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MINERALOGY AND GEOCHEMISTRY OF THE HUSSAINIYAT KARST BAUXITES AND ZABIRA STRATIFORM BAUXITE IN NORTHERN ARABIAN PENINSULA

Khaldoun S. Al-Bassam[*]

ABSTRACT

Two early Cretaceous bauxite deposits in Northern Arabian Peninsula are studied in this paper; the Zabira sratiform deposits and the Hussainiyat karst deposits. The textural constituents are similar in both deposits; colloform grains (pisoids and ooids) are dominant, but they are better developed in the stratiform bauxite suggesting higher maturation. Boehmite and gibbsite are the only bauxite minerals; the former is dominant in the karst bauxite whereas the latter is dominant in the stratiform bauxite. Various amounts of kaolinite are retained in these bauxites. Hematite and anatase are accessary minerals. The former is more enriched in the stratiform bauxite; inherited from source rocks.

Compared to source rocks, Fe, Ni and to some extent Co were depleted during bauxitization in both types of bauxite deposits, whereas Ga and Zr were enriched together with Al. Uranium was depleted in the stratiform bauxites and enriched in the karst bauxite relative to source rocks, whereas Cr behaved oppositely; both elements are controlled by oxidation potential during bauxitiztion. The hidden karst bauxites have suffered less diagenetic and epigenetic modifications relative to the exposed stratiform bauxites. Resilication is one of the diagenetic modifications found in the stratiform deposits only. Epigenetic calcite, alunite and gypsum were introduced later in both deposits under arid climate.

معدنية وجيوكيميائية البوكسايت الخسفي في الحسينيات والبوكسايت الطباقي في الزبيرة، شمال شبه الجزيرة العربية

المستخلص

تمت دراسة راسبين من رواسب البوكسايت الطباشيرية المبكرة في شمال شبه الجزيرة العربية وهما راسب البوكسايت الطباقي في الزبيرة وراسب البوكسايت الخسفي في الحسينيات. المكونات النسيجية متشابهة في الراسبين حيث تسود الحبيبيات الغروية (الحمصيات والسرئيات) غير انها اكثر تطوراً في البوكسايت الطباقي مما يشير الى درجة اعلى من النضوج. البوهمايت والجبسايت هما المعادن البوكسايتية الوحيدة في كلا الراسبين ويسود الأول في البوكسايت الخسفي في حين يسود الثاني في البوكسايت الطباقي. هناك بقايا من الكاؤولينيات بكميات مختلفة في هذه الرواسب البوكسايتية ويمثل كل من الهماتايت والاناتيز معادن مرافقة ويوجد الأول بوفرة في البوكسايت الطباقي موروثاً من الصخور المصدرية.

بالمقارنة مع الصخور المصدرية فان الحديد والنيكل والكوبلت قد تناقصت تراكيزها اثناء عملية تكون البوكسايت في كلا النوعين في حين ازداد تركيز كلا من الغاليوم والزركونيوم مع زيادة تراكيز الألمنيوم. تناقص تركيز اليورانيوم في البوكسايت الطباقي وازداد في البوكسايت الخسفي بالمقارنة مع الصخور المصدرية، في حين كان تصرف الكروم على العكس من ذلك ويعتقد أن جهد التأكسد اثناء عملية التحول الى بوكسايت قد أسهم في هذه الاختلافات بين النوعين من البوكسايت.

لوحظ ان البوكسايت الخسفي المطمور قد تعرض الى عمليات تحويرية اقل من البوكسايت الطباقي المكشوف وتمثل اعادة تكوين السيليكا إحدى تلك العمليات التحويرية الشائعة في البوكسايت الطباقي وقد تكونت معادن ثانوية المنشأ مثل الكالسايت والالونايت والجبسم تحت ظروف مناخية جافة في كلا الراسبين.

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[*] Chief Researcher, State Co. of Geological Survey and Mining, P. O. Box 986, Baghdad, Iraq.

INTRODUCTION

The discovery of bauxite deposits in east Mediterranean area is relatively recent. The Zabira stratiform deposits were discovered in Saudi Arabia in 1979 by Riofinex geologists (Lozej, 1981), whereas the Hussainiyat karst deposits were discovered in Iraq about ten years later by GEOSURV geologists (Mustafa, 1991). In the mean time, bauxite showings were outlined in Syria and Palestine (Valeton, et al., 1983 and Goldbery, 1979). The age of bauxitization event seems comparable in some of these deposits and probably related to a unique rain-forest climatic event which is suggested to have occurred in this part of the world for a limited time during the early Cretaceous (Al-Amiri, 1994).

The age of the Zabira bauxites was suggested as Aptian - Albian on the basis of pollen analysis of the underlying and overlying rock units (Norris, 1980). The same age was suggested for the Hussainiyat karst bauxites on the basis of logical interpretation of available evidence on its stratigraphic position, geological features, paleoclimatic conditions, etc. (Al-Bassam, 1996). Mustafa et al. (1995) shares the author's opinion in this suggestion, but Al-Atia and Saadalla (1995) believe that the age of the Hussainiyat bauxites is Jurassic. Obviously, more than one opinion was forwarded to solve the age problem, but the majority are in favour of an early Cretaceous age for these karst bauxites.

Previous work on the petrology and geochemistry of these two deposits include those carried out on the Hussainiyat karst bauxites by Mustafa et al. (1995), Al-Ani (1996), Ali (1997), Yakta (1997) and Al-Sayegh et al. (1998), and those carried out on the Zabira bauxite by Rainy (1982), Laville (1982) and Bowden (1981). Mustafa et al. (1997) tried to compare texture, mineralogy and chemical composition of both deposits.

The difference in type and bauxitization processes of these two deposits, their close geographic and tectonic setting, as well as their comparable age inspired this study to correlate a stratiform – type bauxite with karst bauxite deposits in terms of bauxite classification, maturity, texture, mineralogy, chemical characteristics, geochemical evolution and epigenetic modifications. This study is based on more than 50 rock samples collected by the author from both deposits including source rocks. Most of the samples were collected from measured outcrop sections (Zabira), mine working faces and boreholes (Hussainiyat). Mineralogical and chemical analyses were performed in GEOSURV laboratories. Additional data on chemical analysis were adopted from previous works to serve the purpose of this study (Al-Ani, 1996 and Ali, 1997).

GEOLOGICAL SETTING

Both deposits are located in the Stable Shelf of the Arabian Platform, within marine sedimentary rocks (Fig. 1). The Zabira bauxite profile was developed on an angular unconformity surface, where late Cretaceous rock units (Wasia and Aruma Formations) are unconformably overlying clastic units of late Triassic, early and middle Jurassic and early Cretaceous age which are stratigraphic equivalents of Minjur, Marrat, Dhruma, Tuwaiq and Biyadh Formations (Bowden, 1981 and Black et al., 1982). The bauxite profile extends in outcrops for about 125 km. along the strike of the overlying rock units with some erosional discontinuities (Fig. 2). This discontinuous character led to the identification of three sectors, named as North, Central and South Zones (Black et al., 1982). These zones show some differences in lithology of bauxite and country rocks in the Zabira deposits.

On the other hand, the Hussainiyat karst bauxite was developed in fossil karsts, tens of meters deep and hundreds of meters wide, within the Ubaid Formation carbonates (early Jurassic) in areas where maximum intersection of fractures and faults exist (Fig. 3). The top of the Ubaid Formation is marked by an erosional unconformity, partly overlain by the Hussainiyat Formation which consists of fluvial clastics (at base) and marine carbonates (at top). The clastics are kaolinitic clay, with quartz – sand lenses. The base is marked by organic – rich black kaolinitic mud (Mustafa et al., 1994). The karst bauxites are found in the exposed parts of the Ubaid Formation only. Non has been found within or underneath the Hussainiyat Formation.

