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MINERALOGY, GEOCHEMISTRY, AND THE ORIGIN OF LOWER CLASTIC UNIT IN HUSSAINIYAT FORMATION (EARLY JURASSIC) WESTERN DESERT OF IRAQ

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ABSTRACT

A mineralogical and geochemical study has been done on (20) Hussainiyat Formation (Early Jurassic) samples in western Iraq. Mineralogical analysis of clays by X-ray diffraction (XRD) shows that the predominant clay mineral is kaolinite and traces of montmorillonite-illite mixed layer with palygorskite. The non-clay minerals are mostly quartz, goethite, hematite, and anatase. Heavy minerals were separated from (sandstone) clastic samples and studied by both polarized and reflected microscopes. These heavy minerals are detected in fewer than 1% quantities and consist of silicates and oxides. The most common of these mineral grains are stable heavy minerals ZTR (zircon, tourmaline, rutile) and apatite, staurolite, and garnet, which indicate that the acidic granite rocks with almost metamorphic rocks were a source of kaolinite. In a geochemical study by XRF, claystone samples were analyzed for SiO_2, Al_2O_3, TiO_2, Fe_2O_3, MgO, CaO, Na_2O, K_2O, MnO, P_2O_5, and L.O.I. kaolinite (claystone) of the Hussainiyat Formation contains a high concentration of iron, which is interbedded with kaolinite as hematite, goethite, and limonite. Kaolinite occurs as kaolinitic pellets and as nuclei of the majority of ironstone ooids and pisoids, together with the alternating concentric laminae of their cortices. Manganese is associated with the kaolinite of the Hussainiyat due to its high iron content.

The present study showed that the kaolinite deposits within the Hussainiyat Formation are less mature than other clays (montmorillonite-illite mixed layer and palygorskite), because the Hussainiyat Formation suffered from less intense chemical weathering, leading to the dissolution of only alkalis and earth alkali metals but not iron. However, the alumina is still stable with li, due to their high resistance, the alumina is still stable with little silica to form kaoliniteintensive chemical weathering, and kaolinite builds by Si and Al. This is because these two oxides are, typically, stable within different physical and chemical weathering. After kaolinite, the rest only gibbsite and boehmite bauxite mineral at the end of the intensive chemical weathering.

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معدنية وجيوكيميائية وأصل الوحدة الفتاتية السفلى في تكوين الحسينيات (الجوراسي المبكر) – الصحراء الغربية في العراق

رنا عباس علي و حسن كطوف جاسم

المستخلص

نفذت الدراسة المعدنية والجيوكيميائية على (20) عينة من تكوين الحسينيات (الجوراسي المبكر) في غرب العراق. أظهر التحليل المعدني للمعادن الطينية بواسطة جهاز حيود الاشعة السينية (XRD)، ان المعدن الطيني السائد هو معدن الكاؤولينايت كما تم العثور على نسب قليلة من المعادن المختلطة من الالايت – مونتمورلونايت مع نسبة أقل من الباليغورسكايت. المعادن غير الطينية هي في الغالب الكوارتز والجيوثايت والهيماتايت والاناتيز. تم فصل المعادن الثقيلة من العينات الفتاتية (الرملية) ودراستها بواسطة كل من المجهر المستقطب والمجهر العاكس. المعادن الثقيلة موجودة بتراكيز اقل من 1%، توجد بشكل اساسي على شكل سليكات وأكاسيد، وهذه الحبيبات المعدنية الشائعة تشمل المعادن الثقيلة المستقرة (الزركون و التورمالين والروتايل) والابتايت والستورولايت والعقيق. يشير وجود معادن ثقيلة مقاومة للتجوية مثل الزركون والاناتيز الى ان صخور الجرانيت الحمضية مع صخور متحولة غالبا كانت مصدرا للكاؤولينايت. بالنسبة للدراسة الجيوكيميائية بواسطة XRF. تم تحليل العينات لـ SiO_2 و Al_2O_3 و TiO_2 و Fe_2O_3 و MgO و CaO و Na_2O و K_2O و MnO و P2O5 و L.O.I. يحتوي الكاؤولينايت في تكوين الحسينيات على تركيز عال من الحديد المتداخل مع الكاؤولين مثل الهيماتايت والجيوثايت والليمونايت. يقع الكاؤولينايت على شكل دمالق كاؤولينيتية وكنوى لاغلبية سرئيات ودمالق الصخور الحديدية جنبا الى جنب مع صفائح متحدة المركز متناوبة مع القشرة. يرتبط المنغنيز مع الكاؤولينايت في تكوين الحسينيات بسبب احتوائه على نسبة عالية من الحديد. أظهرت الدراسة الحالية ان رواسب الكاؤولينايت في تكوين الحسينيات أقل نضوجا من الاطيان الاخرى (معادن مختلطة مونتمورلونايت والايت)، لان تكوين الحسينيات قد عانى من التجوية الكيميائية الاقل شدة أدى الى اذابة وانحلال القلويات والفلزات القلوية الارضية فقط ولكن ليس الحديد. ومع ذلك، لاتزال الالومينا مستقرة مع القليل من السليكا لتكوين الكاؤولينايت بسبب مقاومتها العالية. دائما ما يكون الكاؤولين ناتجا عن التجوية الكيميائية الشديدة، ويتكون الكاؤولين بواسطة Si و Al. هذا لان هذين الاوكسيدين يكونان عادة مستقرين في ظروف التجوية الفيزيائية والكيميائية المختلفة. يكون الباقي فقط، بعد معدن الكاؤولين, معدن الجيبسايت والبوكسايت البوهميت في نهاية التجوية الكيميائية الشديدة.

INTRODUCTION

Western Iraq's, Early Jurassic, Hussainiyat Formation (Fm.), is exposed northeast of the Rutba, particularly, along wadi Hussainiyat (Fig.1). It is limited to the southern section of the region and extends in an E – W band 15 kilometers long and 2 – 3 kilometers broad. This formation is represented by the mixed siliciclastic-carbonate succession of the Hussainiyat Fm. This succession lies within the stable shelf of Iraq (Bellen *et al.*, 1959). The Hussainiyat Fm. is notable for being one of the Arabian Peninsula's few Jurassic sedimentary ironstone deposits (Petranek and Jassim, 1980). It is underlain by Ubaid Formation (Early Jurassic, Liassic) age and it is overlain by Amij Formation (Bajocian) (Buday and Hak, 1980; Al-Naqib *et al.*, 1985 and 1986).

The formation was separated into two major lithological lithostratigraphic units: the clastic bottom unit and the carbonate top unit. The current study focuses just on the lower unit. The lower unit consists of different clay, siltstone, and sandstone cycles. The upper carbonate unit of this formation is made up mainly of hard dolomites with bioturbation and fossiliferous in places (Al-Ani, 1996; Al-Gibouri and Gayara, 2011). The type section is situated in wadi Hussainiyat, about 10 Km from the convergence with wadi Hauran in the west. The thickness of the formation is variable from 120 m in the north to a few meters in the Rutba area (Al-Mubarak, 1983) (Fig.2).

The aim of this study was mainly to identify clay minerals and non-clay that would be useful for establishing the genesis of these clays more clearly.

Al-Mubarak (1983) gave the name of the Hussainiyat to the Upper Ubaid Formation, previously suggested by Buday and Hak (1980). Most geologists are concerned with the Hussainiyat Formation's lower clastic unit due to its economic importance where substantial iron ore deposits and clays were concentrated (Vasiliev *et al*., 1965; Skocek *et al*., 1971; Jassim *et al*., 1981; Al-Hashimi and Skocek, 1981; and Al-Bassam and Tamar agha, 1998). The Hussainiyat pisolitic Formation was thought to be of shallow marine origin by early scholars (Vasiliev *et al*., 1965; Skocek *et al*., 1971; Buday and Hak, 1980). Later scholars, on the other hand, were more inclined toward continental deposition (Petranek and Jassim, 1980; Jassim *et al*., 1981; Al-Hashimi and Skocek, 1981; Yakta, 1981, 1984; and Tobia, 1983), that the formation was derived from Gaara Formation (Permian), exposed in the northwest. Al-Bassam and Tamar agha (1998) found that the clastics were generated from a range of parent rocks, including low and middle-grade metamorphic, intermediate igneous, and pre-existing Nubio-Arabian Shield deposits.

Sedimentological research was conducted on the Hussainiyat Formation by Al-Naqib *et al*., (1985 and 1986) and Al-Naqib (1994). Al-Naqib (1994) classified the clastic unit into five lithofacies depending on lithological varies, sedimentary structures, and grain size; they are claystone, silty claystone, clay siltstone, fine-very fine-grained sandstone, and medium-coarse grained and pebbly sandstone.

