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DETERMINATION OF RARE EARTHS AND OTHER TRACE ELEMENTS IN NEOPROTEROZOIC-EOPALEOZOIC DYKES FROM CEARÁ STATE, BRAZIL, BY NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

Trace elements such as rare earths, U, Th, Ta, Ba and Hf can be very useful in petrogenetic studies of igneous and metamorphic rocks, giving information about the origin and evolution of magmas. Instrumental Neutron Activation Analysis (INAA) is an accurate and precise for trace element analysis in geological samples, and provides the information required for this kind of studies. In this study, rare earths and incompatible trace elements were determined by INAA in the geological reference materials GS-N and BE-N, to quality control, and for the investigation of acid dykes of neoproterozoic-eopaleozoic ages, which outcrop in the Médio Coreaú and Ceará Central domains from the Borborema Province (Ceará State). The powdered samples (particle sizes less than 100 mesh), crushed by using a mechanical agate mortar grinder, were irradiated at the IEA-R1 nuclear reactor at IPEN-CNEN/SP, and the induced activity was measured by high resolution gamma-ray spectrometry. The accuracy and precision of the method were evaluated and preliminary results of dyke samples are presented.

1. INTRODUCTION

Trace elements are present in rocks and minerals in very low concentrations (mg kg^{-1} or ng kg^{-1}), and accurate and precise analytical techniques are required for their reliable determination. Instrumental Neutron Activation Analysis (INAA) is a well known precise and accurate analytical technique for trace elements determination in geological samples [1].

The geochemical behavior of trace elements such as Ba, Rb, Ta, Th, U, Hf, Cs, Sc, Co and rare earth elements (La, Ce, Nd, Sm, Eu, Tb, Yb e Lu), can be very useful in petrogenetic studies of igneous rocks, since they allow the evaluation and the extent of the main processes involved in the generation and differentiation of magmas. They are also used in igneous and metamorphic rocks to predict the nature of source materials, giving information about their chemical and mineralogical composition [2].

The Neutron Activation Analysis consists of irradiating the sample with neutrons in a nuclear reactor and measuring the induced activity in a high resolution detector.

During the final stages of Western Gondwanaland amalgamation an expressive intrusive magmatic activity took place, giving rise to intermediate and acid dykes of neoproterozoic-eopaleozoic ages, which outcrop in the Médio Coreaú and Ceará Central domains from the Borborema Province (Ceará State). Despite the importance of those dykes to elucidate the geodynamic processes involved in the supercontinent assembly, there are only few geochemical studies about them. Considering the ability of rare earths and other incompatible trace elements such as U, Th, Ta, Ba and Hf to provide constraints about the origin and evolution of magmas, their concentrations were determined by neutron activation analysis. The rare earth element normalized to chondrite as well as other incompatible trace element diagrams will be used to obtain information about the tectonic processes involved in the dyke emplacement [2]. The characterization of the sources that originated the magmatism and the knowledge of the magmatic differentiation extent are essential to better understand the geodynamical processes related to the Western Gondwana assembly [3, 4].

2. PRINCIPLE OF THE METHOD

In the comparative INAA, samples and standards are submitted to a neutron flux originated by a nuclear reactor. Nuclear reactions give rise to radioactive isotopes of elements present in the sample [5]. The induced gamma-ray activity is measured in an hyperpure Ge solid state detector coupled to a multichannel analyser and associated eletronics. The gamma-ray spectra are analysed by softwares which identify the photopeaks of the produced radioisotopes. Since sample an standard are irradiated together, at the same irradiation conditions, the concentration of the element of interest is calculated by comparing the activity obtained in each peak of the sample and of the standard, by using the following expression:

$$C_a^i = \frac{A_a^i \, w_s \, C_p^i \, e^{\lambda t}}{A_p^i \, w_a} \tag{1}$$

Where: $C_a^i =$ concentration of the element in the i in the sample, $C_p^i =$ concentration of the element i in the standard, $A_a^i =$ counting rate of the radioisotope i in the sample at the time t = t, $A_p^i =$ counting rate of the radioisotope i in the standard at the time t = 0, $\lambda =$ decay constant of radioisotope and w_s and $w_a =$ weight of the standard and the sample.

