

Identification of different origins of Pb in a tailing deposit of an old Uranium mine (*Urgeiriça - Central Portugal*) and assess to environmental impact – Isotope evidence

Rui Santos^a and Tassinari, C. C. G^b.

^a Laboratório do LNEG, S. Mamede de Infesta, Rua da Amieira,
Apartado 1089, 4466-956 S. Mamede de Infesta, Portugal.

E-mail: rui.santos@ineti.pt; Fax: +351 229 514 040; Tel: +351 220 400 000

^b Centro de Pesquisas Geocronológicas do Instituto de Geociências da USP, Brasil

Pb isotope ratios and bulk metal concentrations, both determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), have been used to identify different sources for Pb present in a huge (5Mton) tailing deposit and to assess to water environmental impact from an abandoned Uranium mining in the Central Region of Portugal. To carry out this research, samples from 10 core drill holes in the tailing deposit were collected. In 7 areas surrounding the mine site samples were collected to characterize the regional rocks background, which was defined as being of 28 ± 1 ppb for Pb bulk concentration, ratios of $1,264 \pm 0,001$ for $^{206}\text{Pb}/^{207}\text{Pb}$ and of $1,962 \pm 0,003$ for $^{208}\text{Pb}/^{206}\text{Pb}$. In order to understand Pb isotope distribution inside the mine dump, simple mixing/mass balance models were used to fit experimental data, involving: (i) background component as defined above; (ii) Uranium ores (Pitchblende) characterized by $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of $1,914 \pm 0,003$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of $1,235 \pm 0,002$ and (iii) an unknown Pb source (*Fonte 5*) characterized by $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of $3,079 \pm 0,007$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of $0,715 \pm 0,001$. This unknown source that shows higher radiogenic ratios, also found in water analysis from monitoring water drill hole located in a very specific position in the dump, is probably related with residues from other uranium mines in the region, exploited in the past and transported to *Urgeiriça* mine for chemical processing. Model application to the available data points made possible to describe the overall deposition system, in terms of isotopic characterization, as 69% from background source (regional granites and ore body host rocks), 25% from Uranium minerals (Pitchblende) and only 6% from material came from other Uranium mines in the region. These figures, that seem to be compatible with the mining history in the region, were used in this paper to show in what extent a Quadrupole ICP-MS can supply isotopic data enough accurate for Pb origin identification as tracer for environmental control. The second goal of this study was to assess the environmental impacts on the surroundings. There were collected 16 well water samples around the tailing deposit and along the principal watercourse (*Rib.ª da Pantanha*) that represent the principal way of pollution dispersion along 4 km. The Pb isotopic data reveals that the pollution was concerned only in the beginning of the stream and not on the surroundings. However, the Uranium content found reveal that the pollution was more extent in the stream, concerned to the distinct chemical behavior of these two metals in water.

1. INTRODUCTION

Pb is considered one of the most common contaminants for ecosystems. However, the knowledge of the concentration of this element by itself does not supply enough evidence of its probable anthropogenic origin, since natural processes can equally increase the appearance of local high Pb concentrations. Correct identification of Pb sources and paths in the environment is a prerequisite for designing any corrective action for land recovery and rehabilitation. The important potential of Pb isotopes for this purpose acting as fingerprint, has been recognized for some decades (Chow and Johnstone, 1965). Such affirmation is sustained by the premise that the Pb will show isotope ratios significantly different according to its provenience – natural or anthropogenic – age and geochemistry, because the abundance of Pb different isotopes results from the radioactive decline of isotopic ^{238}U , ^{235}U and ^{232}Th to ^{206}Pb , ^{207}Pb and ^{208}Pb , respectively, throughout the geologic time. The isotope ^{204}Pb does not have radiogenic behavior and so, its abundance has remained constant since the beginning of the Earth formation.

Pb isotope signature has been applied with undeniable success in the identification of Pb sources in diversified areas. The information obtained from isotope ratios is more valuable than the bulk concentration of this element, a Pb isotope ratios are able to vary in a significant way according to natural processes (Helland, et al., 2002) and to the fact that isotope abundances of Pb are not affected for any physical or chemical process in the terrestrial environment.

Innumerable works using Pb isotope ratios have been published in many applications, such as atmospheric aerosols (Faure, 1986; Sturges and Barrie, 1987; Erel et al., 1997; Monna et al., 1997; Mukai et al., 2001; Simonetti et al., 2004), gasoline (Lord, 1994; Hurst, 2000; Åberg et al., 2001), natural and saline waters (Miyazaki and Reimer, 1993; Halicz et al., 1994; Barrett et al., 1999; Murphy and Hall, 2000; Roy and Négrel, 2001; Benkhedda et al., 2004; Cheng and Foland, 2005), soils (Bjørlykke et al., 1993; Munksgaard and Parry, 1998; Monna et al., 2000a; Probaska et al., 2000; Teutsch et al., 2001; Emmanuel and Erel, 2002; Kaste et al., 2003; Ettler et al., 2004; Haack et al., 2004; Moura et al., 2004), sediments (Chiaradia et al., 1997; Munksgaard et al., 1998; Kawamura et al., 1999; Monna et al., 1999; Monna et al., 2000b; Bindler et al., 2001; Erel et al., 2001; Munksgaard et al., 2003; Ettler et al., 2006; Gioia et al., 2006), digested samples (Cumming and Richards, 1975; Wiedenbeck et al., 1995) and inks (Chiaradia et al., 1997a; Chiaradia et al., 1997b; Gulson et al., 1997). These studies constitute mere examples of the ample diffusion and great evidence of the use of Pb isotope ratios as tracer for environmental purposes. Isotopic studies in abandoned mines areas are still important to study and prevent dispersion of metal contamination in the environmental.

The Portuguese National Uranium Enterprise (ENU) has had been exploiting Uranium in the *Urgeiriça* mine since 1912 until late nineties, along with other mines in the region, like Quinta do Bispo and Cunha Baixa. All chemical treatments were processed in the *Urgeiriça* Chemical Plant. In result of the mining activities about 5 Mton of residues are currently deposited in tailing deposit next to the old mines (Exmin, 2001). These geological waste materials, frequently with significant contents of dangerous chemical products, as well as radioactive elements, are exposed to external geodynamic processes that promote the transference of these elements to different environmental compartments.

Therefore, this area is considered an important pollution focus where new strategies of analysis, like Pb isotope characterization will be able to supply new, accurate and useful information.

The present study aims to complement earlier works by using Pb isotope data since they can be used as an indicator of anthropogenic contribution in the *Urgeiriça* mine and more particularly to investigate the impact of his tailing deposit on the surrounding environmental.

2. GEOLOGICAL SETTING

The Old *Urgeiriça's* mine is located in central part of mainland Portugal, near to the city of Nelas. The region compresses granites and other rocks (Fig. 1), and is integrated into the so-called Região Uranífera das Beiras (Junta de Energia Nuclear, 1968), which occupies an area of around 10,000 km². Inserts an approximate quota area, 400 m, which rises slightly flattened to the East and is deeply torn by the docked valleys of Mondego and Dão rivers, NE-SW. In this flattened region, the Serra da Estrela and Serra do Caramulo horsts made part of the Iberian Meseta.

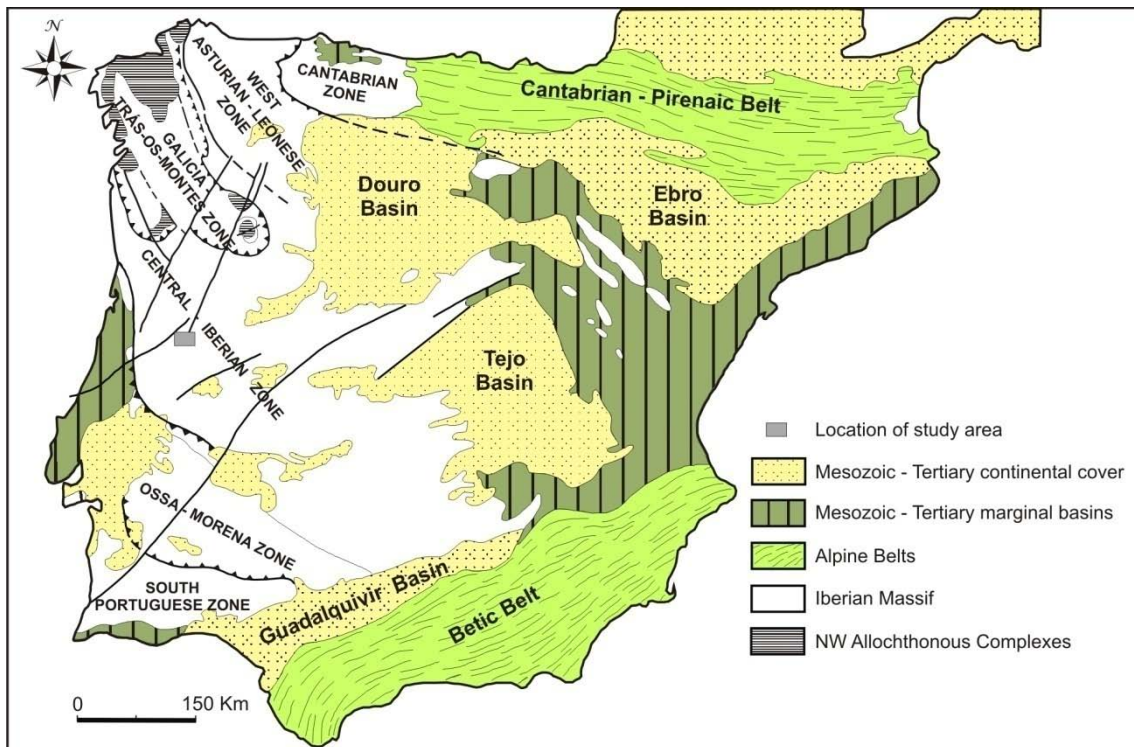


Fig. 1: Location of *Urgeiriça* Mine in the Iberian geological context according to Julivert (Julivert, 1974), modified by Farias (Farias et al., 1987) and Pereira (Pereira, 1987).

