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A Baseline Study on Levels of Uranium, Thorium and Lead Isotope Ratios in Sediment from the Sebou Estuary in the North-West of Morocco

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Abstract

Inductively coupled plasma – quadruple mass spectrometry was used for determination of uranium and thorium concentrations and lead isotope compositions in surface deposits and a sediment core for the intertidal zone of the Sebou Estuary located in the northwestern Morocco. The results showed that U and Th concentrations were respectively in the ranges of 0.79 to 1.14 $\mu g.g^{-1}$ and 3.75 to 5.14 $\mu g.g^{-1}$, while the vertical distribution presented important fluctuations throughout the core. Lead isotope ratios ($^{208}Pb/^{204}Pb$, $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$) did not show any significant spatial variability along the covered area within the estuary, and the values found were characteristic of Pb generated mainly from natural sources. The data produced in this study were the first such data for sediment from the Sebou Estuary, and the results could be considered as baseline values for future environmental impact assessments.

1. Introduction

The Sebou catchment is the second largest basin in Morocco, draining 40000 km^2 and running some 600 km from its source at over 2800 m altitude in the middle Atlas Mountains to the Atlantic Ocean in the Northwest. On its way, it suffers from pollution from the cities due to domestic and industrial activities, and from the most important agricultural area (the Gharb coastal plain) to which it provides with irrigation water. Social and economic development is threatened by increasing deterioration of water quality which constitutes a major environmental issue. Domestic and industrial sewage from Fez city, located at some 160 km from the Sebou estuary, is directly discharged into the Sebou River. Several water quality studies have been conducted in this area and have demonstrated the presence of many toxic chemicals generated mainly by textile and tanneries activities [1, 2].

The sediment is an important compartment in estuarine environments since it represents a good indicator of the state of anthropogenic pollution of rivers and coastal habitats. The fine fraction of sediment particles acts as a sink of trace pollutants within such systems and a delayed source of these pollutants through adsorption/desorption and redissolution processes [3]. On the other hand, pollutant concentrations in water are constantly changing due to the mixing of seawater and river inputs under tidal dynamics [4]. Consequently, detection of pollution in this compartment results less representative than in sediment in which concentrations can also vary in time but with a rate much lesser than in water. For this reason, estuarine surface sediment has always been the physical compartment of choice in assessing pollution, while bottom cores are usually used for determining historical records of pollutants delivery to such important ecosystems. The Sebou Estuary has been recently the subject of a study to assess levels of metal concentrations and radionuclide activities in sediments [5], but no data are available for uranium and thorium concentrations in this coastal system. These radioelements are important for monitoring natural radioactivity and understanding their behaviour in such tidal environment. The origin of U and Th found in estuarine bed sediment is mainly due to weathering of terrestrial rocks, and their mobility and distribution depend on the chemical constituents of the surrounding aquatic environment [6].

Environmental contamination by Pb has several sources such as waste burning, combustion of fossil fuels, urban and industrial discharges. Three radiogenic stable isotopes of Pb are present in the environment, ^{206}Pb, ^{207}Pb and ^{208}Pb, being end-members of ^{238}U, ^{235}U and ^{232}Th decay chains, respectively, and one non-radiogenic isotope, ^{204}Pb. Lead isotope ratios have been extensively used in environmental studies as indicators of anthropogenic contribution to the Pb budget in the sediment [7, 8, 9,10].

The purpose of this study was to characterize for the first time the state of the environment in terms of U, Th and Pb concentrations and lead isotopic ratios in sediments from the Sebou Estuary. Another objective is the use of Pb isotopic fingerprints to determine the still unknown level of Pb pollution in the studied area. Inductively coupled plasma – quadruple mass spectrometry (ICP-QMS) was used in this work, being a powerful technique in multi-elemental analysis which offers high sensitivity and ultra-low background allowing to measure extremely small concentrations of elements in a large variety of matrices [11].

2. Materials and methods

2.1. Sampling and samples pre-treatment

A sediment core of 60 cm was retrieved in 2009 at low tide (the water depth was about 1 m) from the right bank of the Sebou Estuary using an Uwitec gravity corer of 10 cm internal diameter. Five surface samples were also collected at low tide from marginal areas. The sampling locations are shown in Figure 1. The sediment core was sectioned into 2 cm slices immediately after retrieval to avoid particles redistribution, and then transported to the laboratory for pre-treatment and conditioning prior to elemental analyses. Each one of the resulting sub-samples along with the surface samples were dried in an oven at a constant temperature of 65°C until constant weight.

