ARTICLE

Investigations into Pb isotope signatures in groundwater and sediments in a uranium-mineralized area

Investigações isotópicas de Pb em águas subterrâneas e sedimentos de uma área mineralizada em urânio

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ABSTRACT: This work presents the investigation in an environment that contains uranium deposits by using Pb isotope signatures. The study area, southeast of Brazil, is characterized by the lack of surface water and, as a consequence, the groundwater plays an important role in the economy of the region, such as the supply to the uranium industry and, above all serving the needs of the local population. The objective of the present investigation is the determination of the signatures of Pb in groundwater and sediments as well as the identification of environments under influences of geogenic and/or anthropogenic sources. It was determined that the Pb in the majority of sediments was geogenic in origin. Although data from the literature, related to the environmental studies, consider $^{206}Pb/^{207}Pb$ isotopic ratio values below or close to 1.2 as an indicative of anthropogenic Pb, the $^{206}Pb/^{207}Pb$ determined for the majority of groundwater samples ranged from 1.14 to 1.19, and are similar to the data reported for rocks samples (1.09 to 1.96) from area with U mineralization. It was also determined that the anthropogenic influence of the uranium was restricted to a single sampling point within the mining area.

KEYWORDS: Lead stable isotopes; Anthropogenic; Geogenic; Radiogenic Pb; Environmental monitoring.

RESUMO: *Este trabalho investiga um ambiente caracterizado por depósitos de urânio usando assinaturas isotópicas de Pb. A área de estudo apresenta escassez de água superficial, sendo assim, a água subterrânea adquire importância, não só, para o desenvolvimento econômico referente à exploração de urânio, mas, sobretudo, para a sobrevivência e fixação da população local. O objetivo da investigação é a caracterização das assinaturas de Pb em águas subterrâneas e sedimentos, bem como a identificação de ambientes com influências de fontes geogênicas e/ou antropogênicas. Em relação aos sedimentos, verificaram-se que suas assinaturas sofreram influência das fontes geogênicas presentes no contexto geológico e, que o enriquecimento antrópico em urânio foi restrito a um único ponto de amostragem na área da mina. Embora dados na literatura, relativos a estudos ambientais, consideram valores de razões $^{206}Pb/^{207}Pb$ ≤ 1,20 como indicativo de Pb antropogênico, foi determinado para a maioria das águas subterrâneas razões $^{206}Pb/^{207}Pb$ entre 1,14 e 1,19, sendo similares aos dados reportados para as rochas (1,09 a 1,96) na área mineralizada em U.*

PALAVRAS-CHAVE: *Isótopos estáveis de Pb; Antropogênico; Geogênico; Pb radiogênico; Monitoramento ambiental.*

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INTRODUCTION

Lead isotopic studies provide a convincing approach to studying and tracing the geogenic and/or anthropogenic sources of Pb in different environmental matrices, i.e., waters, soils, sediments, rocks, aerosols, peat deposits, tree rings (plants) etc (Bollhöfer *et al.* 1999, Bollhöfer & Rosman 2000, 2001, Chen *et al.* 2005, Gioia *et al.* 2006, 2010, Gulson *et al.* 2007, Komárek *et al.* 2008, Rosman *et al.* 1993, 2000, Rosman & Taylor 1998). In addition, it is particularly useful to demonstrate and identify the anthropogenic input from different sources of Pb from various mining activities, such as uranium/thorium mining and others with potential to generate Naturally Occurring Radioactive Materials (NORM) (Chow *et al.* 1975, Gulson *et al.* 1989, 1992, Bollhöfer & Martin 2003, Moraes *et al.* 2004, Ketterer *et al.* 2010, Vecchia 2015, Vecchia *et al.* 2015). The isotopic composition of Pb is not significantly affected by physical-chemical fractionation processes and it is present in the environment as 4 main isotopes: ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb. The radiogenic isotopes ^{206}Pb, ^{207}Pb, and ^{208}Pb are products of radioactive decay of ^{238}U, ^{235}U, and ^{232}Th. The majority of the available isotopic studies of Pb in the environment has investigated the Pb arising from a geologic environment containing ^{238}U, ^{235}U, and ^{232}Th in concentrations typical of the earth's crust. Few published studies (Gulson *et al.* 1989, 1992, Bollhöfer 2003, Bollhöfer & Martin 2003, Ketterer *et al.* 2010, Vecchia 2015) have investigated radiogenic Pb from areas with U/Th mineralization or the Pb from areas where the radioactive elements U and/or Th may be associated with the exploited ores. The Pb isotopic compositions of U- and Th-rich environment are significantly different from a geologic environment containing U and Th relative to the crust's composition. The typical ranges of Pb isotopic ratios found in natural materials such as ores and rocks are: 14–30 for ^{206}Pb/^{204}Pb, 15–17 for ^{207}Pb/^{204}Pb, and 35–50 for ^{208}Pb/^{204}Pb, although values outside of these ranges are not uncommon. However, the Pb from each ore Pb-rich ore body carries a particular isotopic signature fixed at the time of its formation (Doe 1970, Sangster *et al.* 2000, Bollhöfer & Rosman 2001, Veysseyre *et al.* 2001). In contrast the uranogenic Pb signature, derived by radioactive decay from U, is characterized by higher ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{207}Pb/^{206}Pb ratios and little or no relative increase in ^{208}Pb/^{204}Pb or ^{208}Pb/^{207}Pb.

Uranium mining is generally a matter of concern for the population that lives in its surroundings (Gulson *et al.* 2005). The stakeholders are commonly apprehensive about the possibility of the environmental contamination due the mining and metallurgical processes. Disagreements are not unusual and sometimes difficult to resolve. Pb isotopic composition emerges as a reliable and precise technique able to elucidate this kind of problem as it determines the sources and pathways of the potential contaminants. This technique was employed for the first time in the Lagoa Real Uranium Complex (Brazil) as a tool to indicate whether the elements uranium (^{238}U and ^{235}U) and/or thorium (^{232}Th) were derived from geogenic or anthropogenic sources. This environmental research is considered of extreme importance as the uranium mineralized area is characterized by surface water scarcity (Vecchia 2015, Vecchia *et al.* 2015), and, as a consequence, the aquifers are crucial for the economy of the region as they supply the processing of uranium ore as well as the needs of the population. Therefore, the main objectives of this investigation were the characterization and determination of the Pb isotopic signatures in groundwater and sediment in order to indicate areas that have undergone changes in the Pb isotopic signatures due to anthropogenic sources or those, which have preserved their original features (geogenic sources).

STUDY AREA AND LOCAL GEOLOGY

Pb isotopic compositions of groundwater samples and sediments were determined in one area of 1200 km^2 at Lagoa Real Uranium Complex, Bahia State, Brazil (Fig. 1). This is the main active site of uranium processing in Brazil and South America. This complex is geologically identified as a Gneissic-Granitic Complex with ages between 1.72 and 1.77 Ga (Cordani *et al.* 1992), where granites, gneisses and albitites are the principal lithologies of the region and represents the geogenic sources.

