Comun. Serv. Geol. Portugal, 1987, t. 73, fasc. 1/2, pp. 11-19

Comunicações dos Serviços Geológicos de Portugal

Radioemanometry, Gamma-Spectrometry, Fluorimetry, Neutron Activation and Numerical Taxonomy Methods in an Uranium Prospection Program. A Study of Rebolia Sediments (Portugal)

By

M. I. PRUDÊNCIO*, M. A. GOUVEIA*, JOAQUIM MARÇALO*,
E. ALBUQUERQUE BARROSO** & M. CAJÃO**

Key-words: Uranium prospecting; sedimentary geological formations; field gamma and radon detection; fluorimetry; neutron activation analysis; gamma-spectrometry; numerical taxonomy.

Abstract: Field gamma and radon detection, concentration of 23 elements, namely Na, K, Sc, Cr, Mn, Fe, Co, Zn, As, Rb, Cs, Ba, La, Ce, Nd, Eu, Tb, Yb, Lu, Hf, Ta, Th and U, radioactive equilibrium and soluble and total uranium were determined in soils of Rebolia area during the previous phase to execution of geological reconnaissance drillings of a DGGM uranium ore exploration program. The results were subjected to cluster analysis and principal components analysis. Four major clusters were recognized, roughly related with lithology and with uranium anomalies in sedimentary formations of Rebolia area.

Palavras-chave: Prospecção de urânio; formações geológicas sedimentares; detecção de radioactividade no campo e do radão; fluorimetria; análise por activação com neutrões; espectrometria-gama; taxonomia numérica.

Resumo: Fez-se o estudo de amostras de solos da região de Rebolia na fase de prospecção local, ou seja anterior à fase de reconhecimento por sondagens, de um programa de prospecção de urânio da DGGM. Procedeu-se à determinação da radioactividade no campo e à detecção do radão, bem como de 23 elementos, nomeadamente Na, K, Sc, Cr, Mn, Fe, Co, Zn, As, Rb, Cs, Ba, La, Ce, Nd, Eu, Tb, Yb, Lu, Hf, Ta, Th e U, equilíbrio radioactivo e ainda dos teores de U lixiviável e total nas amostras de solos.

Fez-se uma análise dos dados aplicando aos resultados obtidos um método de análise grupal e a análise em componentes principais.

Reconheceu-se a existência de quatro grupos de amostras que apresentam uma certa relação com a litologia e ainda com anomalias de U nas formações sedimentares da área de Rebolia.

INTRODUCTION

In the course of the exploration phase of DGGM uranium ore program of sedimentary formations (1982-1984), the Rebolia area, situated in the south slope of Cabeça Gorda structure (sheet 19 C – Figueira da Foz of «Carta Geológica de Portugal», scale 1:50 000) was chosen for a more complete study.

As a matter of fact, not only radioemanometry was applied, but also neutron activation analysis and gamma-spectrometry for the determination of numerous major and trace elements and radioactive equilibrium in soil samples of the area. All the results were processed by methods of multivariate analysis, namely cluster analysis and principal components analysis.

The aim of this work is to investigate the contribution of these methods to this kind of studies, specially for the discrimination between lithologic and metallogenetic anomalies.

* Departamento de Química, ICEN, LNETI, 2685 Sacavém, Portugal.
** DGGM, Serviço de Fomento Mineiro e Indústria Extractiva, Rua Diogo Couto, 1, Lisboa, Portugal.

