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Of Trace Elements In Phosphate Ores**

by

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# Activation Analysis As A Tool For The Assignment Of Mode Of Occurrence Of Trace Elements In Phosphate Ores

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## ABSTRACT

An efficient calcination process for calcareous phosphate ores is studied as a base for the present work. The net result of the behaviour of the constituent minerals is given.

As determined by a nondestructive neutron activation analysis technique, the trace elements, Ce, Lu, U, Cr, La, Hf, Zr, Sc and Co are found to be associated with the phosphate mineral while Eu is present in the gangue minerals, as calcite, dolomite, clay and iron oxides. The two elements Ba and Fe are incorporated in both the gangue and the phosphate minerals.

## INTRODUCTION

Apatite (the major mineral constituent of phosphate rock) is host to many substitutions by cations, anions, and anionic radicals that resemble its normal constituents in size and charge (1). Accordingly, apatite proves to be a useful environmental indicator.

The major and minor element composition of phosphorites is naturally of more than academic interest in view of the use of these rocks in the manufacture of fertilizers and phosphoric acid and also because of the feasibility of the byproduct extraction of vanadium, uranium (2), fluorine (3) and the rare earth elements (4). Thus many authors (5-9) have studied the distribution of trace elements in different deposits spectrochemically.

In the present study the distribution and abundance of trace elements in the phosphate mineral or gangue minerals prove to be use-

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ful, since some of these trace elements such as iron if found in the phosphate minerals are incorporated in the phosphate fertilizer and hence are of great value to certain soils (10). To the knowledge of the present authors no similar study as the present one has been done before, except for uranium and phosphorus which are determined chemically during the physical upgrading of phosphatic sandstone of Egyptian Qatrani ore by flotation (11).

Phosphate ores are usually associated with calcareous materials mainly calcite, dolomite and rarely siderite which lower the phosphate grade. The method used for upgrading these ores is accomplished by calcination to decompose the carbonate into oxides then quenching and washing removing the oxide as a milky solution to obtain the maximum phosphate oxide ratio. In the present work, calcination of the phosphate rock is chosen as the proper technique to separate the phosphate mineral from the gangue minerals.

The development of high resolution Ge (Li) detectors for gamma spectrometry, and efficient data processing systems for spectral analysis, have made instrumental neutron activation analytical methods a powerful analytical tool for multielement determinations (12).

Fortunately, the elements, P,C,O,F and Ca which are considered an interfering elements are either a beta emitter or gamma emitter of a very short half-life; hence their activities decay to negligible proportions before commencing measurements, since a decay time of two days was used. Accordingly, matrix interference was negligible. There was no interference of phosphorous by its bremsstrahlung due to the high resolution of the detector used and the peak to compton area is very high.

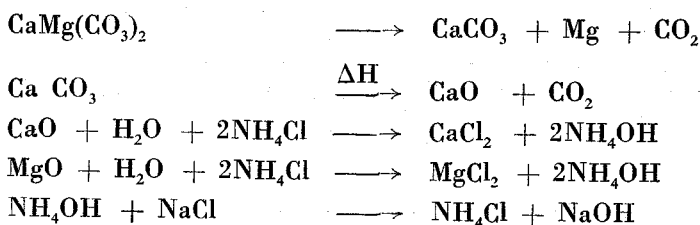
### Experimental

The phosphate ore presently investigated is a representative sample from Wassif Mine (Red Sea Coast). Calcination of the studied sample was performed using a locally made tube furnace of 60 cm long, 2.5 cm internal diameter. It was connected with a liquid flowmeter to adjust the flow of oxygen gas through the furnace.

A flow rate of  $\frac{1}{2}$  L / min was found suitable. The temperature was kept constant at 940 °C for half an hour during the experiment by

means of an automatic regulator. 25 g. sample was placed in a fused magnesite boat and inserted inside the tube furnace.

The calcined sample was removed from the furnace while hot in 25 ml of distilled water, washed 4 times while stirring for 5 min. with 50 ml solution of (50 g  $\text{NH}_4\text{Cl}$  / 1). The latter has greatly facilitated the elimination of the lime and magnesia produced during calcination. For the purpose of recycle the produced  $\text{NH}_4\text{OH}$  could be distilled off and allowed to react with rock salt regenerating  $\text{NH}_4\text{Cl}$  and  $\text{NaOH}$ . The overall reactions involved could be summarized in the following equations.



