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# MÖSSBAUER EFFECT OF THE ORIGIN OF THE COLOUR IN THE ANCIENT EGYPTIAN BLACK WARE

## Introduction

An important archaelogical problem is the origin of black colour of the Ancient Egyptian pottery. The origin of this colour is not yet clarified. Lucas /1/ attributed the colour to be due to baking in smoky fire, that is to bake the pots first in a fire as hot as could be obtained then to blacken them after the baking by exposing to dense smoke. Petrie /2/ and Forsdyke (3) stated that smoke cannot penetrate pottery and that the phenomenon is not due to the smoke but is caused by reducing gases accompanying the smoke. These gases convert the red oxide of iron present into a black modification, which is either ferrous oxide /4/, magnetic oxide /5/ or partly to ferrous oxide and partly to magnetic oxide /6/.

In addition to the completely black pottery there is other kind which is partly black and partly red. The Badarian and predynastic black and red wares take the form of a black top, with often also black interior, to an otherwise red vessel. Lucas had suggested that blackness in this type of pottery is also due to carbon, i.e., a smoke black and not an oxide of iron black, as often stated.

In 1969 Cousins and Dharmawardena /7/ measured the Mössbauer effect spectra of a sample of a red sandy ware with a black interior which was excavated at Cheam. This sample showed a magnetic spectrum for the red outer layer and two non-magnetic components corresponding to 27 % of the iron as $Fe^{3+}$ and 73 % as $Fe^{2+}$. They related these results to the oxidizing conditions existing in the kiln during firing.

In the present work it was decided to study the origin of this black colour by the ME, IR spectroscopy and the x-ray diffraction. Shreds from the Badarian and twelve dynasty wares were measured which are black from the rim as well as the interior and red from the exterior. Other black sherds from the Roman and Modern periods were studied for comparison.

## Experimental technique and results

a) Mössbauer measurements

Samples were prepared from the powder scraped from the black interior surface and anothers from the red exterior surface. The room temperature ME spectra of the red and black parts of representative samples from different periods are shown in figures 1, 2, 3 and 4.

b) IR measurements

The potassium bromide disc technique was used and a summarization of the position of maximum absorption of the bands is presented in table I.

c) x-ray measurements

Some samples were examined by scanning their untouched black or red surfaces. In other samples fine powders from the black and red core were measured. Representative diffraction patterns are shown in figure 5 and 6 and the results are presented in table II.

## Discussion and conclusion

From the ME results of the Badarian sample (figure 1), it is seen that the spectrum of the red part showed more than one magnetic component of about 15 % of the total iron present (the appearance of 8 lines with different widths indicates the overlaping of more than one magnetic component). From the x-ray results of this sample, one concludes that these magnetic components are due to $\alpha$-$Fe_2O_3$ and $Fe_3O_4$. From table III the red part gave also a non-magnetic component having QS = 0.97 mm/sec and IS = 0.53 mm/sec characteristic of $Fe^{3+}$ ions in octahedral site. On the other hand, the black part showed a magnetic component of about 12 % only, and a new non-magnetic one of 14 % having isomer shift = 1.26 mm/sec, QS = 2.43 mm/sec characteristic of $Fe^{2+}$ ions. The same results are obtained from the x-ray diffraction of this sample (figure 5) which showed a sharp decrease in the intensity of $\alpha$-$Fe_2O_3$ with increase in the intensity of $Fe_2SiO_4$ in comparison with the red sample. These results are contradicting Lucas suggestion that the conditions in which this pottery was coloured were not reducing conditions and that the black colour is due to the penetration of smoke through the pores of the pots, i.e., due to carbon black only. It is not also in complete agreement with Petrie and Forsdyke who related the colour to the reduction of the ferric oxide to, ferrous or magnetic oxides. Because the ferrous oxide is not stable and cannot exist as free oxide, also from our ME and x-ray results the intensity of the magnetic oxide does not increase by reducing the ferric oxide during the blakening as another ferrous compound appeared.

The ME spectrum of the red part of the twelve dynasty sample (figure 2) showed a magnetic component of about 40 % of the total iron present and two non-magnetic ones characteristic of $Fe^{3+}$ ions in octahedral and tetrahedral sites (table III). On the other hand, the black part of this sample showed a decrease in the intensity of the ferric iron (magnetic and non-magnetic) with the appearance of a ferrous component. When the black part of this sample had been heated in open air to 650 °C for 3 hours, it became red and gave the spectrum characteristic of ferric component only. The x-ray diffraction pattern, of the two parts of this sample showed a sharp decrease in $\alpha$-$Fe_2O_3$ when going from the red to the black part. From these results and from the deep black colour of the pots of this Dynasty which have the same appearance as those of the Badarian, one can relate both types to the same method of production.

