

## Alterações recentes nas razões isotópicas de Pb em sedimentos do Canhão Submarino de Cascais (Portugal)

### *Recent changes in lead isotopic signature in sediments of the Cascais Canyon (Portugal)*

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**Abstract:** Temporal variations in lead concentrations and stable lead isotopic ratios ( $^{206}\text{Pb}/^{207}\text{Pb}$ ,  $^{208}\text{Pb}/^{206}\text{Pb}$ ) in two sediment cores from the Cascais Canyon shows changes in sources of Pb during the last two centuries. The increase of total Pb contents with the evolution of  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio recorded in both cores reveals the increase of Pb from industrial sources. Nevertheless, this increase is lower in deeper core location (252-32) due to dilution and mixing with uncontaminated marine materials. An isotopic shift towards lower  $^{206}\text{Pb}/^{207}\text{Pb}$  in the shallower core (252-35) during the 1970s may reflect the increasing number of vehicles in the Lisboa area during that time.

**Palabras clave:** Margem Portuguesa, sedimentos marinhos, isótopos estáveis de chumbo, chumbo

**Key words:** Portuguese Margin, marine sediments, stable lead isotopes, lead

### 1. INTRODUCTION

Lead is one of the most spread contaminants with distinct multiple anthropogenic sources (combustion of alkyl-leaded gasoline, coal burning and ore smelting) that have been released in large amounts to the environment since the Roman times, having a new increment with the beginning of the Industrial Revolution. Lead has four stable isotopes:  $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$ , being the last three final end-members of the  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{232}\text{Th}$  decay chains. Anthropogenic Pb emissions are characterized by distinct Pb isotopic signatures, depending on the variety of lead ores used in the industry. The significant differences in the Pb isotopic composition between natural and anthropogenic sources together with large Pb anthropogenic contributions when compared to natural Pb emissions, makes both efficient tracers for anthropogenic influences in environmental studies (e.g. Gobeil *et al.* 1995, Ferrand *et al.* 1999, Ritson *et al.* 1999, Miralles *et al.* 2004, Miralles *et al.* 2006).

Submarine canyons are considered as pathways for transport and dispersal of both natural and contaminated materials from shelf areas to the deep

ocean (e.g. Mullenbach and Nittrouer, 2000, de Stigter *et al.* 2007, Palanques *et al.* 2008). In a recent work, Richter *et al.* (2009) studied the role of the Nazaré Canyon and the Setúbal-Lisboa canyons system in offshore contaminants dispersal, using Pb and stable Pb isotopes from surface sediments. They found an anthropogenic Pb signature in the Setúbal-Lisboa canyons system, consistent with the proximity of industrialized and populated areas (Tagus and Sado estuaries). Furthermore, an efficient transfer of contaminated sediments from both rivers to the adjacent shelf, builds here a preferential accumulation area, as documented in previous works (e.g. Jouanneau *et al.* 1998, Mil-Homens *et al.* 2009). The Cascais Canyon, is a short feature 70 km in length, also located in this shelf area. Due to its position, this submarine canyon represents an additional target to evaluate the role of canyons in carrying contaminated materials from the shelf to deeper areas of the Portuguese Margin. This will be achieved in the present work through the determination of total Pb concentrations and stable Pb isotopic ratios during the last 200 years in two short sediment cores from the Cascais Canyon.

## 2. MATERIALS AND METHODS

Two short sediment cores (252-32 and 252-35) were taken, among others, with a multicorer, along the axis of the Cascais Canyon, during the cruise CANYONS2006 onboard the RV Pelagia (Fig. 1), in 2006. Each core was split, described, cut in 1 cm thick slabs and refrigerated (ca. 4°C). After, sediment samples were freeze-dried, ground and homogenized.