3. MATERIALS AND METHODS

3.1. Study area and sampling

The Fig. 2 shows a map of the mining site, where the tailing deposit is well seen (detail c). Ores exploited in *Urgeiriça*, or transported from other mines in the region, were ground at fine sizes in order to allow the operation of leaching processes for uranium recovery. The tailings dump is constituted by very fine sand (below 1 mm) reject by that treatment. Historical records also indicate that a few tons of high-grade uranium ore, not milled yet, are still deposited nearby the mine facility (Pereira, 2004).

For water monitoring purposes, the enterprise made a set of 10 vertical core drills crossing the tailing deposit until the bedrock – Fig. 2c shows the locations of these cores.

For the purpose of this research, in what concerns to the Pb distribution inside the tailing deposit, our team was allowed to collect solid samples from each core at different depths as well as one water sample by core hole. All this samples were analyzed for chemistry and for Pb isotope characterization. All data from chemical analysis were projected according to their depth inside the dump. For Pb isotope characterization of the tailing deposit, regional and local possible Pb sources were identified at first.

For environmental purpose were collected 16 well water samples around the tailing deposit and along the principal watercourse (Rib.^a da Pantanha). The well depths vary between 5 to 100 meters.

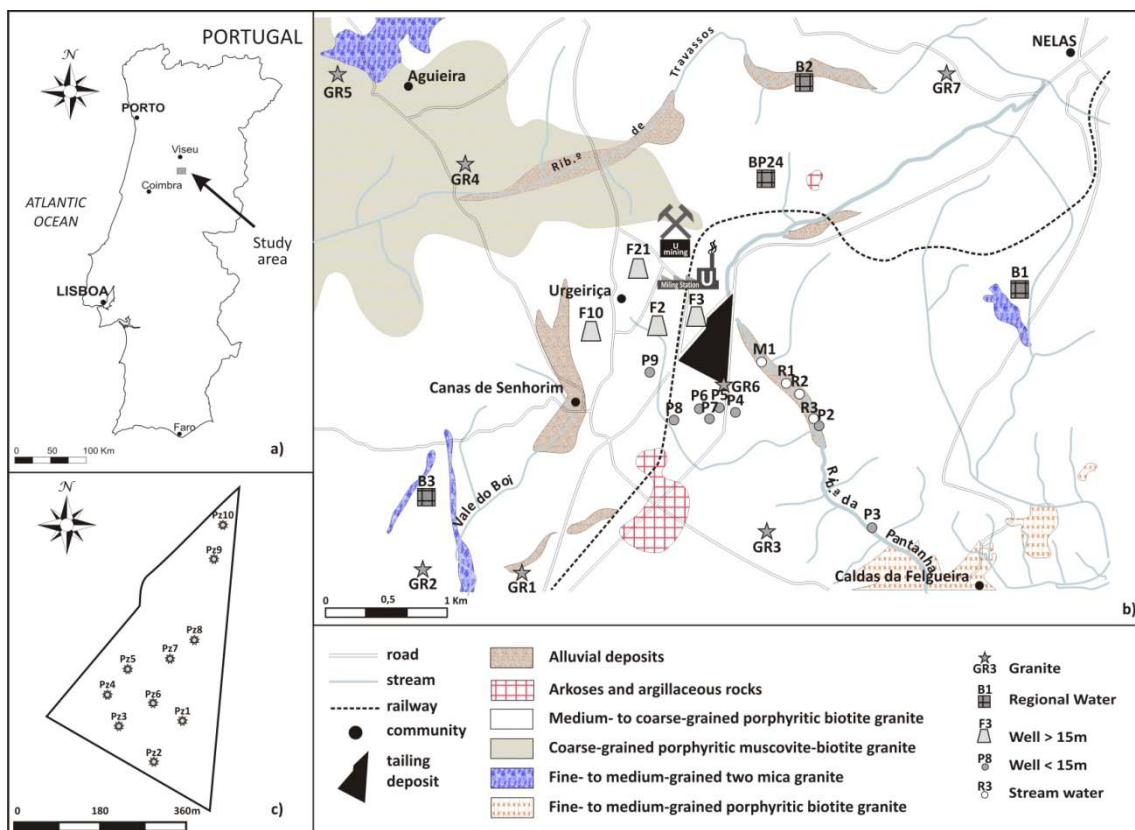


Fig. 2: Location of the study area: a) *Urgeiriça* Mine in the Central Region of Portugal; b) Detail of the study area showing all collected samples; c) Detail of 10 core drills in the tailing deposit.

For background Pb geogenic characterization seven regional rocks (Granites) were geologically surveyed and sampled for 3 Kg sample each. For Uranium minerals (Pitchblende, Autunite, Torbernite and other secondary minerals) and Galena characterization, about 500 mg of sample were collected from the INETI Laboratory Museum in São Mamede de Infesta, where *Urgeiriça* Mine is well represented. All samples were finely ground in an agate mortar to about 100% below 200 mesh.

All water samples were collected to 1,5 L PET bottles for chemical and Pb isotope determination. These samples were filtrated through a membrane (hydrophilic polyether sulfone) of 0,1 μm porosity (Acrodisc filters from Pall Corporation) and preserved with HNO_3 at 2% (v/v). The filtered water cores deposit was preserved for posterior Pb metal and isotope ratios analysis.

3.2. Samples Preparation

To dissolve the solid samples a tri-acid attack in a Teflon reactor were used 00 mg of sample was weighed (previously ground to 200 mesh and dried at 105 $^{\circ}\text{C}$); 5 mL of acid HNO_3 ultrapure and 2 mL of HF p.a. plus concentrated had been added; the Teflon reactor was closed and heated at 170 $^{\circ}\text{C}$ during 24 hours in a bath of sand. After this period, the acid solution was evaporated until dryness at 80 $^{\circ}\text{C}$. Then, 3 mL of HCl had been added; again the Teflon reactor was closed and placed during a second period of 24 hours in bath of sand at 150 $^{\circ}\text{C}$. After this second period of time, it was evaporated until dryness at 80 $^{\circ}\text{C}$. The residue was retaken with 1 mL of HCl and 1 mL of HNO_3 and quantitatively transferred to polypropylene pipe of high density with ultrapure water. The final volume of 50 mL was filled with ultrapure water.

Finally, a 25 ppm standard solution of certified Pb isotope ratios were also prepared from NBS 981 isotope Pb standard from NIST using ultra pure HNO_3 obtained by double sub-boiling distillation in a Duopor system (Milestone) and deionized water produced by a Milli-Q Elemental system (Millipore), with resistivity better than 18 $\text{M}\Omega\ \text{cm}$.

3.3. Analytical procedure

All samples were analyzed for 35 metals. However, for easily interpretation only Pb and Uranium compositions are represented (Table 1). For Pb isotope analysis, samples were diluted in PFA volumetric flasks to reach a final Pb concentration of about 25 ppm. Before filling the flasks to the mark with HNO_3 2% (v/v), appropriate volumes of Uranium stock solution were introduced in order to keep a constant Uranium concentration in samples and isotope standard. For this purpose, samples and standards were grouped into three different batches concerning to Uranium concentrations. Mass bias was calculated for each pair of isotopes $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ and the interpolated measured ratios were compared with the certified values. Mass bias corrections were individually carried out for each ratio via the specific mass bias interpolated factor, defined according to the procedure previously develop (Santos et al., 2007). The mass discrimination factor was evaluated at regular intervals along the working day and particularly before, between and after the measurement of real samples (Santos et al., 2007).

Blocks of ten measurements have been used to obtain data for all standards, blank and samples. The isobaric interference of ^{204}Hg on ^{204}Pb was corrected by monitoring ^{202}Hg and correcting the mercury contribution using a $^{204}\text{Hg}/^{202}\text{Hg}$ ratio of 0,23. The blank Pb content was always discounted in all analyzed solutions. The mass bias correction was accomplished by external standardization, wherein the concerned isotope ratio was measured in NBS 981

standard solutions matched according to sample matrices and analyzed just before and after the sample that was being corrected.

Table 1: Pb and U composition of all collected samples.