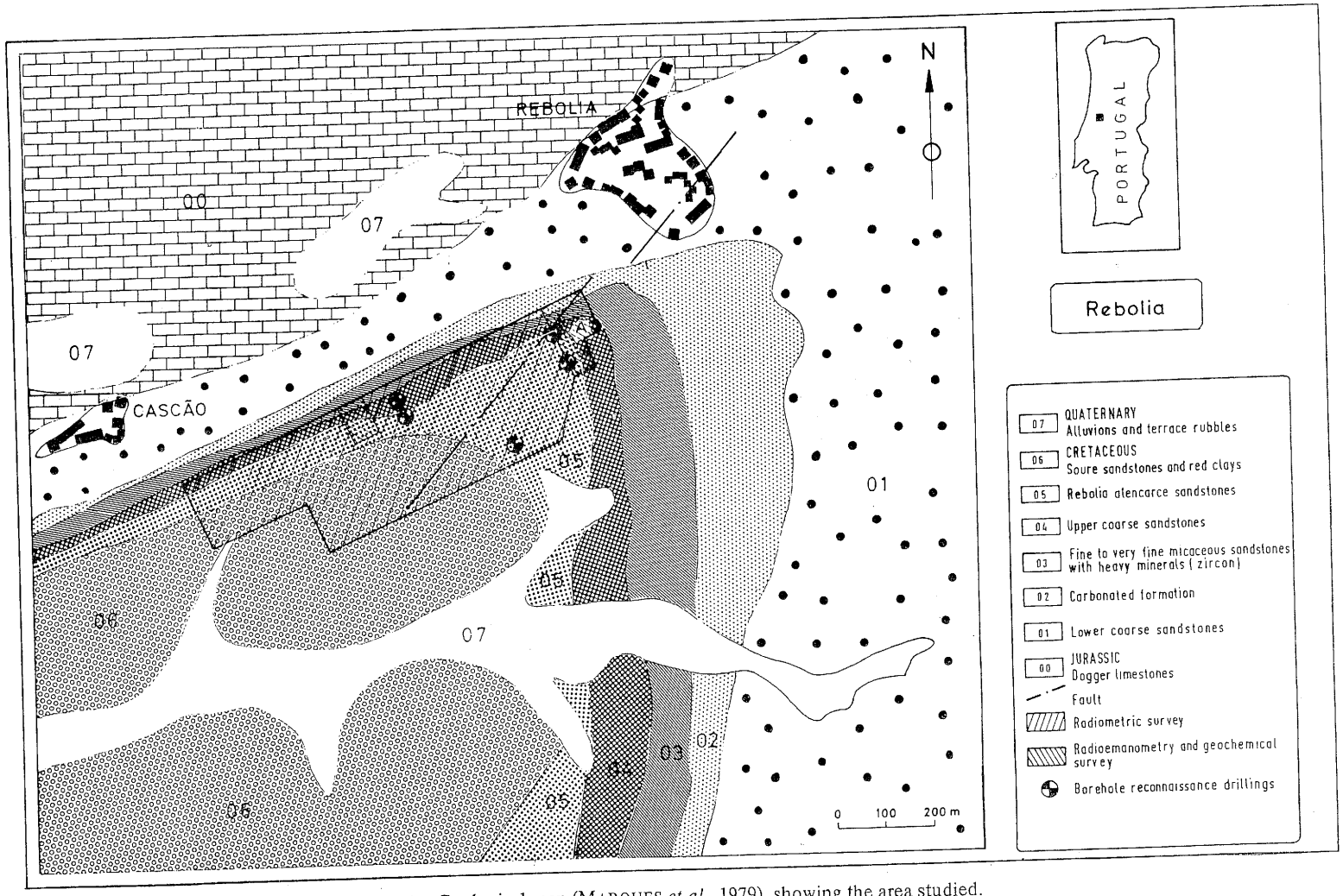

Fig. 1 – Geological map (MARQUES *et al.*, 1979), showing the area studied.

FIELD METHODS AND ANALYTICAL TECHNIQUES

In figure 1 are represented the geological formations of the Rebolia region together with the areas where radioemanometric and geochemical surveys were done in a more detailed phase for uranium exploration purposes. The localization of the soil sampling survey, subject of this work, is indicated by the letter A. The geological formations have been characterized previously by J. CORREIA MARQUES *et al.* (1979) (fig. 1).

The geral tectonics structure of the region is conditioned, westward by the salt dome of Soure, at north by Cabeça Gorda anticline and at east by the fractures of Sicó massif. The geometry of the anomalous area is fundamentally related to the Rebolia sincline which has the axis inclined toward Soure salt nucleus.

In the area studied the distance between profiles was five meters, and in each two meters into profiles a measurement station was localized.

In each station two kinds of measurements were made: the total gamma activity, using Saphymo – SPP2 – NF NaI(Tl) scintilometer and the integral alpha activity, using a EDA RD-200 emanometer. For the second method three successive measurements were made (MATOLIN, 1982).

Soil samples were collected 30 cm deep at the stations previously refered but as the points of a square net, 10 m by 10 m, and in other points where radiometry showed anomalies. The soil samples, in number of 109, were submitted to the analytical treatment described below.

Twenty three elements, namely Na, K, Sc, Cr, Mn, Fe, Co, Zn, As, Rb, Cs, Ba, La, Ce, Nd, Eu, Tb, Yb, Lu, Hf, Ta, Th and U were determined using the instrumental neutron activation analysis (INAA) method (CABRAL *et al.* 1979; GOUVEIA *et al.*, 1986; PRUDÊNCIO *et al.*, 1986). All irradiations were done in the core grid of the Portuguese Research Reactor (RPI) at a neutron flux of 1.6×10^{11} n cm^{-2} s^{-1}. The IAEA SOIL-5 and NBL Fosfated Rock standards were used as the reference samples.

Leachable and total uranium in the soil samples were determined by fluorimetry in SFMIE Laboratory (DGGM, Lisbon), using a «Nucleometer» FPDTU 1 reflection fluorimeter (CAJÃO, 1969).

The radioactive equilibrium in the soil samples (expressed as *P*, which is 1 for samples in radioactive equilibrium and smaller or bigger than 1 as the samples contain ^{226}Ra in defect or excess) was determined, as previously described in detail (MARÇALO & MATOS, 1984), by gamma-spectrometry, using a 4" x 4" NaI(Tl) detector.

METHODS OF DATA ANALYSIS

The data used in this study are the results obtained by using the several methods refered (Table I). Thus the original data matrix has 109 soil samples to be grouped and 30 variables.

Standardization of variables was applied in order to equalize the size of each variable (SNEATH & SOKAL, 1973).

Only one dissimilarity coefficient was calculated, namely the Pearson correlation coefficient.

Cluster analysis was carried out by using the sequential agglomerative hierarchic method – UPGMA (unweighted pair-group method using arithmetic averages). The results were represented by a phenogram. The cophenetic correlation coefficient between the dissimilarity values implied by the phenogram and those of the original dissimilarity matrix was calculated.

Ordination of samples was carried out by employing principal components analysis (PCA). The variance accounted for a given number of principal components was calculated.

In order to investigate the correlations between the variables, cluster analysis (UPGMA), using the R technique and the correlation coefficient to estimate the similarity between variables, was employed. The results were represented by a phenogram and the cophenetic correlation was calculated.

Computations were carried out on a NORD-560 computer by employing the NTSYS programs system (ROHLF *et al.*, 1982).

Two programs were used, namely Profile and Maplot, of the MICROGAS program system prepared in 1980 by Queen's University, Kingston, Ontario, under IAEA Research Contract. The programs were run at the SFMIE.

