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STUDY OF THE BEHAVIOUR OF RARE
EARTH ELEMENTS AND OTHER   ELEMENTS
IN ROCKS FROM A PETROLEUM ORE
BY NEUTRON ACTIVATION ANALYSIS

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Introduction

The agricultural and industrial development verified in Cuba, mainly in the last years, has incremented the interest for mineral prospection in order to find energetic alternative sources, supplying a part of the internal demand.

For this reason several works studying the para-autoctonal horizon in different petroleum ores from north-western of Cuba were realised [1].

However, this paper discusses the vertical behaviour of the concentration for certain elements using the INAA in seals and collector rocks taken from different depths to establish the presence of microelements which affect the geophysical methods, specially those which have large neutron absorption cross section.

On the other hand, the knowledge of the concentrations of rare-earth elements and other traces in rocks is of great interest in the field of geoscience.

Trace elements including U, Th, Ba, Sc, Rb, Ta, Cs, Co, Hf, and REEs have been extensively used in petrogenetic studies of igneous, metamorphic and sedimentary rocks. They allow the evaluation and the extent of the main processes involved in the generation and differentiation of layer and melts. They are also used in the study of rocks to predict the nature of sources materials, giving information about their chemical and mineralogical composition.
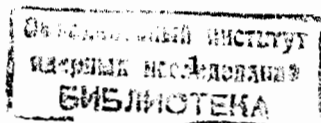
Neutron activation analysis has been widely used in the determination of these elements in rocks due to its high sensitivity as well as good precision and accuracy [2-7]. It is readily capable of simultaneous determination of many elements at parts per million (ppm) and parts per billion (ppb) levels, often without destruction of the sample, and may be applied for the determination of a wide range of elements in rocks, including most lantanides.

The aim of this work is to present and discuss the results of a series of measurements which have been realised in six sample rocks corresponding to different depth from the same well in a region to north-western of Cuba. The behaviour of the element composition at all depths, referred to the element concentration in the major depth is also shown, in order to know how the element distribution changes and to see how is affected by the different types of rocks in the well.

At the same time the behaviour of the REEs at different depths is presented. The ratio between the REEs and vanadium contents and between the REEs and condrites contents were calculated with the purpose of knowing: firstly, how the concentrations change with respect to the content of petroleum in the different layers and, secondly, to have an idea for the evaluation of the main processes in the generation and differentiation of the melts and to know the nature of source material.

Experimental

-Principle of comparative Neutron Activation Analysis Method:

In this method, standards containing known amounts of the elements of interest are submitted to a neutron flux together with the samples. Thus, the induced activities are measured under equal conditions using Ge(Li) detectors.

Since each radioisotope has its characteristic half-life and energy (or energies) of gamma radiation it is possible, in general, to identify the isotope of the element. The amount of this element in the sample is considered as directly proportional to the counting rate of gamma radiation.

When the samples and standards are irradiated together at the same irradiation time and neutron flux conditions, the concentration of a particular element is obtained by comparing the counting rates of the sample and of the standard spectra. This concentration, C(i), is calculated from the expression:

$$\frac{C(i)}{C(i)_s} = \left[\frac{A_m(i) - \sum_k A_m(k) \cdot FCS(k)}{A_s(i) - \sum_k A_s(k) \cdot FCS(k)} \right] \times \left[\frac{Tm_m \cdot m_s \cdot FCF}{Tm_s \cdot m_n} \right] \times e^{\frac{\ln 2 \cdot Delt}{T_{1/2}}}$$

where $A_m(i)$ and $A_s(i)$ are the areas of the photo-peaks in the sample and on the standards, respectively. The index "k" refers to the reference intensity lines of other lines which energetically interfere with element i. Factor FCS(k) takes into account the efficiency and absolute intensity corrections. Tm_m and Tm_s are the effective measurement times of the samples and of the standards, respectively. FCF is the correction due to neutron flux in the container. $T_{1/2}$ is the half-life of the radioisotope. DELT is the difference between samples and standard cooling times. $C(i)_s$ is the element concentration in the standard. Data of studied elements were taken from [8].

-Sample preparation:

The rocks from the petroleum wells that arrived in coarser fragments were first broken with a hammer and then crushed to smaller fragments in the porcelain mortar until a reasonable size for grinding in a mechanical agate mortar was obtained.

After grinding the rocks, the treatment was continued in a manual agate mortar, until the powder passed trough a 150 mesh nylon sieve. This final treatment was considered necessary to assure a reasonable homogeneity of the material.

Contact with the metallic parts was avoided as much as possible, since the problem of contamination of the samples by forcing elements can be very serious at this level of granulometry.

References materials were not submitted to any further treatment, since they were already received as fine powder. For the relative neutron activation analysis the certified material IAEA/SOIL-7 [9] was used. The use of this standard for the determination of elemental concentration in rocks, is justified in [1].

-Irradiation:

Aliquot of about 100-300 mg of the powder rock samples were weighted in pre-cleaned Al foils (long irradiation) or polyethylene packets (short irradiation). They were thus placed inside vessels of the same materials, specially developed for use in the nuclear reactor IBR-2 from the Neutron Physic Laboratory of JINR, Dubna, USSR [3].

A total of twelve samples, corresponding to six different depths from the same well into the east beach region of Havana were analyzed. The mean depths, lithology and types of layers are shown in Table 1.

The irradiation times of the samples and standards were selected according to the elemental concentration and half-life, divided in short (1-5 minutes) and long (72 hours) irradiations. The cooling and measuring times of the short irradiated samples were 5-15 minutes and 5-10 minutes respectively.

