

STUDY OF RARE EARTH ELEMENTS, URANIUM AND THORIUM MIGRATION IN ROCKS FROM ESPINHARAS URANIUM DEPOSIT, PARAIBA - BRAZIL

Cirilo C.S. Conceição

Instituto de Radioproteção e Dosimetria -IRD
Av. Salvador Allend, S/N - Jacarepaguá
Rio de Janeiro, Brazil
CEP.: 22780-160
cirilo@ird.gov.br

ABSTRACT

The determination of Rare Earth Elements as natural analogue in patterns geologic has grown as a tool for predicting the long-term safety of nuclear disposal in geological formation. Migration of natural radionuclides is one of the most serious problems in the waste deposit from nuclear fuel cycle. Rare Earth Elements show the same kinetic behavior in rocks as natural radionuclides. This similar property of the analogues allows perform studies and models on the subject of radionuclides migration. The aim of this study was to determine the distribution of Rare Earth Elements in rocks located at Espinharas – Paraíba – Brazil, uranium deposit. In this work are presented the results from the study above the distribution of rare earth elements in function of the degree of mineralized rocks, composition and the conditions of radioactive equilibrium of the uranium and thorium in some fractures on the rocks from radioactive occurrence of Espinharas-Brazil. The results show that there is a correlation of heavy Rare Earth Elements, uranium and Thorium concentrations to oxidation factor of the rocks. However this correlation was not observed for light Rare Earth Elements. It means that heavy Rare earth Elements follow the natural radionuclides in oxidation process of rocks. The samples were analyzed by ICP-MS, alfa and gamma spectrometry, X-ray diffraction and fluorimetry.

1. INTRODUCTION

The greatest interest in the determination of rare earth elements (REE) is dedicated to geological materials, especially for studies petrogenetics, although it had increased the interest in exploration, modeling for studies of migration of radionuclides in the environment and geochemical studies on the evolution of the earth. The rare earth elements are a group of 14 naturally occurring chemical elements (from La to Lu), which exhibit chemical and physical properties very similar. This uniformity arises from the nature of their electronic configurations, due to the oxidation state 3+ and the small but constant decrease in ionic radius as a function of atomic number. The values of ionic radius and the concentrations of rare earth elements in some types of rocks can be seen in table 1.

As the similarity of their chemical behavior, they may be partially fractionated through various petrology and mineralogy processes. Studies on migration to elements that are not normally found in nature, such as Np, Am, Pu and Cm, are studied from Th, U and rare earth elements, which elements are suggested as "Chemical Analogues". In the present study sought to verify the feasibility of using the method of ICP-MS to perform the chemical analysis of elements and analyze the behavior of REE in a fracture in the rocks and mineral related not changed from a natural radioactive deposit.

Table 1. Values of ionic radius and average concentration of rare earth elements

Element	REE Ionic radius [Å]	Chondrites [$\mu\text{g g}^{-1}$]	Granite [$\mu\text{g g}^{-1}$]	Basalt [$\mu\text{g g}^{-1}$]
La	1.03	0.33	55	6.1
Ce	1.01	0.87	104	16
Pr	0.99	0.13	12	2.7
Nd	0.983	0.63	4.7	14
Sm	0.958	0.20	8	4.3
Eu	0.947	0.077	1.1	1.5
Gd	0.938	0.28	7.4	6.2
Tb	0.923	0.050	1.1	1.1
Dy	0.912	0.34	6.2	5.9
Ho	0.901	0.077	1.5	1.4
Er	0.890	0.23	4.2	3.6
Tm	0.880	0.035	0.69	0.60
Yb	0.868	0.22	4.3	3.2
Lu	0.861	0.034	0.68	0.55

Ref.: [1] Henderson, P. -Rare Earth Element Geochemistry -Developments in Geochemistry -Elsevier 1984

1.1. Studied area

The uranium of Espinharas is located close to the village of São José de Espinharas, 25 km from the city of Patos, state of Paraíba (PB)-Brazil. Its geographical position is: longitude 6°51'00"; latitude 37°20'00" in area of relatively flat topography, with small variations, where the average altitude is 200 meters above sea level. In Figure 1, you can see the location of the occurrence of Espinharas. The mineralized area extends up to northeast and southeast, where the Village of São José de Espinharas as reference.

