicates that *Chaetoceros* R.S. and some morphotypes are useful tracers of palaeoupwelling conditions on the NW Iberian margin. The other proxies considered show consistent patterns indicating high productivity on the Galician shelf during the last 500 years, from the onset of the humid event. This fact is due to the intensification of the upwelling phenomena related to prevailing N–NNE winds controlled by the position and strength of the Azores High.

In brief, marine productivity in this area is triggered by two processes that increase the nutrient availability for phytoplankton growth: nutrient input by river discharge and/or coastal upwelling. Both processes are linked to changes in the position and strength of the atmospheric pressure systems and NAO regime.

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Erratum

Bernárdez, P., González-Álvarez, R., Francés, G., Prego, R., Bárcena, M.A. and Romero, O.E. 2008: Palaeoproductivity changes and upwelling variability in the Galicia Mud Patch during the last 5000 years: geochemical and microfloral evidence. *The Holocene* 18, 1207–1218. (Original DOI: 10.1177/0959683608096596)

On page 1211, part of Table 1 missing. The complete table is shown below.

Table 1 Comparison of the analytical results of the certified reference material PACS-2 (NRCC, Canada) with the measured data

PACS-2	Al (mg/g)	Fe (mg/g)	Mn (mg/g)	Cu (μg/g)	Pb (μg/g)
Measured value	67.6±3.9	41.6±2.0	0.48±0.04	318±47	186±11
Certified value	66.1±5.3	40.9±0.6	0.44±0.019	310±12	183±8

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