

## MINERALOGY OF PLYGORSKITE-RICH CLAYSTONE IN GERCUS FORMATION, DOHUK GOVERNORATE, NORTHERN IRAQ

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### ABSTRACT

Seventeen geological sections were studied in the Gercus Formation, east of Dohuk city, with sampling of all exposed palygorskite-rich claystone beds. The thickness of these beds ranges between few centimeters to three meters. Forty eight claystone samples were analysed by X-ray diffraction and five of these samples were examined by transmission electronic microscopy. Mineralogically, these claystones consist basically of palygorskite, montmorillonite and dolomite with small amounts of kaolinite, quartz, chlorite, calcite and feldspar.

For the first time in Iraq, this study succeeded in separating the palygorskite from the other associated minerals in the claystones. Eight samples were purified to separate the palygorskite using a developed purification procedure. The percentage of the palygorskite in the separated samples ranged between 90 – 100%. The separated palygorskite was studied minerlogically by X-ray diffraction, thermogravimetric analysis and Infrared.

The palygorskite is well crystalline and includes several forms of water which were lost when heated above 900 °C. Palygorskite appears as elongated authigenic fibers aggregated forming weak bands; each band includes 2 – 12 fibers or more. The lengths of the fibers are mostly less than 8 µm and the width is about 0.1 µm mainly with straight edges and euhedral shape. Various patterns were observed in the studied palygorskite represented by short palygorskite fibers emerge from the montmorillonite grains. This feature and the sharp peaks of XRD and infrared patterns promote the authigenic formation of the studied palygorskite from montmorillonite in a shallow marine (restricted) environment in a warm temperature and high pH value as well as the enrichment of Mg in the sedimentary basin. The direct precipitation theory for the formation of the studied palygorskite cannot be applied. The origin of montmorillonite is detrital, transported to the depositional basin from the weathering of continental detritus.

معدنية الصخور الطينية الغنية بالباليغورسكايت ضمن تكوين الجركس  
في محافظة دهوك، شمال العراق

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### المستخلص

تم تغطية تكوين الجركس في المنطقة الواقعة شرق مدينة دهوك بسبعة عشر مقطع جيولوجي مع نمذجة كل الطبقات الطينية الظاهرة الغنية بالباليغورسكايت. يتراوح سمك هذه الطبقات بين عدة سنتيمترات إلى ثلاثة أمتار. تم دراسة ثمانية وأربعون نموذج طيني بواسطة الأشعة السينية وخمسة منها فحصت بواسطة المجهر الإلكتروني النافذ.

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تتكون الصخور الطينية المدروسة بصورة رئيسية من المعادن التالية: الباليغورسكايت، مونتوريلوناييت والدولومايت بالإضافة إلى نسبة قليلة من الكوارتز، الكلورايت، الكالسيت والفلدسبار.

نجحت هذه الدراسة ولأول مرة في العراق بفصل معدن الباليغورسكايت من المعادن المرافقة له في الصخور الطينية. من خلال استعمال الطريقة المطورة في هذه الدراسة حيث تمت تنقية معدن الباليغورسكايت لثمانية نماذج طينية ونسبة تراوحت بين (90 – 100%).

تمت دراسة الباليغورسكايت المنقى معدنيا بواسطة جهاز حيود الأشعة السينية، التفاضل الحراري والأشعة تحت الحمراء. الباليغورسكايت ذو تبلور جيد ويحوي عدة أشكال من الماء يفقدها جميعا إذا سخن إلى 900 درجة مئوية. يتواجد الباليغورسكايت على شكل ألياف طولية مكانية المنشأ تتجمع مكونة حزم ضعيفة، كل واحدة منها تتكون من (2 – 12) من هذه الألياف أو أكثر. طول الألياف لا يزيد عادة عن 8 مايكرون وعرضها بحدود 0.1 مايكرون وغالبا مايكون شكلها منتظم وبحواف مستقيمة. من الملاحظات المهمة والمشخصة في هذه الدراسة هو تنوع ألياف قصيرة للباليغورسكايت من حبيبات المونتوريلوناييت وبأنماط مختلفة. هذه الظاهرة إضافة إلى المنحنيات الحادة لمخططات حيود الأشعة السينية والأشعة تحت الحمراء تشير إلى نشوء الباليغورسكايت موضعيا من المونتوريلوناييت في بيئة بحرية ضحلة (محصورة) ودافئة وبظروف قاعدية تتوافق مع إغناء بنسبة المغنسيوم في حوض الترسيب. استبعدت هذه الدراسة فرضية الترسيب المباشر لتكوين الباليغورسكايت وبيئت ان المونتوريلوناييت فتاتي الأصل انتقل إلى حوض الترسيب عن طريق تجوية الفتاتيات الرسوبية.

