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ON PLACER ILMENITE COMPOSITION

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ABSTRACT

A selected pure sample of fresh ilmenite was examined by activation analysis technique to study its complete chemical composition. The method produced a very wide spectrum which cannot be obtained by any other methods. About 20 trace elements have been estimated against the standard W1. Before activation analysis of the sample an infrared spectrogram was obtained in order to confirm its purity. The studied ilmenite sample was found to contain high chromium content. This could reveal in a decisive way its origin from the basaltic rocks of Ethiopia, Sudan, and Upper Egypt.

INTRODUCTION

The importance of ilmenite stems from its major abundance in the beach sands of the delta on the Mediterranean Sea. The sands originally transported by the River Nile and when reaching the outlet to Mediterranean Sea the abrupt change in water current velocity gives the conditions to deposit the heavy minerals along the continental shelf. The heavy minerals were subjected to different natural, physical and chemical sorting during transportation. This process led to the concentration of insoluble minerals which underwent a second concentration process mainly by specific gravity [FARAG, 1958]. The beach sands are enriched in heavy minerals by undertow action of the waves and at the River mouth a further elutriation takes place by the north westerly winds which spread the beach sand over the spit [SHUKRI, 1980].

The content of the Egyptian black sands shows: ilmenite 0—37.6%, magnetite 0.2—15.20%; zircon 0.02—3.00%, monazite 0.01—0.40%, rutile 0.06—0.70%, garnet 0.05—1.7%, spinel 0—0.2%, amphiboles 4.4—14.8%, pyroxenes 1.58—7.4%, biotite 0.30—1.7%, epidote 0.60—1.24%, staurolite 0—0.65%, sillimanite 0.05—0.20%, olivine 0—0.04%, tourmaline 0—0.40%, sphene 0—0.63%, quartz 15—87.3%, feldspars 0.88—3.9%, glauconite 0—0.27%, calcite 0—1.0% [WASSEF, 1964].

Ilmenite is mostly black with bluish or violet tint. Some of altered grains are dull black. In case of leucoxene grains the yellowish white colour is predominant.

According to EL HINNAWI [1964] the chemical composition of the Egyptian placer ilmenite using the emission spectrography was as follows:

SiO_2 0.25%, TiO_2 43.73%, Fe_2O_3 24.04%, FeO 30.63%, MnO 0.20%, MgO 0.65%. The trace element are estimated by the figures: Al 400 ppm, Ca 300 ppm, Co 200 ppm, Cr 400 ppm, Cu 30 ppm, Mn 1500 ppm, Nb 600 ppm, Ni 100 ppm, Pb 250 ppm, Sn 50 ppm.

The ilmenite optical properties are highly affected by its chemical composition. This ilmenite with appreciable amounts of Fe_2O_3 in solid solution has a lighter colour and weaker reflection pleochroism and anisotropism than normal ilmenite. On the other hand ilmenite grains which probably contain geikielite in solid solution show a darker colour [BOCTOR, 1966].

Most of ilmenite grains are irregular in shape angular to subangular and some grains are rounded. The ilmenite grains show the L/B (Length—Breadth) ratio between 2:1, among them the majority have L/B ratio between 1:1, and 2:1. The fresh or homogeneous ilmenite may reach about 61.14% of the total ilmenite present in the black sand deposits [MIKHAIL, 1971].

HAMMOUD [1975], in his study on a highly purified dry ilmenite sample and by X-ray fluorescence has mentioned that the composition of this sample shows: Fe_2O_3 18.63%, FeO 31.18%, TiO_2 46.24%, MnO 1.35%, MgO 0.64%, Al_2O_3 0.87%, Cr_2O_3 0.28%, V_2O_5 0.14%, CaO 0.12%, SiO_2 0.32%, P_2O_5 0.04%, and trace of Nb, Co, Ni, Zn, Mo and Zr. Traces of chromospinel sometimes with ilmenite exsolution bodies and hematite with pseudobrookite intergrowth are present [EL GORESY, 1962].

