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Sea-level rise and anthropogenic activities recorded in the late Pleistocene/Holocene sedimentary infill of the Guadiana Estuary (SW Iberia)

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ABSTRACT

This study reviews data on sea-level rise during the last 13000 yr cal. BP (13 kyr) as recorded in the estuarine sediments of the Guadiana River (SE Portugal, SW Spain). We combined new data from a 63 m-long borehole, drilled through the entire postglacial sedimentary sequence, with information on five previously studied cores. By integrating sedimentological, geochemical and palaeontological proxies, we were able to make a palaeoenvironmental reconstruction of the Guadiana terminal palaeovalley during the last 13 kyr and propose a curve of sea-level rise for the SW Iberian Atlantic margin. Our foraminifera-based palaeoecological reconstruction, anchored to a ^{14}C age model, reveals rapid sea-level rise from 13 kyr, interrupted during the Younger Dryas and resuming ca 11.5 kyr. The pace of marine transgression slackened ca. 7.5 kyr and since then has progressed upwards at a rate of 1.2 mm yr^{-1}.

Holocene–Anthropocene sediments from two boreholes were also analysed to assess the timing, levels and sources of trace metals produced by acid mine drainage from the Iberian Pyrite Belt. Study of metal/aluminium ratios through the profiles allowed background metal concentrations to be estimated from lithostratigraphic units older than ca. 5 kyr (i.e. unaffected by anthropogenic activities). Human activities are especially evident from 4.5 kyr (the beginning of the Copper Age), with anthropogenic sources of metal fluxes prevailing over natural sources (especially Pb, Co, Ni, and Mn, and, to a lesser extent, Zn, Cu, and Ni). Mining activities became particularly intensive between the late Bronze Age and the Roman period (3–1.5 kyr), when the highest metal enrichment factors were recorded: $EF_{Pb} \approx 2$, $EF_{Cd} > 10$, $EF_{Cr} \approx 2$, $EF_{Cu} \approx 3$, $EF_{Zn} = 1.4$.This study reveals the utility of postglacial sedimentary records for reconstructing historical changes in regional water-sediment quality and separating natural and anthropogenic sources of geochemical contaminants.

1. Introduction

The rapid rise in sea-level that occurred following the last glacial maximum (LGM) created tens of metres of vertical accommodation space for sediments deposited in fluvial palaeovalleys. In particular, the deeply incised terminal segments of river valleys provide excellent conditions for the uninterrupted accumulation and preservation of continuous records of sedimentation, evolving progressively from fluvial to estuarine/marine. Estuarine sedimentary archives usually contain abundant ^{14}C-datable items and may be seen as complementary to the classical, coral-based records used in sea-level reconstructions, like those in Barbados (Fairbanks, 1989) and Tahiti (Bard et al., 1996, 2010). On the Spanish side of Gulf of Cadiz, the process of postglacial coastal sedimentation has been reviewed by several authors (e.g. Goy et al., 1996; Dabrio et al., 2000; Zazo et al., 2005, 2008). Postglacial sea-level rise also induced changes in human settlement patterns (Turney and Brown, 2007), and adaptations to marine transgression (Rolett et al., 2011) through differentiated dispersal patterns and social structures (Fa, 2008). Marine resources made an important contribution to the human diet, especially after 10 kyr when terrestrial resources became depleted due to overpopulation (Cohen, 1977). The importance of marine resources in the Mesolithic diet has been demonstrated through the isotopic composition of bones (e.g., Mannino and Thomas, 2001; Fischer et al., 2007). Considering the limitations on the transport and preservation of food, humans probably spent large amounts of time near the coast (Fischer et al., 2007). Between 8500 and 5630 years cal. BC, a marine diet composed mainly of species occurring on intertidal rocky substrates sustained Mesolithic

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populations along the SW Portuguese coast (Dean et al., 2011). Shell middens, some of them including artefacts dated to 8–7 ka BP, reflect the vital importance of marine sources for pre-historic communities (Bailey and Flemming, 2008) and can be used as a proxy for coastline evolution (e.g., Pavlopoulos et al., 2010).

Due to strong chemical gradients and dynamic mixing of continental and marine waters, estuaries have a great capacity for the accumulation of contaminant elements introduced by anthropogenic activities, both within the catchment and the estuary itself (Weistein, 1996; Sanger et al., 1999; Spencer et al., 2003). Since these areas are often places of intense human and animal activity, playing an important role in the maintenance of ecological diversity through their provision of shelter and food to numerous species, contamination levels are of particular interest in estuarine environments (Rae, 1997; Price et al., 2005). Over millennia, human activities like forest clearing, mining, waste dumping and metallurgy have accelerated the supply of heavy metals to coastal areas. Interpretation of the human influence, however, requires knowledge of natural reference (background) concentrations, which can be obtained from the pre-anthropogenic part of the estuarine sedimentary record.

Trace metals in the water column generally tend to be adsorbed onto fine, chemically active particles in suspension, which are subsequently accreted to the sedimentary column. Sedimentation of these metal-adsorbing particles incorporates the historical record of the sources (both local and regional) of contaminant input into the host sediment (Hwang et al., 2009). Where ^{14}C-datable items are abundant, these sedimentary archives may therefore provide time-resolved information for the reconstruction of historical changes in water quality, local sedimentation and sea-level rise (Hartmann et al., 2005; Cantwell et al., 2007; Baker et al., 2010). In estuaries affected by acid mine drainage (AMD), natural salt-induced coagulation/precipitation processes, through which suspended elements in particulate matter are incorporated onto sediments (Stecko and Bendell-Young, 2000), are altered. These environments are characterized by high sulphate, metal and metalloid concentrations, the behaviour of which is controlled by changes in pH and salinity. As a result, all these behavioural modifications may be reflected in the geochemical characteristics of the sediments (Borrego et al., 2004).