## INTRODUCTION

The Gercus Formation outcrops over wide areas of north and northeast parts of Iraq. The studied area lies to east and southeast of Dohuk city. The studied area is about 90 Km<sup>2</sup>, limited by 36° 48' 00" – 36° 53' 00" N, and 43° 12' 00" – 43° 02' 30" E, within the High Folded Zone (Buday and Jassim, 1987 and Fouad, 2012). The following folds are recognized within the map area; Zawita, Shaikhan and Dohuk anticlines. The studied area consists of high mountains series and deep valleys (Fig.1). The maximum and minimum elevations, within the area are 1338 m and 590 m (a.s.l.) respectively. The exposed formations are (from older to younger); Shiranish, Kolosh, Khurmala, Gercus, Pila Spi and Fatha (Fig.2).



Fig.1: Landsat image of the study area (Google Earth, 2015)

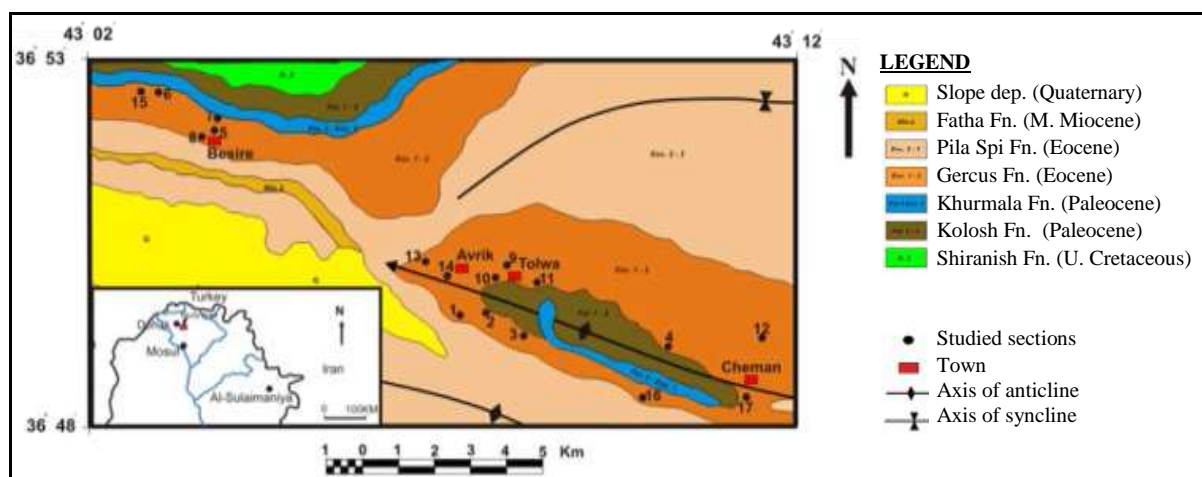


Fig.2: Location and Geologic map of the study area showing location of studied sections (modified after Sissakian, 1995)

## PREVIOUS WORK

There are several studies on the mineralogy of the palygorskite in the Gercus Formation, the most important of which are:

- Al-Rawi (1980) studied the petrology and sedimentology of the Gercus Formation, northern Iraq. He showed that the major amounts of the clay fraction from marl and siltstone beds in Gercus Formation are palygorskite and chlorite.
- Dhannon and Al-Dabbagh (1988), discussed the geochemistry of the palygorskite-bearing rocks (from rock fragments and the cement material) in the conglomerate, which lies at the top of the Gercus Formation, north Iraq. They showed that the palygorskite is formed by alteration of serpentine bearing mineral sediments, which are transported from the Arabian Shelf and ophiolites and ultramafic rocks of Zagros Thrust Zone of northeast Iraq and Iran.
- Hasso and Al-Naqib (1995), discussed the petrology of the clastic members of the Gercus Formation in Atrush area. They suggested that the main source of these clastics is sedimentary rather than igneous and metamorphic rocks.
- Al-Sayegh (1996), discussed the geochemical correlation between four localities where Gercus Formation is exposed, in northern Iraq. He suggested that the sediments of the Gercus Formation are derived from older nearby rocks and these sediments were deposited mainly in fluvial and deltaic environment.
- Jabbo and Kadhum (2007), noticed the presence of light green rocks, during the collection of samples from the claystone beds within the Gercus Formation, in Talwa area near Dohuk city. XRD analyses showed that they mainly contain palygorskite and montmorillonite.
- Al-Qayim *et al.* (2008), studied the Flysch – Molasse sediments of the Paleogene forland basin of North Arabia, Shiranish area, North Iraq. He mentioned that the palygorskite is restricted to the uppermost part of the Gercus Formation only.

