

1 **A high-resolution Holocene record on the Southern Brazilian shelf:**
2 **paleoenvironmental implications**
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22 ABSTRACT

23 A high resolution multi-proxy record has been used to determine environmental changes during the Holocene on
24 the southern Brazilian shelf. Present oceanographic conditions reveal wind and freshwater input as determinants
25 of short-term productivity changes in the study area. Thus, magnetic susceptibility and grain size parameter
26 variations, together with proxies of productivity (organic carbon, carbon accumulation rate, Ba, Sr and Ca
27 content, Ba/Al, Ba/Ti and Al/Ti ratios) were analyzed and compared with proxies of redox condition (V/Ti
28 ratio), terrigenous input (Fe/Ca and Ti/Ca ratios) as well as other Element/Ti ratios, in order to evaluate the
29 paleoceanographic and paleoclimatic changes over the period.

30 Sediment samples were taken every 2 cm along the 506 cm long core and AMS radiocarbon datings were
31 undertaken every 50 cm.

32 The core covers a time interval of about 7,650 years, with sedimentation rates varying from 0.025 to 0.250
33 cm.yr⁻¹, which represent time intervals of between 8 and 80 years per sample. There is a clear change in the
34 sedimentation rate at about 2,800 years B.P.

35 All grain size and elemental results indicate the occurrence of conspicuous changes between 5,200 and 5,000 yr
36 B.P. as well as between 3,000 and 2,800 yrs B.P.. A comparison of our results with palynological information
37 available for the continental areas suggests that the sedimentary changes in this last interval may be correlated
38 with the onset of modern climatic conditions in South America and, especially, with the onset of the Plata Plume
39 Water, a water mass that carries cold, less saline waters towards the north. Minor changes are observed at ca
40 1,500 years B.P. and are correlated with an increase in atmospheric humidity.

41 A time series analysis undertaken of the several proxies indicates the occurrence of Sub-Milankovitch cycles
42 which may be compared with those reported for the Northern Hemisphere.

43

44 INTRODUCTION

45 The present oceanographic conditions give the southern Brazilian shelf a privileged status for the study of short-
46 term (seasonal and decadal) changes in the wind-driven currents and freshwater discharge regimes of the
47 Southwestern Atlantic Ocean. In this area, the wind-dependent northward displacement of cold and less saline
48 waters originating in the Río de La Plata and the discharge of the southern Brazilian lagoons (Piola et al., 2000;
49 Piola and Romero, 2004) control the seasonal variation in primary productivity (Ciotti et al., 1995).
50 Sedimentological evidence of the northward displacement of this water flow is to be observed both in the
51 organic and inorganic constituents of the bottom sediments and can be traced as far north as the 24°S parallel
52 (Mahiques et al., 1999; 2004). Also, this northward flow, which was originally attributed to the Malvinas
53 Current, has been used to explain the occurrence of cold water foraminiferal forms on the Southwestern Atlantic
54 Shelf (Stevenson et al., 1998)

55 Assuming that the Río de La Plata river mouth has undergone only very slight changes in its geographical
56 position over the last 7,500 years (Cavallotto et al., 2004; Violante and Parker, 2004), that the relative sea-level
57 crossed its present height approximately at this time (Mahiques and Souza, 1995) and that later oscillations in the
58 Holocene sea-level were unable to expose significant portions of the shelf (Suguio and Martin, 1978; Angulo et
59 al., 1999), we may assume that middle and late Holocene paleoceanographic changes on the Southwestern
60 Atlantic shelf were mainly dependent on the wind regime and terrigenous input and that millennial variations in
61 the sedimentary pattern may be assumed to have resulted from variations in this wind-driven water mass.

62 The aim of this work is to identify environmental Holocene changes on the Southwestern Atlantic shelf based on
63 a high-resolution, multi-proxy analysis of a sediment core, sampled from a location in an area of high level of
64 primary productivity, determined by the displacement of the northward flow described above.
65 Paleoproductivity, redox conditions and terrigenous input proxies, together with grain-size and magnetic
66 susceptibility variations were considered so as to permit the analysis of the main temporal changes and
67 variability as well as to correlate with the known climatic changes that affected the South American continent
68 during the Holocene. This work constitutes a first attempt at the utilization of a multiproxy approach in
69 paleoenvironmental studies on the Southwestern Atlantic shelf.