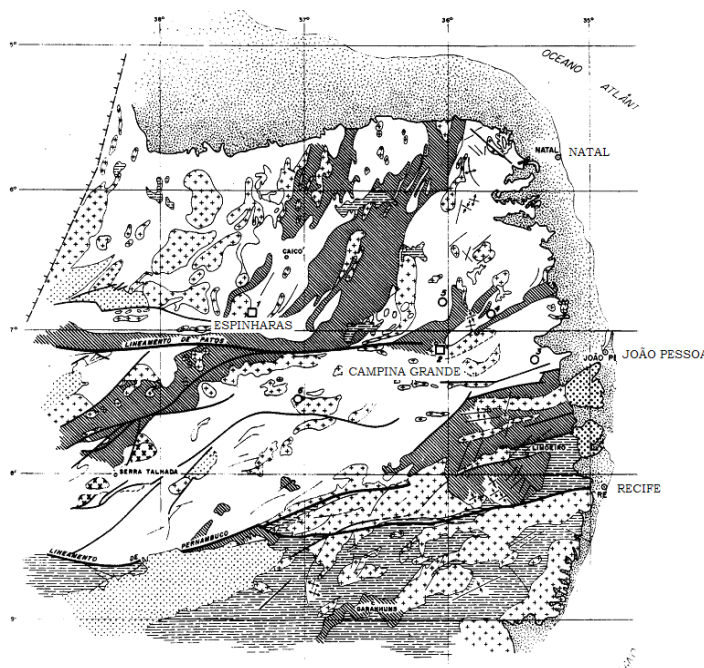


Figure 1. Location of the studied area

The origin of the call series Ceará, according Ferreira & Albuquerque [2] is divided into two groups: Group Caicó and Group Seridó, occurred between 750 and 1100 Ma. The deposit of Espinharas belong to the complex called "Caicó", which is in lower pre-Cambrian of northeastern Brazil, which includes, prominent rock type amphibole-biotite gneiss, amphibolites and some tactites. The metamorphic action, which led to all kinds lithological rocks, occurred between 700 and 750 Ma, the first building structural patterns and, second, the call was being granites fase. After extensive field work done by NUCLAN, where studies have been conducted petrographic, geochemical and macroscopic identification of samples collected in the field of holes survey, detailed studies indicated that the mineralized area is of metamorphic origin, were affected by mineralizing solutions, regardless of nature of the rock origin. These studies also indicated that the uranium mineralization is associated with the process of metasomatism changes as the most recent geological event of the area, dating from approximately 600 to 700 Ma [2,4,5].

1.2. Samples

The samples were selected for this study corresponding to the fissure that can be observed in Figure 2, and the drilling of holes by the surveys carried out to study the radioactive deposit by NUCLAN. The fissure in this study is the most important and extensive part of the radioactive deposit, allowing further study the issue of mobilization of elements, taking into account the aspect of action of metasomatism. Considering that the metasomatic process was not taken to the maximum intensity, which would allow a visual identification due to the homogeneous appearance and color typical of each primary altered rock, the samples were identified by X-ray diffraction, allowing a better characterization of them.

