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**DETERMINATION OF RARE EARTHS AND OTHER TRACE  
ELEMENTS IN THE BRAZILIAN GEOLOGICAL STANDARDS  
BB-1 AND GB-1 BY NEUTRON ACTIVATION ANALYSIS**

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## ABSTRACT

Neutron activation analysis of the Brazilian geological standards basalt BB-1 and granite GB-1 provided by Instituto de Geociências da Universidade Federal da Bahia, has been carried out. The concentration values of ten rare earth elements (La, Ce, Nd, Sm, Eu, Gd, Tb, Dy and Lu) and other trace elements (U, Th, Ba, Sc, Rb, Ta, Cs, Co and Hf) have been determined.

The results were obtained with a good precision (standard deviation less than 15%). For the rare earth and some other trace elements, there are already some proposed values, and data showed, in general, a good agreement with published values.

## RESUMO

Os padrões geológicos brasileiros, basalto BB-1 e granito GB-1, fornecidos pelo Instituto de Geociências da Universidade Federal da Bahia, foram analisados pelo método de análise por ativação neutrônica. Foram determinadas as concentrações de dez elementos terras raras (La, Ce, Nd, Sm, Eu, Gd, Tb, Dy e Lu) e de outros elementos traços, tais como U, Th, Ba, Sc, Rb, Ta, Cs, Co e Hf.

Os resultados obtidos apresentaram boa precisão, com desvios padrões inferiores a 15% e, no caso das terras raras e de alguns outros elementos traços, para os quais já existem dados publicados, mostraram valores concordantes.

## INTRODUCTION

Trace elements, including U, Th, Ba, Sc, Rb, Ta, Cs, Co, Hf and rare earth elements (REE), have been extensively used 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 melts. They are also used in igneous and metamorphic rocks to predict the nature of source materials, giving information about their chemical and mineralogical composition (e.g. Allègre & Minster, 1978; Hanson, 1978; Frey, 1979; Hanson, 1980; Haskin, 1984).

Neutron activation analysis has been widely used in the determination of these elements in rocks due to its high sensitivity as well as good precision and accuracy (Vasconcellos & Lima, 1978; Henderson & Williams, 1981; Potts, 1983; Marques *et al.*, 1988). It is readily capable of simultaneous determination of many elements at parts per million (ppm), some at parts per billion (ppb) levels, often without destruction of the sample.

Instrumental neutron activation analysis (INAA) may be applied for the determination of a wide range of elements, including most lanthanides, in rocks. However, this method presents some difficulties. A neutron activated rock sample has a very complex gamma-ray spectrum, with a high activity during the first days after irradiation, which may produce spectral interferences. The good resolution now available in modern planar detectors has done much to reduce the problem of the mutual interferences of photopeaks. Computer programs also allow the solution of partially interfering peaks. However, important interferences still exist for the REE. A selection of the most important ones in INAA is published elsewhere (Vasconcellos *et al.*, 1986).

In the case of rocks containing uranium, the determination of REE is disturbed by fission-produced rare earths of by  $^{239}\text{Np}$ , originating from  $^{238}\text{U}$ . Radioisotopes such as  $^{140}\text{La}$ ,  $^{141}\text{Ce}$ ,  $^{153}\text{Sm}$  and

$^{147}\text{Nd}$ , which are often used in the analysis of their corresponding elements, are common fission products.

Therefore, several methods of group separation of lanthanides for neutron activation analysis are reported in the literature (Csajka, 1973; Wyttenbach *et al.*, 1983; Bishop & Hughes, 1984).

Almost all the analysis carried out by means of neutron activation analysis are done on a comparative basis. This means that adequate standards, with well known, accurate and precise concentration values of the elements of interest are fundamental for a successful and reliable analysis.

Usually, a multielementar standard is used, consisting either of calibration standards, prepared from stock solutions, containing known quantities of trace elements, or of reference standard rocks. Nevertheless, well analyzed geological standards, such as W-1, BCR-1, G-2 and AGV-1, provided by the United States Geological Survey (USGS) are very difficult to obtain, being almost exhausted. Therefore available geological standards, with well known concentration values, are of great importance in the analysis of geological samples.

Even if a geological standard with recommended values is used, the analysis of another reference standard, accomplished simultaneously with the analysis of the samples, is useful since it can be used to check the obtained values.

