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Study of Trace and some Rare Earth Elements of Hussainiyat Karst Bauxite, Iraq: Leaching Efficiency

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ABSTRACT

Karst-filling bauxite deposits of early Cretaceous age are widespread in Hussainiyat area to the northeast of Al- Rutba city within the Iraqi Western Desert. Karstified carbonate host rocks represented by the dolostone of the Ubaid Formation (Early Jurassic) contain bauxite lenses preserved inside the karst together with kaolinitic bauxite, kaolinitic clays and sands belonging to the lower clastic unit of the overlying Hussainiyat Formation (Lower-Middle Jurassic). Normative mineralogy reveals that boehmite (up to 47%) and to a lesser extent gibbsite (up to 19%) are the main bauxitic minerals with kaolinite (28%), hematite (2.8%), anatase (up to 4.1%) and calcite (0.4%) as the main accessory minerals. Plots of chemical data against increasing grade of bauxitization show that Al, Ti, Zr, Nb, V, Hf, Th, U, Ga, Cr, Co, Cu, As and W were immobile and highly enriched, whereas SiO_2, Fe_2O_3, CaO, K_2O, Na_2O, MgO, MnO, Ni, Mo and Gd were mobilized and depleted. Variation diagrams of certain immobile elements indicate that bauxite precursor might be shale derived from acidic granodiorite or its metamorphosed equivalent.

Keywords: Karst bauxite, trace elements, Hussainiyat, Iraq.

دراسة العناصر الأثرية وبعض العناصر الارضية النادرة لرواسب بوكسايت الحسينيات الخسفي/العراق: كفاءة الخلب

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الملخص

تنتشر رواسب البوكسايت الخسفي والتابعة للعصر الطباشيري في الصحراء الغربية العراقية في منطقة الحسينيات الواقعة شمال شرق مدينة الرطبة. إن الصخور المضيفة هي الصخور الكاربوناتية المتخسفة السطح والمتمثلة بصخور الدولوستون التابعة لتكوين عبيد (الجوراسي المبكر) والحاوية على عدسات من صخور البوكسايت محفوظة داخل الخسفات يصاحبها صخور بوكسايت طيني، اطيان غنية بالحديد، أطيان كاؤولينية وصخور رملية تابعة للوحدة الفتاتية السفلى لتكوين الحسينيات (الجوراسي الاسفل–الاوسط).

بينت نتائج التحليل الكمي للأطوار المعدنية إن معدن البوهيمايت (يصل إلى ٤٧%) وبدرجة أقل معدن الجبسايت (يصل الى ١٩%) هي المعادن البوكسايتية الرئيسية يصاحبها معادن اضافية تشمل الكاؤولينايت (٢٨%)، الاناتيز (٤.١%)، هيمتايت (٢.٨%) والكالسايت (٠.٤%).

أوضحت نتائج تباين تراكيز العناصر مع زيادة شدة عملية البكستة ان العناصر Zr, Ti, Al, W, As, Cu, Co, Cr, Ga, U, Th, Hf, V, Nb كانت غير متحركة فازدادت تراكيزها، بينما عناصر Gd, Mo, Ni, MgO, Na_2O, K_2O, CaO, Fe_2O_3, SiO_2 قد تحركت ونقصت تراكيزها. أشارت مخططات التباين لعناصر أثرية معينة وغير متحركة الى ان الصخور التي تحولت الى بوكسايت تعود لصخور طفل مشتقة من صخور الكرانودايوريت الحامضية أو صخورها المتحولة.

الكلمات الدالة: بوكسايت خسفي، عناصر أثرية، الحسينيات، العراق.

INTRODUCTION

Karst-related bauxite deposits were discovered in 1990 in Hussainiyat area about 65 km northeast of Rutba city (Fig. 1) within the Iraqi Western Desert by the geologists of the Iraqi Geological Survey (GEOSURV) during their extensive investigations in the area (Mustafa, 1991). These bauxite deposits are found to occur as lenses preserved inside fossil karsts developed within the carbonate (dolostone) beds of the Early Jurassic Ubaid Formation. Kaolinitic clay with flint appearance was considered to be the potential protolith of the Hussainiyat bauxite deposits (Mustafa *et al.*, 1997 and Al-Bassam, 2005).

Proposed models regarding karst-related bauxite deposits emphasize in situ alteration and accumulation of residual components from the leaching of either the karst-host limestone and/or the sediments filling the karst especially in case of deep sinkholes where the resulted bauxite material may remain in place after the leaching of the source rocks (Bardossy, 1982, Valeton *et al.,* 1987, and D'Argenio and Mindszenty, 1995).

There are numerous geochemical studies of many bauxite deposits in the world (e.g., Kolesnikov *et al.,* 1969, Parshakov *et al.,* 1976, Boski and Herbosch, 1990, Boulange *et al.,* 1996, MacLean *et al.*, 1997, Hill *et al.,* 2000, Kurtz *et al.,* 2000, Ozturk *et al.,* 2002, Abedini *et al.,* 2008, Rafieli *et al.,* 2008, Calagari *et al.,* 2010, Esmaeily *et al.,* 2010, and Ayorinde, 2011). Some of these studies had used successively the dispersion patterns of trace and rare earth elements in bauxites as indicators to the type of the deposit and their precursor and to give important clues to elucidate their geochemical characteristics. The remainders were concerned with the distribution and mobile/immobile behavior of these elements during processes involved in the complex phenomenon of bauxitization.

In this paper, geochemical analysis of 11 major and 25 minor, trace and some rare earth elements was carried out, in an attempt to identify the immobile elements and apply their variation to trace the bauxite precursor and to follow mineralogical and geochemical evolution with increasing grade of bauxitization.