Type	Provincience	Ref#	[Pb] / $\mu\text{g.L}^{-1}$	[U] / $\mu\text{g.L}^{-1}$	Type	Provincience	Ref#	[Pb] / mg.Kg^{-1}	[U] / mg.Kg^{-1}	Type	Ref#	Profile	[Pb] / mg.Kg^{-1}	[U] / mg.Kg^{-1}		
WATER SAMPLES	Regional Waters	B1	0,126 ± 0,002	1,01 ± 0,07	ROCKS and MINERALS	GRANITES	GR 1	25 ± 3	<51 ± -	TAILING CORES	PZ 4	4-1	133 ± 17	143 ± 19		
		B2	0,118 ± 0,001	0,30 ± 0,02			GR 2	25 ± 3	<51 ± -			4-2	129 ± 17	213 ± 28		
		B3	<0,1 ± -	<0,4 ± -			GR 3	24 ± 3	<51 ± -			4-3	138 ± 18	177 ± 24		
		BP24	0,080 ± 0,001	1,35 ± 0,09			GR 4	35 ± 5	<51 ± -			4-4	270 ± 35	212 ± 28		
	WELL < 15 m	M1	<1,2 ± -	250 ± 17			GR 5	29 ± 4	<51 ± -			4-5	292 ± 38	181 ± 24		
		R1	<0,1 ± -	91 ± 6			GR 6	28 ± 4	<51 ± -			4-6	1069 ± 138	209 ± 28		
		R2	<0,2 ± -	124 ± 8			GR 7	30 ± 4	<51 ± -		PZ 5	5-1	183 ± 24	106 ± 14		
		R3	<0,1 ± -	82 ± 5		Secondary	3794 ± 490	77550 ± 10354	5-2			197 ± 26	172 ± 23			
		P2	0,0510 ± 0,0006	5,1 ± 0,3		Torbernite	140 ± 18	192150 ± 25656	5-3			142 ± 18	137 ± 18			
		P3	0,0550 ± 0,0007	39 ± 3		Autunite	1269 ± 164	327750 ± 43761	5-4			216 ± 28	150 ± 20			
		P4	<0,05 ± -	0,57 ± 0,04		Pitchblende	10990 ± 1421	127650 ± 17044	5-5			281 ± 36	189 ± 25			
		P5	0,099 ± 0,001	3,6 ± 0,2		Galena	199700 ± 25813	7610 ± 1016	5-6			682 ± 88	232 ± 31			
		P6	<0,05 ± -	<0,2 ± -		WATER CORES DEPOSIT	Pz 1	338 ± 44	354 ± 47		PZ 6	6-1	66 ± 9	139 ± 19		
		P7	0,148 ± 0,002	2,0 ± 0,1			Pz 3	1266 ± 164	450 ± 60			6-2	80 ± 10	113 ± 15		
	P8	<0,05 ± -	0,29 ± 0,02	Pz 4			199 ± 26	344 ± 46	6-3			83 ± 11	78 ± 10			
	P9	0,0550 ± 0,0007	0,48 ± 0,03	Pz 5			385 ± 50	465 ± 62	6-4			89 ± 12	81 ± 11			
	WELL > 15 m	F2	0,84 ± 0,01	422 ± 28		PZ 7	Pz 7	87 ± 11	277 ± 37		7-1	95 ± 12	86 ± 12			
		F3	<0,05 ± -	5,8 ± 0,4			Pz 10	155 ± 20	552 ± 74		7-2	109 ± 14	102 ± 14			
		F10	0,730 ± 0,009	7,3 ± 0,5			TAILING CORES	Ref#	Profile		[Pb] / mg.Kg^{-1}	[U] / mg.Kg^{-1}	PZ 7	7-3	94 ± 12	101 ± 14
	F21	0,362 ± 0,004	5,4 ± 0,4	PZ 1		1-1		110 ± 14	214 ± 29		7-4	543 ± 70		111 ± 15		
	CORES WATER	F1 A	17,2 ± 0,2	2,1E+04 ± 1410		PZ 1		1-2	127 ± 16		257 ± 34	PZ 8	8-1	229 ± 30	241 ± 32	
		F3 A	31,3 ± 0,4	2,7E+04 ± 1823		PZ 1		1-3	141 ± 18		167 ± 22		8-2	165 ± 21	208 ± 28	
		F4 A	46,5 ± 0,6	536 ± 36		PZ 2		2-1	77 ± 10		124 ± 17		8-3	150 ± 19	202 ± 27	
		F5 A	61,4 ± 0,7	1,2E+03 ± 79		PZ 2		2-2	85 ± 11		93 ± 12		8-4	153 ± 20	176 ± 24	
		F7 A	5,57 ± 0,07	4,3E+03 ± 286		PZ 2		2-3	66 ± 8		76 ± 10		8-5	161 ± 21	172 ± 23	
		CORES WATER	F10 A	5,46 ± 0,07		32 ± 2		PZ 3	3-1		168 ± 22	266 ± 36	PZ 9	9-1	143 ± 18	154 ± 21
								PZ 3	3-2		120 ± 16	329 ± 44		9-2	50 ± 6	1336 ± 178
								PZ 3	3-3		139 ± 18	235 ± 31	PZ 10	10-1	142 ± 18	261 ± 35
											10-2	40 ± 5		208 ± 28		

4. RESULTS AND DISCUSSION

4.1. Pb isotope composition of regional rocks

In the first part of results interpretation, all possible Pb sources were evaluated. As natural Pb sources were considered the geological background, reported by the average of the seven granite samples collected in the involving area (Table 2) and by the different Uranium ores; (i) the primary Pitchblende or Uraninite (UO₂ - the main ore of Uranium that occurs in this mining exploration); (ii) the secondary like Autunite (Ca(UO₂)₂(PO₄)₂·10-12(H₂O)) and Torbernite (Cu(UO₂)₂(PO₄)₂·8-12(H₂O)) and (iii) other minerals designated by Secondary that belong to the *Urgeiriça* paragenesis. Galena (PbS) was considered as a natural Pb source.

Table 2: Pb isotope ratios and Pb, Th and U concentrations (*with standard deviation*) of seven Regional Granites and Minerals of U and Pb in the *Urgeiriça* region.

Ref ^a	[Pb] / µg.L ⁻¹	[Th] / µg.L ⁻¹	[U] / µg.L ⁻¹	²⁰⁶ Pb: ²⁰⁴ Pb	²⁰⁷ Pb: ²⁰⁴ Pb	²⁰⁸ Pb: ²⁰⁴ Pb	²⁰⁶ Pb: ²⁰⁷ Pb	²⁰⁸ Pb: ²⁰⁶ Pb	
GRANITES	GR 1	25 ± 3	13 ± 3	<51 ± -	21,595 ± 0,069	15,888 ± 0,058	39,540 ± 0,185	1,359 ± 0,003	1,834 ± 0,007
	GR 2	25 ± 3	5 ± 1	<51 ± -	19,258 ± 0,054	15,746 ± 0,065	39,471 ± 0,210	1,223 ± 0,003	2,051 ± 0,011
	GR 3	24 ± 3	6 ± 1	<51 ± -	19,157 ± 0,031	15,704 ± 0,041	39,058 ± 0,137	1,219 ± 0,002	2,040 ± 0,007
	GR 4	35 ± 5	1,7 ± 0,4	<51 ± -	19,436 ± 0,071	15,789 ± 0,052	38,617 ± 0,167	1,231 ± 0,002	1,988 ± 0,007
	GR 5	29 ± 4	3,1 ± 0,7	<51 ± -	20,815 ± 0,052	15,840 ± 0,028	38,788 ± 0,144	1,314 ± 0,002	1,863 ± 0,006
	GR 6	28 ± 4	12 ± 3	<51 ± -	19,533 ± 0,057	15,703 ± 0,050	38,837 ± 0,205	1,243 ± 0,002	1,987 ± 0,007
	GR 7	30 ± 4	10 ± 2	<51 ± -	19,837 ± 0,059	15,748 ± 0,055	39,138 ± 0,134	1,259 ± 0,003	1,973 ± 0,003
Mean (GR)	28 ± 4	7 ± 2	<51 ± -	19,947 ± 0,057	15,774 ± 0,051	39,064 ± 0,171	1,264 ± 0,002	1,962 ± 0,007	
MINERALS	Secondary	3794 ± 490	<2 ± -	77550 ± 10354	107,1 ± 0,2	20,180 ± 0,056	38,525 ± 0,098	5,304 ± 0,010	0,360 ± 0,001
	Torbernite	140 ± 18	<2 ± -	192150 ± 25656	10372 ± 182	523 ± 9	42 ± 1	19,816 ± 0,064	0,0040 ± 0,0001
	Autunite	1269 ± 164	<2 ± -	327750 ± 43761	9266 ± 268	493 ± 14	56 ± 2	18,773 ± 0,026	0,0060 ± 0,0001
	Pitchblende	10990 ± 1421	<2 ± -	127650 ± 17044	31,124 ± 0,060	16,257 ± 0,040	38,430 ± 0,096	1,914 ± 0,003	1,235 ± 0,002
	Galena	199700 ± 25813	<2 ± -	7610 ± 1016	18,409 ± 0,037	15,645 ± 0,038	38,361 ± 0,080	1,176 ± 0,003	2,084 ± 0,005

According to the values found in the background granites, we can say that the majority of Pb isotope ratios are very similar, however two granites (GR1 and GR5) a little bit more radiogenic were found. The reported Pb isotope ratios for the background are $^{206}\text{Pb}/^{204}\text{Pb} = 19,947 \pm 0,057$; $^{207}\text{Pb}/^{204}\text{Pb} = 15,774 \pm 0,051$; $^{208}\text{Pb}/^{204}\text{Pb} = 39,064 \pm 0,171$; $^{206}\text{Pb}/^{207}\text{Pb} = 1,264 \pm 0,002$ and $^{208}\text{Pb}/^{206}\text{Pb} = 1,962 \pm 0,007$.

As expected, extremely radiogenic ratios for Autunite and Torbernite, with $^{206}\text{Pb}/^{204}\text{Pb} = 9266 \pm 268$ and $^{206}\text{Pb}/^{204}\text{Pb} = 10372 \pm 182$, respectively, were obtained. These Uranium minerals together with the Pitchblende were recovered by the chemical processing during the industrial activity. Although the industrial plant met a requirement of maximum recovery of these ores, some losses inevitably left in the residues are contributing to enhance environment impact in the area.

4.2. Tailing deposits profiles

In Fig. 3, Pb concentrations *versus* Pb isotope ratio ($^{206}\text{Pb}/^{207}\text{Pb}$) for the several layers of the 10 cores sampled in the tailing deposit are illustrated according to the values obtained in table 3. The ratio $^{206}\text{Pb}/^{207}\text{Pb}$ was chosen since it reveals more information of the uragenic Pb present in this type of deposit.

Data illustrated in Fig. 3 allow some consideration about the panorama found in the polluting focus. Three different situations between Pb concentration and $^{206}\text{Pb}/^{207}\text{Pb}$ ratio can be found: (i) an homogeneous behavior in cores 2, 6 and 8; (ii) an inverse relationship in cores 1, 3, 7 and

10; and (iii) a direct relationship seems to happen in the cores 4, 5 and 9. In this last case, whenever Pb concentration increases (reaching values of 682 the 1069 ppm for cores 5 and 4, respectively) the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio always follow this increase, reaching radiogenic values, particularly over the cores 4 and 5, between fifteen and twenty five meters height (like a “sandwich section”). This fact can probably support that we are in presence of another radiogenic source.

In all cores Pb concentrations and the corresponding $^{206}\text{Pb}/^{207}\text{Pb}$ ratios were different of one's found in background (average of seven granites), fact that makes for the existence of possible mixtures with other radiogenic sources of the region.

Table 3: Pb concentration and isotope ratios of the several tailing cores profiles.