71 STUDY AREA

72 The northernmost part of the Southern Brazilian margin is known as the São Paulo Bight, which is an arc-shaped
73 feature extending from 23°S to 28°S (Zembruski, 1979) (Figure 1).

74 The ocean floor of the São Paulo Bight shows a rather complex morphology involving channels, canyons, and
75 considerable variations in the slope morphology (Furtado et al. 1996). The shelf break is located at a water
76 depth of approximately 140 meters with the upper slope showing an average gradient of approximately 1:55. On
77 the inner shelf the sedimentation is mainly determined by the Plata Plume Water flow (Möller Jr. et al., under
78 revision) which carries sediments from the Río de La Plata and, to a lesser extent, from the southern Brazilian
79 coastal lagoons (Mahiques *et al.*, 2004). On the middle and outer shelves as well as on the upper slope the
80 sedimentary processes are influenced by the flow of the Brazil Current (BC) along the western Atlantic
81 continental margin (Mahiques et al. 2002, 2004).

82 The distribution of surface sediments on the Southeastern Brazilian margin was extensively studied during the
83 70's and is described in the papers of Rocha et al. (1975) and Kowsmann and Costa (1979). In general, the
84 present sea-floor is covered by very fine siliciclastic sands and silts, with variable amounts of clay and calcium
85 carbonate. Coarser sediments and carbonate gravel and boulder facies, found on the outer shelf, represent less
86 than 5% of the present bottom sediments and are generally related to relict sediments, deposited under lower sea-
87 level conditions. More recently, Mahiques et al. (2002, 2004) have re-evaluated the sedimentary characteristics
88 of the Southeastern Brazilian shelf and proposed hydrodynamic models for the sediment deposition in the area.

89 The displacement of the La Plata Plume over the continental shelf is highly dependent on both river discharge
90 and wind regime. Piola and Romero (2004) report a 1000-km displacement of the plume during the winter
91 season, extending as far north as 27°S, and a retreat to 32°S during summer, associating this variability with the
92 influence of the along-shore wind stress. Also, in a multi-year study, using satellite images, Gonzalez-Silvera et
93 al. (2006) recognized a marked temporal variability of the plume, the most effective northward penetration of the

94 plume occurring under conditions of high river discharge and southerly winds. Under El Niño conditions,
95 characterized by the blockage of the southerly winds, the plume extends southward.

96 97 METHODS

98 A 506-cm piston core was sampled at the coordinates 26°59'16.8"S – 048°04'33.6"W, at a water depth of 60
99 meters, onboard the R.V. "Prof. W. Besnard". Prior to its opening the core was analyzed for magnetic
100 susceptibility using a Bartington MS2C sensor.

101 At the laboratory the core was sub-sampled continuously at intervals of 2cm, sub-samples being immediately
102 frozen for further freeze-drying.

103 Due to the lack of suitable carbonate materials (e.g. foraminifers, mollusks), approximately 7 grams of total
104 sediment at each 50 cm was separated for AMS radiocarbon dating at Beta Analytics. Calibrated ages were
105 calculated using the Calib software, version 5.0.2html, available at <http://calib.qub.ac.uk/calib/>, with the standard
106 marine correction of 408 years and a regional reservoir effect of $\Delta R=82.0\pm 46$, corresponding to the average
107 value of three samples reported by Angulo et al. (2005) to the area, and the Marine04 Calibration Dataset
108 (Hughen et al., 2004).

109 Grain-size analysis was performed in a Malvern Mastersizer 2000, on decarbonated samples.

110 Organic carbon was determined in a LECO CNS2000 analyzer. Approximately 200 mg of dry sediment of each
111 sample was treated with 10% hydrochloric acid in order to remove calcium carbonate, and then freeze-dried and
112 analyzed. LECO soil standards and blanks were analyzed as controls for each set of 30 samples. Organic carbon
113 accumulation rate ($_{org}C\ AR$), in $g.cm^{-2}.kyr^{-1}$, was calculated in accordance with the formula described in Grant
114 and Dickens (2002):

$$115$$
$$116 \text{ } ({}_{org}C\ AR) = (\%{}_{org}C) / 100 * SR * DBD * 1000$$
$$117$$