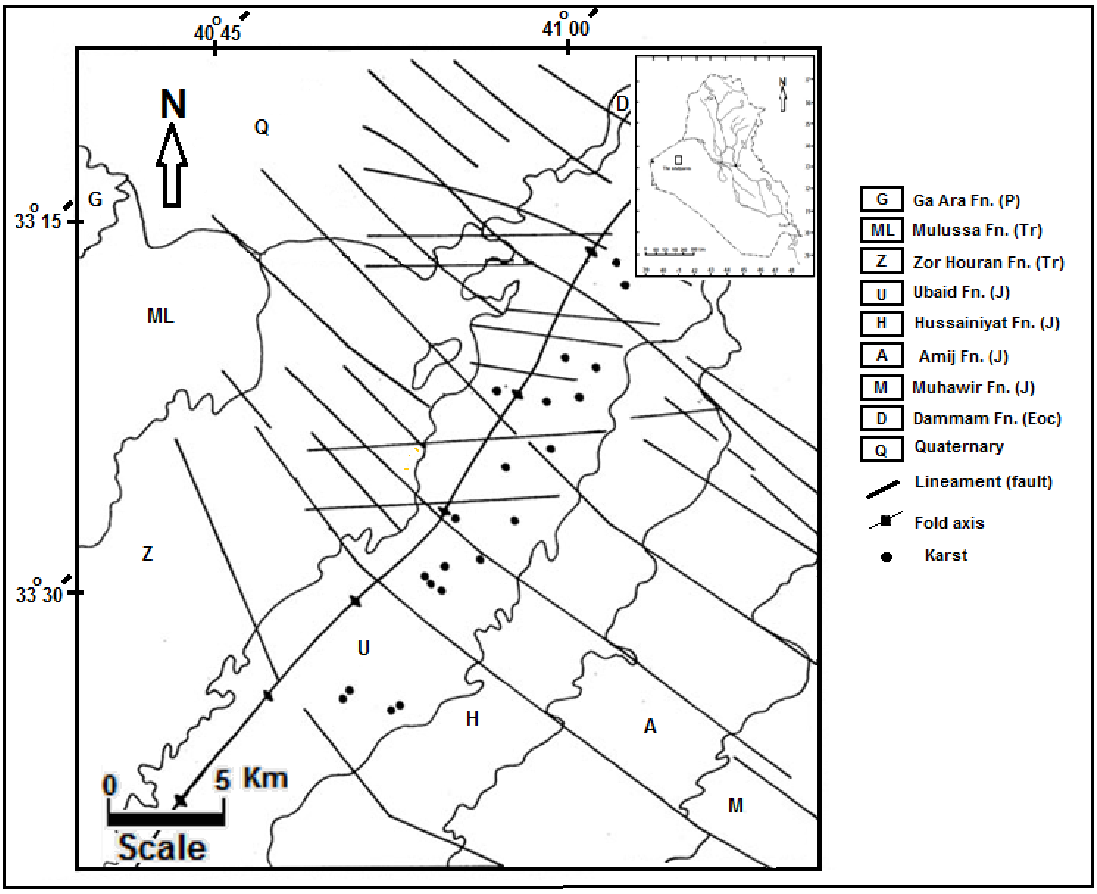


Fig. 1: Location and Geological Map of the Studied Area, Taken from Al-Bassam, 2005. with Slight Modification.

GEOLOGICAL SETTING

The Iraqi Western Desert is located within the stable shelf that represents the external edge of the Nubia-Arabian Platform. It is characterized by its thin sedimentary cover that was affected by many vertical faults resulted from the vertical movements in the area. Rutba Uplift is the main structure in the area with the Ga′ara high and Horan anticlinorium forming its upper part (Qassir *et al.,* 1992). The principal rock formations in the area are: Zor Hauran Formation (Triassic), Ubaid Formation (Jurassic) and Hussainiyat Formation (Jurassic) (Fig. 1).

Early Cimmerian Orogeny took place during Late Triassic-Early Jurassic and as a result a basin was formed between the Ga′ara and the Horan masses that had accommodated the deposits of the Jurassic formations. Deposition of the Jurassic formations is accompanied by many repeated Epiorogenic pulses of the Rutba Uplift causing successive events of transgression and regression of the Jurassic Sea. This was inferred from the cyclic characteristic of the sediments of the Jurassic formations that are composed of two main units; lower clastic unit and upper carbonate unit. Ubaid Formation, the host to the Hussainiyat karst bauxite deposits, is the oldest Jurassic formation (Liassic-Bajocian) in the area, deposited in Horan Basin and consists of dolomite, marl and dolomitic marl of fluvial and tidal-supratidal environment. Following the deposition of Ubaid Formation, a long period of sea regression occurred exposing the surface of the dolomite of Ubaid Formation to karst weathering (Qassir *et al.,* 1992). As a result, undulations and depressions were formed as a sign of the initiation of karstification that had not developed deeply in this early stage due to the deposition of the other Jurassic formation (Mustafa *et al.,* 1994).

During Late Jurassic-Early Cretaceous, the area was affected by the Late Cimmerian Orogeny (collision of Arabian-Turkish-Iranian plates) and consequently many faults and anticlines were formed and had led to a relative uplift of the Horan Basin marking a second major stop of sedimentation in the area. This was accompanied by deep erosion leaving parts of the surface of carbonate of Ubaid Formation to expose again to deep weathering furnished by contemporaneous change in climatic conditions towards wet and warm tropical climate. Accordingly, karstification continued in deepening while sediments of the clastic unit of the Hussainiyat Formation were depositing at the same time in the area and filled the karsts (Mustafa *et al.,* 1994). This was followed by bauxite formation within the karsts and deposition of the sediments of the Al-Ghar Formation (Miocene) as the upper most layers that preserved the bauxite. The last event was erosion and opening of the karsts that exposes the bauxite deposits to surface.

DEPOSIT CHARACTERISTICS

The karsts hosting the bauxite deposits were reported to occur strictly in an area lies at the conjunction of Wadi Hauran and Wadi Hussainiyat (Fig. 1), where maximum intersections of lineaments, fractures and major faults exist (Al-Ameri, 1978, Mustafa, 1991, Qassir *et al.,* 1992, Mustafa *et al.,* 1994, and Mustafa *et al.,* 1995). (Etabi *et al.*, 1984, and Mehdi *et al.,* 1993) have pointed to the occurrence of this karstification phenomenon within the exposed parts of the Ubaid Formation only and stressed on its absence elsewhere within the unexposed dolostone of the Ubaid Formation and also underneath the Hussainiyat Formation. A detailed study by(Mustafa and Jibrail, 1996) described these karsts as deep paleo sinkholes extending parallel to the general trend of the faults in the area (NW-SE), and exhibiting variable shapes (circular, elliptical and arc), variable sizes (<0.01-1.25 km^2) and variable depths (4-105m). They suggest five stages for the complete development of karstification and bauxitization in the area. The layers of the karst-filling sediments had inherited the general shape of the karst and appear concaving upwards (Fig. 2). They are characterized by fining upwards cyclicity and show an internal layering divided by (Mustafa *et al.*, 1994) into three distinct zones (A, B and C) according to their lithology. Zone (C), the lower zone and is up to 35m thick, consists of white quartzose sandstone (bottom) followed by multi-colored kaolinitic clay.

Zone (B), the bauxitic zone and is up to 70m thick, and consists of white and multi-colored sandstone (bottom) followed by bauxitic clay. This is followed upwards by lenses (1-40m thick) of white-pink oolitic and pisolitic bauxites with occasional calcite veins followed by white-pink bauxitic clay and finally kaolinitic clay with flint containing plant remains at the top. Zone (A), the overburden zone up to 85m thick and consists of multi-colored quartzose clayey sand layer (bottom), followed by dark red-brown clay layer containing quartzose sandstone and enclosing two horizons of brecciated iron-oxide minerals. This is followed by a layer of yellow quartzose sands cemented by kaolinitic clay and topped with fine red clay mottled by greenish gray color. These sediments are unconformably underlain and overlain by Ubaid Formation (Lower Jurassic) and Ghar Formation (Middle Miocene) respectively.