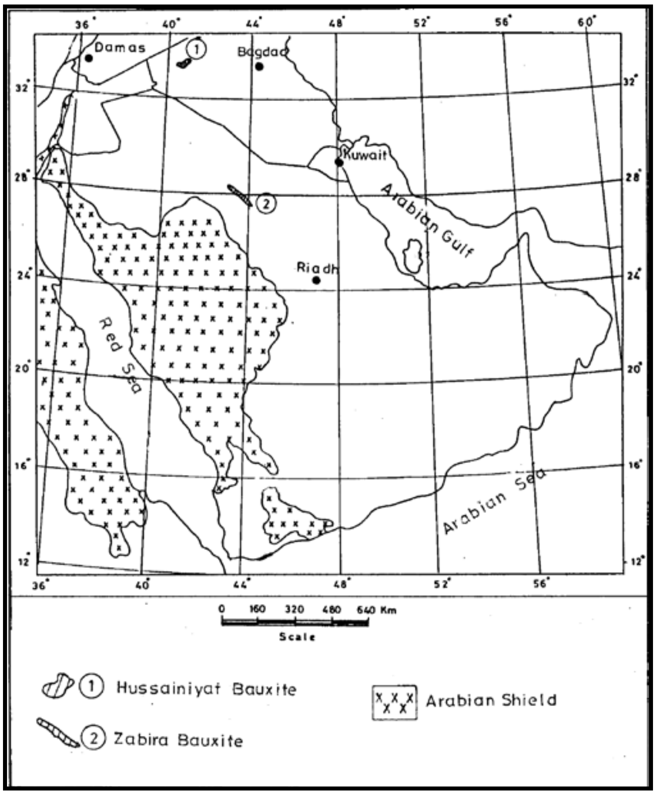

Fig. 1: Location map

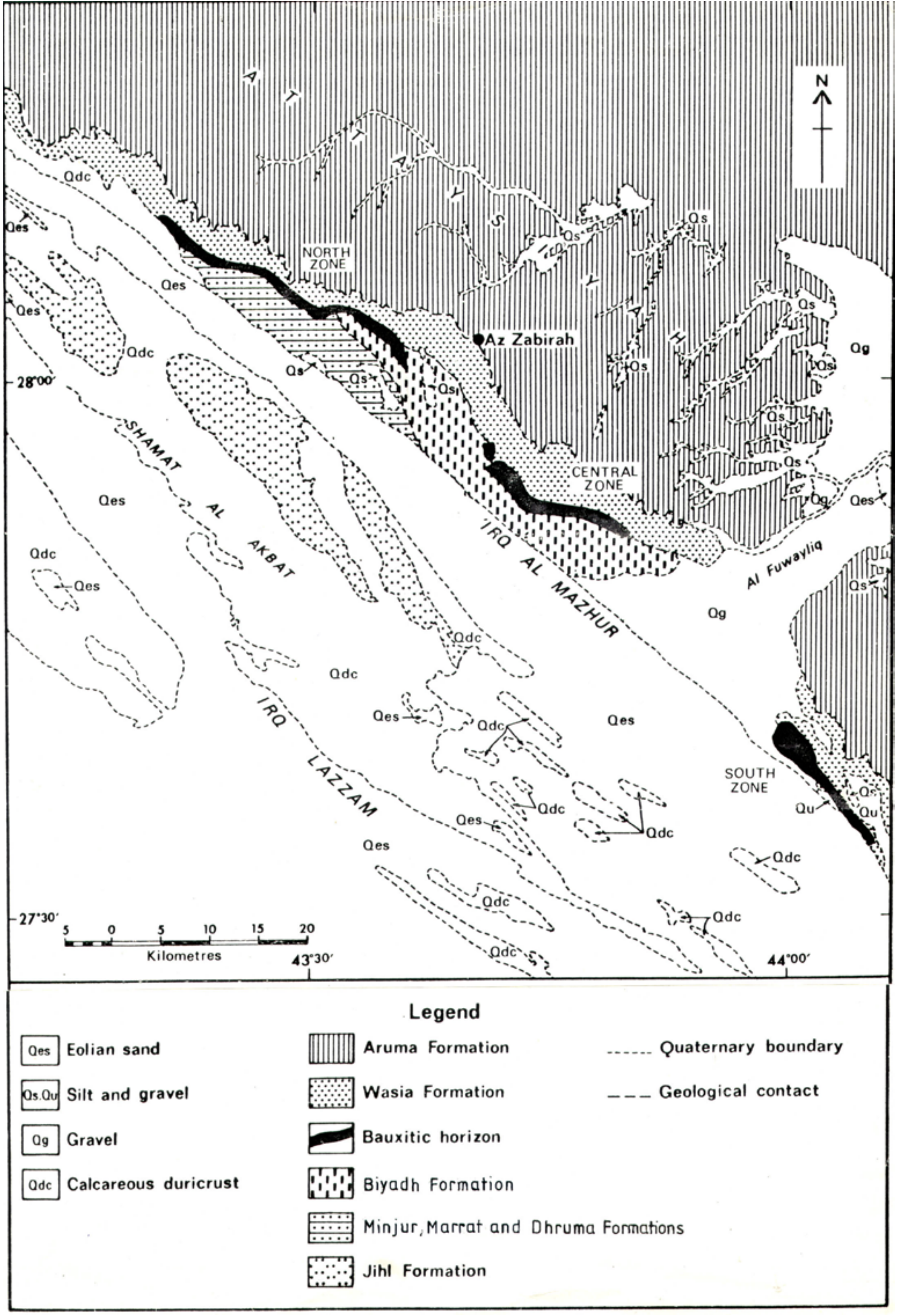

Fig. 2: Geological setting of the Zabira bauxite deposit (Black et al., 1982)

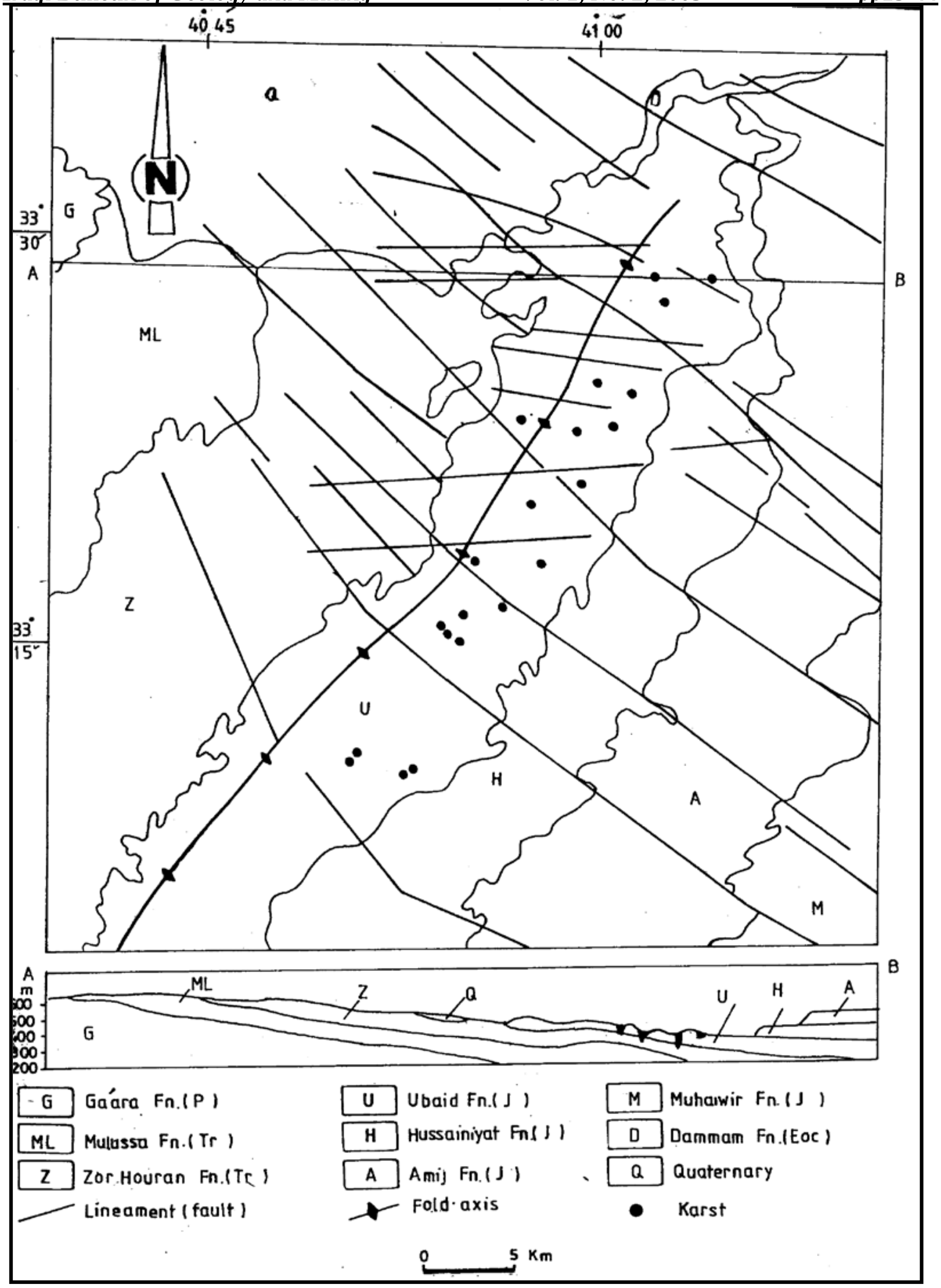

Fig. 3: Geological and lineaments map of the Hussainiyat karst area (Mustafa et al., 1994)

THE BAUXITE PROFILES

The bauxite profile in the Zabira stratiform deposit is about 6m. thick in average(Fig.4) and was developed on two different rock types (Bowden , 1981 and Black et al., 1982). It is developed on permeable sandy kaolinitic rocks, where the contact with the bauxite is gradational, marked by gradual decrease of pisolites content. It is also developed on impermeable ferruginous kaolinitic rocks, where the contact is sharp and marked by pisolites development within the basal rocks, in fractures, cavities, etc. The true bauxite is mainly pisolitic, red, violet, yellow and pink in color, overlain by kaolinitic claystone. Diagenetic processes have influenced the upper part of the bauxite profile by resilication and calcrete development.

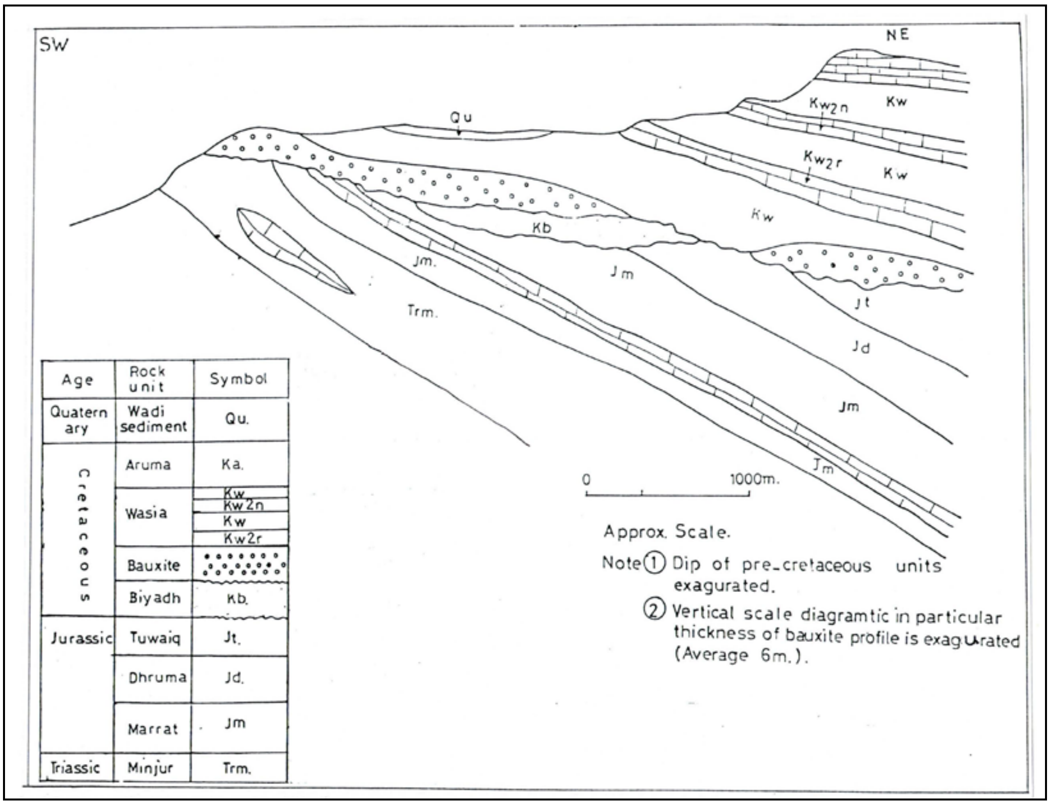

Fig. 4: Schematic geological cross section in the Zabira bauxite deposit (Bowden, 1981)

The bauxite–bearing karst-fill deposits of the Hussainiyat exhibit similar pattern of sedimentary secession in most of the investigated karsts. The filling sediments are usually concave upwards, having the general shape of the karst. They were divided into three parts (A, B and C) according to lithology (Mustafa, et al., 1994) (Fig.5). Zone (C) is up to 35 m. thick and consists of white fining upwards quartzose sandstone, overlain by varicolored, mottled kaolinitic clay. Zone (B) is up to 70m. thick and consists of quartzose sandstone at base, topped by kaolinitic clay, followed upwards by bauxitic clay and flint clay with plant remains, pyrite and Fe-oxides. This unit grades upward into oolitic – pisolitic bauxite, which has a lenticular shape (1-40m. thick) with plant remains at the upper part. This is overlain by bauxitic clay. Zone (A) is up to 85m. thick and represents the upper unit of the karst – fill succession. It consists of quartzose sandstone at base, occasionally clayey, overlain by dark red, oolitic-kaolinitic clay, occasionally sandy with two horizons of ferruginous breccia. The upper part of this zone consists of ferruginous multicolored sandstone, topped by kaolinitc claystone.