On the other hand, spectrum of the Roman sample (figure 3) which is completely black, but dark grey to bluish and not deep black as the Badarian and twelve dynasty pots did not show a magnetic component and all the iron present gave the parameters characteristic of ferrous ions only. The same results were obtained from x-ray diffraction of this sample (figure 6) which showed the lines characteristic of the ferrous compounds: olivine, $FeOAl_2O_3$ and traces of $Fe_2SiO_4$, but did not show the lines characteristic of $\alpha$-$Fe_2O_3$.

The spectra of the Modern sample (figure 4) showed very interesting results which assure the direct relation between the colour of the pottery and the type of existing iron. This sample has a black outer surface which appeared to be coated with some material. This surface showed a single ME peak at the the velocity 0.16 mm/sec. Under this surface there is a very thin pale brown layer which gave beside the magnetic component a strong ferrous component and a less intense ferric one. On the other hand, the bulk of the sherd which is dark grey to bluish similar to the Roman sample, showed three ferrous components and a very weak magnetic one.

From the x-ray results this magnetic component is due to $Fe_3O_4$. When samples of these two latter periods were heated at 650 °C, in open air the modern sample became red and gave the lines characteristic of $\alpha$-$Fe_2O_3$ in the x-ray diffraction while, the Roman sample was not affected. These results indicate that the pots of these two periods were manufactured under reducing condition, at very high temperature specially the Roman pots which has glasy appearance. It can be suggested also that the colour in these two periods is due to the ferrous compounds mainly. From the ME work of Cousins and Dharmawardena, the black sample which showed spectrum containing ferrous and ferric components, when baked in air at 700 °C the iron became entirely ferric, and the colour of the sample changed to buff. This result confirms that the black colour in Mediaeval English pottery is due ferrous compounds also.

The colour of the Badarian and the Twelve Dynasty is deep black and it can not be suggested that it is due to ferrous compounds only but may be partly due to ferrous compounds and partly to carbon. Since this type of pots is coloured by first producing completely red ware then in a second process blackening the interior and rim by subjecting them to the action of dense smoke. So this smoke can penetrate the pores of the pots and aid in intensifying the colour due to ferrous compounds /6/. From our IR measurments the bands characteristic of the free carbon were very weak and from the ignition loss analysis of these samples the loss due to carbon was very weak (about 1 %). From all these results we cannot support Lucas suggestion that carbon alone is the cause of the black colour, but it can be suggested that the colour is due to the reduction of the ferric oxide to ferrous compounds and the few percentage of carbon that penetrated the pots as smoke aid in intensifying the black colour.

Acknowledgement

The authors are grateful to Dr. S.A. Saleh for providing the archaelogical samples and the x-ray measurements and to Dr. F.M. Taiel for the IR measurements.

References

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TABLE I Results of I.R. measurements

| Sample | Band (1) $cm^{-1}$ | Band (2) $cm^{-1}$ | Band (3) $cm^{-1}$ | Band (4) $cm^{-1}$ | Band (5) $cm^{-1}$ | Band (6) $cm^{-1}$ | Band (7) $cm^{-1}$ | Band (8) $cm^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| Red part | 465 (s) | 553 (m) | 590 (vw) | 790 (w) | 920 (w) | 1040 (cs) | 1470 (vw) | 1625 (w) |
| Black part | 470 (m) | 540 (w) | 570 (vvw) | 780 (vw) | 880 (w) | 1030 (s) | 1240 (vw) | 1610 (w) |
| Identification | $Fe_2O_3$ | | | $SiO_2$ | | | $CO_3$ | |

TABLE II Results of X-Ray measurements

| Sample | Badarian | Twelve Dynasty | Roman | Modern |
|---|---|---|---|---|
| Red | $\alpha$-$Fe_2O_3$ . $Fe_3O_4$ | $\alpha$- $Fe_2O_3$, $Fe_4O_4$ geethite and traces of muscovite | | |
| Black | $Fe_3O_4$, $Fe_2SiO_4$ | muscovite and minor traces of $Fe_3O_4$ + goethite | olivine $FeOAl_2O_3$ and $Fe_2SiO_4$ | augite, traces of magnetite and minor traces of $Fe_2SiO_4$ |

Note: All the red and black samples contain -quartz as major quantity and the plagioclase series with different quantities from period to another according to the kind of the clay used.

