

## Trace and major elements in rock samples from Itingussú River Basin, Coroa-Grande, Rio de Janeiro

D. R. Araripe,<sup>1\*</sup> L. F. Bellido,<sup>3</sup> S. R. Patchineelam,<sup>2</sup> A. V. B. Bellido,<sup>2</sup> M. T. Guimarães,<sup>4</sup> M. B. A. Vasconcelos<sup>5</sup>

<sup>1</sup> Departamento de Química Analítica, Universidade Federal Fluminense, Niterói, 24020-007, Brazil

<sup>2</sup> Departamento de Geoquímica, Universidade Federal Fluminense, Niterói, 24020-007, Brazil

<sup>3</sup> Instituto de Engenharia Nuclear, C.P. 68550, Rio de Janeiro, Brazil

<sup>4</sup> Centro de Pesquisas Minerais, Rio de Janeiro, 22290-240, Brazil

<sup>5</sup> Instituto de Pesquisas Energéticas e Nucleares, São Paulo, 05508-900, Brazil

(Received April 6, 2006)

The goal of the present work was to determine the concentration of 23 elements by instrumental neutron activation analysis in rock samples from the vicinity of Itingussú River, in order to investigate the contribution of trace and major elements from the local lithology to the river basin. The Itingussú River Basin ends in a mangrove area not yet largely impacted by antropogenic activities. So far, there are no data for the concentration of trace elements in that region, even though these data are important to the understanding of the influence of the rocks on the composition of the mangrove sediments. The results showed some enrichment of Th and some light rare earths, probably because of the presence of the mineral allanite and other accessory minerals, as identified by petrographic analysis.

### Introduction

The Itingussú drainage basin is situated in the Coroa-Grande district, Sepetiba Bay, south of Rio de Janeiro. It belongs to the Rio Negro Complex, a granitic pre-cambrian embasement already well described by CASTRO et al.<sup>1</sup> It is a small bay of drainage that ends in a mangrove, extending from Itacuruçá to the Coroa-Grande district.<sup>2</sup> This area is not yet largely affected by antropic action, however, it was recently found that the elemental concentrations of some sediment samples collected nearby on an eastward industrial region were unusual.<sup>3,4</sup> Since there is a lack of data concerning trace element concentrations in that area, it seems important to evaluate their influence and the contribution of the local lithology.

It was found to be possible to combine the determination of trace element concentrations with petrographic data in the classification of geological material. In this way, this work has succeeded in the characterization of the rock samples of the Itingussú River Basin by applying multivariate statistical analysis to the concentration of 23 chemical elements determined by instrumental neutron activation analysis (INAA).

### Experimental

#### Sample collection

The Itingussú River Basin is situated at 22°44'–22°55' SL and 44°53'–43°55' WL (Fig. 1), and has no more area than 10 km<sup>2</sup>.

The Itingussú River has clear water with three falls.

Nine rock samples were collected from points chosen using existing geological maps. They were the main examples of the local lithotypes. Because the major crystal observed was smaller than 1 cm, the total volume of the rocks did not exceeded 200–300 cm<sup>3</sup>. No other kind of rock in the outcrop was different enough to be collected. Also, three samples (R10–R12) were collected from the riverbed, and an altered rock (R13) was collected on the ground of the soil profile (Table 1). These samples were appropriately cut for petrographic analysis and a fraction of them powdered for INAA.

#### Activation analysis

The comparative method was used in the present work. Each sample and standard G2 (USGV) was weighed around 200 mg and irradiated at the IEA-R1 research reactor of the Institute of Nuclear Energy and Research (IPEN). The irradiations were carried out with a neutron flux of 10<sup>12</sup> n·cm<sup>-2</sup>·s<sup>-1</sup>. For the analysis of short-lived radionuclides the irradiation time was 1.5 minutes and the activities were counted for 4 minutes; for long-lived radionuclides the irradiation time was 8 hours and after 10 days of cooling time the activities were counted for 5,400 seconds.

#### Detection and measurement system

The irradiated samples were counted in coaxial HPGe detectors (Ortec), and also in low energy photon detector GAMX (Canberra). The resolution for the 1,332.5 keV gamma-ray of <sup>60</sup>Co was 2.8 keV and 1.8 keV, respectively. The same geometry was used for samples and standards.