Ref ^a		[Pb]/ $\mu\text{g.L}^{-1}$	Depth Profile / m	$^{206}\text{Pb}:^{204}\text{Pb}$	$^{207}\text{Pb}:^{204}\text{Pb}$	$^{208}\text{Pb}:^{204}\text{Pb}$	$^{206}\text{Pb}:^{207}\text{Pb}$	$^{208}\text{Pb}:^{206}\text{Pb}$	
TAILING CORES	PZ 1	1-1	110 ± 14	18,1	23,532 ± 0,079	15,873 ± 0,053	38,661 ± 0,120	1,482 ± 0,002	1,643 ± 0,004
		1-2	127 ± 16	9,6	22,434 ± 0,082	15,864 ± 0,037	38,658 ± 0,137	1,414 ± 0,004	1,722 ± 0,005
		1-3	141 ± 18	5,0	21,535 ± 0,111	15,768 ± 0,053	38,613 ± 0,208	1,365 ± 0,005	1,795 ± 0,005
	PZ 2	2-1	77 ± 10	19,9	21,379 ± 0,079	15,802 ± 0,032	38,720 ± 0,167	1,353 ± 0,005	1,813 ± 0,006
		2-2	85 ± 11	11,1	21,258 ± 0,068	15,832 ± 0,033	38,767 ± 0,137	1,342 ± 0,004	1,826 ± 0,006
		2-3	66 ± 8	3,2	21,164 ± 0,050	15,817 ± 0,049	38,862 ± 0,153	1,338 ± 0,004	1,838 ± 0,004
	PZ 3	3-1	168 ± 22	12,6	22,700 ± 0,097	15,791 ± 0,066	38,499 ± 0,190	1,437 ± 0,005	1,695 ± 0,007
		3-2	120 ± 16	7,4	23,710 ± 0,045	15,978 ± 0,026	38,871 ± 0,146	1,484 ± 0,002	1,639 ± 0,006
		3-3	139 ± 18	2,6	22,710 ± 0,071	15,799 ± 0,024	38,606 ± 0,220	1,437 ± 0,004	1,700 ± 0,008
	PZ 4	4-1	133 ± 17	25,7	23,697 ± 0,089	15,835 ± 0,056	38,882 ± 0,236	1,496 ± 0,004	1,640 ± 0,005
		4-2	129 ± 17	20,9	25,976 ± 0,058	16,040 ± 0,041	39,279 ± 0,094	1,619 ± 0,004	1,512 ± 0,003
		4-3	138 ± 18	15,7	37,515 ± 0,169	16,664 ± 0,077	39,369 ± 0,240	2,251 ± 0,006	1,049 ± 0,003
		4-4	270 ± 35	11,7	33,415 ± 0,078	16,425 ± 0,045	38,761 ± 0,080	2,034 ± 0,003	1,160 ± 0,002
		4-5	292 ± 38	6,9	39,448 ± 0,135	16,792 ± 0,058	39,031 ± 0,192	2,350 ± 0,008	0,991 ± 0,004
		4-6	1069 ± 138	2,1	24,865 ± 0,077	15,921 ± 0,029	38,372 ± 0,304	1,561 ± 0,004	1,545 ± 0,012
	PZ 5	5-1	183 ± 24	25,5	22,914 ± 0,109	15,886 ± 0,070	39,120 ± 0,216	1,442 ± 0,003	1,706 ± 0,007
		5-2	197 ± 26	20,7	23,219 ± 0,075	15,909 ± 0,037	39,222 ± 0,200	1,458 ± 0,005	1,687 ± 0,008
		5-3	142 ± 18	16,9	34,716 ± 0,203	16,487 ± 0,082	39,214 ± 0,247	2,105 ± 0,004	1,130 ± 0,004
		5-4	216 ± 28	12,3	32,897 ± 0,125	16,419 ± 0,067	39,038 ± 0,160	2,003 ± 0,005	1,186 ± 0,004
		5-5	281 ± 36	9,1	30,779 ± 0,078	16,294 ± 0,049	38,915 ± 0,096	1,888 ± 0,004	1,264 ± 0,003
		5-6	682 ± 88	4,3	26,335 ± 0,120	16,030 ± 0,039	38,375 ± 0,397	1,640 ± 0,007	1,458 ± 0,010
	PZ 6	6-1	66 ± 9	18,2	23,152 ± 0,078	15,866 ± 0,046	38,648 ± 0,133	1,459 ± 0,002	1,671 ± 0,003
		6-2	80 ± 10	13,4	22,021 ± 0,074	15,849 ± 0,042	38,776 ± 0,154	1,390 ± 0,004	1,762 ± 0,005
		6-3	83 ± 11	7,9	22,558 ± 0,073	15,895 ± 0,040	38,815 ± 0,124	1,419 ± 0,002	1,723 ± 0,005
		6-4	89 ± 12	1,6	23,126 ± 0,090	15,847 ± 0,046	38,596 ± 0,134	1,459 ± 0,004	1,669 ± 0,004
	PZ 7	7-1	95 ± 12	18,5	21,905 ± 0,043	15,772 ± 0,041	38,617 ± 0,104	1,388 ± 0,002	1,763 ± 0,003
		7-2	109 ± 14	13,7	21,563 ± 0,069	15,811 ± 0,037	38,714 ± 0,166	1,363 ± 0,003	1,791 ± 0,005
		7-3	94 ± 12	8,9	21,533 ± 0,062	15,826 ± 0,042	39,022 ± 0,171	1,359 ± 0,003	1,810 ± 0,006
		7-4	543 ± 70	4,1	20,082 ± 0,091	15,674 ± 0,064	38,268 ± 0,264	1,280 ± 0,005	1,905 ± 0,007
	PZ 8	8-1	229 ± 30	21,0	22,015 ± 0,060	15,777 ± 0,060	38,580 ± 0,150	1,394 ± 0,003	1,754 ± 0,007
8-2		165 ± 21	15,4	22,520 ± 0,090	15,827 ± 0,074	38,574 ± 0,271	1,423 ± 0,003	1,713 ± 0,008	
8-3		150 ± 19	11,1	23,100 ± 0,087	15,830 ± 0,064	38,680 ± 0,185	1,459 ± 0,003	1,674 ± 0,006	
8-4		153 ± 20	7,9	22,209 ± 0,066	15,763 ± 0,043	38,607 ± 0,228	1,408 ± 0,004	1,737 ± 0,012	
8-5		161 ± 21	1,7	23,188 ± 0,102	15,881 ± 0,040	38,805 ± 0,176	1,460 ± 0,004	1,672 ± 0,007	
PZ 9	9-1	143 ± 18	7,2	22,744 ± 0,053	15,764 ± 0,044	38,351 ± 0,154	1,442 ± 0,003	1,685 ± 0,006	
	9-2	50 ± 6	4,2	21,711 ± 0,051	15,755 ± 0,042	38,598 ± 0,088	1,378 ± 0,003	1,778 ± 0,003	
PZ 10	10-1	142 ± 18	3,2	23,608 ± 0,105	15,838 ± 0,045	38,569 ± 0,240	1,489 ± 0,005	1,634 ± 0,006	
	10-2	40 ± 5	2,2	25,220 ± 0,114	16,010 ± 0,051	38,743 ± 0,125	1,575 ± 0,003	1,536 ± 0,004	

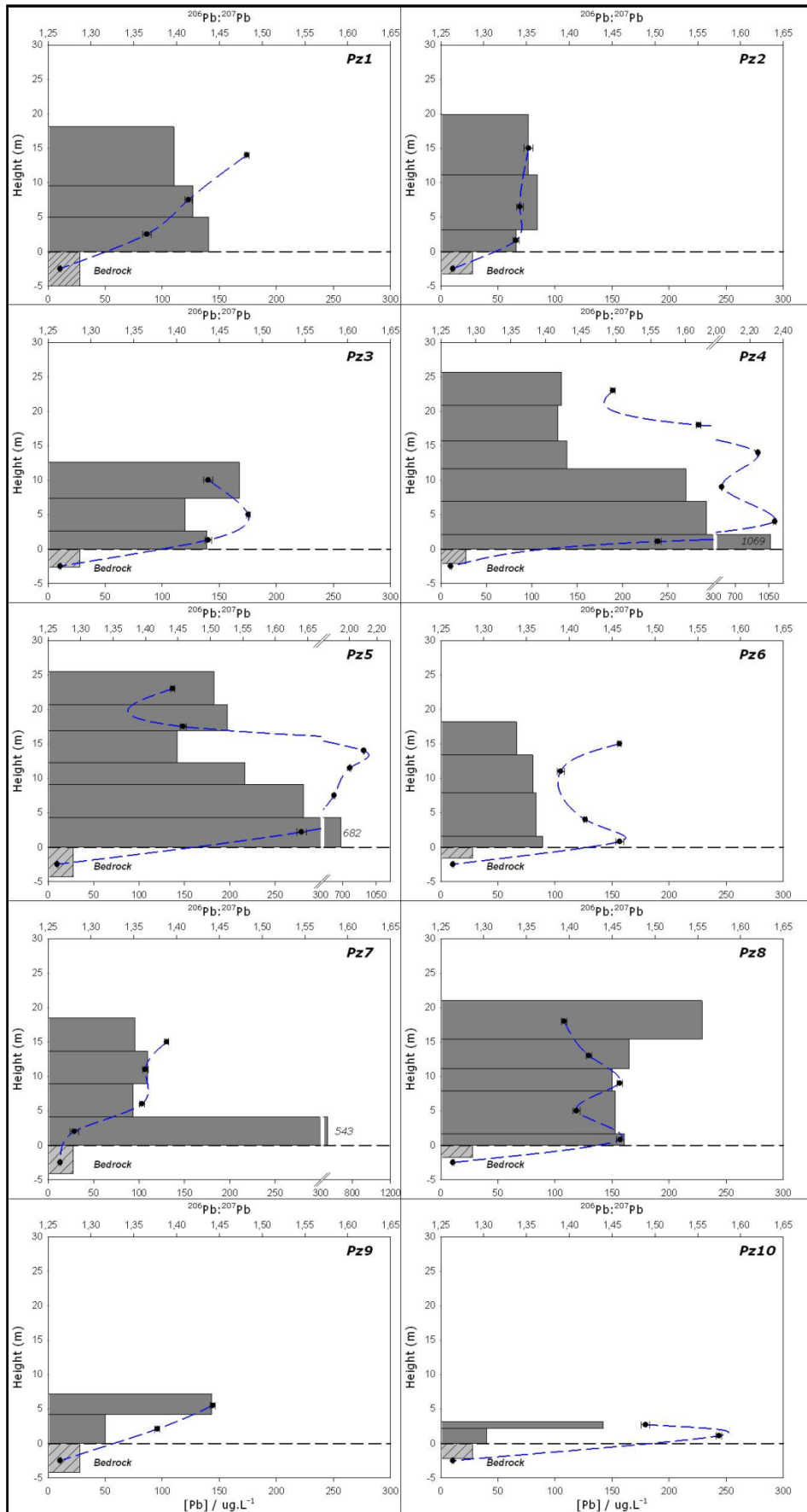


Fig. 3: Illustration of the several tailing profiles according to Pb concentration and $^{206}\text{Pb}/^{207}\text{Pb}$ versus height.