**TABLE III** **The MB parameters of representative sample from different periods**

| Period | Sample | (H) KOe | IS (mm/sec) | OS (mm/sec) | Type of iron | % component / Total iron |
|---|---|---|---|---|---|---|
| Badarian | Red part | (507 (497 | | | $Fe^{3+}$(mag.) | 45 % |
| | | | 0.53 | 0.97 | $Fe^{3+}$(non-mag.) | 55 % |
| | Black part | 502 | | | $Fe^{3+}$(mag.) | 12 % |
| | | | 0.49 | 0.89 | $Fe^{3+}$(non-mag.) | 74 % |
| | | | 1.26 | 2.43 | | 14 % |
| | Red part | 512 | | | $Fe^{3+}$(mag.) | 40 % |
| | | | 0.32 | 1.20 | $Fe^{3+}$(non-mag.) | 25 % |
| | | | 0.30 | 0.40 | $Fe^{3+}$(non-mag.) | 35 % |
| Twelve Dynasty | Red part | 512 | | | $Fe^{3+}$(mag.) | 25 % |
| | | | 1.28 | 1.92 | $Fe^{2+}$(non-mag.) | 21 % |
| | Black part | | 0.36 | 1.76 | $Fe^{3+}$(non-mag.) | 19 % |
| | | | 0.32 | 0.64 | $Fe^{3+}$(non-mag.) | 35 % |
| Roman | Bluish grey | | 1.16 | 1.92 | $Fe^{2+}$(non-mag.) | |
| | | | 1.12 | 0.88 | $Fe^{2+}$(non-mag.) | |
| | Black surface | 525 | | | $Fe^{3+}$(mag.) | |
| | | | 0.16 | Zero | (non-mag.) | |
| | Pale brown layer | 500 | | | $Fe^{3+}$(mag.) | |
| | | | 0.96 | 2.64 | $Fe^{2+}$(non-mag) | |
| | | | 0.56 | 0.80 | $Fe^{3+}$(non-mag.) | |
| Modern | Bluish grey | 475 | | | $Fe^{3+}$(mag.) | |
| | | | 1.04 | 2.80 | $Fe^{2+}$(non-mag.) | |
| | | | 1.20 | 1.68 | $Fe^{2+}$(non-mag.) | |
| | | | 1.12 | 0.72 | $Fe^{2+}$(non-mag.) | |