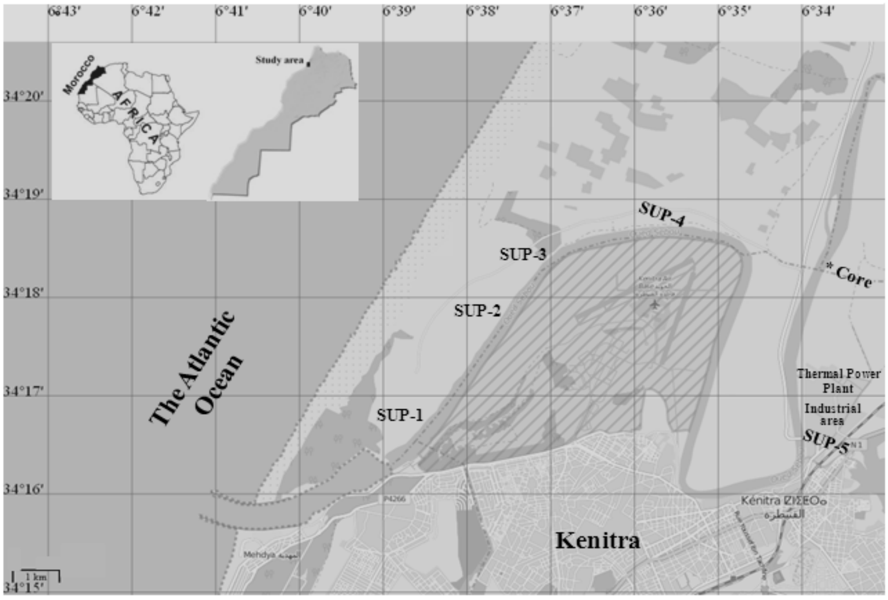

Figure 1: Map of the study area showing the sampling locations.

2.2. ICP-QMS measurements

Uranium, thorium and Pb-isotopic ratios were measured by ICP-QMS following microwave-assisted digestion. The digestion method was based in the U.S.E.P.A 3050 methodology (U.S.E.P.A, 1998), then modified by Hassan *et al.,* (2007) [12]. An aliquot of the sample was diluted in 1% HNO_3 until a final dilution factor of 3500 mL/g was achieved. The recovery of Pb using this methodology for the certified reference samples (IAEA SL-1, estuary sediment samples) was almost 100%.

An Agilent 7500c ICP-Quadrupole MS was used for Pb-isotopic ratio determination. The instrument is provided with an Octopole reaction system, which operated in He-mode at 3.5 mL/min. A conventional Babington nebuliser was used for multi-element analysis and the analytical running (three replicates per analysis) was performed according to the U.S.E.P.A. 200.8 protocol. Lead isotopic ratios were measured using the standard mode (no reaction gas) with a PFA micro-nebuliser after optimisation of the counting time for masses 206, 207 and 208 (five replicates per analysis). Lead concentration in the solutions was in the range of 5-10 ng/mL and the relative uncertainty (1-σ) was in the range of 0.3-0.5%. Two certified reference samples, NIST SRM-1646 and IAEA SL-1, a lake and an estuary sediment sample, respectively, were used for element recoveries determination and also to correct the Pb isotope ratios for mass bias [13].

3. Results and discussion

Uranium, thorium, lead concentrations and lead isotope ratios in surface samples collected along the Sebou Estuary are presented in Table 1. These are to our knowledge the first such data for sediment from this estuary, and the results could be considered as baseline values for future assessment studies. The mean concentrations of uranium and thorium were respectively 0.91 and 4.34 $\mu g.g^{-1}$ with the highest values recorded in the location Sup-3, being generally similar to the mean worldwide concentrations reported for non-contaminated sediments [14]. Uranium concentrations were lower than Th concentrations in each sediment sample and the ratios Th/U were fairly constant. It is well documented in the scientific literature that uranium is much more soluble than thorium in estuarine waters, since the distribution coefficient, k_d, of Th is greater by four order of magnitude than that of U [15]. Consequently, they exhibit different geochemical behaviour in estuarine systems. Indeed, U is much less adsorbed onto surface particles than Th which is practically transported with tidal currents in the particulate form. Nevertheless, some parameters such as Eh and pH conditions, HCO_3^- availability, iron hydroxides, organic matter and uranyl-carbonate are the main factors influencing uranium concentrations and migration in estuarine waters [16, 17].