The measurement of the long irradiated samples was realized in three cycles:

Table 1

Characteristics of the studied rocks

Sample	Lithology	Layer	Depth (m)
1	calcareous + clay + silice + dolomite	seal	1648
2	calcareous + clay + dolomite	"	1808
3	calcareous + clay	"	1993
4	calcareous + clay	"	2160
5	calcareous + silice + clay	"	2311
6	calcareous	collector	2421

a.-) After 8 days (measuring time: 30 min.).

b.-) After 15 days (measuring time: 30 min.).

c.-) After one year to improve the accuracy in the determination of the elemental concentration for ^{152}Eu, ^{134}Cs, ^{182}Ta, and ^{60}Co. , with one hour of measuring time.

The characteristics IBR-2 (Channel I) epithermal neutron flux characteristics used in this work are described in [10]. Epithermal irradiation suppresses activation of some strong interfering elements for analysis of REEs, Uranium, Thorium, etc.

-Gamma spectrometry measurement:

Measurements were performed using Ge(Li) detectors with 3 keV resolution for 1332 keV gamma line of ^{60}Co. Detectors were connected to a standard CAMAC 4096 channels ADC and to a PC/XT computer.

The gamma spectra were processed using a modified version of ACTIV program [11,12] written in FORTRAN. This program locates peak positions and calculates gamma ray energies and net areas.

Results and discussion.

Forty eight activation spectra were worked out. The analytical peaks with statistical error less than 15 % in a 70-1830 keV energetic range were analyzed.

The obtained elements, active isotopes, half-life, reference material element concentrations (g/g) and its errors are show in Table 2. The order of elements in Table 2 corresponds to descendant element concentration obtained for the productive or collector (2421 m) layer (see Table 1). Dashed

Table 2

Determined elements by INAA

	Element	Nuclide	T1/2	Eγ(KeV)	SOIL-7(g/g)	Error(%)
1	Si	S31	2.6 h	1266.2	1.8e-1	2.8
2	Ca	Sc47	3.35 d	159.4	16.3E-1	1.5
3	Fe	Fe59	44.5 d	1099.2	2.57E-2	0.2
4	Mg	Mg27	9.46 m	1014.4	11.3E-3	0.9
5	Al	Al28	2.24 m	1778.9	47.0E-3	1.1
6	K	K42	12.36 h	1524.7	12.2E-3	0.8
7	Na	Na24	15.02 h	1369.0	2.4E-3	4.1
8	Sr	Sr85	64.84 d	514.0	1.08E-4	10
9	Mn	Mn56	2.58 h	1810.7	6.31E-4	0.6
10	V	V51	3.75 m	1434.1	6.6E-5	10.6
11	Cl	Cl38	37.5 m	1642.0	-------	----
12	Zn	Zn65	243.9 d	1116.0	1.04E-4	2.9
13	Ba	Ba131	11.8 d	496.3	1.59E-4	20
14	Nd	Nd147	10.98 d	531.0	3.0E-5	23
15	Ce	Ce141	32.5 d	145.4	6.1E-5	10
16	La	La140	40.27 h	1596.5	2.8E-5	3.6
17	Mo	Mo99	66.0 h	140.5	2.5E-6	20.0
18	As	As76	26.32 h	559.1	1.34E-5	1.5
19	Rb	Rb86	18.66 d	1076.6	5.10E-5	1.0
20	U	Np239	2.36 d	228.2	2.6E-6	25.0
21	Co	Co60	5.27 y	1173.1	8.90E-6	8.9
22	Gd	Tb161	6.9 d	74.6	-------	----
23	Ga	Ga72	14.1 h	834.0	10.0E-6	20.0
24	Sm	Sm153	46.7 h	103.2	5.1E-6	10.0
25	Br	Br82	35.3 h	776.5	7.00E-6	14.3
26	Sb	Sb124	62.2 d	1691.0	1.7E-6	5.9
27	Sc	Sc46	83.83 d	889.2	8.3E-6	12.4
28	Hf	Hf181	42.4 d	482.0	5.1E-6	5.8
29	Cs	Cs134	2.06 y	604.7	5.40E-6	13.6
30	Tm	Tm170	128.6 d	84.3	-------	----
31	Yb	Yb169	32.02 d	177.2	2.4E-6	16.3
32	Th	Pa233	27 d	311.9	8.2E-6	16.1
33	Tb	Tb160	72.3 d	879.4	6.0E-7	16.7
34	Ta	Ta182	115 d	1121.3	0.52E-6	25.0
35	Eu	Eu152	13.33 y	1407.5	1.0E-6	20.0

lines in the places of the concentrations indicate that this element was not in the standard and its concentration was calculated by the absolute method using the algorithm described in [13].

Table 3 shows the element concentration and its errors between parentheses, except the group of Rare Earth Elements which appear below. The Si, Al and Mg concentrations were evaluate using the interfering factor, according to the neutron energetic spectra [14].

In the quantitative determination prevailed as major elements, Si, Ca, Fe and Al, as minor elements Mg, K, Na and Cl and remainder was obtained as trace elements. The distribution of the concentration values obtained by INAA in rocks from petroleum ores according to their depths is presented in Figure 1. The order of the elements in Figure 1 corresponds to the order in Table 2.

The elements can be divided in three great groups according to their concentration values in each depth:

1.- A maximum intermediate of element concentration in the productive layer. In this group only V, Sr and Sb, which are typical in the petroleum composition, are fixed (V-group).

2.- An intermediate maximum of element concentration in depth 1993 m (seal), and 2421 m.(collector). The elements are: U, Mn, Si, Ca, Sc, Mg, As, Mo and Cl (U-group).

3.- An intermediate maximum at 2160 m (seal). The elements are: Co, Zn, Ga, Br, Rb, Hf, Ta, Cs, Th, Na, Al, Ba, Ca and REEs (Co-group).