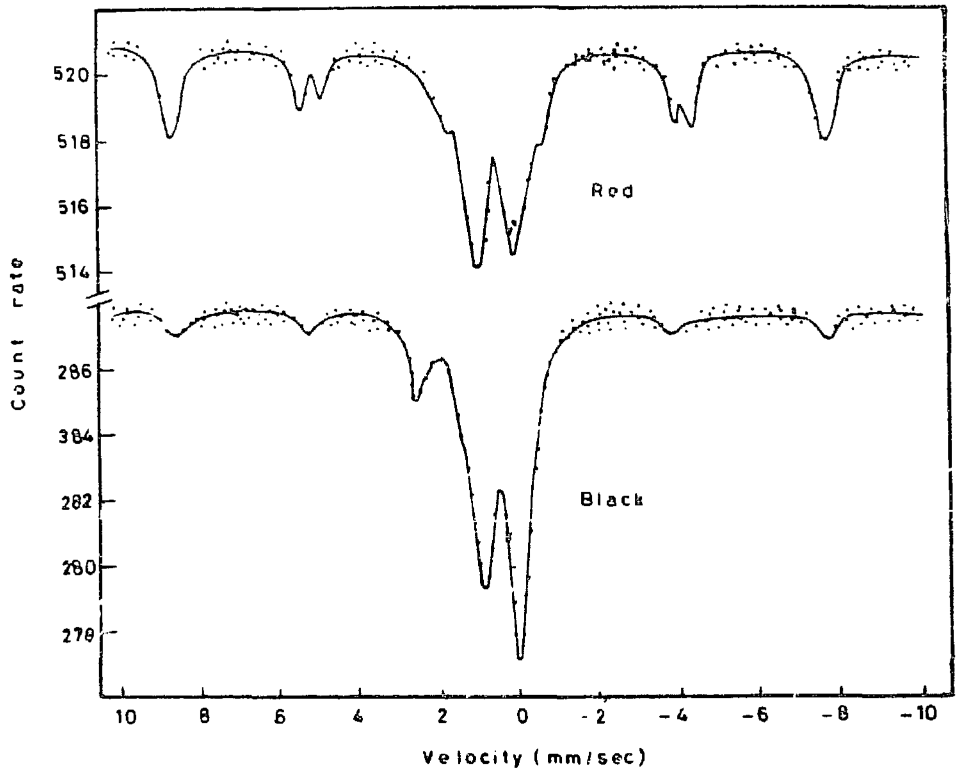


**Fig.1.** The Mössbauer spectra of a Badarian sample. The upper spectrum is for the red part and the lower one for the black part

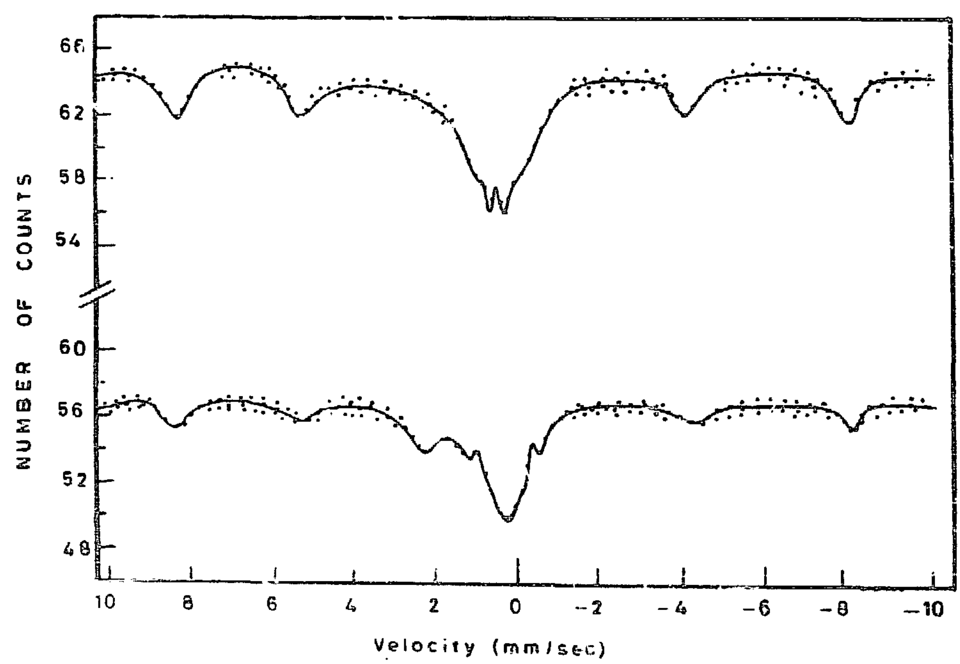


**Fig.2.** The Mössbauer spectra of a twelve dynasty sample, the upper spectrum is for the red part and the lower one is for the black part