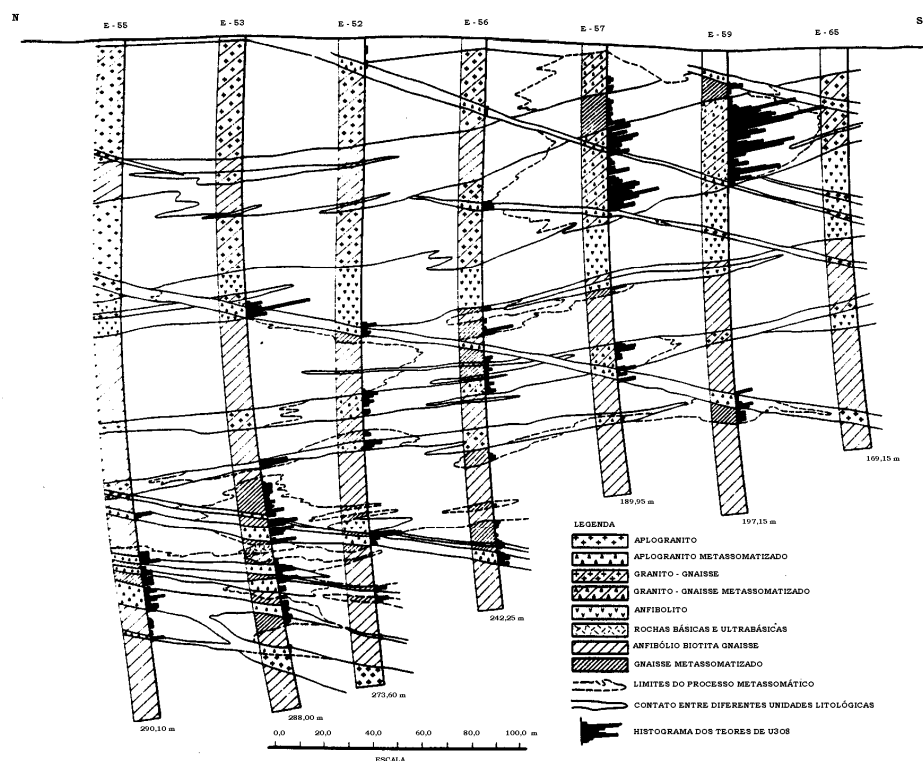


Figure 2. Details of the drilling holes in the study area

The representative samples of the rock body and its corresponding minerals in the fracture were selected and analyzed. The rock samples were selected according to Table 2, where the types can be observed lithological boundaries locations.

Table 2. Pre-existing rocks and equivalent metassomatic rocks

A) Pre-existing Rocks	B) Equivalent Metasomatic Rocks
1) Amphibole biotite gneiss	Mineralised gneiss (Group 1)
2) Granite-gneiss	Albite (Group 2)
3) Aplogranite	Albite (Group 2)
4) Amphibolites	* Mineralized amphibolites (Group 3)

* No metasomatic changes as the other rocks.

Group 1: Most of the samples from a lithological consist mainly of plagioclase, albite or albite-oligoclasio, which are products of changing the aplogranite. The main characteristic of these rocks is to provide a porous appearance with numerous vacuoles, a result of the removal of grains of quartz in equigranular texture. The vacuoles are mostly filled by recrystallized quartz, calcite, and a lesser amount of kaolinite, alteration of feldspars in common.

Group 2: The albite is the result of the change of granitic gneiss, richer in quartz and feldspar, presenting a lesser number of samples, since most samples are of origin of the rock changes (originally aplogranite), as mentioned in the previous item. Maintains the same mineralogical composition of albite, except the presence of biotite, which gives a more reddish color to them.

Group 3: The amphibolites were the rock that has undergone minor metasomatic changes. The location of holes and depth of samples can be seen in Table 3.

Table 3 - location of holes and depth of samples

Location (holes)	Depth (m)
EBH-52	119-126
EBH-53	110-119
EBH-57	136 -142
EBH-59	142 -149

2.0 METHODOLOGY AND EXPERIMENTAL PROCEDURE

2.1. Samples preparation

The dissolution of the rocks was made from approximately 0.250 g of sample homogenized, and digested in teflon vessel on the heating plate, with appropriate amount of hydrochloric acid, nitric acid, perchloric acid and hydrofluoric acid. The digestion was performed for 12 hours and then brought to dryness on a heating plate at 150 °C to decompose and evaporate fluorides, chlorides and perchlorates. The residue was dissolved with 2 ml of nitric acid and 0.5 ml of hydrogen peroxide and taken to dryness on a heating plate. Again resumed the residue in 2 ml of nitric acid and brought to the volumetric flask of 50 ml.

Note: The waste of fluoride may precipitate the rare earth elements, and chlorides can form diatomic species in plasma interfering with the determination of rare earth elements (REE).

2.2. Methodology and instrumentation

The determination of rare earth elements, we used a mass spectrometer with inductively coupled plasma (ICP-MS), CIEX/PERKIN-ELMER model ELAN 5000. Calibration of equipment and analysis of reference materials: For the calibration of equipment, a standards Merck cocktail was used. To compensate for any variation in sensitivity, efficiency of the nebulizer, salinity and other effects of the matrix, the internal standard was used. For REE determination of the ICP-MS, internal standard have been used by many researchers, can be some work carried out by Longerich [6] with the addition of ^{147}Sm and Balaran [7] with the addition of ^{115}In . In both cases, necessary corrections of the readings of the samples and patterns by varying the sign of the internal standard were made. The ^{115}In is particularly suitable for this purpose in analysis of geological samples (geochemical analysis), mainly due to its low natural occurrence (abundance of $\sim 80 \text{ ng.g}^{-1}$) and also because of its low ionization potential for the 1st (5.79 eV) and high potential for 2nd ionization (18.86 eV), much higher than the ionization potential of the argon plasma (15.76 eV). The ^{115}In form mainly single charged species and the concentration of double-charge is negligible. The ^{115}In is located near the middle of the mass range of interest, with isotopic abundance of about 96% [4]. In the case of samples of this work, dilutions were performed between 1.000 and 25.000. This is due to the fact that, in order to measure the REE without resorting to chemical separations had to be digested sample masses of about 250 mg in 50 ml of solution. Corrections due to the formation of refractory oxides and doubly charged ions are other important factors in setting the parameters of measurement. For the application of this technique of measurement was observed carefully various methodologies [7-11], and that applied in this work is an adaptation to existing conditions of the laboratory and the nature of the samples. To demonstrate the use of this methodology for their analytical quality, ie accuracy and reproducibility, were analyzed the geological rock standards BCR-1, G-2 and GSP-1, from the United States Geological Survey (USGS). Results of measurements are presented in tables 3, 4 and 5.