\* E-mail: drararipe@vm.uff.br

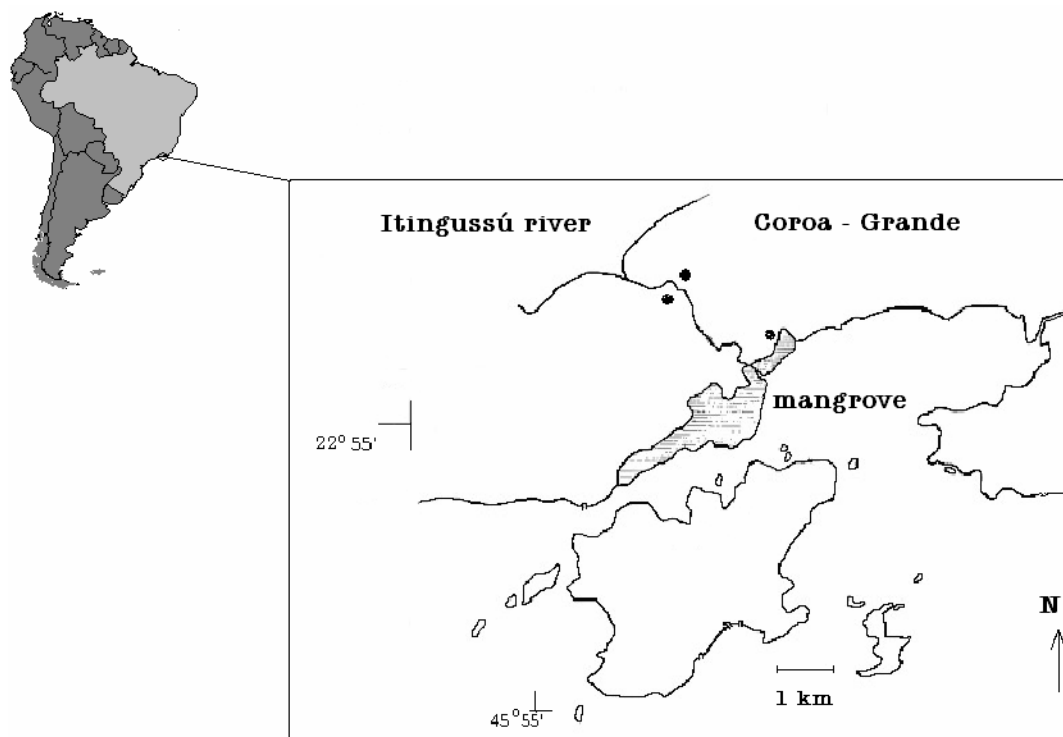


Fig. 1. Localization of the Itingussú River Basin; sites of sampling are marked with black circles

Table 1. Denomination and field description of the lithotypes collected

R1	Mesocratic rock
R2	Leucocratic rock, with feldspate porfiroblastes
R3	Hololeucocratic rock
R4	Mesocratic rock, biotite enriched
R5	Leucocratic rock
R6	Diabase
R7	Diabase. There are milimetric amigdales.
R8	Feldspate gneiss with biotite (leucocratic rock)
R9	Pegmatite vein, that cuts all embasement
R10	Like R1, more weathered
R11	Lixiviated gneiss
R12	Porfiritic stile, very lixiviated

The gamma-spectra were analyzed with the GRGAN code. This programme allows to choose the background of each photopeak, which was specially selected to be free of interferences.<sup>5-8</sup> The spectra collected with the Canberra system (Genie2k) were converted to a CHN format for the GRGAN programme.

#### Statistical treatment

Statistica 5.0 multivariate statistical packet was used. After descriptive statistics and Pearson methods, cluster analysis with Wards subroutine was employed for identification of elemental correlations with normalized data.

#### Results and discussion

The petrographic results can be found in Table 2. No petrographic analysis was done for samples R10 to R13, because they were similar to the other rocks in a structural sense. It can be seen the presence of accessory minerals that contain rare earth elements in these structure, due to the long term replacement.<sup>9,10</sup> One of these minerals is allanite, common in igneous rocks. There were other minerals as apatite, titanite, and zircon, probable hosts of these elements.<sup>11-13</sup> The tonalitic gneiss showed significant amounts of allanite and zircon. The two samples of diabases were somewhat different from each other, probably related to hydrothermal alteration, suggested by the alkaline amigdales in sample R7.