RESULTS AND DISCUSSION

In figure 2 are presented the geological limits of the area studied. The values marked, corres-

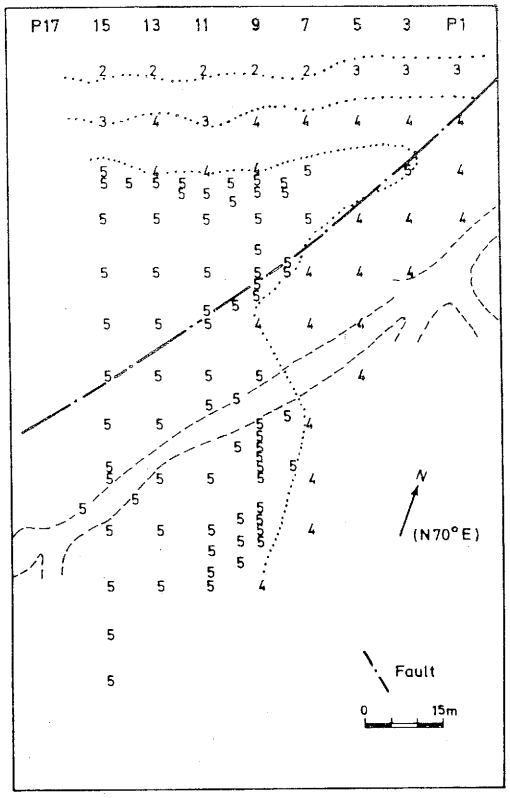

Fig. 2 – Geology of the area studied (see fig. 1 for geological units).

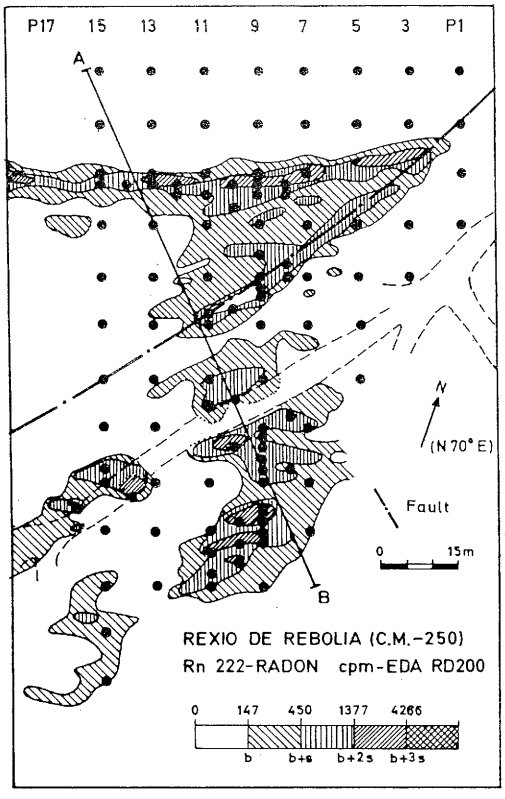

Fig. 3 – Radon contour map.

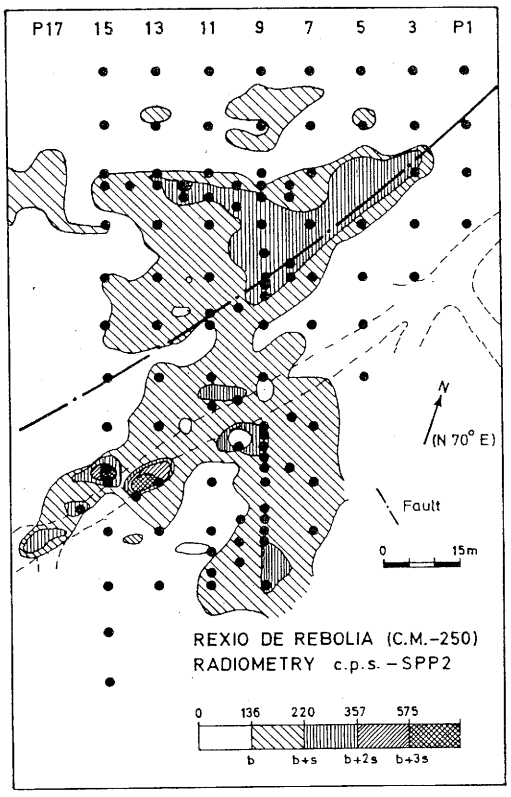

Fig. 4 – Radiometry contour map.

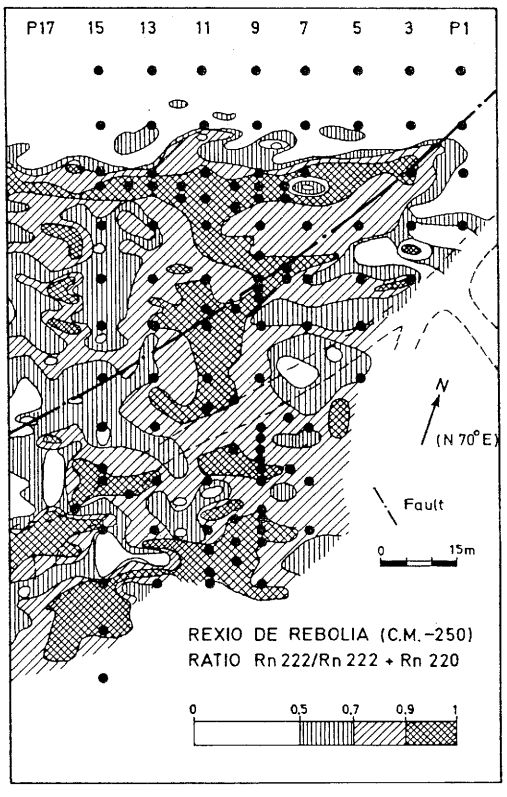

Fig. 5 – Ratio contour map.