Table 3. Results of measurements and geological references to standard BCR-1

Element	This work [$\mu\text{g g}^{-1}$]	Ref. a [$\mu\text{g g}^{-1}$]	Ref. b [$\mu\text{g g}^{-1}$]	Ref. c [$\mu\text{g g}^{-1}$]
La	23.34 \pm 0.26	26.00	27.00	26.60
Ce	49.33 \pm 0.58	53.90	53.00	53.80
Pr	6.28 \pm 0.16	7.00	7.00	7.29
Nd	26.24 \pm 0.69	29.00	26.00	29.70
Sm	6.19 \pm 0.20	6.60	6.50	6.70
Eu	1.97 \pm 0.09	1.94	2.00	1.98
Gd	6.33 \pm 0.31	6.60	6.60	6.90
Tb	1.07 \pm 0.06	1.00	1.00	1.00
Dy	6.12 \pm 0.16	6.30	7.00	6.72
Ho	1.23 \pm 0.05	1.20	1.20	1.40
Er	3.71 \pm 0.15	3.59	3.50	3.80
Tm	0.53 \pm 0.02	0.60	0.60	0.57
Yb	3.20 \pm 0.16	3.36	3.40	3.70
Lu	0.47 \pm 0.04	0.55	0.50	0.52

Table 4. Results of measurements and geological references to standard G-2

Element	This work [$\mu\text{g g}^{-1}$]	Ref. a [$\mu\text{g g}^{-1}$]	Ref. b [$\mu\text{g g}^{-1}$]	Ref. c [$\mu\text{g g}^{-1}$]
La	78.14 \pm 0.26	90.00	92.00	80.00
Ce	148.16 \pm 0.58	160.00	160.00	154.00
Pr	14.53 \pm 0.16	19.00	19.00	18.00
Nd	48.15 \pm 0.69	55.00	58.00	58.00
Sm	6.78 \pm 0.20	7.30	7.20	7.00
Eu	1.56 \pm 0.09	1.50	1.40	1.10
Gd	5.44 \pm 0.31	5.00	5.00	4.40
Tb	0.51 \pm 0.06	0.54	0.50	0.44
Dy	1.86 \pm 0.16	2.40	2.30	2.30
Ho	0.31 \pm 0.05	0.40	0.40	0.46
Er	0.91 \pm 0.15	1.20	1.30	1.30
Tm	0.09 \pm 0.02	0.30	0.30	0.33
Yb	0.53 \pm 0.16	0.80	0.86	1.10
Lu	0.10 \pm 0.04	0.10	-----	0.11

Table 5. Results of measurements and geological standard reference for GSP-1

Element	This work [$\mu\text{g g}^{-1}$]	Ref. a [$\mu\text{g g}^{-1}$]	Ref. b [$\mu\text{g g}^{-1}$]	Ref. c [$\mu\text{g g}^{-1}$]
La	158.35 \pm 11.62	196.00	195.00	197.00
Ce	377.32 \pm 25.96	394.00	360.00	390.00
Pr	48.24 \pm 3.80	50.00	50.00	48.00
Nd	181.17 \pm 11.69	188.00	190.00	213.00
Sm	22.61 \pm 1.47	27.10	25.00	26.00
Eu	2.06 \pm 0.13	2.40	2.40	3.00
Gd	16.30 \pm 1.73	15.00	15.00	15.40
Tb	1.54 \pm 0.12	1.30	1.40	1.50
Dy	4.92 \pm 0.42	5.40	5.70	6.60
Ho	0.84 \pm 0.07	0.50	-----	-----
Er	2.47 \pm 0.20	3.00	3.00	3.30
Yb	1.29 \pm 0.14	1.80	1.90	0.85
Lu	0.15 \pm 0.05	0.23	0.20	0.22

Ref. a: K. Govindaraju, Geost Newsletter, Special Issue 8, 3-16 (1984); **Ref. b:** Abbey, Geol. Survey, Can. Pap., 1980, 80-14

Ref. c: Hutton, R.C.; Eaton, A.N.; Gosland, R.M., VG Elemental - England - Applied Spectroscopy, volume 44, Number 2, 1990.