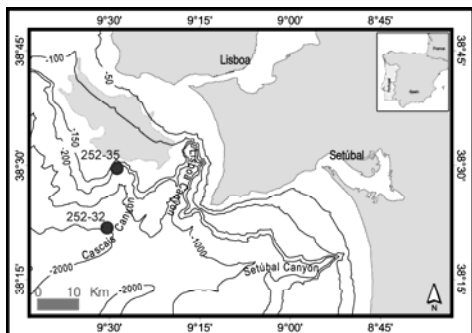


Fig. 1. Location of sites in the Cascais Canyon. The Tagus prodelta (in light grey) surface sediments fall within the class of lithoclastic mud with more than 90% of mud and less than 30% of  $\text{CaCO}_3$  (adapted from the Surface Sedimentary Chart of the Portuguese shelf between Roca and Sines capes, sheet number 5, published by the Portuguese Hydrographic Institute in 2005).

The age models were based on  $^{210}\text{Pb}$  measurements by  $\alpha$ -spectrometry in 12 samples per core. Sediment accumulation rates were determined using the model of Constant Flux and Constant Sedimentation Rate (CF/CS; Appleby and Oldfield, 1992) for core 252-32 and the model of Constant Flux and Constant Sedimentation Rate including a surface mixed layer (SML) on the top (CF/CS<sup>SML</sup>; Carpenter *et al.*, 1982) for core 252-35.

Lead and Li concentrations were measured respectively by Graphite Furnace Atomic Absorption Spectrometry (GFAAS) and Flame Atomic Absorption Spectrometry (FAAS), after total digestion of 0.25 g of grounded sample (< 2 mm) with a mixture of  $\text{HNO}_3$ , HF,  $\text{HClO}_4$  and HCl. Along the entire procedure blank reagent and CRM were carried out. Analytical precision expressed as RSD of 27 replicates of CRM MESS-3 (NRC Canada) was nominally lower than 9%. Bias was estimated comparing the CRM MESS-3 certified values with those obtained being, generally, lower than 4%.

Lead isotopes ( $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ ,  $^{208}\text{Pb}$ ) were determined according to the procedure described in Caetano *et al.* (2007), using a quadrupole ICP-MS X Series from Thermo Elemental equipped with a Peltier Impact bead spray chamber and a concentric Meinhard nebulizer. Briefly, sediment samples were digested with a mixture of 6 ml HF and 1 ml Acqua Regia in closed Teflon bombs at 100°C for 1 hour. Sample solutions were evaporated until near dryness in Teflon vials (DigiPrep HotBlock—SCP Science), redissolved with 1 ml of double-distilled  $\text{HNO}_3$  and

5 ml of Milli-Q water (18.2 M $\Omega$ ), heated for 20 min at 75 °C and diluted to 50 ml with Milli-Q water.

## 3. RESULTS AND DISCUSSION

### Chronology and accumulation rates

The studied cores present an exponential increase in  $^{210}\text{Pb}$  values towards the top. The  $^{210}\text{Pb}$  background ( $^{210}\text{Pb}_{\text{back}}$ ) was not reached in core 252-35. This, together with relatively high sediment accumulation rates (SAR) of  $0.40 \text{ g cm}^{-2} \text{ yr}^{-1}$ , may reflect the proximity of this core to the shelf fine-grained deposit known as the Tagus prodelta. The bottom of the core reaches an age of AD 1940. The relatively lower SAR ( $0.06 \text{ g cm}^{-2} \text{ yr}^{-1}$ ) obtained in core 252-32 indicates a minor input of particles to this section of the Cascais Canyon, practically inactive in terms of sedimentation. Despite the age of bottom samples for core 252-32 over the limit of  $^{210}\text{Pb}$  chronology (about 150 years) and the occurrence of an increase in sand contents in sediments at depths from 29 to 34 cm, it is assumed a constant sedimentation rate along the 1850's.

### Temporal variations of Pb concentrations and Pb/Li ratios

Lead concentrations were similar in both cores (Fig. 2a), with a continuous increase trend towards the surface (Fig. 2a). Core 252-35, however, presents same oscillation compared to core 252-32.