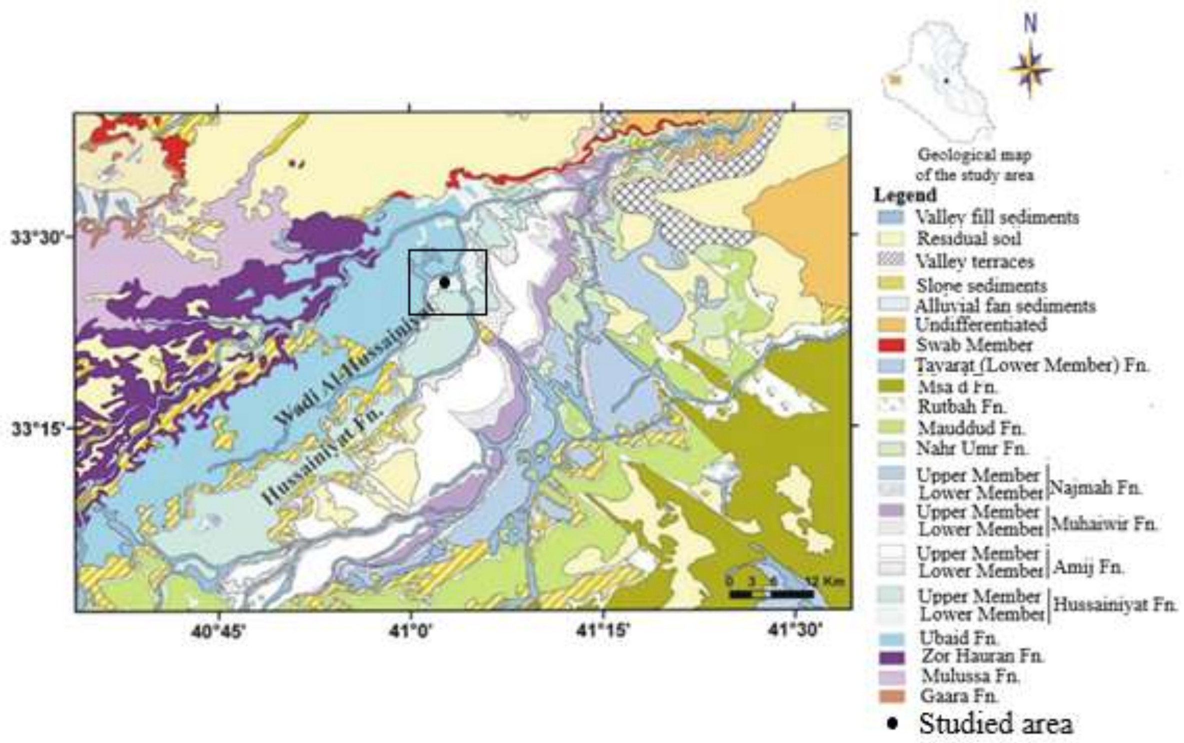

Fig.1: Geological map of the studied area (after Barwary and Slewa, 1997)

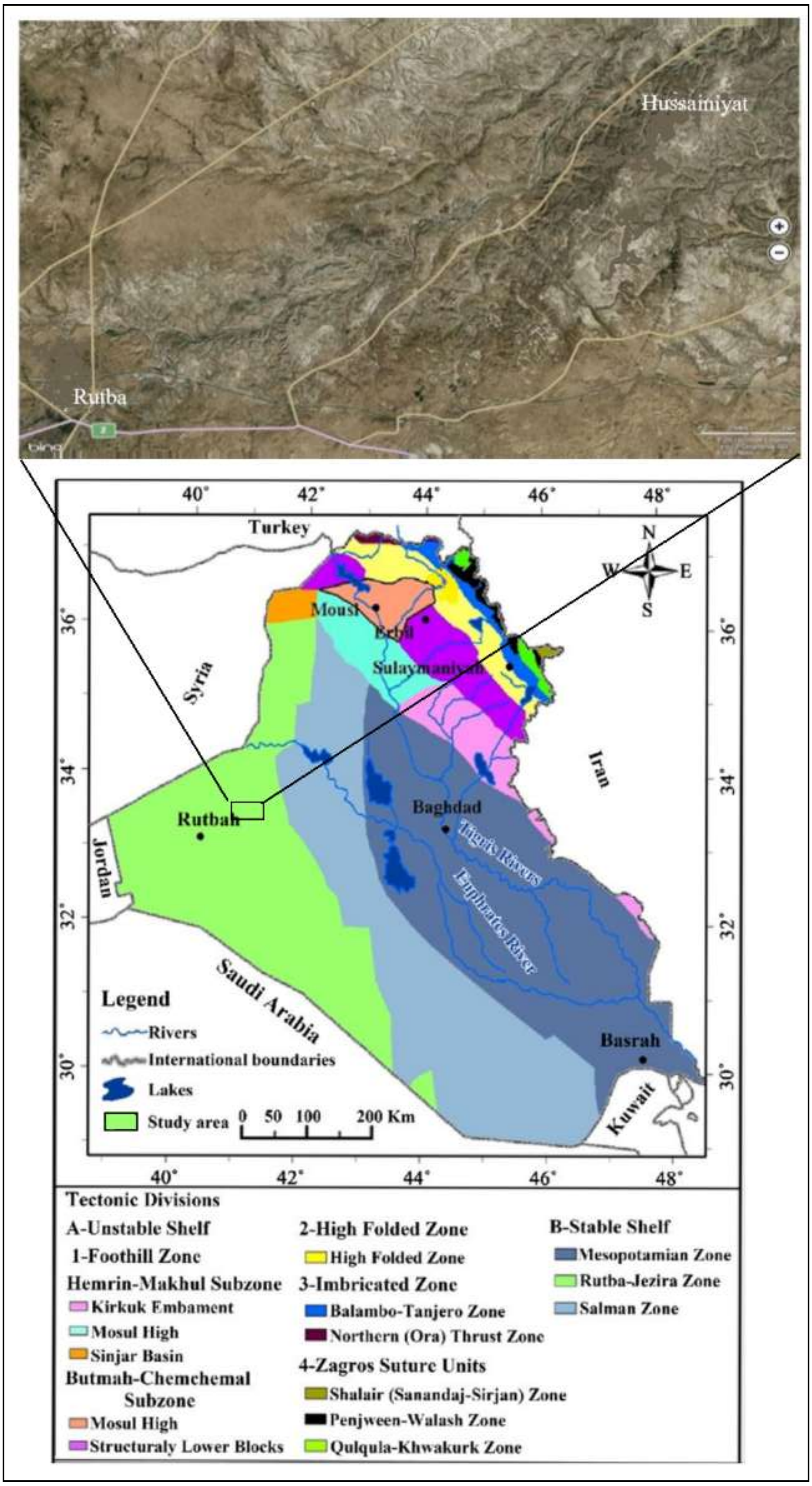

Fig.2: Tectonic map of Iraq, after (Jassim and Buday, 1980 in Jassim and Goff, 2006), showing the location of the Hussainiyat Formation

METHODOLOGY

A total of 20 samples of the Hussainiyat Formation were collected from the lower clastic unit east of Rutba city (Fig.3). The thickness of this unit is about 35 – 40 m. The formation in the studied region is approximately 35 m thick and is composed of clastic and carbonate units. The lower part, with a thickness of 14 m, represents the clastic unit, which consists of a sequence of claystone and sandstone, whose grains vary in size from coarse sand to fine clay. The color of the rocks ranges from red to dark because they contain a percentage of iron minerals, have finning upward cycles, and contain cross-bedding in their upper parts. The carbonate unit consists of dolostone rocks with a thickness of 21 m, which contains chert nodules and crystallized calcite. Each sample was sieved according to the Wentworth size grading scale to separate the sand fraction from silt and clay. As a result, sand with grain sizes ranging from 0.0625 mm to 0.250 mm was separated from the bulk samples and submerged in bromoform liquid (Friedman, 1958).

The heavy minerals split into two halves. The first was put on glass slides, and at least 200 grains were manually identified and counted using binocular microscopic inspection, whereas the second was commonly utilized for polished 2.5 cm diameter parts manufactured using a standard protocol (Craig and Vaughan, 1981). However, the translucent heavy minerals were detected (Fig.4), using a binocular microscope and a polarized microscope, whereas the opaque minerals were identified using a reflected light microscope (Fig.5). The methods of heavy mineral grain identification are described in Mange and Maurer (1992). Major oxides analysis was carried out on 14 samples of kaolinitic clays using XRF. The concentrations of samples and XRD & XRF analyses were measured at the Ministry of Science & Technology, Iraq. Statistical graphs were made using the SPSS statistical program. Thin and polished sections were made in the workshop of the Department of Geology, College of Science, University of Baghdad.