There is no clear cut fossil evidence regarding the age of these deposits. It was suggested as Jurassic by (Al-Atia and Saadalla, 1996) and early Cretaceous by Mustafa et al. (1996) based on geological and paleoclimatic observations. On the other hand, (Al-Rawi *et al.,* 1996) considered it Eocene based on palynological analysis. Despite the above contradicting opinions on the age of bauxitization event, early Cretaceous age (Aptian - Albian) suggested by (Al-Bassam, 2005) seems to be the most widely accepted.

Mineralogy and textures of the Hussainiyat bauxites were well-described by many previous studies (Mustafa *et al.,* 1995, Mustafa *et al.,* 1997, Al-Bassam, 2005 and Tobia, 2005). These studies have shown that Hussainiyat bauxites are dominantly piloids and ooids with some pisoids and in places massive varieties of cryptocrystalline bauxite are also present. Mineralogically, they have shown that the Hussainiyat bauxites consist mainly of boehmite, gibssite, kaolinite, hematite, anatase and secondary calcite based on qualitative (XRD) identification and on quantitative mineralogical estimation (Al-Bassam, 2005).

MATERIALS AND METHODS

In this study three representative bauxite samples were selected (BS.1, BS.2 and BS.3). Chemical analysis of the bulk rock for 36 major, trace and rare earth elements was carried out using Siemens SRS 303 X-ray fluorescence spectrophotometer at the Geological Institute of Bonn University. Mineralogical examination was conducted by applying normative method estimation following the procedure proposed by (Nyobe, 1991) where applicable.

RESULTS AND DISCUSION

Chemical Composition

The results of 11 major element analyses of the studied bauxite samples are presented in Table 1. The main major dominant chemical constituents are Al_2O_3, SiO_2 and H_2O (i.e., loss on ignition LOI, which was assumed chiefly H_2O with no other volatiles). The Al_2O_3 and SiO_2 show a wide range of variation with Al_2O_3 ranges from 39.2-63.19 wt% and SiO_2 content ranges from 12.94 to 37.5 wt% and the LOI value ranges from 16.7 to 18 wt%. The Fe_2O_3 content in these samples is relatively low ranges from 0.56 to 2.76 wt %, while TiO_2 content shows a considerable amount ranges from 2.84 to 4.11 wt%. CaO content ranges from 0.19 to 1.39 wt%, while MgO, MnO, Na_2O, K_2O and P_2O_5 are extremely low (< 1 wt %).

The results of chemical analysis of 25 minor, trace and some rare earth elements (Table 1) show that Zr, V and Cr are the most abundant trace elements in the analyzed samples. The value of Zr ranges from 1531 to 1905 ppm, V content ranges from 372 to 1154 ppm and the Cr concentration ranges from 116 to 300 ppm. Considerable content of Nb, La, Ce and Ga can also be noticed, with their concentrations reach up to 163, 146, 139, 114 ppm respectively. The remaining analyzed trace elements are generally <100 ppm.

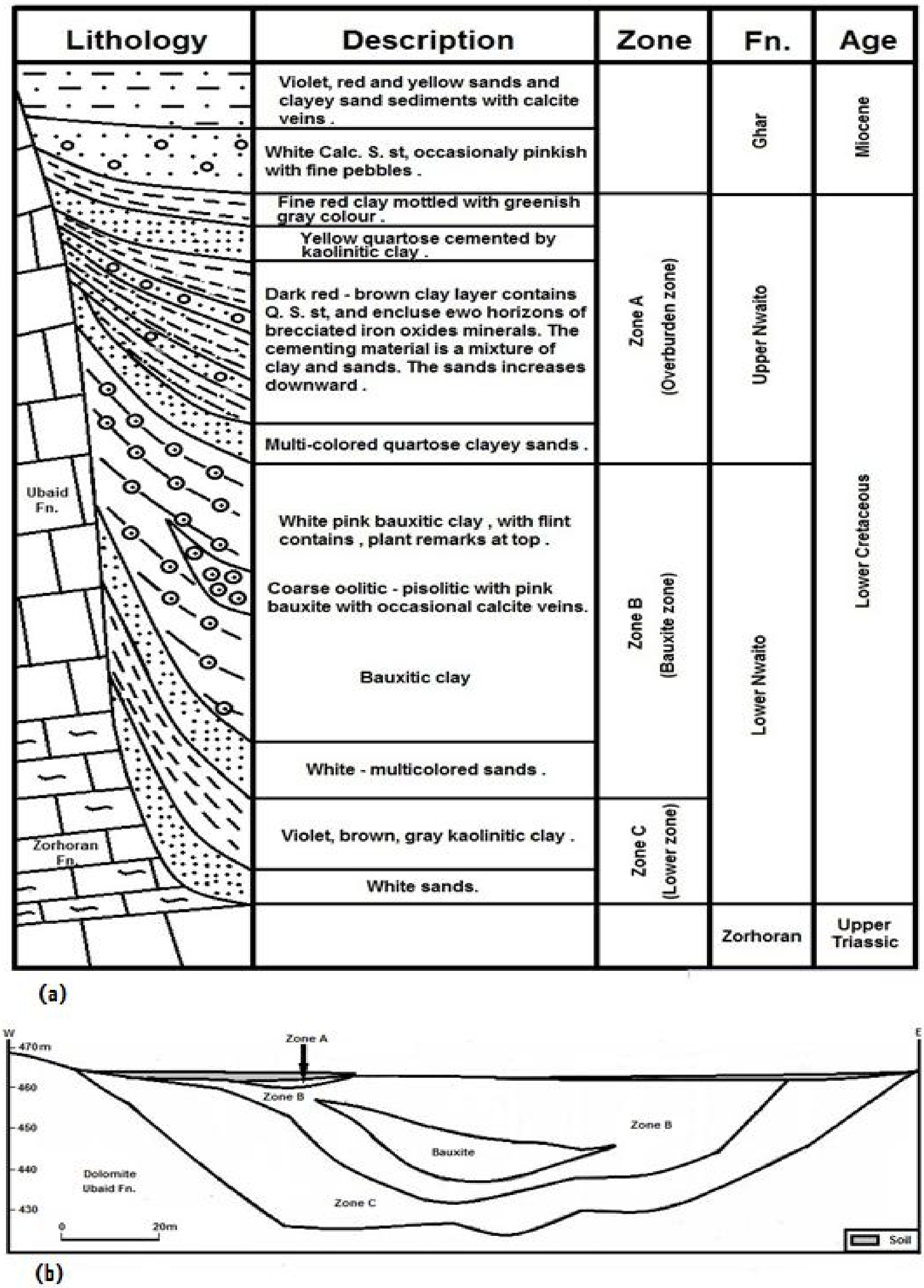


Fig. 2 : **(a)** Ideal section of the sediment filling karst.
(b) Transverse section of the karst (Mustafa and Jibrail, 1996).