The calcined and washed products were dried at  $100^\circ\text{C}$ , purified by bromoform, weighed and analysed.

A number of chemical and instrumental methods of analysis were used for the quantitative determination of major and minor element components of the present phosphate ore, using a strongly cationic ion exchange resin column in the hydrogen form (12). Phosphate ions were determined by the citromolybdate method (13) while sulphate ions by the barium chloride method (14). Calcium, magnesium, iron and aluminium were determined by EDTA titration (15). For the analysis of silica, ferrous iron fluoride, carbon dioxide, organic matter,  $\text{OH}^-$  and  $\text{OH}^+$ , special treatment of a powdered sample was every time used. The procedure used for their determination was described in detail by Shapiro and Brannock (16), sodium and potassium were determined by flame photometrically (17) while titanium was estimated spectrophotometrically (18). Finally chloride ions were analyzed by measuring the turbidity produced by colloidal  $\text{AgCl}$  (19).

From both the obtained chemical analysis results and petrographic examination of representative thin sections the model or normative minerals of the studied ores can be calculated using mostly the assumption adopted by Anwar et al (20).

The distribution and abundance of trace elements in the samples were studied by radioactivation analysis. An international United State Geological Survey (USGS) standard sample (W. 1) was irradiated with each sample. The complete chemical analysis of which is published (21).

A known weight of each sample ( $\sim 0.2$  g) was packed in a thin aluminium sheet, together with the standard. Samples were irradiated in the vertical dry channel of ET. RR-1 reactor of the Nuclear Research Centre at Inshas. Irradiation time was about 35 hours at a neutron flux of about  $10^{22}$  n.  $\text{cm}^2$ .  $\text{sec}^{-1}$ . The delay time was about 48 hours. Gamma spectra from samples and standard were measured using a  $30 \text{ cm}^2$  Ge (Li) detector together with a 4096 PDP-11 / 05 computer based multichannel analyzer (Digital) and the necessary electronics (Nuclear Enterprises-OrtEc and Canberra). A standard curve in the range of the measured isotopes was done before and after each measurement.

The identities of the detected elements producing  $\gamma$ -rays when activated were established by measurements of  $\gamma$ -ray energy and of half life, whereas the concentrations of the elements were calculated for all principal  $\gamma$ -lines by reference to the standard according to the following equation:

$$W_2 = \frac{W_1 A_2 M_1}{A_1 M_2}$$

where  $W_1$  is the known concentration of a certain isotope in the standard.

$W_2$  is the unknown concentration of the same isotope to be determined.

$A_1$  is the calculated area under the known peak after subtracting the

$A_2$  is the calculated area under the known peak after subtracting the background in the standard.

$M_1$  is the weight in gms of the standard sample.

$M_2$  is the weight in gms of the sample under investigation.

Since the half life of the isotopes under investigation is very much longer compared to the measuring periods and a standard is used there is no correction for decay of the activities  $A_1$  and  $A_2$ .

In case of elements which are absent or not quantitatively given in the international standard, spectroscopy pure elements were added as internal standard. For elements which are absent in the international standard and the addition of their spectroscopy pure grade was impossible, equation (5) was used.

It is clear from equation (5) that a correction factor referred to as K factor is used. This factor is mainly due to the change in the absolute value of the neutron flux at the position of irradiation. An isotope of known concentration in the international standard is used. The verification of the used equation is as follows.

$$\text{Activity} = \frac{W}{M} \times N \times a \times \varnothing \times \sigma \times 10^{-24} \times B \times \left(1 - e^{-\frac{0.693t_{ir}}{T_{1/2}}}\right) e^{-\frac{0.693t_d}{T_{1/2}}} \quad (1)$$

$$\text{Activity} \propto \frac{A}{\gamma}$$

$$\text{Activity} = k_1 \times \frac{A}{\varepsilon} \quad (2)$$

Substitution of the value of activity from equation (2) in equation (1) we get

$$\frac{k_1 A}{\varepsilon} = \frac{W}{M} \times N \times a \times \varnothing \times \sigma \times 10^{-24} \times B \times \left(1 - e^{-\frac{0.693t_{ir}}{T_{1/2}}}\right) e^{-\frac{0.693t_d}{T_{1/2}}} \quad (3)$$

from equation (3) we can get the ( $k_1$ ) factor for the known isotope in the standard.