As reported, in some of the core drill (Pz1, Pz3, Pz4, Pz5, Pz7 and Pz10) were possible to collect waters for Pb isotope ratios determination, including in the corresponding suspension in the material. The isotope diagram (Fig. 4) illustrates the isotope ratios for the different materials of these cores and some issues could reveal important questions. It is true that cores Pz1, Pz3, Pz7 and Pz10 show a small dispersion between water, suspension and sections materials. However, two exceptions occur in the Pz7 and Pz10 waters, since they have more radiogenic ratios than solid material. Such facts do not surprise, since it is likely that pluvial waters could percolate through different circuits on distinct zones of the respective profiles and could incorporate different fingerprints or even different source mixtures.

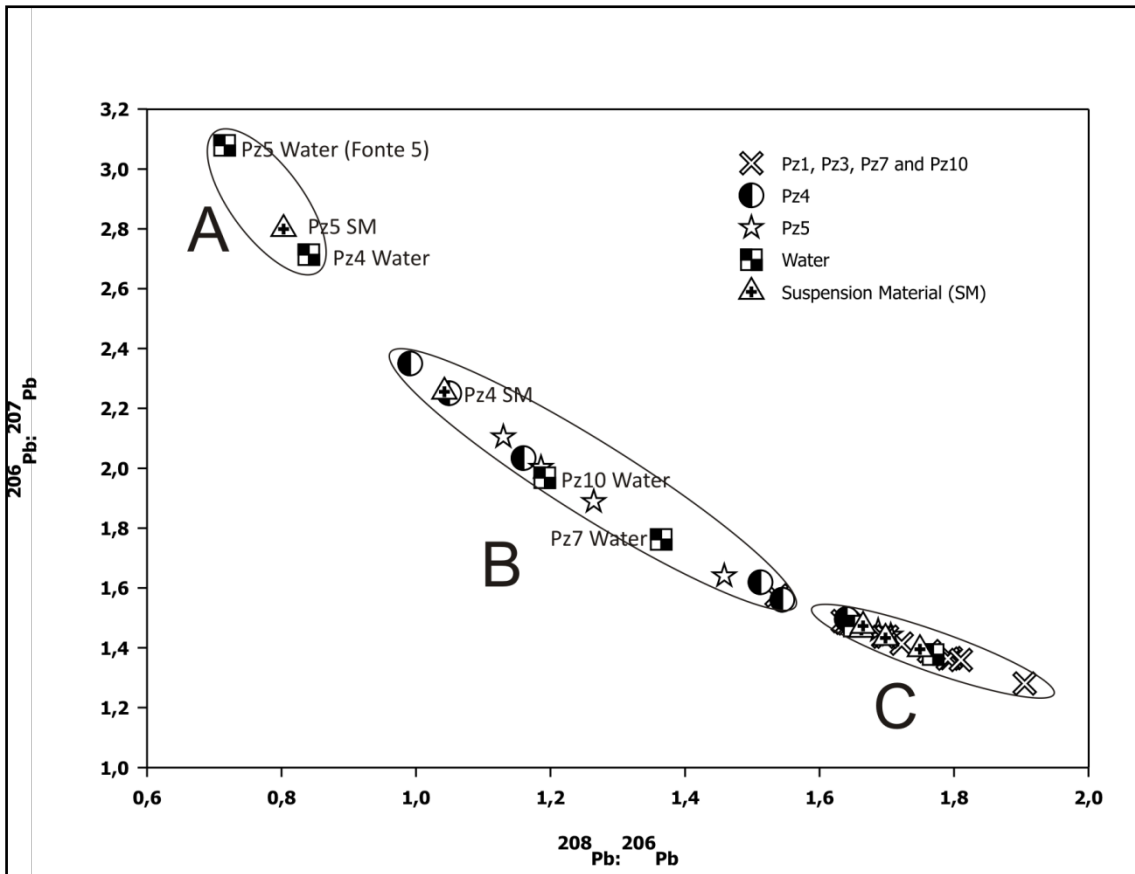


Fig. 4: Pb isotope diagram for tailing cores with respective waters and suspension material. A) Most radiogenic ratios found in water of Pz5, considered as unknown Pb source (*Fonte 5*); B) Heterogeneous isotope ratios in Pz4 and Pz5 layers; C) Homogeneous isotope ratio in Pz1, Pz3, Pz7 and Pz10, except for the Pz7 water, and Pz10 water.

Other cores, like Pz4 and Pz5, show a huge dispersion between their section materials but mainly between their waters and suspension material. These particular cases support the hypothesis that another Pb source proceeding from another place could have been dropped on the tailings deposit.

In almost core drills their suspension materials and the respective water reflect the same isotope ratio of some sections of the core (ex: Pz1, Pz3, Pz7 and Pz10). However, in Pz4 and Pz5, the suspension material present in water could result from any another layer with bigger solubility (ex: Pz4) or, from another source through which water has circulated (ex: Pz5).

There is no doubt that water isotope ratios are an important tool to access other Pb sources presented in the tailing deposit, as water percolates through different circuits. Without those

data it was impossible to identify that another radiogenic material would be present in the tailing deposit.

According to the facts, is essential to admit the presence of another unknown radiogenic material. This new Pb source was designated by *Fonte 5* and has the same radiogenic ratios of Pz5 water, since it was the most radiogenic ratios found in the tailings.

4.3. Pb sources identification on tailings deposit

Accordingly to historical records the mine dump has residues from different Uranium mines of the region, the ranges in isotope ratios of the different layers are a clear evidence of the different Pb sources mixtures deposited there.

In the isotope diagram (Fig. 5) are represented all identified Pb sources and all the samples collected in the tailing deposit. The lack of linearity between samples and Pb sources is a result of a non isotope homogenization – it can be described as “a cold mixture process”.

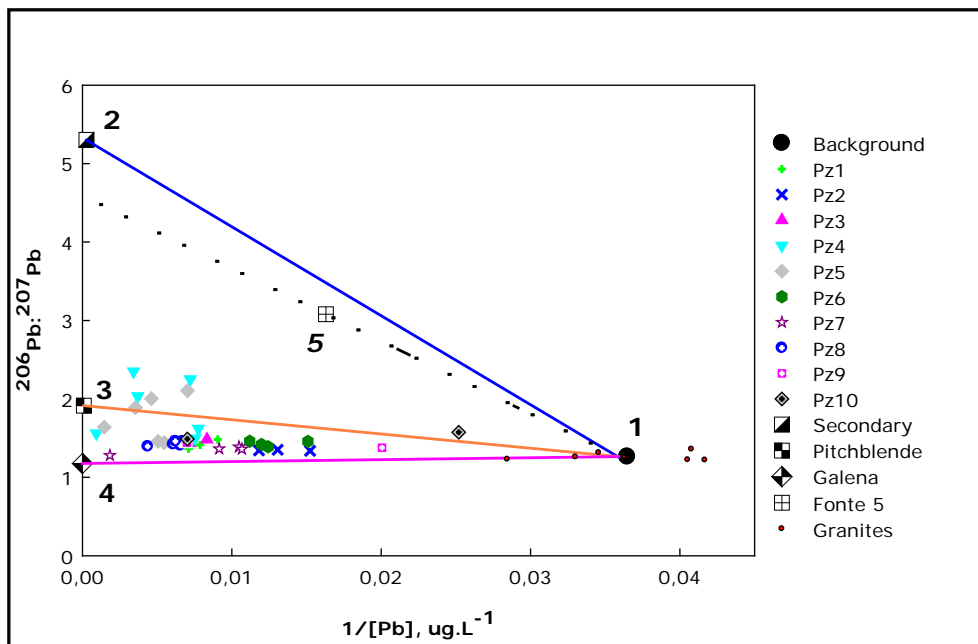


Fig. 5: $^{206}\text{Pb}/^{207}\text{Pb}$ versus $1/[\text{Pb}]$ for all the tailing samples including all the Pb sources: (1) Background; (2) Secondary.; (3) Pitchblende; (4) Galena and (5) *Fonte 5* (Pz5 water).

Accordingly to the behavior of the collected samples only three Pb sources (Background, Pitchblende and *Fonte 5*) were selected as being present. The other two sources were rejected because Galena has Pb isotope ratios less radiogenic than Regional Granites as expected, since Galena is a Pb mineral that stops its isotopic evolution at the moment that as formed. The Secondary Minerals source was rejected too because of its radiogenic behavior higher than *Fonte 5*. However, it could be present in low quantities in the mixtures of the tailing deposit.

Fig. 5 shows that isotope ratios for some layers in the cores 4 and 5 are more radiogenic than Pitchblende itself and the reason for this could be a possible mixture between *Fonte 5* and Pitchblende or, alternately, involving *Fonte 5* and the Background. For the rest of the profiles it seems to be a credible hypothesis that mixture between Pitchblende and Background could explain the obtained isotope ratios.

Although interpretation of natural data is always a difficult task, a isotope diagram of $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{207}\text{Pb}$ (Fig. 6) from all data points analyzed could be an interesting tool to clarify which Pb sources will be responsible for the environmental impact.