Table 1: Concentrations of Th, U, Pb-isotopic ratios and Pb concentrations in surface sediment samples collected along the Sebou Estuary.

	U ($\mu g.g^{-1}$)	Th ($\mu g.g^{-1}$)	Th/U	$^{208}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	Pb ($\mu g.g^{-1}$)
SUP-1	0.79	3.75	4.75	38.52	1.19	2.47	19.61
SUP-2	0.86	4.86	5.65	38.55	1.19	2.47	16.96
SUP-3	1.14	5.14	4.51	38.88	1.19	2.47	19.14
SUP-4	0.93	4.1	4.41	38.32	1.18	2.47	24.91
SUP-5	0.82	3.85	4.69	38.33	1.19	2.48	14.85
min	*0.79*	*3.75*	*4.41*	*38.32*	*1.182*	*2.468*	*14.85*
max	*1.14*	*5.14*	*5.65*	*38.88*	*1.189*	*2.476*	*24.91*
mean	*0.91*	*4.34*	*4.80*	*38.52*	*1.187*	*2.473*	*19.09*
StDev[*]	*0.14*	*0.62*	*0.49*	*0.23*	*0.003*	*0.003*	*3.76*

[*] *Standard Deviation*

Only slight spatial variation was observed for both U and Th concentrations in samples collected from intermediate zones along the study area, the only exception being the highest concentrations for both elements in the sample SUP-3. Th/U ratios were ranging from 4.41 to 5.65 suggesting that the deposited sediment in the Sebou Estuary has its origin from the continental area. Indeed, values between 3.5 and 4 were reported for upper continental crust [18], while ratios higher than 4 suggest intense weathering. This is in good agreement with the fact that the samples were collected after a flooding event which resulted in massive inputs of particles from the surrounding area to the Estuary. Furthermore, in estuarine systems, large U and Th fractions are usually found associated to heavy minerals, such as zirconite and monazite, which are quite insoluble, and Th/U ratios in these minerals are higher than 1.

Figure 2 depicts concentration profiles of U and Th in the sediment core. Thorium vertical distribution presented important fluctuations with depth and several maxima and minima. Thorium concentrations increase slightly in the first 6 cm, decrease substantially to a peak of minimal concentration at 23 cm, and then increase. Thereafter, concentrations oscillate till the bottom within a relatively narrow range between 4.2 and 5.17 $\mu g.g^{-1}$. On the other hand, U presented large variations throughout the core, as shown in the corresponding profile plotted in Figure 2, with a concentration of 6 $\mu g.g^{-1}$ in the upmost layer, which decreased until 20 cm depth to reach values less than the limit of detection of the equipment used (some $ng.g^{-1}$) between 20 and 40 cm. The deficiency of uranium in these layers could be interpreted by the fact that post-depositional desorption and/or redissolution of U minerals, in particular uranyl carbonate minerals, had taken place within the sediment core. Thus, the downward diffusive fluxes of U in sedimentary layers have resulted in a highest concentration (more than 7 $\mu g.g^{-1}$) at 40 cm depth, beneath which concentrations decreased substantially downcore to reach values of the order of 1 – 2 $\mu g.g^{-1}$. This behaviour has already been reported in the scientific literature in similar environments

[19, 20]. Concentration values of both U and Th over the core were similar to those found in non-contaminated coastal ecosystems, indicating that the anthropogenic component was negligible in the sediment matrix. The worldwide averaged values are 2.83 $\mu g.g^{-1}$ and 7.4 $\mu g.g^{-1}$ for U and Th, respectively [14].