## FIELD GEOLOGY

The Gercus Formation is exposed in different parts of the studied area, in most parts of Shaikhan anticline and the southern limb of the Zawita anticline. Generally, the formation forms slopes and badlands due to its soft clastic rocks. The formation consists of fining upward cyclothems. The thickness of the formation is variable in the studied area, in the northwest, near the Besire village it is about 430 m thick and decreases southeastwards. The formation, consists mainly of red clastics, carbonate and rare conglomerate beds with two

beds of gypsum in the upper part of the formation. A brief description of the beds is as follows:

▪ **Claystones and Mudstones**

These are the basic components of the formation. They represent more than 70% of the formation thickness. These beds occur in the lower and middle parts more than they do in the upper part. The thickness range from 0.3 – 10.0 m. A red color is predominant, especially in the upper part, while the middle part is varicolored (green, gray and rarely violet and other colors), (Fig.3). The palygorskite is present in these beds as horizons of various thicknesses ranging from a few centimeters to 3.0 m, (mostly 0.3 – 1.0) m. The palygorskite horizons are characterized by dark green or red colors, become pale when exposed to air. The palygorskite is soft with greasy texture and conchoidally fractured.

▪ **Sandstones**

Sandstone beds can be found widely in the upper part of the Gercus Formation. They represent about (15 – 20) % of the total formation thickness. Generally, red is the dominant color, with green and gray colors in the lowermost part of the formation. They are mainly fine to medium grained and occasionally coarse grained, rarely with pebbles, especially in the upper part. The thickness of these beds ranges from 0.4 to 8.0 m.

▪ **Carbonates**

They represent (5 – 10) % of the total formation; they are composed of dolomite, marl and rarely limestone. Thickness of these beds ranges from a few centimeters to 2.0 m. Dolomite and limestone are characterized by light gray color, hard to very hard, finely crystalline, medium to thinly bedded and porous.

▪ **Conglomerates and Gypsum**

Few conglomerate horizons are found in the Gercus Formation in addition to two beds of gypsum in the upper part of formation.



Fig.3: Varicolored claystone beds at the middle part of the Gercus Formation

## METHODS OF STUDY

Ninety five mudstone samples are collected from seventeen sections. Forty eight samples were examined by X-ray diffraction using Shimadzu 6000 diffractometer. The clay fraction ( $-2\ \mu\text{m}$ ) was separated from all samples and oriented specimens for XRD analyses by gravity settling on to glass slides. Additional XRD scans were obtained after ethylene glycol treatment and after heating to  $550\ ^\circ\text{C}$ . A quantitative estimate of the whole rock mineralogy was determined from XRD data by measuring the area under the peak, according to Al-Janabi *et al.* (1993). Eight samples were investigated by FTIR type (Shimadzu-8400 S), for wave numbers, ranging between  $250$  and  $4000\ \text{cm}^{-1}$ . Five samples were investigated by Transmission Electronic Microscopy using Philips (TEM) type (C-M-10). Thermo gravimetric Analysis (TGA) curve was carried out by taking  $1.0$  gram from the purified sample, dried at  $105\ ^\circ\text{C}$  for 2 hours and weighted. Then, the temperature was raised to  $200\ ^\circ\text{C}$  for one hour and the sample was weighted, then heated at  $300\ ^\circ\text{C}$  for 1 hour and the weight was recorded and so on until  $1000\ ^\circ\text{C}$ . The rate of the heating was  $5\ ^\circ\text{C}/\text{min}$ . All these analyses were performed in the central laboratories of GEOSURV, IRAQ, except the Infra red analyses which were performed in the laboratories of the College of Science/ Baghdad University and some of the X-ray diffraction analyses were performed in the laboratories of the Iraqi Ministry of Science and Technology.

## MINERALOGY

### ▪ X-Ray Diffraction Analysis

The mean content of the clay minerals in the analysed samples is about 59% ranging between 29 and 81%. The results showed the presence of different clay and non-clay minerals (Table 1).