3. EXPERIMENTAL

3.1. Sample Preparation

Aliquots of about 600g of the sample are crushed, quartered, grinded (< 100 mesh) and homogenized. Aliquots of about 100mg of the powdered sample were wrapped in pre-cleaned polyethilene envelops and were placed in aluminum containers (rabbits) developed for irradiation in the nuclear reactor IEA-R1.

The standards used were the reference materials basalt BE-N and granite GS-N, provided by ANRT. They present the same physical characteristics of the sample providing similar irradiation and counting conditions.

3.2. Irradiation and Counting

One hundred to one hundred and fifty mg of each sample and of the reference materials were accurately weighed in polyethylene bags. Samples and reference materials were irradiated for 8 hours at a thermal neutron flux of 10^{13} $cm^{-2}s^{-1}$ at the IEA-R1 nuclear reactor of IPEN. The measurements of the induced gamma-ray activity were carried out in a gamma-ray spectrometer with a GX20190 hyperpure Ge detector (Canberra). The radioisotopes used and their main nuclear characteristics are presented in Table 1. The software used for gamma-ray spectrum analysis was the VISPECT, developed at the LAN-IPEN. To evaluate the precision and accuracy of the methodology, the reference materials GS-N and BE-N were analysed.

Table 1 – Radioisotopes used, their main nuclear characteristics and time of decay before counting

Element	Radioisotope	Half-life	Energy (keV)	Decay after irradiation (d)
Ba	^{131}Ba	11.5 d	496.3	15-20
Ce	^{141}Ce	32.5 d	145.4	15-20
Co	^{60}Co	5.24 a	1332.2	15-20
Cr	^{51}Cr	27.8 d	320.0	15-20
Cs	^{134}Cs	2.7 y	795.8	15-20
Eu	^{152}Eu	12.2 a	1407.5	15-20
Fe	^{59}Fe	45.1 d	1098.6	15-20
Hf	^{181}Hf	44.6 d	482.2	15-20
La	^{140}La	47.27 h	328.6 1595.4	5
Lu	^{177}Lu	6.75 d	208.4	5
Nd	^{147}Nd	11.1 d	91.4 531.0	5 15-20
Rb	^{86}Rb	18.66 d	1076.6	15-20
Sb	^{122}Sb ^{124}Sb	2.70d 60.2d	564.2 1691.0	5 15-20
Sc	^{46}Sc	83.9 d	889.4	15-20
Sm	^{153}Sm	47.1 h	103.2	5
Ta	^{182}Ta	115.1 d	1188.8 1221.6	15-20
Tb	^{160}Tb	73 d	879.4	15-20
Th	^{233}Pa	27 d	311.8	15-20
U	^{239}Np	2.35 d	277.5	5
Yb	^{175}Yb ^{169}Yb	101 h 30.6 d	396.1 197.8	5 15-20
Zn	^{65}Zn	245 d	1115.4	15-20

4. RESULTS AND DISCUSSION

The results obtained for the reference material GS-N and BE-N are presented in Table 2. The results are mean of 4 replicates and the associated error is the standard deviation. The results agree with certified values, with bias < 13%, and the coefficients of variation < 17%. Except for Cs, which presented higher bias mainly in GS-N. This may be due to the fact that the concentration level is very close to the analytical detection limit (0.2 mg/kg). Figure 1 and 2 show the results obtained in relation to certified values. The correlation coefficients of the straight-line fits are higher than 0.999 for both GS-N and BE-N.