NORMATIVE MINERALOGY

In order to clarify the association between the analyzed trace and major elements with the bauxite mineral composition, a quantitative mineral estimation is needed. However, visual modal estimates are difficult to make because of the very fine cryptocrystalline nature of the Hussainiyat bauxite constituents, and XRD gives qualitative estimation of the mineralogical components. Alternatively, a CIPW-derived petrochemical calculation procedure was proposed by (Nyobe, 1991) for the conversion of whole-rock chemical analyses of bauxites and related materials into normative mineralogical suites. In this regard, normative minerals of the Hussainiyat bauxite were calculated quantitatively from the present bulk chemical analyses after considering the mineral phases identified by earlier workers based on XRD study (Al-Bassam, 2005 and Tobia 2005). The minerals are computed in cation percent, which is close to modal estimation, and assumptions in the calculations are as follows:

Al_2O_3 is attributed to boehmite, gibbsite and kaolinite.
SiO_2 is attributed to kaolinite.

The remainder of the loss in weight of ignition (L.O.I) after subtracting CO_2 loss for calcite is assigned to H_2O loss from boehmite, gibbsite and kaolinite.

Fe_2O_3 is attributed to hematite.
TiO_2 is attributed to anatase.
CaO is attributed to calcite.

The results show that boehmite and gibbsite are the main bauxitic minerals while kaolinite, anatase, hematite and calcite represent the non-bauxitic mineral assemblages in the analyzed samples (Table 2).

Table 1: The Chemical Analysis of Hussainiyat Bauxites. PAAS (Post Archean Australian Shale) Data from (Taylor and McLennan, 1985), SR Data from (Al-Bassam, 2005). B.d. = Below Detection limit, (-----) = Not Analyzed.

Sample No.	**BS.1**	**BS.2**	**BS.3**	**PAAS**	**SR**
SiO_2 wt%	12.94	34.6	37.5	62.4	44.49
Al_2O_3	63.19	42.5	39.2	18.78	32.95
TiO_2	2.86	4.11	2.84	0.99	2.18
Fe_2O_3	2.76	1.18	0.56	7.18	4.79
CaO	0.23	0.19	1.39	1.29	0.37
MgO	0.2	0.17	0.16	2.19	-----
MnO	0.01	0.01	0.01	0.11	-----
Na_2O	0.13	0.15	0.06	1.19	-----
K_2O	0.02	0.01	0.01	3.68	-----
P_2O_5	0.04	0.05	0.03	0.16	-----
L.O.I	17.62	16.7	18	6	13.42
Total	99.8	99.67	99.76	97.86	98.2
Ki	0.21	1.45	1.7	-----	-----
As ppm	13.6	4.86	3.28	-----	-----
Ba	62.3	77	61.1	650	-----
Co	57.9	b.d.	1.9	23	36
Cr	299.5	134	116.4	110	201
Cs	14.28	10.83	0.7	15	------
Cu	99.5	28.6	29.7	50	-----
Ga	114.2	50.1	38.3	-----	50
Hf	37.17	43.6	28.9	5	-----
Mo	3.46	b.d.	1.38	-----	-----
Nb	149.1	163.4	124.2	1.9	-----
Ni	32	48.3	68.8	55	59
Pb	15.9	6.9	17.5	-----	-----
Rb	0.9	b.d.	b.d.	160	-----
Sr	30.9	58.3	24.5	200	96
Th	40.71	14.83	19.4	14.6	-----
U	15.23	7.71	6.71	3.1	4
V	1153.7	540	372.3	150	-----
W	42.52	15.71	11.35	0.43	-----
Zn	16	7.6	18	85	-----
Zr	1530.9	1905.3	1153.4	210	652
La	4.5	146.2	21.3	38.2	-----
Ce	16.1	139.1	51.9	79.6	-----
Nd	32.1	65.01	21.97	33.9	-----
Gd	b.d	16.65	13.28	4.6	-----
Y	54.93	63.01	54.05	27	-----

Table 2: Normative Mineralogical Content of Hussainiyat karst Bauxite.

Mineral %		BS.1	BS.2	BS.3
Bauxitic Minerals	Boehmite	46.98	2.64	5.64
	Gibbsite	18.75	16.61	7.33
	Total	65.73	19.25	12.97
Non-bauxitic Minerals	Kaolinite	27.84	74.41	80.65
	Anatase	2.86	4.11	2.84
	Hematite	2.7	1.18	0.56
	Calcite	0.4	0.33	2.48

Boehmite content varies from 2.64 to 46.98 normative % and gibbsite ranges from 7.33 to 18.75 normative%. Increasing in the amount of bauxitic normative minerals reflects increasing in the total Al_2O_3 wt % and can be explained by stages of evolution of bauxitization process. During the early bauxite-forming stage, silica is leached from kaolinite to produce bauxite where gibbsite is prevailing over boehmite, and continued loss of silica from kaolinite produced bauxite rocks with boehmite as the dominant mineral (MacLean *et al.,* 1997).

$$\underset{\text{Kaolinite}}{Al_2Si_2O_5(OH)_4} + 3H_2O = \underset{\text{boehmite}}{2AlO(OH)} + \underset{\text{(aqueous)}}{2H_4SiO_4}$$

Bauxite Lithology

Trivariate plot for the bauxite data on the $(Al_2O_3+TiO_2)$ - SiO_2 -Fe_2O_3 diagram of (Balasubramaniam *et al.*, 1987), shows that they are siliceous bauxite (BS.1) and bauxitic clay (BS.2 and BS.3) (Fig. 3).

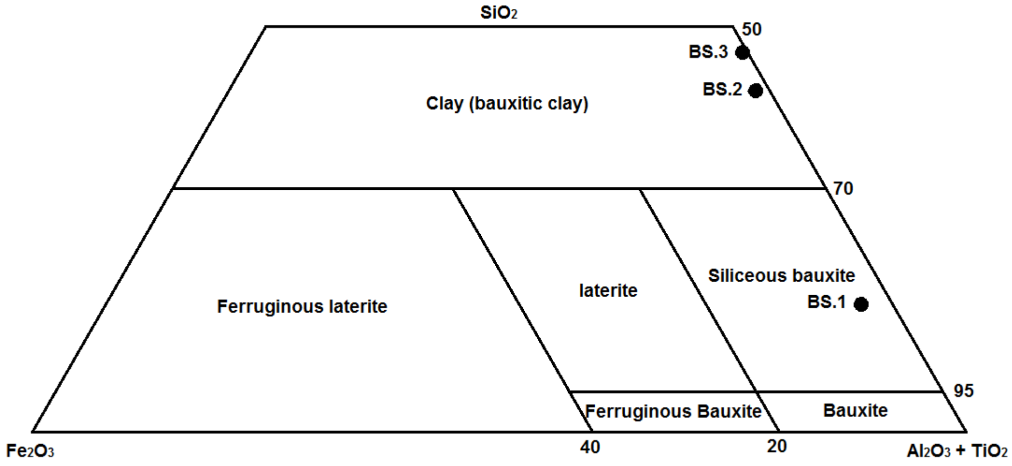


Fig. 3 : Hussainiyat Bauxite Lithology on the Ternary Plot for the System SiO_2-Fe_2O_3-$(Al_2O_3+TiO_2)$.