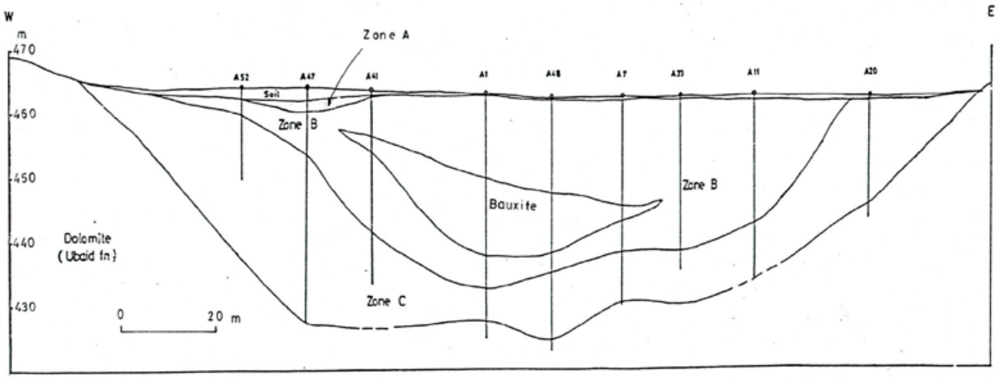

Fig. 5: Cross section showing zonation in the karst-fill deposits of the Hussainiyat bauxite (Mustafa et al., 1994)

SOURCE ROCKS

Source rocks of the Zabira stratiform bauxites are well-defined by previous workers as the Triassic to early Cretaceous underlying rocks equivalent to Minjur, Marrat, Dhruma, Tuwaiq and Biyadh Formations (Bowden, 1981 and Black et al., 1982). On the other hand, source rocks of the Hussainiyat karst deposits are believed to be the neighbouring kaolinite-rich clastics of the Hussainiyat Formation (Jurassic) (Mustafa et al., 1991, Mustafa et al., 1995, Al-Ani, 1996 and Ali, 1997).

Al-Bassam (1997) showed great mineralogical and geochemical similarities between the karst-fill deposits and the neighbouring clastics of the Hussainiyat Formation, and suggested the latter as source rocks for the former. However, Al-Atia and Saadalla (1995) suggested that the clastics of the karst-fill deposits and those of the Hussainiyat Formation came from the same source and were deposited simultaneously. They suggested the pre-Triassic, kaolinite-rich clastics, especially those of the Ga'ara Formation (Permo-Carboniferous), as source rocks.

PETROGRAPHY

The present study have shown that both bauxite deposits are pisoidal- ooidal in texture, with some other colloformic textures related to bauxitization processes as well as to some diagenetic and epigenetic modifications (Figs. 6 and 7). In the Zabira stratiform bauxites, pisoids are the dominant textural constituent. They generally range in diameter from 1 to 5 mm., but some of them may reach up to 15 mm. (megapisoids according to Bardossy, 1982).

The pisoids in the Zabira bauxite are brown in color with internal layering of cryptocrystalline bauxite minerals, iron oxide and kaolinite. They have sharp contact with the matrix or cement. They commonly show radial or rounded senistral cracks and irregular internal channels of lighter color (Fig. 6). Broken pisoids with ferruginous cement are occasionally found, whereas composite pisoliths are rare.

Ooids range in size from 0.1 to 1 mm., having similar internal structure as in the pisoids. In addition, various colloform grains of irregular shape are common. Those usually have diffused contact with the matrix. Irregular grains of kaolinitic clay are also common. Few grains of zircon and tourmaline are often found. The matrix mostly consists of bauxitic clay or clayey bauxite and occasionally of iron oxide. Resilication of the bauxite in some samples left some pisoids floating in a "kaolinitic" matrix formed by resilication of a precursor bauxitic matrix. Secondary calcite is found in some samples as cement filling small fractures.

In the Hussainiyat karst bauxite, peloids and ooids are more dominant than pisoids (Fig. 7), a feature also noticed by previous workers (Mustafa et al., 1995 and Yakta, 1997). Massive (structureless) varieties of cryptocrystalline bauxite are also present. The ooids are lacking concentric layering and, instead, have single central grain, enveloped by a cryptocrystalline bauxite coat. The pisoids show diffused internal structures but a few of them have concentric layering and they occasionally contain dark iron oxide. The outer boundaries of the grains are sometimes diffused, but may show sharp contact with the matrix in some samples. Composite pisoliths are present and some pisoids show irregular internal channels and radial or rounded senistral cracks, similar to those found in the Zabira bauxite. These cracks resemble the "contraction cracks" described by Keer (1977).

The matrix in the Hussainiyat bauxite is similar to that in the Zabira bauxite, consisting of kaolinitic bauxite or bauxitic clay, seldomly rich in iron oxide. Generally, the textural components in the Hussainiyat bauxite are less developed relative to the Zabira bauxite. The former have suffered less diagenetic and epigenetic modifications including resilication, which was not noticed in the Hussainiyat bauxite.

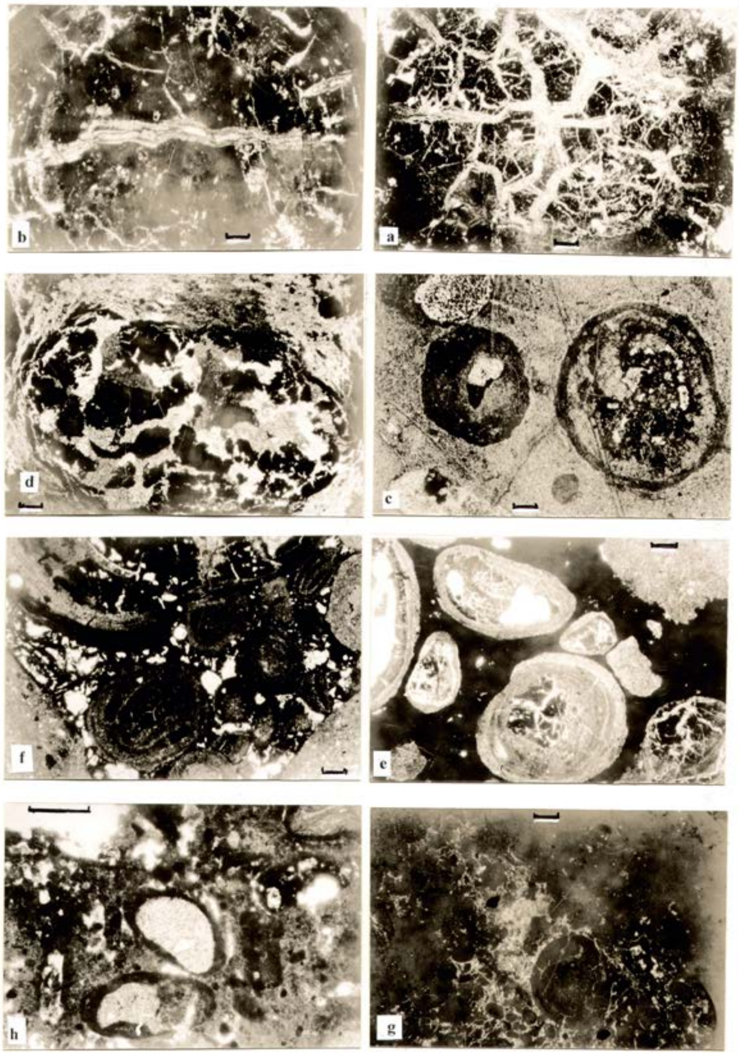

Fig. 6: Petrographic constituents of the Zabira bauxite (Bar = 1 mm)

(a) Large bauxitic pisoid cut by irregular internal channels (PL) .
(b) Large bauxitic pisoid with radial senistral cracks (PL) .
(c) Bauxitic pisoids in a resilicated bauxitic matrix (PL) .
(d) Bauxitic pisoids showing leaching features of Fe- oxide (XN) .
(e) Bauxitic pisoids cemented by iron oxide (PL) .
(f) Reworked bauxitic pisoids (PL) .
(g) Bauxitic pisoids, peloids and ooids with bauxite matrix showing the anisotropy of gibbsite (XN) .
(h) Bauxitic pisoids in a matrix of bauxite and iron oxide (PL) .

Fig .7

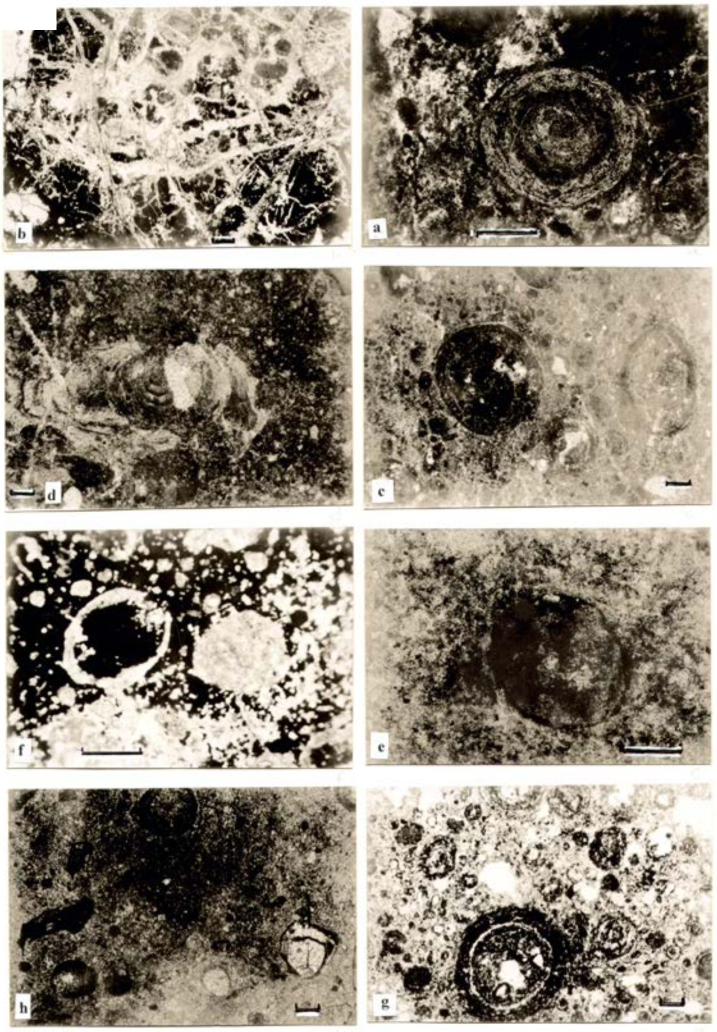

Fig .7: Petrographic constituents of the Hussainiyat bauxite (Bar = 1 mm).