In all cases, the order of the fluctuation is not large, therefore we do not observe variations in the element concentration which can affect the record in the nuclear sounding
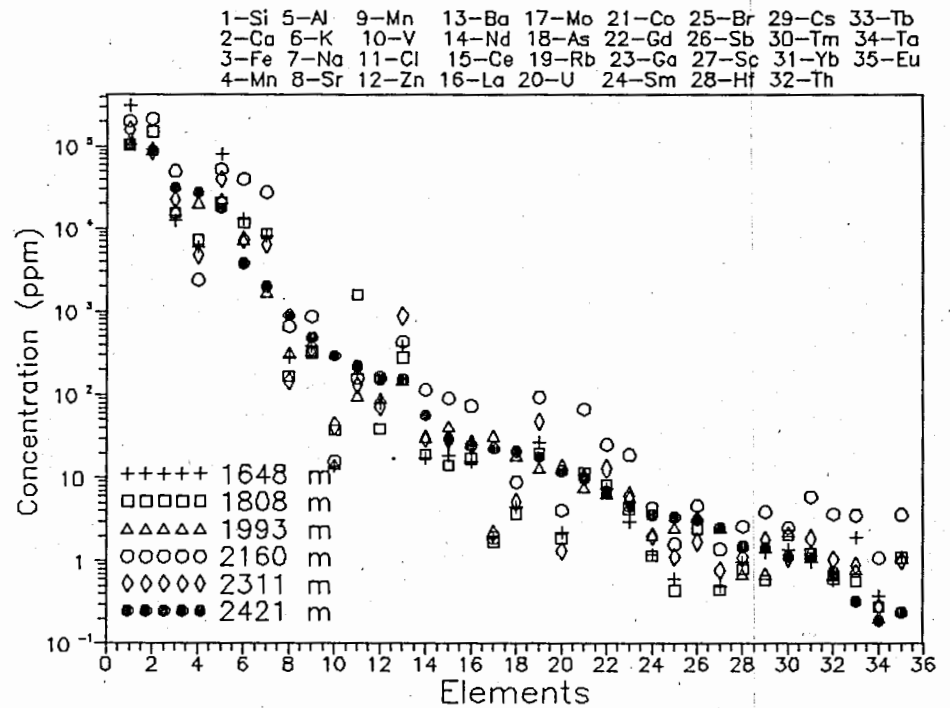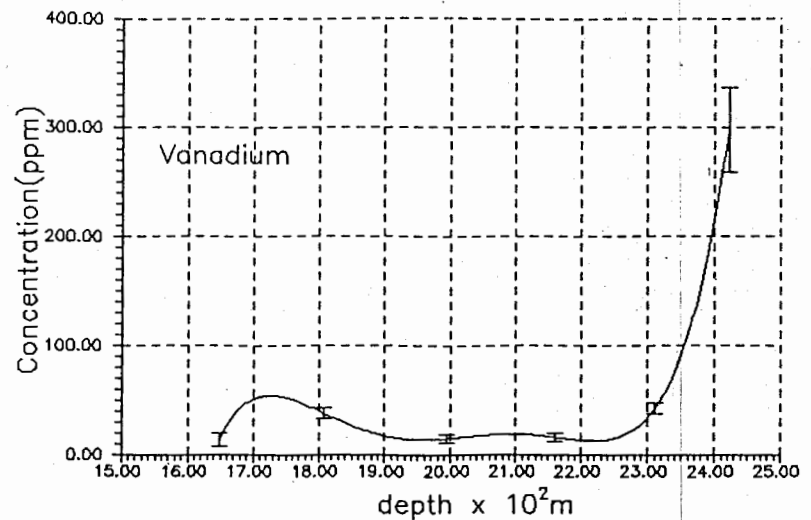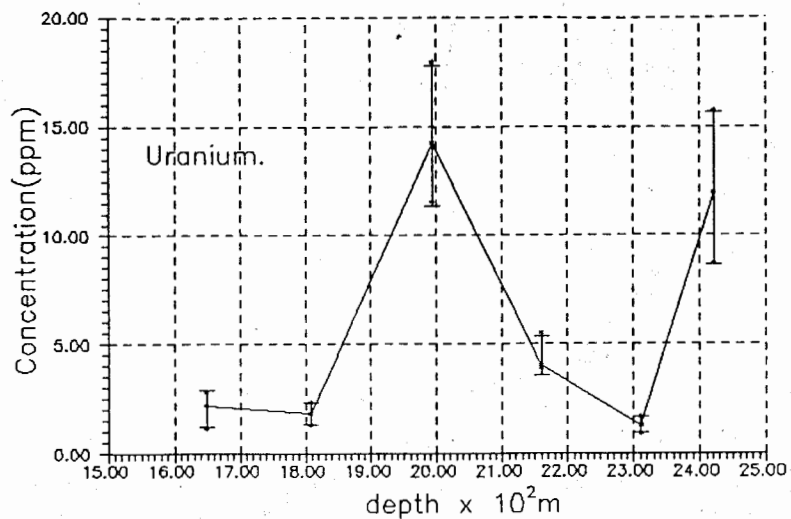
1—Si	5—Al	9—Mn	13—Ba	17—Mo	21—Co	25—Br	29—Cs	33—Tb
2—Ca	6—K	10—V	14—Nd	18—As	22—Gd	26—Sb	30—Tm	34—Ta
3—Fe	7—Na	11—Cl	15—Ce	19—Rb	23—Ga	27—Sc	31—Yb	35—Eu
4—Mn	8—Sr	12—Zn	16—La	20—U	24—Sm	28—Hf	32—Th	

Concentration (ppm) vs Elements

+++++ 1648 m
□□□□□ 1808 m
△△△△△ 1993 m
○○○○○ 2160 m
◇◇◇◇◇ 2311 m
●●●●● 2421 m

Fig 1

Vanadium

Concentration(ppm) vs depth x 10^2m

Fig 2(a)