According to the classification of Valeton (1972) using the factor (ki) that equals the molecular ratio of (SiO_2 / Al_2O_3), the analyzed bauxites are low quality bauxite (BS.1), Bauxitic clay (BS.2) and clay (BS.3).

Immobile Elements

In order to trace the Hussainiyat bauxite precursor by applying immobile elements geochemical approach, it is necessary to examine the mobility of the elements during bauxitization process. In this regard, (MacLean, 1990) and (MacLean *et al.,* 1997), considered elements to be immobile only when their distribution produces a linear array that passes through the origin of their binary plot. Accordingly, in this study, the mobility of the present elements is examined by plotting each element against Al_2O_3 for all bauxite units (Fig. 4). As it is evident from this figure, Ti, Zr, Th, Cr, Ga, Hf, Nb, V, U, W, Cu, Co, As, Cs and Y produce linear high correlated trend that passes through the origin indicating that they were immobile and therefore highly enriched as a residual elements during bauxitization process. However, a slight scatter differences can be noticed in some of these plots that can be attributed to minor mobility or slight source rock inhomogeneity (Maclean *et al.,* 1997) or it might be due to sampling bias or analytical error. In contrast, SiO_2, Fe_2O_3, Ni, Sr, Zn and Ba reveal negative correlation with Al_2O_3 and are therefore considered mobile and were leached. MgO, MnO, Na_2O, K_2O and CaO are nearly disappeared indicating that they were extremely mobile. On the other hand, Rb, Mo and Gd were erratic probably because of their very low concentrations that are generally close to or below their detection limits. The remainder, such as La and Ce are randomly distributed and exhibit very weak correlation with Al_2O_3 and TiO_2.

Source Rock

There is more than one opinion regarding the parent rocks of the Hussainiyat bauxite deposits. The bauxite precursor was believed to be the adjacent Jurassic kaolinite-rich clastics of the Hussainiyat Formation (Mustafa *et al.,* 1997 and Al-Bassam, 2005) whereas, (Al-Atia and Saadalla, 1996) emphasized that the Pre-Triassic, kaolinite-rich clastics of the Ga‘ara Formation was the source rocks for both the Hussainiyat and the bauxite. However, in this study, the concentrations of certain trace elements of the analyzed bauxite were employed in an attempt to trace the nature of their likely precursor rocks. Plots of the Hussainiyat data on the binary Cr/Ni correlation diagram (Fig. 5) proposed by (Schroll and Sauer, 1968) show that they are close to the karst bauxite field and that shale and/or slate might be the possible parent rocks. On the other hand, on the ternary Zr-Cr(Ni)-Ga diagram of (Balasubramaniam *et al.,* 1987), the parent rocks of Hussainiyat bauxite should have a composition close to the acidic and metamorphic rocks (Fig. 6).