$$k_2 = k_1 \times \frac{\text{measured area of the peak after subtracting the background (2)}}{\text{measured area of the peak after subtracting the background (1)}} \quad (4)$$

from equation (4) we can obtain the ( $k_2$ ) factor of the isotope in the sample, and equation (3) becomes,

$$\frac{k_2 A_2}{\epsilon} = \frac{W_2}{M} \times N \times a \times \phi \times \sigma_c \times B \times \left( 1 - e^{-\frac{0.693 t_{ir}}{T_{1/2}}} e^{-\frac{0.693 t_d}{T_{1/2}}} \right) \quad (5)$$

where  $A_2$  is the area of the peak after subtracting the background,

$W_2$  = is the unknown concentration,

$M$  = Molecular weight

$N$  = Avogadro number ( $6.023 \times 10^{22}$ )

$a$  = percent abundance

$\sigma_c$  = the neutron capture reaction cross sections in barns  
( $10^{-22} \text{ cm}^2$ )<sup>22</sup>

$\phi$  = thermal neutron flux<sup>22</sup> neutron  $\text{cm}^{-2} \text{ sec}^{-1}$ .

$t_{ir}$  = irradiation time in min,

$t_d$  = Decay time in min,

$T_{1/2}$  = Half life in mins<sup>23</sup>,

$B$  = Branching ratio<sup>23</sup>,

= Relative efficiency of the Ge (Li) detector taken from the efficiency curve<sup>22</sup>.

$k_2$  = Correction factor taken from equation (4).

## RESULTS AND DISCUSSION

Complete chemical analysis of the final calcined phosphate concentrate together with the original ore sample as well as their calculated potential mode of minerals are reported in Table (1). Nuclear data for the elements determined together with their concentrations are given in Table (2). Gamma spectra obtained from a standard W. 1. and the studied phosphate samples are shown in Figs. (1-3).

As shown from Table (1) the ore sample contains 8.19 % dolomite and 4.30 % calcite and hence calcination should be used in the present study. Moreover, the calcined ore contains 9.20 % silicate and silica, accordingly the purification of the phosphate mineral by bromoform is essential before its analysis. The phosphate mineral (Collophane) increased from 66.40 to 84.13 % upon calcination, i.e. an increased factor of 1.27.



Table 1. Chemical Assay and Potential Mode of Minerals for Wassif Original and Calcined Ore.

Element %	Safaga ore (Wassif)		Potential Mode of Minerals %	Safaga ore (Wassif)	
	Bulk	Calcined		Bulk	Calcined
SiO <sub>2</sub>	12.03	8.48	T. C. P. (Ca <sub>3</sub> PO <sub>4</sub> ) <sub>2</sub>	59.73	76.01
P <sub>2</sub> O <sub>5</sub>	27.36	34.87	CaF <sub>2</sub>	6.67	8.12
CaO	43.14	45.96	Collophane	66.40	84.13
MgO	1.78	—*	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·CaF <sub>2</sub>		
FeO	0.42	—	CaSO <sub>4</sub> ·2H <sub>2</sub> O	3.34	4.35
Fe <sub>2</sub> O <sub>3</sub>	1.18	0.86	Gypsum		
Al <sub>2</sub> O <sub>3</sub>	0.79	1.19	CaCl <sub>2</sub>	—	—
Na <sub>2</sub> O	0.22	0.15	Dolomite		
K <sub>2</sub> O	0.02	—	CaMg (CO <sub>3</sub> ) <sub>2</sub>	9.19	—
SO <sub>3</sub>	1.55	2.07			
F <sup>-</sup>	3.25	3.25	Calcite, CaCO <sub>3</sub>	4.230	—
Cl <sup>-</sup>	0.26	0.34			
CO <sub>2</sub>	6.55	0.79	Fe <sub>2</sub> O <sub>3</sub> ·3H <sub>2</sub> O	0.90	—
OH <sup>-</sup>	0.58	—	Organic Matter	0.47	—
Organic Matter	0.47	—	Silicate + SiO <sub>2</sub>	14.84	9.20
OH <sup>+</sup>	7.50	0.80			
<b>Total</b>	<b>99.88</b>	<b>98.96</b>	<b>Total</b>	<b>99.20</b>	<b>99.62</b>

+ (—) not detected.