RESULTS AND DISCUSSION

Mineralogy of Clays

Claystone rock beds vary in color from red to reddish-brown, violet, and pink. The coloring is due to iron impurities. They are generally soft, ferruginous, highly weathered, and highly fractured (Fig.6a and b). The fractures are usually filled with secondary gypsum or calcite. The claystone is occasionally silty to sandy and in places contains lenses of siltstone and/ or sandstone; the lenses range from a few meters to a few hundred meters in length, and 0.1 m to 1.0 m in thickness.

To study these clays concerning genesis, this present work was initiated mineralogically. The clays were studied using an X-Ray diffractometer (Fig.7 and 8). The heavy minerals were extracted, identified, and interpreted with relevance to genesis. Any grains that may be indicative of the light fraction are studied.

Mineralogical analysis of clays shows that the predominant clay mineral is kaolinite. Traces of montmorillonite-illite mixed layer and palygorskite were also found (Fig.8). The claystone exhibits a shiny, wavy luster and contains a few scattered detrital quartz and silt grains. Claystones are of variable color, structure, and texture. It contains often authigenic concretions formed of ferric oxides and ferruginous oolites and pisolites (Fig.9c and e). The claystone was mostly disordered kaolinite and contained in some parts traces of rootlets, plant debris (Fig.6e), and burrows (Fig.6d) as well as iron pisolites (Fig.6c), which are also a good indicator of pedogenization of an alluvial plain (Tobia *et al.*, 2019). Poorly crystallized or disordered kaolinite and quartz are the major non- ferruginous minerals that exist in the ironstones. The kaolinite is, basically, disordered especially in the reddish-brown mudstone than in the white mudstone. The non-clay minerals are composed mainly of quartz and heavy minerals (goethite, hematite, and anatase).

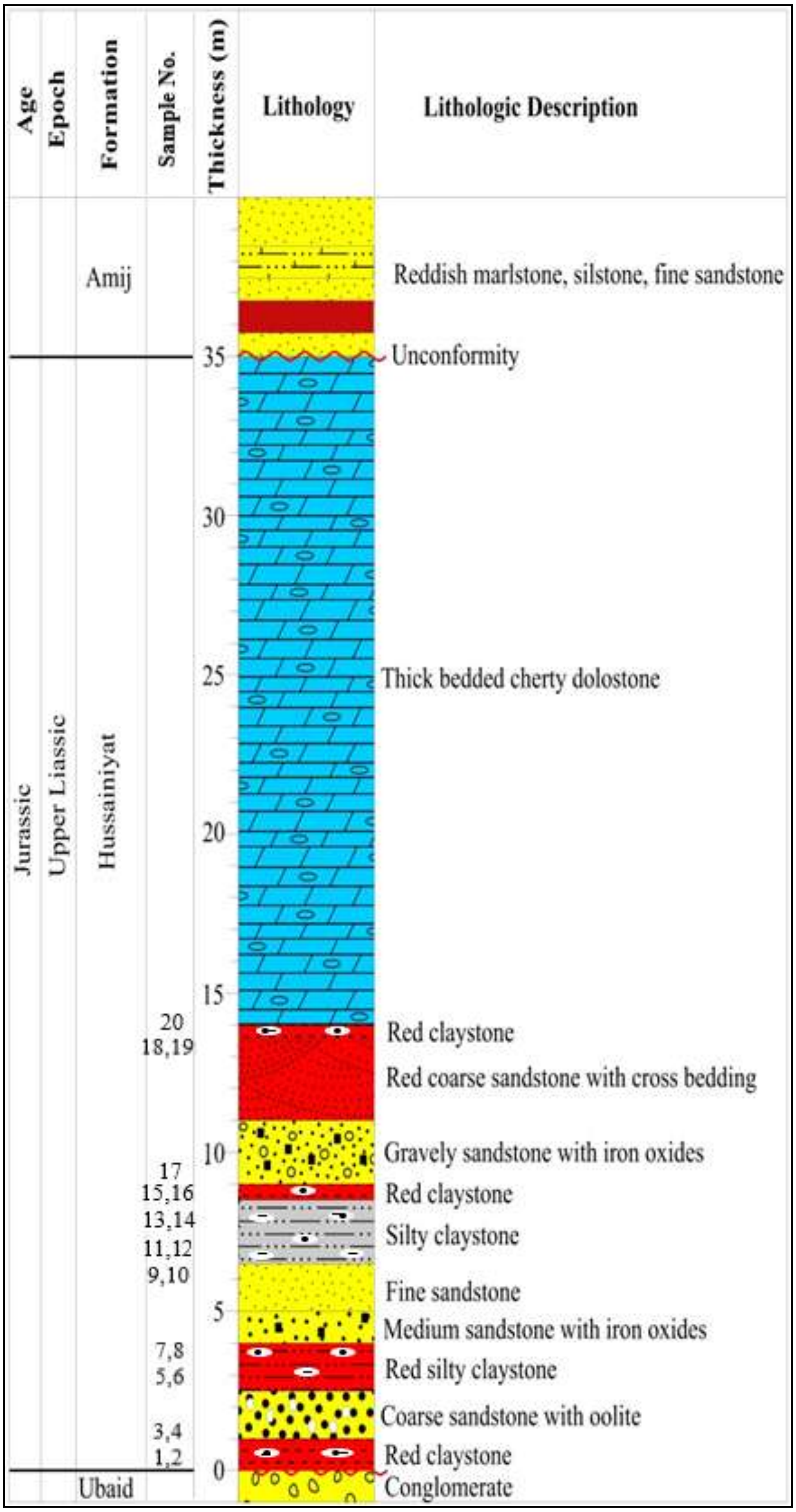

Fig.3: Stratigraphic column of the studied section

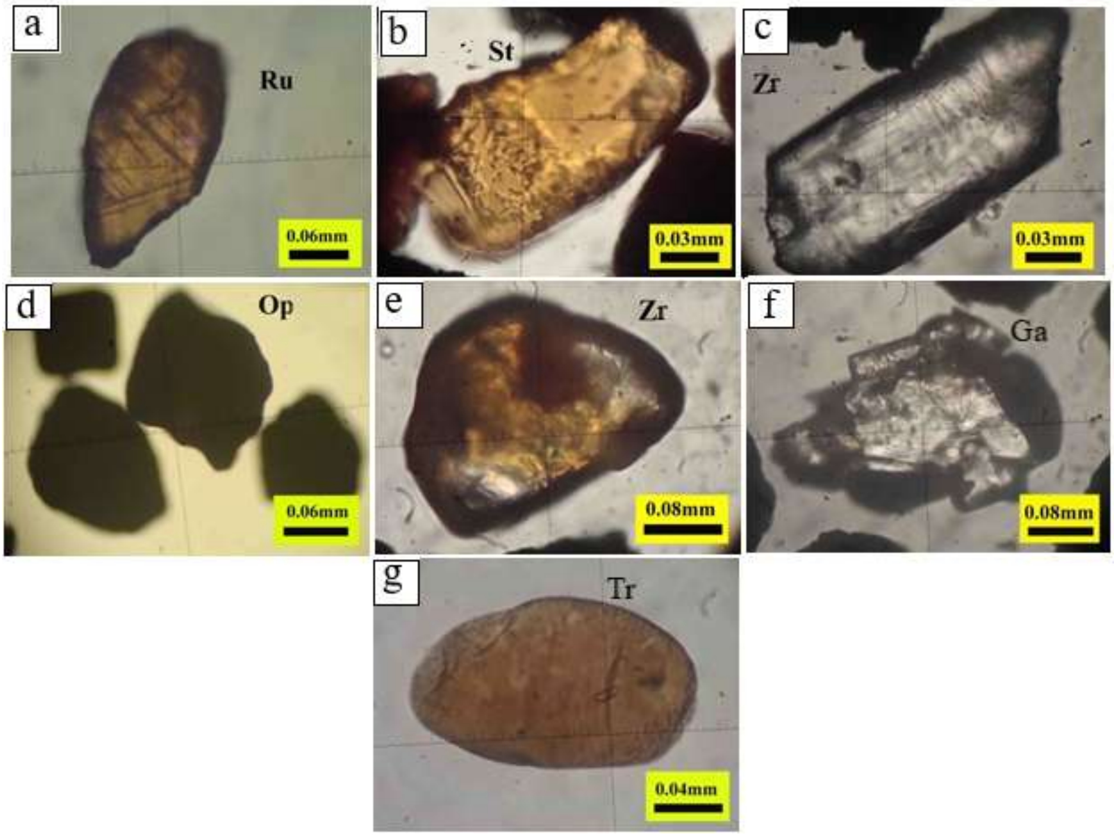

Fig.4: Translucent heavy minerals suit in polarized light.
A) Subhedral- anhedral brown rutile. **B)** Irregular, angular, fractured grain staurolite. **C)** Euhedral prismatic colorless zircon. **D)** Opaque minerals. **E)** Anhedral light brown zircon. **F)** Irregular, angular, fractured grain garnet. **G)** Dark brown sub-rounded tourmaline