TABLE I

Mean, standard deviation, sample size, minimum and maximum values for the variables and mineralized sample contents

Variable	Mean	Standard Deviation	Sample Size	Minimum	Maximum	Mineralized Sample
Na	.11236E+00	.60923E−01	108	.2000E−01	.3130E+00	.5000E−01
K	.17286E+01	.10153E+01	108	.3230E+00	.5640E+01	.6880E+00
Fe	.15811E+01	.10415E+01	108	.1620E+00	.5050E+01	.3290E+01
Sc	.42824E+01	.26745E+01	108	.5000E+00	.1200E+02	.1200E+02
Cr	.20010E+02	.11340E+02	108	.3960E+01	.5570E+02	.4600E+02
Mn	.10400E+03	.11614E+03	108	.3800E+01	.8380E+03	.2980E+02
Co	.30212E+01	.24376E+01	108	.4710E+00	.1750E+02	.3320E+01
Zn	.28236E+02	.18031E+02	103	.5520E+01	.8420E+02	.4660E+02
As	.31857E+02	.60464E+02	108	.1950E+01	.5640E+03	.8830E+02
Rb	.14408E+03	.89821E+02	108	.2860E+02	.5130E+03	.1130E+03
Cs	.11358E+02	.69995E+01	108	.1980E+01	.3170E+02	.2370E+02
Ba	.24953E+03	.10140E+03	108	.7030E+02	.5240E+03	.7140E+03
La	.29906E+02	.11365E+02	108	.5530E+01	.7060E+02	.4790E+02
Ce	.59331E+02	.22647E+02	106	.1140E+02	.1280E+03	n.d.
Nd	.28439E+02	.11242E+02	106	.4990E+01	.6190E+02	n.d.
Eu	.53903E+00	.29950E+00	108	.1050E+00	.1460E+01	.3440E+01
Tb	.47414E+00	.23727E+00	108	.9490E−01	.1510E+01	.1730E+01
Yb	.16475E+01	.69722E+00	108	.2660E+00	.3760E+01	.6440E+01
Lu	.23697E+00	.98462E−01	108	.4110E−01	.6230E+00	.9160E+00
Hf	.52024E+01	.20549E+01	108	.1190E+01	.1200E+02	.3770E+01
Ta	.20652E+01	.97485E+00	108	.2150E+00	.4650E+01	.3230E+01
Th	.15117E+02	.57698E+01	108	.3070E+01	.3180E+02	.2030E+02
UN	.27394E+02	.47009E+02	108	.2110E+01	.2930E+03	.8820E+03
P	.88657E+00	.21082E+00	108	.5000E+00	.1300E+01	.5900E+00
SPP2	.20889E+03	.23693E+03	108	.7000E+02	.2300E+04	.2000E+04
RN222	.62594E+03	.10059E+04	108	.0000E+00	.6949E+04	n.d.
RN220	.54482E+02	.63840E+02	108	.0000E+00	.3390E+03	n.d.
RN/THOR	.74491E+00	.28174E+00	108	.0000E+00	.1000E+01	n.d.
UL	.78120E+01	.20439E+02	108	.2000E+00	.1580E+03	.8500E+03
UT	.18916E+02	.38055E+02	108	.8000E+00	.2870E+03	.9100E+03

n.d. — not determined.

pondent to the stations established, refer to the geological units (fig. 1).

Mean, standard deviation, sample size and minimum and maximum values for each variable are shown in Table I. The results of Na, K and Fe are in percentage and the results Sc to UN (U concentration determined by INAA) as well as of UL and UT (leachable and total U respectively, determined by fluorimetry) are in ppm. SPP2 (total gamma activity) is expressed in cps, and ^{220}Rn and ^{222}Rn are in cpm. Together with these values the results for a mineralized sample, collected in a trench between profiles 13 and 14 (fig. 2), are presented.

Figures 3, 4 and 5 show the contour maps of SPP2, ^{222}Rn and RN/THOR in the area studied. Figure 6 shows a cross-section between points A and B indicated in figure 3. Radon contour map (fig. 3) confirms the location of the fault deduced by J. MARQUES *et. al.* (1979).

The result of UPGMA clustering of the samples is presented in figure 7. The cophenetic correlation coefficient was 0.64, indicating a weak agreement of the phenogram with the original correlation matrix. However, the results obtained agree well with the geological evidence. In fact, four major clusters are discerned: a cluster A litologically related with three geological formations, namely carbonated (2), fine to very fine micaceous sandstones (3) and upper coarse sandstones (4) units in the most sloping part of the area (fig. 6); a cluster B specially related with background values obtained in Rebolia Alencarce sandstones (unit 5); and clusters C and D related with uranium anomalies. The anomalous uranium concentrations appear related with the erosion surface situated

between upper coarse sandstones (unit 4) and Rebolia Alencarce sandstones (unit 5) – group D; and with black shales with carbonaceous material which is below the erosion surface (fig. 6) – group C. These groups were marked in the map of figure 8.

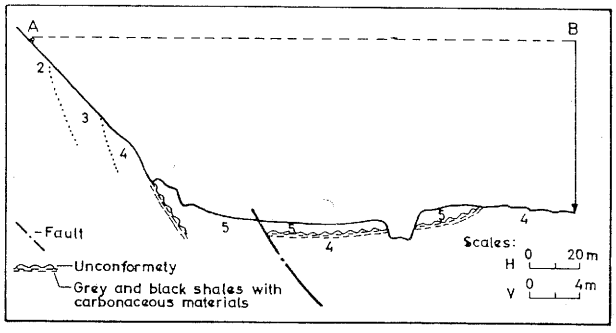

Fig. 6 – Cross section A-B (see fig. 3).