Note: For each standard, there were 5 samples independent digestion.

2.3. Methodology and equipment used in the determination of thorium and uranium

The implemented method in the radiochemical laboratory of IRD-CNEN, it is the same developed in the PUC laboratories by Mickleley [14] and Valley [15], with the introduction of small changes in the final part of the one, mainly in the assembly of sources after chemical separation of radionuclides of interest. This method based on the extraction of uranium and thorium with a solution of 0.1 M in cyclohexane TOPO, re-extraction the Thorium with 0.3 M solution of H_2SO_4 and co-precipitation it with solution of LaF_3 with 500 mg.g^{-1} , the uranium is re-extracted with 1 M solution of NH_4F , eliminating polonium (^{210}Po is a spectral interference) by spontaneous deposition on the scraps of copper, followed by reduction of U^{+6} to U^{+4} with the addition TiCl_3 15% solution and the co-precipitation with LaF_3 solution with 500 mg.g^{-1} . The uranium is co-precipitate with the solution of LaF_3 with 500 mg.g^{-1} , then filtered on cellulose acetate membrane with pore size of 0.1 μm and 25.4 mm (1 inch) diameter. The filters are then mounted on metal disks of same diameter, covered with thin adhesive layer and then taken to dry before being measured by detecting alpha, the following system of measures: the alpha spectrometer ORTEC, composed of two surface barrier type detectors with 1 inch in diameter. Previous work carried out by Silveira [3] and Valley [15] where was studied the linearity of the response to sources of uranium and thorium in terms of mass deposited on filters, provide new calibration curves, since the masses of these elements deposited on sources assembled for this work are of the same order of magnitude. In the determination of uranium, a tracer was added, so that could be made the necessary corrections on the chemical yields in the chemical separation used. The ^{232}U tracer was used with approximate 0.25 Bq. The values of the activities of the filter samples and standards were obtained from the relationship between the total counts of the peaks of the isotopes ^{238}U and ^{234}U with ^{232}U tracer and activity of tracer added. The determination of thorium by alpha spectrometry, the radioisotope ^{234}Th was used as a tracer to estimate the performance of the chemical yield of the method. The ^{234}Th was measured in a system with proportional-type detector, where the rate of counting of the filters ^{234}Th sources of mounted samples were considered to be directly proportional to the standard filters prepared only with standard solutions of ^{234}Th . Unlike the ^{232}U tracer in determining spectroscopic detection of alpha for uranium which serves the same time to determine the chemical yield and efficiency of the detector, the tracer is ^{234}Th in determining spectroscopic detection of alpha to report, only to determine the chemical yield, and the efficiency of the detector determined separately through filters sources prepared with standard solutions of ^{232}Th . (For the preparation of the standards of thorium, the standard sources were prepared from a standard solution concentration of ^{232}Th with 807 Bq.g^{-1} , and taking an aliquot of this solution with amount of thorium and taken to polyethylene tubes, 25 ml solution directly in support of 0.3 M H_2SO_4 , and then co-precipitated with solution of LaF_3 . The chemical yield can be accompanied also here with the addition of tracer ^{234}Th . The seven standards prepared with the same characteristics of the samples were measured in the barrier detectors surface with the characteristics already presented previously and the average efficiencies were: detector A ($h = 0.1671 \pm 0.0037$), and detector B ($h = 0.1829 \pm 0.0030$). Analysis of geological standard reference sample of S-2 of the IAEA, was performed to test the reliability of the method. Table 6 we can be seen the results obtained with 4 (four) independent analysis of the reference sample.

Table 6 - Results of the analysis of the standard S-2 – IAEA

Nr	% of U (mg l ⁻¹)	Ratio ²³⁴ U : ²³⁸ U	Ratio ²³⁰ Th : ²³⁸ U
1	2,664.1	0.989	0.975
2	2,709.3	1.020	0.996
3	2,597.3	1.023	1.048
4	2,435.4	0.980	1.010
2,601.5 ± 119,9		1.006 ± 0.020	1.007 ± 0.031

3. RESULTS

The distribution of rare earth elements, uranium and thorium in the fracture study are compared with crystalline rocks that have not been changed by metasomatic process.