Catchments of the Iberian Pyrite Belt in SW Iberia have been widely documented on account of their massive sulphide deposits and associated intensive mining. The extraction of minerals from these deposits dates back to the age of the Iberians and Tartessos, some 5000 years ago (Davis et al., 2000; Leblanc et al., 2000; Nocete et al., 2005). Acid discharges from these mineral extractions into the river network almost inevitably left a chemical imprint in the geological record. Hence, sedimentary geochemistry should be a powerful tool to trace environmental changes in the area, induced both by natural and anthropogenic causes. Previous investigations have indeed shown that study of sediments at depth may help establish the effects of natural and anthropogenic processes in sedimentary environments (van Geen et al., 1997; Leblanc et al., 2000; Borrego et al., 2004; Price et al., 2005; López-Gónzalez et al., 2006; Chatterjee et al., 2007; Viguri et al., 2007; Hwang et al., 2009).

Various studies have examined aspects of coastal sedimentation systems in the vicinity of the Guadiana River, which crosses the final section (Fig. 1) of the Iberian Pyrite Belt. For example, Morales (1993) and Morillo et al. (2004) provided geochemical data on sediments at the coast near Huelva, González et al. (2007) characterized sediments on the Gulf of Cádiz shelf, and Ruiz (2001) made an assessment of estuarine pollution levels. González-Vila et al. (2003) and Polvillo et al. (2009) presented data on organic geochemical markers to infer aspects of the history of vegetation, diagenesis of organic matter and possible anthropogenic interference, as well as on climatic and environmental changes (mainly derived from changes in sea-level) during the Holocene–Anthropocene.

Historically, the waters in the Lower Basin of the Guadiana River have received acid input from mining activity (Delgado et al., 2009), thus the surface sediments of the estuary contain significant levels of contamination associated with this input (Delgado et al., 2010, 2011). However, there are no detailed data concerning the post-glacial input of toxic metals to the estuary. A thorough examination of historic variations in contaminant elements and the establishment of the background metal concentrations are important precursors to an assessment of anthropogenic impact on these environments (Mil-Homens et al., 2006). Such studies may also provide valuable data on the behaviour of metals in estuarine settings that have been historically affected by AMD.

Given the exceptionally long sedimentary record accumulated since the LGM in the Guadiana River Estuary, the present study aims to bring together existing information on sedimentary evolution in the area and to propose the first regional curve for postglacial sea-level rise (SLR) in the Gulf of Cádiz, embracing the terminal Pleistocene and Holocene. From a geochemical perspective, our goal is to establish background values for contaminant elements and discriminate between natural and anthropogenic inputs of these elements into the system. This information will complement an existing pollen-based reconstruction of environmental change in the Lower Guadiana Basin, as proposed by Fletcher et al. (2007).

1.1. *Study area and historical perspective*

The Guadiana River is the fourth-longest river on the Iberian Peninsula, with a total length of 810 km. The last 200 km stretch forms a natural border between Portugal and Spain. In geological terms, the estuary is located almost entirely in the Central Domain (Iberian Pyrite Belt) of the South-Portuguese Zone (Simancas and Pérez Estaún, 2004). Its Late Quaternary geological framework has been described in several previous works (Boski et al., 2002, 2008; González-Vila et al., 2003; Delgado et al., 2009). In a physical sense, the Guadiana Estuary covers the zone of tidal influence extending 50 km upstream of the point where the river debouches into the Atlantic Ocean (Ruiz et al., 1996) (Fig. 1). The main estuarine channel varies in depth between 2 and 14 m and experiences a semi-diurnal mesotidal regime, with maximum spring-tide amplitude reaching 3.44 m (Garel et al., 2009). A schematic cross-section, based on exploratory geotechnical drilling and seismic profiles, shows that the estuary's palaeovalley was 600 m wide and approximately 70 m deep, 8 km north from the mouth (Boski et al., 2002). In contrast to the sedimentary infill characteristic of other estuaries in the region (soft, unconsolidated sediments from the Plio-Pleistocene accumulated in large, shallow structures valleys: Borrego et al., 1999), the Guadiana has thick (70–80 m) Lateglacial and Holocene deposits, enabling high-resolution temporal analysis of the sedimentary record (Boski et al., 2002). For the purpose of this study, core materials from two deep boreholes were used: CM5 and CM6, which define a NW–SE cross-section approximately 9 km upstream from the mouth (Fig. 1).

The Iberian Pyrite Belt (IPB), through which the Guadiana runs, is one of the most important metallogenic provinces in the world, with original reserves of about 1700 million tonnes of sulphides (Sáez et al., 1999). In line with archaeological evidence, the extraction of minerals in the IPB started in the third millennium BC, and focused on the production of copper (Davis et al., 2000; Leblanc et al., 2000; Nocete et al., 2005). During the first millennium BC, silver was targeted. Silver and gold extraction developed on a larger