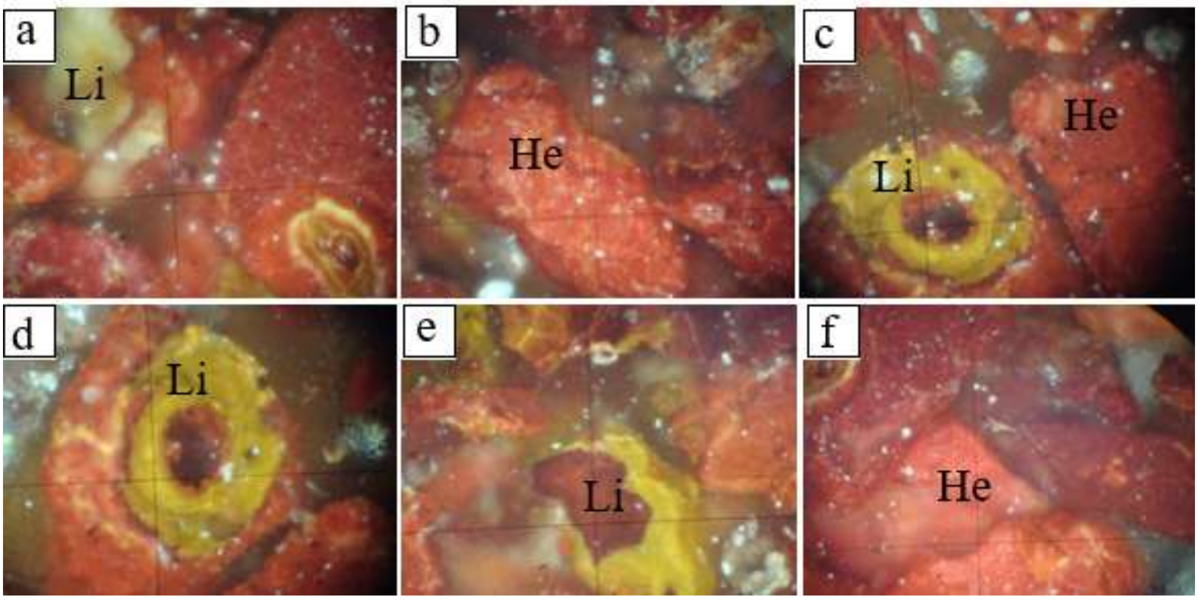

Fig.5: Opaque heavy minerals suit in the reflected light (10X).
A, C, D, E) Yellow of a mixture of hydrated iron (III) oxide- hydroxides (limonite). **B, C, F)** Blood red iron oxide (hematite)

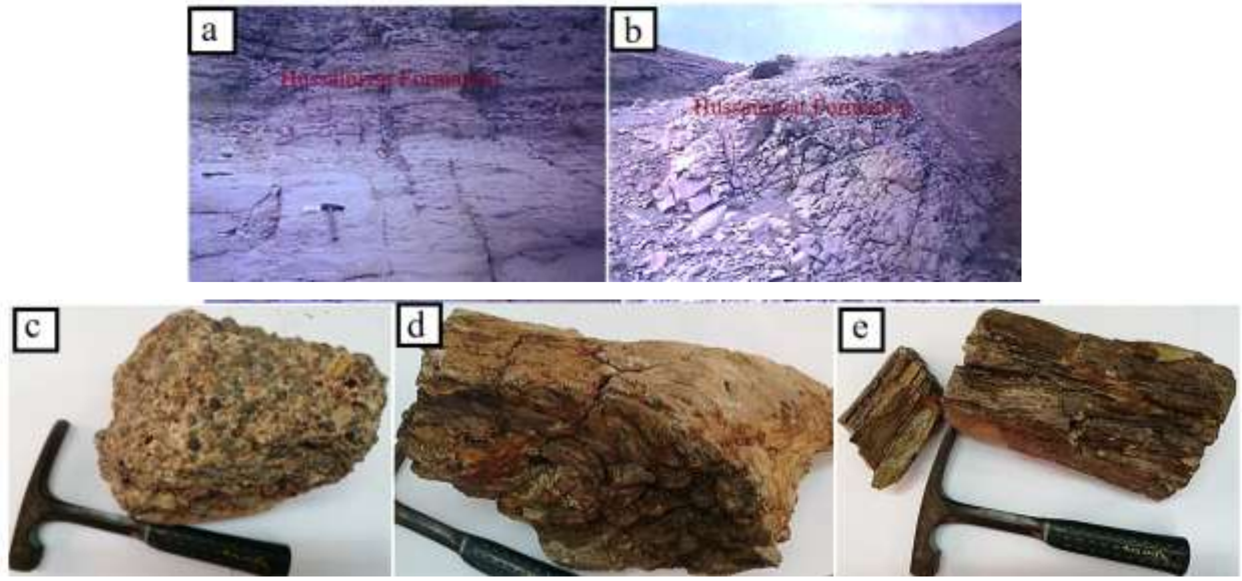

Fig.6: **A and B)** Outcrops of the Hussainiyat Fm. in Wadi Al- Hussainiyat. **C)** Pisolitic iron. **D)** burrows. **E)** traces of rootlets, and plant debris

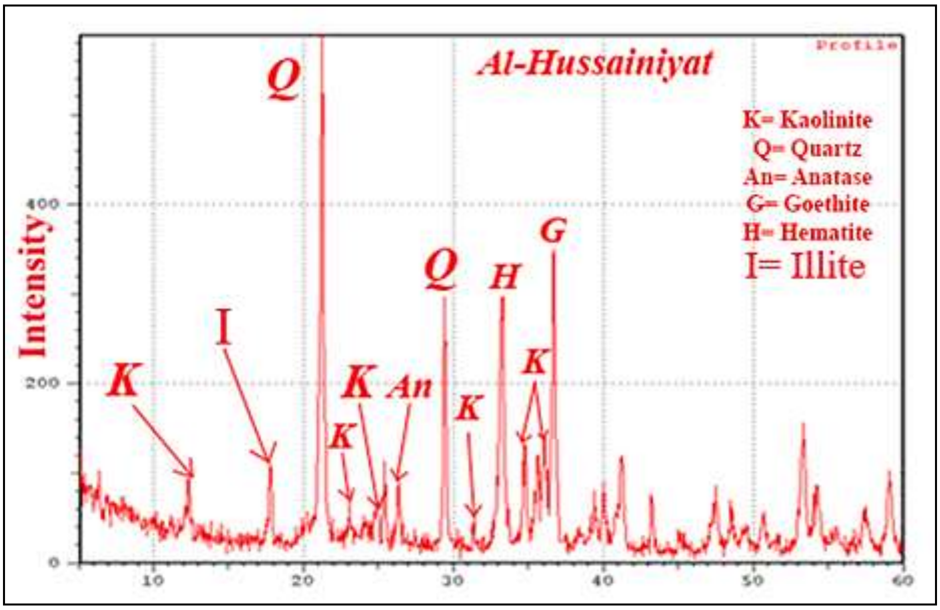

Fig.7: XRD pattern of a bulk sample of Al-Hussainiyat Fm.

The sedimentation of claystone lithofacies is from suspension and deposits fine away from the channel of the flood plain. Deposition may be from water due to overbank flooding with may be of wind-blown origin near shore (Tobia *et al*., 2019), when homogeneous silt, commonly colored red is abundant. Kaolinite is almost the only clay mineral found in the studied rocks, with traces of a mixed layer of illite-montmorillonite. It appeared at first basal reflection (001) in the spacing of approximately (7.12 A°) (Fig.8). This mineral, treated by 3 stages of XRD normal, glycolated, and heating to 550 ºC, showed kaolinite not affected by ethylene glycol but disappeared when heated to 550 ºC due to decomposition of crystal system. Kaolinite clay minerals can originate from varied rock types (Tamar-Agha *et al*., 2019).