The Brazilian geological standards, basalt BB-1 and granite GB-1, provided by the Instituto de Geociências da Universidade Federal da Bahia were analyzed by the neutron activation method. The elements U, Th, Ba, Sc, Rb, Ta, Cs, Co, Hf and ten REE (La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Yb and Lu) were determined. In the case of Gd and Dy, where spectral interferences did not allow the use of INAA, a chemical separation was necessary. For the Gd, a procedure similar to that described by Atalla *et al.* (1985) was

employed. This method has been also applied by Figueiredo *et al.* (1987) in the analysis of Gd in the French geological standard GS-N.

For the element Dy, a chemical procedure based on the coprecipitation of the REE with ferric hydroxide was employed. In this case, a pre-irradiation separation method was applied due to the short half-life of the radioisotope  $^{165}\text{Dy}$  (2.3 hours), which does not allow a long procedure after sample's activation.

Some data for concentration values in BB-1 and GB-1 standards are already reported in the literature (Dutra, 1984, 1988; Linhares, 1987). The aim of this work is to provide results in order to give a contribution to the concentration values proposed for these standards. Some data for not yet analyzed elements are presented and, for the REE and some other traces, a comparison with literature data is made.

## PRINCIPLE OF THE METHOD

Samples, along with separate standards, are placed in a neutron flux, originated by a nuclear reactor, where nuclear reactions give rise, in general, to radioactive isotopes of the elements present.

After irradiation, gamma radiations emitted by the radioactive isotopes are discriminated, measured and compared with the radiations of the standards. Discrimination and intensity measurement of the gamma radiations are commonly performed using lithium-drifted germanium (Ge-Li) or hyperpure germanium (Ge) solid state detectors coupled to a suitable counting device such as a multichannel analyzer.

Each radioactive isotope has its own characteristic energy (or energies) of gamma radiation, so it is possible, in general, to identify the presence of a particular isotope while the intensity of that radiation is directly proportional to the amount of that isotope present.

Since sample and 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 spectra, by using the following expression:

$$C_a^i = \frac{A_a^i \cdot w_p \cdot C_p^i \cdot e^{\lambda \cdot t}}{A_p^i \cdot w_a}$$

where:

$C_a^i$  = concentration of the element  $i$  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  $t = 0$

$w_p$  and  $w_a$  = weight of the standard and the sample

$\lambda$  = decay constant of the formed radioisotope

$t$  = decay time

## EXPERIMENTAL

### Instrumental Neutron Activation Analysis (INAA)

Aliquots of about 100 mg of powdered rock samples were wrapped in pre-cleaned Al foil and were placed inside aluminum cans, developed for use in the nuclear reactor IEA-R1.

The standards used were those provided by the United States Geological Survey — USGS (AGV-1, BCR-1 and G-2), due to their recommended concentration values (Abbey, 1980; Gladney *et al.*, 1983; Govindaraju, 1984). Furthermore, they present the same physical characteristics of the sample, providing similar irradiation and counting geometries.

Samples and standards were both submitted to thermal and epithermal irradiation under a thermal flux of about  $10^{12}$  to  $10^{13}$   $\text{ncm}^{-2}\text{s}^{-1}$ , from 8 to 72 h, depending on the concentration of the analyzed elements. In epithermal neutron irradiation, the thermal neutron component of the neutron flux is eliminated by using cadmium sheet as shield.

After irradiation, samples and standards were allowed to decay from about 5 days up to a month.

Countings were carried out using a solid state ORTEC Ge(Li) detector, with a resolution of 2.8 keV peak of  $^{60}\text{Co}$ . Also a ORTEC hyperpure Ge detector with a resolution of 0.58 keV for the 122 keV peak of  $^{57}\text{Co}$  was used. The detectors were connected to a 4096 channel pulse-height analyzer. Counting times varied from 20 min to 16 h.

The assignment of the energies of the several peaks in the gamma spectrum and the calculation of the corresponding areas were performed by means of a PDP-11/04 minicomputer using the "Geligam" program in ORACL language, developed by ORTEC.

Table 1 shows the radioisotopes used to calculate the concentration of the analyzed elements as well as their nuclear data and the irradiation and counting conditions. An asterisk denotes the conditions that gave the best values. The absence of asterisk means that similar results were obtained.

### Chemical procedure

#### Analysis of Gd

A radiochemical procedure was applied for the particular determination of Gd. INAA did not present satisfactory results for this element, due to spectral interferences of radioisotopes  $^{233}\text{Pa}(\text{Th})$  and  $^{182}\text{Ta}$  in the gamma spectrum of  $^{153}\text{Gd}$ .