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Fig 2(b) — Uranium

Concentration(ppm) vs depth x 10^2 m

Fig 2(c) — Cobalt

Concentration(ppm) vs depth x 10^2 m
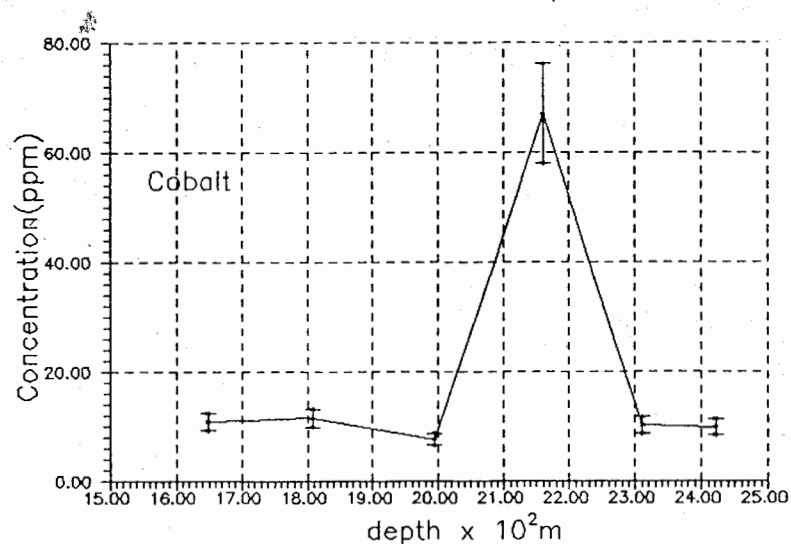
Table 3

Element Concentration whithout REEs (in ppm)

Depth-> Elem ↓	1648 m	1808 m	1993 m	2160 m	2311 m	2421 m
Si	3.14E+5 (11.8)	1.04E+5 (11.8)	1.22E+5 (12.6)	2.02E+5 (11.8)	1.57E+5 (11.9)	1.08E+5 (11.4)
Ca	9.36E+4 (7.3)	1.51E+5 (7.2)	9.13E+4 (7.4)	2.15E+5 (7.3)	8.77E+4 (7.3)	8.96E+4 (7.6)
Fe	1.26E+4 (14.3)	1.54E+4 (13.0)	1.68E+4 (5.6)	4.95E+4 (5.1)	2.26E+4 (6.6)	3.13E+4 (4.8)
Mg	5.9E+3 (10.2)	7.30E+3 (10.9)	2.05E+4 (16.5)	2.40E+3 (16.6)	4.80E+3 (14.6)	2.73E+4 (11.4)
Al	8.01E+5 (8.6)	2.08E+4 (8.7)	2.30E+4 (9.1)	5.17E+4 (8.7)	4.00E+4 (8.8)	1.75E+4 (9.3)
K	1.28E+4 (14.8)	1.17E+4 (14.5)	7.30E+3 (15.1)	3.96E+4 (15.2)	7.38E+3 (14.9)	3.80E+3 (15.8)
Na	8.17E+3 (4.5)	8.70E+3 (4.6)	1.70E+3 (5.8)	27.40E+3 (4.7)	6.40E+3 (4.7)	2.00E+3 (5.0)
Mn	3.86E+2 (4.3)	3.19E+2 (4.5)	3.43E+2 (4.5)	8.77E+2 (3.6)	3.68E+2 (3.8)	4.89E+2 (4.3)
V	13.6 (18.3)	37.6 (13.0)	14.6 (18.5)	15.8 (18.4)	42.4 (12.7)	2.98E+2 (13.1)
Cl	1.80E+2 (19.8)	1.60E+3 (15.0)	99.2 (20.2)	1.59E+2 (15.7)	1.33E+2 (20.3)	2.21E+2 (15.8)
Zn	78.7 (11.4)	38.6 (8.1)	90.4 (12.4)	1.62E+2 (10.6)	71.1 (11.3)	1.53E+2 (11.5)
Ba	3.81E+2 (22)	2.82E+2 (25)	1.54E+2 (25)	4.34E+2 (26)	8.87E+2 (229)	1.52E+2 (26)

Table 3 (cont)

Element Concentration whithout REEs (in ppm)

Depth-> Elem ↓	1648 m	1808 m	1993 m	2160 m	2311 m	2421 m
Mo	1.9 (21.7)	1.7 (21.3)	32.0 (20.1)	1.9 (21.4)	2.1 (22.6)	22.8 (20.1)
As	4.5 (6.6)	3.7 (5.4)	18.7 (6.7)	8.9 (6.7)	5.1 (5.9)	20.9 (6.2)
Rb	26.9 (11.2)	19.6 (11.2)	13.3 (10.1)	94.7 (10.7)	47.5 (14.7)	17.9 (12.8)
U	2.2 (27.8)	1.8 (27.8)	14.2 (27.7)	4.0 (27.9)	1.3 (27.9)	12.0 (27.8)
Co	10.9 (17.9)	11.5 (16.2)	7.7 (17.8)	67.1 (15.1)	10.3 (15.9)	9.9 (17.4)
Ga	7.4 (24)	8.1 (24)	6.6 (24)	25.1 (23)	13.0 (22)	6.8 (24)
Br	1.2 (14.6)	1.6 (14.4)	2.1 (14.5)	4.3 (14.5)	2.0 (14.5)	3.6 (14.4)
Sb	0.6 (8.3)	0.4 (14.7)	2.5 (8.2)	1.6 (15.2)	1.1 (14.6)	3.3 (7.6)
Sc	4.5 (15.5)	3.7 (15.8)	1.9 (17.5)	16.5 (14.9)	4.1 (15.3)	2.7 (17.8)
Hf	1.0 (7.9)	0.8 (8.5)	0.7 (8.5)	2.6 (6.2)	1.1 (7.2)	1.5 (7.8)
Cs	1.3 (16.1)	0.6 (17.1)	0.7 (17.3)	3.9 (15.7)	1.8 (15.8)	1.4 (16.3)

Depth-> Elem ↓	1648 m	1808 m	1993 m	2160 m	2311 m	2421 m
Th	0.6 (26.6)	0.6 (26.4)	0.7 (26.8)	3.7 (26.2)	1.0 (26.3)	0.7 (26.8)
Ta	0.4 (25.4)	0.3 (25.2)	0.2 (25.7)	1.1 (25.1)	0.3 (25.2)	0.2 (25.7)

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In Figures 2(a, b, c) we present, as an example, the characteristic distribution for these groups, using the more representative elements (V, U and Co).