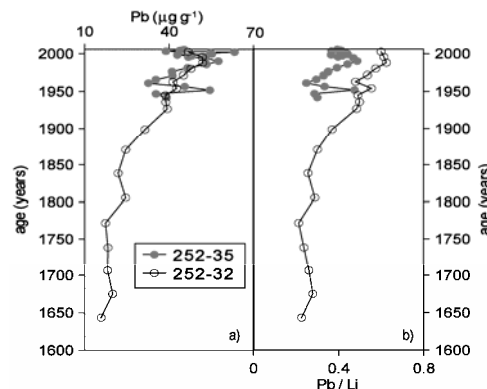


Fig. 2. Vertical profiles of Pb concentrations (a) and Pb ratios to Li in the studied cores (b). The geochronology for each core is derived from  $^{210}\text{Pb}$ .

With the goal of compensating for effects of grain-size variability, the total Pb contents were normalised against Li which is often used as a proxy for grain size (Loring, 1990). Thus, after Li-normalisation, Pb has an increasing up-core trend in both cores not associated with sediment texture (Fig. 2b), but probably resulting from contaminated sediments transferred from the Tagus Estuary to the adjacent shelf area. The slight Pb enrichment at 1950 AD is also observed by Mil-Homens *et al.* (2009) in cores from the Tagus Prodelt revealing an extension of contamination through the canyon to deeper parts of the ocean.

### Pb isotopic compositions

In core 252-32,  $^{206}\text{Pb}/^{207}\text{Pb}$  isotope ratios show a clear trend from more radiogenic values older than AD 1850 decreasing progressively until AD 1970, and remaining stable to the Present-day. AD 1850 sets a date for the onset of industrial-sourced Pb, with low  $^{206}\text{Pb}/^{207}\text{Pb}$  isotope ratios (Fig. 3a). Core 252-35 exhibits lower  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios (i.e. more contaminated) than in core 252-32, since AD 1975, which is attributed to low efficiency in transport of contaminants to depth and/or dilution by more radiogenic and uncontaminated sediments, at least (Fig. 3b). AD 1975 corresponds to a sharp increase in the usage of vehicles in Portugal and consequent input of less radiogenic Pb from gasoline additives (close-up in Fig. 3a). Higher-resolution analyses at core 252-35, allow to detect a slight reversal of the long-term decreasing trend in isotopic ratios after 1990AD, coincident with the gradual phase-out of leaded gasoline that was completely eliminated in 1999 (Roma-Torres *et al.*, 2007) and with political legislation to decrease industrial emissions (e.g. coal combustion).

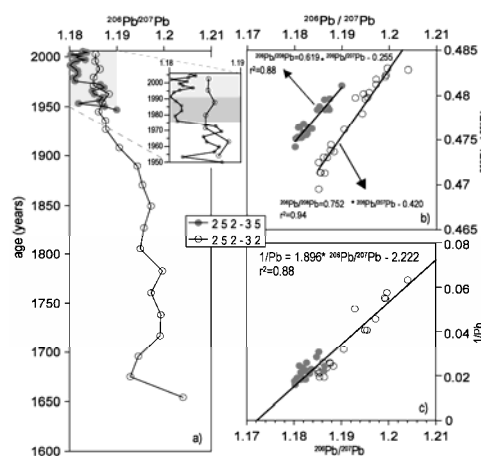


Fig. 3. Variations of Pb isotopic ratios ( $^{206}\text{Pb}/^{207}\text{Pb}$ ) vs. approximate year of sedimentation (a), three isotope plot for cores 252-32 and 252-35 (b) and  $^{206}\text{Pb}/^{207}\text{Pb}$  vs. inverse of Pb concentrations ( $1/\text{Pb}$ ) (c).

The isotopic signatures obtained in both cores suggest binary mixing between natural and anthropogenic Pb isotopic end members (Fig. 3b and Fig. 3c). Nevertheless, distinct mixing lines are observed for each core.