### A. Clay Minerals

— **Palygorskite:** The X-Ray diffraction results showed palygorskite with characteristic peaks at  $10.5$ ,  $6.4$ ,  $5.4$ ,  $4.5$ ,  $3.6$  and  $3.2\ \text{\AA}$  for  $110$ ,  $200$ ,  $130$ ,  $040$ ,  $240$  and  $400\ \text{hkl}$  respectively. Glycolation had minor effect, where the  $110$  reflection became  $10.7\ \text{\AA}$ . At  $550\ ^\circ\text{C}$  the  $10.5\ \text{\AA}$  peak was noticeably shifted to about  $10.0\ \text{\AA}$  and the peak suffered significant reduction in intensity (Fig.4), due to further dehydration and possible folding of the structure (Soong, 1992). Depending on the width of  $110$  peaks in the midhigh, it is possible to determine the crystallization degree of the palygorskite (Kubler, 1964 in Mohammed, 1993). From X-ray diffractograms of the studied samples, it can clearly be noticed that the palygorskite peak is sharp and consequently reflects high degree of crystallization. In the studied area, the palygorskite average content in bulk claystone samples is about 25% and ranges from 4 to 53%, while in clay fraction of claystone samples it is about 43% and ranges between 14 and 75% (Table 1).

— **Montmorillonite:** Palygorskite and montmorillonite are the most common clay minerals present in the claystone horizons of the Gercus Formation in the studied area. The average content of montmorillonite is about 23% in bulk claystone samples and ranges between 5 and 53%, while in clay fraction, montmorillonite average content is about 40% and ranges between 16 and 80% (Table 1). On XRD diffractograms of air-dried oriented samples, montmorillonite is characterized by its  $001$  reflection at  $(14 - 15)\ \text{\AA}$ . This d-space is an indicator for Ca-Mg-montmorillonite type (Nelson, 2003), when saturated with ethylene glycol it swells to about  $17\ \text{\AA}$ ; when it is heated to  $550\ ^\circ\text{C}$  the  $001$  reflection collapses to about  $(10\ \text{\AA})$ . This collapse is often related to the dehydration the smectite (Poope *et al.*, 2002). Other reflections are found at  $(5.1, 3.05)\ \text{\AA}$  for the  $003$  and  $006\ \text{hkl}$ 's respectively (Fig.4).



— **Kaolinite:** Its X-ray diffraction patterns is characterized by 001 reflection at (7.0) Å, natural and when glycolated. This reflection disappears when heated to 550 °C. Reflections of 002 and 003 hkl appear at (3.57 and 2.36) Å respectively (Fig.4). Kaolinite average content in the studied claystone samples is about 9% and ranges from 0.0 to 20%, while in clay fraction kaolinite average content is about 15% and ranges between 0.0 and 35% (Table 1).

— **Chlorite:** It is characterized by the peaks at (14, 7, 4.7 and 3.5) Å corresponding to (001, 002, 003 and 004) hkl reflections, respectively. The (001) montmorillonite peak and (001) kaolinite peak are identical with the 001 and 002 hkl reflections of the chlorite. Chlorite can be distinguished from montmorillonite by the expansion of the later to 17 Å or more, when the sample is glycolated to be distinguished from kaolinite by heating to 550 °C, the later collapses at this degree only. As a result of this identification method, only five samples appear to contain chlorite with a range of 7 to 12% (Table 1). Therefore, chlorite is the least clay mineral identified by XRD in this study with an average of 1% (in the bulk samples).

## **B. Non-Clay Minerals**

— **Dolomite:** It is the most abundant non-clay mineral in the studied claystones. The average dolomite content in the bulk claystone samples is about 23% (Table 1). The X-ray diffractograms showed dolomite with characteristic peaks at (2.89 and 2.19) Å for (104 and 113 hkl) reflections (Fig.5).

— **Calcite:** Generally, it is present in a small amount. According to the XRD results, about quarter of the studied samples contain calcite. Its average content in all studied samples is about 3% (Table 1). Calcite is characterized by the peak of 3.04 Å for the 104 hkl reflection (Fig.5).

— **Quartz:** It is present in an average of 11% and ranges between (0.0 – 22) % (Table 1). Quartz is characterized by the peaks (3.34 and 4.26) Å for hkl reflections (101 and 100) respectively (Fig.5).

— **Feldspar:** It was identified as plagioclase which is characterized by the peak (3.2) Å for the (002) hkl reflection (Fig.5). The average content is about 4%; ranging between 0 and 15% (Table 1).