The granitoids of Lagoa Real Uranium Complex, generically called São Timóteo Granite, are immersed in the form of lenses in gneissic rocks (homogeneous orthogneisses), probably caused by the deformation of granites (Maruéjol 1989). The uranium bearing rocks, called U- albitites, are hosted in gneisses (having abrupt contacts), related to shear zones and Na-Ca metasomatism processes (Maruéjol *et al.* 1987). As the U-albitites are the main hosts of the uranium mineralization, they have been extensively studied by several authors, including Costa *et al.* (1983), Lobato (1985), Maruéjol *et al.* (1987) and Lobato and Fyfe (1990). Geochronological investigations at the Lagoa Real Uranium Complex was carried out by Cordani *et al.* (1992) aiming at producing data from Pb isotopic compositions of the rocks such as granite type São Timóteo (undeformed granites) and orthogneiss (deformed granites and associated U-mineralization) considered the most important geogenic sources characteristic of the region. The analyzed

orthogneiss samples by Cordani *et al.* (1992) are unweathered, and are obtained from drill cores in zone of U mineralization. They are from a depth of 50 to 110 m below the surface. Therefore, Pb isotopic signatures data reported by Cordani *et al.* (1992) were used in the present study as reference for geogenic sources.
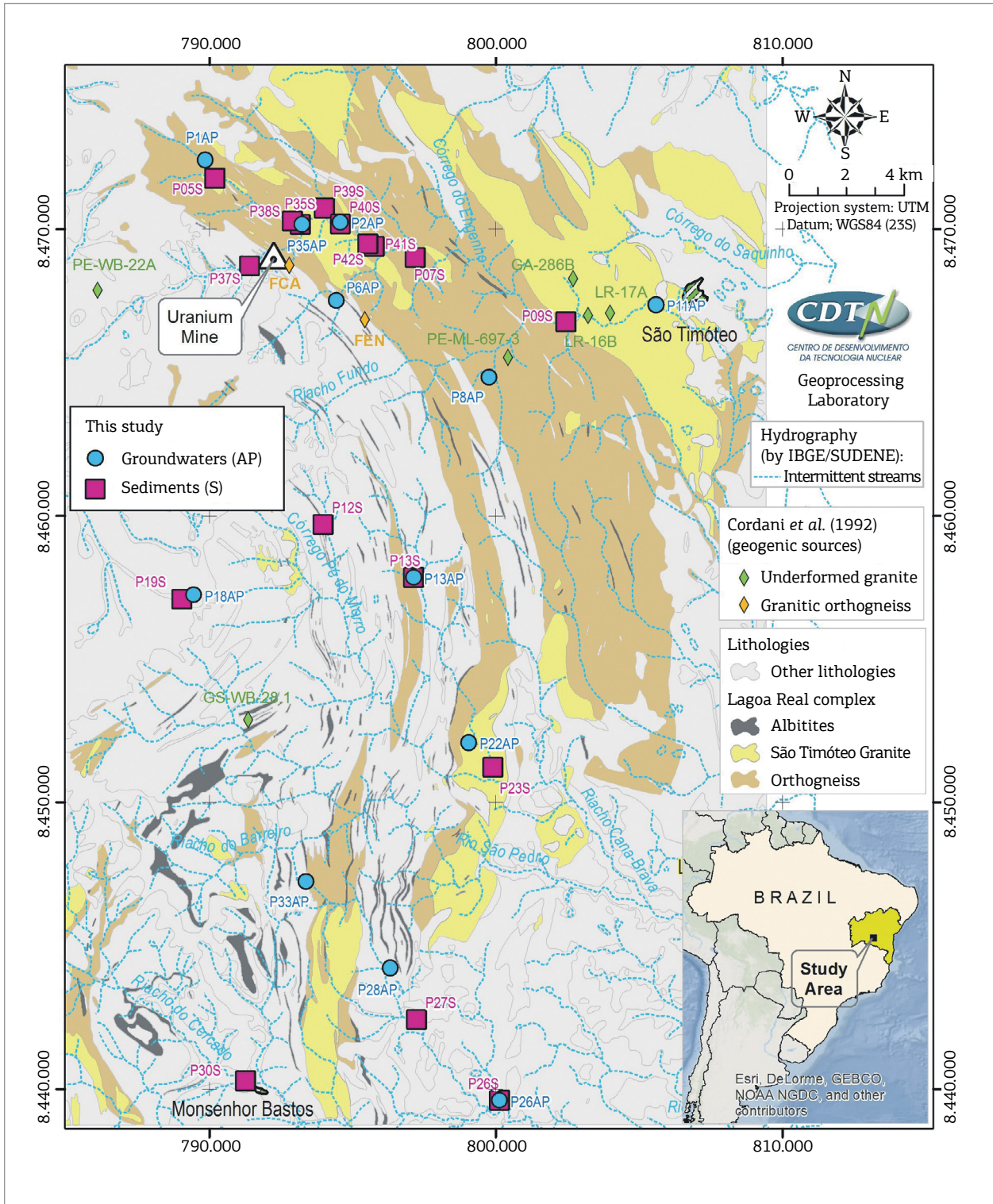

Figure 1. Simplified geologic map with the main lithologies representative of the geogenic sources in the Lagoa Real Uranium Complex: Albitites, Orthogneiss and São Timóteo Granites and the sample locations of sediments and groundwater. (*) vectorized from the geologic map 1:50.000, modified by Costa *et al.* (1985).

Maruéjol *et al.* (1987) carried out a systematic geochemical study of the Lagoa Real Complex and observed a large variation in Th contents (5 to 76 ppm), whereas the U contents were more limited in range. Th/U ratios were found to vary from 4 to 10 similar to most altered granites and this variation was attributed to the probable preferential loss of U over Th from metamict secondary minerals (e.g. allanite, Nb ± Ti REE minerals) throught the preferencial leaching of U (Iyer *et al.* 1999).

The study area is located in the Brazilian semi-arid region characterized by a marked water deficit, with an average annual rainfall of around 700 mm, with high variability in the spatial and temporal distribution of rainfall (annual seasonality) (Vecchia 2015). According to Lamego Simões *et al.* (2003), the dominance of the crystalline rocks, which predominates in the semi-arid region, presents fracture-type aquifer systems with low productivity, where the wells are generally associated with flows of less than 3 m³/h (< 0.0 m³/s). The climatological and hydrological characteristics, associated to the conformation of the regional relief with flows to Atlantic slope, give rise to a hydrographic network in which intermittent drainage are common (Fig. 1), whose discharge occurs only during restricted periods of torrential rain (Lamego Simões *et al.* 2003). Complementary hydrological data of the study region can be seen in Vecchia (2015).

EXPERIMENTAL METHODS

Sampling

Groundwater and sediment sampling points were selected according to regional hydrology and geology, including points at the mining area and points located downstream and upstream of U anomalies. In Lagoa Real, all areas that have higher uranium contents than 1500 ppm are considered anomalies. The selection of environmental matrices of groundwater and sediment for this Pb isotope study was justified by the shortage of surface water. The location of sampling points along with two different matrices made it possible to achieve a reliable geographical representation ensuring a good spatial distribution of the data. Therefore, the scarcity of surface water did not have any interference in the investigation and characterization of this environment. Considering the low precipitation in the region, 700 to 800 mm, concentrated in the wet season (December to January) and the intermittent flow of the rivers, the wet season was defined as the only period for sampling. Thirty samples were analyzed; 12 of groundwater (AP) and 18 of sediments (S) as shown in Figure 1. The sampling points were georeferenced using GPS (Global Positioning System).

The sampling and preservation of water samples were performed according to procedures recommended by the Environmental Agency of the State of São Paulo – CETESB (2011) and Veridiana *et al.* (2008). Water samples in a volume of 1 L were collected in low-density polyethylene (LDPE; Nalgon®) bottles, which were previously washed with deionized water (Milli-Q equipment Millipore®) and detergent; *ca.* 50 mL of an acid mixture of 25% HCl + HNO₃ was added to the bottles and heated at 40°C for 2 days. After that, they were left for two days in an exhaustion hood. The bottles were then rinsed three times with H₂O MQ; *ca.* 50 mL of 25% HCl was added to the bottles and they were heated on a hot plate (40°C) for 2 days. After the bottles had sat for 2 days in an exhaust hood, the solutions were discarded and the bottles were rinsed three times with deionized water; bottles were filled with 1% pure nitric acid and sealed until use; just before sampling, the solutions were discarded and the bottles were rinsed three times with deionized water, dried in a class-100 clean bench under laminar flow and sealed.