EXPERIMENTAL

Sample preparation

The ilmenite sample presently investigated was separated from the black sand deposit on the Mediterranean Sea beach. Frantz isodynamic separator was used in 0.1 amp., 3° tilt, and 15° slope. After separation the fraction was purified by bromoform (2.85) to reject the highly altered grains. Moreover, the foreign grains were rejected by picking under the stereomicroscope. The purity of the sample was confirmed by its infrared pattern *(Fig. 1)*.

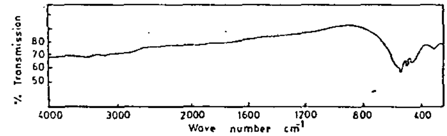

Fig. 1. Infrared spectrogram of the ilmenite

Activation analysis

A known weight of the sample was packed in a thin aluminium sheet together with the standard sample and irradiated in the vertical dry channel of ET RR-1 reactor of Nuclear Research Center at Inshas. Short irradiation time of 4 hours favour the shorter life isotopes. On the other hand, by irradiating long enough for 32 hours to induce sufficient activity of the longer life isotopes and by deferring examination time until the shorter life isotopes has decayed, the longer life product can be favoured. For the very short half-life isotopes as ^{28}Al, ^{52}V, ^{27}Mg, and ^{51}Ti a rabbit system should be used. Unfortunately this system is unavailable at our reactor. Accordingly these elements were determined spectrophotometrically [SHAPIRO and BRANNOCK, 1962].

An international United States Geological Survey (USGS) standard sample (W_1) was used. Its complete chemical analysis is shown in Table 1.

TABLE 1

Chemical analysis of standard sample W1

Element	W1	Element	W1	Element	W1 (ppm)
SiO_2	52.58	CaO	10.92	Ba	130
Al_2O_3	14.94	Li_2O	—	Be	1
TiO_2	1.08	Na_2O	2.15	Bi	n.d.
ZrO_2	0.022	K_2O	0.63	Co	44
SnO_2	0.0003	Rb_2O	0.0022	Cr	110
V_2O_5	0.045	BaO	0.00006	Cs	5
Cr_2O_3	0.016	SrO	0.021	Cu	110
R.E.ThO_2	—	H_2O^+	0.45	La	n.d.
UO_2	—	Ignition		Li	—
NiO	0.0097	loss	0.08	Mn	1320
CuO	0.0138	(H_2O^-)		Ni	76
BeO	0.0003	P_2O_5	0.14	Rb	20
CoO	0.0056	CO_2	0.07	Sc	34
PbO	0.0006	F	0.03	Sr	180
ZnO	0.014		—	Ti	6500
As_2O_3	—		100.02	V	250
Fe_2O_3	1.38			Y	19
FeO	8.71			Yb	3
MnO	0.17			Zn	110
MgO	6.52			Zr	160

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

$$W_2 = \frac{W_1 A_2 M_1}{A_1 M_2} \tag{1}$$

Where:

W_1 = the known concentration of certain isotope in the standard,
W_2 = the unkown concentration of the same isotope to be determined,
A_1 = the calculated area under the known peak after subtracting the background in the standard,
A_2 = the calculated area under the same peak after subtracting the background in the sample,
M_1 = the weight in gms of the standard samle,
M_2 = the weight in gms of the examined sample.

In case of elements which are absent or not quantitatively given in the international standard, spectrally pure elements were added as internal standard. In this case equation (1) is also valid after computing A_1 for the standard.

For elements which are absent in the standard and the addition of their spectrally pure grade was impossible, the general equation of decay and growth [TAYLOR, 1964] has been modified to suit our application. A correction factor K_2 which takes into consideration the change in the absolute value of neutron flux at the position of irradiation has been added [GUIRGUIS *et al.*, 1979]. This resulted in the following expression:

$$W_2 = \frac{A_2 K_2 M}{E} \left[1/Na\Phi\delta CB(1 - e^{\frac{-0.693 t_{ir}}{T1/2}} \cdot e^{\frac{-0.693 t_d}{T1/2}}) \right] \tag{2}$$

where:

W_2 = unknown concentration,
A_2 = area under the peak after subtracting the background,
M = molecular weight,
E = relative efficiency of the Ge(Li) detector taken from the efficiency curve [ESSA et al., 1974],
N = Avogadro's N*o* (6.023×10^{23}),
a = percent abundance [LEDRER and HOLLANDER, 1967],
Φ = thermal neutron flux (10^{12} neutron cm^{-2} sec^{-1}),
δC = neutron capture reaction cross sections in barns ($10^{-24}cm^2$),
B = branching ratio [PEAKFIND and ISOQUAM, 1975],
t_{ir} = irradiation time in minutes,
t_d = decay time in minutes,
$T\frac{1}{2}$ = half life in minutes [PEAKFIND and ISOQUAM, 1975].