The irradiated sample and standard were

attacked with a HF-HNO<sub>3</sub>-HClO<sub>4</sub> mixture in a teflon coup inserted in a stainless steel bomb, for 5 h at about 100°C. After total dissolution of the rock the mixture was slowly heated in a sand bath and evaporated to dryness. The residue was taken up in 20 ml of water to which some drops of HCl and HNO<sub>3</sub> were added.

The solution was transferred to a 60 ml centrifuge tube and the REE were coprecipitated with Fe(OH)<sub>3</sub> by addition of ammonium hydroxide. Separation of the precipitate was made by centrifugation.

The Fe(OH)<sub>3</sub> precipitate was dissolved with

Table 1 — Radioisotopes used and main energies of the analyzed elements. Irradiation and counting conditions.

Element	Radioisotope	Energy (keV)	Type of irradiation	Decay intervals (days)	Type of detector
La	<sup>140</sup> La	815.5, 1595.4	T, E*	4-7	Ge(Li)
Ce	<sup>141</sup> Ce	145.4	T	15-30	Ge*
		145.4	E*	15-30	Ge(Li)
Nd	<sup>147</sup> Nd	91.4	T	4-20	Ge*
		531.0	T, E	4-20	Ge(Li)
Sm	<sup>153</sup> Sm	47.0, 69.6, 103.0	T	4-7	Ge*
		103.0	E	4-7	Ge(Li)
Eu	<sup>152</sup> Eu	45.4, 121.8	T	15-30	Ge
		1407.5	T	15-30	Ge(Li)
Gd	<sup>153</sup> Gd	97.5, 103.2	T	30-60	Ge(Li)
Tb	<sup>160</sup> Tb	298.6, 879.4	T, E*	15-30	Ge(Li)
Dy	<sup>165</sup> Dy	94.7	T	30 min	Ge
Yb	<sup>169</sup> Yb	50.7, 63.0	T	15-30	Ge*
		177.0, 197.8	T	15-30	Ge(Li)
Lu	<sup>177</sup> Lu	113.0, 208.4	T	15-20	Ge, Ge(Li)
U	<sup>239</sup> Np	277.5	E	4-7	Ge(Li)
Th	<sup>233</sup> Pa	311.5	E	15-30	Ge(Li)
Ba	<sup>131</sup> Ba	496.3	E	15-30	Ge(Li)
Rb	<sup>86</sup> Rb	1076.6	E	15-30	Ge(Li)
Ta	<sup>182</sup> Ta	1188.8	E	15-30	Ge(Li)
Hf	<sup>181</sup> Hf	482.2	E	15-30	Ge(Li)
Cs	<sup>134</sup> Cs	795.8	E	15-30	Ge(Li)
Co	<sup>60</sup> Co	1332.4	E	15-30	Ge(Li)
Sc	<sup>46</sup> Sc	889.4	T, E	15-30	Ge(Li)

\* Irradiation and counting conditions that provided the best results  
E, epithermal activation; T, thermal activation

For each sample treated, one standard (AGV-1 in this case) was simultaneously processed in exactly the same way.

#### Analysis of Dy

For the determination of Dy, a pre-irradiation separation method was employed to eliminate interferences from elements that provide high activity from the irradiated rock during the first hours after irradiation, like <sup>24</sup>Na.

Samples and the AGV-1 standard were treated before irradiation as described above, except for the use of an HAP column. In this case, only the coprecipitation of the REE with ferric hydroxide was performed. The procedure of precipitation of the Fe(OH)<sub>3</sub> was repeated twice. The precipitate was separated by centrifugation, dried for about 8 h in a stove at about 100°C and transferred to polyethylene vials of high purity, for irradiation.

HClO<sub>4</sub> 6M and the resulting solution was percolated through a column containing 5 cm<sup>3</sup> of hydrated antimony pentoxide (HAP), previously treated with a solution of HClO<sub>4</sub> 6M to retain various interfering radioisotopes, mainly <sup>233</sup>Pa, <sup>182</sup>Ta and <sup>46</sup>Sc.

A second precipitation of Fe(OH)<sub>3</sub> was performed in the effluent solution by addition of ammonium hydroxide. After centrifugation, the Fe(OH)<sub>3</sub> precipitate was dried at about 100°C in a stove, for 8 h. Finally, it was transferred to polyethylene counting vials and counted in the Ge(Li) detector.

A calibration standard, consisting of a stock solution containing known quantities of Dy and Eu was also prepared. An aliquot of this solution was pipetted in the same type of polyethylene vial used for the samples, and was irradiated together with them.