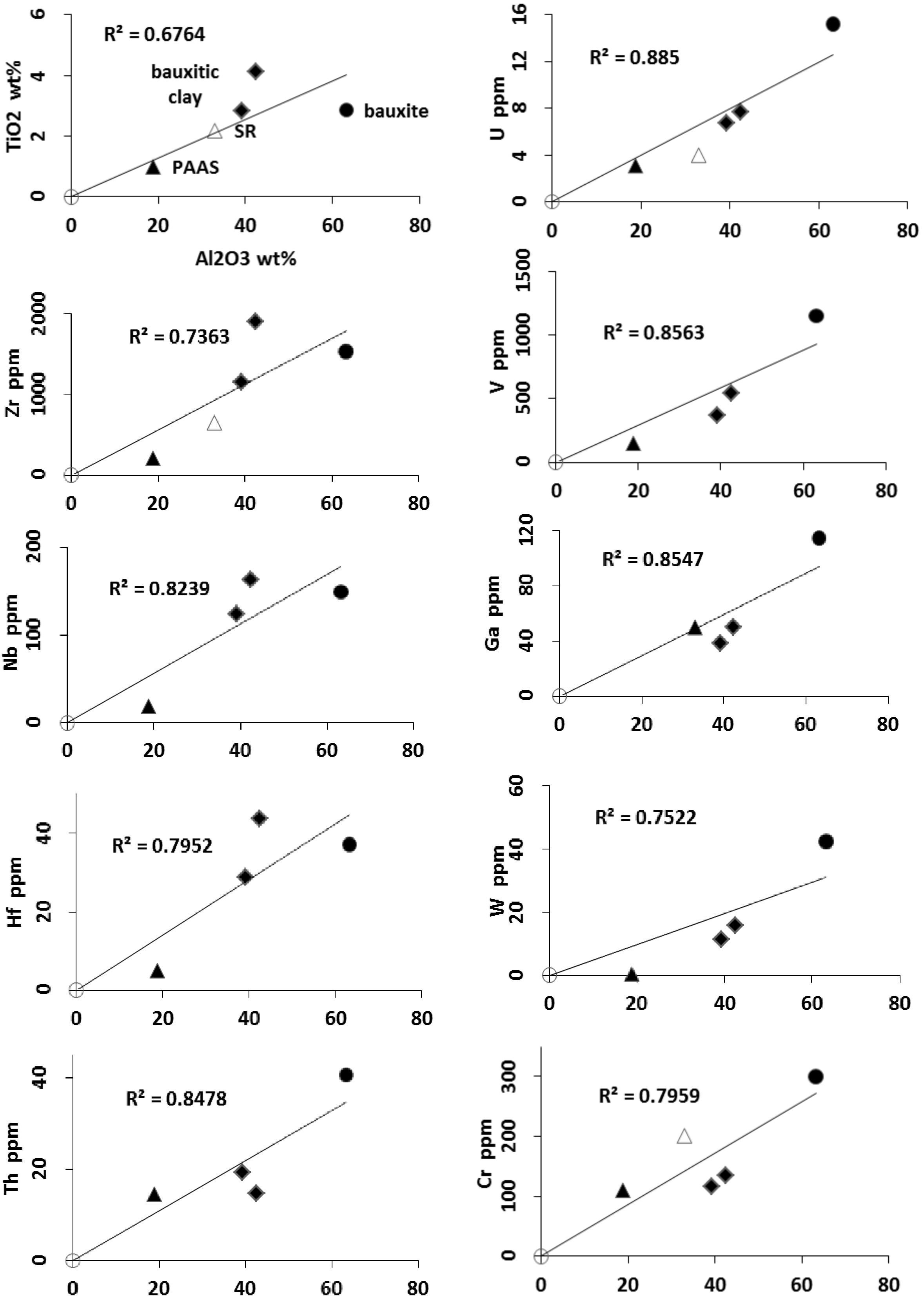
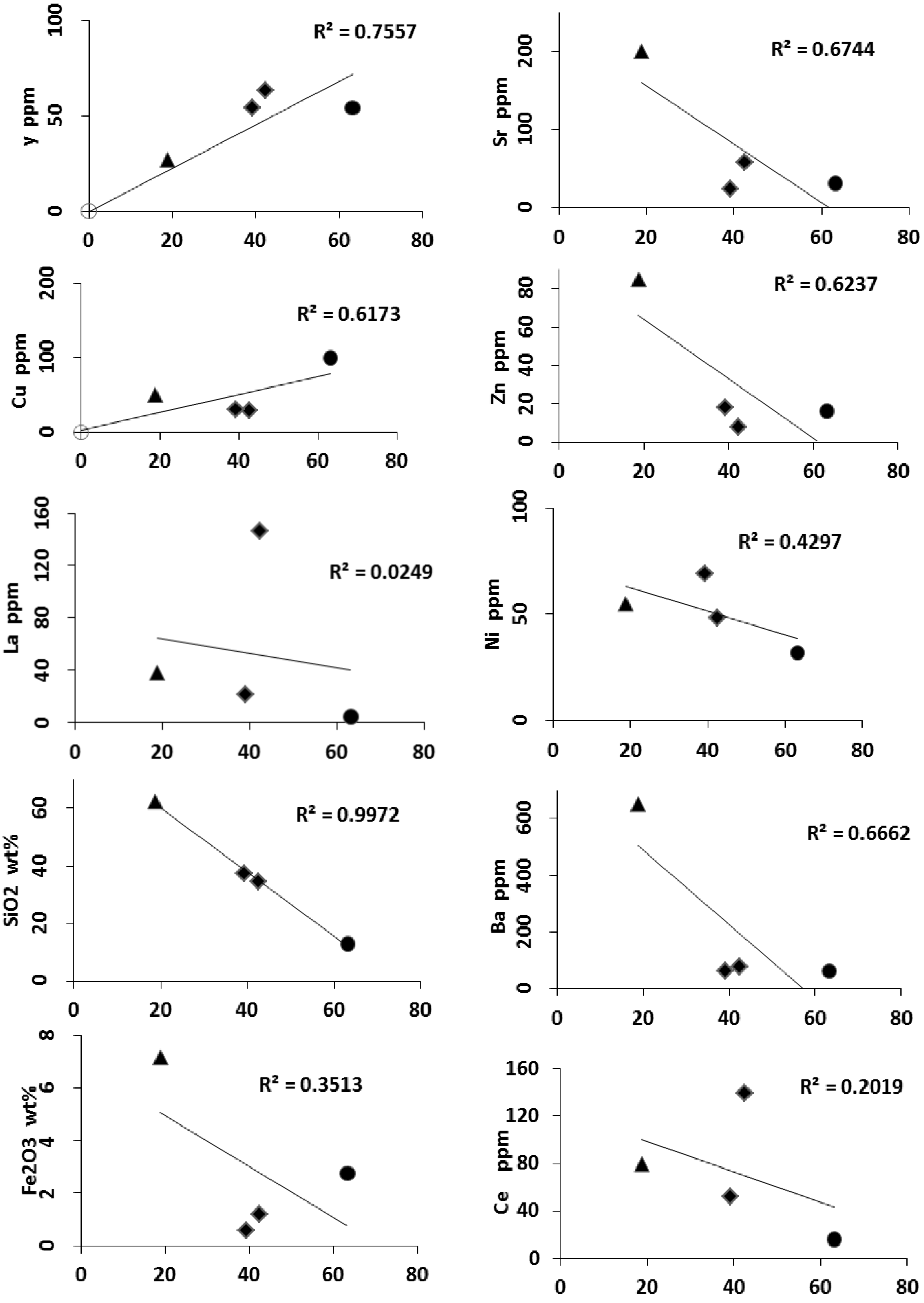


Fig. 4: Binary Plots of some Major and Trace Elements Against Al_2O_3 wt%.

Cont. Fig. 4


y ppm
R² = 0.7557
Sr ppm
R² = 0.6744
Cu ppm
R² = 0.6173
Zn ppm
R² = 0.6237
La ppm
R² = 0.0249
Ni ppm
R² = 0.4297
SiO2 wt%
R² = 0.9972
Ba ppm
R² = 0.6662
Fe2O3 wt%
R² = 0.3513
Ce ppm
R² = 0.2019
0
20
40
60
80

