SUPERGENE ALTERATION OF MAGNETITE AND PYRITE AND THE ROLE OF THEIR ALTERATION PRODUCTS IN THE FIXATION OF URANIUM FROM THE CIRCULATING MEDIA.

BY

M.A. EL GEMMIZI

Nuclear Materials Authority

Cairo- Egypt.

ABSTRACT.

In most of the Egyptian altered radioactive granites, highly magnetic heavy particles were found to be radioactive. They are a mixture of several iron oxide minerals which are products of supergene alteration of the pre-existing hypogene iron-bearing minerals especially magnetite and pyrite. The end products of this supergene alteration are mainly hydrated iron oxide minerals limonite hematite and geothite. During the alteration, deformation and defects in the minerals structure took place , thereby promoting diffusion of the substitutional and interstitial ions (uranium) to words these sites

The mechanism of the alteration of the hypogene iron-bearing minerals; magnetite and pyrite to form the secondary minerals hematite, limonite and geothite; the role of these minerals in fixing uranium from the ciculating media as well as the applicability of these minerals as indicators to the radioactivity of the host rocks were discussed.

INTRODUCTION

It is quite common that in all the altered rocks magnetite and to some extent pyrite which are present as accessories are suffering from some degrees of alteration. Magnetite and pyrite in the altered granite of Wadi Nugrus, El Missikat and El Aradyia, Eastern Desert was found by (1 & 2) to possess several degrees of alteration and crystal deformation. This means that both minerals are sensitive to postdepositional environmental changes.

The granites of the present study were described as altered granites overlained by metasediments and underlained by magmatic bodies which invaded the granites itself by sills. This situation indicates that the rocks in question were subjected to heat and pressure, which are the principal agents of deformation of magnetite and pyrite. On the other hand, the radioactivity of the studied rocks was said to be postdepositional, and is limited in those parts of the rocks that suffer from shearing and structural deformation, while the other parts are not radioactive i.e. the radioactivity is not original in the rocks.

The aim of the present study is to show how the magne : and pyrite transformed to their alteration products (the highly magnetic particles) and the rule of the different stages of alterations in capturing uranium from the circulating media.

MINERALOGICAL STUDIES

Represented samples from the altered granite of Wadi Nugrus, El Missikat , El Aradyia, El Shallal, Oblisk, Um Akl, El Hudi and Abu Aggad localities, Eastern Desert, Egypt were collected, crushed and subjected to up grading by gravity techniques using Wilfley Table. The up graded accessories were magnetically defferntiated into different magnetic fractions from which the highly magnetic parts were subjected to mineralogical investigations.

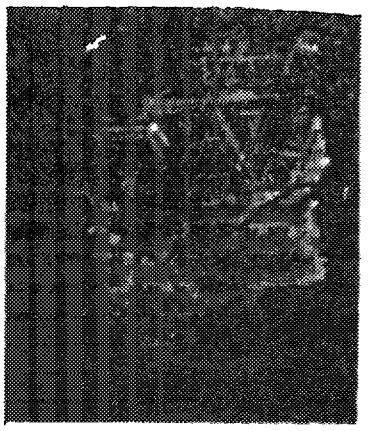
The highly magnetic parts were found to be composed mainly of unhederal flaky (specular) particles and deformed cubes. Both types seem dull brown, unsorted ,sherinked and are relatively of coarser grain size than the other unaltered magnetite, fresh pyrite and other accessories. In most cases both types are represented by fragments. The euhederl particles are mainly pseudomorphous geothite and limonite after pyrite, while those after megnetite are quite rare.

Polished surfaces of these particles were prepared,and their studies revealed that the altered magnetite particles show different degrees of alteration. Principally the alteration began by martitization either through the particles boundaries, through the cracks sides or through the cubic plains (Fig.1, a &b) where martite phase seems lighter than the magnetite phase. Martitization proceeded until the whole particles became martite and the previously martitized areas were hydrated into limonite or geothite (Fig. 1, c) where the black hydrated areas are confined to the cubic plains, the first martitized zones. The hydration process proceeded until the whole particles became hydrated; Fig. 1,d shows an advanced stage of hydration.