The results obtained for the REEs require special interest due to their extensive use in petrogenetic studies and its high neutron absorption cross sections. Table 4 shows the concentration values of the REEs: La, Ce, Nd, Sm, Eu, Gd, Tb, Tm and Yb at each depth. The numbers between parenthesis represent the total calculated errors. Figure 3a shows the concentration of REEs in ppm vs depth in semi-logarithmical scale using as parameter the different elements. Three groups can be distinguished in this distribution. The standard deviation for each group is shown. The criterion to separate these groups was the proximity in their concentration values. The distribution groups are:
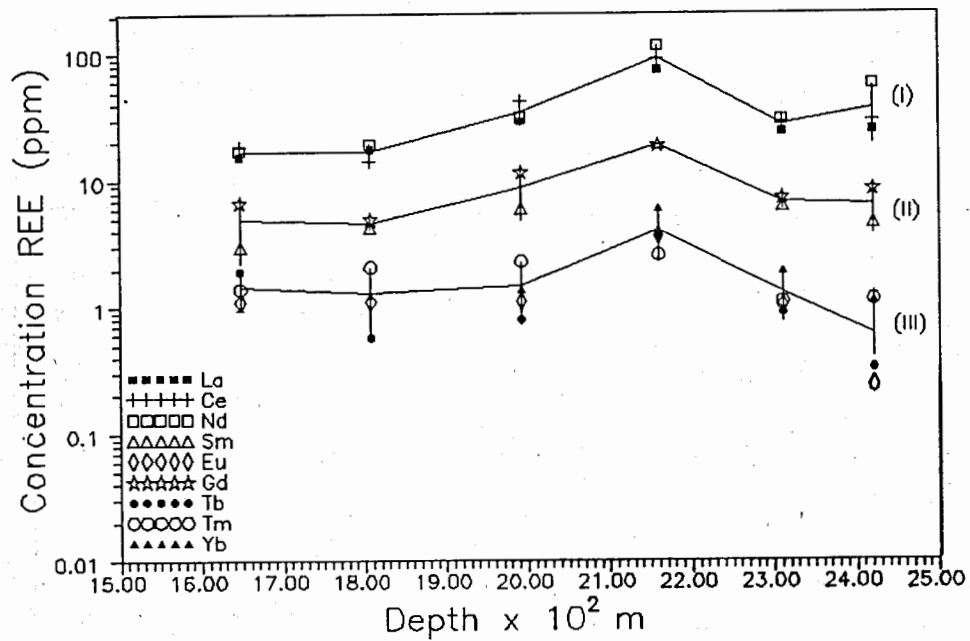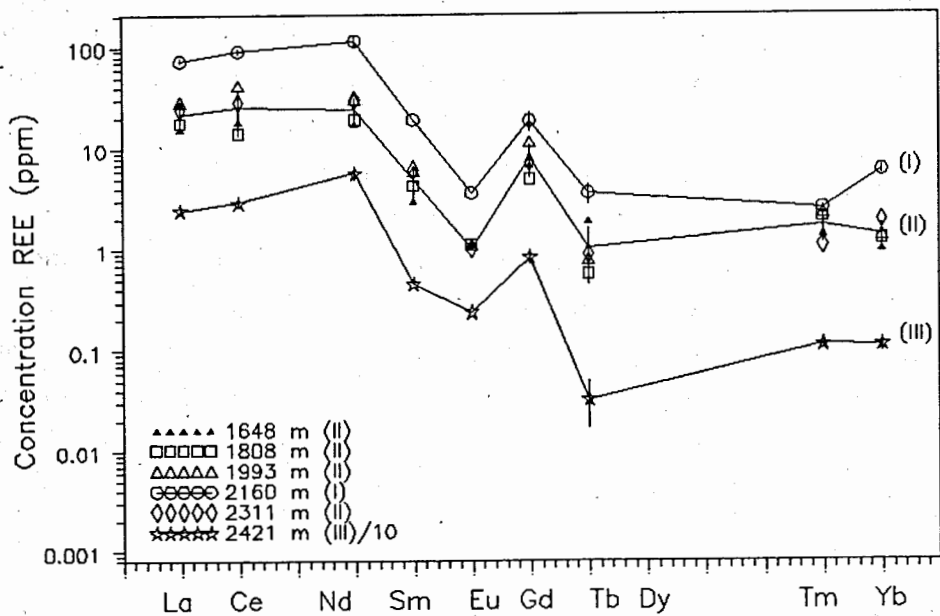
Fig 3(a)

Fig 3(b)

Table 4

Concentration of REEs and Condrites (in ppm)

Depth-> Elem ↓	1648 m	1808 m	1993 m	2160 m	2311 m	2421 m	Condrites
La	15.5 (4.1)	17.7 (3.9)	28.8 (4.0)	73.1 (3.8)	24.0 (3.8)	24.6 (4.2)	0.3
Ce	18.2 (18.5)	14.1 (20.6)	41.7 (20.5)	90.5 (15.3)	28.7 (16.3)	29.2 (19.4)	0.5
Nd	17.2 (24.8)	19.2 (28.3)	30.7 (19.9)	114.6 (14.2)	29.7 (14.3)	56.6 (17.4)	0.6
Sm	3.0 (10)	4.3 (14)	5.9 (12)	18.8 (12)	6.1 (13)	4.6 (11)	0.2
Eu	0.11 (22.5)	0.11 (22.5)	0.11 (22.7)	0.361 (18.7)	0.10 (27.0)	.024 (25.9)	0.08
Gd	6.76 (20.7)	4.92 (20.3)	11.45 (21.6)	18.55 (20.4)	7.23 (20.6)	8.36 (20.4)	0.4
Tb	1.89 (18.0)	0.57 (17.7)	0.79 (18.4)	3.58 (17.4)	0.89 (18.3)	0.33 (19.4)	0.05
Tm	1.38 (15.0)	2.06 (14.9)	2.26 (14.9)	2.53 (14.7)	1.08 (14.6)	1.13 (14.4)	0.04
Yb	0.98 (20.2)	1.23 (20.5)	1.35 (20.4)	5.93 (19.4)	1.88 (20.1)	1.11 (22.6)	0.2

I.- La, Ce and Nd

II.- Sm and Gd.