118 where SR is the sedimentation rate ($cm.yr^{-1}$) obtained from the age model and DBD is the dry bulk density
119 ($g.cm^{-3}$), calculated from:

$$120$$
$$121 DBD = (1 - \square / 100) * \square_s$$
$$122$$

123 where \square is the wet porosity and \square_s is the density of the sediment particles, previously determined as $2.35\ g.cm^{-3}$.
124 The wet porosity (\square) was calculated using the formula proposed by Clifton et al. (1995):

$$125$$
$$126 \square = [(W/100) * \square_s] / \{ [(W/100) * \square_s] + [1 - (W/100)] * \square_w \}$$
$$127$$

128 where W is the water content (in weight %), \square_s the density of the sediment particles, i.e. $2.35\ g.cm^{-3}$, and \square_w the
129 density of the pore water, assumed to be $1.0\ g.cm^{-3}$.

130
131 Elemental analysis (Al, B, Ba, Ca, Cr, Fe, Mg, Mn, Sr, Ti, V) was performed using the ICP-OES technique.
132 Approximately 1 g of dry sediment was digested with 10 mL of 1:1 HNO₃ at 95°C for 15 minutes. After cooling,
133 another 5 mL of concentrated HNO₃ was added and the solution heated for 30 minutes. This second procedure
134 was repeated until the digestion of the sample was complete. 2 mL of water and 3 mL of 30% H₂O₂ were added
135 under heating until the elimination of the organic matter was complete. The solution was then filtered through a
136 Whatman 41 filter and 10 mL of concentrated HCl was added to the digestate. Finally the solution was filtered
137 again in a Whatman 41 filter and the filtrate was collected in a 100 mL volumetric flask. The volume was
138 completed and the solution analysed in a Perkin Elmer Model 2100 DV ICP-OES. Measurement precision for all
139 elements was better than 5%. Method accuracy was obtained by analysing certified sediment (HR1) and
140 conformed by joining proficiency promoted by RTC, NELAP (National Environmental Laboratory Accreditation
141 Programme) accredited.

142 143 144 RESULTS AND DISCUSSION

145 *Age Mode and, Sedimentation Rates*

146 Table 1 presents the results of radiocarbon datings. There was no age inversion in the radiocarbon datings.
147 The establishment of a reliable model for depth-age relationships is a key question for all the studies involving
148 sediment accumulation and has been recently criticized by Telford et al. (2004). A basic assumption determined
149 by these latter authors is that age-depth models are only meaningful and useful when established using calibrated
150 radiocarbon ages. In order to evaluate the effect of the age-depth models on the values of sedimentation rates
151 and, consequently, sediment accumulation, we tested several interpolation procedures (polynomial, linear
152 interpolation between radiocarbon values, cubic spline and mixed effect). Polynomial, linear interpolation and
153 cubic spline models were calculated using the DepthAge software, developed by Louis Maher Jr. and available
154 at the INQUA file boutique at <http://www.geology.wisc.edu/~maher/inqua.html> (last accessed December 15,
155 2006) . The mixed-effect model was calculated by means of the Cagedepth and Cagenew functions as described
156 by Heegard et al. (2005) and available at <http://www.uib.no/bot/qeprg/Age-depth.htm> (last accessed January 3,
157 2007).

158 As stated by Grant and Dickens (2002), the linear interpolation leads to artificial sedimentation rate values, and,
159 in our case, there was no significant difference among the 4th order polynomial, cubic spline and mixed effect
160 estimates, with a correlation coefficient higher than 0.999. Nevertheless, due to the possibility of a better error
161 estimation in this last model, we chose the mixed-effect procedure for the depth-age modelling.

162 The core covers an age range of 7,650 years with sedimentation rates varying from 0.025 to 0.250 cm.yr⁻¹, which
163 represent a time interval of between 8 and 80 years for each sample, the main changes having occurred at around
164 3,000 yr B.P (Figures 2 and 3). The changes in sedimentation rates observed in this study seem dramatic for such
165 a short time period. Nevertheless, this has already been verified in other shelf and upper slope areas. Knies
166 (2005) observed changes in sedimentation rates by a factor of 12 between the Holocene and older layers in shelf
167 sediments off northern Norway. The same behavior has been observed for an equivalent period on the shelf off
168 NE Iceland (Andresen et al. 2005).