(a) Bauxitic pisoid showing concentric internal layering (PL).
(b) Large bauxitic pisoid showing radial and rounded cracks (PL).
(c) Bauxitic pisoids and peloids embeded in a kaolinitic bauxite matrix (PL).
(d) Bauxitic colloforms in a bauxitic clay matrix (PL).
(e) Bauxitic pisoid in a flint clay matrix (PL).
(f) Bauxitic pisoids and peloids in a matrix of iron oxide (PL) .
(g) Bauxitic pisoids , ooids and peloids containing some heavy minerals and iron oxide(PL).
(h) Bauxitic pisoids and peloids in a bauxitic clay matrix containing zircon and tourmaline (PL).

MINERALOGY

In view of the cryptocrystalline nature of the bauxite minerals in both deposits, thin section study was not helpful in the mineral identification. X- ray diffraction was used to identify the mineralogy qualitatively and the chemical analysis was used for the quantitative estimation of the mineral constituents following a procedure developed by the author (Al- Bassam, 1997).

In order to follow the mineralogical development during bauxitization stages all samples were classified according to Valeton (1972), using the factor (Ki) which is:-

$$\mathbf{Ki = [(SiO_2 / Al_2O_3) \times 1.78]}$$

Accordingly, five classes were defined by Valeton (1972), these are:-

* High Quality Bauxite (HQB) → Ki < 0.2
* Low Quality Bauxite (LQB) → Ki 0.2 – 0.5
* Kaolinitic Bauxite (KB) → Ki 0.5 – 1.0
* Buxitic clay (BC) → Ki 1.0 – 1.5
* Clay (C) → Ki 1.5 – 2.0

However, some of the studied non – bauxitic samples contained free silica as quartz, which lead the author to add another class to Valeton's classification called here "silty clay" with Ki > 2.0 in order to cover these samples.

The mineralogical study show that the Zabira and the Hussainiyat bauxites consist mainly of boehmite, gibbsite, kaolinite, hematite, anatase and secondary calcite (Table1).Quartz may occur in some samples as well as in source rocks.

Table 1: Mineral content of various rock types in the Zabira and Hussainiyat deposits

Zabira deposit

Minerals %	HQB	LQB	KB	BC	C	SC	SR	Range (Ki<1.0)
Kaolinite	9.50	16.90	31.50	58.20	74.30	76.80	41.50	6.3-42.5
Bauxite	69.60	50.30	34.60	21.00	3.00	-	-	27.7-79.7
Boehmite	12.80	23.10	14.90	6.80	1.00	-	-	0.0-43.9
Gibbsite	56.80	27.20	19.70	14.70	2.00	-	-	7.3-79.7
Hematite	14.90	24.20	13.20	14.60	15.00	12.90	33.90	0.5-41.1
Anatase	14.40	2.30	1.30	2.10	3.30	2.20	1.00	0.4-3.5
Calcite	1.70	4.50	15.50	2.20	2.80	3.90	15.90	0.8-37.6
Quartz	-	-	-	-	-	4.20	4.40	-

… continue table 1

Hussainiyat deposit

Minerals %	LQB	KB	BC	C	SC	SR	Range (Ki<1.0)
Kaolinite	27.70	46.90	70.10	89.00	86.00	82.40	17.0-60.9
Bauxite	63.50	46.30	22.70	3.30	-	-	33.0-75.8
Boehmite	52.40	32.50	11.40	2.50	-	-	4.9-64.4
Gibbsite	11.10	13.80	11.30	0.80	-	-	0.0-44.1
Hematite	1.90	1.40	2.30	2.20	4.00	4.80	0.2-7.3
Anatase	2.50	2.60	2.10	2.10	2.40	2.20	1.2-6.0
Calcite	2.80	1.40	0.60	1.80	2.70	0.70	0.3-6.4
Quartz	-	-	-	-	2.00	6.60	-

SR	Source Rocks	
SC	Silty Clay	(Ki> 2.0)
C	Clay	(Ki 1.5-2.0)
BC	Bauxitic Clay	(Ki 1.0-1.5)
KB	Kaolinitic Bauxite	(Ki 0.5-1.0)
LQB	Low-Quality Bauxite	(Ki 0.2-0.5)
HQB	High- Quality Bauxite	(Ki<0.2)

Bauxite minerals:- The bauxite minerals content varies from 28% to 80% in the Zabira samples with Ki< 1.0 (Table 1). Boehmite content varies from 0 to 44% and gibbsite content from 7.3% to 80% in the same samples. Boehmite is dominant in the central zone (average 62% of the bauxite minerals), whereas gibbsite is dominant in the southern and northern zones (average 54% and 76% of bauxite minerals, respectively). The average of the three zones is in favour of gibbsite which is typical of stratiform bauxites. The HQB is remarkable for the high gibbsite content averaging (82%) as compared to LQB (54%), KB (57%) and BC (70%) of the total bauxite minerals.

The vertical distribution of gibbsite and boehmite in the bauxite profile of the Zabira deposit does not follow a specific pattern. Boehmite is enriched in the middle of the profile in the central zone; gibbsite is especially enriched in the upper part in the northern zone, whereas gibbsite is dominant throughout the whole profile in the southern zone (except the basal part). Gibbsite is dominant in the overlying and underlying bauxitic clays in the three zones (Fig. 8).

The intermineral correlation coefficients (Table 2) show a strong negative correlation between bauxite minerals (total) with kaolinite and calcite and weakly negative with hematite. On the other hand, boehmite correlations are different than gibbsite; it is positively correlated with anatase whereas gibbsite is negatively correlated. This may indicate that boehmite and anatase formed together in the early stages of bauxitization. They require weakly oxidizing and

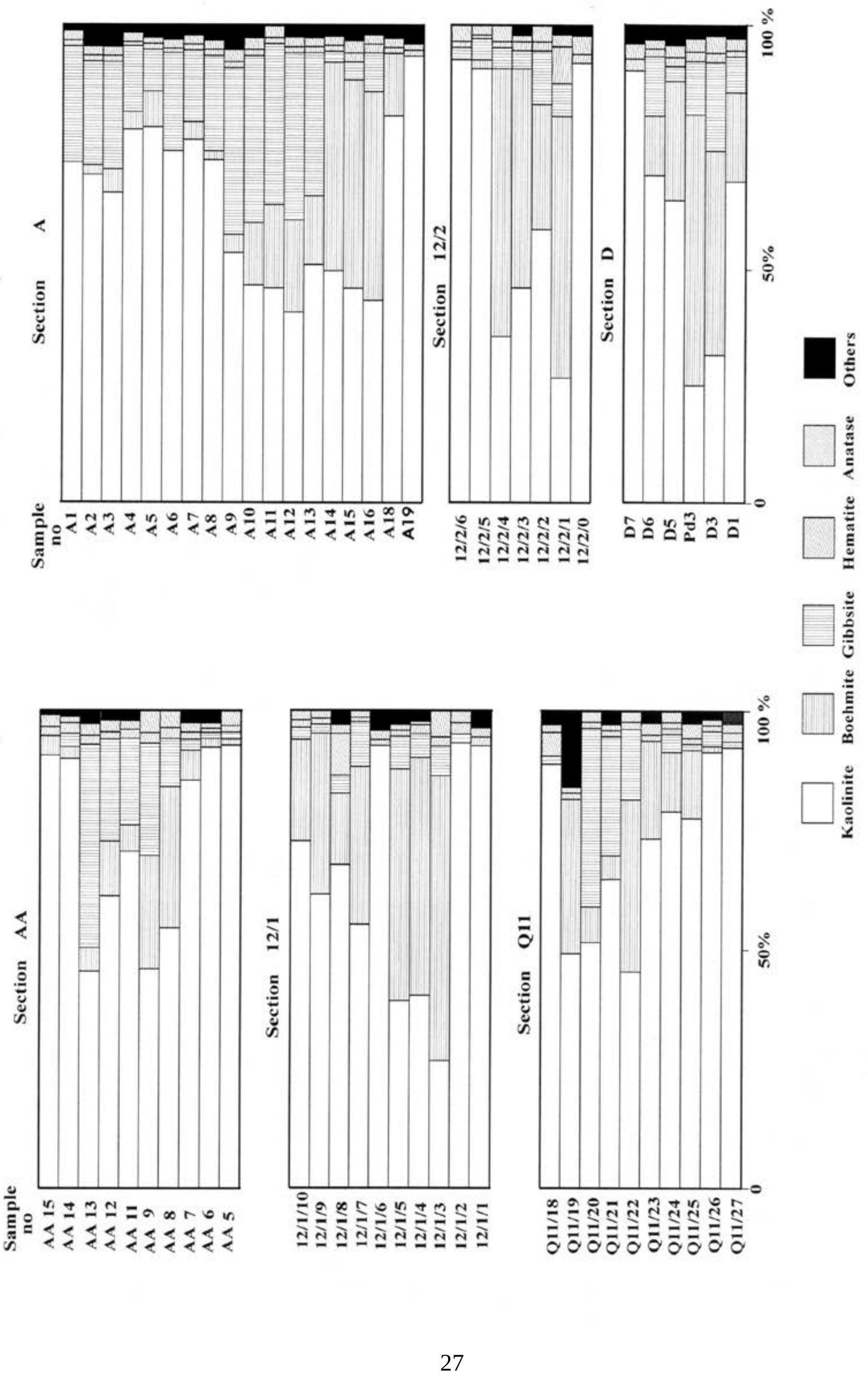

Fig .8: Vertical distribution of minerals in the Hussainiyat deposit generally neutral pH according to Valeton (1972). Gibbsite may have formed in the later stages by the hydration of boehmite, which explains the negative correlation between gibbsite and boehmite. The overwhelming presence of gibbsite in the Zabira bauxite is demonstrated by the positive correlation of bauxite minerals (total) with gibbsite.

In the Hussainiyat karst bauxite, bauxite minerals (total) vary from 33% to 75.8% (average 63.5%) in the LQB, 46.3% in the KB and 22.7% in the BC (Table1). Boehmite is the dominant bauxite mineral here. It has an average of 82.5% of total bauxite minerals in the LQB, 70.2% in the KB and 50.2% in the BC. This is one of the important mineralogical differences between the Hussainiyat karst bauxite and the Zabira stratiform bauxite, such difference between the two bauxite types was also noticed by Mustafa et al. (1997) and was found else where in the world and considered a characteristic difference between karst and stratiform (platform) bauxite deposits (Bardossy, 1982).

The distribution of boehmite and gibbsite in the karst deposits is not uniform. Boehmite average content varies from 40% to 88% of the total bauxite minerals. A vertical distribution pattern was identified; gibbsite content increases in the upper parts of the bauxite profiles, (the same was noticed by Mustafa et al., 1997) as well as in the bauxitic clay (Fig. 9). Boehmite content increases in the higher grades of bauxite, where maximum leaching and draining have occurred. This is different than the trend found in the Zabira deposits where gibbsite is enriched in the higher grades of bauxite. Mustafa et al. (1997) found that boehmite in the Hussainiyat deposits is dominant in the center of the bauxite lenses.