During field sampling, bottles were rinsed three times with sample water before collection. 1 L samples were collected in duplicate and the ones that presented clear and free from particles were acidified with nitric acid (HNO₃ – Fluka), refrigerated at 4-10°C and packed for shipping. Water samples were sent to isotopic Pb analysis and geochemistry analytical.

Approximately 1 kg of sediments samples representative of the regional lithologies (Fig. 1) were collected in depth from 50 to 80 cm using a cylindrical collector, and transferred to low-density polyethylene (LDPE; Nalgon®) containers. Subsequently, these samples were dried, disaggregated, homogenized and sieved. Fractions < 63 μm were sent to isotopic Pb and chemical analysis.

Pb Isotopic Geochemistry Analytical Procedure

Pb isotopic ratios of groundwater and sediments were determined through Thermal Ionization Mass Spectrometry (TIMS), using a multi-collector Finnigan MAT 262 at the Geochronological Research Center of the University of São Paulo (USP). Precision in isotope ratio measurements to samples P37S to P42S and P35AP was 0.008%, 0.010% and 0.032% amu⁻¹ (1SD) for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios, respectively, assessed by repeated measurements (n = 80) of NBS 981 (between January and December from 2013). For the other samples, mass fractionation was 0.003%, 0.003 % and 0.010% amu⁻¹(SD) for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios, respectively, determined by repeated measurements (n = 60) on NBS 981 (between January and April from 2012). The Pb analytical blank for the all procedures was typically lower than 200 pg.

Sediments Sample Treatment and Pb, U and Th Geochemistry Analytical Procedure

For determining the Pb in sediments (< 250 Mesh Tyler), the samples were weighed (0.2500 g) and transferred to 20 mL test tube in aqua regia (nitric acid and hydrochloric acid) was added and kept in a water bath (75ºC ± 5ºC) for 2 hours, with stirring every 30 minutes. After finished, the sample cooled to ambient temperature and it was added 20 mL of ultrapure water. The tube was capped and homogenized. After decant, the Pb concentration was determined in ICP-MS.

For the determination of U and Th in sediment samples (< 250 Mesh Tyler), each samples were weighted (0.1000 g) and transferred to graphite crucible and lithium metaborate was added. It was molten in a muffle (950 ± 25ºC) and transferred immediately to the beaker containing nitric acid solution and tartaric acid. It was kepted under stirring until complete dissolution. The dissolved mass was transferred to 100 mL volumetric flask and completed with the solution of nitric acid and tartaric acid. It was homogenized and diluted for determination of U and Th elements in ICP-MS.

Pb, U and Th analyzed in water and sediments samples by Inductively Couple Plasma Mass Spectrometry (ICP-MS), according to procedures recommended by the U.S. EPA 2008, through PerkinElmer - ELAN DRC-e, using a Standard 3 da PerkinElmer – 10 mg/L (Pb) and Standard 2 da PerkinElmer – 10 mg/L (U e Th).

RESULTS AND DISCUSSION

The isotopic data from this study were plotted on $^{208}Pb/^{204}Pb$ *versus* $^{206}Pb/^{204}Pb$ diagram (Fig. 2) that also includes a comparison with isotope ratios:

1. the geogenic Pb data in granite type São Timóteo (undeformed granites) and orthogneiss (deformed granites and associated U-mineralization) available for the Lagoa Real Uranium Complex (U-mineralized area) (Cordani *et al.* 1992) and

2. data from anthropogenic contamination of U (uranogenic Pb) associated with U containing accessory minerals in a Ti ore refining process discharge (NORM waste) (Ketterer *et al.* 2010).

Figure 2 shows that, in general, the sediment samples exhibit Pb isotopic ratios higher than the groundwater samples. The majority of the sediment values are close to the geogenic reference data reported by Cordani *et al.* (1992) for this U-mineralized area, which indicates a geogenic behavior of these signatures. That is, the elevated isotopic ratios have been generated probably in situ at the time of
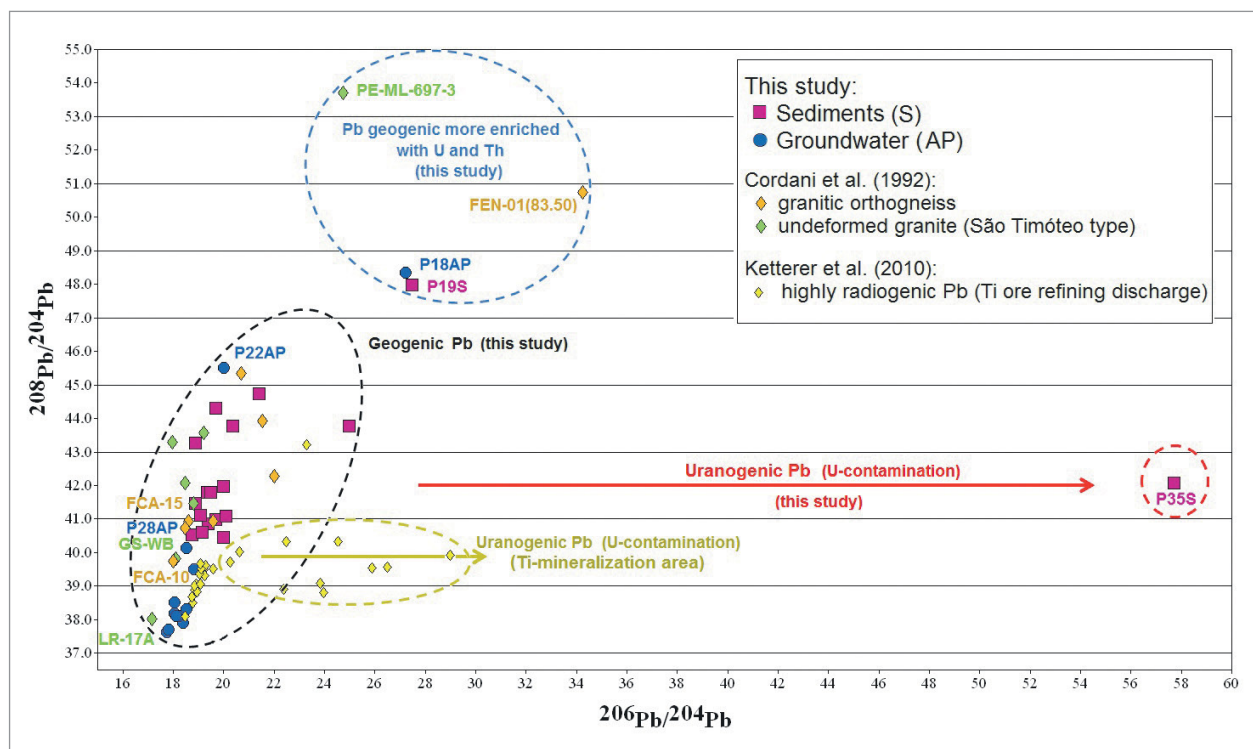

Figure 2. $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram for groundwater, sediment and rocks samples in the U-mineralized area investigated and the Pb isotopic data from the literature.

formation of the rocks. On the other hand, the Pb isotopic ratios of the majority groundwater samples (except P18AP and P22AP) are close to the geogenic data reported by Cordani *et al.* (1992) for the samples FCA-15, GS-WB-28, FCA-10, and LR-17A.