The chemical concentrations for the 23 determined elements are presented in Table 3, the overall uncertainties (1 sigma) are better than 10%. The results show high concentration of Th and some light rare earth elements in samples R2, R3 and R8, named leucocratic rocks in the campaign classification. Probably its accessory minerals were a product of magma with an enriched crustal component made during the formation of this rocks.

In most of the samples, very low concentrations of uranium was found (around  $2\text{--}4\text{ mg}\cdot\text{kg}^{-1}$ ). In only one sample of the altered rock R13, was found  $11.5\text{ mg}\cdot\text{kg}^{-1}$ . This rock was collected from a saprolite situated in a lower part of the basin. Its localization suggests that this uranium was preconcentrated in the saprolite by its retention through percolating water in the argillous minerals or ferric oxide-hydroxides, associated with the depletion of rock volume through weathering.

In general, the samples are similar to some commercial granites from the Rio de Janeiro State and the biotite granodiorite of Minas Gerais State, which are enriched with thorium and uranium with a maximum concentration of  $4\text{ mg}\cdot\text{kg}^{-1}$ .<sup>14</sup>

The normalization graphics for the trace element concentrations of the differentiated rocks related to the upper continental crust values of CONDIE (UCC)<sup>15</sup> are shown in Figs 2 to 4. As it can be seen in Fig. 2, the samples R3 and R8 were enriched with light rare earth elements and thorium. The pegmatite R9 revealed a poor mineralogical matrix. The normalization graphics of a more enriched rock (R2) found in this work is in Fig. 3.

The diabbases samples showed an enrichment of trace elements in the normalization graphic related to concentrations of the medium composition of basalts (Fig. 4), and high concentrations of large ions lithophile elements (LILE), namely Cs, La, Rb, Sb and Ba. The index factor of Eu suggests a positive anomaly of this element.

The final result of the statistical treatment of our data allowed the construction of a dendrogram (Fig. 5) that agrees well with the petrographic analysis. Samples R6 and R7 are classified in the same group, as expected. The hololeucocratic rocks R3 and R9 (a pegmatite vein), and the weathered rocks, R13 and R11, are well defined in a group of rocks depleted in the major elements. Rock R13 was classified with sample R3, more enriched with immobile trace elements. In the dendrogram, there are two other subgroups: an intermediate one, composed of the granodiorite gnaisses (R5, R8 and R12) and the last one, a group of mesocratic rocks (R1, R4 and R10). R2 sample is so different from all the lithotypes collected, that the dendrogram classified it as an outlier between the mafic group and the more felsic group.