Table 2: Mineral correlation coefficients

Zabira deposit (16 samples)

	KA	HE	AN	BA	BO	GB
HE	-0.41					
AN	-0.04	0.30				
BA	-0.67	-0.19	0.03			
BO	-0.34	0.03	0.51	0.28		
GB	-0.38	-0.19	-0.34	0.72	-0.46	
CA	-0.02	-0.25	-0.41	-0.34	0.01	-0.32

Hussainiyat deposits (38 samples)

	KA	HE	AN	BA	BO	GB
HE	-0.06					
AN	-0.21	-0.24				
BA	-0.98	0.07	0.22			
BO	-0.66	0.50	0.05	0.65		
GB	-0.23	-0.56	0.18	0.27	-0.56	
CA	-0.26	-0.05	-0.06	0.10	0.20	-0.14

KA: Kaolinite, HE: Hematite, AN: Anatase.
BA: Bauxite minerals (total), Bo: Boehmite
GB: Gibbsite, CA: Calcite

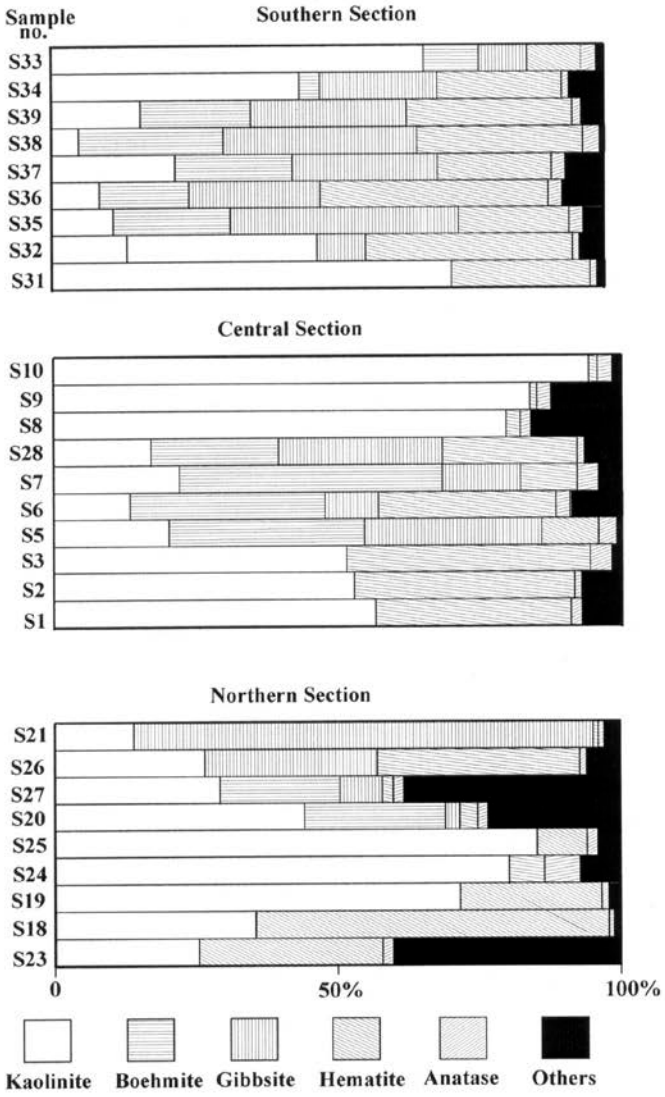

Fig.9 : Vertical distribution of minerals in the Zabira deposit.

The correlation of bauxite minerals is negative with kaolinite (Table 2). This relation is especially clear in the case of boehmite rather than gibbsite, which may indicate that boehmite formed first by leaching of silica from the kaolinite precursor and gibbsite formed later by the hydration of boehmite. A positive correlation exists between boehmite and hematite which suggests that their formation was controlled by similar factors (Valeton, 1972). On the contrary, the relation of gibbsite with hematite is negative, suggesting younger stage of formation for the gibbsite, similar in this respect to the Zabira bauxites. The overwhelming presence of boehmite over gibbsite in the Hussainiyat bauxites is demonstrated by the positive correlation of boehmite with total bauxite minerals content.

Non-bauxitic minerals:- Kaolinite, hematite, anatase and secondary calcite are the main non-bauxitic minerals in both deposits with minor amounts of alunite, gypsum and palygorskite of late epigenetic origin. Kaolinite content in the Zabira bauxite (Ki < 1.0) ranges from 6% to 43%. It is negatively correlated with hematite and bauxite minerals. In the Hussainiyat bauxite, kaolinite ranges from 17% to 60.9% of the rock constituents, revealing higher content than the Zabira bauxites, which may be explained by the higher contents of bauxite minerals and hematite in the Zabira deposits. Kaolinite is negatively correlated with all other minerals, especially with boehmite.

Hematite is the main Fe-mineral in the studied stratiform and karst bauxites, present in the pisoids, ooids and matrix. The Zabira bauxite contain higher amounts of hematite than the Hussainiyat bauxites, ranging in the former from 0.5% to 41.1% compared to 0.2-7.3% in the latter. There is no clear pattern in the vertical distribution of hematite in the Zabira bauxite profiles, but a general trend of enrichment was noticed in the lower parts. The high Fe-content in the underlying source rocks seems to have played a significant role in this respect. Hematite is positively correlated with anatase; both may precipitate under oxidizing, neutral to weakly alkaline conditions (Valeton, 1972).

In the Hussainiyat deposit, hematite content decreases as bauxite minerals increase. Source rocks contain about 4.8% hematite, depleted to 1.9% in the higher grade bauxite (LQB). This trend of continuous Fe-leaching during bauxitization suggests reducing conditions during the process. Hematite content is higher in the pisoidal-ooidal bauxites than in the massive varieties. Generally, it is more concentrated in the basal parts of the profiles. It shows positive correlation with boehmite, suggesting conjunct origin in the early stages, but negative with gibbsite; the later- formed mineral. Anatase is found in considerable quantities in the Zabira bauxites (0.3-3.5%) and in the Hussainiyat bauxites (1.2-6.0%). The variation in the anatase content is partly related to source rocks in the former. It is generally present in higher amounts at the middle of the profile. Anatase is positively correlated with boehmite in the Zabira deposits, but shows no significant correlation with any of the minerals in the Hussainiyat deposits.

Calcite is the most significant of the secondary minerals in both types of bauxite. It is found in excessive amounts in the Zabira bauxites (Ki <1.0) ranging from 0.8% to 37.6%, increasing as bauxite grade increases. In the Hussainiyat deposits it is found in lesser amounts, ranging from 0.3% to 6.4% in the bauxite samples (Ki <1.0). Calcite is found filling cavities and cracks developed during and after bauxitization.

CHEMICAL COMPOSITION AND GEOCHEMICAL ASSOCIATIONS

More than 50 samples of various grades of bauxite, bauxitic rocks and source rocks from both deposits were analyzed in this study for: SiO_2, Al_2O_3, Fe_2O_3, TiO_2, CaO, L.O.I., Zr, Cr, Ni, Co, Ga, Sr and U (Table 3). In addition, raw data from previous analysis of more than 120 specimens from the Iraqi deposits were also used (Al-Ani, 1996 and Ali, 1997). In the present study, average chemical analysis of samples from the underlying rocks was used to represent source rocks for the Zabira bauxites and average chemical composition of samples collected from the kaolinitic rocks of the neighbouring Hussainiyat Formation was used to represent source rocks for the Hussainiyat bauxites.

Table 3: Chemical analysis of various rock types in the Zabira and Hussainiyat deposits

Zabira Bauxite

Wt %	HQB	LQB	KB	BC	C	SC	SR
SiO_2	4.37	7.75	14.50	26.77	34.16	39.46	23.48
Al_2O_3	50.62	44.92	37.97	38.12	31.04	30.70	16.58
Fe_2O_3	14.90	24.18	13.16	14.61	14.95	12.89	33.87
TiO_2	1.40	2.25	1.97	2.10	3.26	2.19	0.96
CaO	0.92	2.50	8.69	1.24	1.58	0.85	8.93
LOI	24.79	16.39	21.49	15.14	13.26	12.71	14.45

ppm	HQB	LQB	KB	BC	C	SC	SR
Zr	475	2353	2168	863	437	1584	168
Cr	150	264	222	154	166	172	68
Ni	12	13	5	5	8	9	21
Co	50	74	49	34	58	35	162
U	1.9	1.6	0.3	0.4	0.4	1.3	2.9
Sr	2531	500	1944	285	313	212	218
Ga	54	98	99	73	59	59	45
ki	0.15	0.31	0.68	1.25	1.96	2.29	2.52

No. of Samples	2	9	3	2	2	6	4
Cr/ Ni	12.5	20.3	44.4	30.8	20.8	19.1	3.2
Co/ Ni	4.2	5.7	9.8	6.8	7.3	3.9	7.7

… continue table 3

Hussainiyat Bauxite

Wt %	LQB	KB	BC	C	SC	SR
SiO_2	12.75	21.00	32.23	40.93	41.59	44.49
Al_2O_3	62.94	55.43	45.08	38.25	34.40	32.95
Fe_2O_3	1.91	1.45	2.33	2.17	3.98	4.79
TiO_2	2.54	2.59	2.10	2.13	2.36	2.18
CaO	1.18	1.14	0.34	0.98	1.49	0.37
LOI	16.17	16.74	15.74	13.90	14.13	13.42

ppm	LQB	KB	BC	C	SC	SR
Zr	1477	1689	1331	1002	1022	652
Cr	214	108	88	80	162	201
Ni	30	21	30	45	54	59
Co	32	20	16	33	40	36
U	11.5	7.4	5.6	5.0	4.7	4.0
Sr	51	87	76	70	103	96
Ga	238	252	144	94	75	50
ki	0.36	0.68	1.27	1.90	2.15	2.40

No. of Samples	11	29	28	45	38	11
Cr/ Ni	7.1	5.1	2.9	1.8	3.0	3.4
Co/ Ni	1.1	1.0	0.5	0.7	0.7	0.6

Major oxides:- Apart of a few secondary minerals, the mineralogy of the studied bauxites is relatively simple and the geochemical association of major oxides can be easily traced to mineral composition. Silica, when present, is linked to kaolinite in all samples except non-bauxitic source rocks where silt- size quartz shares some of the silica. Alumina is shared mainly between bauxite minerals, when present, and kaolinite. Small amounts of alumina are incorporated in secondary alunite in a few samples, especially found in the Zabira bauxites. Iron is mainly present as hematite, and minor amounts in goethite or pyrite; rarely found in both deposits. Titanium is present as anatase, which is formed as a result of alteration of primary Ti-minerals, such as rutile and illmenite, during bauxitization (Valeton, 1972). Minor amounts of rutile may resist alteration and remain in these rocks as a rare residual mineral. Calcium is linked to secondary calcite. It is however, of primary origin in source rocks of the Zabira bauxites (Marrat Formation). Some secondary gypsum share minor amounts of Ca too. The loss in weight upon ignition at 1000 C^o (L.O.I) is a combination of H_2O loss from bauxite minerls and kaolinite , as well as CO_2 loss from calcite .