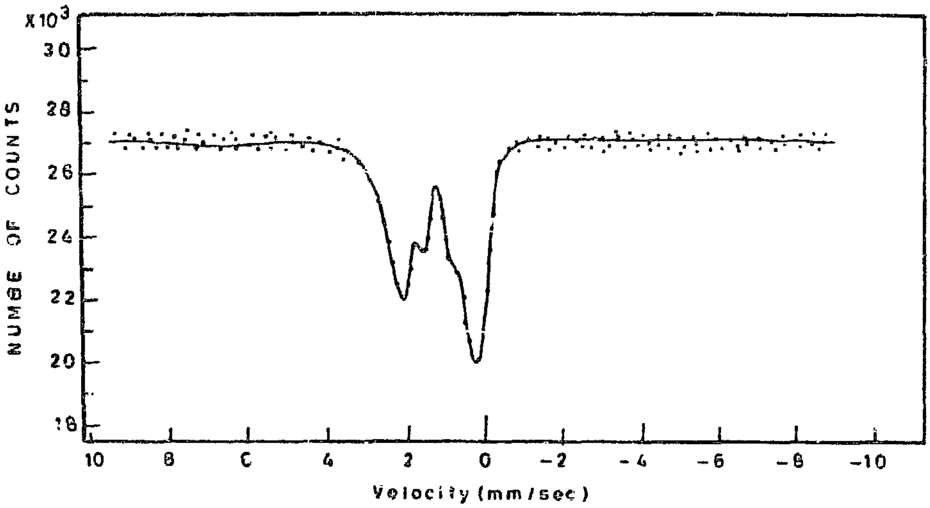


Fig.3. The Mössbauer spectrum of a Roman sample

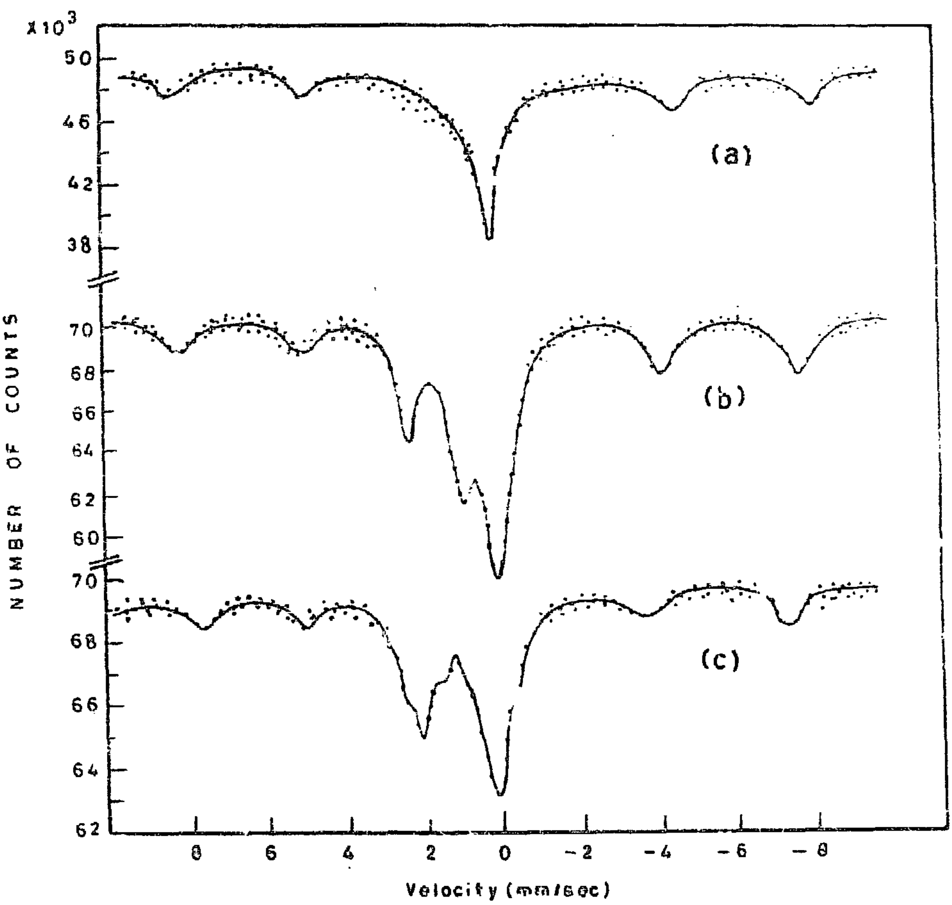


Fig.4. The Mössbauer spectra of a modern sample
a) The spectrum of the outermost black surface
b) The spectrum of a pale brown layer under the surface
c) The spectrum of the bluish grey body