169 *Grain size*

170 Almost all of the parameters show a pattern of three time intervals, with transitions occurring between 5,200 and
171 5,000 yrs B.P. and 3,000 and 2,800 yrs B.P.

172 This pattern is reflected in the grain-size (Figure 3). From the base to ca. 5,200 yrs B.P., sediments are
173 essentially composed of sandy silts, with clay content varying from 5 to 10% and sands ranging from 20% to
174 40%. A progressive increase in the silt content, followed by diminishing sand (10 to 25%) values is found from
175 this date up to 3,000 yrs B.P. Finally, after this age, the grain size remains approximately constant, as observed
176 by the mean diameter and silt content, this latter corresponding to more than 80% of the grain size distribution.

177
178 *Terrigenous input and redox proxies and other Element/Ti ratios* (Figure 3)

179 Terrigenous input has been evaluated through the use of the magnetic susceptibility values and Fe/Ca and Ti/Ca
180 ratios (Arz et al., 1998). There is an expected significant correlation (R=0.82) between the Fe/Ca and Ti/Ca
181 ratios, with a much smaller but significant correlation between magnetic susceptibility and those elemental
182 ratios. As a rule, terrigenous input, as defined by the Fe/Ca and Ti/Ca ratios, follows a pattern which is similar to
183 that observed in the grain size, with the occurrence of three phases in the time interval considered. Higher
184 terrigenous input appears to have occurred during the Late Holocene.

185 The vanadium content and, specifically, the V/Ti ratio has been used as a proxy for the redox condition (Moreno
186 et al., 2004). Together with Cr/Ti, B/Ti, Mg/Ti and Mn/Ti ratios, they all exhibit the same three-phase division
187 stated above, with a highly significant correlation among these ratios and sedimentation rate.

188
189 *Productivity proxies* (Figures 4 and 5)

190 Barium is one of the most widely used proxies for estimating paleoproductivity (Dymond et al., 1992; Paytan et
191 al., 1996). Nevertheless, the number of its adepts (Jacot Des Combes, 1999; 2005; Calvert and Fontugne, 2001;
192 Pfeifer et al., 2001; Prakash Babu et al., 2002; Wei et al., 2003) is as large as is the number of its detractors
193 (Averyt and Paytan, 2004; Anderson and Winckler, 2005; Mora and Martinez, 2005) for its use as a reliable
194 indicator of variations in productivity over time. The problems reported are related to the impossibility of
195 calculating Ba_{xs} values from the Ba/Al ratios (Kasten et al., 2001; Moreno et al., 2004), either due to the

196 reactivity of the aluminium, to its use as a “normalizing” element, to the absence of regional Ba/Al background
197 values, or even to inconsistencies in the algorithms used for the productivity estimates.
198 Averyt and Paytan (2004), indicate discrepancies in the results obtained from the different parameters related to
199 the barium content, as well as to the Al accumulation rate and Al/Ti ratio. In a more general analysis, Anderson
200 and Winckler (2005) criticize the utilization of the Ba/Ti and Al/Ti ratios which may be influenced by the spatial
201 and temporal variability in the Ti flux. According to the authors, the dissolution of CaCO₃ during the Holocene
202 might be responsible for the increase in the concentrations of barite as well as for the excess in aluminium,
203 which might raise difficulties regarding the utilization of these proxies in paleoproductivity estimates. Also,
204 Pattan et al. (2003), studying glacial-interglacial variations in the southeastern Arabian Sea, indicate that the
205 Al/Ti ratio cannot be used as a reliable paleoproductivity proxy.

206 Concerning our data the following questions must be addressed:

207 1) May we use Al as a reliable normalizer element? Murray and Leinen (1996), analysing samples from the
208 Equatorial Pacific, reported anomalous values in the Al/Ti ratio, related to the non-terrigenous character of the
209 aluminium. In order to evaluate this aspect of our samples, we plotted Al vs Ti, assuming that this last element is
210 exclusively terrigenous and non-reactive (Figure 4a). The correlation may be considered statistically significant
211 (0.797). Nevertheless, when we compare the Ba content, as well as Ba/Al, Ba/Ti and Ba/Ca ratios, with the
212 organic carbon and carbon accumulation rate (Figures 4b to 4i), the Ba/Al plots exhibit the smallest values of
213 correlation, despite being statistically significant. Further, it is worth noting that several plots, such as Ba vs.
214 _{org}C showed a dispersion which is not explicable by a linear equation, but probably only by a polynomial or
215 exponential equation. Actually, there is a clear temporal dependence in the relationship between Ba and Ba-
216 related parameters with _{org}C and carbon accumulation rate.

