J Radioanal Nucl Chem (2015) 304:1053–1058
DOI 10.1007/s10967-015-3934-7

Rare-earth elements in uranium deposits in the municipality of Pedra, Pernambuco, Brazil

Kennedy Francys Rodrigues Damascena · Romilton dos Santos Amaral · José Araújo dos Santos Júnior · Frederico Antonio Genezini · Alberto Antônio da Silva · Rômulo Simões Cezar Menezes

Received: 4 September 2014 / Published online: 14 January 2015
© Akadémiai Kiadó, Budapest, Hungary 2015

Abstract In the present study, soil and rock samples were collected from uranium deposits in the city of Pedra, Pernambuco, Brazil. These samples were analyzed using neutron activation analysis to identify the occurrence of rare-earth elements (REE). The most abundant elements found were Ce, Nd and La, with concentrations 12 times higher than the average in the earth's crust and 4.6 times higher than values reported in worldwide studies, including Brazil. Nonetheless, further studies to examine the economic feasibility of mining REEs from this site are necessary.

K. F. R. Damascena (✉) · R. dos Santos Amaral · J. A. dos Santos Júnior · A. A. da Silva
Grupo de Radioecologia (RAE), Departamento de Energia Nuclear (DEN), Universidade Federal de Pernambuco (UFPE), Av. Prof. Luiz Freire, 1000-Cidade Universitária, Recife, PE 50740-540, Brazil
e-mail: kennedy.eng.ambiental@gmail.com

R. dos Santos Amaral
e-mail: romilton@ufpe.br

J. A. dos Santos Júnior
e-mail: jaraujo@ufpe.br

A. A. da Silva
e-mail: alberto.silva@barreiros.ifpe.edu.br

F. A. Genezini
Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN-SP), Av. Professor Lineu Prestes 2242, São Paulo, SP 05508-000, Brazil
e-mail: fredzini@ipen.br

R. S. C. Menezes
Grupo de Pesquisa da Fertilidade dos Solos/Radioagronomia, Departamento de Energia Nuclear (DEN), Universidade Federal de Pernambuco (UFPE), Av. Prof. Luiz Freire, 1000-Cidade Universitária, Recife, PE 50740-540, Brazil
e-mail: rmenezes@ufpe.br

Keywords Rare-earth elements · Neutron activation analysis · Gamma spectrometry · Primordial radionuclides

Introduction

Rare-earth elements (REE) have been treated as a strategic issue and even one of "national sovereignity" by the governments of some countries. This treatment has occurred because REEs have been used for a variety of reasons in several areas, especially in the oil industry, which employs catalysts to refine oil that contains some of these elements. In addition, REEs are widely applied in the electronic industry and are considered as essential resources in the production of equipment, such as high definition TV's, smartphones, tablets, computers and many other products [1]. According to Alonso et al. [2], the future demand for REE may increase up to 2,600 % over the next few decades due to the possible increase in the production of electric cars and wind turbines, which use dysprosium (Dy) and neodymium (Nd).

Currently, the global demand for REEs is approximately 150,000 tons per year, and the great majority of this amount is produced in China [3]. This situation places China in a dominant market position that directly affects the prices of the items in the international market. This effect on price was recorded in 2010, when the prices of some of these elements significantly increased after the export restrictions by China [4]. To reduce this dependence, several countries, including Brazil, have been conducting research to discover new areas for the potential exploitation of these elements.

Some studies have indicated that coal deposits may be considered as new sources for the recovery some REEs as a by-product [5, 6]. However, the operation of coal mines with high concentrations of REEs is a complex issue, since high concentrations of these elements in the environment may be harmful to human beings and animals [7]. Another strategy to meet part of the supply is to stimulate the recycling of REE from electronic waste, but in general there is a lack of incentives for the recycling route [8]. Meanwhile, the federal government in Brazil (through the Ministry of Mines and Energy and the Ministry of Science, Technology and Innovation), such as other countries, has been conducting studies that will serve as a basis for developing a policy for exploring and extracting these elements. Some of these studies have indicated that the occurrences of these elements in Brazil are associated with radioactive minerals [9]. For example, monazite is a radioactive mineral in a rare-earth orthophosphate formation with a thorium content of between 0.1 and 30 % and up to 1.5 % of natural uranium [10]. Studies in other regions of the world, such as the study by Popic et al. [11] conducted in Norway, also reported high levels of REEs in reservoirs of thorium and uranium.