It is also observed in Figure 2 that one sample of sediment (P19S) and other of groundwater (P18AP), from the same geographical coordinate, exhibit similar signatures with high $^{208}Pb/^{204}Pb$ ratio (within the region outlined in blue). In fact, their compositions are comparable to the two samples of geogenic reference from this U-mineralized area (Cordani *et al.* 1992) whose isotopic composition is naturally enriched in U and Th. So, the high $^{208}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ ratios presented by these two different environmental matrices arise from in situ radioactive. According to Gulson *et al.* (1989) the lead isotope characteristics of rocks and/or ore body that have been in contact with groundwater for sufficient time to permit dissolution of lead (and other elements) will determine the fingerprint of the water system. Therefore, with the exception of P18AP and P22AP samples, the groundwater samples despite having

less radiogenic isotopic compositions compared to sediment samples and the other rock samples, are characterized by geogenic sources (FCA-15, GS-WB-28, FCA-10, LR-17A) located in the field delimited (dashed lines), as shown in Figure 2.

Figure 2 also shows that a single sediment sample, P35S, is different from all the other samples. Its $^{206}Pb/^{204}Pb$ ratio of 57.7 is significantly different from the others sediment ratios, which varied from 18.7 to 25.0. The high $^{206}Pb/^{204}Pb$ and low $^{208}Pb/^{204}Pb$ ratios are characteristic of isotopic signature of uranium ores (area outlined in light green) (Ketterer *et al.* 2010, Gulson *et al.* 1989, 1992, Bollhöffer & Martin 2003) even though this sample contain about 28.5 mg U/kg.

Table 1 summarizes the results of the chemical analysis for the U, Th e Pb in sediments and water samples and Iyer *et al.* (1999) data measured by the X-ray Fluorescence in rock samples (Cordani *et al.* 1992) from the Lagoa Real Uranium Complex. It is observed that the U concentrations found in sediments (5.9 – 28.5 mg/kg) are higher when compared to concentrations determined by Iyer *et al.* (1999) in orthogneiss type rocks collected by Cordani *et al.* (1992).

Table 1 - Concentrations data for U, Th and Pb in mg/kg for sediments and in µg/L for water samples (this study - ICP-MS results) and in mg/kg for rock samples (Cordani *et al.*, 1992) – Lagoa Real Complex, Bahia – Brazil.

Sediments samples	U	Th	Pb	Water samples	U	Th	Pb	Rock samples*	U	Th	Pb
P05S	8.20	23.4	11.0	P1AP	14.5	0.005	0.28	Orthogneiss			
P07S	5.87	28.2	22.1	P2AP	4.13	0.005	0.22	FEN-01 (54.50)	3.3	16.8	25.3
P09S	7.13	37.0	28.8	P6AP	10.5	0.005	1.04	FEN-01 (79.75)	2.1	29	24.3
P12S	17.15	63.6	26.1	P8AP	0.15	0.006	0.25	FCA-03 (88.25)	1.7	14.8	20
P13S	10.25	43.1	28.0	P11AP	4.91	0.005	0.21	FCA-15 (97.50)	2.8	8.9	25.2
P15S	6.41	59.9	21.9	P13AP	0.17	0.15	0.49	FEN-01 (81.75)	3.5	8.8	22
P19S	20.38	130.2	45.6	P18AP	2.0	1.13	2.77	FEN-01 (83.50)	–	–	–
P23S	7.57	43.1	23.3	P22AP	0.41	1.92	0.79	FCA-10 (116.25)	< 1	5.3	15.6
P26S	9.91	63.6	29.6	P26AP	37.0	0.005	0.31	FCA-13 (66.50)	< 1	6.4	22.2
P27S	9.97	69.2	26.6	P28AP	0.44	0.024	0.18	São Timóteo Granite			
P30S	9.16	57.0	25.3	P33AP	5.34	0.016	0.23	PE-WB-22A	–	–	–
P35S	28.52	38.2	26.1	P35AP	–	–	–	GS-WB-28.1	–	–	–
P37S	–	–	–					PE-ML-697-3	–	–	–
P38S	–	–	–					LR-16B	–	–	–
P39S	–	–	–					LR-17A	–	–	–
P40S	–	–	–					GA-286B	–	–	–
P41S	–	–	–					GA-798	–	–	–
P42S	–	–	–								

*Concentration of U, Th and Pb from rock samples determined by the X-ray Fluorescence technique (Iyer *et al.*, 1999).

According to the U and Th mobility studies reported by Iyer *et al.* (1999), the orthogneiss samples exhibited a loss of 68 to 86% (U) at various depths for the two places (FCA and FEN). Considering that:

1. orthogneiss have high mobility for U;
2. the U concentrations in sediments vary depending on the concentrations of this element in rocks and
3. the conditions of Eh and pH determine the existing U concentrations in environmental matrices, the U

concentration values found in this study in sediments samples and partly in groundwater samples can be justified by all of the considerations and not only the mobility of U in orthogneiss (Iyer *et al.* 1999). Except for the P35S sample, which has the highest content of U (28.5 mg/kg), the sediment samples showed consistent Pb isotopic signatures with geogenic sources (granites and orthogneiss), more details in Figure 3.
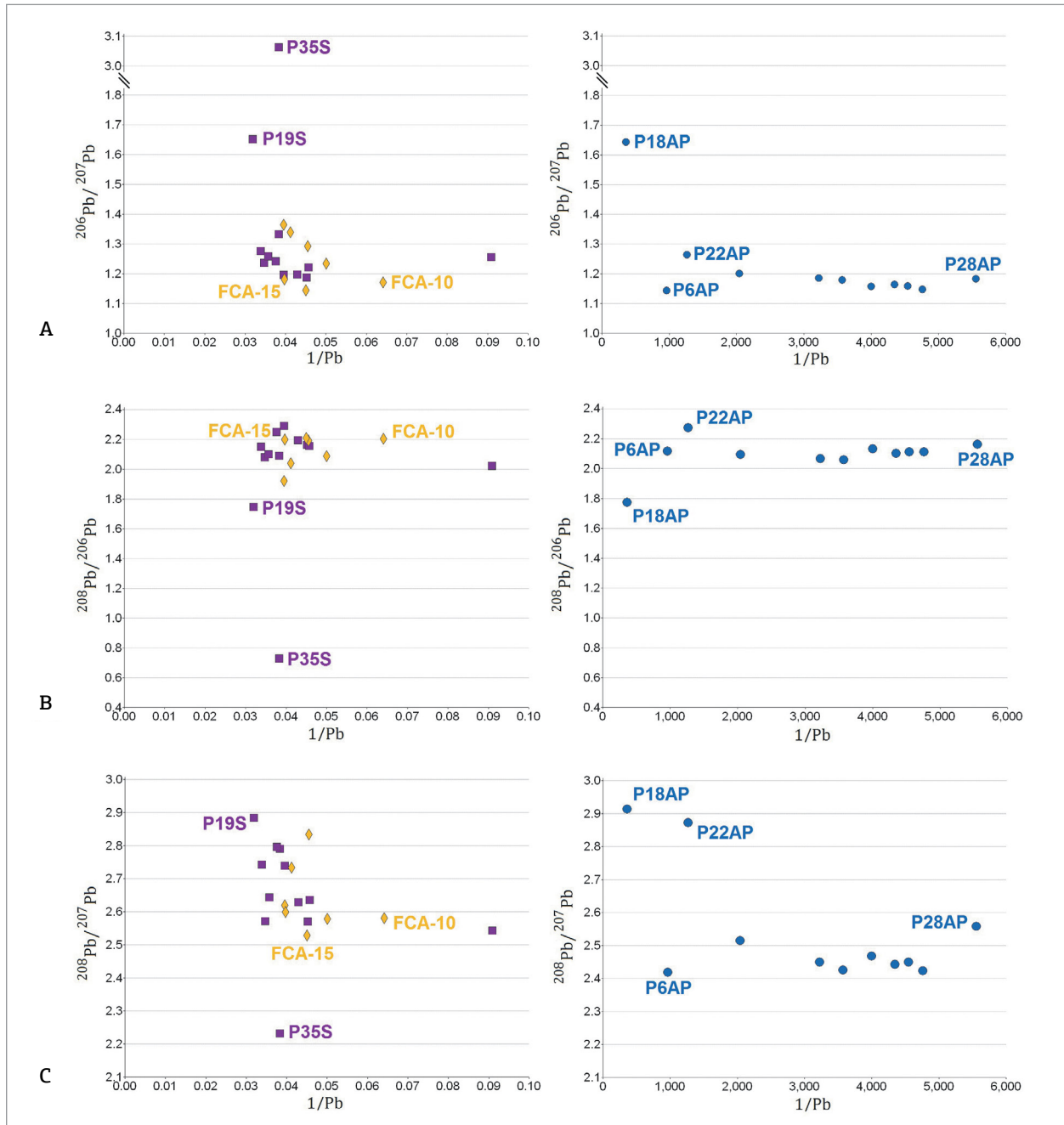
Figure 3. ^{206}Pb/^{207}Pb (A), ^{208}Pb/^{206}Pb (B) and ^{208}Pb/^{207}Pb (C) isotopic ratios versus the inverse Pb concentration (mg/kg) for orthogneiss samples and sediment on the left and groundwater on the right (mg/L). Evidence of anthropogenic U contamination for P35S.