217 2) May we calculate Ba_{xs}? None of our Ba/Al values is greater than 0.0075, which may be considered as a
218 terrigenous background value (Taylor and McLennan, 1985) or even higher than 0.0028, found by Klump et al.
219 (2000) in the Chilean continental margin surface sediments. Hence, and due to the lack of regional background
220 values for Ba/Al, the determination of Ba_{xs} and the calculation of paleoproductivity is somewhat deficient.
221 Nevertheless, it is possible, at least, to compare data qualitatively in order to establish temporal changes in
222 productivity.

223
224 As observed in almost all of the other parameters, the paleoproductivity proxies exhibit a temporal variation
225 characterized by two main changes at the intervals 5,200-5,000 and 3,000-2,800 years B.P. From the base of the
226 core to 5,200-5,000 years B.P. organic carbon and carbon accumulation rates, as well as Ba, Al and Ca exhibit
227 their lowest values. The interval between 5,000 and 3,000 years is characterized by low but increasing values in
228 organic carbon and carbon accumulation rate. The Ba/Ti and Ba/Ca ratios show their lowest values in this
229 interval, indicating a correspondingly lower productivity period during the Holocene in the area. There was a
230 significant increase in productivity after 3,000 years B.P., as shown by the behavior of organic carbon, carbon
231 accumulation rate, barium, aluminium and other Ba and Al ratios. This increase coincides with the increase of
232 the terrigenous input and sedimentation rate in the area.

233 234 *Climatic changes*

235 As a rule we observe important environmental variations during the Holocene, not only in the productivity but
236 also in the terrigenous input and shelf dynamics. Some events are very well marked, the break in the depositional
237 process prior to and after the transition of 3,000-2,800 years B.P. being the most conspicuous. The causes of the
238 oscillations observed along the core may be analysed from the point of view of the climatic variability affecting
239 South America, the main factor of which is the wind regime (Ledru et al., 1996, 1998; Behling, 1997, 1998;
240 Gaiero et al., 2004; Gilli et al., 2005).

241 Ledru et al. (1996), in a description of the climatic variability of the last 55,000 years in Southeast Brazil,
242 describe the occurrence of a drier and warmer period, between 7,000 and 4,000 years B.P., followed by a
243 subsequent increase in moisture, as a consequence of oscillations in the position of the Inter Tropical
244 Convergence Zone (ITCZ). In a more detailed paper, Ledru et al. (1998) describe a persistent increase in
245 moisture, from 7,000 years B.P. up to the present, by virtue of changes in the wind regime, dominated by the
246 advance of polar masses. The role played by the wind has also been stressed by Behling (1997, 1998), who

247 described the northward advance of the *Araucaria* forests, from 2,850 years B.P. to the present, resulting from
248 the intensification of the wind regime, increase in moisture and decrease in atmospheric temperature.
249 It is thus, in view of the modern controls of the productivity on the shelf, that our results permit us to infer
250 paleoclimatic changes, associated with the wind regime and continental input. As a rule, the period of lower
251 productivity corresponds to the interval between 5,200 and 3,000 years, which may be compared with the lower
252 humidity values on the continent as well as weaker winds over the South American continent. The increase in
253 moisture and the intensification of the southerly winds, as related by the authors above, led to an environmental
254 change in the shelf regime, with a consequent increase in sedimentation rates, productivity and terrigenous input.
255 Oscillations occurred after 3,000 years, as shown by the decrease in several parameters at ca 1,500 yrs B.P.,
256 which also agree with the paleoclimatic inferences set out by Behling (1997).

257

258 *Time Series Analysis*

259 The occurrence of cycles in the Holocene climate and ocean circulation has been reported by Bond et al. (1997),
260 who identified a $1,470 \pm 500$ -year periodicity in the North Atlantic surface winds and hydrography. This cyclicity,
261 which has been attributed to solar activity, has also been lately identified in other parts of the world, thus giving
262 it a global character (Russell and Johnson, 2005).