This association of the REE and radioactive minerals was one aspect that motivated the choice of the area of the present study for further investigation. The municipality of Pedra, which is located in the semiarid region of Pernambuco state, is known for the occurrence of a significant radioactive anomaly of U and Th in amphibolitic silicate rocks and granitic calcium, respectively [12, 13], despite the fact that this U and Th deposit only covers a small area. Another aspect that motivated this study was the lack of studies that have determined the existence of these elements in the area and (if present) their respective concentrations. With this information, we expect that studies can be performed to assess the technical and economical feasibility of extracting elements in the future, which would imply economic development for the region.

There are numerous techniques for determining the presence and concentrations of REE in the environment [14]. In the present study, these tests were performed by using the neutron activation analysis (NAA) technique followed by high resolution Gamma Spectrometry. This methodological sequence was chosen because they are non-destructive techniques with high sensitivity for detecting several elements [15, 16].

Materials and methods

Study area

The study area is located in the Ipanema Valley in the semiarid region of the state of Pernambuco, specifically in the city of Pedra. The geographical location of the study area is at a latitude of approximately 08°29.817′ S and a longitude of approximately 36°56.450′ W (WGS 84 datum) as expressed in Fig. 1. The city is located at 593 m above sea level. From a geological point of view, the municipality is inserted in the Borborema Province and is composed of rocks from the Cabrobó and Belém do São Francisco Intrusive Suite leucocratic peraluminous complex containing granitic rocks of the Indiscriminate and Calcialcalina suite. Major soil types in the region include Luvisols, Planosols and Regolitic Neosols, with the latter representing the soil type in the study area [17, 18].

From a socioeconomic perspective, the Municipality of Pedra has a total estimated resident population of 21,558 inhabitants, of whom 57.3 % live in urban areas. The population density of this area is 24.7 inhabitants per km^2. Among the economic activities of the municipality, 65.3 % are represented by agriculture, especially dairy farming, which is the main source of revenue, with a monthly production of approximately 2.2 million liters of milk [13].

Sample collection, treatment and conditioning

Sample collection was conducted in an area of approximately 2 km^2 that included granite outcrops and amphibolitic calcium silicate. Overall, 115 soil samples were collected that originated from 23 different points and 55 rock samples that were collected from 11 outcrops. Each collection point was marked in a 5 × 5 m grid and divided into quadrants. At each point, 5 samples were collected. Before sampling, the points were previously cleaned. Next, a sample of approximately 5.0 kg was collected at each point at a depth of 30–50 cm, which corresponded to the C horizon.

During the collection of rock samples, the granite outcrops and amphibolitic calcium-silicate rocks that existed within the area were prioritized. From the 11 outcrops, six corresponded to granite outcrops and five corresponded to calcium-silicate amphiboles. Samples of approximately 10 kg were collected from each outcrop, disregarding the weathered surfaces.

After collection, the soil samples were pre-treated as follows: drying at 60 °C; lump breaking; sieving; homogenization; quartering and particle size reduction to obtain particles smaller than 63 µm. The rock samples were crushed and pulverized so that they had the same grain sizes as the soil samples. All of these actions were conducted in partnership with the Laboratory for Mineral Technology at the Department of Mining Engineering of the Federal University of Pernambuco.