Table 2. Nuclear Data and Concentration Results of Trace Elements In the Studied Phosphate Samples.

Element	Product	Half-life	Photo peaks used in Kev.	Conc. p.p.m.	
				Wassif original	Wassif calcined
Cerium	<sup>143</sup> Ce	33.0h	144.9	4.76	6.04
Barium	<sup>131</sup> Ba	11.6d	56.55, 373.1, 396.3	948.94	361.1
	<sup>133</sup> Ba	1.62b	275.9, 496.3		
Lutetium	<sup>174</sup> Lu	143d	176.7		
	<sup>177m</sup> Lu	155b	113, 128.6, 204.3	1	1.3
Uranium	<sup>239</sup> Np	2.35d	228.1	64	72
Chromium	<sup>51</sup> Cr	27.8d	320.1	114.79	149.6
Lanthanum	<sup>140</sup> La	1.672d	328.8, 482.2	127.33	160.70
			815.8		
Hafnium	<sup>175</sup> Hf	70d	343.6	0.59	0.75
	<sup>181</sup> Hf	42.5d	133.0, 482.2		
Zirconium	<sup>93</sup> Zr	65.5d	724.2, 756.9	156.22	198
Europium	<sup>154</sup> Eu	7.8y	1274.8	4.81	—+
	<sup>152</sup> Eu	14.1y	1407.9		
Scandium	<sup>46</sup> Sc	84d	889.3, 1120.5	7.15	9.76
Tin	<sup>125</sup> Sn	9.62d	1087.4	1.91	2.26
Colbalt	<sup>60</sup> Co	5.26y	1173.2, 1332.5	3.33	2.56

+ (—) not detected

It is clearly seen from Table (2) that the trace elements Ce, U, Hf, Lu, La, Zr, Sc, Cr and Co increased with the same factor of the phosphate mineral concentration (1.27). This might suggest that these elements probably owe their abundance to the phosphate mineral itself.

Barium is actually one of the elements reported to be associated with the phosphate mineral itself. It undoubtedly substitute for Ca in the mineral. However, its decrease in the calcined phosphate product indicates that it has been partially replacing Ca in the calcite and dolomite structure of the gangue ore.

Europium like other rare earth elements should substitute Ca in the apatite lattice (1). However, its complete absence in the calcined product suggests that Eu might be associated with the eliminated minerals as calcite, dolomite and the organic matter.