263 More recently this single-dominant period cyclicity has been questioned by Clemens (2005), who indicated the
264 occurrence of two stronger spectral peaks, at 1,667 and 1,190 years. The author suggests that millennial variability
265 is determined by nonlinear interactions (heterodyning) between centennial periodicities due to solar activity.

266 In order to evaluate the occurrence of cycles in the sedimentation of the study area a time series analysis (Lomb
267 periodogram) was undertaken with the aid of the software PAST (Hammer et al., 2001). Prior to analysis the
268 data were detrended in order to remove the effect of very low frequencies (e.g. periods longer than the time
269 span) on the results. Also, in order to reduce noise, a Principal Component Analysis (PCA) was performed with
270 the standardized values including all of the elements, and the Axis-1 (83% of the total variance) scores were
271 submitted to spectral analysis. Axis-1 corresponds mainly to the input of Fe and Al, which may be assumed that
272 the terrigenous input is the most important factor in the variability of the system.

273 An example of the results is shown in Figure 6 and the significant frequencies ($p \leq 0.05$) for each parameter are
274 presented in Table 2 with the highest peak highlighted.

275 The spectrograms for most of the elements as well as for the PCA scores show five main periodicities:

276 a) 3,880 to 6,700 years, accounting for the low frequency oscillations. These periods are too long compared with
277 the time series for them to give reliable information concerning periodicity;

278 b) 2,360 to 2,820 years (centered at 2,680 yr B.P., according to the PCA analysis), observed at its highest power
279 in Cr, Fe, magnetic susceptibility, sedimentation rate and PCA Axis-1 score. This cycle may be compared with
280 the 2,750-year cycle observed both in the GISP-2 ice core and Santa Barbara Basin sediment core (Nederbragt
281 and Thurow, 2005);

282 c) 1,600 to 1,910 years (centered at 1,848 yr B.P.), as identified in Mg. This cycle is found in most of the
283 elements but we cannot assume that this cycle corresponds to the $1,470 \pm 500$ year-cycle of Bond et al. (1997;
284 2001). On the other hand, Clemens (2005) observes a conspicuous 1,667 year-cycle in the records of Hulu Cave
285 and GRIP;

286 d) 1,220 to 1,310 years (centered at 1,276 yr B.P.), found to be the most powerful cycle in Al distribution. We
287 may not discard this as the second harmonic for the 2,360-2,820 year-cycle. It may also be compared with the
288 1,160-1,190 year-cycle reported by Clemens (2005), for the GRIP and Hulu Cave $\delta^{18}\text{O}$ records;

289 e) 880 to 1,030 years (centered at 1,030 yr B.P.), as observed in Sr, Ti and V. This cycle may be compared with
290 the 1,000-year cyclicity reported for thermohaline circulation (Chapman and Shackleton, 2000), GISP-2 $\delta^{18}\text{O}$
291 and atmospheric $\Delta^{14}\text{C}$ (Nederbragt and Thurow, 2005) and North America temperatures (Viau et al., 2006),
292 among others. This cycle is still maintained on several parameters (Axis-1 of the PCA, B, Sr, Mn and Ti) when
293 the periodogram is executed for the most recent interval, i.e. coretop to 3,000 yrs B.P.

294

295 CONCLUSIONS

296 A high-resolution Holocene multiproxy record obtained for the first time on the Southwestern Atlantic shelf
297 allowed us to recognize the main changes in the wind and La Plata river discharge. Two transitions, at 5,200-

298 5,000 and 3,000-2,800 yrs B.P. mark the boundaries of three time intervals with different sedimentary
299 characteristics, related to environmental changes.
300 The interval between 5,200 and 3,000 yrs B.P. marks the period of lowest terrigenous input and productivity,
301 which may be associated with the weakening of southerly winds and a decrease in humidity in South America,
302 as confirmed previously in the palynological record for the continent.
303 The period after 3,000 yrs B.P. marks the highest terrigenous input and productivity, corresponding to the
304 establishment of the modern conditions of wind and river discharge. At least one interval of the weakening of the
305 climatic conditions could be observed in this period.
306 The time series analysis allowed us to recognize four significant cycles, which may be compared with the
307 cyclicity described by several other authors, mainly in the northern hemisphere. The significant cycles centered
308 on 2,680, 1,848, 1,276 and 1,030 found in the spectrograms of several parameters are comparable to those of
309 GISP-2, GRIP, Hulu Cave, Santa Barbara basin, $\Delta^{14}\text{C}$ and North American temperatures.
310 Despite their significant correlation with orgC and carbon accumulation rates, the utilization of Ba and Ba-related
311 ratios as proxies for productivity have only been used qualitatively by the present authors. Regional studies are
312 needed in order for us to be able to understand of the background terrigenous values of barium and,
313 consequently, Ba_{xs} , better.