After treatment, approximately 1.5 g of each sample was stored in a polyethylene container. These samples were sent to the Laboratory of Neutron Activation Analysis (LNAA) located at the Center of Nuclear Research Reactor (CNRR) of the Energy Research Institute and Nuclear

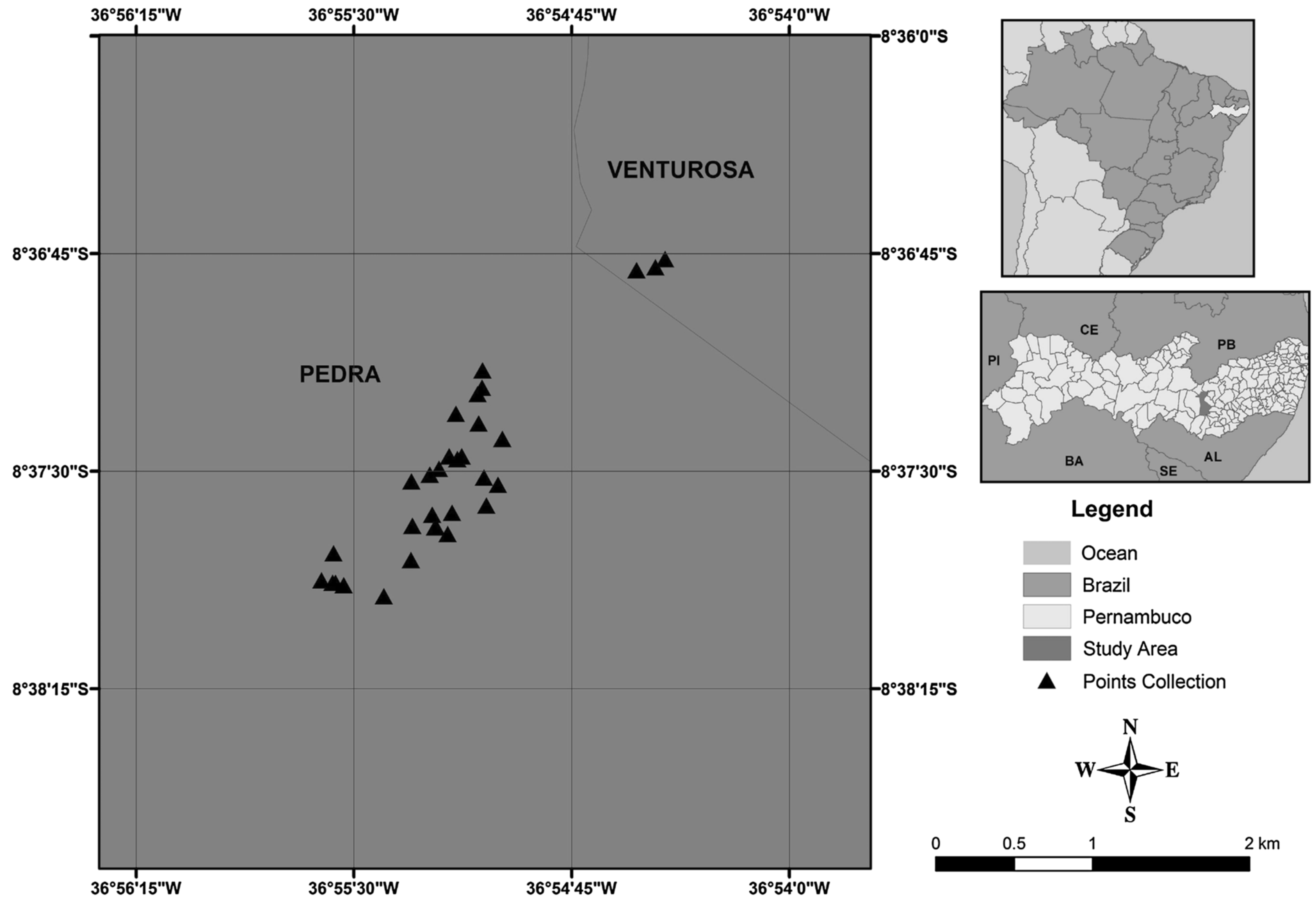


Fig. 1 Map containing the location of the study area and sampling points georeferenced

(IPEN) of the National Nuclear Energy Commission (CNEN) in São Paulo, where the neutron activation gamma spectrometric analyses were performed.