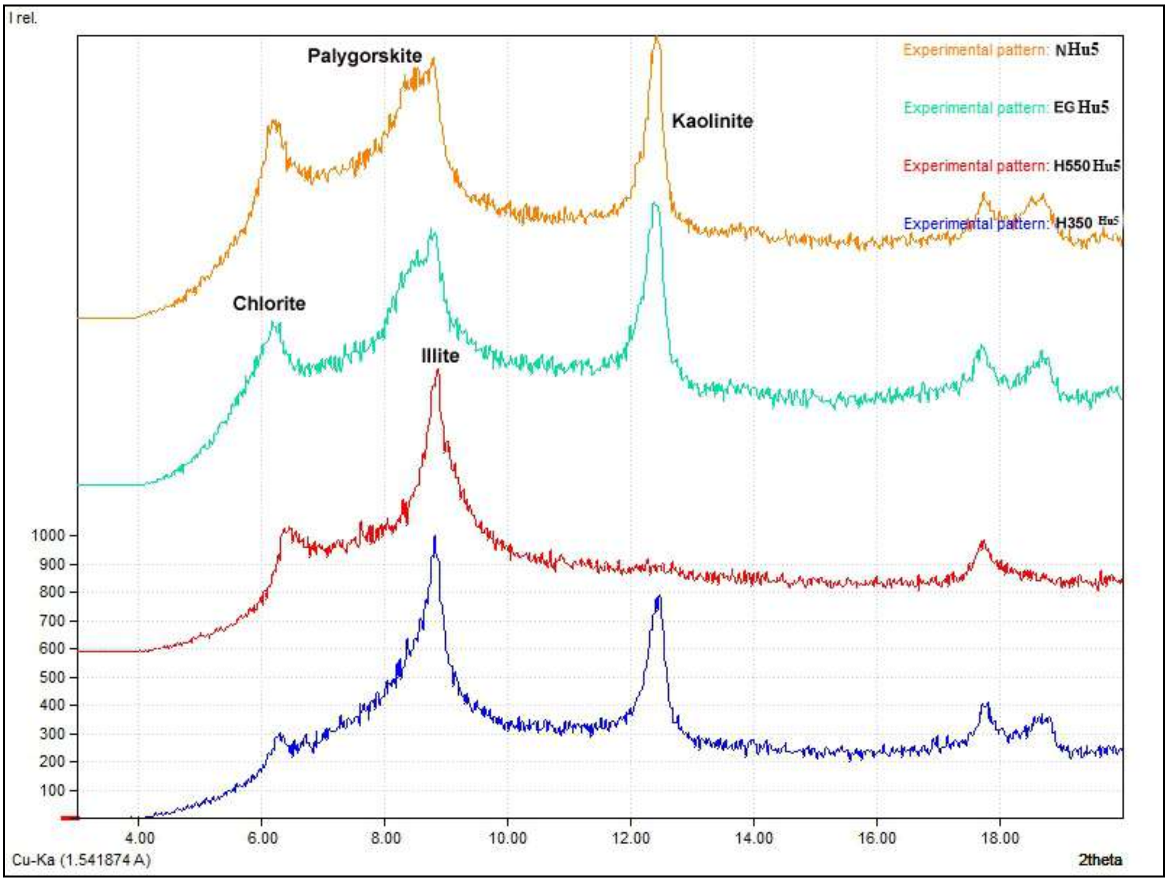

Fig.8: XRD pattern (3 stages: normal, glycolated, and heating to 550 ºC) of red Al-Hussainiyat claystone

Kaolinite can also be found as reworked pieces, in situ (neoformed) oolites and pisolites, and as late-diagenetic infilling of void spaces and micro-fissures. Individual kaolinite crystals range in size from 2 to 5µm, with a community of smaller grains that cannot be identified under the microscope. Kaolinite within fissures or syneresis cracks are generally coarser-grained (still clay size), and more idiomorphic. The percentage of Kaolinite in the formation is (25 – 80) with an average of about 40, in the studied rocks demonstrated in XRD analysis. The mode of occurrence of kaolinite in the studied rocks is variable. It occurs associated with the iron oxide minerals (goethite, hematite, and limonite) in their various forms (Fig.5 and 9d). It also occurs as kaolinitic pellets of oval, rounded, or elongated shape (Fig.9c). The kaolinite and kaolinitic particles may play a role in how hydrated ferric oxide moves and how it is put down (Luo *et al*., 2019). Kaolinite is the dominant clay mineral in humid tropical latitude areas, particularly, in major rivers and well-drained regions of tropical weathering (Dera *et al*., 2009). The variation in the terrigenous clay composition of input may reverse short-term variations in the rainfall intensity.

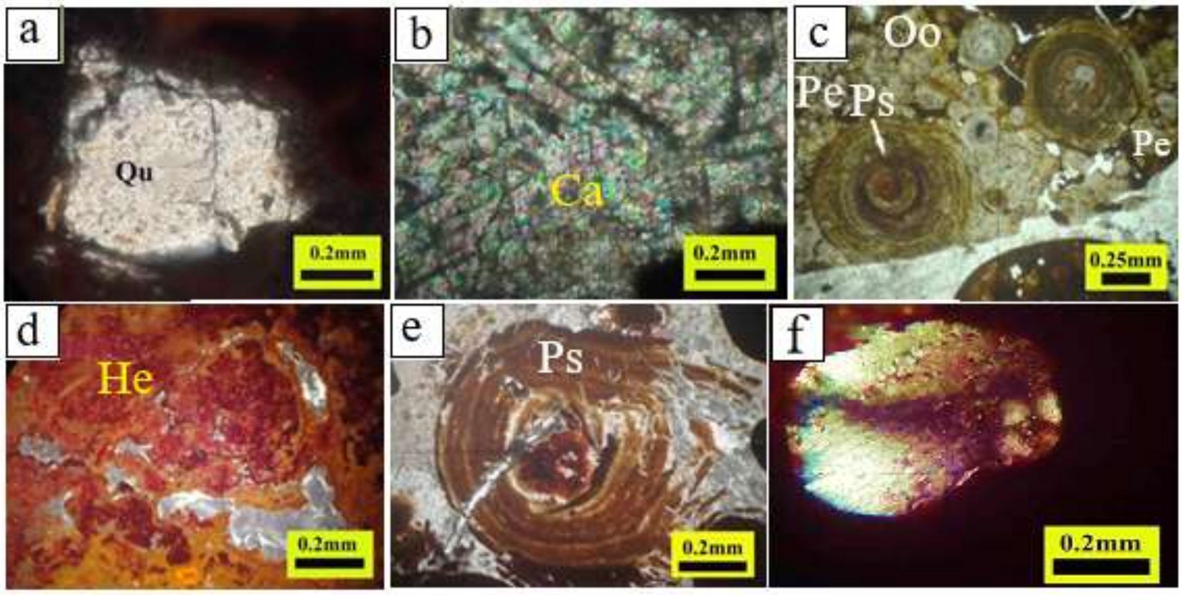

Fig.9: Non-clay minerals suits in thin sections (XPL).
a) Sub-rounded to sub-angular detrital quartz grain. **b)** Sparry calcite cement, viewed between crossed polars, shows high order birefringence colors. **c and e)** Concentric textures of pisolites (Ps), oolites (Oo) and kaolinitic pellets (Pe). **f)** undulous extinction of quartz

When an igneous rock alters into clay, some of the minerals that were phenocrysts in the original rock will remain in the clay bed if the alteration has taken place in situ. The heavy minerals recovered from the clay will be those that were present in the mother rock, and if the alteration has taken place somewhere else and then transported, the clay will be contaminated with minerals that were not present in the parent material that gave rise to the clay but introduced during transportation and deposition periods (Aboudi Mana *et al*., 2017). These normal detrital components are most likely to have come from the associated sediment, such as sandstone that overlies and underlies the clay horizons. Among the non-clay minerals present in these clays is the anatase (TiO_2), which was the titanium mineral detected in the studied rocks in addition to rutile (Fig.7). The relatively small content of anatase in the Hussainiyat Formation is directly related to the TiO_2 content of the parent rock, which is characteristic of the graintiod-derived kaolinitic deposits. Calcite ($CaCO_3$) was discovered in the form of cement or vein let. The source of calcite was either from the precipitated lime-mud of the warm shallow shelf area or detrital carbonate fragments and grains deposited as extra clasts (especially, in the upper part of clastic facies) and were dissolved and reprecipitated by the sparry calcite during lithification (Fig.9b). Quartz (SiO_2), among the light minerals, is the most abundant. It occurs in silt and sand fractions and is the most stable of all minerals under depositional conditions. The quartz particles are usually sub-rounded to sub-angular (Fig.9a). Some grains exhibit an undulous structure (Fig.9f), indicating probably metamorphic origin. The sedimentary ironstone returns chiefly to the iron oxides and is controlled by the existence of hematite and goethite, existing as pisolites, oolites, concretions, and ferruginous clay (Fig.9c and e). The ironstone matrix is formed of clay and sand whereas sometimes the matrix is composed of kaolinite and carbonate material. Pisolites are ideally prevalent over oolites which varied in size. The size of pisolite is often over 1 cm in diameter, while oolites are less than 2 mm in diameter in the studied samples.