Trace elements:- Correlation coefficients (Table 4) show that Zr, Cr and Ga are mainly related to boehmite in both deposits. On the other hand Sr is positively correlated with gibbsite which supports the suggestion that gibbsite formed later, probably at the same time when calcite (Sr – host) was introduced to the system . Strontium is also related to calcite as shown in the Hussainiyat samples.

Table 4: Trace elements correlation coefficients

Zabira (16 samples)

	Co	Ni	Sr	Zr	Cr	U	Ga
KA	-0.43	-0.22	0.03	0.02	-0.20	-0.38	-0.05
HE	0.95	0.10	-0.48	-0.35	-0.14	0.12	0.07
AN	0.35	0.25	-0.43	0.51	0.30	0.70	0.43
BA	-0.15	0.07	0.41	0.22	0.16	0.40	-0.13
CA	-0.23	0.09	-0.18	-0.00	0.24	-0.22	0.20
BO	0.10	0.19	-0.12	0.64	0.68	0.53	0.69
GB	-0.21	-0.07	0.46	-0.26	-0.34	-0.11	-0.62
Co	1.00	0.08	-0.45	-0.25	-0.09	0.22	0.13
Ni	0.08	1.00	-0.67	0.01	0.42	0.07	0.27
Sr	-0.45	-0.07	1.00	0.09	-0.13	-0.20	-0.13
Zr	-0.25	0.10	0.09	1.00	0.66	0.44	0.57
Cr	-0.09	0.42	-0.13	0.66	1.00	0.20	0.73
U	0.22	0.07	-0.20	0.44	0.20	1.00	0.36
Ga	0.13	0.27	-0.13	0.57	0.73	0.36	1.00

Hussainiyat (28 samples)

	Co	Ni	Sr	Zr	Cr	U	Ga
KA	-0.49	0.31	0.03	-0.61	-0.73	-0.32	-0.35
HE	-0.10	-0.48	-0.29	0.07	-0.10	-0.48	-0.66
AN	0.07	0.14	0.04	0.16	0.00	0.38	0.54
BA	0.47	-0.39	-0.09	0.70	0.74	0.31	0.41
CA	0.15	0.33	0.39	-0.28	0.09	0.01	-
BO	0.19	-0.63	-0.42	0.54	0.37	-0.10	0.38
GB	0.27	-0.37	0.43	0.08	0.35	0.47	0.31
Co	1.00	-0.22	-0.24	0.24	0.63	0.52	-
Ni	-0.22	1.00	0.62	-0.61	-0.30	0.21	0.69
Sr	-0.24	0.62	1.00	-0.26	0.01	-0.08	0.61
Zr	0.24	-0.61	-0.26	1.00	0.55	0.23	0.87
Cr	0.63	-0.30	0.01	0.55	1.00	0.34	-0.77
U	0.52	0.21	-0.08	0.23	0.34	1.00	0.66
Ga	-	0.69	0.61	0.87	-0.77	0.66	1.00

Uranium behavior is different in the two deposits. It is associated with boehmite in Zabira and with gibbsite in the Hussainiyat. This may suggest epigenetic enrichment of uranium in the karst bauxite, which could have taken place during hydration of boehmite to form gibbsite, especially in the upper parts of the bauxite profiles. Uranium and gallium are positively correlated with each other and both are positively correlated with anatase, suggesting enrichment, as residual elements, during bauxitization.

Cobalt association is also variable; it is related to hematite in the Fe-rich Zabira bauxites, which illustrates the common geochemical affinity of Co to the iron family. On the other hand, Co is associated with the bauxite minerals in the Fe-poor Hussainiyat bauxites, suggesting incorporation in bauxite ooids and pisoids. Nickel is associated with kaolinite and calcite in the karst bauxites of Hussainiyat. Part of Ni was retained in the mother rock (kaolinite) whereas the mobilized part of Ni was incorporated with secondary calcite in epigenetic stages. The trace elements Ga, Zr, Cr, Co and U form a geochemical group with similar mineral associations in the Hussainiyat bauxites. They are enriched in the bauxites relative to source rocks. The group can be separated into two subgroups: the first includes Ga and Zr which are associated with boehmite as residual elements. The second includes Co and U which are associated with gibbsite as a later stage of enrichment, mostly took place under reducing conditions.

A second geochemical group was identified in the Hussainiyat bauxites which includes Ni and Sr and seems to have been controlled by epigenetic processes. Both elements are negatively correlated with the bauxite minerals. In the Zabira bauxites, Ga, Zr, Cr and U represent a geochemical group associated with boehmite. Cobalt is related to hematite and Sr is related to gibbsite.

GEOCHEMICAL EVOLUTION

In order to study the development in chemical composition in the various stages of bauxitization, average chemical composition of each type of rock (as defined by Valeton's, 1972 classification) was derived and compared, taking the composition of source rocks as starting point. In this way it was possible to follow all modifications on the chemical composition of source rocks during various stages of bauxitization (Figs. 10-22).

Major oxides:- The behavior of alumina and silica is discordant in both deposits. The former increases and the latter decreases as bauxitization intensity advances. The Hussainiyat samples are richer in alumina and silica as compared to Zabira samples , which can be attributed to the original composition of source rocks in the two deposits . The Zabria source rocks are remarkably rich in iron oxide, which is, though highly depleted in the first stage of bauxitization, remains higher than the Hussainiyat samples throughout all stages of bauxitization. The main phase of iron depletion have taken place in the early stage of bauxitization , which may suggest reducing conditions at the beginning (Petersen , 1971) . No signficant changes were noticed in Fe_2O_3 concentration in the later stages except some Fe – enrichment in the (LQB) of the Zabira bauxites.