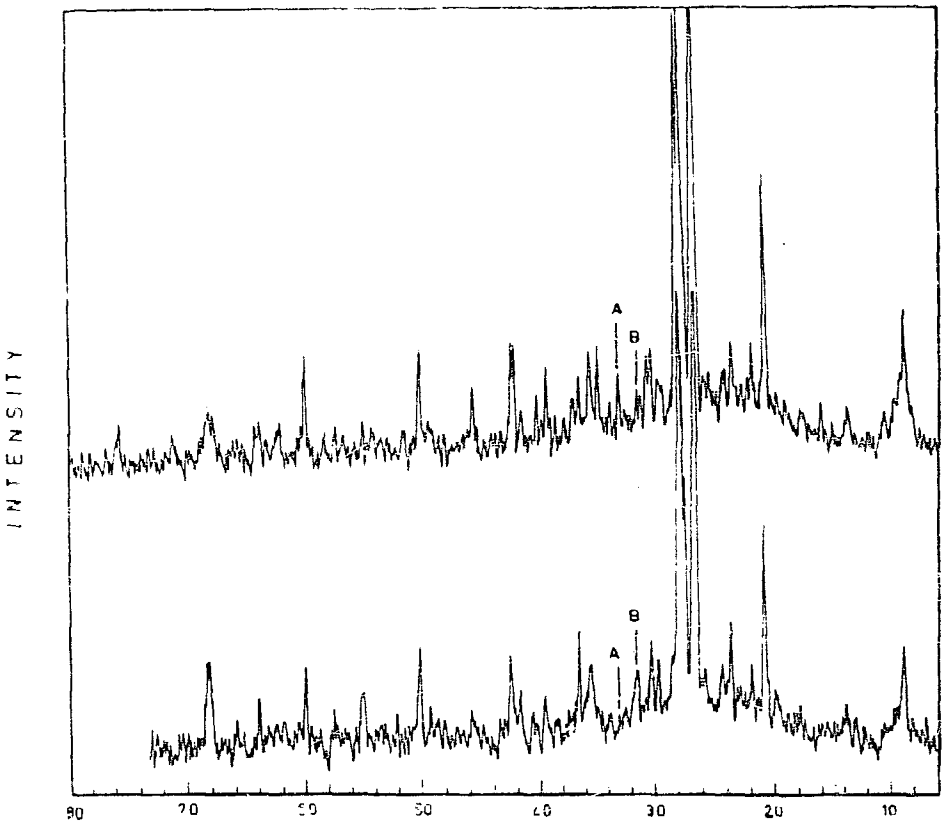


Fig.5. The X-ray diffraction patterns for a Badarian sample. The upper pattern for the red part and the lower one for the black. (A) represents the main line of $\alpha$-$Fe_2O_3$ and (B) that of $Fe_2SiO_4$

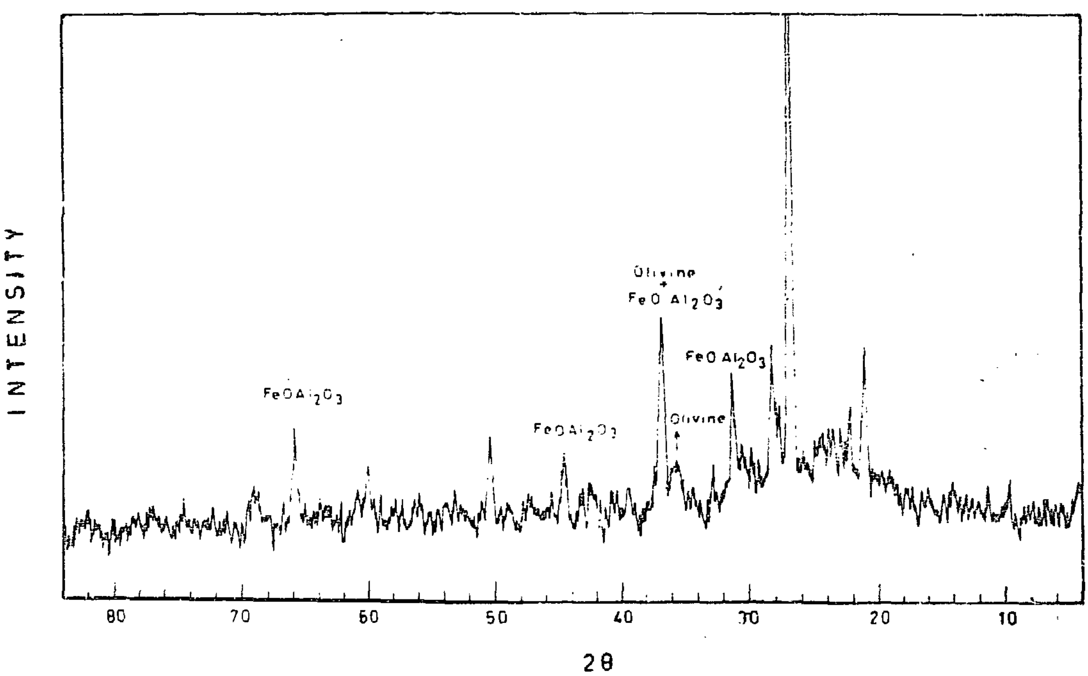


Fig.6. The X-ray diffraction pattern of the Roman sample