III.- Eu, Tb, Tm and Yb.

All groups exhibit a maximum concentration at 2160 m. The third and fourth groups have a rapid decrasing after this depth.

Fig 4(a)

Fig 5(a)

Fig 4(b)

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Fig 5(b)

17
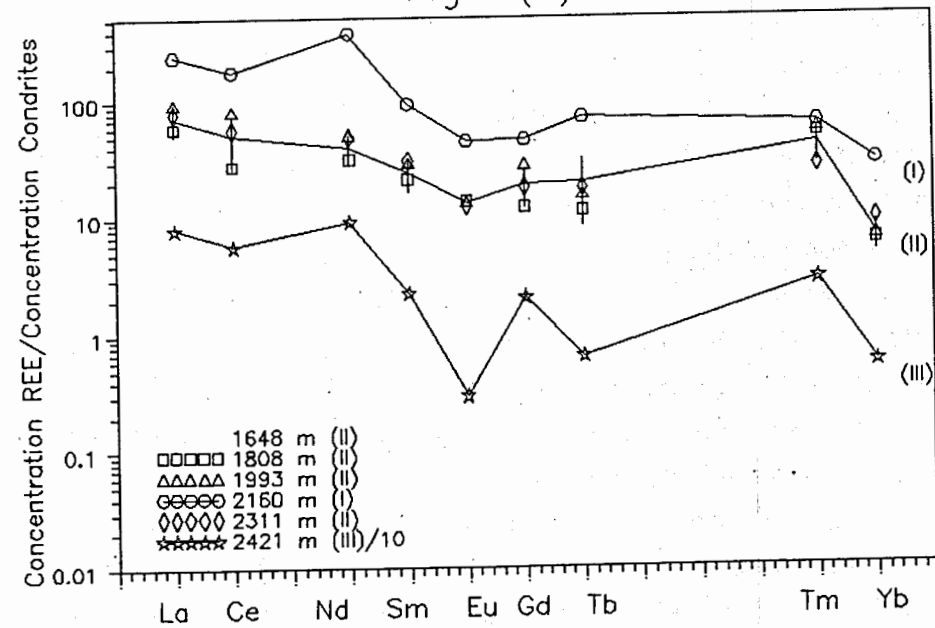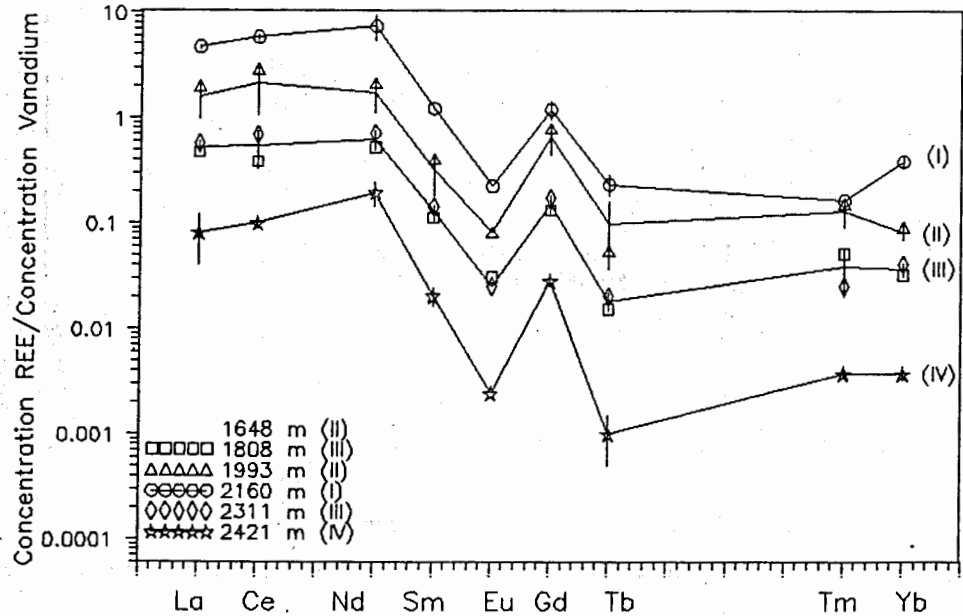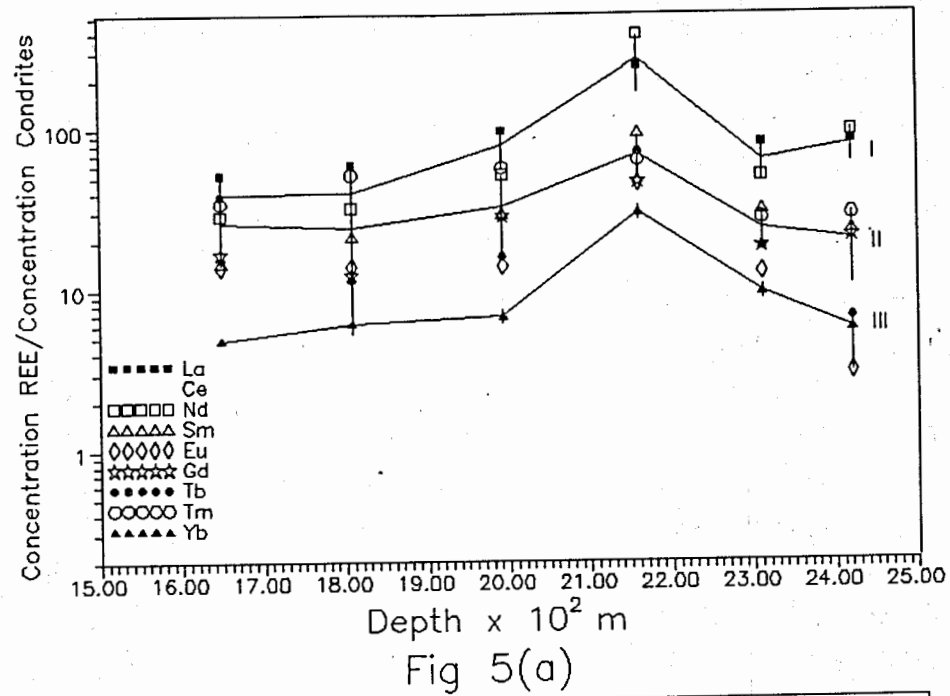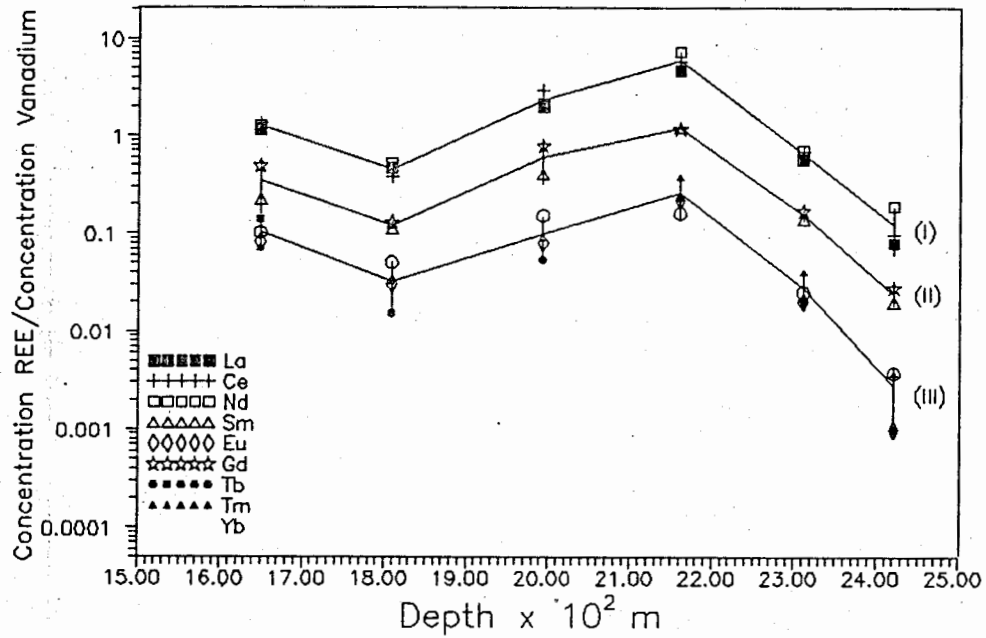
The concentration of REEs vs. elements using as parameters the different depths is shown in Figure 3b. In this case the values of element concentration were grouped according to the proximity in the concentration values between the different depths. These groups are:

