

Boski T.¹, Wilamowski A.², Veiga-Pires C.¹, Moura D.¹, Gonzalez Villa F.³, Polvillo O.³

Geochemical and mineralogical characterization of Holocene sedimentary sequences from two estuaries in Algarve

¹CIMA – Centro de Inv. Marinha e Ambiental, Universidade do Algarve, 8000-117 Faro, Portugal, E-mail: <u>tboski@ualg.pt;</u>

²Institute of Geological Sciences PAS, Twarda 51/55, 00-818, Warszawa, Poland; ³Instituto de Recursos Naturales y Agrobiologia de Sevilla, IRNAS-CSIC, Seville, Spain.

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Abstract

The present study embraces analyses of mineralogy, granulometry, organic biomarkers, elemental chemistry and foraminifera assemblages in sediments from two major estuaries in the S. Portuguese coast. These sediments accumulated during the postglacial sea-level rise, dating back to ca 13000 cal BP in the Estuary of Guadiana and ca 8000 cal BP in the Estuary of Boina-Arade river system.

The mineralogical and geochemical characteristics reflect the superimposed signatures of environmental conditions prevailing in the estuaries and in the drainage basins throughout the Holocene.

The change in organic carbon accumulation rates in the estuaries on a global scale and throughout the postglacial period may explain the variations in the atmospheric CO_2 content.

The area of the Arade Estuary

The Boina-Arade Estuary is located at the confluence of two fluvial systems: a) the rivers of Odelouca and Arade which mainly drain the Paleozoic slates and grauwackes substratum and Lower Jurassic volcanosedimentary terrains and b) the Boina River which drains nepheline syenites of the Monchique Massif as well as the surrounding Carboniferous slates and grauwackes and the Lower Jurassic volcano-sedimentary complex at the river confluence. The actual estuary that occupies the Boina-Arade paleovalley received the Holocene sedimentary sequence whose thickness does not exceed 35 m in the deepest zones, as registered from destructives geotechniques boreholes data. We present here the results of partial analyses of two continuous cores which crossed the Holocene sequence until the Pre-Quaternary substratum. In the P5 core (Boina River), the sedimentary column, which spans 20 m accumulated during ca 8500 years, starts with a sequence of inter-bedded layers

of sandy-pebbles and silty-clays that corresponds to a transitional period from fluvial to estuarine regime.

It is followed by a period of silty-clay deposition during a regime of fast sea level rise. The top 6 meters of the sequence are mainly sandy and represent the progressive infilling of the estuary with material from the continental shelf after the sea level stabilization in the Upper Holocene.

The sediment clay fraction is made of illite, interstratified and kaolinite with mean contents of 65%, 23% and 11%, respectively. In the light fraction of sandy layers, feldspars (both plagioclases and orthoclases) and hydro-muscovite, originating in slates or feldspar alteration, are abundant. The heavy minerals with a contribution of 10 to 19% of total weight are very abundant.

The iron oxi/hydroxides are predominant and their source lies probably in the altered basic rocks from the volcano-sedimentary complex. Pyrite, which is also abundant in the heavy fraction, comes from the reaction between the already mentioned iron and the sulfur



Figure 1. Heavy fraction (bromoform) content in the cores from the Arade Estuary

microbial sulphato-reduction released during processes. Pyrite occurrence is frequent as foraminifera test infillings. The rest of the heavy mineral assemblage is made of pyroxenes and amphiboles (predominantly alkaline), titanite, biotite, all originating from the Monchique Massif and some minerals originating from the slate-grauwacke substratum such as andalusite and epidotes. The sedimentary sequence from Odelouca-Arade River estuary (P2) is similar to the above-described sequence. While the clay mineralogy from both areas does not reveal significant differences, the sandy fraction mineralogy in P2 differs from the on of Boina area as follows: quantitatively smaller heavy mineral fraction (fig. 1), more rounded quartz grains and quantitatively fewer minerals originating from the nepheline massif. The behavior patterns of Sr, Ca, Fe, Ba, Al and Ti elements as well as some of their ratios were analyzed in the clayey samples. In core P2, Sr and Ca values undergone a significant increase around 7 ka (interpolated) although no change in their ratio was observed. This behavior reflects probably the contribution of foraminifera tests. Indeed, according to data obtained in other estuaries from this region, they would be in the maximum of marine influence. As an indicator of fluvial input, the iron presents a slightly later peak than the one observed for Sr and Ca. The simultaneous increase of Ti/Al ratio also indicates an increase of detrital input into the estuary and its progressive infilling.

The area of the Guadiana Estuary

During the last 4 years, a series of boreholes has been carried out with the aim to recognize the structure, mineralogy and geochemistry of the sedimentary sequence of the Guadiana River estuary (Boski et al., 2002). The deepest core, which will be discussed hereafter, reached the slate-grauwacke substratum at a depth of 52 m, corresponding to 13000 years. The studied sequence starts with sandy fluvial deposits in which, besides quartz, lithic grains and hydromicas are predominant. The rest of the sequence, up to the surface, is mainly silty-clay sediment composed of illite, interstratified and kaolinite, with mean contents of 58%, 29% and 12%, respectively. In this sequence, the benthic foraminifera analysis reveal three main steps for the estuary's evolution: confined, open to marine circulation and confined during terminal infilling. Regarding the geochemistry of the organic fraction, the lower section of the sequence (up to ca 15 m deep) is characterized by a mean organic carbon (OC) content \approx 1.1% and by the persistent occurrence of phytol, a marine phytoplankton biomarker coming from the incomplete degradation of chlorophyll (Gonzalez Vila et al., 2003). Pyrite, which is an indicator of reducing conditions, has also been observed in several levels of this section together with sulphur contents above 1% of dry weight. In the section comprised between 15m deep and the surface, mean OC content is $\approx 1.8\%$ and resinic acids (ex. abietic) are always present whereas the presence of phytoplankton biomarkers is less evident. The comparison of these characteristics in the two sections of the sedimentary column clearly indicates a change in the quality of the OC retained in sediments. More labile organic matter (OM) originating from phytoplankton would have contributed to the lower section, whereas in the upper section (Upper Holocene) the OM would have

been more refractory, i.e. terrigenous. The analyses of organic carbon accumulation rate in the sediments recovered from the 4 boreholes of the Guadiana River estuary is represented in figure 2.

Despite of the considerable OC content variations, the mean accumulation rate during the rapid mean seal level (MSL) rise is almost three times higher than the one during the following Upper Holocene, going from 280g OC m²yrs⁻¹ to 86 g OC m²yrs⁻¹, respectively. This difference can be extrapolated to any estuarine area and has a very important meaning regarding the global Carbon cycle. In a first approximation, it can namely explain the lower atmospheric CO₂ content (180-200 ppmV) during glacial periods than during interglacial periods (280 ppmV) (Schlesinger, 1997). According to this hypothesis, when terrestrial organic matter (TOM) is freely delivered to ocean's pelagic zones (glacial period), it allows a



Figure 2. Organic carbon accumulation rates in the sediments from Guadiana River estuary.

higher primary marine productivity, which will absorb an additional quantity of carbon dioxide. On the opposite, organic matter retention in estuaries would deprive the ocean of fertilizer, contributing for a decrease in primary production and in carbonates and, consequently, a post-glacial increase in atmospheric CO_2 content (del Giorgio and Duarte, 2002).

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