From the plot of  $^{206}\text{Pb}/^{207}\text{Pb}$  versus inverse of Pb ( $1/\text{Pb}$ ) it is observed a strong relationship (Fig. 3c). The intersection with x-axis gives the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio of Pb derived from anthropogenic sources (1.172). This value is more radiogenic than the results obtained by Richter *et al.* (2009) in sediments from the Nazaré, Lisboa and Setúbal canyons ( $(^{206}\text{Pb}/^{207}\text{Pb})_{\text{ant}}=1.143$ ) and by Caetano *et al.* (2007) inside the Tagus Estuary. Moreover, ratios are relatively higher than the isotopic signature of atmospheric Pb in aerosols collected in the last decade in Western Europe (Veron *et al.*, 1999;

Bollhofer and Rosman, 2001), suggesting the mixture of high radiogenic background Pb and low radiogenic contaminant Pb emissions of alkyllead gasoline (1.06-1.09; Gobeil *et al.*, 2001).

The average  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios for sediments older than AD 1800 is 1.1990, which is slightly less radiogenic than the value of 1.2050 obtained by Richter *et al.* (2009) for deep levels (prior AD 1000) of piston core 204-31 (38°22'N; 9°20.5'W) collected in the Lisbon Canyon at 1710 mwd. The difference between the two values indicates that core 252-32 (except for the bottom sample) does not reach the natural background Pb ( $(^{206}\text{Pb}/^{207}\text{Pb})_{\text{back}}$ ), and suggests inputs of Pb enriched particles to the marine environment prior to the Industrial Revolution.

### Estimation of anthropogenic Pb in sediments

The estimation of the fraction of anthropogenic Pb ( $\% \text{Pb}_{\text{ant}}$ ) in each sample can be determined applying the formula and end-member values ( $(^{206}\text{Pb}/^{207}\text{Pb})_{\text{back}}=1.2050$  and  $(^{206}\text{Pb}/^{207}\text{Pb})_{\text{ant}}=1.143$ ) of Richter *et al.* (2009). The results show that core 252-35 has high percentage of Pb of anthropogenic origin in agreement with its proximity to the Tagus Estuary (Fig. 4). These values of  $\% \text{Pb}_{\text{ant}}$  are however approximately three times lower than those obtained by Sundby *et al.* (2005) in two salt marshes of the Tagus Estuary, possibly indicating a greater dilution by uncontaminated marine materials.

$$\% \text{Pb}_{\text{ant}} = \left[ \text{Pb} \right] \cdot \left( \frac{(^{206}\text{Pb}/^{207}\text{Pb})_{\text{back}} - (^{206}\text{Pb}/^{207}\text{Pb})_{\text{sample}}}{(^{206}\text{Pb}/^{207}\text{Pb})_{\text{back}} - (^{206}\text{Pb}/^{207}\text{Pb})_{\text{ant}}} \right)$$

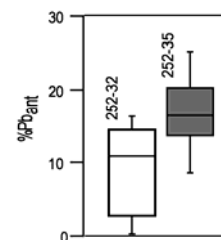


Fig. 4. Box-and-whisker plot representing the fraction of anthropogenic Pb ( $\% \text{Pb}_{\text{ant}}$ ). Box-and-whisker plots show the minimum, maximum, median, and lower and upper quartiles for a variable. The box represents the interquartile range that contains 50% of values. The whiskers are lines that extend from the box to the highest and lowest values. The line across the box indicates the median.

### 4. Conclusions

Despite the relatively low accumulation rates obtained in the deep core, Pb isotopic ratios validate the role of Cascais Canyon as a conduit of contaminated materials derived primarily from the Tagus Estuary to the Tagus Prodelta, and then flushed to deeper parts of the ocean. The decrease of the anthropogenic Pb fraction with water depth is explained by both the major distance to the source and also dilution and mixture with uncontaminated marine materials during sediment transport and deposition.

The small shift to less radiogenic Pb isotopic signatures from core 252-35 during mid 1970's until the beginning of the 1990's may indicate the augment of the consumption of leaded gasoline as a result of the increasing number of vehicles that happened in the Lisboa area at that time. After the 1990s, the Pb isotopic signature tends to increase possibly reflecting the use of unleaded gasoline.

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