Polished surface studies of the pyrite particles indicated that the transformation of pyrite to limonite and geothite was caused by two processes. The first process is the hydration of the sherinked particles through the surface shrinks and parallel to the particle boundaries (Fig. 2,a), where the whole particle is transformed into the highly magnetic material (fresh pyrite is non-magnetic). Remnant of the original pyrite was detected in some polished surface (Fig. 2,b). On the other hand, the study of the polished surfaces of the fragmental particles after pyrite indicated that these fragments were transformed into limonite and geothite through the reduction of pyrite to pyrrhotite by releasing some of its sulfur content, followed by hydration of pyrrohitite phase. Fig. 2,c shows the characteristic wavy structures of formation of pyrrhotite (pale light), remnants of pyrite (bright light) and hydration products (blacks).. The end product of both ways of alteration of pyrite is the hydrated iron oxides (limonite and geothite), which are responsible for the magnetic property of the pseudomorph.

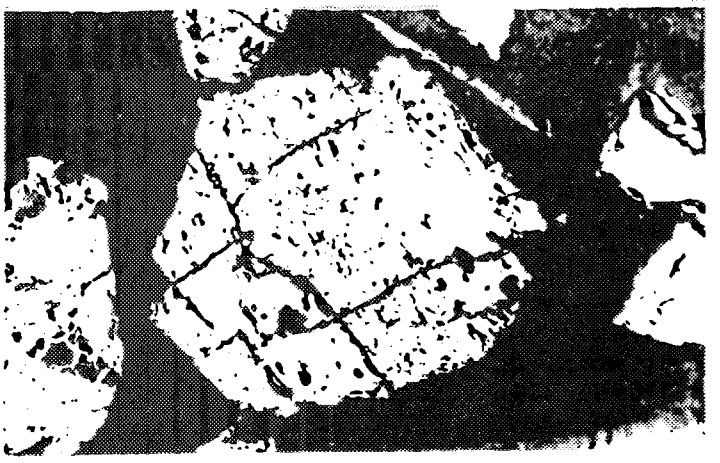
RADIOACTIVITY STUDIES

The separated highly magnetic particles were subjected to radioactivity measurements using different techniques for each group of samples. Those separated from Nugrus Rock were measured by the nuclear emulsion plates (glass slide) and found to contain up to 0.53 % eU while the non-altered magnetite and pyrite (fresh) were not radioactive. Meanwhile, the latter particles are smaller in particle sizes and represented by euhederal crystals. Furthermore, magnetite and pyrite that separated from the non-radioactive parts of the succession of Nugrus group are fresh , euhederal and with smaller particle sizes than those separated from the radioactive units of the group (1).

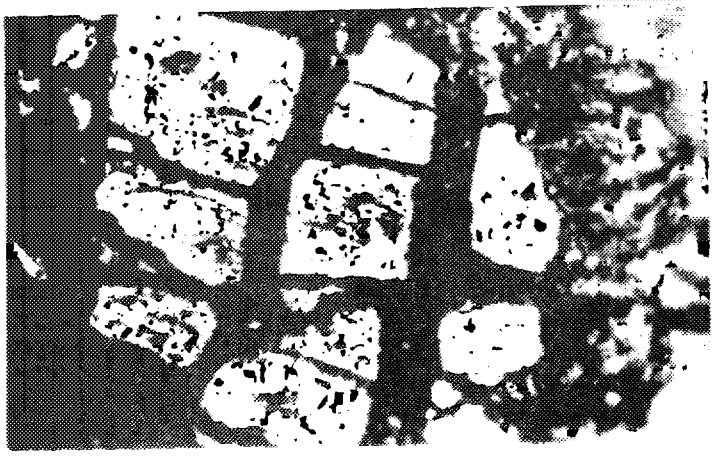


(a)

(b)

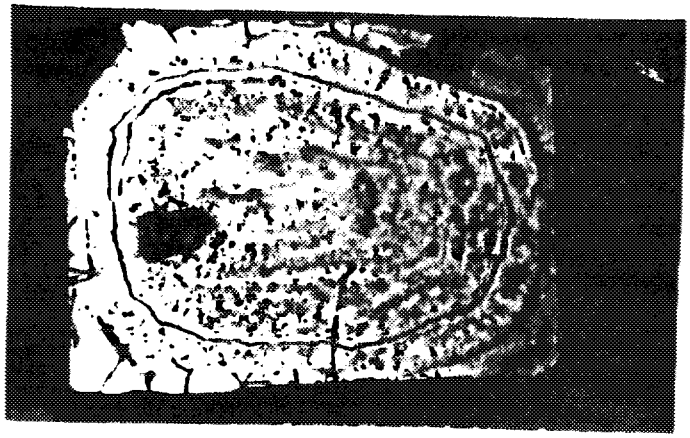


(c)