RESULTS AND DISCUSSION

Nuclear data for the elements determined is shown in Table 2 and their concentration are given in Table 3. Gamma spectra obtained from standard W1 and the studied ilmenite sample are shown in *Figs 2, 3,* and *4.*

The infrared spectrogram of the ilmenite sample is shown in *Fig. 1.* The strong absorption band around 530 cm^{-1} may be due to TiO linkage while the two medium absorption bands at 460—440 cm^{-1} and 325 cm^{-1} may be due FeO linkage. In fact

TABLE 2

Nuclear data of the elements detected

Element	Product	Half life		Photo peaks used in keV
Scandium	^{46}Sc	83.9	d	889.3, 1120.5
Chromium	^{51}Cr	27.8	d	320.1
Iron	^{59}Fe	44.6	d	1099.3, 1291.6
Cobalt	^{60}Co	5.26	y	1173.2, 1332.5
Strontium	^{85}Sr	64.5	d	514
Zirconium	^{95}Zr	68.6	d	724.2, 756.9
Niobium	^{94}Nb	20 000	y	871.1
Silver	^{110}Ag	260	d	763.9
Barium	^{131}Ba	11.6	d	373.1
	^{133}Ba	1.62	d	56.8, 275.9
	^{133}Ba	7.2	y	160.7
Lanthanum	^{140}La	1.672	d	328.8, 815.8, 1596.6
Europium	^{154}Eu	7.8	y	1274.8
	^{152}Eu	12.7	y	1407.9
Ytterbium	^{175}Yb	4.21	d	112.4, 122.9, 144.9 153.1, 396.3
	^{169}Yb	32	d	61.2, 86.2, 196
Lutetium	^{177}Lu	155	d	204.3
Hafnium	^{181}Hf	42.5	d	133.0, 482.2
	^{175}Hf	70	d	343.6
Tantalum	^{182}Ta	115	d	1189, 264.4
Gold	^{198}Au	64.8	h	412
Terbium	^{160}Tb	72.3	d	879.3
Cerium	^{143}Ce	33.0	h	57.4, 664.2
Silicon	^{31}Si	2.62	h	1266
Copper	^{64}Cu	12.80	h	511
Manganese	^{56}Mn	2.28	h	848
Nickel	^{65}Ni	2.569	h	1114

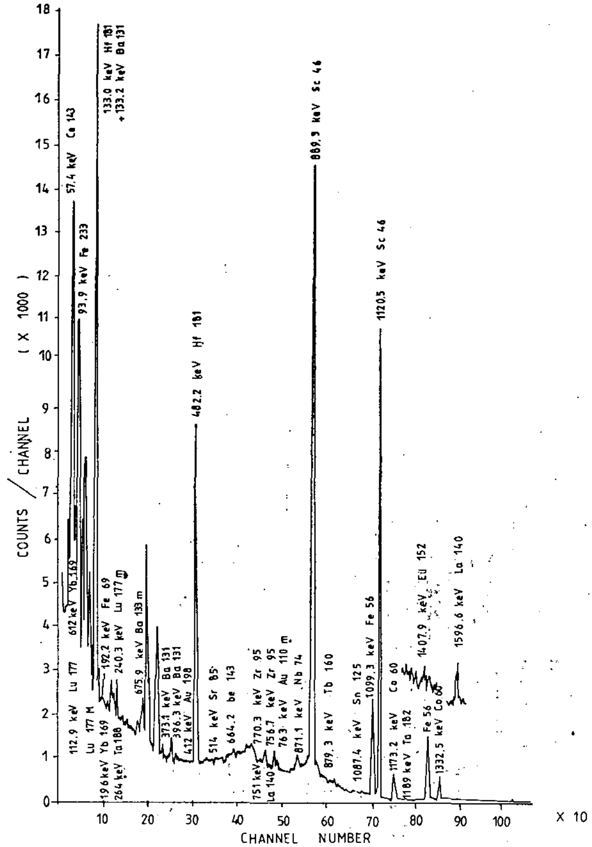

Fig. 2. Gamma-ray spectrum of irradiated standard sample W1 (irradiation time 35 hours, decay time 48 hours)