Table 2 – Results for the REE and some other trace elements in the geological reference materials GS-N and BE-N (ANRT) compared with certified values $\mathbf{mg\ kg^{-1}}$

Element	BE-N		GS-N	
	This work	Certified Values	This work	Certified Values
Ba	1062±27	1025±30	1391±52	1400±44
Ce	149±2	152±4	137±1	135±7
Co	59.1±0.8	60±2	65.8±0.7	65±4
Cr	349±8	360±12	56.1±0.6	55±4
Cs	0.56±0.06	0.8±0.1	8±3	5.4±0.3
Eu	3.56±0.07	3.6±0.2	1.71±0.02	1.70±0.06
Hf	5.60±0.08	5.6±0.2	6.0±0.2	6.2±0.3
La	89±8	82±2	73.6±0.4	75±3
Lu	0.218±0.002	0.24±0.03	0.20±0.03	0.22±0.03
Nd	65.9±0.3	67±2	55±4	49±2
Rb	52.5±0.9	47±2	165±2	185±5
Sc	22.8±0.3	22±2	7.0±0.1	7.3±0.4
Sm	12.3±0.8	12.2±0.3	7.7±0.1	7.5±0.2
Ta	5.9±0.1	5.7±0.4	2.5±0.1	2.6±0.2
Tb	1.3±0.2	1.3±0.1	0.7±0.1	0.60±0.04
Th	10.6±0.1	10.4±0.7	40.5±0.7	41±4
U	2.2±0.1	2.4±0.2	7.5±0.9	7.5±0.8
Yb	1.78±0.03	1.8±0.2	1.3±0.1	1.4±0.2
Zn	117±1	120±13	50±1	48±3

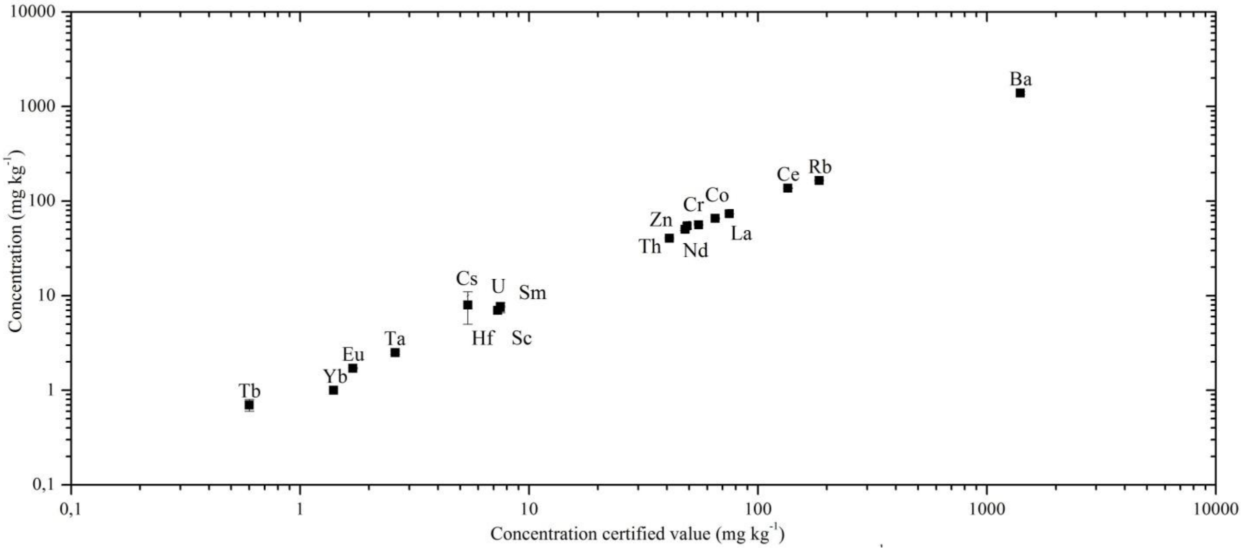

Figure 1. Values obtained for the reference material GS-N in relation to certified values. The uncertainty is 1σ.