Irradiation was performed in the IEA-R1 reactor, under a thermal flux of  $4.4 \times 10^{11}$  ncm<sup>-2</sup>s<sup>-1</sup>, for 30 min.

Countings were carried out about one hour after irradiation using an hyperpure germanium detector.

The concentrations of the elements Eu and Dy were calculated by comparing the activities obtained for the 121 keV peak of <sup>152</sup>Eu and for the 97.4 keV of the <sup>165</sup>Dy, in the samples and in the calibration standard. The AGV-1 standard was used to check the obtained data for the Brazilian geologic standards.

The chemical yield was calculated com-

Table 2 — Results for the REE and some other trace elements in the geological standards GB-1 and BB-1 (ppm) compared with literature values.

Element	GB-1		BB-1	
	This work	Literature	This work	Literature
La	66 ± 3 (14)	63 <sup>a</sup>	32 ± 2 (14)	31.8 <sup>a</sup>
Ce	119 ± 4 (15)	108 <sup>a</sup>	68 ± 4 (15)	63.3 <sup>a</sup>
Nd	38 ± 6 (19)	39 <sup>a</sup>	32 ± 5 (18)	32.7 <sup>a</sup>
Sm	6.6 ± 0.5 (13)	7.8 <sup>a</sup>	6.7 ± 0.6 (18)	8.1 <sup>a</sup>
Eu	0.98 ± 0.05 (18)	0.97 <sup>a</sup>	1.60 ± 0.09 (16)	1.6 <sup>a</sup>
Gd	3.9 ± 0.1 (5)	3.9 <sup>a</sup>	5.6 ± 0.6 (5)	6.0 <sup>a</sup>
Tb	0.40 ± 0.02 (15)		0.88 ± 0.07 (15)	
Dy	1.8 ± 0.2 (5)	1.6 <sup>a</sup>	5.3 ± 0.1 (5)	5.1 <sup>a</sup>
Yb	0.73 ± 0.09 (9)	0.61 <sup>a</sup>	2.6 ± 0.2 (13)	2.5 <sup>a</sup>
Lu	0.12 ± 0.01 (8)	0.079 <sup>a</sup>	0.42 ± 0.04 (11)	0.34 <sup>a</sup>
U	5.8 ± 0.5 (7)		1.42 ± 0.05 (7)	
Th	36.3 ± 0.5 (6)		7.4 ± 0.1 (7)	
Ba	634 ± 11 (7)	15-850 <sup>b</sup>	531 ± 15 (7)	65-767 <sup>b</sup>
Rb	236 ± 4 (7)	224 <sup>b</sup>	76 ± 2 (7)	63 <sup>b</sup>
Ta	4.30 ± 0.01 (7)		1.21 ± 0.01 (6)	
Hf	5.6 ± 0.2 (7)		4.83 ± 0.08 (6)	
Cs	6.9 ± 0.1 (7)		1.20 ± 0.07 (7)	
Co	3.20 ± 0.08 (7)	2-10 <sup>b</sup>	32.8 ± 0.3 (7)	30-40 <sup>b</sup>
Sc	2.22 ± 0.08 (15)		29 ± 3 (15)	35 <sup>b</sup>

*a*, Dutra (1984); *b*, Linhares (1987)

Figures in parenthesis correspond to the number of determinations

paring the concentration values obtained for the element Eu, by instrumental neutron activation analysis, and by the pre-irradiation separation method.

## RESULTS AND DISCUSSION

The results obtained for the REE in the BB-1 and GB-1 standards are shown in Table 2, as well as reported values presented by Dutra (1984). Table 2 also shows the concentration values obtained for the other trace elements analyzed in this work and those proposed by Linhares (1987).

It can be seen that data were obtained with good precision, with standard deviations less than 15%.

For the REE, the results presented in general a good agreement with published values with relative errors less than 13%. Nevertheless some discrepancies were obtained for Sm, Yb and Lu. In the case of Sm, results were about 15% lower than those reported by Dutra (1984), in both analyzed standards. The high discrepancy obtained for Yb and Lu in the GB-1 standard is not very significant considering their low concentrations (< 1 ppm for Yb and about 0.1 ppm for Lu).

In order to provide a better comparison between REE concentration values obtained for the Brazilian standards in this work and literature values, chondrite-normalized diagrams were made (Fig. 1). The concentration values of the REE in the chondrites used in the diagrams are those reported by Boynton (1984).