### CONCLUSION

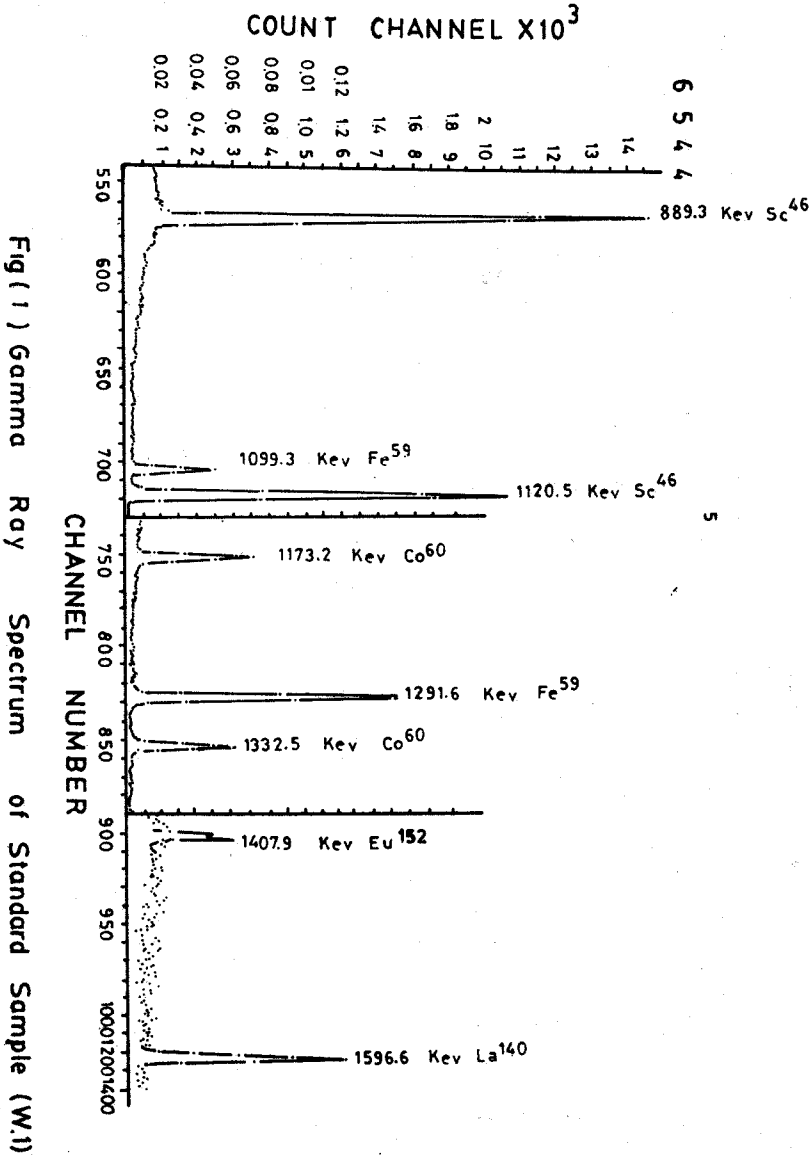
Calcination, quenching and ammonium chloride washing operations proved to be successful beneficiation method for calcareous phosphate ores.

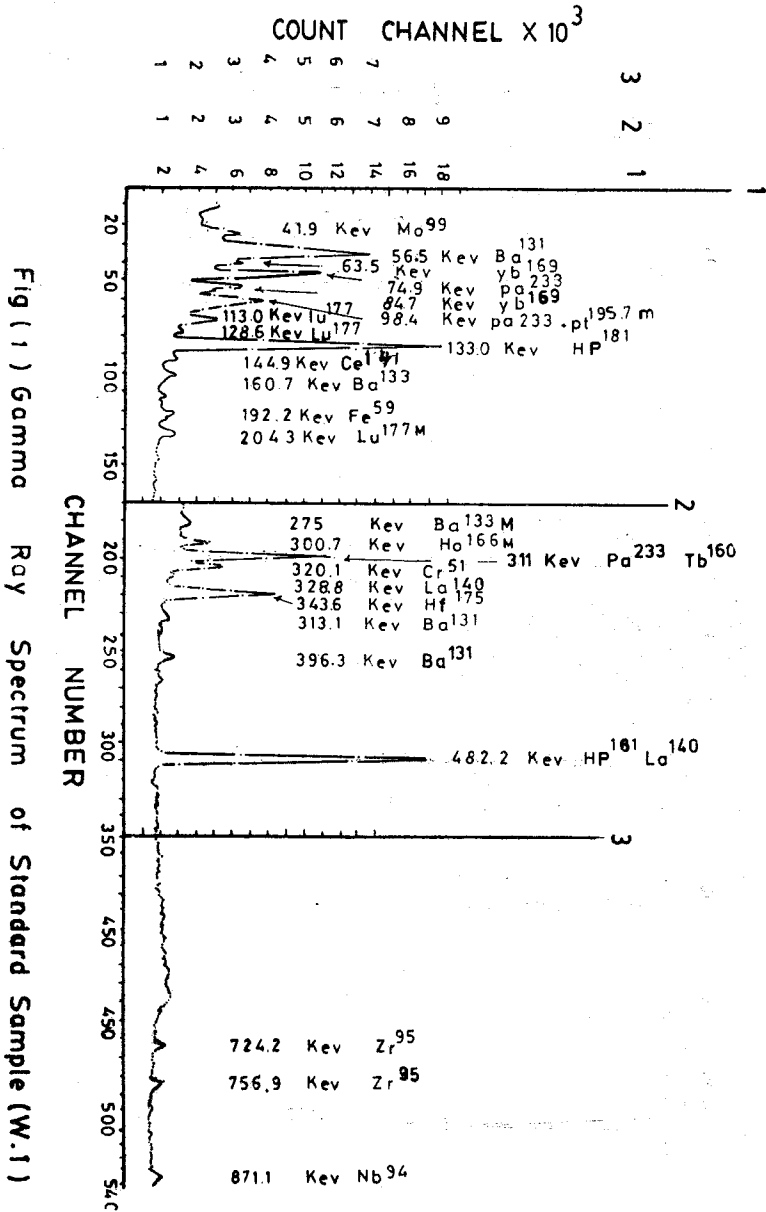
On the other hand, it is plausible that neutron activation analysis is a powerful non-destructive technique for the determination of elements particularly the rare earths. As shown from the results 0.59 part per million of Hafnium could be analyzed in the original sample.