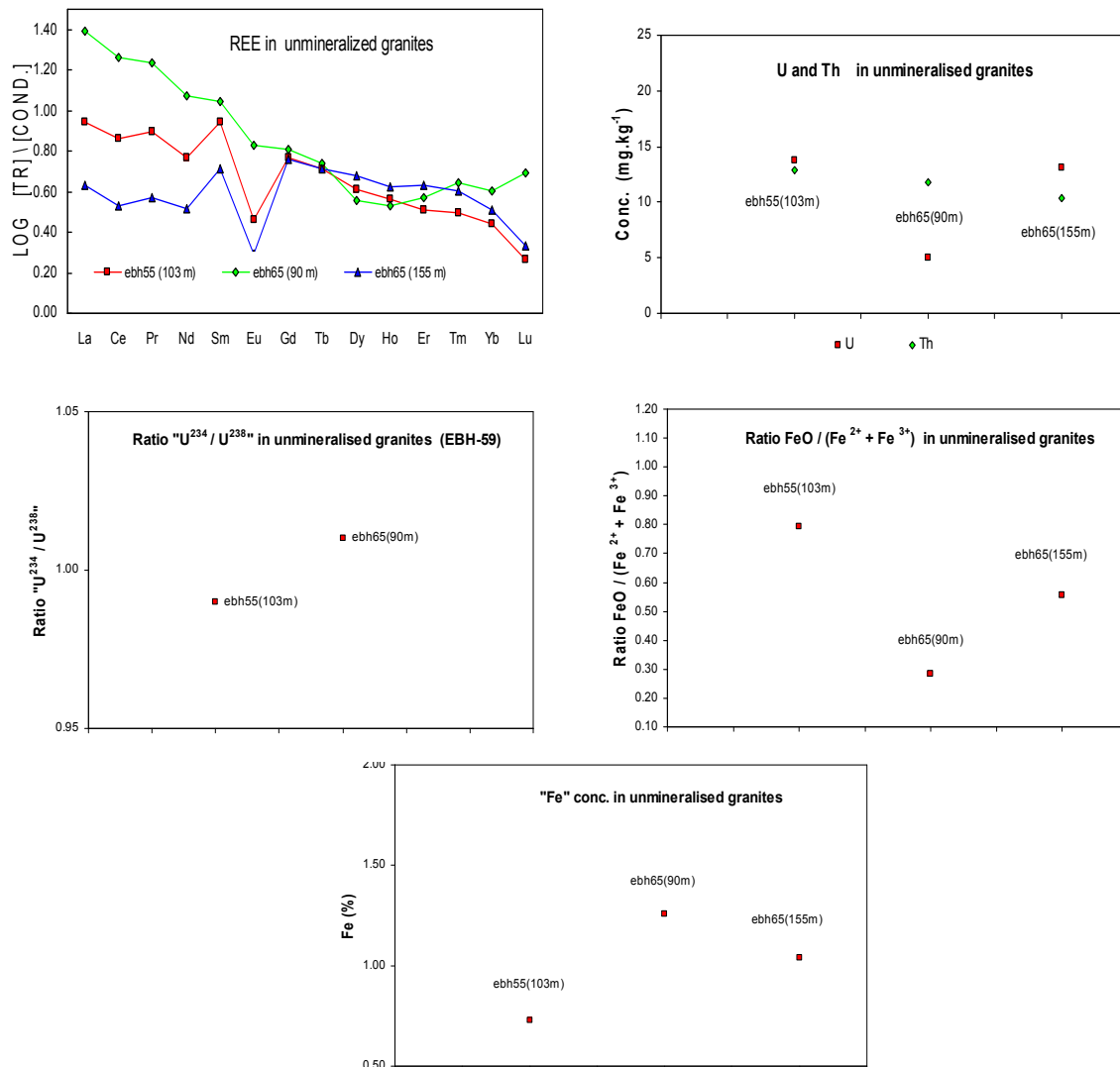


Figure 3. Samples of unmineralized granites

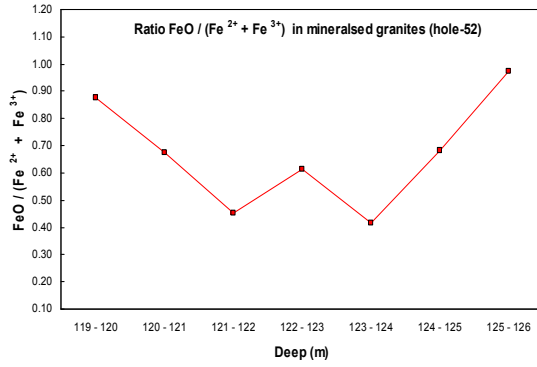
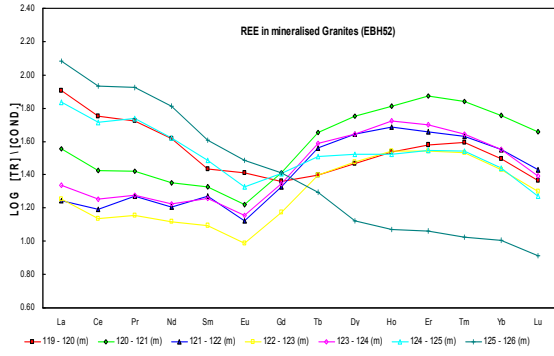