For the BB-1 standard, it can be seen that both patterns are very similar and that the obtained values present a coherent distribution pattern.

For the GB-1 standard there is a difference between the REE patterns after the element Dy. Since the element Tm was not analyzed, more important discrepancies were obtained for Yb and Lu. Nevertheless, in this range of concentration (< 1 ppm) some discrepancies are expected.

For the elements Ba, Co, Rb and Sc the results agree, in general, with reported values (Linhares, 1987). For Ba and Co, the data are within the range of concentration presented by different analytical techniques. In the case of Ba the results, in both standards, are in accordance with those obtained by X-ray fluorescence spectrometry and optical emission spectrography (GB-1: 587 → 850 ppm; BB-1: 380 → 767 ppm). In the particular case of the element Co in the GB-1 standard, the concentration is of the same order of magnitude as that determined by optical emission spectrography (2 ppm).

For the element Tb and the other trace elements also analyzed there are not yet literature values for the Brazilian standards.

This work brought a contribution to the proposed values for the geological standards BB-1 and GB-1, giving new data for not yet analyzed elements and confirming some literature values.

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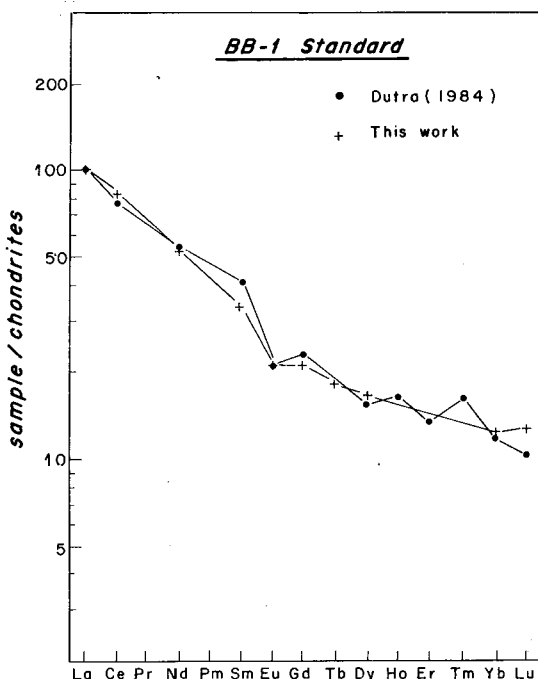
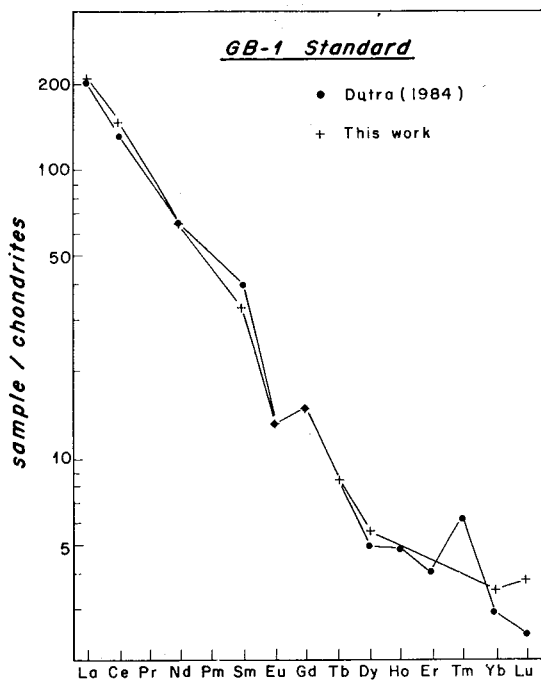


Figure 1 — Chondrite-normalized REE distribution patterns of GB-1 and BB-1 standards. Comparison with literature values.