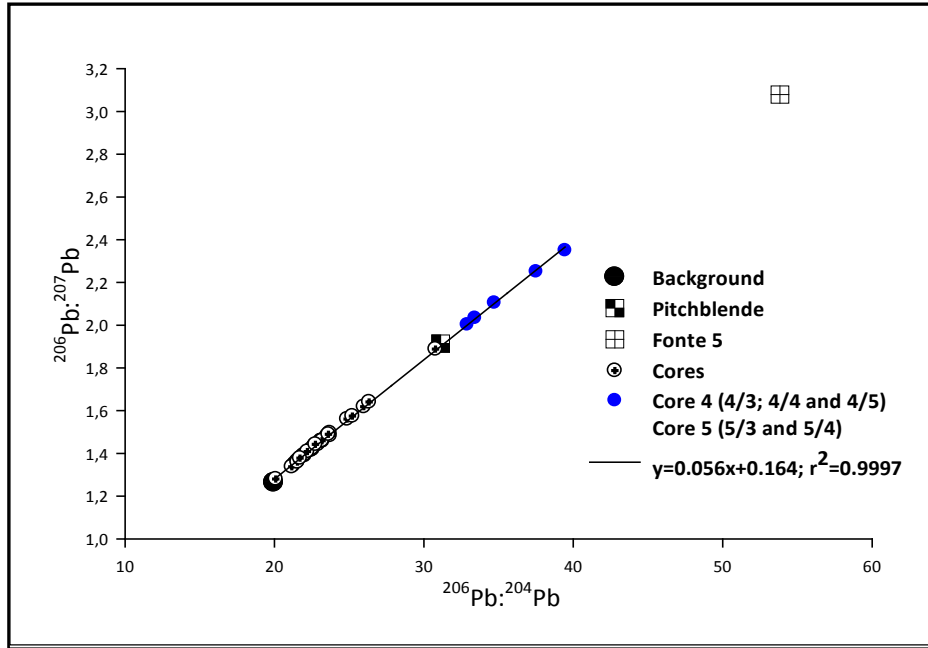


Fig. 6: $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{207}\text{Pb}$ for all the tailing samples including the Pb sources: Background; Pitchblende and Fonte 5 (Pz5 water).

In accordance to the Fig. 6, profiles 4/3, 4/4, 4/5 for Pz4 core and 5/3 and 5/4 for Pz5 core will represent only one set, resulting from a probable mixture between Pitchblende and Fonte 5, or alternative, between Background and Fonte 5. For all other data points they line up ($r^2 = 0,9997$) between Background and Pitchblende, and show that their Pb isotope ratios result probably from this mixture. So, no other source of Pb needs to be mentioned in order to interpret the tailings deposit composition.

4.4. Binary mixing model

After the identification of the probable Pb sources, the contribution of each source for the bulk composition can be approximated by fitting a simple binary mixing/mass balance model to the available data, considering different sources previously recognized. However, these models work satisfactory only if the isotope signatures of the contributors (ex: pollutant and natural background) are significantly different, like in our case study. The binary model was used according with the following expression (Faure, 1986):

$$\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_{\text{Sample}} = \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_A f_A \left(\frac{\text{Pb}_A}{\text{Pb}_{\text{Sample}}}\right) + \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_B (1-f_A) \left(\frac{\text{Pb}_B}{\text{Pb}_{\text{Sample}}}\right);$$

The expression contains two kinds of weighting factors: f_A and $(1-f_A)$ express the abundance of component A and B, whereas $\text{Pb}_A/\text{Pb}_{\text{Sample}}$ and $\text{Pb}_B/\text{Pb}_{\text{Sample}}$ are the fractions of Pb in the sample

contributed by component A and B, respectively. $\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_{\text{Sample}}$, $\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_A$ and $\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_B$ are the Pb isotope ratios in the sample, source A and source B, respectively.

The contributions of each Pb source on the different layer of the tailings deposit (Fig. 7) show some curious considerations, as follows: (i) The majority of the cores are composed by natural Pb (Background); (ii) in almost profiles Pitchblende was present since it was the main Uranium mineral exploited; (iii) cores 4 and 5 reveal that another and more radiogenic Pb source (*Fonte 5*) was deposited there, to be precise between 2,1-15,7 and 9,1-16,9 meters, respectively; (iv) although the former industrial Processing Plant were optimized for Uranium recovery, in some layers we found highly enriched in Pitchblende, as on core 5, layers 4,3-9,1 meters.

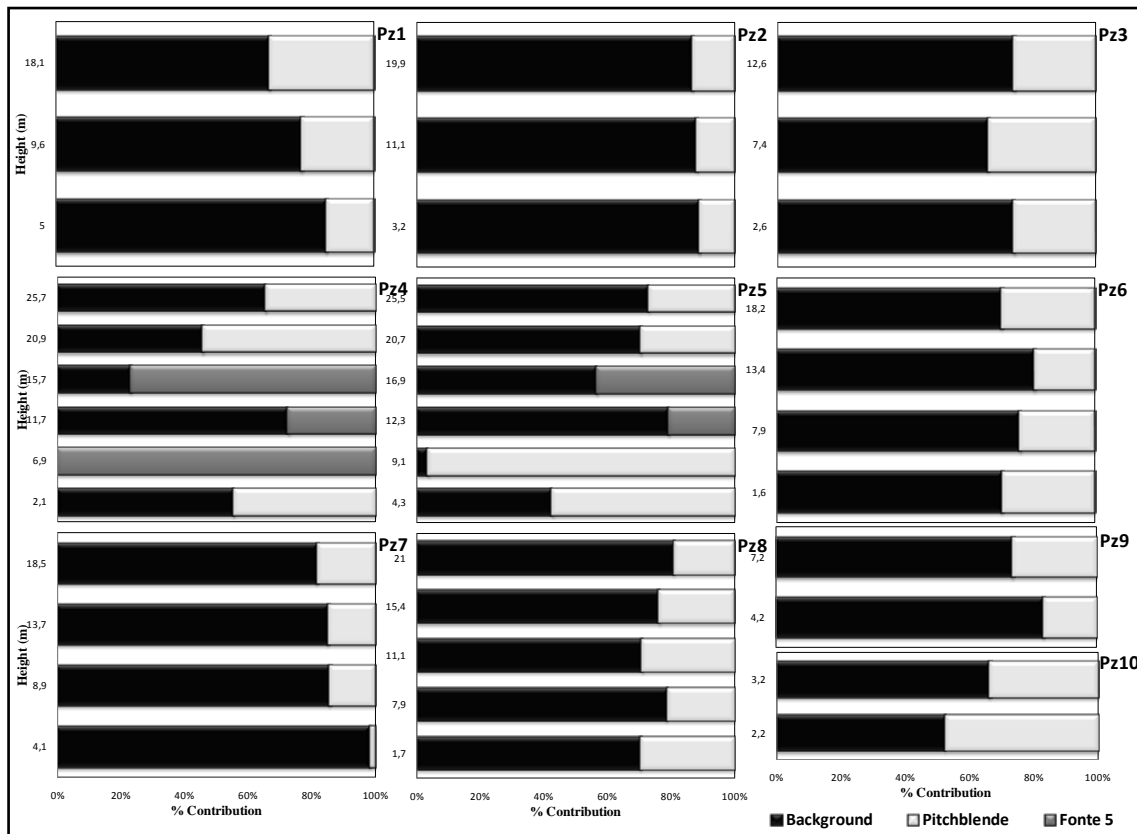


Fig. 7: Fraction of Pb (%) attributed to different sources: Background; Pitchblende and *Fonte 5* in all the cores.

The provenience of such more radiogenic Pb source above referred could be related with the residues of treatment of ores that came from other Uranium mines, or from different ore mixtures, sent at that time to industrial processing plant and deposited on *Urgeriça* tailings deposit.

In a global point of view, Fig. 8 shows that 69% of the 13 Mton in tailing deposit are constituted by Granites (Background); 25% of the rejects are proceeding from the main Uranium mineral (Pitchblende) and 6% derive from the other radiogenic Pb source (*Fonte 5*).

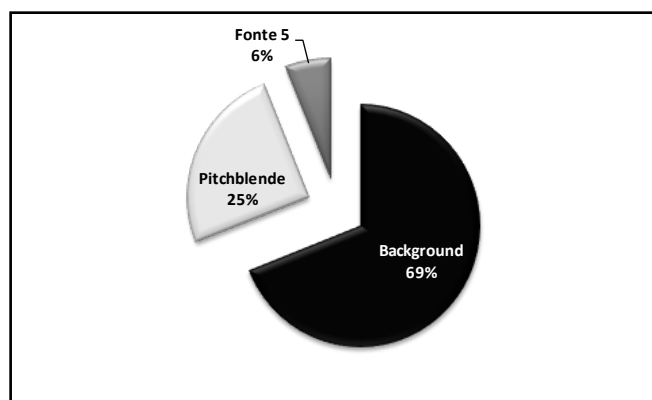


Fig. 8: Contribution (%) of different Pb sources in the tailing deposit.

4.5. Water environmental impact

For the study of the influence of this polluting focus in the water environmental, different kind of water samples were collected: (i) 4 wells till 60 meters depth, for underground waters system; (ii) 8 small wells up to 15 meters depth, for characterization of sub-superficial waters; (iii) 4 collected water points in full riverbed (Ribeira da Pantanha), for evaluation of the quality of surface waters and, (iv) 4 regional waters out of the hydrographic basin where the polluting focus are located to compared the values of water background.

This sampling was planned according to all available information in particular using cartography maps, like ortofotmaps, in conjunction with the geological cartography. The aim of this sampling was the identification and localization of the several transport vectors of these elements. So, we have defined the different hydrographic basins, the main watercourses and the main fracturation, which makes preferably water transport.

The data of the isotopic analysis of Pb ratios found in the colloidal and dissolved water phases (Table 4) were compared in the isotopic diagram of $^{206}\text{Pb} \cdot ^{204}\text{Pb}$ versus $^{206}\text{Pb} \cdot ^{207}\text{Pb}$ (Fig. 9) to the isotopic ratios of the litological background (mean of the seven Granites) and to the main mine ore - the Pitchblende, in a similar way to that used in the characterization of Pb sources present in the tailing deposit.

Table 4: Pb isotopic ratios of water samples: D – Pb dissolved form; C – Pb Colloidal form.