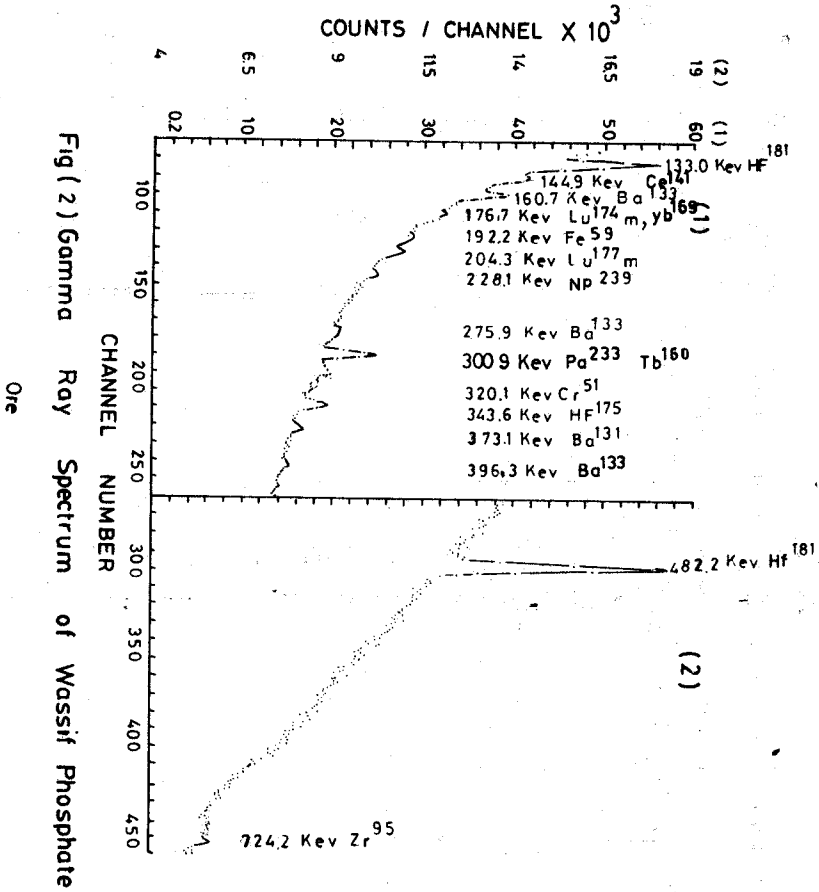
The determination of the concentration of trace elements on the original and calcined sample made possible the assignment of their occurrence, i.e whether in the phosphate mineral or the gangue minerals