Figure 4. Samples of mineralized granites of the hole EBH-52

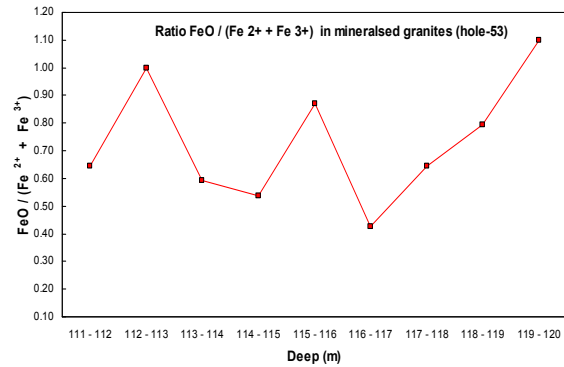
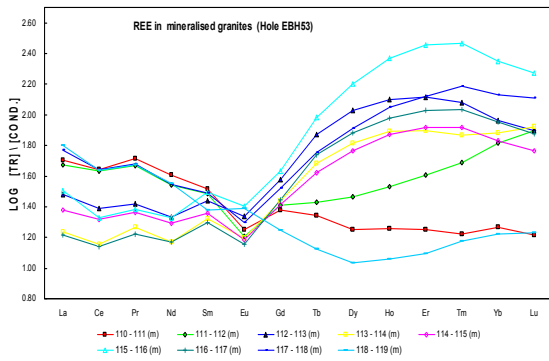


Figure 5. Samples of mineralized granites of the hole EBH-53

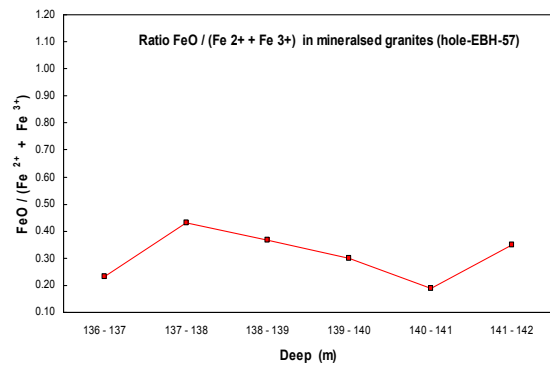
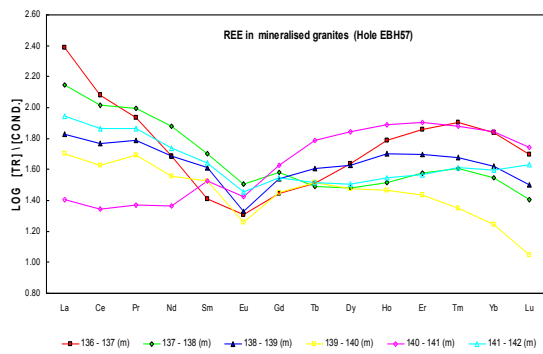