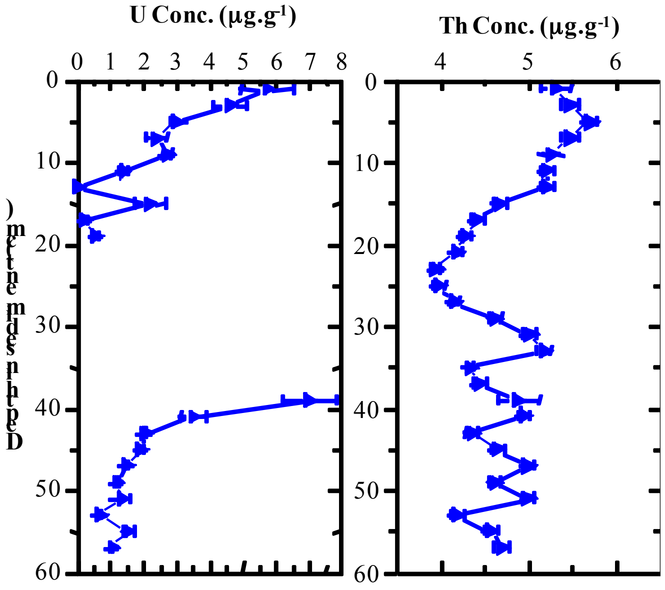

Figure 2: Depth profiles of Th and U concentrations throughout the core collected from the Sebou Estuary. The Y axes correspond to the depth in sediment; 0 cm is the top of the vertical core.

Lead isotope ratios ($^{208}Pb/^{204}Pb$, $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$) and total Pb concentrations measured in surface samples are given in Table 1. Although Pb concentrations exhibited some fluctuations, ranging from 14.85 to 24.91 $\mu g.g^{-1}$ (Table 1, *Stdev* = 3.76), lead isotopic compositions did not show any significant spatial variability along the covered area within the estuary ($^{208}Pb/^{204}Pb$: 38.32 - 38.88, $^{206}Pb/^{207}Pb$: 1.182 - 1.189 and $^{208}Pb/^{207}Pb$: 2.468 - 2.476). This implies that the sediment particles deposited over the studied area have the same origin, and/or the mixing processes induced by tidal dynamics within the estuary have resulted in homogenous distribution of lead isotopes.

Lead concentrations exhibited some spatial variability throughout the study area. The mean value was 19.09 $\mu g.g^{-1}$, with a standard deviation of 3.76, while the earth's crust concentration is 17 $\mu g.g^{-1}$ [21]. It is worth noting that this value is only a crude reference level and, therefore, it would be speculative to conclude whether the values found higher than 17 $\mu g.g^{-1}$ are quantitatively indicative of anthropogenic Pb inputs in the Sebou Estuary. On the other hand, the ratio $^{206}Pb/^{207}Pb$ is widely used to establish the contribution of anthropogenic Pb because of the high accuracy in the analytical measurement of this ratio, and its low sensitivity to changes in the mineralogical composition of the sediment [22]. The values found in this work were around 1.18, while the characteristic $^{206}Pb/^{207}Pb$ ratio associated to Pb generated mainly from natural sources is 1.2 [23]. Therefore, the contribution of anthropogenic input pathways of lead to the sediment, such as leaded gasoline and metal industries, should be minimal in the Sebou Estuary at time of sampling.

In Figure 3 are plotted the vertical distributions of lead isotopic compositions of the sediment core. The $^{208}Pb/^{204}Pb$, $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ranged from 37.85 to 39.23, 1.181 to 1.196 and 2.459 to 2.491, respectively. The values found were similar to background levels reported in the scientific literature [24, 25, 26]. The value of $^{206}Pb/^{207}Pb$ characteristic of natural sources is around 1.22, and this value decreases as the proportion of the anthropogenic component increases in the sediment. The range of variation of this ratio was found in this work close enough to the background value. In addition, the positively correlated relationships between $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ and between $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ (Figure 4) are indicative of the substantial predominance of natural over anthropogenic Pb [27].

The three profiles plotted in Figure 3 were fairly uniform and did not present marked variations throughout the core, within the error ranges, with the exception of the presence of some weakly pronounced peaks of maximal or minimal values. This suggests the absence of noticeable changes of environmental conditions during the time of sediment deposition in the studied area. Nevertheless, it is worth noting that the sampling campaign was carried out following a flooding event, which had produced massive transport and sedimentation of eroded particles within the Estuary [6].