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479 CAPTIONS

- 480 Figure 1. Location of the core analysed in this paper. Seismic line represents a cross-shore chirp (2-8 kHz)
481 profile, showing the bathymetric position of the core sampled. The strong sub-superficial reflector
482 corresponds to the surface developed during the sea-level retreat after Isotope Stage 5e.
- 483 Figure 2. Age-Depth model, based on 11 AMS radiocarbon dating. Interpolation has been obtained with the
484 mixed-effect model as described in Heegard et al. (2005)
- 485 Figure 3. Along-core variation in sedimentation rates, grain-size, terrigenous input and redox proxies and other
486 Element/Ti ratios.
- 487 Figure 4. Dispersion plots of A) Al vs. Ti; B) Ba vs. $_{org}C$; C) Ba vs. carbon accumulation rate; D) Ba/Al vs. $_{org}C$;
488 E) Ba/Al vs. carbon accumulation rate; F) Ba/Ti vs. $_{org}C$; G) Ba/Ti vs. carbon accumulation rate; H)
489 Ba/Ca vs. $_{org}C$ and I) Ba/Ca vs. carbon accumulation rate. Statistically significant values ($p < 0.05$) of
490 Pearson Correlation Coefficient are pointed.
- 491 Figure 5. Along-core variations in organic Carbon ($_{org}C$), total Nitrogen ($_{tot}N$), C/N ratio, carbon accumulation
492 rate (C.A.R.), Al, Ba, Ca and Sr contents, and Ba/Al, Ba/Ca, Ba/Ti and Al/Ti ratios.
- 493 Figure 6. A) Lomb periodogram of the detrended values of Axis 1 Factor Score (83% of the total variance)
494 obtained by a Principal Component Analysis, using elemental values as data source; B) Sinusoidal fit on
495 the same data, using the 2,680, 1,848, 1,276 and 1,030-year cycles.
- 496
- 497 Table 1. Results of AMS radiocarbon datings in the organic matter of selected samples. Calibrated ages were
498 calculated using a SW Atlantic reservoir effect ($\Delta R=87$, $U=46$), using data from www.calib.org
499 (accessed June 15th, 2006).
- 500 Table 2. Significant frequencies obtained in the Lomb Periodogram, for each parameter analysed. Highest peaks
501 of each parameter are highlighted.

502

Depth	Conventional radiocarbon age (yr B.P.)	Error	$\delta^{13}\text{C}$ (‰ PDB)	Calibrated radiocarbon age (yr B.P.)
0-2	1410	40	-19.6	855
50-52	1680	40	-19.8	1155
98-100	2080	50	-19.8	1565
148-150	2560	50	-20.3	2125
198-200	2750	40	-20.9	2370
248-250	3090	50	-20.6	2780
298-300	3230	50	-20.2	2930
352-354	3770	40	-19.6	3595
398-400	4490	40	-19.9	4545
448-450	5340	40	-20.3	5625
504-506	7290	40	-20.4	7665

503

504

Table 1

<u>Al</u>	<u>Ba</u>	<u>B</u>	<u>Ca</u>	<u>Cr</u>	<u>Fe</u>	<u>Mg</u>	<u>Mn</u>	<u>Sr</u>	<u>Ti</u>	<u>V</u>	<u>Sus</u>	<u>C</u>	<u>S</u>	<u>Median</u>	<u>Sed Rate</u>	<u>Axi 1 PC score</u>
6700	6700			6700	6700	6700	6700			6700						667
		5960														
			5360					5360								
												4180	3880	4520		
2550	2680	2820		2550	2680	2550	2680	2550	3150	2550	2820				2360	268
1790	1850			1850	1850	1910	1850	1790		1790		1600				185
1280	1280	1250		1310	1280				1220	1250						128
1050	1030	1030	870	1030	1030			880	1010	1030						103

505

506

Table 2