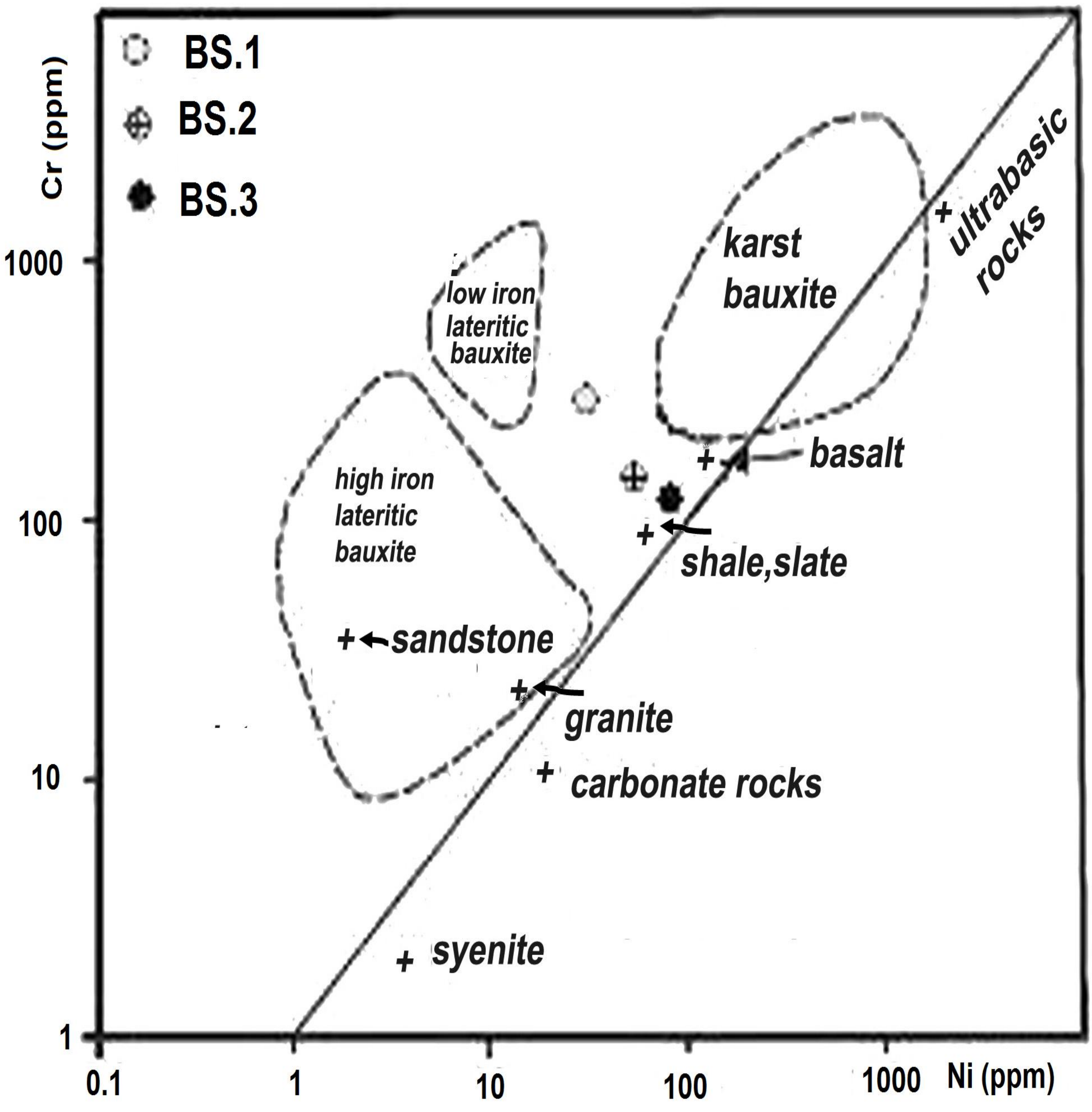


Fig. 5: Binary Correlation Diagram of Cr/Ni in Different Parent Rocks.

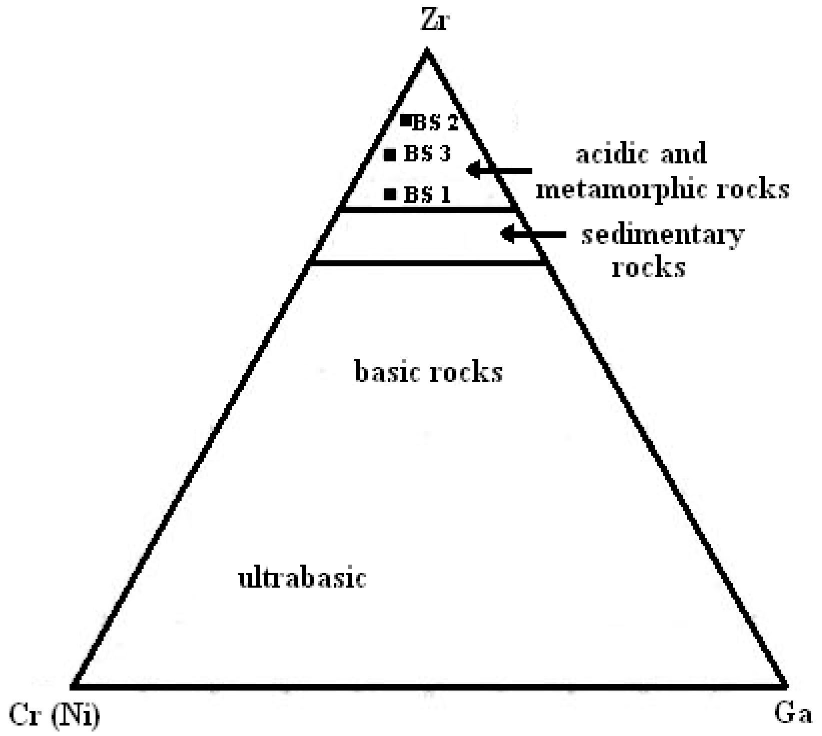


Fig. 6: Ternary Diagram for Bauxites Derived from Different Parent Rocks.

In studies of other bauxite deposits, variations of certain immobile element pairs were used to trace the type of source rock (MacLean *et al.,* 1997, Ozturk *et al.,* 2002, Abedini *et al.,* 2008, Rafieli *et al.,* 2008, Calagari *et al.,* 2010 and Esmaeily *et al.,* 2010). Based on the findings of (MacLean, 1990. and MacLean *et al.*, 1997), single well correlated line (alteration line) that passes through the origin on the immobile element pair plot for all bauxite units indicates one homogeneous source. Whereas, for example, three separate trend lines indicate three different homogeneous sources and finally fan or random distribution indicates that one or more of the sources were heterogeneous.

Taking into consideration the above mentioned discussion regarding the likely bauxite source rocks and by assuming a shale precursor nature for them, elemental Zr versus TiO_2 is plotted (Fig. 7) for all the units including the source rock (SR) suggested by (Al-Bassam, 2005). Additional data regarding the average composition of the Post Archean Australian Shales (PAAS) is also included to testify the shale nature of the bauxite precursor. As only one linear trend with high correlation is evident in this plot, it is reliable to say that these two elements were extremely immobile and that they were residually concentrated in each successive unit (PAAS shale, kaolinitic-rich rock (SR), bauxitic clay and bauxite) on the alteration line.

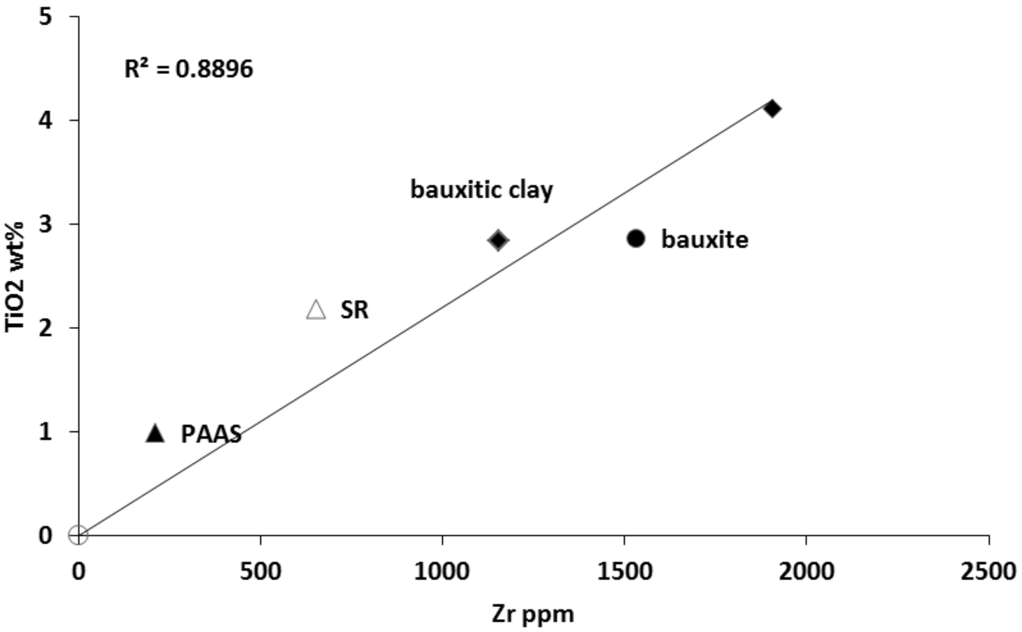


Fig. 7: Plot of TiO_2 Versus Zr for Hussainiyat Bauxite Units.