Table 1: Estimation of mineral constituents of claystone samples (Gercus Formation) in the studied area

Sample No.	Non-clay minerals				Clay minerals				Clay fraction				
	(bulk)		%		(bulk) %				(%)				
	D	C	Q	F	P	M	K	Ch	TC	P	M	K	Ch
1/5	4		21	5	30	33	6		69	44	48	8	
2/5	52		3		13	25	5		43	30	58	12	
3/5	28		19	3	4	21	14	10	49	7	39	32	22
4/5	52		6		12	27	2		41	29	66	5	
5/5	50		3		23	22			45	51	49		
6/5	6	6		7	53	25	3		81	65	31	4	
7/5	48			2	32	15	3		50	62	30	8	
8/5	36	12	5	5	28	8	6		42	66	19	15	
9/5	10	14	21	5	13	20	17		50	26	40	34	
10/5	54				26	19	1		46	56	41	3	

Continue Table: 1

Sample No.	Non-clay minerals				Clay minerals (bulk) %				Clay fraction (%)				
	(bulk)		%										
	D	C	Q	F	P	M	K	Ch	TC	P	M	K	Ch
11/5	54				23	17	6		46	50	39	11	
12/5	14	27	15	15	17	10	2		29	59	34	7	
13/5	22	18	14	8	16	11	11		38	44	29	27	
14/5	18	12		6	42	22			64	65	35		
15/5	52		6	3	6	33			39	16	84		
16/5	13	6	8		25	15	20	13	73	35	19	29	17
17/5	16	8		4	15	54	3		72	21	75	4	
18/5	32		14	4	10	35	5		50	20	70	10	
19/5	14		18	5	32	25	6		63	52	39	9	
20/5	15			6	30	41	8		79	38	52	10	
21/5	25		16		21	33	5		59	36	56	8	
22/5	20	20	8	3	17	27	4		48	35	56	9	
23/5	13	16	13	3	25	12	7	13	57	44	21	12	23
24/5	14	6	20	6	12	39	3		54	22	72	6	
25/5	21	12	4	3	20	36	4		60	33	60	7	
26/5	10		19	9	22	28	12		62	36	44	20	
27/5	23		6	4	22	32	13		67	32	49	19	
28/5	15		6	7	42	21	9		72	58	29	12	
29/5	58				12	20	10		42	29	47	24	
30/5	45		5	2	14	32	2		48	29	67	4	
31/5	11	6	15	11	40	9	8		57	70	16	14	
35/5	16		13	12	28	26	5		59	47	44	9	
4/17	20		10		28	31	11		70	40	44	16	
3/3	10		22	5	21	25	19		63	32	39	29	
2/16	28	5	19	5	32	6	6		44	72	14	14	
6/11	15		19	4	26	15	21		63	42	24	34	
2/12	17		17	3	34	16	13		63	53	26	21	
1/10	8		20	4	11	33	17	7	68	17	48	24	11
2/10	7		18	3	30	26	16		72	42	35	23	
5/10	12		9	5	51	12	11		74	69	16	15	
7/10			20	4	35	23	18		76	46	30	24	
4/1	9		14	8	36	22	11		69	54	33	17	
½	13		9	5	10	31	17	15	73	14	42	23	23
2/2	20		13	5	10	33	19		62	16	53	31	
3/13	30		6		32	21	11		64	50	33	17	
1/13	29		2	9	45	15			60	75	25		
2/13	21	5	9	3	39	5	18		62	63	8	29	
1/14			14	7	51	18	10		79	65	23	12	
Mean	23	3	11	4	25	23	9	1	59	43	40	15	2

**D:** Dolomite, **C:** Calcite, **Q:** Quartz, **F:** Feldspar, **P:** Palygorskite, **K:** Kaolinite, **M:** Montmorillonite, **Ch:** Chlorite, **TC:** Total of clay fractions in the sample