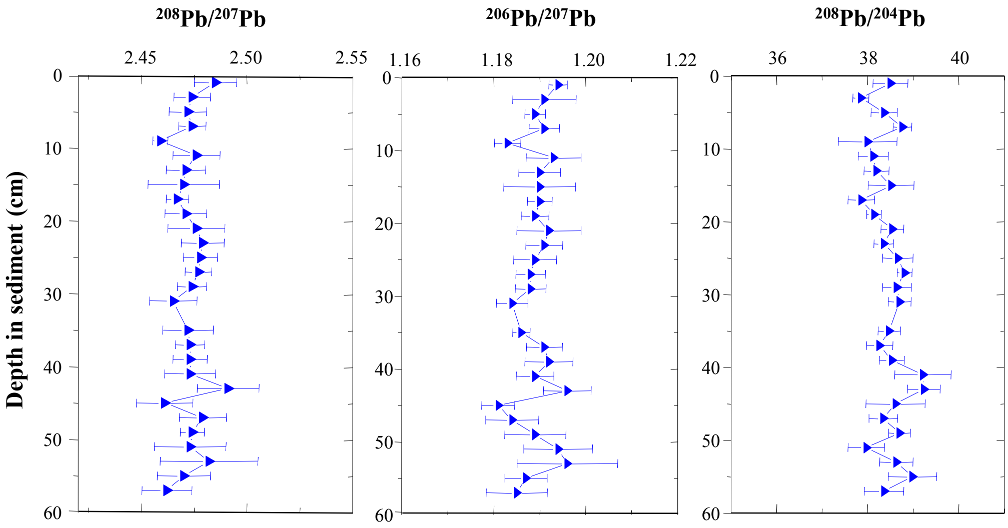

Figure 3: Vertical distributions of lead isotopic compositions in the sediment core collected from the Sebou Estuary. The Y axes correspond to the depth in sediment; 0 cm is the top of the vertical core.

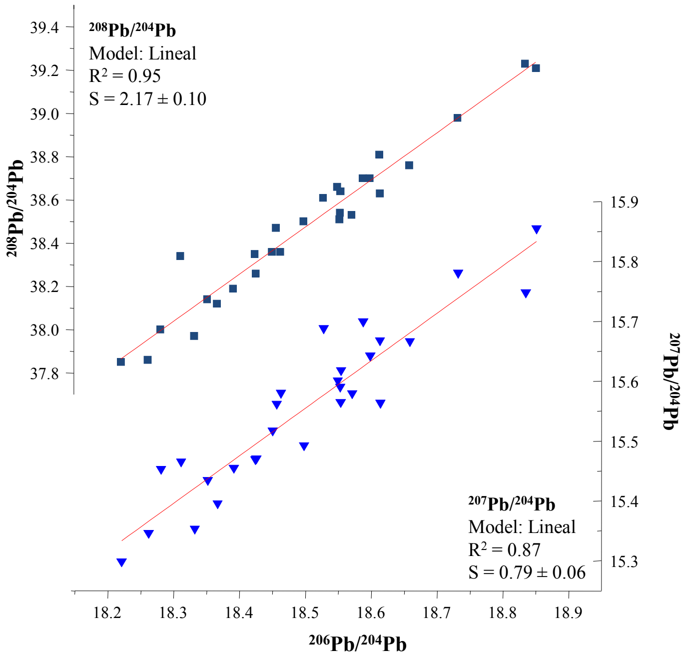

Figure 4: Diagrams of ^{208}Pb/^{204}Pb vs ^{206}Pb/^{204}Pb and ^{207}Pb/^{204}Pb vs ^{206}Pb/^{204}Pb in the sediment core collected from Sebou Estuary. The lines are the best fitting to lineal functions. S is the slope of the linear regression line.

Conclusion

Concentrations of U and Th and Pb-isotopic ratios were assessed for the first time in intertidal surface deposits and a 60 cm sediment core collected from the Sebou Estuary. Concentrations of U and Th were in the range of those reported for non-contaminated sediment, and their vertical distribution presented important fluctuations throughout the core, particularly for U which was attributable to diffusion and redissolution processes. Th/U ratios, being close to those reported for the upper continental crust, suggested that the deposited sediment in the Sebou Estuary has its origin from the continental area. On the other hand, Pb-isotopic ratios and the high correlation found between ^{206}Pb/^{204}Pb and ^{208}Pb/^{204}Pb and between ^{206}Pb/^{204}Pb and ^{207}Pb/^{204}Pb were indicative of the substantial predominance of natural over anthropogenic Pb.

The data produced in this work, being the first such a data, could be referred as a baseline study as it provides background levels of U, Th and Pb-isotopic ratios, against which any future changes due to anthropogenic activities can be assessed.

