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 $^{206}\text{Pb}/^{207}\text{Pb}$ isotopic ratio values below or close to 1.2 as an indicative of anthropogenic Pb, the $^{206}\text{Pb}/^{207}\text{Pb}$ 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 isotôpicas 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, considerem valores de razões $^{206}\text{Pb}/^{207}\text{Pb}$ $\leq$ 1.20 como indicativo de Pb antropogênico, foi determinado para a maioria das águas subterrâneas razões $^{206}\text{Pb}/^{207}\text{Pb}$ 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.
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: 204Pb, 206Pb, 207Pb, and 208Pb. The radiogenic isotopes 206Pb, 207Pb, and 208Pb are products of radioactive decay of 238U, 235U, and 232Th. The majority of the available isotopic studies of Pb in the environment have investigated the Pb arising from a geologic environment containing 238U, 235U, and 232Th in concentrations typical of the earth’s crust. Few published studies (Gulson et al. 1989, 1992, 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 environments 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 206Pb/204Pb, 15–17 for 207Pb/204Pb, and 35–50 for 208Pb/204Pb, 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, Veyssyeure et al. 2001). In contrast the uranogenic Pb signature, derived by radioactive decay from U, is characterized by higher 206Pb/204Pb, 207Pb/204Pb, and 208Pb/204Pb ratios and little or no relative increase in 206Pb/204Pb or 207Pb/204Pb.

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 (235U and 238U) and/or thorium (232Th) 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 km² 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 amphibolites are the principal lithologies of the region and represents the geogenic sources.

The granitoids of Lagoa Real Uranium Complex, generally 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.

This study
- Groundwaters (AP)
- Sediments (S)

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).
**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. 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; Nalgón) bottles, which were previously washed with deionized water (Milli-Q equipment Millipore®) and detergent; 

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 exhaust 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; Nalgón) 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 ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb 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 ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb 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 (75°C ± 5°C) 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 ± 25°C) 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 208Pb/204Pb versus 206Pb/204Pb 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...
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 $^{208}\text{Pb}/^{204}\text{Pb}$ 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 $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ 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 $^{206}\text{Pb}/^{204}\text{Pb}$ ratio of 57.7 is significantly different from the others sediment ratios, which varied from 18.7 to 25.0. The high $^{208}\text{Pb}/^{204}\text{Pb}$ and low $^{206}\text{Pb}/^{204}\text{Pb}$ 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 Pb in sediments and water samples and Iyer et al. (1999) data measured by the X-ray Flourescence 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.

<table>
<thead>
<tr>
<th>Sediments</th>
<th>U (mg/kg)</th>
<th>Th (mg/kg)</th>
<th>Pb (mg/kg)</th>
<th>Water samples</th>
<th>U (µg/L)</th>
<th>Th (µg/L)</th>
<th>Pb (µg/L)</th>
<th>Rock samples</th>
<th>U (mg/kg)</th>
<th>Th (mg/kg)</th>
<th>Pb (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P05S</td>
<td>8.20</td>
<td>23.4</td>
<td>11.0</td>
<td>P1AP</td>
<td>14.5</td>
<td>0.005</td>
<td>0.28</td>
<td>Orthogneiss</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P07S</td>
<td>5.87</td>
<td>28.2</td>
<td>22.1</td>
<td>P2AP</td>
<td>4.13</td>
<td>0.005</td>
<td>0.22</td>
<td>FEN-01 (54.50)</td>
<td>3.3</td>
<td>16.8</td>
<td>25.3</td>
</tr>
<tr>
<td>P09S</td>
<td>7.13</td>
<td>37.0</td>
<td>28.8</td>
<td>P6AP</td>
<td>10.5</td>
<td>0.005</td>
<td>1.04</td>
<td>FEN-01 (79.75)</td>
<td>2.1</td>
<td>29</td>
<td>24.3</td>
</tr>
<tr>
<td>P12S</td>
<td>17.15</td>
<td>63.6</td>
<td>26.1</td>
<td>P8AP</td>
<td>0.15</td>
<td>0.006</td>
<td>0.25</td>
<td>FCA-03 (88.25)</td>
<td>1.7</td>
<td>14.8</td>
<td>20</td>
</tr>
<tr>
<td>P13S</td>
<td>10.25</td>
<td>43.1</td>
<td>28.0</td>
<td>P11AP</td>
<td>4.91</td>
<td>0.005</td>
<td>0.21</td>
<td>FCA-15 (79.50)</td>
<td>2.8</td>
<td>8.9</td>
<td>25.2</td>
</tr>
<tr>
<td>P15S</td>
<td>6.41</td>
<td>59.9</td>
<td>21.9</td>
<td>P13AP</td>
<td>0.17</td>
<td>0.15</td>
<td>0.49</td>
<td>FEN-01 (81.75)</td>
<td>3.5</td>
<td>8.8</td>
<td>22</td>
</tr>
<tr>
<td>P19S</td>
<td>20.38</td>
<td>130.2</td>
<td>45.6</td>
<td>P18AP</td>
<td>2.0</td>
<td>1.13</td>
<td>2.77</td>
<td>FEN-01 (83.50)</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>P23S</td>
<td>7.57</td>
<td>43.1</td>
<td>23.3</td>
<td>P22AP</td>
<td>0.41</td>
<td>1.92</td>
<td>0.79</td>
<td>FCA-10 (116.25)</td>
<td>&lt; 1</td>
<td>5.3</td>
<td>15.6</td>
</tr>
<tr>
<td>P26S</td>
<td>9.91</td>
<td>63.6</td>
<td>29.6</td>
<td>P26AP</td>
<td>37.0</td>
<td>0.005</td>
<td>0.31</td>
<td>FCA-13 (66.50)</td>
<td>&lt; 1</td>
<td>6.4</td>
<td>22.2</td>
</tr>
<tr>
<td>P27S</td>
<td>9.97</td>
<td>69.2</td>
<td>26.6</td>
<td>P28AP</td>
<td>0.44</td>
<td>0.024</td>
<td>0.18</td>
<td>São Timóteo Granite</td>
<td></td>
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<tr>
<td>P30S</td>
<td>9.16</td>
<td>57.0</td>
<td>25.3</td>
<td>P33AP</td>
<td>5.34</td>
<td>0.016</td>
<td>0.23</td>
<td>PE-WB-22A</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>P35S</td>
<td>28.52</td>
<td>38.2</td>
<td>26.1</td>
<td>P35AP</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>GS-WB-28.1</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>P37S</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>PE-ML-697-3</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>P38S</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>LR-16B</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>P39S</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>LR-17A</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>P40S</td>
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<td>–</td>
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<td>P41S</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>GA-798</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>P42S</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<td>–</td>
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<td>–</td>
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</tr>
</tbody>
</table>