## REFERENCES

- ABBEY, S. (1980) Studies in "standard samples" for use in the general analysis of silicate rocks and minerals. *Geostand. Newsl.*, **4**(2):163-190.
- ALLEGRE, C.J. & MINSTER, J.F. (1978) Quantitative models of trace element behavior in magmatic processes. *Earth Planet. Sci. Lett.*, **38**:1-25.
- ATALLA, L.T.; MANTOVANI, M.S.M.; MARQUES, L.S.; SOUSA, M.A. (1985) Determinação de terras raras e outros elementos traços em rochas através de análise por ativação neutrônica. *An. Acad. brasil. Ciênc.*, **57**(1):19-33.
- BISHOP, J.G. & HUGHES, T.C. (1984) Radiochemical neutron activation analysis. Determination of rare earth elements in geological materials with ppb sensitivity. *J. Radioanal. Nucl. Chem. Articles*, **84**(2): 213-221.
- BOYNTON, W.V. (1984) Cosmochemistry of the rare earth elements: meteorite studies. In: P. Henderson (ed.) *Rare earth element geochemistry*. Elsevier, p. 63-114.
- CSAJKA, M. (1973) Fast radiochemical separation of rare earths from rock samples by retention on lanthanum oxalate. *Radiochem. Radioanal. Letters*, **13**(2):151-159.
- DUTRA, C.V. (1984) Método para determinação de traços e subtraços de terras raras em rochas por espectrometria de plasma (ICP) — Aplicação em petrogênese. XXXIII Congr. Bras. Geol., Rio de Janeiro, Anais, 4:4792-4805.
- DUTRA, C.V. (1988) Geoquímica analítica dos elementos de terras raras. Aplicação da espectrometria de plasma — ICP. In: *Geoquímica dos elementos terras raras no Brasil*. CPRM, (in press).
- FIGUEIREDO, A.M.G.; SAIKI, M.; MARQUES, L.S. (1987) Determination of rare earth elements, U and Th in the standard rock GS-N by neutron activation analysis. *Inorganica Chim. Acta*, **140**:285-287.
- FREY, F.A. (1979) Trace element geochemistry: applications to the igneous petrogenesis of terrestrial rocks. *Rev. Geophys. Space Phys.*, **17**(4):803-823.
- GLADNEY, E.S.; BURNS, C.E.; ROELANDTS, I. (1983) 1982 compilation of elemental concentrations in eleven United States Geological Survey rock standards. *Geostand. Newsl.*, **7**:3-226.
- GOVINDARAJU, K. (1984) Compilation of working values and sample description for 170 international reference samples of mainly silicate rocks and minerals. *Geostand. Newsl.*, **8**, special issue.
- HANSON, G.N. (1978) The application of trace elements to the petrogenesis of igneous rocks of granitic composition. *Earth Planet. Sci. Lett.*, **38**:26-43.
- HANSON, G.N. (1980) Rare earth elements in petrogenetic studies of igneous systems. *Ann. Rev. Earth Planet. Sci.*, **8**:371-406.
- HASKIN, L.A. (1984) Petrogenetic modelling — use of rare earth elements. In: P. Henderson (ed.) *Rare earth element geochemistry*. Elsevier, p. 115-152.
- HENDERSON, P. & WILLIAMS, C.T. (1981) Application of intrinsic Ge detectors to the instrumental neutron activation analysis for rare earth elements in rocks and minerals. *J. Radioanal. Chem.*, **67**(2): 445-452.
- LINHARES, P.S. (1987) Estado atual do estudo cooperativo interlaboratorial das amostras padrões granito (GB-1) e basalto (BB-1) do Departamento de Geoquímica do IG-UFBA. I Congr. Bras. Geoq., Porto Alegre, Anais, 2:327-340.
- MARQUES, L.S.; FIGUEIREDO, A.M.G.; SAIKI, M.; VASCONCELLOS, M.B.A. (1988) Geoquímica analítica dos elementos terras raras. Aplicação da técnica de análise por ativação neutrônica. In: *Geoquímica dos elementos terras raras no Brasil*. CPRM (in press).
- POTTS, P.J. (1983) Gamma ray photopeak interferences found in the instrumental neutron activation analysis of silicate rocks. *J. Radioanal. Chem.*, **79** (2):363-370.
- VASCONCELLOS, M.B.A. & LIMA, F.W. (1978) Activation analysis of alkaline rocks. A comparison between destructive and non-destructive methods. *J. Radioanal. Chem.*, **44**(1):55-81.
- VASCONCELOS, M.B.A.; ATALLA, L.T.; FIGUEIREDO, A.M.G.; MARQUES, L.S.; REQUEJO, C.M.; SAIKI, M.; LIMA, F.W. (1986) Alguns aspectos do problema da análise por ativação dos lantanídeos. X Simp. Anual Acad. Ci. Est. São Paulo, Anais, 1:1-19.

WYTTENBACH, A.; MAJO, S.; TOBLER, L. (1983)  
Group separation of rare earth elements by liquid-  
liquid extraction for the neutron activation analysis  
of silicate rocks. J. Radional. Chem., **78**(2):283-294.