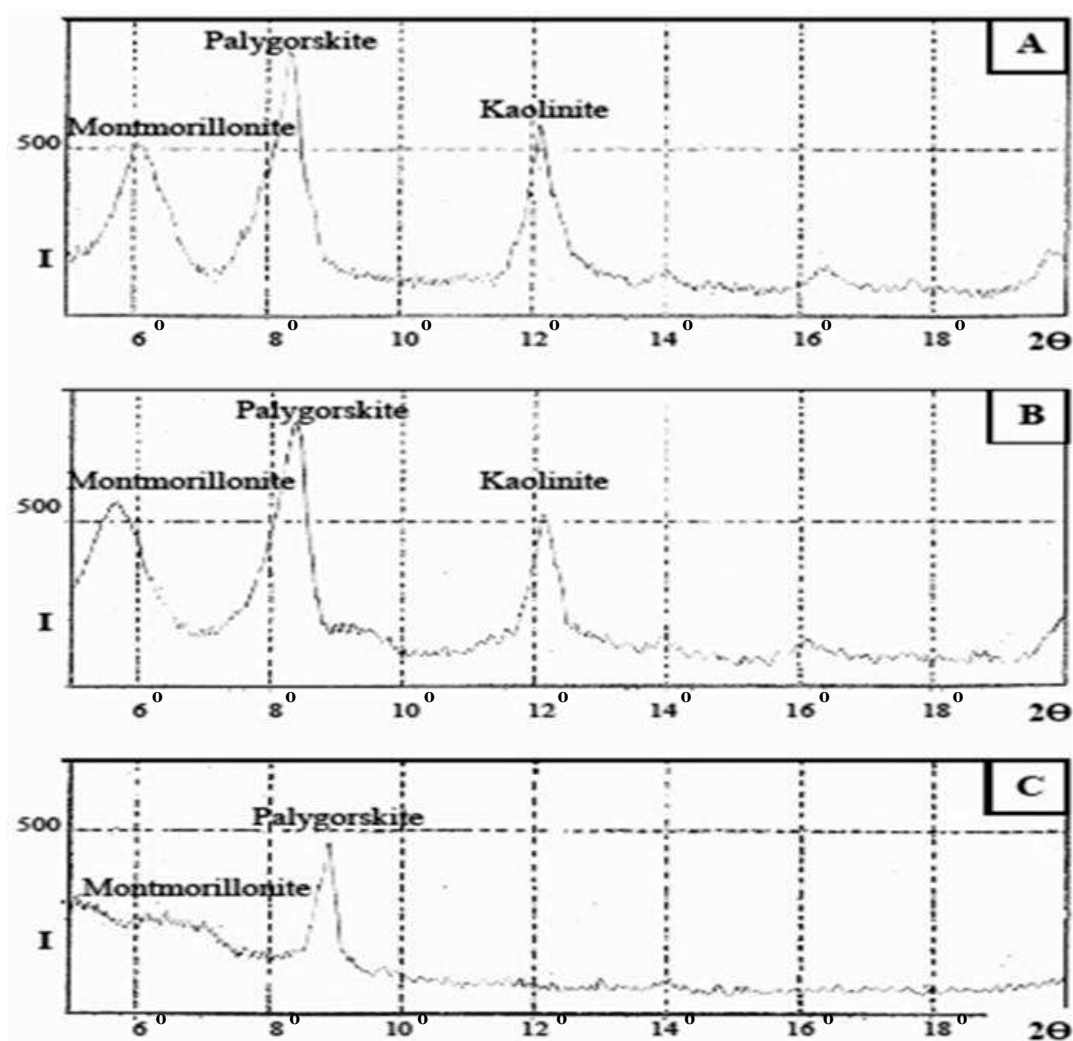


Fig.4: X-ray diffractograms of clay fraction in sample (13/5). **A)** Natural sample, **B)** Glycolated sample, **C)** Heated to 550 °C

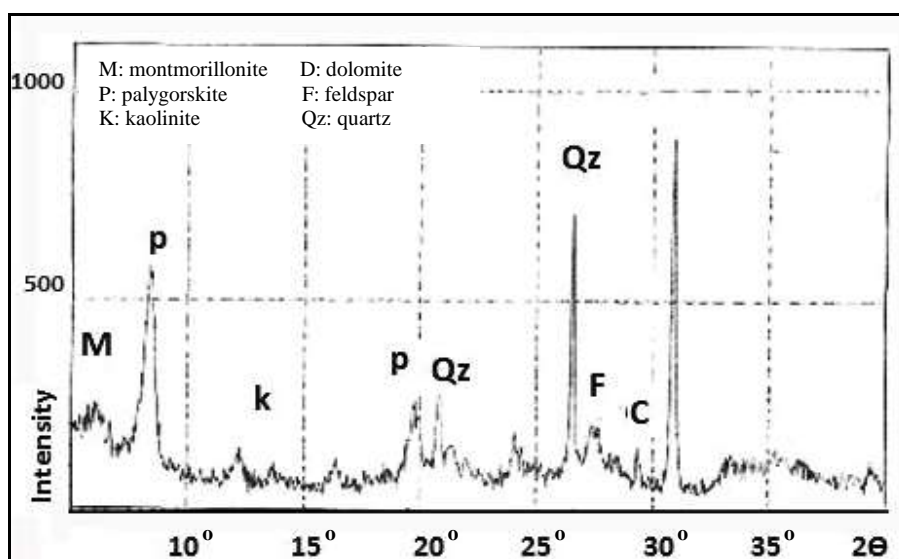


Fig.5: X-ray diffractogram of bulk sample no. 2/13



### ▪ Transmission Electron Microscopy (TEM)

To identify the nano texture of various minerals, five samples were selected for the study by the Transmission Electron Microscopy (TEM). In order to interpret the results of TEM, several published studies, in this field, were reviewed, such as Sindelar (1965); Sudo *et al.* (1981); Welton (1984); Smith and Norem (1986); Mohammed (1993); Al-Na'ami (2003) and Krekeler *et al.* (2004).