I.- 2160 m

II.- 1648, 1808, 1993, and 2311 m

III.- 2421 m

In the third group we can observe the relative deficit of Eu and Tb.

The ratio between the element concentration of REEs and vanadium vs. depth, which is a characteristic element in the petroleum, is shown in Figure 4a. Here is present faster decreasing of the ratio after the maximum at 2160 m. The number of distributions and the element groups are the same as in Figure 3a.

Figure 4b shows the same ratio, but now vs. REEs. Four evident distributions in depth can be observed:

I.-2160 m

II.-1648 and 1993 m.

III.-1808 and 2311 m

IV.- 2421 m

To have a precise idea about the origin of the rocks in the different layers from the petroleum ores, we compared our results with the concentration of REEs in condrites. These concentration values were taken from [15, 16].

Figure 5a shows the ratio between the concentration element REEs and condrites vs depth. The different element groups in this graphic are the same as those presented in Figures 3a and 4a. The behaviour along the different depths resembles that shown in Figure 3a, but the standard deviation between elements is greater than there.

An interesting result can be obtained from Figure 5b. In it we show the ratio between the element concentration of REEs and the condrites vs. REEs, taking as parameter the different depth.

This Figure contains the same groups of depth which are presented in Figure 3b, but now appears depression not only for the Eu and Tb ratios. In this case depression can be observed for the Yb ratio too. Furthermore the depression in the Tb ratio is inverted in the seal layers.

According to [17], the condrites are characterized by their chemical composition, fundamentally for the contents in REEs. The condrites are the witness of the solar system formation. They reflect the primary period of the cloud condensation. Related with the deficit of REEs and fundamentally with the more volatile ones: the Eu and Yb; they were formed from the condensation which took place in the missing refractory REEs. For this reason the Eu and the Yb are the more volatile elements into the group of REEs. This allows to suppose that Eu and Yb were separated from the gas at the time of condensation. This explains the depression in the contents of these elements in the petroleum ore, but this is not so for the Tb.