*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 geo‑genic 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 \(^{206}\text{Pb}/^{207}\text{Pb}\) but low \(^{208}\text{Pb}/^{207}\text{Pb}\) 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 \(^{235}\text{U}\) and \(^{239}\text{U}\) to total Pb in sediments sample.

Figure 3 shows that samples P19S and P18AP from the same area in Lagoa Real Uranium Complex, present \(^{206}\text{Pb}/^{207}\text{Pb}\) and \(^{208}\text{Pb}/^{207}\text{Pb}\) 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 \(^{208}\text{Pb}/^{207}\text{Pb}\) and \(^{206}\text{Pb}/^{207}\text{Pb}\) ratios in the Figure 3.

The P6AP sample showed the lowest value for the ratio \(^{206}\text{Pb}/^{207}\text{Pb}\) (1:14) compared to the investigated samples, consistent with the ratio value \(^{206}\text{Pb}/^{207}\text{Pb}\) (1:14) on the sample orthogneiss FCA-10. Important to mention that the FEN-01 rock samples exhibited isotopic signature \(^{206}\text{Pb}/^{207}\text{Pb}\) between 1.36 and 1.95, being higher than that found for P6AP, collected in the same region. Considering that the sample of groundwater samples reflect their contact with the rocks from the geological context and, that the sample P6A presents \(^{206}\text{Pb}/^{207}\text{Pb}\) 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 \(^{206}\text{Pb}/^{207}\text{Pb}\) versus \(^{208}\text{Pb}/^{207}\text{Pb}\) diagram, the values of \(^{206}\text{Pb}/^{207}\text{Pb}\) ratio for all the samples allowing the distinction of the possible sources (Fig. 4). The \(^{206}\text{Pb}/^{207}\text{Pb}\) 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 \(^{206}\text{Pb}/^{207}\text{Pb}\) values varied from 1.09 to 1.96 for rocks samples from Cordani et al. (1992). Although data from the literature considered that the \(^{206}\text{Pb}/^{207}\text{Pb}\) 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 \(^{206}\text{Pb}/^{207}\text{Pb}\) determined for the majority of the groundwater samples ranged from 1.14 < \(^{206}\text{Pb}/^{207}\text{Pb}\) < 1.19, indicating a shift towards a show less radiogenic isotope signatures in certain regions. The sample P18AP presented the most radiogenic \(^{206}\text{Pb}/^{207}\text{Pb}\) isotope signatures (1.64) and together with the samples P13AP (\(^{206}\text{Pb}/^{207}\text{Pb}\) of 1.20) and P22AP (\(^{206}\text{Pb}/^{207}\text{Pb}\) of 1.26) represent the samples more radiogenic isotope signatures (Fig. 4).

The lowest values of the ratio \(^{206}\text{Pb}/^{207}\text{Pb}\) 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 \(^{206}\text{Pb}/^{207}\text{Pb}\) for the majority of the sediments samples ranged from 1.2 < \(^{206}\text{Pb}/^{207}\text{Pb}\) < 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 \(^{206}\text{Pb}/^{207}\text{Pb}\) 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 \(^{206}\text{Pb}/^{207}\text{Pb}\) versus \(^{208}\text{Pb}/^{207}\text{Pb}\) 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. $^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ diagrams showing the geogenic variability in terms of the ratio $^{206}\text{Pb}/^{207}\text{Pb}$ for groundwater and for sediment samples based on the ratio $^{206}\text{Pb}/^{207}\text{Pb}$ for rocks samples. Evidence of anthropogenic U contamination only for P35S.

Figure 5. $^{206}\text{Pb}/^{207}\text{Pb}$ vs $^{208}\text{Pb}/^{204}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of the 1.5, which is lower than the $^{206}\text{Pb}/^{207}\text{Pb}$ (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 $^{206}\text{Pb}/^{207}\text{Pb}$ ratios for most groundwater samples are in accordance to the $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 of $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{207}\text{Pb}$ and the $^{208}\text{Pb}/^{204}\text{Pb}$ by $^{206}\text{Pb}/^{204}\text{Pb}$ diagrams and the association with the $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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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Pb isotope signatures in a uranium-mineralized area


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