

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

^{a,b}Mil-Homens M, ^bCaetano M, ^{a,c}Costa A M, ^dLebreiro S, ^eRichter T, ^ede Stigter H, ^fTrancoso M, ^eBoer W

Stable Pb isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$), ^{210}Pb , Pb and Li were measured in 7 short marine sediment cores (from N to S; 1 core at the Estremadura Spur, 2 cores at the Cascais Submarine Canyon, 3 cores at the Lisboa-Setúbal submarine canyon system and 1 core at the Sines transect) with the main goal of reconstructing Pb contributions in the last 150 years. Independently of their location, all studied cores are characterized by increasing Pb/Li trends that are not related to grain-size or mineralogical changes in opposition to decreasing trends of $^{206}\text{Pb}/^{207}\text{Pb}$ towards the Present. These trends suggest a change in Pb sources reflecting greater proportion associated with anthropogenic activities. ^{210}Pb -dated sediments older than 1850AD have a variable isotopic composition ($1.188 < ^{206}\text{Pb}/^{207}\text{Pb} < 1.204$) indicating some of these values are less radiogenic than the range proposed for natural end members[1] ($1.205 < ^{206}\text{Pb}/^{207}\text{Pb} < 1.232$), suggesting that natural background sediments were not reached. From

the $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $1/\text{Pb}$ plot, and extrapolating to $1/\text{Pb}=0$, the anthropogenic Pb end member can be represented by a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.174. This result suggests the importance of using Iberian Pyrite Belt ores by chemical plants (pyrite roast facility and metallurgical activities) around the Tagus estuary during the 20th century. These ores are characterized by more radiogenic $^{206}\text{Pb}/^{207}\text{Pb}$ ratios than other sources of anthropogenic lead (e.g. leaded gasoline). The isotopic signatures obtained in all cores suggest binary mixing between natural background and anthropogenic Pb isotopic end members. Assuming this, it is possible to estimate the percentage of anthropogenic Pb associated in each sample, considering the values of 1.174 and 1.205 (upper limit derived from the plot $^{206}\text{Pb}/^{207}\text{Pb}$ ratios vs. Pb, extrapolating to 0 $\mu\text{g.g}^{-1}$ of Pb) for the anthropogenic and natural end member $^{206}\text{Pb}/^{207}\text{Pb}$ ratios, respectively. The results indicate that the percentage of anthropogenic Pb in all studied cores increases towards the Present. The

fraction of anthropogenic Pb in sediments younger than 1950AD ranges between 50% and 70%, revealing the occurrence of anthropogenic Pb contamination. The highest values are obtained in the two shallowest cores of Cascais and Lisboa submarine canyons.

References

- [1] Richter, T.O., de Stigter, H.C., Boer, W., Jesus, C.C., van Weering, T.C.E., 2009. Dispersal of natural and anthropogenic lead through submarine canyons at the Portuguese margin. *Deep Sea Research Part I: Oceanographic Research Papers*, 56(1): 267-282.

^a Laboratório Nacional de Energia e Geologia, I.P., Unidade de Geologia Marinha, Estrada da Portela, Apartado 7586, 2610-999 Alfragide, Portugal (mario.milhomens@lneg.pt)

^b IPMA – Portuguese Institute of Sea and Atmosphere, Av. Brasília, 1449-006 Lisboa, Portugal

^c Laboratório de Arqueociências, IGESPAR, I.P. and LARC/CIBIO/INBIO, Rua da Bica do Marquês, n°2, 1300-087 Lisboa, Portugal

^d Geological and Mining Institute of Spain, OPI, Dept. of Geosciences Research and Prediction – Global Change, C/ Rios Rosas, 23, 28003, Madrid, Spain

^e NIOZ - Royal Netherlands Institute for Sea Research, Department of Marine Geology, P.O. Box 59, 1790 AB Den Burg, Texel, The Netherlands

^f Laboratório Nacional de Energia e Geologia, I.P., Laboratório de Biocombustíveis e Ambiente, Azinhaga dos Lameiros, 1649-038 Lisboa, Portugal