In Figures 6a, 6b and 6c we present the stereometrical projection, in which at the same time appears the concentration of REEs, or ratios, the depth and the element distribution. Specially in Figures 6a and 6b we observe better the maximum in the contents of REEs corresponding to depth 2160 m. We observed furthermore and the rapid decreasing of the ra-
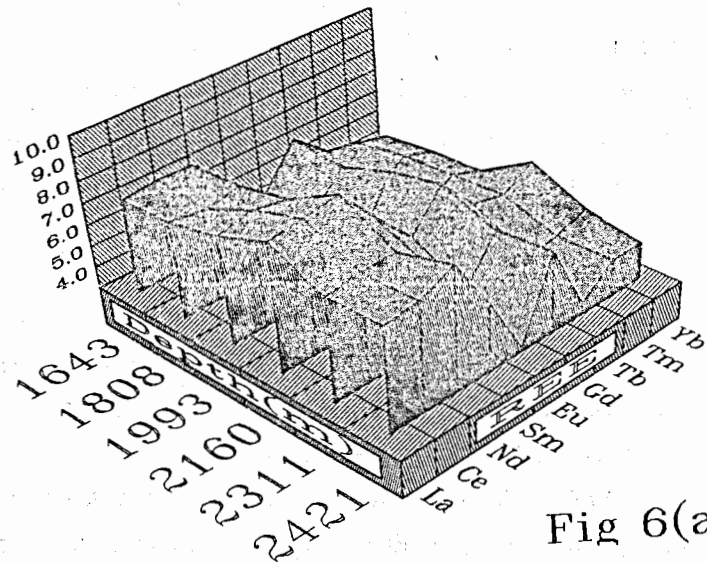
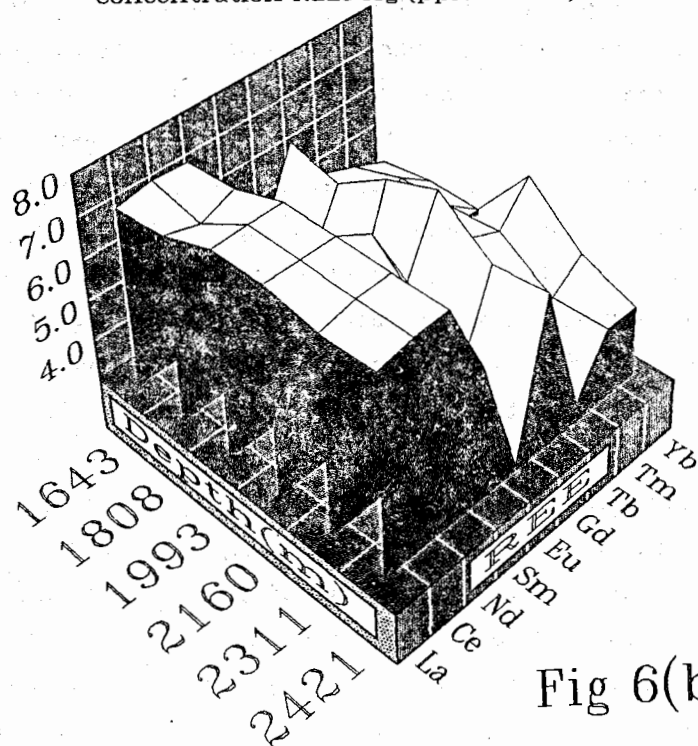Fig 6(a)

Concentration REEs log (ppm x 100)

Fig 6(b)

Concentration REEs/concentration vanadium log (rate x 100)

tio between the REEs/vanadium concentration in Figure 6b. In both cases the visualization of the Eu and Tb valleys is evident.

However, in Figure 6c the superficial landscape is other. New valley for Yb appears and the valley for Tb disappears. Furthermore, the distribution of ratio maxima is different for the previous figures. This allows to suppose that the origin of the REEs contents in the petroleum ore is completely migratory and justify the sedimentary characteristics of the ore in the analysed region.
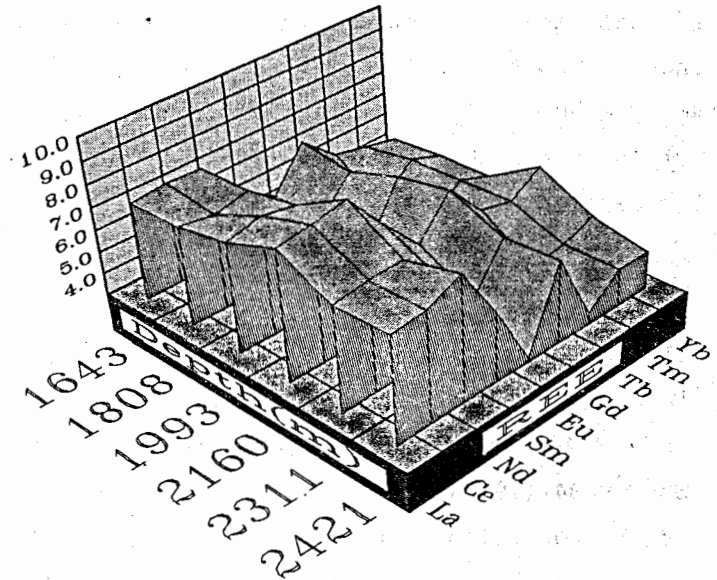

Fig 6(c)

Concentration REEs/concentration codrites log (rate x 100)

Conclusions

1- Six rock samples from a petroleum well at north-western of Cuba were analyzed using instrumental neutron activation analysis. Thirty five elements were fixed.

2- We do not observe large fluctuations in the elements which can affect the record in the nuclear sounding used in the geological prospection.

3- From a particular study of the behaviour of the REEs we observed, that there is a maximum concentration of them at the depth of 2160 m from which a rapid decreasing in the contents of REEs takes place for the majority of these elements. This decreasing is stronger for all REEs when compared with the vanadium content, and element which is a characteristic one for petroleum. This particularity could help at the geological carotage , due to the large neutron cross sections of short-lived REE isotopes, if the NAA is used.

4- From the analysis of the layers characterizing the distribution of the REEs concentration with depth one could confirm the sedimentary origin of rocks in the ore.

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