Plots of the Pb isotopic ratios versus inverse Pb total concentration (Fig. 3) shows for the P35S sample (collected in the drainage that intersects the uranium mining) is characterized by U rich material, with very high $^{206}Pb/^{207}Pb$ but low $^{208}Pb/^{207}Pb$ ratios (Gulson *et al.* 1992). The U concentration for sample P35S is 28.5 mg/kg and it is higher than the concentration of other sediment samples (Tab. 1). This information when associated with isotopic data Pb (Figs. 2 and 3) confirms the anthropogenic influence on U and indicate a significant contribution of radiogenic Pb produced by the concurrent decay of ^{238}U and ^{235}U to total Pb in sediments sample.

Figure 3 shows that samples P19S and P18AP from the same area in Lagoa Real Uranium Complex, present $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios more radiogenic compared to other samples, however, free from anthropogenic influences. The samples P19S, P18AP and P22AP (Tab. 1) have higher values for the concentration of Th, reflecting high $^{208}Pb/^{206}Pb$ and $^{208}Pb/^{207}Pb$ ratios in the Figure 3.

The P6AP sample showed the lowest value for the ratio $^{206}Pb/^{207}Pb$ (1:14) compared to the investigated samples, consistent with the ratio value $^{206}Pb/^{207}Pb$ (1:14) on the sample orthogneiss FCA-10. Important to mention that the FEN-01 rock samples exhibited isotopic signature $^{206}Pb/^{207}Pb$ between 1.36 and 1.95, being higher than that found for P6AP, collected in the same region. Considering that the signature of groundwater samples reflect their contact with the rocks from the geological context and, that the sample P6A presents $^{206}Pb/^{207}Pb$ signature similar to that of the orthogneiss sample FCA-10 (Fig. 3), it is suggested that for the sampling point P6AP, the type of orthogneiss is similar to the FCA-10 sample.

The FCA-15 and FCA-10 orthogneiss samples were highlighted in Figure 3 because they represent the geogenic references with the lowest values of Pb isotopic ratios with Pb concentration data available by Iyer *et al.* (1999). The geogenic references are important to understand the low values of Pb isotopic ratios found for the groundwater samples. Additionally, Figure 3 shows there is no indication that there are uranogenic Pb from such material contaminating the groundwater samples.

Aiming at understanding and characterizing the origin of the isotopic sources, it was highlighted, in a $^{208}Pb/^{204}Pb$ *versus* $^{206}Pb/^{204}Pb$ diagram, the values of $^{206}Pb/^{207}Pb$ ratio for all the samples allowing the distinction of the possible sources (Fig. 4). The $^{206}Pb/^{207}Pb$ ratios were highlighted according to specific range as the values varied from 1.19 to 3.10 for sediments, 1.14 to 1.64 for groundwater and 1.09 to 1.96 for rocks. The ranges were stipulated by considering the difference between values lower than 10%.

Figure 4 shows the discrimination between the possible geogenic sources. The discrimination between these possible sources was determined by considering that the $^{206}Pb/^{207}Pb$ values varied from 1.09 to 1.96 for rocks samples from Cordani *et al.* (1992). Although data from the literature considered that the $^{206}Pb/^{207}Pb$ isotopic ratio below or close to 1.2 is an indicative of anthropogenic Pb, the Pb isotopic ratios for the rocks samples FCA-15 (1.18), GS-WB-28 (1.15), FCA-10 (1.14), and LR-17A (1.09) are observed below to 1.2.

The isotopic $^{206}Pb/^{207}Pb$ determined for the majority of the groundwater samples ranged from $1.14 < {}^{206}Pb/^{207}Pb < 1.19$, indicating a shift towards a show less radiogenic isotope signatures in certain regions. The sample P18AP presented the most radiogenic $^{206}Pb/^{207}Pb$ isotope signatures (1.64) and together with the samples P13AP ($^{206}Pb/^{207}Pb$ of 1.20) and P22AP ($^{206}Pb/^{207}Pb$ of 1.26) represent the samples more radiogenic isotope signatures (Fig. 4).

The lowest values of the ratio $^{206}Pb/^{207}Pb$ was for P6AP, P11AP and P8AP groundwater samples (between the rock samples FCA-10 and LR-17A in the Fig. 4) that are located in the river basin near the U mining facilities (Fig. 6).

On the other hand, the isotopic $^{206}Pb/^{207}Pb$ for the majority of the sediments samples ranged from $1.2 < {}^{206}Pb/^{207}Pb < 1.7$, indicating a shift towards a geogenic isotopic signature (Fig. 4). Consequently, all the sediments were considered environmentally preserved; except for the sample P35S whose $^{206}Pb/^{207}Pb$ ratio of 3.10 is in accordance with the findings of anthropogenic influence (Figs. 4 to 6).

In order to improve the Pb isotopic study, the isotopic data from this uranium mineralized area were plotted on $^{206}Pb/^{207}Pb$ *versus* $^{208}Pb/^{207}Pb$ diagram (Fig. 5) along with data from Cordani *et al.* (1992), and data from Bollhöfer and Martin (2003) (used herein as reference for Pb isotopic signatures for sediments from a U-mineralized area in Australia).

The P35S sample differs from all the other samples as it moved away from the geogenic reference field proposed by Cordani *et al.* (1992), which indicates uranogenic Pb isotopic signature, i.e., Pb evolving in a U-rich and Th- and Pb-poor chemical environment.

The sediment and groundwater samples show less radiogenic isotope signatures when compared to sediment data from Bollhöfer and Martin (2003), which indicate the natural enrichment in U and Th. The samples P19S and P18AP show more radiogenic isotope signatures and lie in the same region of the samples of Bollhöfer and Martin (2003) and the samples FEN-01 (83.50) and PE-ML-697-3 from Cordani *et al.* (1992).