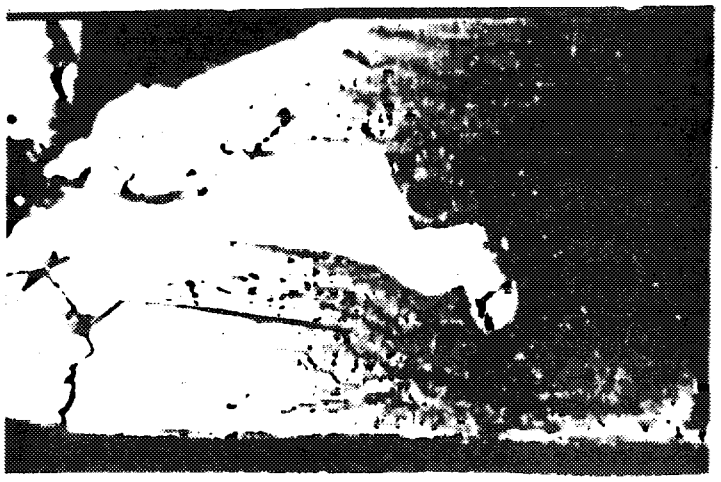


(d)

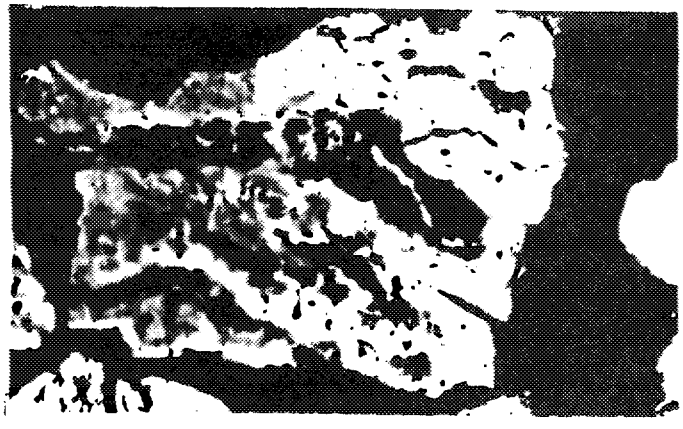
Fig. 1: Stages of supergene alteration of magnetite;
a- Martitization along the cubic planes.
b- Martitization through cracks and grain boundary.
c- Completely martitized grain and beginning of hydration.
d- An advanced hydration stage.



(a)



(b)



(c)

Fig. 2: Supergene alteration of pyrite to geothite ;

a- Complete alteration(altration pattern is parallel to the grain boundary).

b- Partial alteration to geothite with pyritic remnant.

c- Alteration of pyrrhotite after pyrite to geothite with pyritic remnants

The uranium content in the magnetite of the two plutons of El Missikat and El Aradyia by laser method and found to contain from 500 upto 60,000 ppm uranium (2). She added that in some parts magnetite was enriched uranium upto 1:2143 relative to the total radioactivity of the host rock.

The radioactive measurements of the highly magnetic particles separated from El Shallal, Oblisk,Um Akl, El Hudi and Abu Aggag was carried out using a low background Single Channel Analyzer by which the radioactivity is expressed in CPS in order to correlate the CPS of the total heavy accessories in the rocks including the highly magnetic particles and count the contribution percentages of these particles(share %) to the total radioactivity of the bulk heavy accessories. The obtained results were correlated with the field radioactive measurements in the aim to find out the relation between the radioactivity of the highly magnetic particles and the field radioactivity of the rock. The results (Table 1) indicate some parallelism between them.

Table (1) Radiometric Measurments.

Sample	El Shallal	Oblisk	Um Akl	El Hudi	Abu Aggag
Share %	27	26	28	22	20
Field measur. (cps)	185	175	230	100	65

DISCUSSION

The processes of formation of supergene alteration and the formation of the secondary minerals are very complicated. Several explanations have been reported about the supergene alteration of magnetite and pyrite and the formation of hydrated iron oxide minerals. On the basis of the results of mineralogical investigations, the accepted explanation is discussed herein.

The oxidation of magnetite to hematite by addition of oxygen (3), causes an increase of volume of 5.2% takes place. The altered highly magnetic particles in investigation are coarser than the fresh ones. Metasomatic alteration of the rocks has resulted in much of the magnetite becoming martitized (4). The alteration of magnetite to hematite during this process, has penetrated from the preferies of magnetite crystals inwards along (111) plains giving partial pseudomorphism. He added that no crystal of magnetite in such rock have escaped some degree of

martitization and in many, the replacement process is advanced and that martitization is confined only to metasomatized granulite from Matapau.