It can be also concluded that the kaolinitic rich rocks of Hussainiyat clastics is the likely bauxite precursor and that these clastics were originally derived from a shale parent rocks.

Redistribution of Elements during Bauxitization

Previous studies on many bauxite deposits have shown that bauxite is highly enriched in certain immobile trace elements such as Zr, V, Th, Nb, Hf, Cr, Ga, etc., that were named bauxitophilic elements by (D′Argenio and Mindszenty, 1995). It is also known that the distribution of these elements in the bauxitic rocks is controlled by many factors such as the type of the source rock, duration and intensity of bauxitization, resistance to weathering of the primary host minerals, their affinity to the neoformed and resistant minerals, prevailing physiochemical conditions and processes (coprecipitation, substitution and surficial adsorption).Therefore, in the following section, the mineralogical and other possible controls on the distribution of these elements in the Hussainiyat bauxites are discussed.

Major Elements (Al, Si, Fe, Ti)

As it is commonly accepted for all types of bauxite, the results of these elements reveal a conspicuous increase in the less mobile Al_2O_3 and TiO_2 elements concomitant with a clear decrease in SiO_2 and highly mobile alkali and alkaline earth metals (CaO, MgO, K_2O and Na_2O). This indicates the in situ leaching of silica and alkali from the weathered rocks coupled with upgrade build-up of residual alumina and titanium that contribute to the main bauxitic minerals. The Si depletion is resulted from the breakdown of kaolinite and washing of the silica from the suggested precursor kaolinitic clay leaving the residual Al progressively enriched as immobile inert element. Ti enrichment might be attributed to the alteration of ilmenite and/or rutile and formation of neoformed anatase mineral in addition to some detrital rutile. The characteristically low iron content of these bauxite samples (0.56-2.76 wt%) may be caused by its removal as Fe-organic complexes in acid solutions (especially during early stage of bauxitization) and/or it might be removed under reducing conditions as a result of organic decay (Mameli *et al.,* 2007). Within deep developing sinkholes and under reducing conditions with probably circum-neutral pH (4-5) where both Si and Al are insoluble (Fergusson, 1982), an incomplete slow leaching might had taken place giving the Hussainiyat bauxite its siliceous nature.

High Field Strength Elements (Zr, Nb and Hf)

Zirconium, Hf and Nb exhibit considerable enrichment with increasing grade of bauxitization (Fig. 4) reflecting their relative immobile nature. They are good correlated with TiO_2 ($R>0.8$) and with each other and therefore indicate that their distributions were controlled by the residual mineral zircon and/or anatase as was suggested by Lopez *et al.*, (2005) for the Oliete kaolinite deposit/Spain bauxite and by (Rafieli *et al.,* 2008) for the Kisejin bauxite/Iran.

Large Ion Lithophile Elements (Rb, Ba and Sr)

The extreme Rb depletion, moderate Sr and Ba depletion and the negative high correlation of both Sr and Ba with increasing Al_2O_3 suggest that these elements were leached and mobilized in the early stages of alteration of the precursor host minerals in association with the pronounced leaching of Silica, alkali and alkaline earth metals.

Transition Trace Elements (V, Cr, Cu, Co and Ni)

It can be inferred from the high V enrichment in the more bauxitic sample, the positive well correlation of V with increasing Al_2O_3 and its well correlation with Ga that the fixation of V is related to boehmite and gibssite. Also, Cr, Cu and Co exhibit gradual enrichment with increasing Al_2O_3 suggesting their association with the bauxitic minerals. On the other hand, Ni is correlated strongly negative with Al_2O_3 and was mobilized during the alteration of the host minerals (kaolinite and calcite).

Th, U and Ga

The considerable Ga enrichment in the more bauxitic sample and its very well linear correlation with Al_2O_3 (Fig. 4) may indicate its association with boehmite and gibssite either contained in their crystal lattice or adsorbed on them. Uranium and Th show considerable enrichment and are well correlated with Al_2O_3 and with Ga indicating that the distribution of these elements is controlled by boehmite and gibssite minerals.

Rare Earth Elements (REEs)

Among the REEs, only four elements were analyzed in this study (La, Ce, Nd and Gd). They exhibit enrichment (except Gd) towards more bauxitic rocks and show slight correlation with increasing TiO_2 rather than with Al_2O_3 indicating that their mobility is controlled by the mineral anatase. The Gd negative correlation with increasing Al_2O_3 shows that it is mobilized and washed away.

CONCLUSIONS

The concentrations and behaviour of the major and trace elements during the bauxitization in the Hussainiyat samples were rather normal and within the expected trend. The main chemical constituents are Al_2O_3, TiO_2 and H_2O with little Zr, V, Nb and other trace elements. The high residual element concentrations and low alkali metal support an intense chemical weathering origin for the Hussainiyat bauxite precursor. On lithological basis, using $(Al_2O_3+TiO_2)$-SiO_2-Fe_2O_3 triangular diagram, the Hussainiyat bauxites are siliceous bauxites and bauxitic clays.

However, the siliceous nature of these bauxites is attributed to the slow incomplete leaching of silica under reducing condition.

In this study it was possible to delineate and trace mineralogical changes with increasing grade of bauxitization (build-up of Al) presented by a clear gradual increase in normative bauxite minerals (boehmite and gibssite) coupled with a gradual decrease in normative kaolinite.

Single well correlated trends of element pairs for the successive bauxite units indicate that, besides Al; Ti, Zr, Nb, Hf, V, Th, U, Ga, Cr, Co, Cu, As, and W were immobile during bauxitization and are characterized by a gradual increase with increasing grade of bauxitization. On the contrary, SiO_2, Fe_2O_3, CaO, K_2O, Na_2O, MgO, MnO, Ni, Mo and Gd are characterized by a successive loss suggesting that they were mobile during bauxite formation.

Applying immobile elements Plots, it was possible to trace the likely precursor and parent rocks of the Hussainiyat bauxites. From the Zr-Ti binary plot, it was possible to suggest that all the different bauxite units on the alteration line have similar source. Cr-Ni, Zr-Ti and Zr-Cr(Ni)-Ga variation diagrams suggest, that shale of probably acidic and metamorphic provenance, might be the original rocks for the likely bauxite precursor (kaolinitic rocks). Correlations and chemical variations show that, mineral phases besides source rock composition, physiochemical condition, duration and intensity of bauxitization, played an important role in the distribution and mobilization of the trace elements.

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