According to the data presented in Figures 2, 3 and 5, all the sediment samples (except sample P35S) are derived
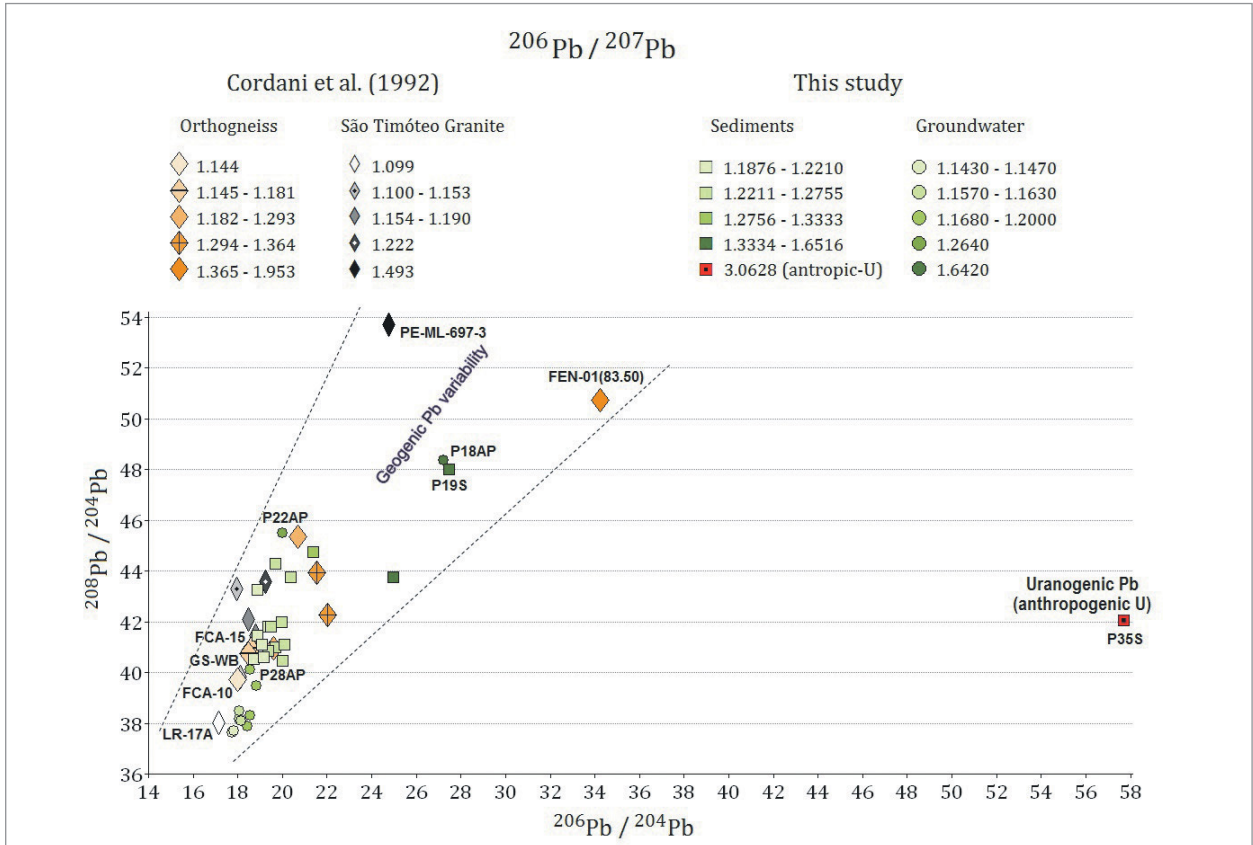
Figure 4. $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagrams showing the geogenic variabililty in terms of the ratio $^{206}Pb/^{207}Pb$ for groundwater and for sediment samples based on the ratio $^{206}Pb/^{207}Pb$ for rocks samples. Evidence of anthropogenic U contamination only for P35S.

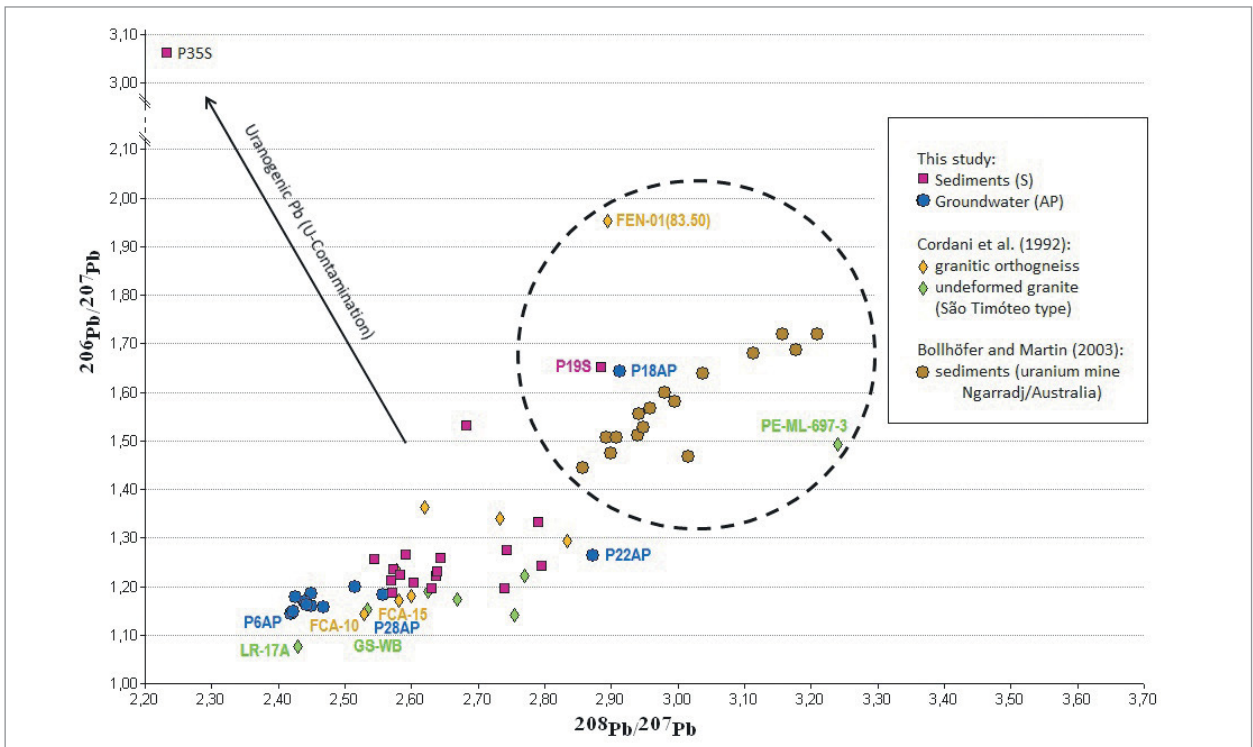Figure 5. $^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{207}Pb$ diagram showing the Pb isotopic signature for samples in the U- mineralized area (Brazil) and also the Pb isotopic data from the literature.

from source materials reflecting the mineralization of the investigated region, i.e., geogenic sources. It is evident that the anthropogenic uranium enrichment is localized as it occurs only for sample P35S, which was collected in the domains of the uranium mining industry (Fig. 6).

Important to note (Fig. 6) that the P37S sample, located upstream of the U mine, has ^{206}Pb/^{207}Pb ratio of the 1.5, which is lower than the ^{206}Pb/^{207}Pb (3.1) ratio of the P35S sample, located downstream the mining facilities.

With respect to groundwater one, Figure 6 shows that Pb isotopic signatures are characteristic of geogenic sources and are widely spread throughout the region of Lagoa Real Uranium Complex. The lowest values of ^{206}Pb/^{207}Pb ratios for most groundwater samples are in accordance to the ^{206}Pb/^{207}Pb ratios of the geogenic sources LR-17A and FCA-10. However, it is strongly recommend a detailed investigation of the potential sources of anthropogenic Pb that can be the main responsible for the lower ^{206}Pb/^{207}Pb ratios found in this area. It is necessary to carry out Pb isotopic analyses in sediments, groundwater, surface water, soils and aerosols. In addition, investigation into other groundwater wells, located in the U mining area where the lower ratio values

^{206}Pb/^{207}Pb were detected is also recommended. One reason for possible anthropogenic interference owes to the fact that both the population and the industry, mainly the uranium mining, make extensive use of the water from the wells. Then, it may be possible to identify the main activities of the industry and/or population contributing to the Pb sources. It is important to assess the Pb isotopic signatures from fertilizers, gasoline and organic solvents used in the metallurgy of U to determine the main agent in the contamination.

