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Temporal evolution of lead isotope ratios in sediments of the Central Portuguese Margin: A fingerprint of human activities

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ABSTRACT

Stable Pb isotope ratios ($^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$), ^{210}Pb, Pb, Al, Ca, Fe, Mn and Si concentrations were measured in 7 sediment cores from the west coast of the Iberian Peninsula to assess the Pb contamination throughout the last 200 years. Independently of their locations, all cores are characterized by increasing Pb/Al rends not related to grain-size changes. Conversely, decreasing trends of $^{206}Pb/^{207}Pb$ were found towards the present. This tendency suggest a change in Pb sources reflecting an increased proportion derived from anthropogenic activities. The highest anthropogenic Pb inventories for sediments younger than 1950s were found in the two shallowest cores of Cascais and Lisboa submarine canyons, reflecting the proximity of the Tagus estuary. Lead isotope signatures also help demonstrate that sediments contaminated with Pb are not constrained to estuarine–coastal areas and upper parts of submarine canyons, but are also to transferred to a lesser extent to deeper parts of the Portuguese Margin.

1. Introduction

Marine sediments play an important role as a sink of particulate material supplied by coastal erosion, and riverine and atmospheric transport. These materials derive from both natural (biological and geological) sources and supplied from anthropogenic activities (Windom et al., 1989). The deposition of particles from both origins makes it difficult to identify and partition each individual source (Soto-Jimenez and Paez-Osuna, 2001). Depending on the existing environmental conditions, sediment particles can also act as a source for contaminants, which can be accumulated and biomagnified by organisms through the food web (Harada, 1995). The use of radioactive isotopes (e.g., ^{210}Pb, ^{137}Cs) coupled with variations in elemental concentrations allows reconstruction of the history of contamination through time, using undisturbed sediment cores (Valette-Silver, 1993), making them environmental archives for past conditions (e.g., Nriagu, 1979). Nevertheless, total Pb concentrations by itself do not correctly reflect contamination sources or their relative contributions, due to the large diversity of sources existing in the environment resulting from anthropogenic activities (e.g., mining, smelting, waste incineration, coal burning, leaded gasoline, leaded batteries, weapons) and natural sources (bedrocks, soils, hydrothermal activity) (e.g., Cheng and Hu, 2010).

The preservation of Pb isotopic signatures of the geological sources (e.g., during weathering, exploitation, industrial production and processing) makes stable Pb isotopes an efficient tool for the research of Pb contamination through the distinction between natural and anthropogenic sources (Harlavan et al., 2010), the identification of Pb sources (Bindler et al., 2001) and the reconstruction of Pb contamination history (Martínez Cortizas et al., 2012; Ritson et al., 1999). Lead (Pb) mainly occurs in the environment in four stable isotopes: ^{204}Pb, ^{208}Pb, ^{207}Pb, and ^{206}Pb. ^{204}Pb is the only primordial stable isotope, with low and approximately constant abundance (1%) on Earth, whereas the three others are derived from the radioactive decay of ^{232}Th, ^{235}U and ^{238}U, respectively (e.g., Komárek et al., 2008). The range of natural ^{208}Pb, ^{207}Pb and ^{206}Pb shows variations of 51.28–56.21%, 17.62–23.65% and 20.84–27.48%, respectively (Rosman and Taylor, 1998). The abundances of Pb isotopes co-vary strongly and depend on when the ore was formed (Cheng and Hu, 2010), not being affected by fractionation in natural and industrial processes, as for Hg (e.g., Jackson and Muir, 2012).

The intense mining activity during the Roman period was responsible for release of great amounts of heavy metals (e.g., Pb, Cu, Zn) into the environment, as a consequence of uncontrolled smelting (e.g., Nriagu, 1996). Additionally, the relative abundance

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of Pb ore deposits and the Pb occurrence within ores mined for other heavy metals, together with easy use of Pb to be smelted and refined, explains its long use by Man (Choi et al., 2007), making this metal a ubiquitous contaminant in the environment. The start of the Industrial Revolution brought an unprecedented demand of Pb (and other heavy metals) and an exponential increase of their emissions (Nriagu, 1996). The discovery of the antiknock property of organolead compounds in the beginning of the 20th century and its use by automobile industry lead to another significant increase in Pb consumption and emissions (Nriagu, 1990). During the peak use of leaded gasoline from the 1940s through the early 1980s, vehicle emissions became the predominant source of Pb to the environment throughout the world (e.g., Juracek and Ziegler, 2006). Modern awareness of the toxicity of Pb (e.g., Jarup, 2003) lead to the gradual ban of Pb additives in western countries during the mid-1970s (Nriagu, 1990). This diminution resulted in the increase of relative contributions of Pb associated with industries to the environment. According to Roma-Torres et al. (2007), the phasing out of leaded gasoline in Portugal happened gradually in the beginning of the 1990s, but was not completed before 1999.

To date, there have been few studies characterizing Pb isotopic ratios in sediments of the Iberian Margin. One of them was focused on the late Quaternary Pb isotope reconstructions of Mediterranean Outflow Water pathways (Stumpf et al., 2010) and another mainly focused on the spatial distribution of natural and anthropogenic Pb sources in surface sediments of the Nazaré and Lisboa–Setúbal submarine canyons (Richter et al., 2009).