PROVENANCE OF THE HEAVEY MINERALS

When an igneous rock, whether acidic or otherwise, undergoes alteration to clay, its original textural character is destroyed. However, some heavy minerals and phenocrysts that were present in the original rock and did not alter will stay in the formed clay if the alteration to clay has taken place in situ (Al-Ani and Sarapää, 2008). On the other hand, if the altered rock has been transported a distance and then deposited in the basin, the formed clay will be mixed with transported detrital (Tamar-Agha *et al*., 2019 and 2020). The heavy minerals with a clastic unit of the Hussainiyat Formation are characterized by the cyclicity of its sediments. It is composed of alternating beds of sandstone and claystone. The heavy minerals within sandstones are sediments of high energy, and the formation of such rather high-grade clay deposits in a high-energy environment is not probable. The content of kaolinite in the clays exceeds 80% of the whole rock in some places, while in the underlying sandstones the content of the kaolinite hardly exceeds a few percentages, as evidenced by the Al_2O_3 % (Al-Ani, 1996).

The heavy minerals exist in concentrations of lesser than 1%. They are chiefly silicates and oxides, and many of them are very resistant to chemical weathering and mechanical abrasion, so, they can last for a very long time. It is common for these mineral grains to be zircon and rutile, as well as tourmaline, apatite, staurolite, and garnet (Fig.4; Table 1). These mineral grains are characterized by their higher specific gravity and tend to be smaller in size. The study of their minerals can give some useful indications of provenance and events in the source area. Heavy minerals are normally used for source rock determination because they supply the mineralogical nature of the source terrains (Boggs, 2001).

Table 1: Percentages of heavy minerals in Al-Hussainiyat Formation;
Hu= Sample No. from stratigraphic section (Fig.3)

Heavy Minerals	**Samples Number**					
	Hu1	**Hu4**	**Hu5**	**Hu9**	**Hu14**	**Hu19**
Opaques	41.5	42.8	44.6	43.5	40.8	43.1
Zircon	14.9	12.3	14.5	10.1	12.6	11.1
Tourmaline	14.7	12.7	10.8	15.4	13.0	15.7
Rutile	11.6	11.4	12.3	12.1	12.5	13.3
Garnet	2.6	3.1	4.5	3.4	2.7	3.4
Pyroxenes	5.8	4.7	3.3	5.7	4.9	4.0
Epidote	3.8	6.5	4.2	5.5	3.2	5.3
Biotite	2.5	3.4	3.7	3.1	4.4	4.8
Muscovite	2.3	2.5	1.2	2.2	3.8	4.1
Others	0.3	0.6	0.9	0.6	0.9	0.5

The opaque minerals are approximately stable and have a high specific gravity due to their iron content. Hematite constitutes the opaquest minerals. The grains opaque are sub-rounded to rounded, and a few grains are angular (Fig.4d). These minerals originated from various rocks (sedimentary rocks, acidic igneous rocks, basic igneous rocks, and metamorphic rocks) (Hibbard, 2002).

Zircon is an ultra-stable mineral, colorless, has a lot of relief, presence of zonation and inclusions, and well-rounded or prismatic grains euhedral-subhedral. The rounded zircon grains in the clay are more abundant than the euhedral ones. Furthermore, the rounded and well-shaped zircons present in the heavy fraction of clay samples may have two origins; the rounded ones have undoubtedly undergone long transportation, probably a few hundred kilometers, while the euhedral zircons show no or very little transportation (Arabian shield) (Fig.4c and e). However, since the majority of the ultrastable minerals are rounded, it indicates that recycling (i.e., sedimentary source rock) is predominant. Euhedral zircon is derived from igneous rocks while rounded zircon originates from metamorphic rocks and maintains roundness in sedimentary rocks (Blatt *et al.*, 1980). Tourmaline, is an ultra-stable mineral and has various colors, but light brown is a more common color, pleochroism, sub-rounded to rounded (Fig.4g). The presence of multi-color tourmaline is indicated that deposits derived from igneous rocks (Bozkaya *et al.*, 2020). Rutile is also an ultra-stable mineral that has a dark color, and angular to sub-rounded shape, and contains striations (Fig.4a). The origin of rutile is igneous and metamorphic rocks (Hibbard, 2002).

Meta-stable minerals involve staurolite, which has golden yellow or yellowish brown, pleochroism, and fractured and angular grains (Fig.4b). The presence of staurolite in deposits is indicated that they are derived from metamorphic rocks (Blatt *et al.*, 1980). Garnet is colorless, isotropic, euhedral crystals, with sharp edges (Fig.4f); originating of garnet from metamorphic and pegmatite rocks (Hibbard, 2002).

Kaolinite clay minerals can be derived from the alteration of acid rocks such as granite or syenitic rocks (Tamar-Agha *et al.*, 2019 and 2020; Klee *et al.*, 2021).

CHEMICAL CHARACTERISTICS

▪ Major Elements Composition

Fourteen claystone samples were analyzed for their major oxides. The elements were analyzed for SiO_2, Al_2O_3, TiO_2, Fe_2O_3, MgO, CaO, Na_2O, K_2O, MnO, and P_2O_5. The results of the major chemical analyses are shown in Table 2. The distribution of the elements with the thickness is shown in Figure 10. The light green area represents the highest concentration of the element in that area.

– **Silica (SiO_2)** The average silica content in the claystone of Hussainiyat Fm. is 38.42% (Table 2). The distribution of silica with the thickness is shown in Figure 10a. This average is lower than the Gaara ironstones and sandy ironstones, as well as the iron-rich beds of the Abha Khamis region, but it is greater than many international ones (Table 3). The presence of detrital quartz grain contributes to the high SiO_2 concentration of these clays and the presence of SiO_2 in the crystal structure of clay minerals. This can be explained by a higher silica content of the parent rock, silica transportation to the depositional basin with clay minerals either fine grains form or colloidal fluids and coating form with Kaolin strata (Li *et al.*, 2018). The distribution of SiO_2 is trimodel with positive skewness (Fig.11A). This distribution reflected the various types of ironstone lithofacies and associated clastic claystone and sandstone facies.

Table 2: Major chemical composition of the kaolinitic claystone in wt.% of Hussainiyat Formation; Hu = Sample No. from stratigraphic section (Fig.3)

Oxides %	**Hu1**	**Hu4**	**Hu5**	**Hu6**	**Hu7**	**Hu8**	**Hu10**	**Hu12**	**Hu14**	**Hu16**	**Hu17**	**Hu18**	**Hu19**	**Hu20**	**Aver. %**
SiO_2	44.5	32.3	40.2	35.4	30.8	42.3	44.7	47.5	35.6	36.5	33.3	37.8	33.6	43.4	38.42
Al_2O_3	16.4	20.0	18.8	24.5	24.3	25.6	21.7	22.4	19.2	24.6	18.8	20.6	26.0	22.4	21.8
Fe_2O_3	19.6	26.3	21.4	22.9	27.5	19.5	17.7	21.8	30.8	24.1	31.4	25.3	25.77	25.66	24.27
TiO_2	1.3	1.1	0.6	1.5	1.6	1.9	1.2	0.8	2.1	1.8	1.0	2.2	1.4	1.7	1.44
MgO	1.8	0.85	1.5	2.2	1.6	1.6	0.5	1.4	3.1	1.8	1.9	1.7	1.3	1.5	1.62
CaO	1.2	0.4	1.0	1.42	1.25	1.13	2.2	0.7	1.15	1.02	1.03	1.19	0.2	1.52	1.10
Na_2O	0.91	0.2	0.4	0.3	0.2	0.5	0.4	0.3	0.3	0.2	0.2	1.5	1.26	0.4	0.5
K_2O	0.1	0.01	0.1	0.2	0.2	0.1	0.23	0.21	0.2	0.13	0.42	0.18	0.5	0.32	0.2
MnO	0.02	0.02	0.02	-	0.02	0.04	0.04	0.03	0.03	0.01	0.05	0.03	0.04	0.05	0.03
P_2O_5	0.08	0.05	0.02	0.08	0.04	0.09	0.06	0.07	0.09	0.05	0.03	0.05	0.08	0.09	0.06
L.O.I	14.0	17.77	15.1	12.39	11.99	5.78	11.1	5.7	6.23	8.89	10.76	9.3	8.86	2.96	10.06
Total	99.9	99.0	99.1	100.8	99.5	98.6	99.8	100.9	98.8	99.1	98.89	99.85	99.01	100	99.53