Procedures for neutron activation analysis and gamma analysis

At the Laboratory of Neutron Activation Analysis, approximately 100 mg of each sample was irradiated for 8 h at the research reactor IEA-R1 at IPEN/CNEN-SP. An average neutron flux of 4.5×10^{12} cm^{-2} s^{-1} was used with the granite GS-N (ANRT) and basalt BE-N (GIT-IWG) reference materials.

After irradiation, the samples were analyzed in a high-resolution gamma spectrometry system with an experimental setup consisting of a HPGe detector (Canberra®, model GX2020) with a resolution of 2.0 keV for the 1,332 keV ^{60}Co energy. This system was connected to a multichannel analyzer with 8,196 channels. These measurements were performed in two stages, with the first count performed 7 days after irradiation and the second count performed 15 days later. For treating and handling the spectra and data analysis, the Genie-2000® (from Canberra®) was used. To minimize dead time, measurements were performed using a geometry of 12 cm from the top of the detector.

Results and discussion

As mentioned earlier, we analyzed environmental rock and soil samples from an area that presents an anomalous occurrence of U. The data obtained from the analysis of the samples will be addressed separately for each analyzed matrix to understand them better.

In Fig. 2, the REE mass fractions along the studied area are observed. In most samples, the REE mass fractions do not exceed 300 mg kg^{-1}.

Table 1 shows the results that were obtained for the different rock types (including granite and amphibolitic calcium silicate) and for the different mass fractions of REE, which depended on the rock type. By analyzing the average mass fractions of the elements that were obtained for each different type of outcrop, it was observed that the amphibolitic calcium-silicate rocks have higher mass fractions of seven of the nine elements (La, Ce, Nd, Sm, Tb, Lu and Sc) relative to the granite rocks, especially for the Ce and Nd, whose average mass fractions were 4.5 and 2.3 times higher, respectively, than the values obtained for the granitic rocks.

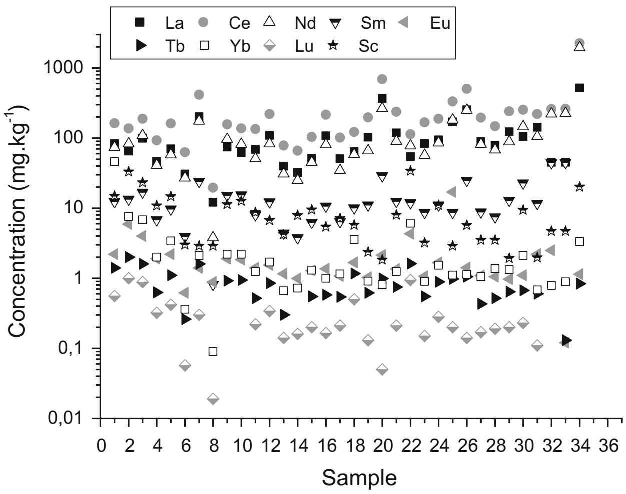


Fig. 2 Mass fractions of rare-earth elements (REEs) in the analyzed environmental matrices

Table 1 Rare-earth elements (REEs) present in rock samples from the municipality of Pedra, Pernambuco, Brazil