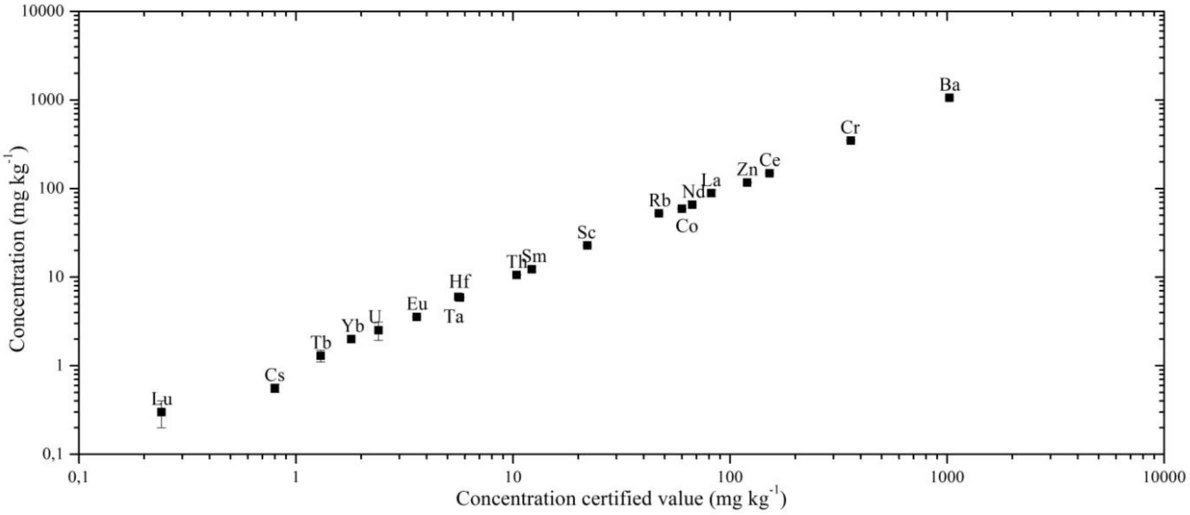

Figure 2. Values obtained for the reference material BE-N in relation to certified values. The uncertainty is 1σ.

The zeta-score criterion [6] is widely used in analytical laboratories to evaluate the accuracy and precision of analytical data, and can be calculated as:

$$z = \frac{C_i - C_{ref\ i}}{\sigma_i^2 + \sigma_{ref\ i}^2} \qquad (2)$$

Where: C_i = obtained concentration for the element i in the reference material, $C_{ref.i}$ = certified value of the element i in the reference material, σ_i = uncertainty in the concentration obtained for the element i in the reference material and $\sigma_{ref.i}$ = uncertainty of the certified value of the element i in the reference material.

The results of z-score obtained are presented in Figures 3 and 4. The zeta-score were all within $|z|<3$, showing that the results are in a confidence level of 99% of the certified value. The elements Rb and Cs presented higher deviations from certified values. Possible spectral interferences will be further investigated.

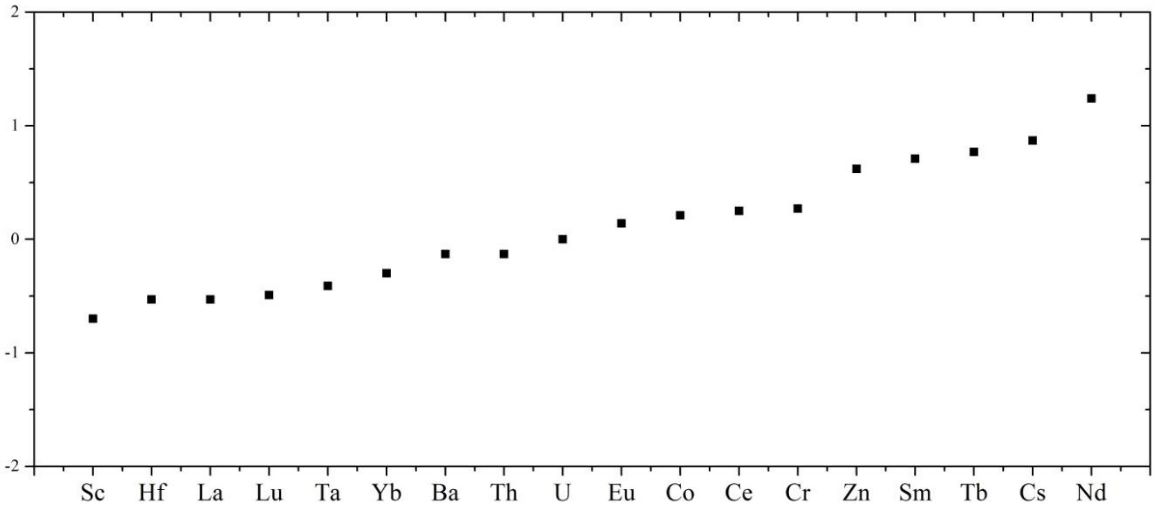

Figure 3. Control chart (zeta-score) for the analysed elements in the reference material GS-N.