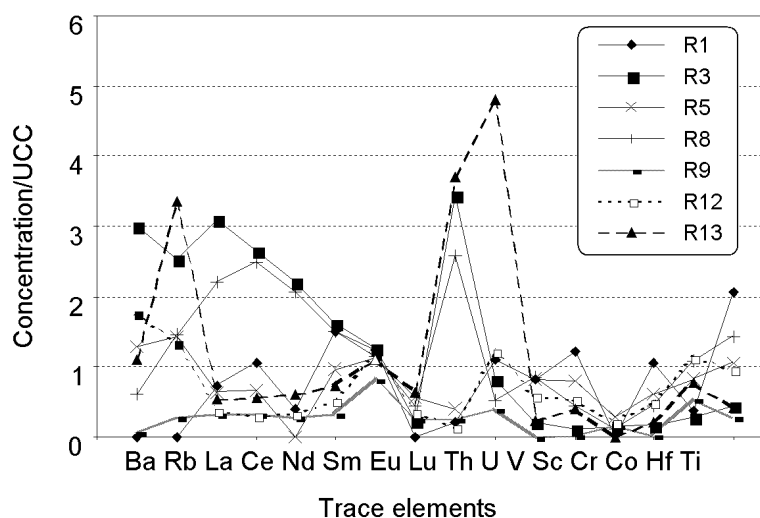


Fig. 2. Normalized values of trace elements of sample rocks

Table 2. Results of the petrographic analysis

Sample	Description
R-01 Diorite quartz	Quartz – biotite – hornblende – plagioclase gneiss. Accessory minerals: opaques, titanite, apatite and allanite. Secondary minerals: sericite and carbonate, alteration products of plagioclase.
R-02 Tonalite gneiss	Biotite – quartz – plagioclase gneiss. Accessory minerals: allanite and zircon are the most abundant; opaques and apatite are the rarest. Secondary clorite, muscovite, sericite and carbonate; the first ones are alteration products of biotite; the other two are alteration products of plagioclase.
R-03 Leuco-granite	Biotite leuco-syenogranite, composed essentially of microcline, quartz, plagioclase and biotite. It shows innumerable microfractures. Scarce accessory minerals: apatite, zircon and opaques. Secondary minerals: clorite, muscovite, sericite and clayminerals
R-04 Diorite quartz gnaiss	Clinopiroxeny – quartz – biotite – hornblende – plagioclase gneiss. Accessory minerals: opaques, titanite, apatite, allanite and zircon. Sericite and carbonate are alteration products of plagioclase; clorite is an alteration product of biotite.
R-05 Granodiorite gneiss	Hornblende – potash feldspate – quartz – biotite – plagioclase gneiss. Accessory minerals: titanite, apatite and zircon; scarce allanite and opaques. Secondary minerals: sericite, clorite and carbonate.
R-06 Diabase	Diabase with ophitic texture, host of plagioclase ~50%; titanipherous augite ~ 45%. Accessory minerals: opaques and apatite.
R-07 Diabase	Diabase with ophitic texture; plagioclase ~42%; titanipherous augite + uralite~40%; biotite ~5%; carbonate+serpentine ~7%; opaque + apatite ~5%. It showed vesicles of carbonate and others of serpentine.
R-08 Granodiorite gneiss	Microcline – biotite – quartz – plagioclase gneiss; composed of plagioclase, quartz, pertitic microcline and biotite. Accessory minerals: apatite, opaque, allanite and zircon. Secondary minerals: sericite, clorite and carbonate.
R-09 Leuco-tonalite	Leuco-tonalite, plagioclase, quartz, microcline and and biotite. Scarce muscovite.

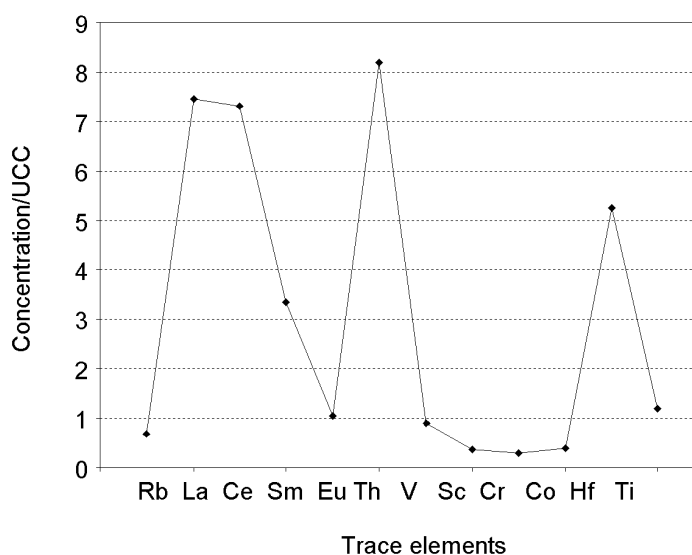


Fig. 3. Normalized values of trace elements of sample rock R2

Table 3. Concentration of inorganic elements in rocks from Itingussú River Basin; major elements (in %) and trace elements (in mg·kg<sup>-1</sup>)