Type	Ref ^a	[Pb] _{Dissol} /μg.L ⁻¹	$^{206}\text{Pb} \cdot ^{204}\text{Pb}$	$^{207}\text{Pb} \cdot ^{204}\text{Pb}$	$^{208}\text{Pb} \cdot ^{204}\text{Pb}$	$^{206}\text{Pb} \cdot ^{207}\text{Pb}$	$^{208}\text{Pb} \cdot ^{206}\text{Pb}$	[Pb] _{Susp} /μg.L ⁻¹	$^{206}\text{Pb} \cdot ^{204}\text{Pb}$	$^{207}\text{Pb} \cdot ^{204}\text{Pb}$	$^{208}\text{Pb} \cdot ^{204}\text{Pb}$	$^{206}\text{Pb} \cdot ^{207}\text{Pb}$	$^{208}\text{Pb} \cdot ^{206}\text{Pb}$	
Regional Water	B1	0,13	18,363 ± 0,054	15,611 ± 0,071	38,272 ± 0,146	1,175 ± 0,003	2,085 ± 0,005	12	19,467 ± 0,104	15,686 ± 0,065	38,266 ± 0,161	1,241 ± 0,004	1,965 ± 0,006	
	B2	0,12	18,315 ± 0,015	15,560 ± 0,013	37,739 ± 0,031	1,1770 ± 0,0001	2,0605 ± 0,0001	5,7	20,501 ± 0,096	15,894 ± 0,061	38,596 ± 0,158	1,291 ± 0,005	1,879 ± 0,003	
	B3	<0,1	18,560 ± 0,072	15,659 ± 0,092	37,788 ± 0,213	1,186 ± 0,004	2,038 ± 0,009	1,4	18,871 ± 0,003	15,602 ± 0,003	38,096 ± 0,006	1,2095 ± 0,00002	2,0187 ± 0,00003	
	BP24	0,08	n.d.						24	19,355 ± 0,065	15,706 ± 0,048	38,311 ± 0,093	1,232 ± 0,003	1,978 ± 0,006
Well < 15 m	M1	<1,2	n.d.						1,4	19,478 ± 0,028	15,644 ± 0,023	38,110 ± 0,057	1,2450 ± 0,0001	1,9561 ± 0,0002
	R1	<0,1	n.d.						5,6	20,268 ± 0,095	15,932 ± 0,081	38,772 ± 0,260	1,271 ± 0,005	1,915 ± 0,010
	R2	<0,2	n.d.						32	20,980 ± 0,084	15,729 ± 0,054	38,204 ± 0,180	1,333 ± 0,004	1,821 ± 0,005
	R3	<0,1	n.d.						40	21,974 ± 0,103	15,819 ± 0,050	38,354 ± 0,204	1,389 ± 0,004	1,745 ± 0,006
	P2	0,05	n.d.						34	21,604 ± 0,083	15,873 ± 0,042	38,561 ± 0,213	1,361 ± 0,004	1,784 ± 0,007
	P3	0,06	n.d.						<0,4	19,112 ± 0,026	15,635 ± 0,022	38,088 ± 0,054	1,2224 ± 0,0001	1,9928 ± 0,0002
	P4	<0,05	n.d.						2,7	19,193 ± 0,095	15,876 ± 0,061	38,701 ± 0,135	1,207 ± 0,004	2,021 ± 0,005
	P5	0,10	17,854 ± 0,092	15,447 ± 0,076	37,521 ± 0,188	1,1543 ± 0,0005	2,1025 ± 0,0007	51	17,794 ± 0,063	15,533 ± 0,068	37,628 ± 0,130	1,145 ± 0,002	2,115 ± 0,004	
	P6	<0,05	n.d.						122	18,144 ± 0,074	15,663 ± 0,045	38,176 ± 0,165	1,158 ± 0,005	2,106 ± 0,008
	P7	0,15	18,637 ± 0,066	15,690 ± 0,057	38,094 ± 0,136	1,1880 ± 0,0004	2,0439 ± 0,0004	22	18,577 ± 0,063	15,698 ± 0,031	38,199 ± 0,124	1,183 ± 0,004	2,056 ± 0,005	
Well > 15 m	P8	<0,05	n.d.						3,2	19,284 ± 0,067	15,876 ± 0,076	38,674 ± 0,182	1,217 ± 0,006	2,001 ± 0,008
	P9	0,06	n.d.						7,9	18,539 ± 0,068	15,692 ± 0,058	38,226 ± 0,147	1,181 ± 0,003	2,062 ± 0,007
	F2	0,84	20,686 ± 0,057	15,756 ± 0,043	38,632 ± 0,088	1,312 ± 0,003	1,867 ± 0,004	17	18,551 ± 0,070	15,648 ± 0,055	37,793 ± 0,225	1,186 ± 0,004	2,042 ± 0,009	
F3	<0,05	n.d.						12	19,131 ± 0,070	15,763 ± 0,077	38,215 ± 0,098	1,214 ± 0,004	1,997 ± 0,006	
F10	0,73	17,585 ± 0,012	15,550 ± 0,011	37,288 ± 0,025	1,1309 ± 0,0001	2,1204 ± 0,0002	245	17,534 ± 0,045	15,558 ± 0,032	37,260 ± 0,095	1,127 ± 0,004	2,125 ± 0,006		
F21	0,36	18,281 ± 0,008	15,565 ± 0,007	37,866 ± 0,016	1,1744 ± 0,0001	2,0715 ± 0,0008	3,7	19,332 ± 0,165	15,819 ± 0,095	38,220 ± 0,326	1,223 ± 0,006	1,982 ± 0,009		

Fig. 9 suggests that mostly Pb isotopic ratios associated to the sampled waters (Dissolve and Colloidal forms) probably resulted from a mixture of the selected two sources (Background and Pitchblende). However, it should be noted that various Pb isotopic ratios shows values below as the defined region's background. This fact deserve some reflection, it could provide an indication of poor representativeness statistical results used in the definition of the region's background or, on the contrary, indicate the presence of other Pb anthropogenic source, directly related with the decomposition of organic matter, nitrogen land and also gaseous emissions from industrial activity or motor vehicles, that could be dragged into the water by means of rain water itself.

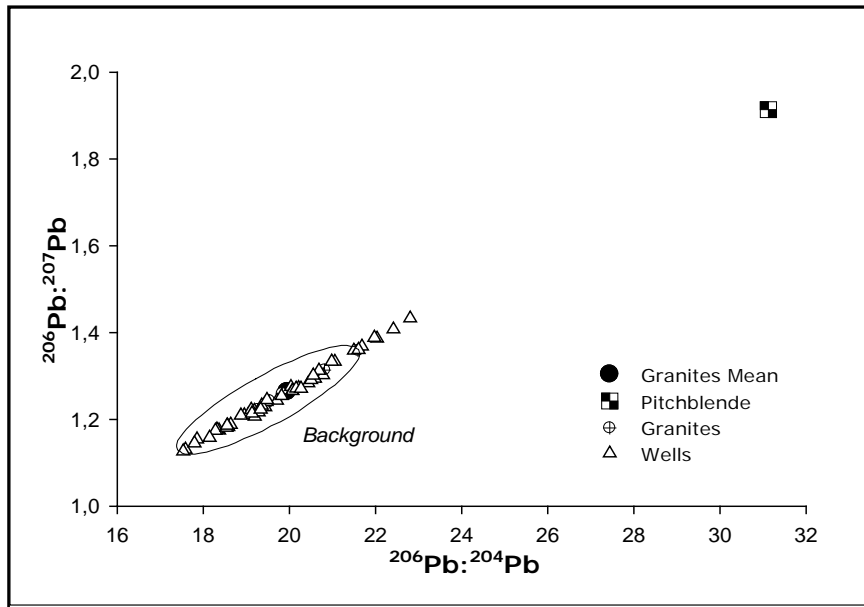


Fig. 9: Isotopic diagram: $^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ of the water samples (*all the wells*) collected on the tailing surroundings compared to the Background family and Pitchblende Pb sources.

This finding was not considered prejudice to the continuation of the analysis of the results, only drove the reformulation of the region's background value. So, we decided to select the Pb isotopic ratios of the less radiogenic granite (GR3) instead of the average value of the seven granites of the region. In this way, we achieved a better definition of the lower limit of background's family and a higher contrast between samples (noted with an asterisk), which possibly shall carry the contribution of other unknown and less radiogenic Pb anthropogenic source.

The contributions of the different Pb sources were obtained (Table 5) in a similar way using the same mixing model as in the tailing profiles. Some samples (marked with asterisk) show a strong suspicious presence of another Pb anthropogenic source.

Table 5: Contribution (%) of Background, Pitchblende and Pb anthropogenic sources (*marked with asterisk*) in the water samples on the two Pb forms. Note: D – Dissolved form < 0,2 µm; C- Colloidal form > 0,2 µm.

Ref. ^a		Dissolved Lead (D)		Colloidal Lead (C)	
		% Background	%Pitchblende	% Background	%Pitchblende
Regional Waters	B1	100*	0	100	0
	B2	100*	0	95	5
	B3	100*	0	100*	0
	BP24	---	---	100	0
On the Riba ^a da Pantanha	M1	---	---	100	0
	R1	---	---	98	2
	R2	---	---	90	10
	R3	---	---	81	19
Well (depth < 15 m)	P2	96	4	85	15
	P3	---	---	100	0
	P4	---	---	100	0
	P5	100*	0	100*	0
	P6	---	---	100*	0
	P7	100*	0	100*	0
	P8	---	---	100	0
	P9	---	---	100*	0
	Well (depth > 15 m)	F2	93	7	100*
F3		---	---	100	0
F10		100*	0	100*	0
F21		100*	0	100	0

Despite the serious difficulties experienced during the experimental phase of determinations of Pb isotopic ratios, motivated by the very low Pb concentration existing in most water samples analyzed, it was still possible to collect a significant isotopic data set for the water environment around *Urgeiriça's* mine. The detailed analysis of these data provides the following information: (i) about half of samples analyzed (more precisely 48%) display isotopic signatures which reflect the existence of a Pb anthropogenic source, which could not be identified. Only 7% of the Pb presented on the remaining samples will come uniquely from the region's background; (ii) same percentage of samples carrying Pb isotopic signatures directly related to the tailing material (mixture of Background and Pitchblende), reached proportion between 2-19% of the main uranium mineral.

In fact, with the exception of samples P2 and F2, the Pb dissolved present in water samples provided consistent information with dominant presence of an unknown anthropogenic source. In the exception samples, we found a direct influence of Pitchblende estimated at 4 and 7%, respectively.