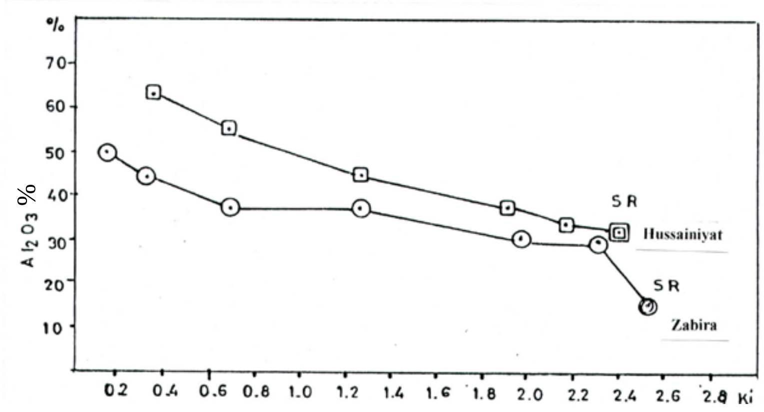

Fig. 10: Alumina distribution

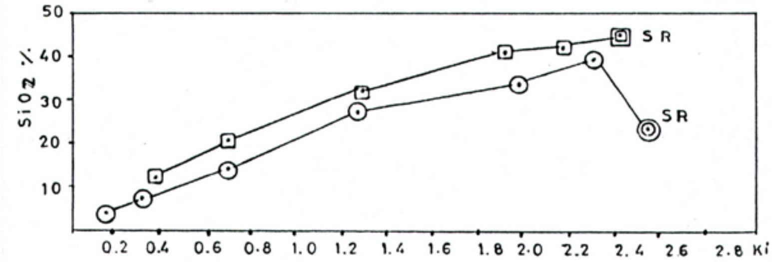

Fig. 11: Silica distribution

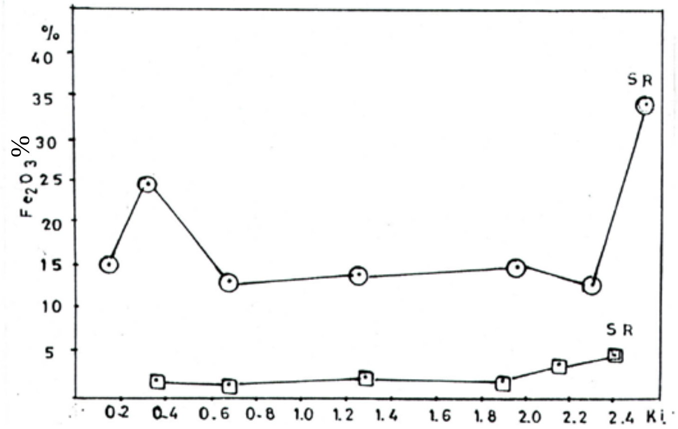

Fig. 12: Iron oxide distribution

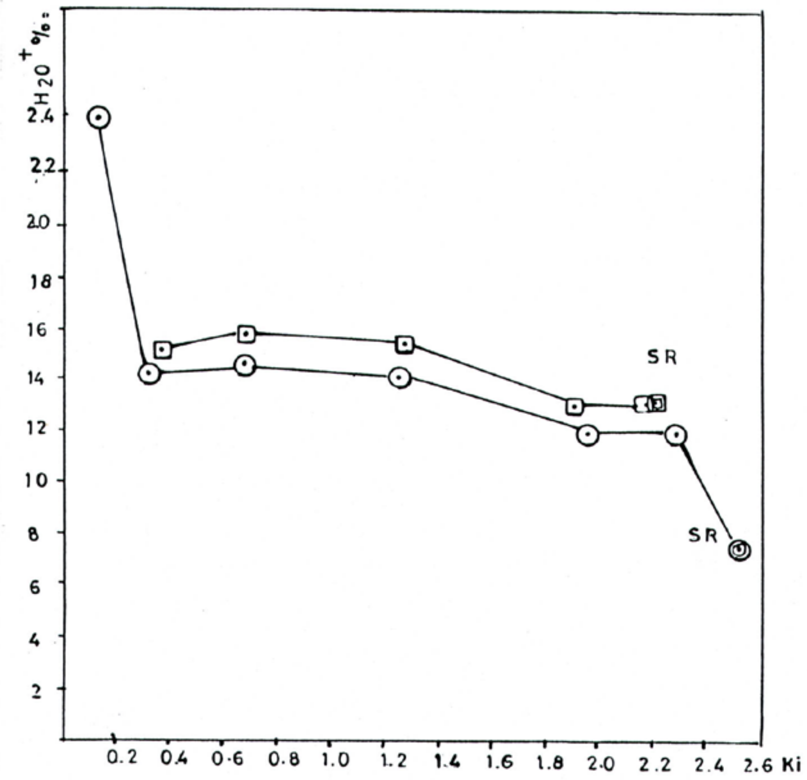

Fig. 13: Water distribution

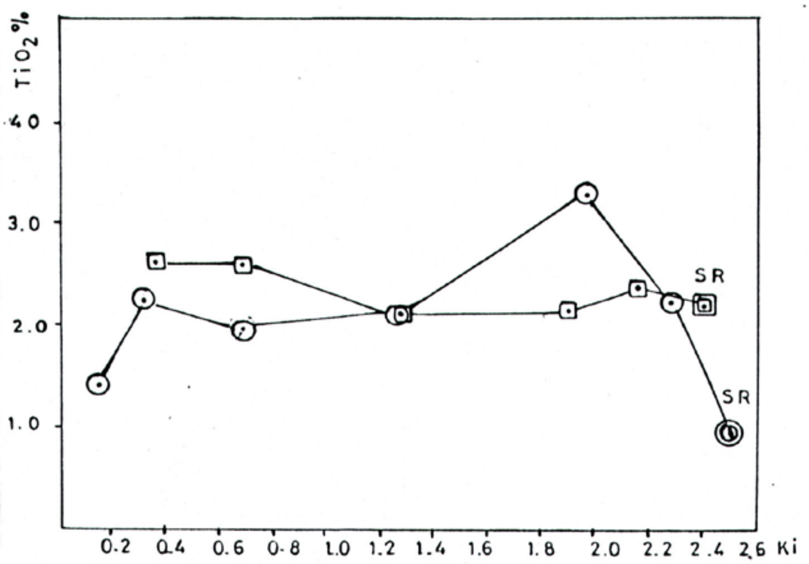

Fig. 14: Titania distribution

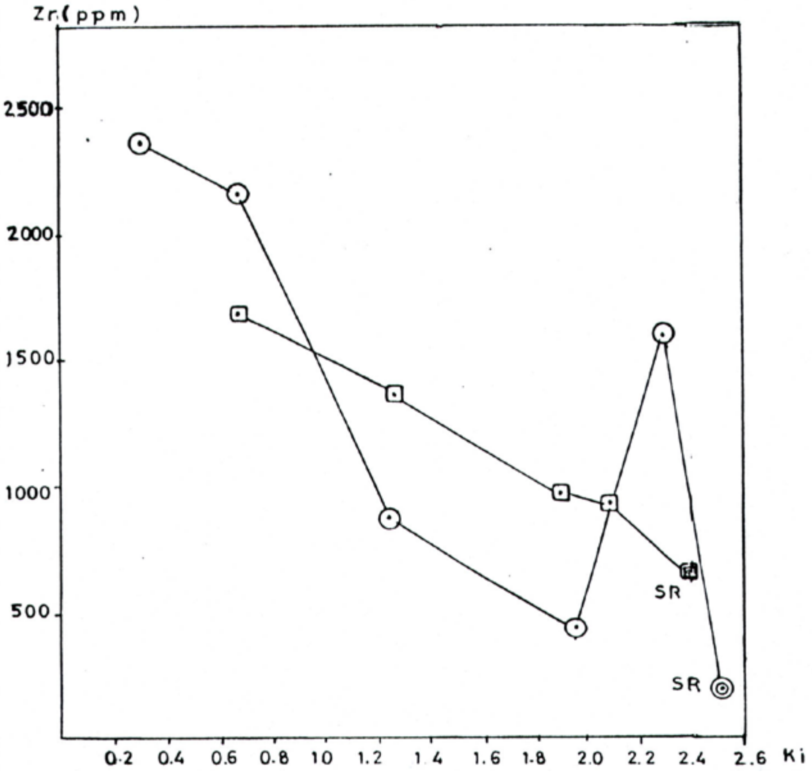

Fig. 15: Zirconium distribution

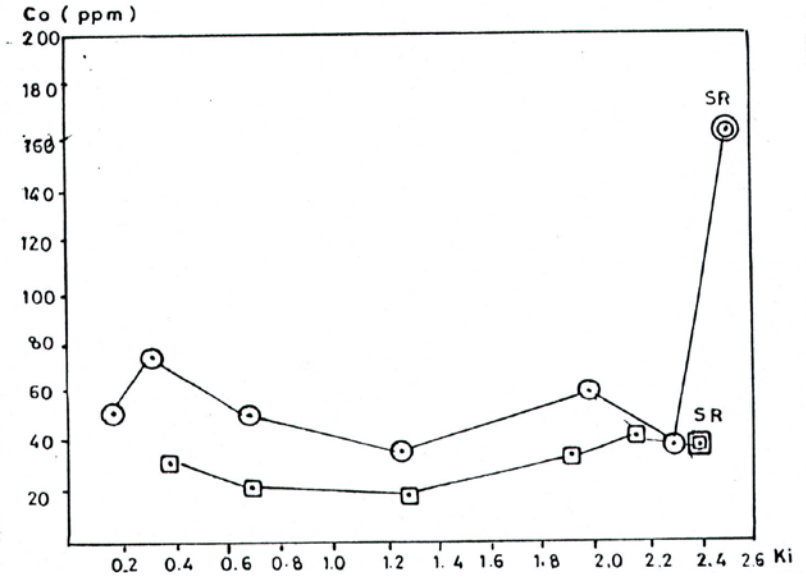

Fig. 16: Cobalt distribution

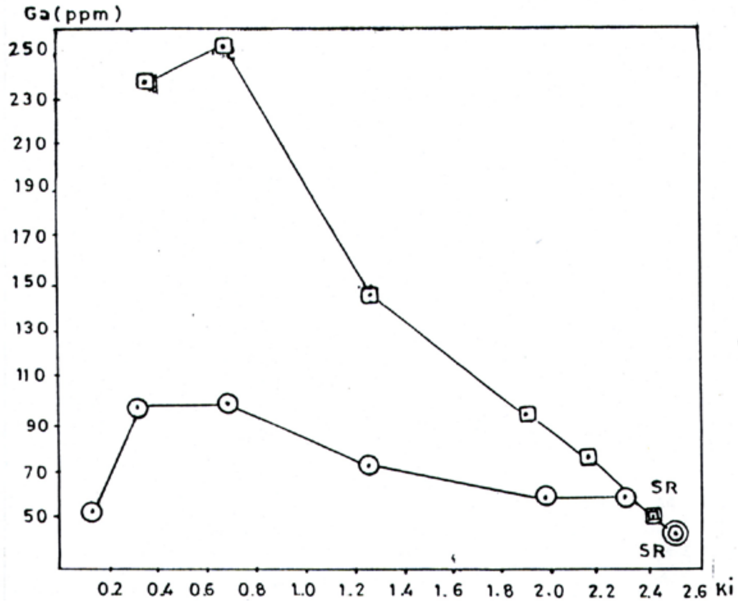

Fig. 17: Gallium distribution

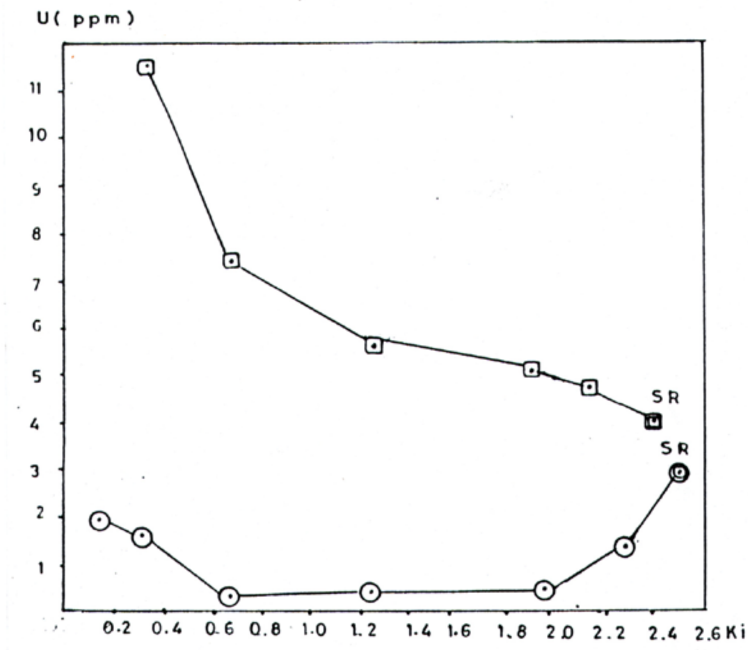

Fig. 18: Uranium distribution

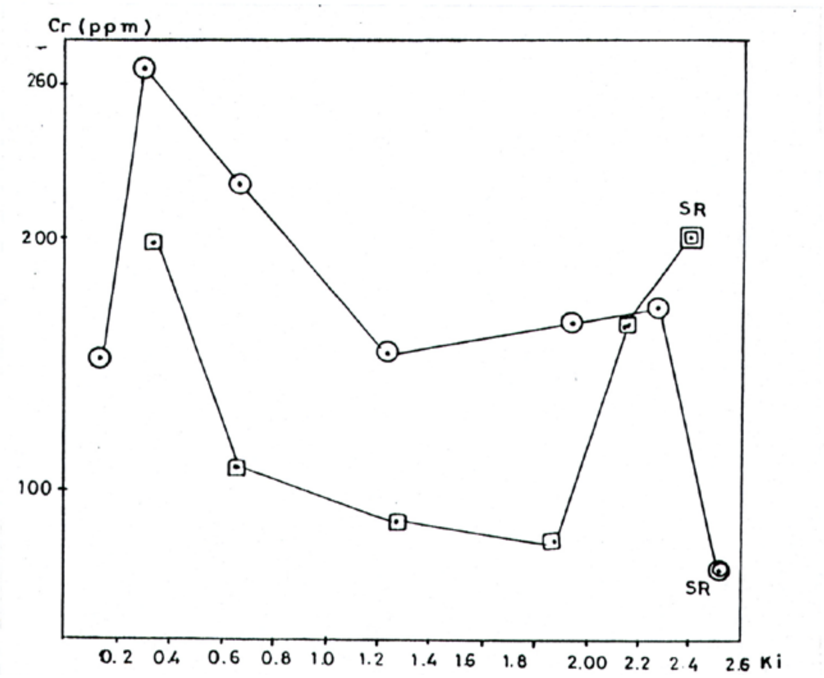

Fig. 19: Chromium distribution

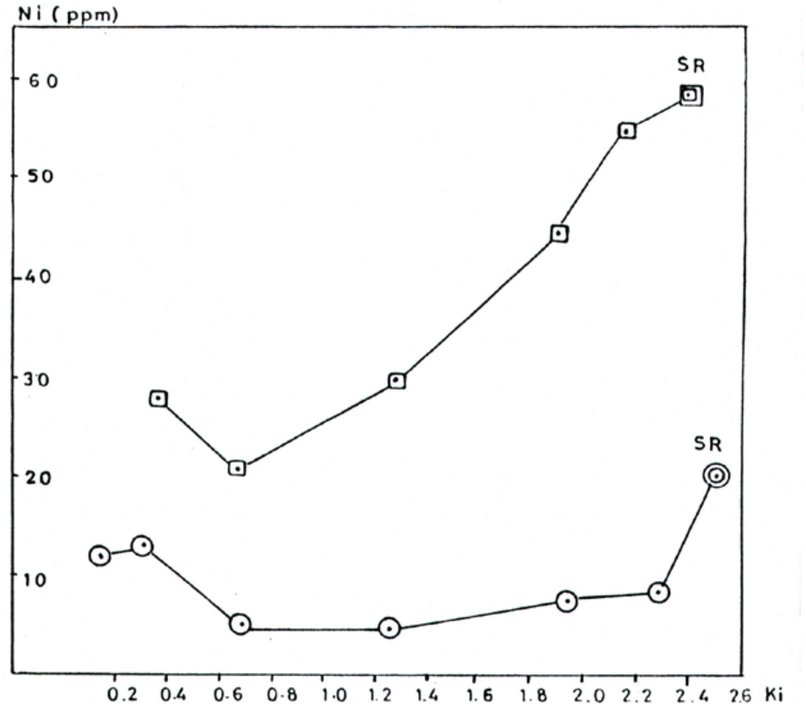

Fig. 20: Nickel distribution

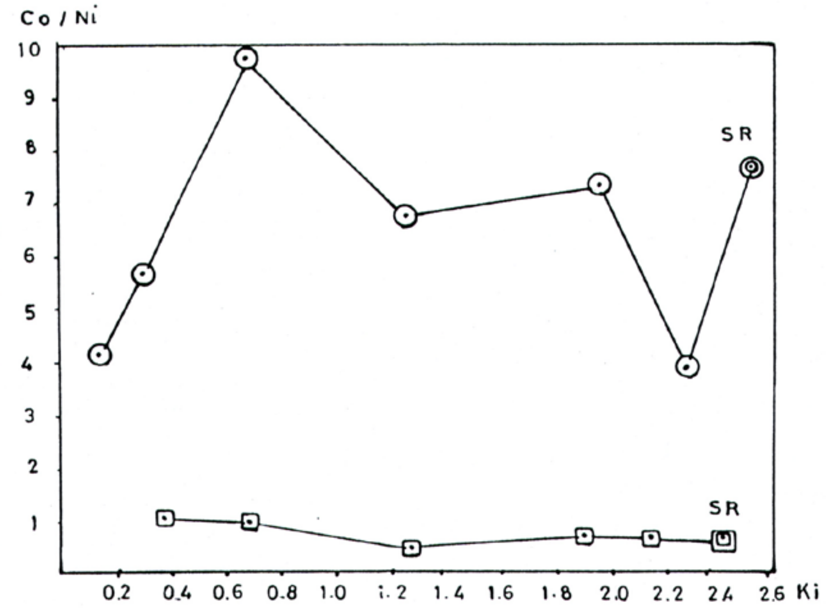

Fig. 21: Co / Ni distribution

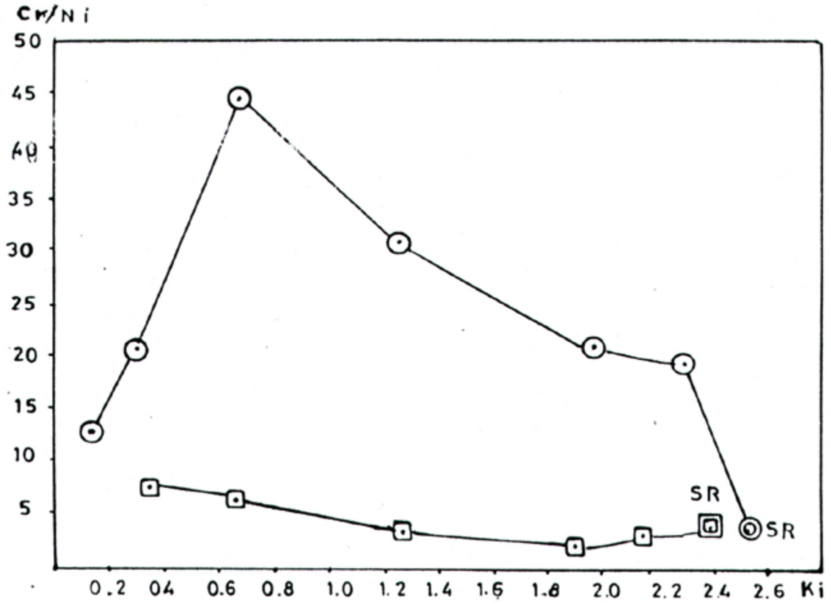

Fig. 22: Cr / Ni distribution

Titania behaves in a similar way in both deposits . It is generally , but not significantly , enriched as bauxitization proceeds , especially when it is compared with source rocks as the case in the Zabira deposit .There is a noticeable increase in the Ti content in early stages of bauxitization in the Zabira deposit which reflects initial dissolution of the easily soluble carbonates present in source rocks and enrichment of the Ti – bearing minerals. This increase is also noticed in the alumina and silica trends in this deposit.

Water content increases as bauxitization proceeds in both deposits, which is explained by the continuous increase in bauxite minerals. The increase is gradual and the trend is concordant in both deposits, except in the final bauxitization stage which produced(HQB)in the Zabira bauxites , where a sharp increase in H_2O^+ content can be noticed and can be explained by the sharp increase in gibbsite content in this type of bauxite .

Trace elements:-The distribution of trace elements show marked differences between stratiform and karst bauxites on one hand and among the various rock classes within each type, on the other hand. The Zabira bauxites are richer in Cr, Co and Sr, whereas the Hussainiyat bauxites are richer in Ni, Ga and U. These differences may be attributed partly to source rock composition and also to the differences in physical and chemical conditions prevailed during bauxitization in the two deposits.

Some trace elements were enriched as bauxitization proceeded, especially those associated with ultrastable minerals like Zr, which is present as zircon in both deposits, or those which have geochemical affinity towards Al and behaved in a similar manner during bauxitization, such as Ga, as well as elements enriched by diagenetic or epigenetic processes such as Sr.

Compared to source rocks, Zr, Cr, Ga and Sr were enriched in the Zabira stratiform bauxite during bauxitization whereas U, Co and Ni were depleted. On the other hand, Zr, Ga and U were enriched in the Hussainiyat karst bauxite relative to source rocks, whereas Cr, Ni and Co were depleted. Hence, both deposits show Ga and Zr enrichment and Co and Ni depletion after bauxitization. The other trace elements (U, Cr and Sr) behaved differently in the two deposits.

Zirconium enrichment during bauxitization is explained by its presence as zircon, the ultrastable and residual mineral, whereas gallium enrichment is explained by its strong geochemical affinity towards Al (Goldschmidt, 1950). The behavior of Cr is different in the two deposits. The original content of Cr in the Hussainiyat source rocks is higher than that in the Zabira source rocks, but it was sharply depleted in the former in the early stage of bauxitization, whereas it was significantly enriched in the latter in the early stage. In the first case it is expected that Cr, loosely attached to kaolinite or to organic matter, was mobilized as bauxitization commenced. In the second case, as the easily soluble carbonates of the source rocks were dissolved in the early stage, leaving most of the Cr-bearing kaolinites unaltered. However, both deposits show gradual Cr increase in the advanced stages of bauxitization. The depletion of Cr in final stage in the Zabira bauxites is explained by the transformation of boehmite to form gibbsite by hydration of the former, which resulted in the dilution of many elements beside Cr. Cobalt and nickel depletion in both deposits may be related to partial leaching of iron oxide during bauxitization. Both elements are part of the iron geochemical family.