	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13
Na, %	3.26	2.64	1.92	2.58	2.50	1.91	1.65	3.04	4.99	3.29	1.99	2.44	0.461
Mg, %	0.663	0.540	0.497	1.003	0.654	2.24	3.65	0.626	0.496	0.649	0.377	0.509	0.524
Al, %	8.07	8.24	14.7	9.92	7.90	6.63	7.71	10.6	10.3	10.4	8.5	10.6	12.4
Fe, %	4.58	2.07	0.96	5.33	3.20	11.2	8.84	2.67	0.55	6.35	0.37	3.22	1.36
Ti, %	0.669	0.391	0.147	0.948	0.338	1.92	1.25	0.466	0.0892	0.641	0.0359	0.307	0.134
Mn	895	439	134	1495	646	1504	1671	609	95.1	877	45.0	344	238
V	70.2	76.8	18.15	151	70.4	449	200	72.7	(1.33)	85	5.80	50.8	19.9
Ba	512	nd	1881	nd	801	578	1042	382	40.5	545	878	1101	689
Cs	3.30	3.52	2.95	4.41	2.90	(0.732)	10.4	3.77	1.0476	3.50	1.03	4.31	4.57
La	23.89	216	90.0	21.0	18.4	36.4	43.3	63.8	10.16	28.4	6.03	9.62	15.4
Ce	58.7	434	158	55.1	38.4	74.7	74.6	147	19.4	64.6	8.66	18.0	33.8
Sm	7.24	16.2	7.85	5.66	4.63	8.46	6.23	7.20	1.55	8.26	0.97	2.53	3.54
Eu	2.06	1.11	1.33	1.47	1.18	2.7	2.59	1.21	0.850	2.08	1.31	1.59	1.15
Dy	2.00	5.31	3.20	6.24	4.01	7.41	5.13	3.34	1.33	2.13	(0.52)	2.44	2.01
Sc	17.4	4.8	1.66	17	10.8	28.1	19.5	6.07	0.189	19.2	0.542	7.03	5.38
Cr	27.6	31.8	16.7	1.7	32.8	38	172	12.2	22.7	25.2	14.3	44.2	5.68
Co	21.6	7.24	2.97	15.2	11.0	40.3	42.4	7.85	0.604	20.3	0.699	8.86	3.79
Rb	94.9	(60)	221	131	125	31.5	66.3	127	23.3	108	171	116	291
Lu	0.343	nd	0.0835	nd	0.190	0.455	0.328	0.149	0.0910	0.474	0.0363	0.122	0.212
Hf	1.72	23.1	1.26	1.89	3.65	6.87	5.32	4.74	1.13	2.19	2.16	4.93	3.41
Th	3.88	74.6	31.4	4.24	3.64	3.27	3.56	23.48	2.377	7.98	3.00	1.27	33.8
U	2.67	nd	1.96	nd	(0.5-1)	ns	ns	1.24	0.981	nd	1.10	2.93	11.5
Nd	10.5	nd	59.6	nd	22.1	24.5	26.4	55.3	7.69	ns	5.53	8.61	16.3

ns: No significant amounts.

(): Semiquantitative measurement.

nd: Not determined.

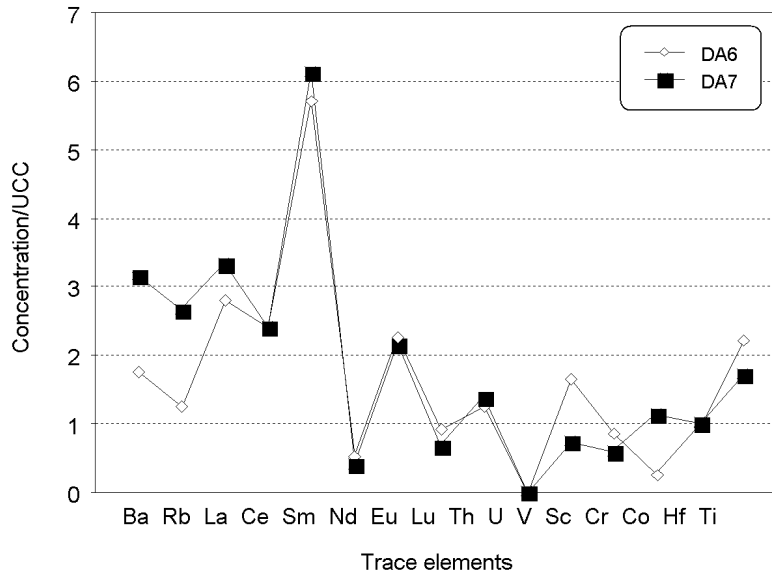


Fig. 4. Normalized values of trace elements of sample rock of diabases against basalts of later Proterozoic