the spectrum is that of a typical ilmenite and is in good agreement with that given by CLAREMCE [1975]. Thus the fresh ilmenite sample used in the present study is very pure.

Major elements

In the present work TiO_2 was found to assay 84.04% while HAMMOUD [1975] and EL HINNAWI [1964] reported a value of 46.25 and 43.73%, respectively. Accordingly the iron content estimated by the activation represents the lowest value (46.98%). It has been concluded from DEAR *et al.*, [1966] that ilmenite is a titanate of ferrous iron ($Fe^{2+}Ti^{2+}O_3$) rather than a double oxide of ferric iron and titanium ($Fe^{3+}Ti^{3+}O_3$). In the present study MnO assays 0.064% indicating a sharp decrease from 1.35 and 0.20%, the value previously reported by HAMMOUD [1975], and EL HINNAWI [1964], respectively. This can be explained by the fact that the elements Ca, Mg, Ni, Cu, Co and Mn can substitute the Fe^{2+} ion in ilmenite [HAMMOUD, 1966] the formula may be fully expressed as (Fe, Mg, Mn) TiO_3 with only limited amount of Mg and

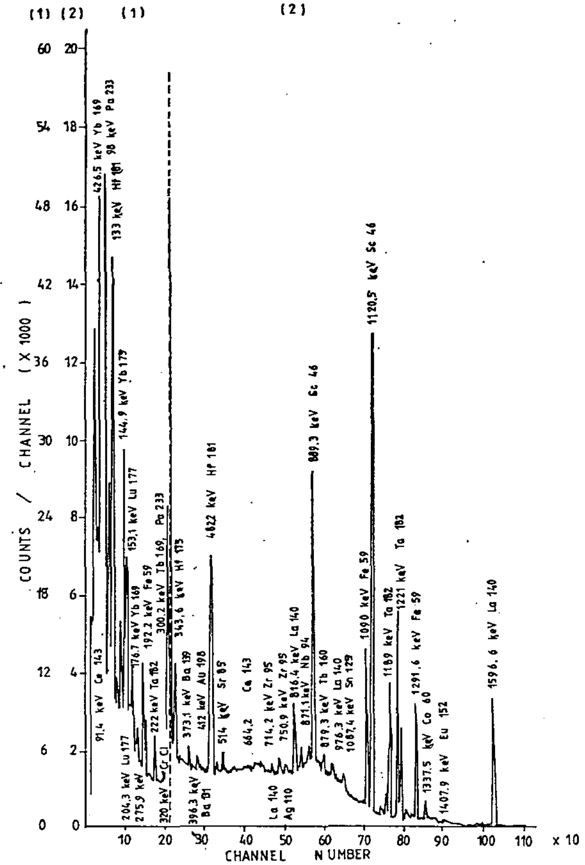

Fig. 3. Gamma-ray spectrum of irradiated ilmenite (irradiation and decay time as in *Fig. 2*)

Mn [Deer *et al.,* 1966]. MgO has actually not been detected in the present work although both Hammoud [1975] and El Hinnawi [1964] ascertained its presence at a value of 0.65 and 0.64%, respectively. Hammoud [1975] gave an average concentration of 0,87% Al_2O_3, 0.14% V_2O_3 and 0.04% P_2O_5, However, this study reveals the complete absence of them.

The analysis of ilmenite showed the presence of 0.34% of Cr_2O_3 indicating the relation between ilmenite and the probable source of the basic rocks. This chromium oxide is estimated as 0.28% by Hammoud [1975], and as 400 ppm chromium by El Hinnawi [1964].

SiO_2 in the studied ilmenite sample assays 0.27%. The figure is actually of the some order of magnitude as that found by El Hinnawi [1964], while its amount up to 0.32% [Hammoud, 1975].