Table 3: Geochemical studies of ironstones in various areas, **A)** Goethitic ironstones/ minette ores/Verte/ Lorrain/ James, 1966. **B)** Chamositic ironstones/ Gottingen/ Germany/ James, 1966. **C)** Those Beauregard ironstones/ marine sedimentary/ France/ Zitzmann, 1977. **D)** Kahlenberg ironstones/ Germany/ Zitzmann, 1977. **E)** Nammen ironstones/ marine sedimentary/ Germany/ Zitzmann, 1977. **F)** Camdag ironstones/ Turkey/ Zitzmann, 1977. **G)** Dolnilom ironstones/ marine sedimentary/ Bulgaria/ Zitzmann, 1977. **H)** Hussainiyat ironstones/ Iraq/ Jawad, 1980. **I)** Pisolitic and oolitic ironstones/ Gaara/ Iraq/ Tobia, 1983. **J)** Total average of Gaara ironstones/ Iraq/ Tobia, 1983. **K)** Sandy ironstones/ Gaara/ Iraq/ Tobia, 1983. **L)** Iron-rich beds/ Abha Khamis area/ Saudi Arabia/ Babalola *et al.*, 2003. **M)** Thuringia ironstones/ Germany/ Mucke and Farshad, 2005. **N)** Benavi ironstone/ Iraq/ Yassin, 2009. **O)** kaolinitic clays/ Hussainiyat Formation/ Iraq/ present study

Elements	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**	**K**	**L**	**M**	**N**	**O**
SiO_2 %	25	21.8	3-13	11	9-11	4.2-20	16.4	48.5	27.5	50.5	55.2	71.5	15.6	3.78	38.42
Fe_2O_3 %	41.6	22.7	24.4 Fe	18.23 Fe	13-15	18-41 Fe	17.7 Fe	18.9	42.5	39.01	35.95	15	41.37	20.44	24.42
Al_2O_3 %	4.6	10.7	-	3-4	1.5-2	3.5-11	-	14.2	7.1	1.855	1.59	4.85	8.75	1.67	21.0
CaO %	4.85	12.2	30-50	30.6	33-36	1.3-36	15.5	2.07	3.2	1.463	1.3	2.3	2.4	39.15	1.10
MgO %	2.1	3.6	-	-	-	-	-	1.7	0.16	0.096	0.1	0.4	2.91	1.05	1.62
TiO_2 %	-	0.53	-	-	0.1Ti	-	-	-	0.43	0.3	0.3	0.33	0.75	0.15	1.44
Na_2O %	-	0.08	-	-	-	-	-	0.7	0.01	0.02	0.02	0.5	0.2	0.14	0.5
K_2O %	-	0.09	-	-	-	-	-	0.549	0.02	0.065	0.06	0.07	0.07	0.06	0.2
P_2O_5 %	1.88	-	-	0.28P	0.19P	0.28P	-	-	0.45	0.432	0.41	0.1	1.02	1.04	0.06
SO_3 %	-	-	-	-	-	-	-	-	6.6	0.123	1.27	-	-	-	-
L.O.I %	7.7	-	-	-	-	-	-	11	11.63	5.06	4.25	5	19.9	31.57	10.07
Mn ppm	-	1600	-	1600	0.11	7000-1200	-	131	47	55	49	-	-	123.9	300
S ppm	0.07	-	-	-	0.14	0.11-0.2	-	-	-	-	-	-	-	214.12	-
Cr ppm	-	240	-	-	-	-	-	310	265	336	356	-	440	749.4	-
Pb ppm	-	-	-	-	-	-	-	15	22	8	7	-	17	<50	-
Co ppm	-	200	-	-	-	-	-	182	84	25	15	-	43	22.64	-
Cu ppm	-	-	-	-	-	-	-	728	23	17	17	-	51	5.42	-
Zn ppm	-	-	-	-	-	-	-	22	16	19.1	19	7.3	201	38.29	-
Ni ppm	-	200	-	-	-	-	-	143	150	56	46	-	208	28	-
V ppm	-	500	-	-	0.33	-	-	434	850	355	290	28	745	800	-

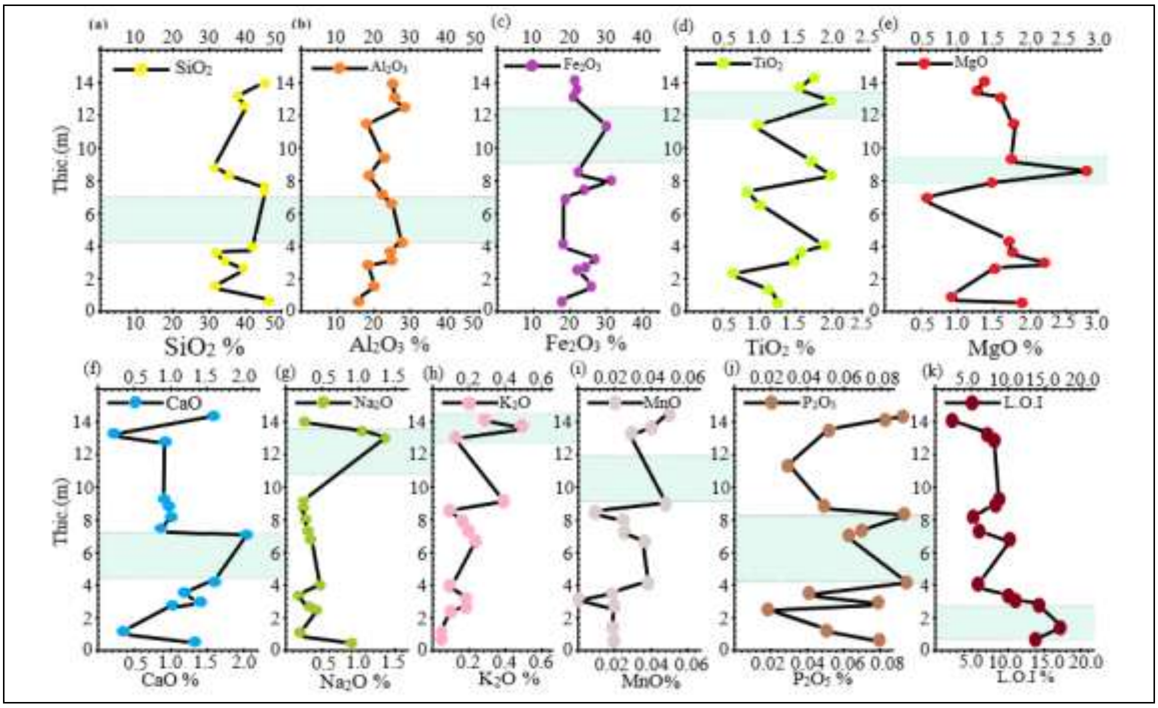

Fig.10: The distribution of the major elements with the thickness of the stratigraphic section (Rutbah area)

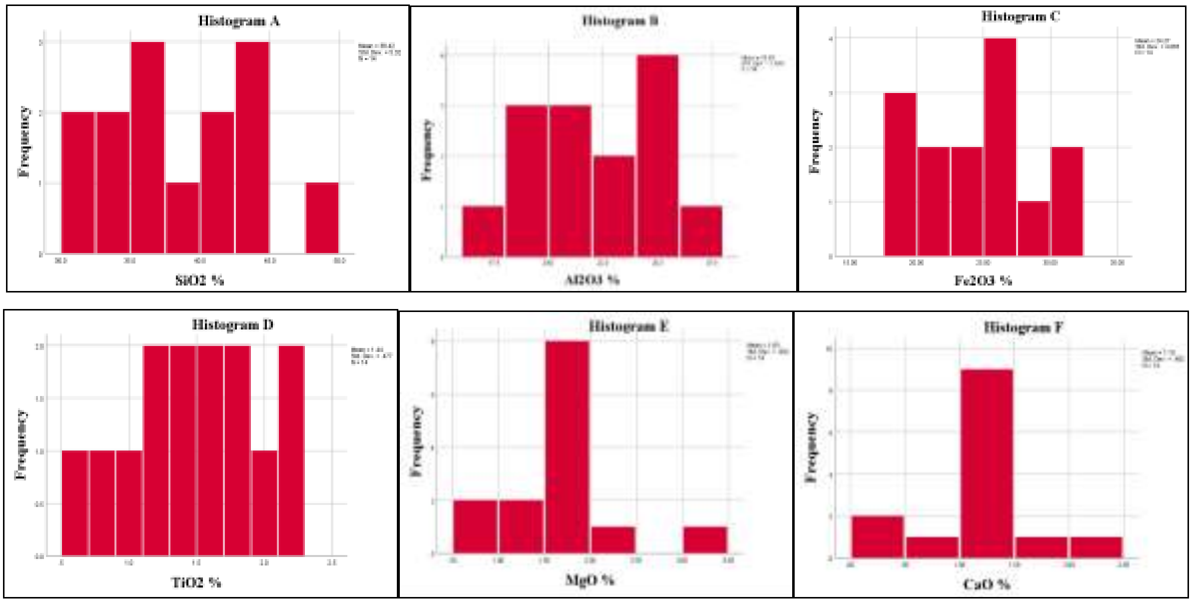

Fig.11: Histogram of the distribution of major chemical composition of the kaolinitic clays of the Hussainiyat Formation

– **Alumina (Al_2O_3)** is a low dissolved element, so, that the alumina is considered resistivity oxides, the process of dissolved or transportation of the alumina includes release from minerals by fluids as a result of gradual weathering of particle rocks with time, and the fluid more acidic, this increases in acidic cause movement of alumina (Luo *et al*., 2019). Increasing Al_2O_3 concentration with the intensity of chemical weathering is accompanied by iron oxide in a depositional environment. The average Al_2O_3 content in the claystone of the Hussainiyat

Formation is 21.8% (Table 2). The distribution of alumina with the thickness is shown in Figure 10b. The frequency distribution of Al_2O_3 in clay ironstone is dimodel (Fig.11B), which reflects the content of Al_2O_3 from claystone facies; this interprets the higher values of Al_2O_3 than many international ones (Table 3).