Palygorskite appears from the present TEM study as elongated fibers, aggregated by weak bands forming bundles. Generally, each band may include 2 – 15 fibers or more. The fibers have mainly straight edges, euhedral lath shapes and elongated (Fig.6A, B and C). Almost all the mentioned references agree that the aggregated euhedral lath shape reflects the authigenic origin, while palygorskite of detrital origin appears mainly as disassembled broken subhedral short fibers. Fibers are mainly less than 8  $\mu\text{m}$  in length and the width is about 0.1  $\mu\text{m}$ . This dimension, when compared with the known dimensions of palygorskite fibers indicates that the studied palygorskite is of short length and thin fibers type. Therefore, the possibility of being directly precipitated chemically from solution, seems to be weak (from these images only), whereas the later mode of formation (direct precipitation) is more likely as it is characterized by long fibers; reaching up to 50  $\mu\text{m}$  in length and up to 0.5  $\mu\text{m}$  in width, similar to the palygorskite deposits of Jabal maqlub (Al-Sayegh *et al.*, 1976) and (Al-Banna, 1977). Shadfan and Dixon (1981) in Singer and Galan (1984) mentioned that palygorskite with short fibers may suggest high Fe content.

In the studied samples, montmorillonite is characterized by dark color and its grains appear as regular flaky subhedral with subrounded shape (Fig.6D), in most cases. This form reflects the detrital origin and transportation to the depositional basin from weathering of continental detritus (Chamley, 1989). Mathieu-Sicaude *et al.* (1951) in Grim (1968) mentioned that the variations in the exchangeable cation in the montmorillonite may be reflected in their appearance in electron micrographs, in which Ca-montmorillonite appears as a mosaic of aggregate, increases in size as the preparatory suspension is aged. Whereas, Na-montmorillonite appears as more or less continuous nebulous film-like assemblages; frequently showing cracks intersecting at 120°. In the studied samples, the montmorillonite grains diameter reaches occasionally 5  $\mu\text{m}$  (Fig.6D). The size and nature of montmorillonite grains complement the XRD results that it is a Ca-type montmorillonite.

In addition to the morphological microscopic characteristics of the palygorskite and montmorillonite, other important textures, where short palygorskite fibers emerge from the montmorillonite grains were observed. This may be attributed to palygorskite originated from the montmorillonite transformation (Tianhu *et al.*, 2004). Various patterns were observed in the supposed relationship between palygorskite and montmorillonite. These forms may be attributed to various stages of transformation. In the early transformation stages, the planner character of the parent montmorillonite is maintained and the palygorskite fibers emerge from the boundaries of the montmorillonite grains (Tianhu *et al.*, 2004) (Fig.7A and B). The following stage shows growth of short fibers outside the grains, with their roots embedded in the transformed grain (Fig.7C). In the later stage of the transformation the palygorskite fibers merge together and become a mosaic weaves texture (Fig.7D).