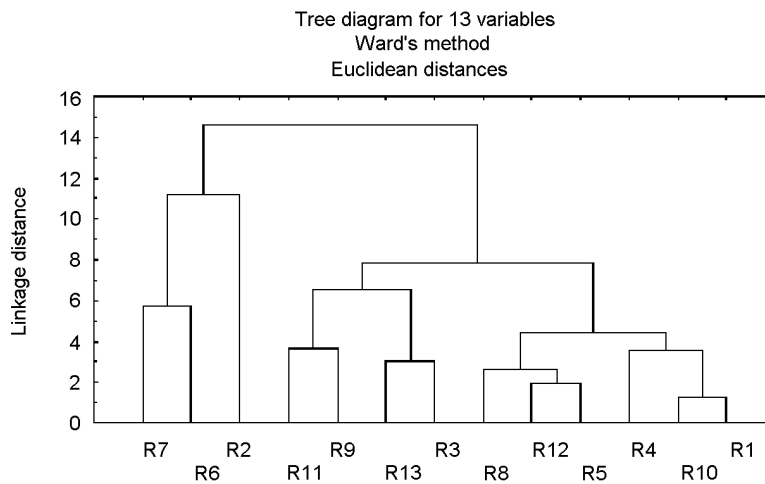


Fig. 5. Dendrogram of the rock samples normalized by z-score

### Conclusions

The application of INAA followed by multivariate statistical analysis succeeded to classify the eight lithotypes collected in the Itingussú River Basin, namely: dioritic-quartz, tonalitic gneiss, leucogranite, quartz-dioritic gneiss, granodioritic gneiss, diabases and leucotonalite (pegmatite that cuts across all of lithotypes).

The presence of allanite, titanite, apatite and zircon like accessory minerals were confirmed by the

petrographic analysis. These minerals can be hosts of rare earth elements and thorium, that will probably contribute to the development of soil and sediments.

Data from the chemical analysis have shown some anomalous enrichment of LREEs and Th, beyond Hf, in the tonalitic gneiss sample, suggesting a mixture of crustal magmas enriched with these elements during the formation of the rock. The leucogranite, altered granodiorite gneiss and diabases also showed enrichment of LRREs and Th.

\*

Sincerely thanks to Dr. André FERRARI, Departamento de Geociências of UFF, Dr. Pierre PERRIN, Departamento de Geoquímica of UFF and to the Radiochemistry Group at Instituto de Pesquisas Energéticas e Nucleares.

### References

1. H. O. CASTRO, M. A. QUEIROZ, in: Congresso Brasileiro de Geologia, Rio de Janeiro, 1984.
2. W. Z. DE MELLO, in: Proc. Intern. Symp. on Perspectives for Environmental Geochemistry in Tropical Countries, Niterói, 1993, p. 165.
3. S. R. PATCHNEELAM, H. C. BEZERRA, S. R. A. SOUZA, V. S. PIRES, F. V. AZEVEDO, *Geochim. Bras.*, 1 (1987) 177.
4. J. C. WASSERMAN, A. M. G. FIGUEIREDO, F. PELLEGATTI, E. SILVA-FILHO, *J. Geochem. Explor.*, 72 (2001) 129.
5. G. R. GILMORE, Technical Report, Universities Research Reactor, University of Manchester, England, 1983.
6. R. M. LATINI, M.Sc Thesis, Department of Geochemistry, Universidade Federal Fluminense, Niterói, 1998.
7. R. M. LATINI, A. V. B. BELLIDO, M. B. A. VASCONCELOS, O. F. DIAS Jr., *Quím. Nova*, 24 (2001) 724.
8. L. F. BELLIDO, B. DE C. AREZZO, *J. Radioanal. Nucl. Chem.*, 100 (1986) 21.
9. W. A. DEER, R. A. MOWIE, J. ZUSMAN, *Rocking-Forming Minerals*, Longmans Group Ltd., London, 1962.
10. C. KLEIN, C. S. HURLBUR Jr., *Manual of Mineralogy*, John-Wiley and Sons, Inc., New York, 1993.
11. V. M. GOLDSCHMIDT, *Geochemistry*, Oxford University Press, London, 1958.
12. P. HENDERSON, *Inorganic Geochemistry*, Pergamon Press, Oxford, 1982.
13. H. ROLLINSON, *Using Geochemical Data: Evaluation, Presentation, Interpretation*, Longmans Group, Essex, 1993.
14. R. M. ANJOS, R. VEIGA, T. SOARES, A. M. A. SANTOS, J. G. AGUIAR, M. H. B. O. FRASCA, J. A. P. BRAGE, D. UZEDA, L. MANGIA, A. FACURE, B. MOSQUERA, C. CARVALHO, P. R. S. GOMES, *Radiat. Meas.*, 39 (2005) 245.
15. K. CONDIE, *Chem. Geol.*, 104 (1996) 1.