The results of ordination by principal components analysis are presented in figure 9. These results are a very useful complement to the previous one. In fact, the proportion of the variance accounted for by the first three principal components is equal to 72.47 %. The relative contribution of the original variables to the first three principal components, as well as the percentages of the total variance they accounted for, are shown in Table II. The first principal component, accounting 47.23 % of the variance is considerably determined by several variables, but specially by Sc, Cr, Co, Fe, Zn, Cs, Ba, rare earths (RE), Ta and Th. The second principal component, accounting 17.54 % of the variance, appears to be principally influenced by U. The third principal component, accounting 7.70 % of the variance is mainly affected by P.

It must be pointed out that the first component appears strongly related with the lithology, while the second component is related with uranium anomalies. The third component is specially related with the radioactive equilibrium, being the principal discriminant variable between groups C and D.

The resulting phenogram of the cluster analysis by using the R technique clustering of the variables is presented in figure 10. The cophenetic correlation coefficient was 0.9, indicating a good agreement of the phenogram with the original dissimilarity matrix.

Fig. 7 – Phenogram of 109 samples based on cluster analysis (UPGMA) of correlations.

Sample concentration maps of UN, UT, UL, P and Fe are shown in figures 11-15.

Concentration distribution along profile 9 were made for selected variables, namely Na, K, Eu, SPP2, ^{222}Rn, UN, UT, UL and P, and are shown in figure 16. It can be easily seen that group C presents P<1, while group D presents P>1. Radioactive equilibrium values greater than 1 may be explained either by deposition of Ra in this area or by lixiviation of U. The second hipothesis is the most likely, in agreement with the lower values of UL in group D.

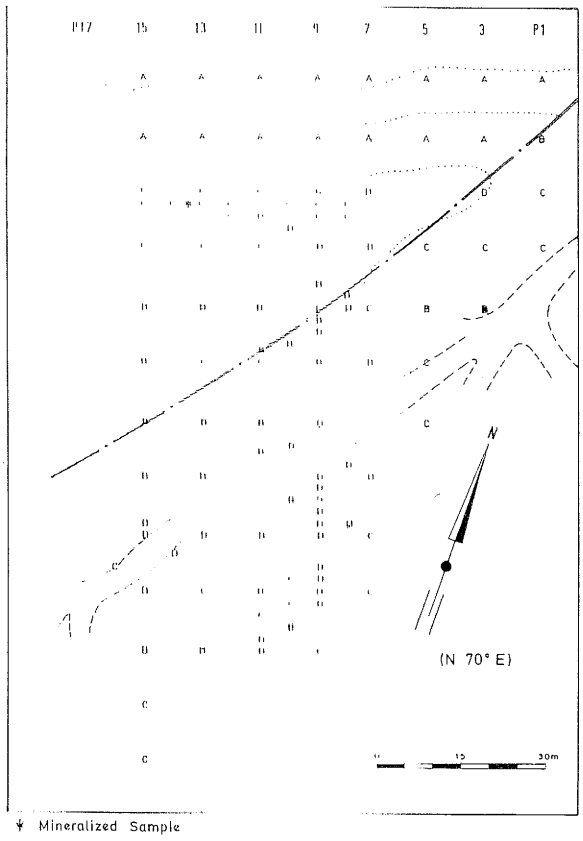

Fig. 8 — Groups map.

TABLE II

Relative contribution of the contributes to first components and relative importance of these components.

	Fact 1	Fact 2	Fact 3
Na	.640	.531	.226
K	.605	.545	.115
Fe	.757	.172	−.393
Sc	.876	.166	−.355
Cr	.840	.112	−.303
Mn	.657	.400	.150
Co	.760	.216	−.212
Zn	.849	.057	−.263
As	.001	.260	−.081
Rb	.724	.429	−.040
Cs	.845	.019	−.370
Ba	.917	.039	.260
La	.906	.056	−.072
Ce	.898	.075	−.020
Nd	.913	.039	.033
Eu	.836	.383	.292
Tb	.798	.233	.305
Yb	.854	.189	.391
Lu	.764	.195	.420
Hf	.613	.381	.193
Ta	.790	.027	−.371
Th	.827	.043	−.228
UN	.345	.926	.142
P	−.209	.117	−.570
SPP2	.207	.750	−.325
RN222	−.001	.656	−.276
RN220	.197	−.001	−.254
RN/THOR	−.563	.527	−.169
UL	.302	.850	.345
UT	.310	.924	.211
eigenvalue	14.17	5.26	2.31
percent of trace	47.23	17.54	7.70
accum. percent.		64.77	72.47