REE	Outcrops	Minimum[a]	Maximum[a]	Average[b]
Granite rocks-mass fractions (mg kg^{-1})				
La	6	12.1 ± 0.1	365.0 ± 6.0	139.4 ± 124.0
Ce	6	19.6 ± 0.5	692.0 ± 18.0	258.3 ± 236.6
Nd	6	3.8 ± 0.7	264.0 ± 12.0	114.6 ± 93.8
Sm	6	0.8 ± 0.0	29.0 ± 0.5	12.1 ± 9.3
Eu	6	0.9 ± 0.0	17.0 ± 0.3	4.4 ± 6.2
Tb	6	<0.1	1.4 ± 0.1	0.9 ± 0.3
Yb	6	0.1 ± 0.0	46.0 ± 0.3	8.7 ± 18.3
Lu	6	<0.1	0.6 ± 0.1	0.2 ± 0.2
Sc	6	1.8 ± 0.1	14.9 ± 0.5	5.0 ± 5.0
Amphibolitic calcium silicate rocks-mass fractions (mg kg^{-1})				
La	5	45.1 ± 0.7	517.0 ± 8.5	145.3 ± 207.9
Ce	5	113.0 ± 3.0	2,243.5 ± 60.5	602.3 ± 919.9
Nd	5	78.0 ± 4.0	1,951.0 ± 133.0	511.6 ± 807.8
Sm	5	<0.5	44.8 ± 0.8	22.9 ± 18.5
Eu	5	0.1 ± 0.0	5.9 ± 0.2	2.8 ± 2.4
Tb	5	<0.1	2.0 ± 0.2	0.9 ± 0.8
Yb	5	0.8 ± 0.1	7.6 ± 0.4	3.7 ± 3.1
Lu	5	<0.1	1.0 ± 0.1	0.4 ± 0.0
Sc	5	4.7 ± 0.2	34.0 ± 1.0	19.3 ± 14.4

[a] Value ± uncertainty

[b] Population average ± population standard deviation

In Fig. 3, a comparative analysis of the results obtained in this study from the rock samples is presented relative to the average REE mass fractions in the earth's crust, according to Oliveira et al. [19]. Most of the elements detected in the area, showed the same order of magnitude in terms of mass fraction. The La, Ce and Nd mass fractions behaved differently, with average mass fractions that were much larger than the average values of the earth's crust. In the granitic rocks, the averages of these elements were 4.0, 3.9 and 2.9 times larger, respectively, than the crust average. Regarding the amphibolitic calcium-silicate rocks, the mean mass fractions of these elements were 4.2, 12.0 and 9.0 times higher, respectively. According to Santos Júnior et al. [13], the rock outcrops in the study area had significant mass fractions of Th (Granitic Rocks-40 mg kg^{-1} on average) and U (amphibolitic Calcium silicate rocks-3,132 mg kg^{-1} on average). The association (ETR-U/Th), as evidenced by the literature [10], possibly justifies the high mass fractions of these REE in the analyzed rock types.

When only considering the soil samples, the average mass fractions were related to each REE that was identified in the study area (Table 2). These data were compared with existing data in the literature and are similar to the mean mass fractions of the REE in the crust [19] that were identified in studies conducted worldwide [20–22]. The Ce, La, Nd, Sm, Eu and Tb REEs presented in this study had average mass fractions that were between 2.8 and 4.6 times larger than those found in the literature (Earth's crust and world studies). The other elements show mean mass fractions in most of the comparisons that were between 0.6 and 0.9 times lower than the reference mass fractions.

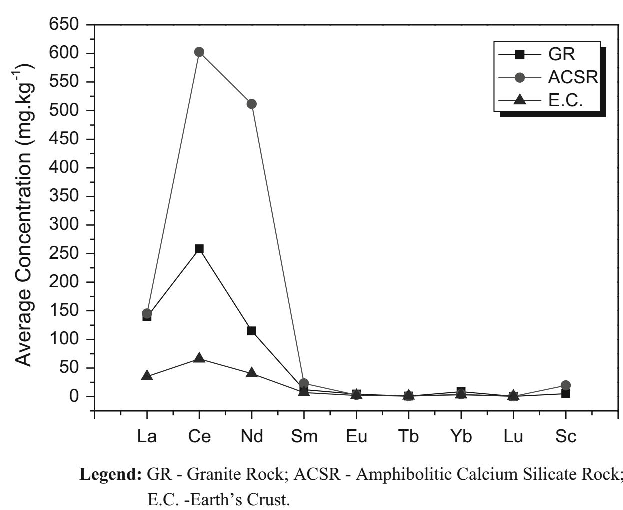


Fig. 3 Comparative analysis of the mean mass fractions of the rare-earth elements (REEs) in the rock samples from the Municipality of Pedra, Pernambuco, Brazil, with the average REEs mass fractions in earth's crust