Isotope analysis undertaken to Pb colloidal reveals, for its part, the contribution of pitchblende signatures found in samples B2 and P2, reaching 15% on the last one. By the fact that attend in a colloidal phase, it is assumed that this Pb had provenance from remobilization phenomena that occurred in water/sediments interface where the Pb is preferably retained, since it made part of the iron-manganese coprecipitate oxide/hydroxide metals. In the case of sample P2, the presence of Pb dissolved and colloidal with isotopic Pitchblende signatures corresponds to 4 and 15%, respectively, gives credibility to the theory that this well be supply by an underground water circuit coming from the tailing surroundings.

In samples collected along the main watercourse we didn't find the minimal Pb concentration required for isotopic analysis. In such samples, where it was only possible to determine lead isotopic ratios in the Pb colloidal, the isotopic data, clearly marked, the influence of pitchblende. Such influence is indicated in samples like R1, R2 and R3. These data reveal possible sediments remobilization phenomena along the bedside and margins of watercourse.

5. CONCLUSIONS

The isotope characterization of the tailing deposit reveals the existence of several Pb sources deposited there. By other hand, this tailing is a typical case of several Pb sources that are not homogenized in terms of present isotopes. So, the definition of the polluting focus was not possible in terms of an "only isotope ratio value", but through mixtures of different Pb sources.

These study reveals something that already was expected, since the U and Pb mobility's are significantly different in the aqueous phase, we only found Pb in half of the picked samples barely in a short distance from focus polluter and in which has still not happened the iron-manganese coprecipitation oxide/hydroxide Fe-Mn (Pb coprecipitates agents). So, the Pb isotopic ratios obtained to check the environmental impact of the polluted focus in the water surroundings area suggest a scatter situation in the main watercourse and in some local points. However, due to reduced mobility of Pb, as evidenced by its low concentrations and/or complete absence of this element in the aqueous phase, the reality may be partial hide. On the contrary, another aspect needs to be emphasized. On the underground (anaerobic situation) the role played by water in Pb isotope ratios data analysis contribute with complementary information about other Pb sources on account of its behavior when percolates throughout porous media

Finally, the reasonable low time needed for analysis achieved by ICP-MS, even when facing difficult matrices with high Uranium content that poses a big challenge because of the space charge and matrix effect already mentioned in previous work (Santos et al., 2007), made possible all the present approach, which points out for the possibility of using these type of data analysis for checking mining exploitation records for environment control.

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References

- Chow, T. J. and Johnstone, M. S. (1965) *Science* **147**, 502
- Helland, A., Göran, A. and Skei, J. (2002) *Marine Chemistry* **78**, 149
- Faure, G. (1986) *Principles of Isotope Geology*. John Wiley & Sons, United States of America, 2nd edition, 310-338
- Sturges, W. T. and Barrie, L. A. (1987) *Nature* **329**, 144
- Simonetti, A., Gariépy, C., Banic, C. M., Tanabe, R. and Wong, H. K. (2004) *Geochimica et Cosmochimica Acta* **68**, 3285
- Mukai, H., Machida, T., Tanaka, A., Vera, Y. P. and Uematsu, M. (2001) *Atmosph. Environ.* **35**, 2783
- Monna, F., Lancelot, J., Croudace, I. W., Cundy, A-B. and Lewis, J.T. (1997) *Environ. Sci. Technol.* **31**, 2277
- Erel, Y., Veron, A. and Halicz, L. (1997) *Geochimica et Cosmochimica Acta* **61**, 4495
- Lord, C. J. III (1994) *J. Anal. At. Spectrom.* **9**, 500
- Åberg, G., Charalampides, G., Fosse, G. and Hjelmseth, H. (2001) *Atmos. Environ.* **35**, 4609
- Hurst, R. W. (2000) *Environ., Forensics* **1**, 11
- Halicz, L., Lam, J. W. H. and McLaren, J. W. (1994) *Spectrochimica. Acta* **49B**, 637
- Miyazaki, A. and Reimer, R. A. (1993) *J. Anal. At. Spectrom.* **8**, 449
- Murphy, E. A. and Hall, G. S. (2000) *Bull. Environ. Contam. Toxicol.* **65**, 314
- Cheng, Z. and Foland, K. A. (2005) *Applied Geochemistry* **20**, 353
- Benkhedda, K., Infante, H. G. and Adams, F. C. (2004) *Analytical Chimica Acta* **506**, 137
- Roy, S. and Négrel, P. (2001) *Sci. Total Environ.* **277**, 225
- Barrett, M. H., Hiscock, K. M., Pedley, S., Lerner, D. N., Tellam, J. H. and French, M. J. (1999) *Wat. Res.* **33**, 3083
- Bjørlykke, A., Vokes, F. M., Birkeland, A. and Thorpe, R. I. (1993) *Econ. Geol.* **88**, 397
- Ettler, V., Mihaljevič, M. and Komárek, M. (2004) *Anal. Bioanal. Chem.* **378**, 311
- Moura, C. A. V., Gandette, H. E., Carvalho, M. C. and Morales, G. P. (2004) *Terrae* **1(1)**, 16
- Haack, U., Kienholz, B., Reimann, C., Schineider, J. and Stumpfl, E. F. (2004) *Geochimica et Cosmochimica Acta* **68**, 2613
- Kaste, J. M., Friedland, A. J. and Stürup, S. (2003) *Environ. Sci. Technol.* **37**, 3560
- Probaska, T., Watkins, M., Latkoczy, C., Wenzel, W. W. and Stingeder, G. (2000) *J. Anal. At. Spectrom.* **15**, 365
- Munksgaard, N. C. and Parry, D. L. (1998) *Sci. Total Environ.* **217**, 113
- Monna, F., Hamer, K., Lévêque, J. and Sauer, M. (2000a) *J. Geoch. Exploration* **68**, 201
- Emmanuel, S. and Erel, Y. (2002) *Geochimica et Cosmochimica Acta* **66**, 2517
- Teutsch, N., Erel, Y., Halicz, L., Banin, A. (2001) *Geochimica et Cosmochimica Acta* **65**, 2853
- Chiaradia, M., Chenhall, B. E., Depers, A. M., Gulson, B. L. and Jones, B. G. (1997) *Sci. Total Environ.* **205**, 107
- Gioia, S. M. C. L., Pimentel, M. M., Tessler, M., Dantas, E. L., Campos, J. E. G., Guimarães, E. M., Marouka, M. T. S. and Nascimento, E. L. C. (2006) *Sci. Total Environ.* **356**, 125
- Ettler, V., Mihaljevič, M., Šebek, O., Molek, M., Grygar, T. and Zeman, J. (2006) *Environ. Poll.* **142**, 409
- Monna, F., Claver, N., Toulkeridis, T. and Lancelot, J. R. (2000b) *Appl. Geochem.* **15**, 1291
- Kawamura, H., Tagomori, M., Matsuoka, N., Takashina, Y., Tawaki, S. and Momoshima, N. (1999) *J. Radioanal. And Nuclear Chemistry* **242**, 717
- Monna, F., Dominik, J., Loizeau, J-L., Pardos, M. and Arpagaus, P. (1999) *Environ. Sci. Technol.* **33**, 2850
- Munksgaard, N. C., Batterham, G. J. and Parry, D. L. (1998) *Marine Pollution Bulletin* **36**, 527
- Munksgaard, N. C., Brazier, J. A., Moir, C. M. and Parry, D. L. (2003) *Aust. J. Chem.* **56**, 233
- Bindler, R., Renberg, I., Anderson, N. J., Appleby, P. G., Emteryd, O. and Boyle, J. (2001) *Atmosph. Environ.* **35**, 4675

- Erel, Y., Dubowski, Y., Halicz, L., Erez, J. and Kaufman, A. (2001) *Environ. Sci. Technol.* **38**, 292
- Cumming, G. L. and Richards, J. R. (1975) *Earth Planet. Sci. Lett.* **28**, 155
- Wiedenbeck, P., Allé, P., Corfu, F., Griffin, W. L., Meier, M., Oberli, F., von Quadt, A., Roddick, J. C. and Spiegel, W. (1995) *Geostandards Newsletter* **19**, 1
- Gulson, B. L., James, M., Giblin, A. M., Sceehan, A. and Mitchell, P. (1997) *Sci. Total Environ.* **205**, 271
- Chiaradia, M., Chenhall, B., Depers, A. M., Gulson, B. L. and Jones, B. G. (1997a) *Sci. Total Environ.* **205**, 107
- Chiaradia, M., Gulson, B. L., James, M., Jameson, C. W. and Johnson, D. (1997b) *Atmosph. Environ.* **31**, 3511
- EXMIN (2001) Estudo Director das Áreas de Minérios Radioactivos, *Internal Report*
- Junta de Energia Nuclear (1968) A Província Uranífera do Centro de Portugal. Suas características estruturais, tectónicas e metalogénicas, Lisboa, 131
- Julivert M., Fontboté J., Ribeiro A. & Conde L. (1974) Memória explicativa del Mapa Tectónico de la Península Ibérica y Baleares. Esc.: 1/ 1000000. *Inst. Geol. Min. España*, Madrid, 133
- Farias, P., Gallastegui, G., González Lodeiro, F., Marquínez, J., Martín-Parra, L.M., Martínez Catalán, J.R., Pablo Maciá, J.G. & Rodríguez-Fernández, L.R. (1987) Aportaciones al conocimiento de la litoestratigrafía y estructura de Galicia Central. *Mem. Museu Mineral. Geol. Fac. Ciências Univ. Porto*, **1**, 411
- Pereira, E.S. (1987) Estudo geológico-estrutural da região de Celorico de Basto e sua interpretação geodinâmica. Ph. D. thesis, Fac. Ciências Univ. Lisboa, Serv. Geol. de Portugal, 274
- Pereira, A.J.S.C., Neves, L.J.P.F., Dias, J.M.M., Campos, A.B.A. E barbosa, S.V.T. (2004) Evaluation of the radiological hazards from uranium mining and milling wastes (Urgeiriça, Central Portugal). *Proceedings of the XI International Congress of the International Radiation Protection Association*, 10
- Santos, R., Machado, M. J., Ruiz, I., Sato, K. and Vasconcelos, M. T. S. D. (2007) *J. Anal. At. Spectrom.* **22**, 1