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References

1. B. Koukal, J. Dominik, D.Vignati, P. Arpagaus, S. Santiago, B. Ouddane, et al., *J. Environ. Pollut.* 131 (2004) 163.
2. L. Giorgetti, H. Talouizte, M. Merzouki, L. Caltavuturo, C. Geri, S. Frassinetti, *Ecotoxicol. Environ. Saf.* 74 (2011) 2275.
3. A. Laissaoui, R. El Mrabet, *Book chapter: Environmental Modelling: New Research. Ed. Paul N. Findley.* (2008) 101-117.
4. M. Ramdani, A. F. Taybi, Y. Mabrouki, B. Haloui, O. El Asri, H. Elmsellem, N. El Khiati, M. Mostareh, Mor. J. Chem. 5 (2) (2017) 227.
5. A. Laissaoui , J.L. Mas, S. Hurtado, N. Ziad, M. Villa, M. Benmansour, *Environ. Monit. Assess*. 185 (2013) 5019.
6. J. Viers, B. Dupre, J. Gaillardet, *Sci. Total Environ.* 407 (2009) 853-868.
7. P.I. Ritson, R.M. Bouse, A.R. Flegal, S.N. Luoma, *Marine Chem.* 64 (1999) 71.
8. G.X. Sun, X.J. Wang, Q.H. Hu, *Environ. Pollut.* 159 (2011) 3406.
9. I.S. Sen, M. Bizimis, S.N. Tripathi, D. Paul, *Atmos. Environ.* 129 (2016) 27.
10. J.K. Park, M.S. Choi, Y. Song, D.I. Lim, *Ocean Sci. J.* 52(2) (2017) 177–192.
11. M.A. AlQutob, H. Shqair, H. Malassa, J.M. Davis , F. Al-Rimawi, J. Mater. Environ. Sci. 7 (9) (2016) 3477.
12. N.M. Hassan, P.E. Rasmussen, E. Dabek-Zlotorzynska, V. Celo, H. Chen, *Water Air Soil Pollut.* 178 (2007) 323.
13. Y. Yip, J. Chung-wah Lamb, W. Tong, *Trends Anal. Chem*. 27 (2008) 460.
14. *UNSCEAR Sources and Effects of Ionizing Radiation. Report to General Assembly, with Scientific Annexes, United Nations, New York* (2000).
15. *International Atomic Energy Agency Technical Reports Series ISSN* 422 (2004) 0074–1914.
16. M.T. Rosing, R. Frei, *Earth Planet. Sci. Lett.* 217 (2004) 237.
17. D. Gorman-Lewis, P.C. Burns, J.B. Fein, *J. Chem. Thermodyn.* 40 (2008) 335.
18. S.M. McLennan, S. Hemming, D.K. McDaniel, G.N. Hanson, M.J. Johnsson, A. Basu, *eds. Geol. Soc. Amer. Spec.* 284 (1993) 21.
19. Y. Zheng, R.F. Anderson, A.V. Geen, M.Q. Fleisher, *Geochim Cosmochim Acta.* 66 (2002) 1759.
20. J.G. Catalano, J.P. McKinley, J.M. Zachara, S.C. Smith, G.E. Brown, *Environ. Sci. Technol.* 40 (2006) 2517.
21. R.L. Rudnick, S. Gao, Ed. R. L. *Rudnick Elsevier 3* (2003) 64.
22. V. Roussiez, W. Ludwing, Probst J.L., Monaco A., *Environ. Pollut.* 138 (2005) 167.
23. J.M. Luck, D.B. Othman, *Chem. Geol.* 182 (2002) 443.
24. M.E. Kylander, D.J. Weiss, A. Martínez-Cortizas, B. Spiro, R. Garcia-Sanchez, B.J. Coles, *Earth Planet. Sci. Lett.* 240 (2005) 467.
25. M. Mil-Homens, C. Vale, P. Brito, F. Naughton, T. Drago, J. Raimundo, B. Anes, S. Schmidt, M. Caetano, *Sci. Total Environ*. 586 (2017) 473-484.
26. P. Álvarez-Iglesias, B. Rubio, J. Millos, *Sci. Total Environ.* 437 (2012) 22.
27. M. Caetano, C. Vale, B. Anes, J. Raimundo, T. Drago, S. Schimdt, M. Nogueira, A. Oliveira, R. Prego, *Deep Sea Res. Part II* 98 (2013) 24.

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