Table 2 Comparison of rare-earth element mass fractions only considering the soil samples: present study x world studies

REE	Soil samples-mass fractions (mg kg^{-1})				
	This study[a]	Earth's crust[b]	Japan[c]	China[d]	Brazil[e]
La	90.9 ± 51.5	35.0	18.0	34.7	24.0
Ce	185.4 ± 103.8	66.0	40.0	74.8	53.0
Nd	81.3 ± 51.5	40.0	18.0	33.0	22.0
Sm	11.5 ± 6.1	7.0	3.7	5.6	2.6
Eu	1.4 ± 0.7	2.1	1.0	1.1	1.1
Tb	0.8 ± 0.4	1.2	0.6	0.8	0.8
Yb	1.7 ± 1.3	3.1	2.0	2.6	<1
Lu	0.2 ± 0.2	0.8	0.3	0.4	–
Sc	7.7 ± 5.0	–	–	–	19.0

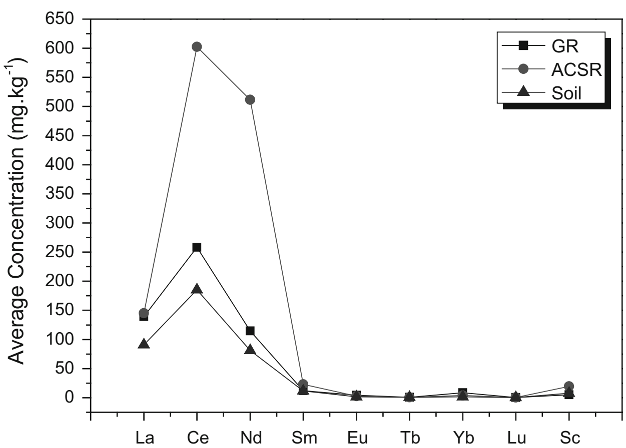
[a] Population average ± population standard deviation

[b] [19]

[c] [20]

[d] [21]

[e] [22]



Legend: GR - Granite Rock; ACSR - Amphibolitic Calcium Silicate Rock.

Fig. 4 Comparative analysis of the average rare-earth elements (REEs) mass fractions between the rock and soil samples-Municipality of Pedra, Pernambuco, Brazil

Figure 4 presents a comparison between the soil and rock samples by using the average REE mass fractions that were identified in the study area. The mass fractions of the rock samples were much higher than those found in the soil samples, especially when compared with the amphibolitic calcium silicate rocks, whose mass fractions were approximately 3.2 times higher in the case of Ce. The significant differences in the REE mass fractions in these environmental matrices can be explained by considering the fact that these rocks represent the forming elements of the soil and REEs are more concentrated. In addition, Ce, La and Nd were observed to show much higher mass fractions than the other REE for both environmental matrices. This finding is confirmed by the literature [10, 19], where it was reported that the light REEs (LREE) (from La to Eu) are usually found in nature in higher mass fractions than the heavy REEs (HREE) (from Gd to Lu).

Conclusions

The results of this study indicated that 9 of the 17 REEs existing in nature were identified in the study area: La, Ce, Nd, Sm, Eu, Tb, Yb, Lu and Sc. The concentrations of REEs that were found demonstrate the importance of this study and confirms the previously identified presence in REE compounds associated with primordial radionuclides, such as U and Th. Among the REEs identified in the study area, Ce, La and Nd showed higher mass fractions, with values that were higher than the averages in the earth's crust (by up to 12 times) and the global averages reported in the literature (by up to 5 times). The remaining REEs were present at mass fractions that were similar to the average levels found on the planet. However, other studies are necessary for extending the area of study and to verify the feasibility of mining the REEs that were found.