Trace elements

The concentration of trace elements is shown in Table 3. According to Braunlow, [1979] the distribution of most trace elements is controlled by substitution for the major elements in crystallizing minerals, thus the divalent ions Ca, Mg, Ni,

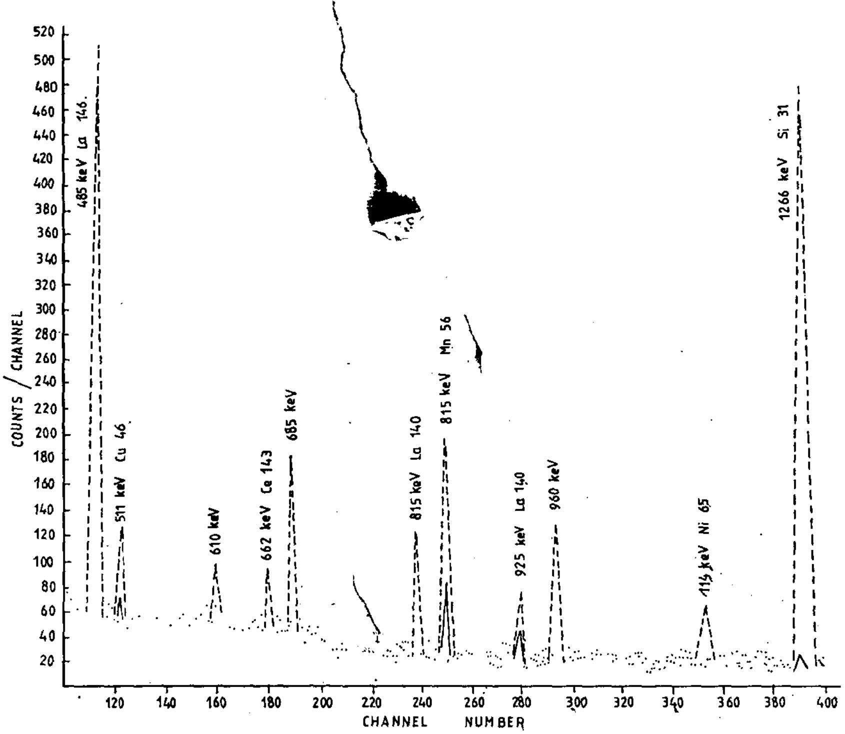

Fig. 4. Gamma-ray spectra of irradiated ilmenite (——) and the standard W1 sample (- - -) (irradiation time 4 hours, decay time 5 hours)

Cu, and Co may substitute Fe^{2+} in space lattice of ilmenite whereas trivalent ions of chromium and vanadium substitute mainly for ferric iron. The concentration of platinoid metals occurs as direct magmatic segregations in layered mafic intrusions [BRAUNLOW, 1979].

TABLE 3

Chemical composition of ilmenite by activation analysis

Element	Concentration %	Element	Concentration (ppm)	Element	Concentration (ppm)
FeO	46.980*	Co	76	Tb	17.713
TiO_2	48.040			La	328.20
SiO_2	0.270	Cu	20	Ta	416.62
Al_2O_3	—	Mn	500	Hf	89.73
V_2O_3	—	Nb	409	Au	0.504
MnO	0.064	Ni	50		
MgO	—			Eu	31.96
Cr_2O_3	0.430	Zr	211.46	Ba	50.00
CaO	—	Sc	34.304	Sr	76.16
P_2O_5	—	Yb	5.97	Ce	80.20
		Lu	0.076		
		Ag	0.036		

* Determined as Fe and calculated as FeO

CONCLUSION

Instrumental neutron activation analysis is a powerful non destructive technique for the determination of elements particularly the earths and platinum metals. As shown from the result a fraction of ppm lutetium and silver could be analysed. The presence of 0.430% chromium oxide have been attributed to the origin of ilmenite as explained by SHUKRI [1950]. The authors [illegible]gest that this ilmenite is derived from the basic rocks of Upper Egypt, Sudan and Ethiopia, as the ilmenite segregates in gabbros and norites [RAGUIN, 1961].

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