The establishment of the first heavy industries along the Tagus shores occurred in the beginning of the 20th century, with the Barreiro chemical complex (pyrite roast plant, chemical and fertilizer industries and a smelter opened in 1961). A boom in production occurred between the forties and the seventies and the Soda Póvoa chloralkali plant stopped using Hg in their processing first in the 1980s. Since the middle of the eighties occurred the improvement of industrial and domestic effluent treatment and modification of the manufacturing processes of some industrial sources. The intense urban growth of the Lisboa and Setúbal areas (ca. 2.8 million inhabitants, 72%, in the Lisboa metropolitan area) occurred mainly between the sixties (1.5 million) and the eighties (2.5 million). The increase of population together with better financial conditions and the opening of one of the Tagus bridges in 1966 led to an increasing number of vehicles in the area.

The legacy of polymetallic contamination (including Pb) in sediments has been documented for the Tagus estuary (Canário et al., 2005; Caetano et al., 2007; Cobelo-García et al., 2011; Figuères et al., 1985; Sundby et al., 2005; Vale et al., 2008), adjacent shelf areas (Jouanneau et al., 1998; Mil-Homens et al., 2009), and submarine canyons and slope areas of the Portuguese Margin (Costa et al., 2011; Jesus et al., 2010; Mil-Homens et al., 2013; Richter et al., 2009). Previous studies (de Stigter et al., 2011; Jesus et al., 2010) considered present-day down-canyon transport through the Lisboa and Setúbal submarine canyons to be very limited, in contrast to their role as important sediment conduits during glacial periods.

The data presented in this article complement the results obtained in two previous studies (Costa et al., 2011; Mil-Homens et al., 2013). Costa et al. (2011) represented the first part of the study that intended to characterize both spatially and temporarily the grain-size and geochemical composition of sediments. The obtained results suggested that although canyons are preferential conduits to transport sediments to the deep sea when compared to the slopes, heavy metals (such as Hg, Pb and Zn) derived from human activities have reached both domains with different intensities down to a depth of 2000 m water depth (mwd). The spatial and temporal distributions of total Hg concentrations raised a set of questions that we have discussed using stable Hg isotopic ratios (Mil-Homens et al., 2013). The idea was to explore whether mass-dependent fractionation (MDF) and mass-independent fractionation (MIF) of Hg isotopes can be used for differentiating between distinct pathways (fluvial vs. atmospheric). The obtained results allowed us to distinguish between areas dominated by detrital (e.g., Cascais submarine canyon, CSC) vs. hemipelagic (Estremadura Spur) sedimentation, and to demonstrate anthropogenic Hg and Pb enrichment in recent marine sediments. By measuring stable Pb isotopic ratios ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$) in sediments covering different environmental settings of the Portuguese Central Margin (slope vs. canyon and shallow vs. deep canyon locations) the data obtained led to the hypothesis that distinct sources of Pb may be present in the slopes contrasting to submarine canyons. This study reports the Pb isotopic composition ($^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$) of seven short marine sediment cores, five of them collected from the CSC and Lisboa–Setúbal submarine canyon system. In these submarine canyons, sediments and associated contaminants from the Tagus and Sado estuaries are likely to accumulate. Another two cores were collected in areas dominated by hemipelagic sedimentation, the Estremadura Spur and Sines slope. Therefore, the main aim of this study is to use Pb concentrations and Pb isotopic ratios to reconstruct in detail the historical Pb contamination for the last 200 years, identifying possible sources of Pb deposited in marine sediments of the central Iberian Margin where the Tagus River (the second largest drainage area of the Iberian Peninsula with 81,351 km^2) is the main terrestrial pathway of suspended sediments and contaminants transport to the adjacent coastal area. An estimation of the Pb contribution derived from anthropogenic sources is also performed. The integration of stable Pb isotopic ratios with total Pb concentrations provides a better understanding of Pb accumulation in marine sediments on distinct areas of this sector of the Portuguese Central Margin.

2. Materials and methods

2.1. Sampling locations

The morphological and sedimentological aspects of the central western Portuguese Margin are described in detail in previous studies (Arzola et al., 2008; de Stigter et al., 2007, 2011). Briefly, the Estremadura spur, a protruding segment of the continental margin, is marked by the predominance of hemipelagic sediments as a result of limited terrigenous sediment supply, being separated from the narrower shelf and gentle slope of the southern sector of the margin by the Cascais (CSC), Lisboa (LSC) and Setúbal (SSC) submarine canyons. The CSC is the shortest and steepest submarine canyon of the Central Portuguese Margin. It is located NW of the LSC and SSC, being separated from them by a narrow spur, the Afonso Albuquerque Plateau. The LSC and SSC are two independent branches converging at 2000 mwd. The three SC terminate at the Tagus Abyssal Plain. The terrigenous supply is mainly dominated by the Tagus River. The present day mean annual discharge close to the river mouth in Lisboa is about 500 $m^3 s^{-1}$ (e.g., Benito et al., 2003). Secondary contributions come from the Sado River (present day mean annual discharge 40 $m^3 s^{-1}$ (e.g., Vale et al., 1993). Previous studies identified the accumulation of fine-grained materials (e.g., Tagus prodelta) in the shelf areas adjacent to both river mouths (Jouanneau et al., 1998; Mil-Homens et al., 2009). Additionally, the positioning of the CSC and LSC heads, at the southern limits of the Tagus prodelta, suggests that riverine particles reach these areas.

2.2. Sediment sampling

The seven short sediment cores investigated in this study were collected onboard RV Pelagia in 2002, 2003 and 2006 during