The dynamic metamorphism is capable for producing mineral changes, thermal energy expands the mineral lattice and promotes solid solution, Deformation introduces defects in mineral structure, thereby promoting diffusion of substitutional and interstitial ions towards these sites. This means that the altered and deformed mineral lattices are ready to accommodate foreign ions (5).

The *alteration of magnetite takes* place by *martitization and/or maghematization*, alteration of maghemite, hydration of maghemite and hematite and possibly magnetite and formation of specularite(6). He further explained that martitization along the cracks and inclusions represent the first stage in the oxidation of magnetite. Martitization first takes place along the grain boundaries and may then proceeds either zonally or along the cubic plains forming the typical widmannstattan pattern. The process may continue until it reaches the stage where only minute remnants of magnetite occur in a network of martite lamellas. Maghemite is, however a metastable phase which in turn alter to hematite. This explanation is in close resemblance with that found in the present study.

On the other hand, (4) observed crystals of pyrite which originally are surrounded by thin crust of limonite and contain rounded bodies of pyrrhotite.and many of the pyrite grains in polished section to have narrow rims of hematite or wholly replaced the hematite which is presumed to be secondary after pyrite.Furthermore, (7) reported photomicrographs resembling those detected in the present study especially those of alteration,by hydration and replacement of magnetite by geothite.

Sulphide ores were found by (8) *to* oxidize to sulphate which are soluble in acid solution. The surrounding carbonate rock immediately reacts with these solution to neutralize any formed acid. Ferric iron is not soluble and is precipiteted almost as hydrous oxides, the end product is limonite which fix uranium by adsorption. He mentioned that finally divided geothite and hematite remove radioactive elements from solution. On the other hand, (9) remarked that metamorphism causes the breakdown of pyrite and formation of pyrrhotite which is not a primary mineral in metamorphic rocks (10). Sulfur was released by metamorphic breakdown of pyrite. In non-metamorphic pyrite deposit, there is a lack of pyrrhotite (11). He added that pyrrhotite was produced, by reduction, by heating pyrite with coal i.e. reduction.

Accordingly, it can be explained that pyrite was either broken down to form pyrrhotite which explain the confinement of pyrrhotite to the altered fragments of pyrite, or oxidized to sulphate followed by precipitation of hydrous ferric oxide in the same site. The breakdown product of pyrite (pyrrhotite) was latter altered to the hydrous iron oxides.

Collectively speaking, in the studied rocks, both magnetite and pyrite followed different ways through their transformation to hydrous iron oxides. Both minerals are not primarily radioactive or at least were not as radioactive as their altered products. Meanwhile, the radioactivity of the host rocks are postdepositional which mean that most of the radioactivity in the secondary highly magnetic particles that separated from the studied rocks were accepted during their formation from the primary magnetite and pyrite by alteration. Furthermore, and according to the last finding it can be concluded that both minerals can fix uranium from the surrounding media during their alteration.

CONCLUSION

The outcome of the present study can be summarized in the following points:

1-Magnetite and pyrite can not survive the alteration effects of the host rocks but altered to hydrated iron oxides.

2- Uranium in the circulating media could be fixed by some way in or on one or more stages of the alteration of magnetite and pyrite

3- The radioactivity of the alteration products of magnetite and pyrite are in some ways comparable with the field radioactivity of the host rocks.

4- Uranium content or at least great part of it in the alteration products of magnetite and pyrite is postdepositional and not primary in the parent minerals.

REFERENCES

(1) M.A. El Gemmizi; Ph.D.Thesis, Fac.Sci.Cairo Univ.; (1979).
(2) N.A. Ahmed; M.Sc.Thesis, Fac. Sci. Cairo Univ.(1991).
(3) J.W. Gruner; Econ.Geol.; 21,375; (1926).
(4) G. Baker; Am.Miner.; 37,7&8, 567; (1952).
(5) J.A. McDonald; Mineral Deposita. 2; (1967).
(6) Wc.J. Van Rensburg; Ann. Geol.S.Afr.; 5,93; (1966).

(7) N.Morimoto, A.Gyobu, H.Mukaiyama,and E.Izawa;Econ.Geol.;70,824; (1975).
(8) P.B. Barton; Econ.Geol.; 51, 178; (1956).
(9) T.F. Bates, N.J.M., Crossford and J.M. Allan; Mineral Deposita,12,143;(1977).
(10) R.L. Santon; McGraw Hill Company, New York; (1972).
(11) I.B. Lambert; J.Geol.Soc.Auster.; 20,2; (1973).