CONCLUSIONS

The use of the ^{206}Pb/^{207}Pb *versus* ^{208}Pb/^{207}Pb and the ^{208}Pb/^{204}Pb *vs* ^{206}Pb/^{204}Pb diagrams and the association with the ^{206}Pb/^{207}Pb ratios makes it possible to determine areas with anthropogenic U, as well as areas with Pb originated from geogenic sources. The availability of reference data from literature, mainly geogenic for U, and their association with the obtained data ensured a fair assessment of the present isotopic investigation. In particular, the association of all these data proved to be very important to elucidate
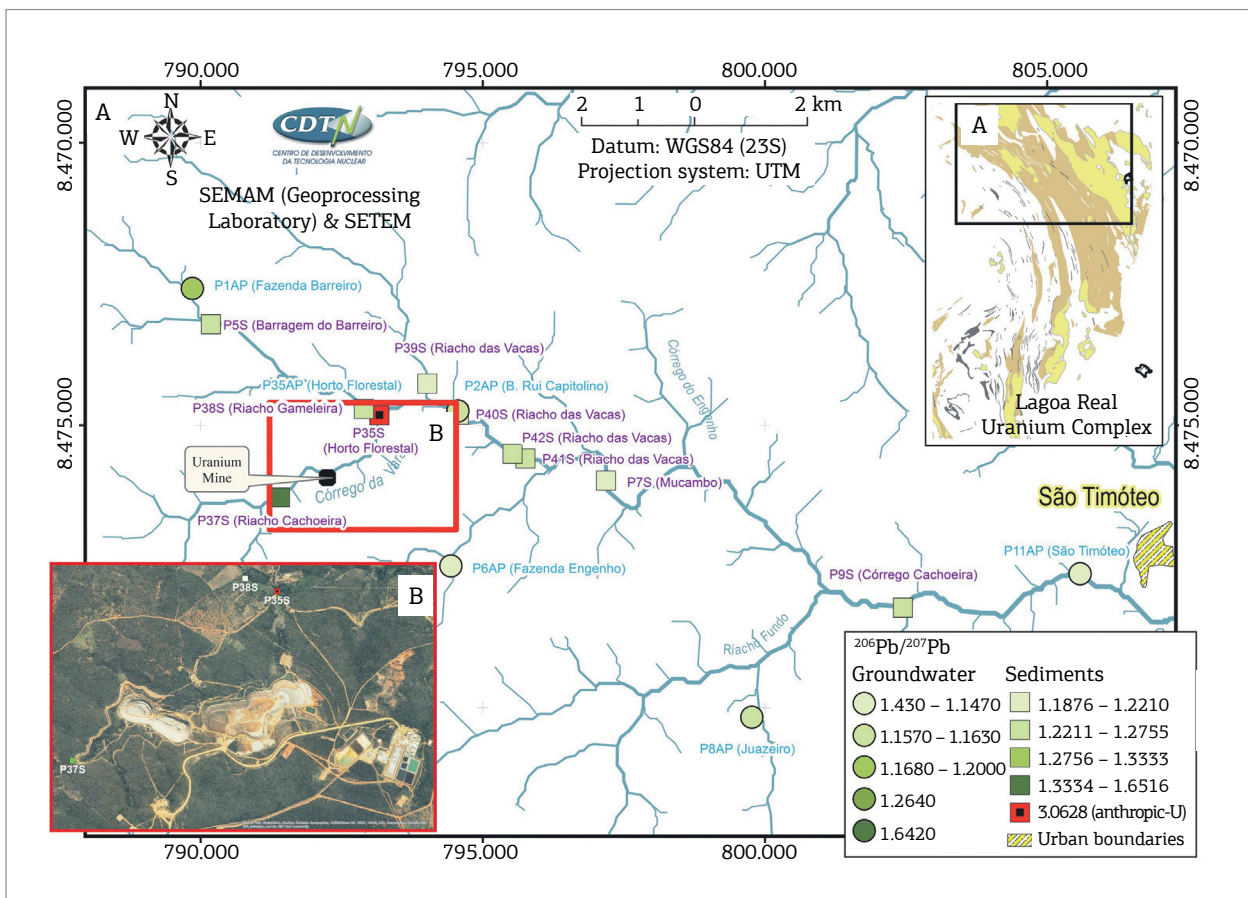

Figure 6. Isotopic ^{206}Pb/^{207}Pb ratio distribution from groundwater and sediment samples from the watershed in the northern region of the study area (A) and around the uranium mining industry area showing the contaminated location (B).

the contamination and environmental monitoring of Lagoa Real Complex. The following points should be stressed:

1. There is a great variation of the Pb isotopic signatures for both sediment and groundwater samples related to the geogenic sources (representative of the regional lithologies), however, the variation for the sediments is significantly higher;

2. Among the geogenic sources, it was observed that the Pb isotopic signatures for the matrices sediments and groundwater, from the same geographical coordinate, indicated a natural enrichment in U and Th;

3. The values of the majority of the Pb isotopic signatures for groundwater are considered low, however, they are in accordance with the geogenic sources of the region;

4. One sediment sample, collected in the U mining area, presented isotopic Pb signature typical of anthropogenic sources in U, i.e., U-contamination. Therefore, the use of Pb isotopic signatures demonstrated to be very effective in discriminating geogenic from anthropogenic sources in one U-mineralized area.

The investigations into Pb isotope signatures in groundwater and sediments in a uranium-mineralized area indicated a preservation of the Lagoa Real Complex. Although preserved, it is necessary environmental monitoring to ensure the exploitation of uranium with social and environmental responsibility. Furthermore, due to its independence of natural environmental processes and of the type of environmental matrices, this technique also proved to be an invaluable analytical method for regions with shortage of surface water. It is important to mention that Pb isotopic signatures can also be useful to indicate an anthropic enrichment in radionuclides (mainly U and Th – the natural generators of radiogenic Pb) present in NORM wastes generated by ore processing, such as Fe, Mn, Cu, Au, Al, Ta/Nb, Ag, Ni, Mo, Zn, Sn, Ti, Zr , Phosphate and Rare Earths ores.

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REFERENCES

Bollhöfer A. 2003. The *use of lead isotopes for research and monitoring the environmental impacts of uranium mining*. Internal report. Australia, Environmental Research Institute of the Supervising Scientist Department of the Environment and Heritage, Australian Government, 24p. Available from: <http://www.environment.gov.au/system/files/resources/00220cf6-cd5b-4852-a21c-b9db53ff975b/files/ir462.pdf>. Accessed on: 2013 Oct. 20.

Bollhöfer A., Chisholm W., Rosman K.J.R. 1999. Sampling aerosols for lead isotopes on a global scale. *Analytica Chimica Acta*, **390**:227-235.

Bollhöfer A., Martin P. 2003. *Radioactive and radiogenic isotopes in Ngarradj (Swift Creek) sediments:* a baseline study. Australia, Environmental Research Institute of the Supervising Scientist Department of the Environment and Heritage, Australian Government, 21p. Available from: <https://www.environment.gov.au/system/files/resources/e443a2eb-d1dc-49a4-8974-54f61d7ef686/files/ir404.pdf>. Accessed on: 2013 Oct. 20.

Bollhöfer A. & Rosman K.J.R. 2000. Isotopic source signatures for atmospheric lead: the Southern Hemisphere. *Geochimica Cosmochimica Acta*, **64**(19):3251-3262.

Bollhöfer A. & Rosman K.J.R. 2001. Isotopic source signatures for atmospheric lead: the Northern Hemisphere. *Geochimica Cosmochimica Acta*, **65**:1727-1740.