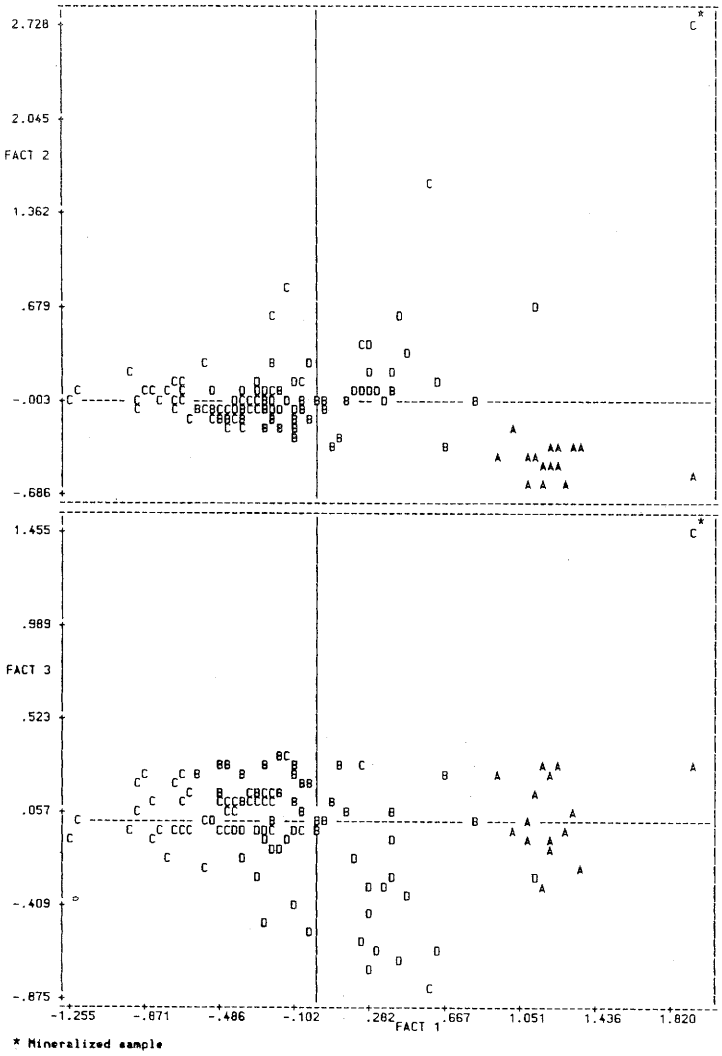

Fig. 9 — Ordination plots from principal components analysis.

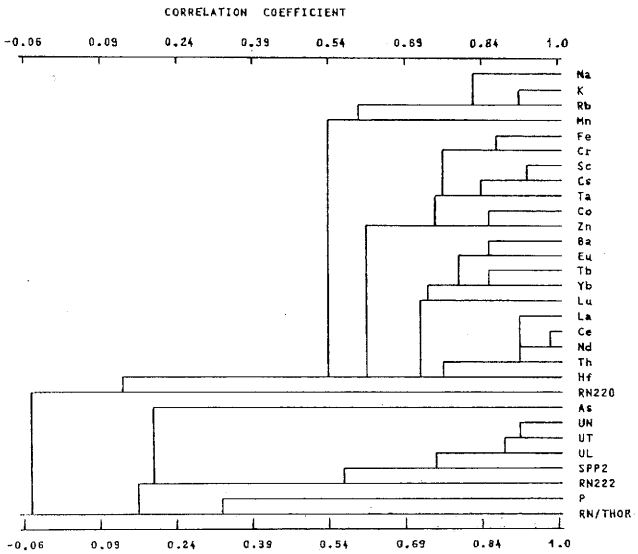

Fig. 10 — Phenogram of 30 variables based on cluster analysis (UPGMA) of correlations.

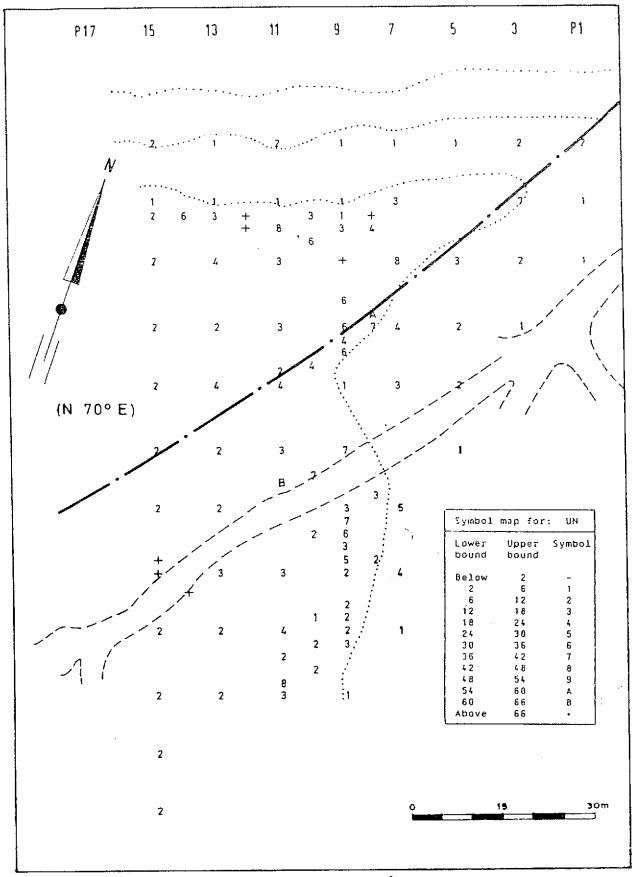

Fig. 11 – Sample concentration map of UN.