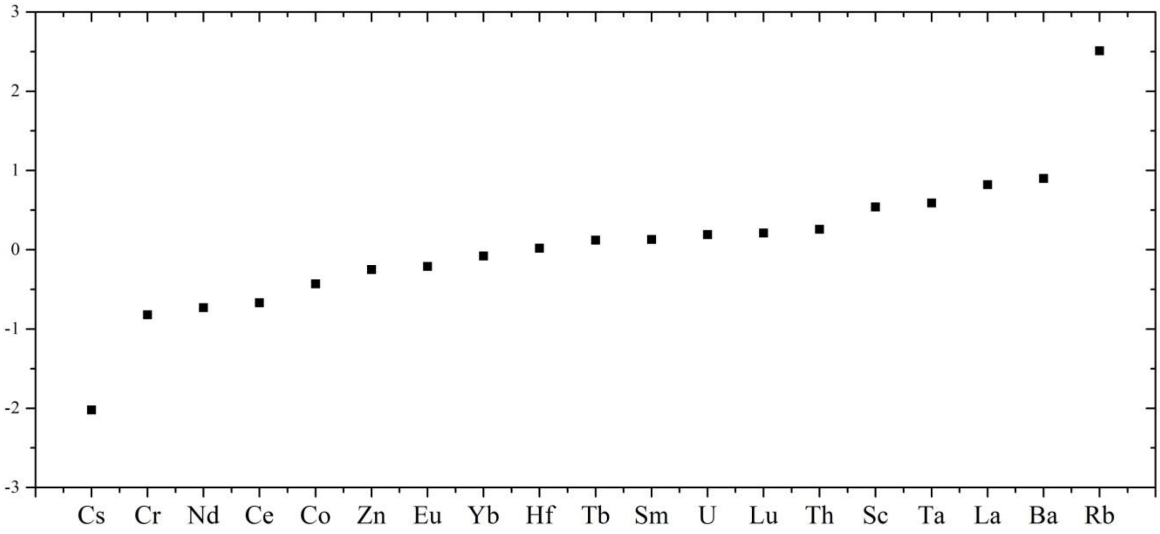

Figure 4. Control chart (zeta-score) for the analysed elements in the reference material BE-N.

To illustrate the results in the dyke samples, the concentration of trace elements obtained in one typical dyke sample is presented in Table 3. The results represent a single measurement and the associated error is the standard deviation. These data will be used to investigate the genesis of the dykes from Ceará State [3, 4].

Table 3 – Results for the REE and some other trace elements in a typical dyke sample. The uncertainty is 1σ.

Element	Concentration mg kg^{-1}
Br	0.32±0.06
Ca	12990± 1083
K	67366 ± 11431
La	152±1
Lu	2.0±0.3
Na	25673± 289
Sb	0.4±0.4
Sm	23.0±0.5
U	3.0±0.2
Yb	15±2
Ba	888±30
Ce	307±9
Co	2.9±0.2
Cr	7.0±0.4
Eu	2.1±0.1
Fe	16378 ± 197
Hf	16.2±0.5
Nd	137.6±0.3
Rb	96±4
Sc	1.2±0.1
Ta	2.8±0.2
Tb	3.2±0.3
Th	17.0±0.9
Zn	34±3

5. CONCLUSIONS

The obtained results showed that the methodoly is adequate to provide reliable results for trace elements in the investigated samples. The results will be used in quantitative modelling of the petrogenetic process that originate the dykes from Ceará State, as well as to decipher the tectonics related to the amalgamation of Western Gondwana. The obtained data will be integrated to paleomagnetic studies in order to the investigate possible temporal evolution of the igneous activity, allowing a better understanding about the geodynamical processes involved in the magma genesis of those dykes .

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