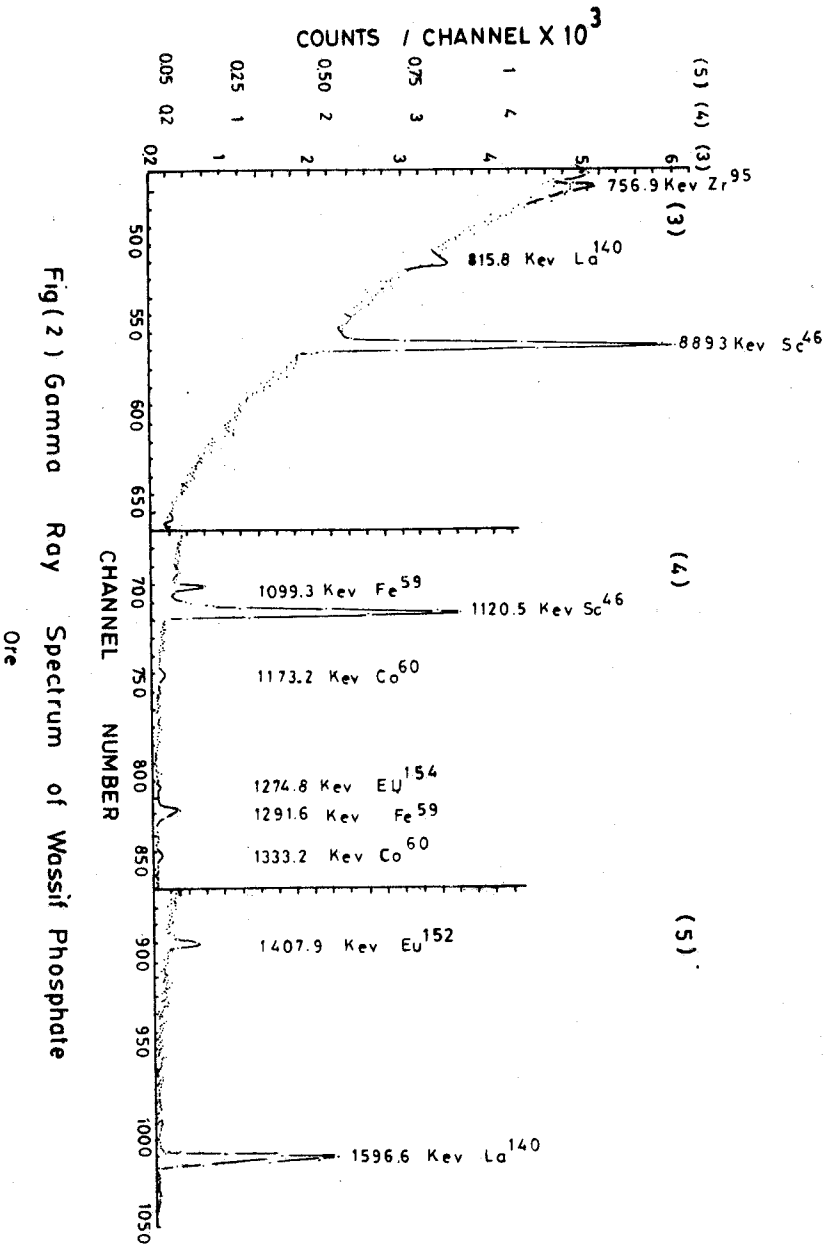
### ACKNOWLEDGMENT

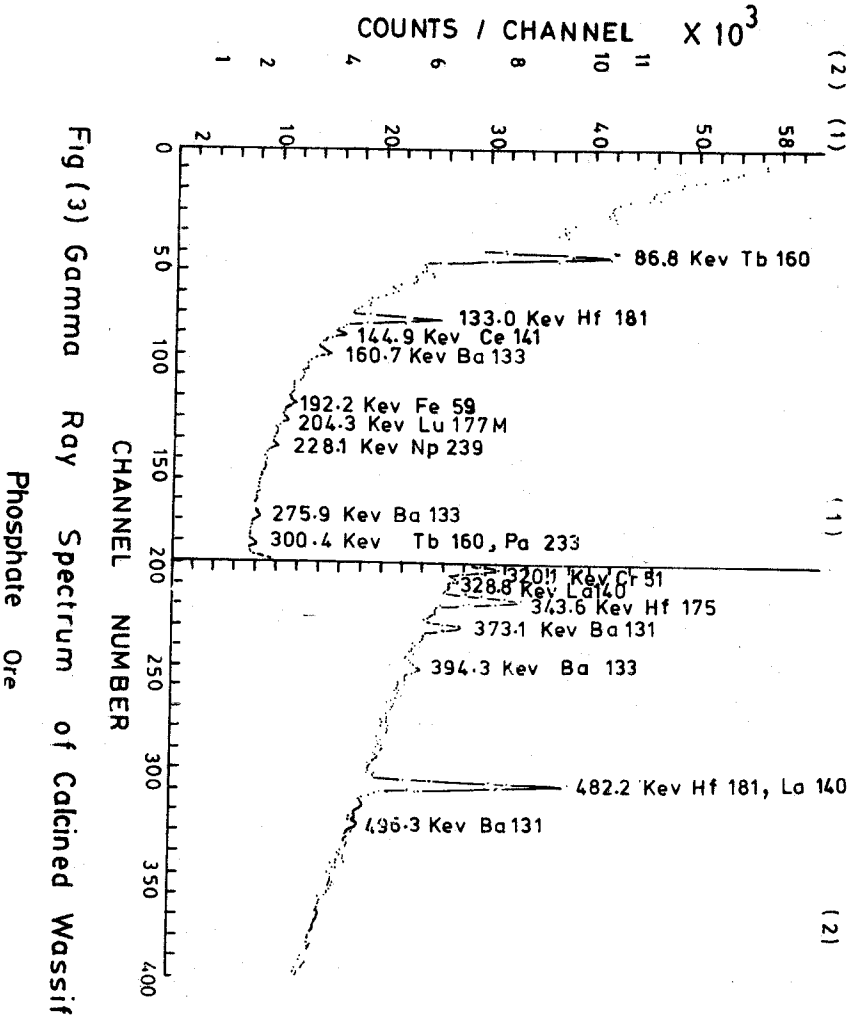
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