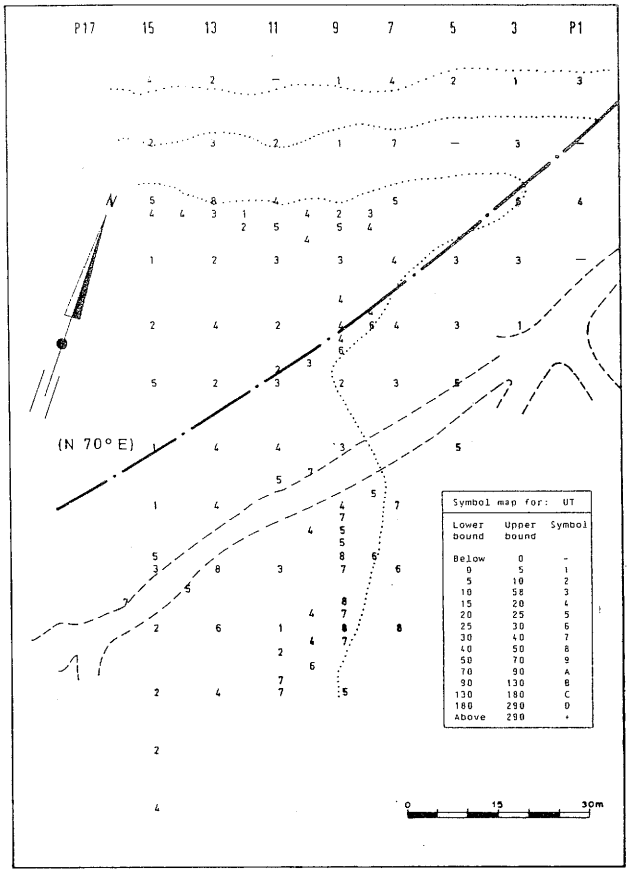

Fig. 12 – Sample concentration map of UT.

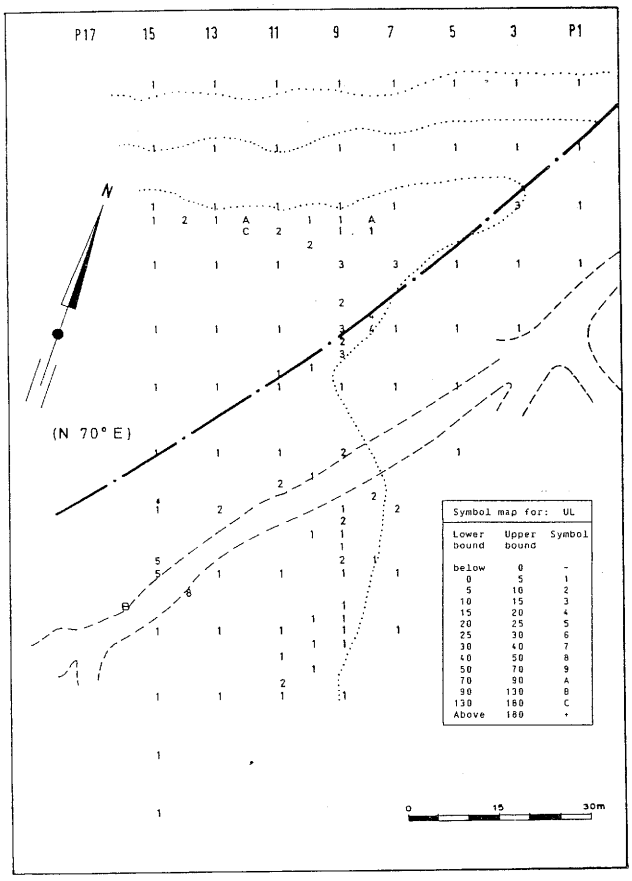

Fig. 13 – Sample concentration map of UL.

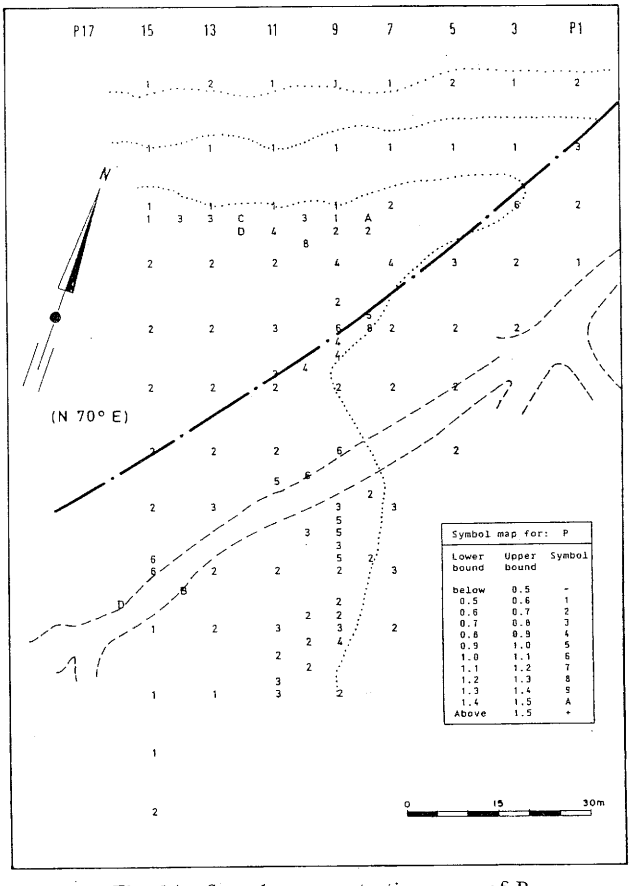

Fig. 14 – Sample concentration map of P.