Figure 6 - Samples of mineralized granites of the hole EBH-57

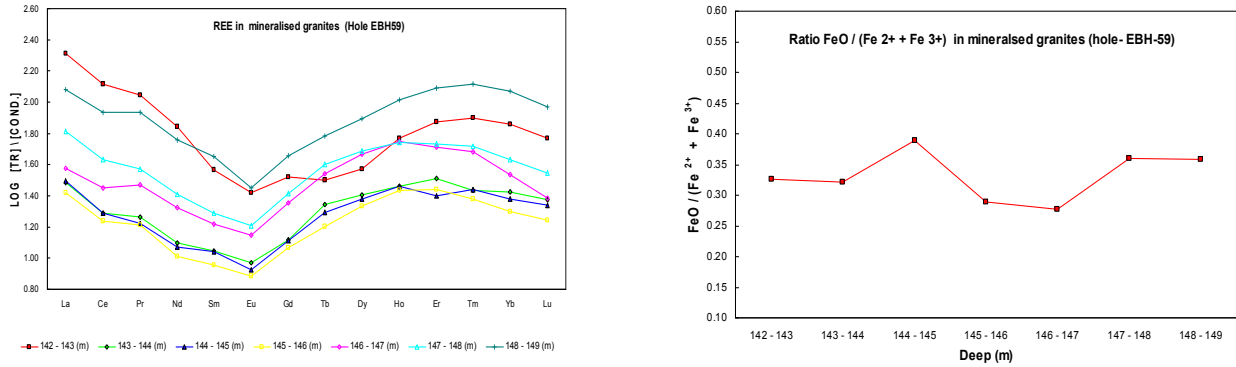


Figure 7 - Samples of mineralized granites of the hole EBH-59

3. CONCLUSIONS

The ICP-MS is an instrumental analytical technique that allows measurements of rare earth elements (REE), which brings a significant gain in terms of detection limit and speed up the chemical analysis of these elements, especially the elimination of pre-concentration steps used in other methodologies. The analysis of geological standard samples showed that the methodology applied is appropriate to the objectives of the work. Changes in methodology for determination of uranium and thorium were effective, allowing reduction of steps in the process of separation, without losing in terms of analytical quality.

The concentrations of mineral elements of fracture vary widely when compared with their concentrations in their original rocks. The values for uranium, range from 5 mg.l⁻¹ in the rock not changed until 3.700 mg.l⁻¹ in the albited rock, however, vary dramatically in the grounds of the unit ²³⁴U: ²³⁸U, happening the same with the Thorium from 11 mg.l⁻¹ to 1.550 mg.l⁻¹ in altered equivalent rocks. As for REE, the levels in the samples are changed significantly higher than in similar rocks not altered, as can be seen in the corresponding graphs, where the samples of mineral fracture, it changes the profile of heavy REE and attached to the uranium oxidation of rocks. Note that the levels of light REE, the accompanying changes in the concentrations of iron in the samples, and the heavy REE, accompanying the removal of iron samples, justifying the comments made by Landstron (14) that the oxy - hydroxides of iron are the main traps for light REE t, and the heavy REE co-precipitation or adsorbs to the phases of carbonate.

REFERENCES

1. Henderson, P. -Rare Earth Element Geochemistry -Developments in Geochemistry - Elsevier 1984
2. Santos, L. C. S.; Mineralização de urânio ligada a metassomatismo sódico, espinharas -PB. Revista Bras. de Geociências, 15(1):9-17, 1985.
3. Silveira, C. L. P. -Geoquímica da mineralização metassomática de Espinharas (PB). Tese de Doutorado -PUC -1986.
4. Ballhorn, R. K.; Suckau, V. -Geology of the Espinharas uranium deposit, Brazil. IAEA-AG- 62/27
5. Hoffinan, U.H.; Sigers -"Valuation Report 11 - Espinharas". Rel. interno da NUCLAN, 1981.
6. Longerich, H.P.; Fryer, B.J.; Strong, D.F.; Kantipuly, C.J. -Effects of operating condition of the Rare Earth Elements by ICP-MS, Epect. Acta, 1987, Voto 42B, pp 75-92.
7. Balaran, V.; Manikyamba, C.; Ramesh, S.I.; Anjalah -Rare Earth Elements determination in iron-formation reference samples by ICP-MS - Atomic Spectroscopy, 1992, volume 13, n° 1.
8. Jarvis, K.E. -Determination of Rare Earth Elements in geological samples by ICP-MS - Journal of Analytical Atomic Spectroscopy, Oct. 1989.
9. Jarvis, K.E. -ICP-MS: "A new technique for the rapid or ultra-trace level determination of REE in geological materials, 1988, Chem. Geol., 68, pp 31-39.
10. 1 O) Lichte, E.F.; Meier, aL.; Crock, J.G. - Determination of RRE in geological samples by ICP-MS, Anal. Chem. 1987,59, 1150-1157.
11. Date, A. R.; Hutchinson, D. -Determination of RRE in geological samples by ICP-MS, Journal of Anal. Atom. Spect., April 1987, voto 2
12. Miekeley, N.; Bastos, K.F. -"Introdução de metodos para determinação de razões isotópicas de U e Th por espectroscopia alfa e aplicação no estudo da migração destes elementos numa ocorrência radioativa -PUC-RJ -1981 -I Encontro Reg. Quím.
13. Vale, M.G.R.; Miekeley, N. -"A simple method for determination of U and Th by alpha spect. and spectroscopy in environmental samples", IV Simposio sobre química nuclear, radioquímica y química de reacciones, p.49, Mexico, 1982.
14. Landstron, O.; Tullborg, E. -"The influence of fracture mineral/groundwater interaction on the mobility of U, Th REE and other trace elements. - SKB -Technical Report 90-37, 1990. Sweden.