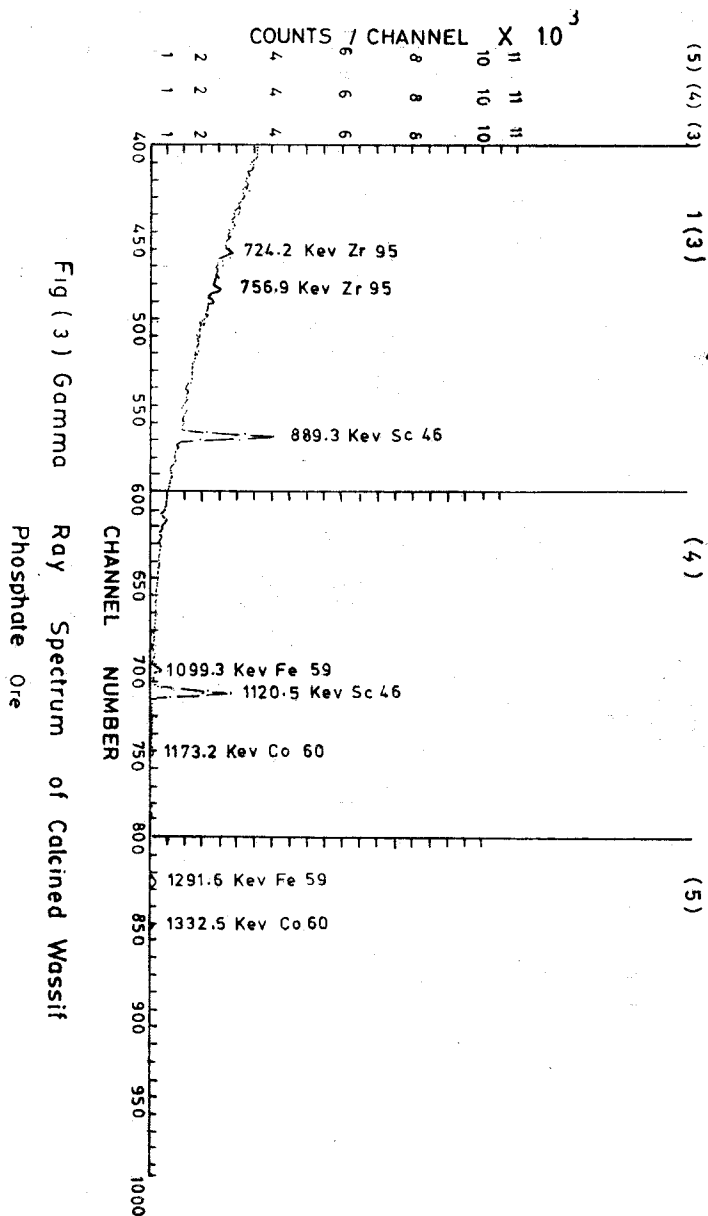














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