The difference in uranium behavior is explained by its geochemical characteristics; it tends to be mobilized under oxidizing conditions, which were apparently dominant in the Zabira bauxites. Moreover, part of uranium may have been leached from these stratiform bauxites by epigenetic processes, where slightly alkaline and oxidizing conditions prevailed, evidenced by the precipitation of calcite. On the other hand, uranium was successively enriched in the Hussainiyat deposits as bauxitization proceeded, which can be explained by the reducing conditions prevailed during bauxitization, evidenced by the common presence of organic and plant remains in the karst deposits. Strontium is one of the highly mobile elements in nature. It is expected that Sr was leached away of the system in the early stages of bauxitization, similar to Ca. However, it was introduced again to the bauxite deposits during epigenesis where it was associated mainly with calcite. Hence, more Sr was found in the Zabira bauxites, as it was more affected by epigenetic processes and contains more calcite as a secondary mineral.

The Co/ Ni ratio is highly different in both deposits. It is about eight times higher in the Zabira stratiform deposits than the Hussainiyat karst deposits. The high Co/Ni ratio in the former is due to the low Ni content, inherited from source rocks. However, the Co/ Ni ratio in the Hussainiyat bauxites is within the values generally reported for sedimentary rocks, which are less than 1.0. The Cr/ Ni ratio also varies in the two deposits**.** It is higher in the Zabira bauxites, although source rocks in both deposits show close Cr/ Ni values. Nickel depletion during bauxitization in the Zabira deposits is the main reason for the higher Cr/ Ni ratio in this deposits.

CONCLUSIONS

- Bauxitization in the Zabira and Hussainiyat deposits went through several stages, each had its impact on the mineral and chemical development of these deposits. Diagenetic and epigenetic modifications have further influenced textural and mineralogical characteristics of the bauxite deposits.
- The wet and warm climatic conditions, dominated the region at that time (Aptian - Albian) were occasionally interrupted by short periods of seasonal aridity, which left its signature on the bauxite profiles in both deposits.
- Source rocks composition have played an important role in determining chemical and mineralogical composition of the studied bauxites. In addition, the different mode of formation (type) of the two deposits have induced further

differences, caused by variation in Eh, pH, drainage, leaching intensity, etc., during the various stages of bauxite formation.

- Framework textural constituents (pisoids and ooids) are better developed in the Zabira stratiform bauxites relative to the Hussainiyat karst bauxite, suggesting higher maturation levels in the former, induced by more leaching and colloids formation.
- The studied karst bauxites are dominated by boehmite, whereas the stratiform bauxites are dominated by gibbsite. Petrographic observations show that boehmite formed first accompanied by hematite and anatase. Gibbsite formed later, most probably from the hydration of boehmite.
- Iron – rich source rocks and subaerial oxidizing conditions gave rise to ferruginous bauxites in the Zabira stratiform deposits. In contrast, the Hussainiyat karst deposits are relatively poor in Fe. They were developed under generally reducing conditions, and were derived from relatively Fe-poor source rocks.
- Compared to source rocks, Fe, Ni and to some extent Co were depleted during bauxitization in both deposits, whereas Ga and Zr were enriched together with alumina. The former group is more mobile as compared to the residual character of the latter group. Gallium follows Al, whereas Zr is present in the ultrastable zircon.
- Oxidation conditions of bauxitization in the Zabira deposits led to the depletion of uranium. In contrast, uranium was enriched, relative to source rocks, in the Hussainiyat deposits. Reducing conditions in the latter hindered uranium mobilization. For the same reason, Cr was relatively enriched, as a residual element in the Zabira bauxites and was depleted in the Hussainiyat bauxites.
- The Hussainiyat karst bauxites have suffered less diagenetic and epigenetic modifications in texture, mineralogy and chemical composition relative to the Zabira stratiform bauxites. Reslilication is common in the upper parts of the Zabira deposits. It took place in the early stages of diagenesis under semi-wet conditions. Calcite, alunite and gypsum were introduced later in both deposits, filling cracks and fractures, under arid or semi-arid conditions. Strontium enrichment took place during these epigenetic stages in association with secondary gypsum and calcite. Calcrete formed in the final stages, capping the bauxite profile in some parts of the Zabira deposits.

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