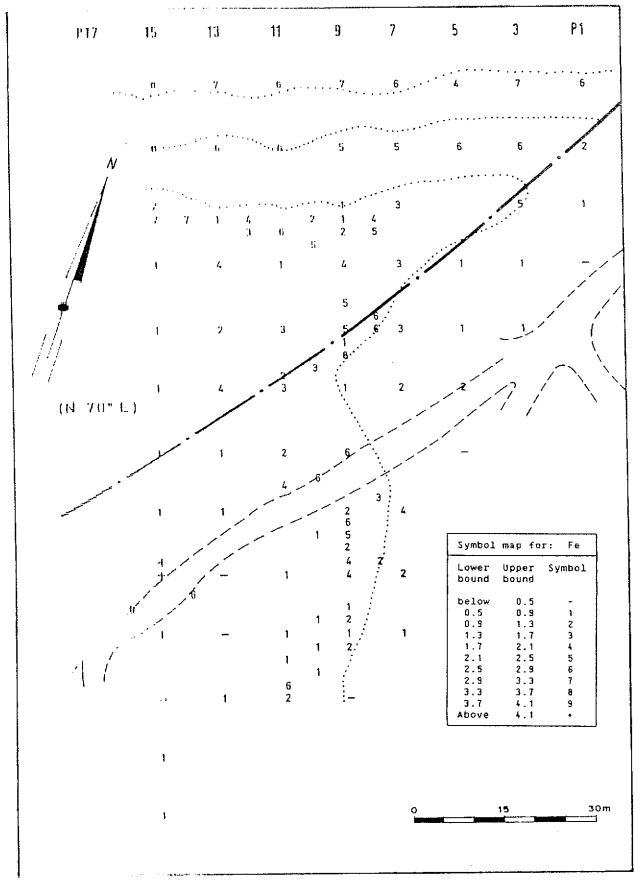

Fig. 15 – Sample concentration map of Fe.

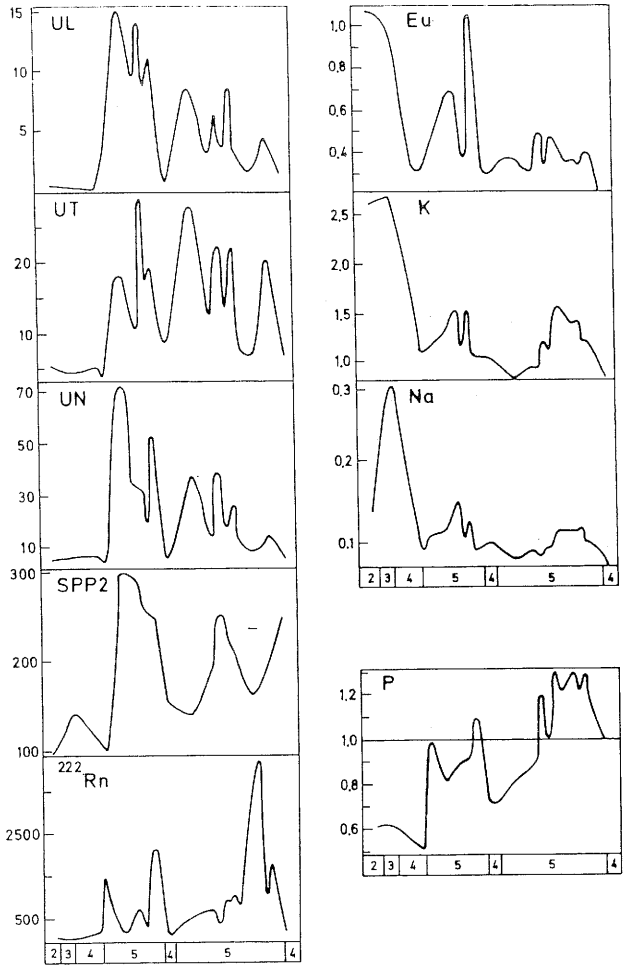

Fig. 16 – Concentration distributions of SPP2, ^{222}Rn, UN, UT, UL, P, Eu, K and Na along profile 9 (see fig. 1 for geological units).

ACKNOWLEDGEMENTS

We thank the LNETI Reactor Department for irradiation facilities.

REFERENCES

CABRAL, J. M. P., GOUVEIA, M. A. & PRUDÊNCIO, M. I. (1979) – Determinação de terras raras e doutros oligoelementos em rochas por activação com neutrões térmicos. *Bol. Mus. Lab. Miner. Geol. Fac. Ciênc. Lisboa,* **16** (1): 205-218.

CAIÃO, M. M. (1969) – Relatório do Estágio no Comissariado de Energia Atómica de França. Report of Junta de Energia Nuclear.

GOUVEIA, M. A., SEABRA e BARROS, J., TAVARES, M. JESUS & FREITAS, M. (1986) – Combination of neutron activation, atomic absorption spectroscopy and conventional methods in the elemental analysis of silicate rocks. *Journ. Radioanal. Nuclear Chemistry,* Articles, 97(2): 265-270.

MARÇALO, J. & MATOS, A. PIRES DE (1984) – Aplicação da espectrometria gama à determinação de urânio, tório e rádio em amostras geológicas. *Comun. Serv. Geol. Portugal,* Lisboa, **70**: 103-109.

MARQUES, J. A. CORREIA, SOARES, A. FERREIRA, GODINHO, M. M. DIAS, J. M. MATOS & CAJÃO, M. M. (1979) – Contribuição para o estudo da distribuição hidrogeoquímica do urânio na orla meso-cenozóica ocidental portuguesa. *Comunic. Serv. Geol. Portugal,* Lisboa, **LXIV**: 151-176.

MATOLIN, W. (1982) – Emanometry in uranium exploration. IAEA Report of a mission to Portugal.

PRUDÊNCIO, M. I., GOUVEIA, M. A. & CABRAL, J. M. P. (1986) – Instrumental neutron activation analysis of two french geochemical reference samples – Basalt BR and Biotite Mica-Fe. *Geostandards Newsletter,* X (1): 29-31.

ROHLF, F. J., KISHPAUGH, J. & KIRK, D. (1982) – NTSYS manual. Dep. Ecology and Evolution, The State University of New York at Stony Brook.

SNEATH, P. H. A. & SOKAL, R. R. (1973) – Numerical Taxonomy. The Principles and Practice of Numerical Classification. San Francisco, W. H. Freeman and Company (Ed.).

Manuscript received July. 1987