CETESB – Companhia de Tecnologia de Saneamento Ambiental. 2011. *Guia nacional de coleta e preservação de amostras:* água, sedimento, comunidades aquáticas e efluentes líquidos. 2ª ed. São Paulo, CETESB; Brasília, Agência Nacional de Águas, Ministério do Meio Ambiente, 325p.

Chen J., Tan M., Li Y., Zhang Y., Lu W., Tong Y., Zhang G. 2005. A lead isotopic record of Shangai atmospheric led emissions in total suspended particles during the period of phasing out of leaded gasoline. Atmospheric Environment, **39**:1245-1253.

Chow T.J., Snyder C.B., Earl J.L. 1975. United Nations FAO and International Atomic Energy Association Symposium, Vienna, Austria (IAEA-SM-191/4). *Proceedings*. p.95-108.

Cordani U.G., Iyer S.S., Taylor P.N., Kawashita K., Mcreath I. 1992. Pb-Pb, Rb-Sr, and K-Ar systematic of the Lagoa Real uranium province (south-central Bahia, Brazil) and the Espinhaço Cycle (ca. 1.5–1.0 Ga). *Journal of South American Earth Sciences*, **1**:33-46.

Costa P.H., Andrade A.R.F., Lopes G.A., Souza S.L. 1985. Projeto Lagoa Real. Mapeamento Geológico, 1:25000, texto e mapas. Companhia Baiana de Pesquisa Mineral, Salvador, v. 1.

Costa P.H., Vianna I., Lopes G.A., Souza S. 1983. Projeto Lagoa Real. Mapeamento Geológico 1:50000. Companhia Baiana de Pesquisa Mineral, Salvador.

Doe B.R. 1970. *Lead Isotopes*. Berlin, Springer-Verlag, 137p.

Gioia S.M.C.L., Babinski M., Weiss D.J., Kerr A.A.F.S. 2010. Insights into the dynamics and sources of atmospheric lead and particulate matter in São Paulo, Brazil, from high temporal resolution sampling. *Atmospheric Research*, **98**:478-485.

Gioia S.M.C.L., Pimentel M.M., Tessler M., Dantas E.L., Campos J.E.G., Guimarães E.M., Maruoka M.T.S., Nascimento E.L.C. 2006. Sources of anthropogenic lead in sediments from an artificial lake in Brasília, central Brazil. *Science of the Total Environment*, **356**:125-142.

Gulson B.L., Korsch M.J., Dickson B., Cohen D., Mizon K.J., Davis M.J. 2007. Comparison of lead isotopes with source apportionment models, including SOM, for air particulates. *Science of the Total Environment*, **381**:169-179.

Gulson B.L., Mizon K.J., Dickson B.L., Korsch M.J. 2005. The effect of exposure to employees from mining and milling operations in a uranium mine on lead isotopes—a pilot study. *Science of the Total Environment*, **339**:267-272.

Gulson B.L., Mizon K.J., Korsch M.J. 1989. Lead isotope as seepage indicators around a uranium tailings dam. *Environmental Science & Technology*, **23**:290-294.

Gulson B.L., Mizon K.J., Korsch M.J., Carr G.R., Eames J., Akber R.A. 1992. *Lead isotope results for waters and particulates as seepage indicators around the Ranger uranium tailings dam – a comparison with the 1984 results*. Report 95 Supervising Scientist Canberra.

Iyer, S.S., Babinski, M., Marinho, M.M., Barbosa, J.S.F., Sato, I.M., Salvador, V.L. 1999. Lead isotope evidence for recent uranium mobility in geological formations of Brazil: implications for radioactive waste disposal. *Applied Geochemistry*, **14**:197-221.

Ketterer M.E., Lane D.A., Jordan J.A. 2010. Unusually Radiogenic Lead (Pb) in Ashtabula River Sediments: An Isotopic Tracing Case Study Using Quadrupole ICP-MS. The *Open Chemical and Biomedical Methods Journal*, **3**:202-209.

Komárek M., Ettler V., Chrastný V., Mihaljevič M. 2008. Lead isotopes in environmental sciences: a review. *Environment International*, **34**:562-577.

Lamego Simões F.F.F., Fernandes H.R.S.M., Franklin M.R., Flexor J.M., Fontes S.L., Pereira F.S.R., Nascimento F.M.F. 2003. Impactos de Mineração e Sustentabilidade no Semi-Árido. Estudo de caso: Unidade de Concentração de Urânio – URA (Caetité, BA). Centro de Tecnologia Mineral – CETEM – Ministério da Ciência e Tecnologia. *In*: Simpósio Brasileiro de Recursos Hídricos, 15., 2003, Curitiba. *Comunicação técnica*. Porto Alegre, ABRH, 18p.

Lobato L.M. 1985. Metamorphism, metassomatism and mineralization at Lagoa Real, Bahia, Brazil. PhD Thesis, University Western Ontario, Ontario. 306 p.

Lobato L.M., Fyfe W. 1990. Metamorphism and mineralization at Lagoa Real, Bahia, Brasil. *Economic Geology*, **5**:968-989.

Maruéjol P. 1989. *Métasomatose alkaline et minéralisations uraniferes: les albitites du gisement de Lagoa Real (Bahia, Brésil) et exemples complémentaires de Xihuasham (SE Chine), Zheltorechensk (Ukraine) et Chhuling Khola (Nepal central)*. These de doctorat, Centre de recherché Sur la Géologie de L'Uranium – CREGU. Nancy, France, 428p.

Maruéjol P., Cuney M., Fuzikawa K., Netto A.M., Poty B. 1987. The Lagoa Real subalkaline granitic complex (south Bahia, Brazil): A source for uranium mineralizations associated with Na-Ca metassomatism. *Revista Brasileira de Geociências*, **17**(4):578-594.

Moraes R.P., Figueiredo B.R., Lafon J.M. 2004. Pb-isotopic tracing of metal-pollution sources in the Ribeira Valley, southeastern Brazil. *Terrae*, **1**(1):A19-A26.

Rosman K.J.R., Chisholm W., Boutron C.F., Candelone J.P., Görlach U. 1993. Isotopic evidence for the source of lead in Greenland snows since the late 1960s. *Nature*, **362**:333-335.

Rosman K.J.R., Taylor P.D.P. 1998. IUPAC table of isotopic compositions of the elements. *Pure and Applied Chemistry*, **70**:217-235.

Rosman K.J.R., Van de Veld K., Boutron C.F. 2000. A two century record of lead isotopes in high altitude Alpine snow and ice. *Earth and Planetary Sciences Letters*, **176**:413-424.

Sangster, D.F., Outridge, P.M., Davis, W.J., 2000. Stable lead isotope characteristics of lead ore deposits of environmental significance. *Environment Reviews*, **8**:115-147.

Vecchia A.M.D. 2015. *Investigações Isotópicas de Pb em Águas Subterrâneas e Sedimentos – Província Uranífera de Lagoa Real – (Bahia)*. Tese de Doutorado, Centro de Desenvolvimento da Tecnologia Nuclear, Comissão Nacional de Energia Nuclear, Belo Horizonte, 222p.

Vecchia A.M.D., Rodrigues P.C.H., Ladeira A.C.Q., Rios F.J. 2015. Interpretação de dados isotópicos de Pb em diferentes ambientes investigativos visando o diagnóstico de fontes geogênicas e/ou antrópicas. *Geonomos*, **22**(2):77-90.

Veridiana M., Babinski M., Ruiz I., Sato K., Souza S., Hirata R. 2008. Analytical procedures for determining Pb and Sr isotopic compositions in water by ID-TIMS. *Química Nova*, **31**(7):1836-1842.

Veysseyre A.M., Bollhöfer A.F., Rosman K.J.R., Ferrari C.P., Boutron C.F. 2001. Tracing the origin of pollution in French Alpine snow and aerosols using lead isotopic ratios. *Environmental Science & Technology*, **35**:4463-4469.

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