Acknowledgments The authors thank the Federal University of Pernambuco, Nuclear Energy Department (DEN) and the Institute of Nuclear Energy Research (IPEN) of the National Nuclear Energy Commission (CNEN) for providing the available infrastructure. In addition, the authors thank the Coordination of Improvement of Higher Education Personnel (CAPES) for the granted scholarship and the Foundation for Science and Technology of the State of Pernambuco (FACEPE) for the financial resources from the grant APQ-0548-3.09/12.

References

1. Resende LV, Morais CA (2010) Miner Eng 23:277–280
2. Alonso E, Sherman AM, Wallington TJ, Everson MP, Field FR, Roth R, Kirchain RE (2012) Environ Sci Technol 46:3406–3414
3. Liang T, Li K, Lingqing W (2014) Environ Monit Assess 186:1499–1513
4. Ting MH, Seaman J (2013) Asian Stud Rev 37(2):234–252. doi:10.1080/10357823.2013.767313
5. Seredin VV, Dai S (2012) Int J Coal Geol 94:67–93
6. Seredin VV, Dai S, Sun Y, Chekryzhov IY (2013) Appl Geochem 31:1–11
7. Ardejanii FD, Rooki R, Shokri BJ, Kish TE, Aryafar A, Tourani P (2013) J Environ Eng 139:896–907
8. Binnemans K, Jones PT, Blanpain B, Gerven TV, Yang Y, Walton A, Buchert M (2013) J Clean Prod 51:1–22
9. Pinto FG, Lepri FG, Silva JBB, Costa LM (2010) Curtius A J 43(6):949–959. doi:10.1080/00032710903491062
10. Abrão A (1994) Química e tecnologia das Terras Raras. Série da Tecnologia Mineral. N° 66. CETEM/CNPq, Rio de Janeiro, Brasil
11. Popic JM, Salbu B, Strand T, Skipperud L (2011) J Environ Monit 13:1730–1738

12. Santos Júnior JA, Cardoso JJRF, Silva CM, Silveira SV, Amaral RS (2010) J Radioanal Nucl Chem 269(2):451–455
13. Santos Júnior JA, Amaral RS, Silva CM, Menezes RSC (2010) Rad Meas 45:861–864
14. Dai J, Wang D, Wang R, Chen Z (2013) J Appl Remote Sens. doi:10.1117/1.JRS.7.073513
15. Lima RB, Yoriyaz H, Hernandes AC, Madi Filho T (2003) Rev Bras Pesqui Desenvolv 5:43–48
16. Shinde AD, Acharya R, Verma R, Reddy AVR (2012) J Radioanal Nucl Chem 294(3):409–412
17. Araujo Filho JC, Burgos N, Lopes OF, Silva FHBB, Medeiros LAR, Melo Filho HFR, Parahyba RBV, Cavalcanti AC, Oliveira Neto MB, Silva FBR, Leite AP, Santos JCP, Sousa Neto NC, Silva AB, Luz LRQP, Lima PC, Reis RMG (2000) Boletim de Pesquisa N° 11. Embrapa Solos, Rio de Janeiro
18. Santos HG, Jacomine PKT, Anjos LHC, Oliveira VA, Lumbreras JF, Coelho MR, Almeida JA, Cunha TJF, Oliveira JB (2013) Sistema Brasileiro de Classificação de Solos. Embrapa Informação Tecnológica, Brasília
19. Oliveira KAP, Menezes MABC, Von Sperling E, Jacomino VMF (2012) J Solid Waste Technol Manag 38:202–210
20. Ran Y, Liu Z (1999) J Rare Earth 17:213–217
21. Liang Tao, Zhang Shen, Wang Lijun, Kung Hsiang-Te, Wang Yuqi, Aitang Hu, Ding Shiming (2005) Environ Geochem Health 27:301–311
22. Menezes MABC, Palmieri HEL, Leonel LV, Nalini JRHA, Jaćimović R (2006) J Radioanal Nucl Chem 270(1):111–116