– **Iron** exists in both ferrous and ferric iron and is relevant, essentially, to iron oxide and hydroxide minerals, such as goethite, hematite, and probably some magnetite and limonite in the studied samples. (Fe^2) oxide is considered to be the primary minerals during weathering processes and alteration to other iron oxides, such as hematite and goethite, accompanied by clay minerals as colloidal fluid form or coated of clay minerals as iron oxides and hydroxides (Tobia *et al*., 2019; Moinevaziri and Mirza, 2021). The iron is found as either an essential component, such as hematite and goethite, or partial substitution of Al^3 by Fe^3 in the lattice structure of Kaolinite. The distribution of iron with the thickness is shown in Figure 10c. Fe_2O_3 is trimodality distributed and refers to poly sources of iron content, the first that represents the claystone associated with the iron ore. The others are representing the ironstone (iron oxides, hydroxides, and other minerals), including iron-bearing clay minerals (Fig.11C). The average Fe_2O_3 content in the claystone of the Hussainiyat Formation is 24.27% (Table 2). Based on this average and when compared to other ironstones from across the world, claystone from the Hussainiyat Formation is one of the medium-grade ironstones, with a greater iron concentration than other international ironstones but lesser than ironstones Gaara, Iraq (Tobia, 1983), goethitic ironstones, minette ores, Verte, Lorrain (James, 1966), Thuringia ironstones, Germany (Mucke and Farshad, 2005).

– **Titanium oxide (TiO_2)** includes in most residual sediments and sedimentary rocks as structural Ti4 in silicate and as free oxides. It ranges from less than 0.5% in scarcely weathered temperate soils to up to 25% in highly weathered ferruginous latosols of Hawaii (Li *et al*., 2018). Most of the TiO_2 presented in the studied samples is anatase, though a minor amount of rutile is present in some deposits. The rutile is most probably inherited from source rocks and the anatase authigenically by the chemical weathering of Ti-bearing minerals. The distribution of titania with the thickness is shown in Figure 10d. TiO_2 distribution is binary modal (Fig.11D). The average TiO_2 content in the claystone of Hussainiyat Formation is 1.44% (Table 2). TiO_2 content of the claystone is higher than Gaara and Benavi ironstone in Iraq and many international ironstones (Table 3).

– **Magnesium oxide (MgO)** is a very dissolved component as a result of weathering and erosion processes, which decreases its concentration in clays, MgO content in kaolinitic clays is less than 1% (Bleam, 2017). The presence of Mg in the studied samples is related to the presence of carbonate minerals (dolomite and sub-ordinate calcite) as well as to the presence of irregular mixed layer clays. The distribution of magnesia with the thickness is shown in Figure 10e. MgO distribution is unimodal with maximum frequency at class interval 1.37 – 2.24 % (Fig.11E). The average MgO content in the claystone of Hussainiyat Formation is 1.62% (Table 2). This average is greater than Gaara ironstones, comparable to Iraq's Benavi ironstones, and lower than many worldwide ironstones (Table 3).

– **Calcium oxide (CaO)** and secondary gypsum presence are related to the CaO concentration. The secondary gypsum is normally present along fractures and in weak areas. It normally replaces the claystone components and thinks to have formed through the diagenetic processes. The distribution of quicklime with the thickness is shown in Figure 10f. The frequency distribution of CaO content is a unimodal distribution with a symmetrical curve; the maximum frequency is at the class interval of 0.9 – 1.6 % (Fig.11F) within

Hussainiyat Formation. The average CaO content in the claystone of the Hussainiyat Formation is 1.10% (Table 2). This concentration is comparable to the CaO content of Ga'ara, Iraq (Tobia, 1983), and the iron-rich beds of the Abha Khamis region, Saudi Arabia (Babalola *et al.*, 2003), Thuringia ironstones/ Germany (Mucke and Farshad, 2005) and lower than more other international ironstones (Table 3).

– **Sodium oxide (Na_2O)** The low values of sodium oxide (av. = 0.5%) reflects the scarcity of evaporate minerals in the studied area (Table 2). This percentage is normal in comparison with other ironstones (Table 3). The distribution of sodium oxide with the thickness is shown in Figure 10g.

– **Potassium oxide (K_2O)** The low content of potassium oxide (av. = 0.2%), (Table 2), maybe return to substantial leaching and chemical weathering, that breaks illite and feldspar as well as the cyclic sedimentation to which the studied formation has been subjected. This average is comparable to the K_2O content of Gaara and Benavi ironstones, as well as the K_2O content of the majority of international ironstones (Table 3). The distribution of potassium oxide with the thickness is shown in Figure 10h.

– **Manganese oxide (MnO)** The positive correlation for manganese oxide with Fe in the Hussainiyat Formation is due to the geochemical similarity in behavior of Mn and Fe, where there is the possibility of Mn transportation as coatings for iron oxides, as well as the possibility of Fe^{+2} substitution by Mn^{+2} into iron oxides with Fe^{+2} in their structures. The average MnO content in the claystone of the Hussainiyat Formation is 0.03% (Table 2). This concentration is close to Benavi ironstones and the study of Jawad (1980), and higher than Gaara, Iraq (Tobia, 1983), Nammen ironstones, marine sedimentary, Germany (Zitzmann, 1977), while it is quite low when compared to international ironstones (Table 3). The distribution of manganic oxide with the thickness is shown in Figure 10i.

– **Phosphorus pentoxide (P_2O_5)** concentration in the Hussainiyat Formation is in the range (0.02 – 0.09 %) with an average of 0.06% (Table 2). It is lesser than international ironstones (Table 3). The phosphate minerals are adsorbed by iron hydroxides (Flores *et al.*, 2021). The distribution of phosphorus pentoxide with the thickness is shown in Figure 10j.

– **Loss on ignition (L.O.I)** involves combined water and other volatile components such as CO_2 and SO_3. It is in the range (5.7 – 17.77 %) with an average of (10.06%), this average is approximately equal to the Gaara ironstones in the western desert and a few higher than many international ironstones, while it is lesser than Benavi ironstone in Northern Iraq. The distribution of loss on ignition with the thickness is shown in Figure 10k.

CONCLUSIONS

Kaolinite claystone in the Hussainiyat Formation is less mature than other clays attributed to the prevalence of iron minerals, which implies a lesser impact on chemical weathering. Granitoids (intermediate and acidic igneous rocks) and reworked sediments make up the majority of the mother rocks. The ultra-stable minerals zircon, tourmaline, and rutile are the primary detrital accessories discovered in the Hussainiyat Formation sandstones. This suite of minerals is found in practically all types of rocks and may be used to determine the genesis of source rocks. Nonetheless, rounded grains suggest extended transportation or reworking of pre-existing sediments. Kaolinite is rare to generate authigenically since it is formed by the decomposition of feldspars and ferrous minerals. These minerals should be observed in sandstone rather than claystone, but the Hussainiyat Formation sandstone facies is clean (high mineralogical and textural maturity) and includes uncommon feldspars and kaolinite. Although the disintegration of a few feldspar particles after their deposition is not completely ignored, it is thought that the majority of the kaolinite was transported in an authigenic manner. There are two methods for kaolinite to develop. The first extensive weathering of the Arabian Shield calcareous rocks, causes metals and alkaline metals to dissolve and iron and alumina to remain. The second is formed by the alteration of feldspar from the Arabian Shield by running rivers, which results in lateritic soil from granitic acidic rocks. The chemical composition of kaolinite ironstone is distinguished by a comparatively high concentration of SiO_2, Fe_2O_3, Al_2O_3, and TiO_2 and a low concentration of MgO, CaO, Na_2O, and K_2O. The presence of kaolinite is linked to the enrichment of Al_2O_3. The variance in the chemical composition of the investigated claystone presumed source rocks can be explained by a decrease in some elements in the source area and by specific locatives in the deposition location.

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