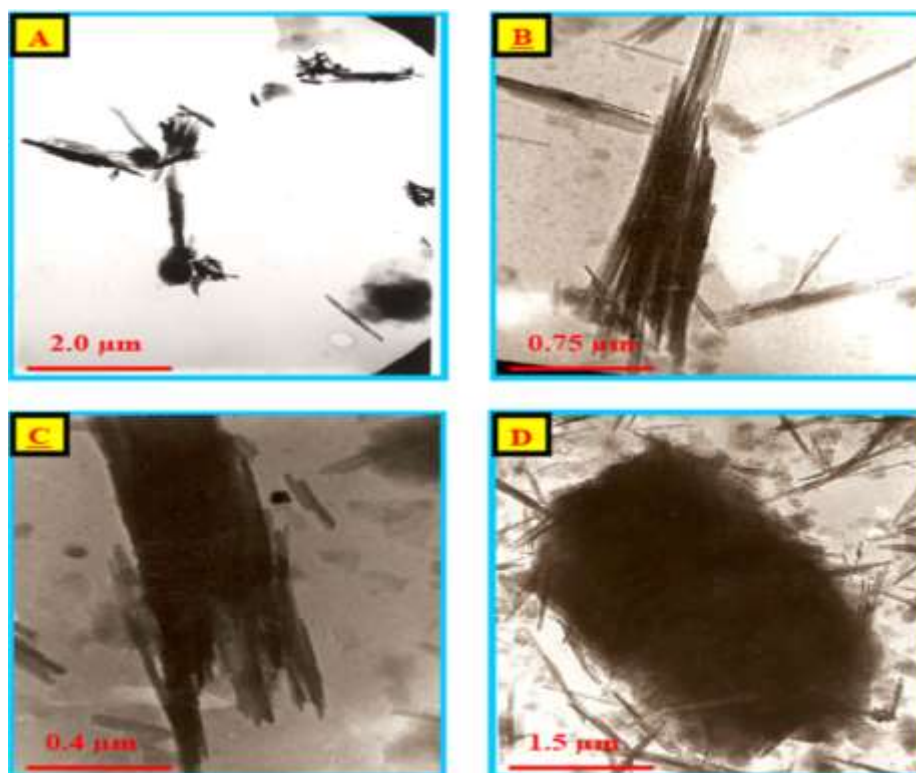


Fig.6: Transmission electron micrographs showing A, B and C) Palygorskite laths aggregated. D) Montmorillonite

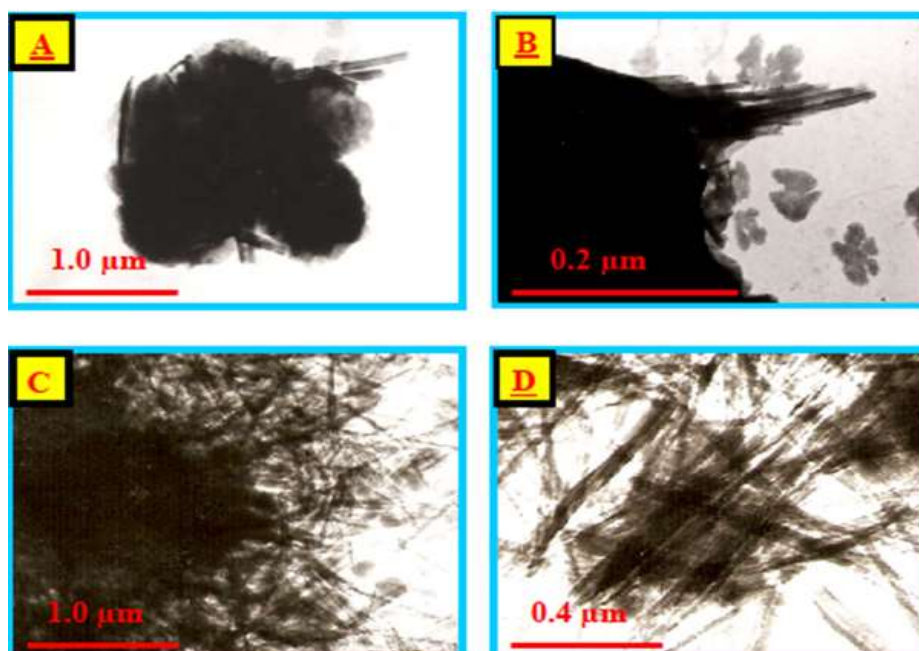


Fig.7: Transmission electron micrographs showing, A and B) The palygorskite fibers are emerging from the boundaries of the montmorillonite grains. C) The following stage of montmorillonite transformation. D) Mosaic weaves texture of palygorskite fibrous.

## DETAILED STUDY OF PLYGORSKITE

### ▪ Palygorskite Separation

Separation of the palygorskite from other minerals is very important, because the highest percentage of palygorskite in the studied sample rarely exceeds 50% (Table 1). Al-Ajeel *et al.* (2008), based on Paul *et al.* (2000) and Robert *et al.*, (2002), purified palygorskite-montmorillonite clays from other minerals using a palygorskite raw clay sample, collected from the Digma Formation in the Iraqi Western Desert. They used a wet method for processing naturally occurring palygorskite claystone and found that the percentage of palygorskite in the rocks can highly be raised.

In the present study, palygorskite from Gercus Formation was isolated following the above procedure, after improving the method by adding several steps to remove the montmorillonite and dolomite. One sample (No. 1/14) (Table 2 and Fig.8A) was selected as a test sample to apply the laboratory purification process. The process comprised the following steps:

1. Preparation of clay slurry by mixing 50 gm of crushed palygorskite raw claystone, with tap water (total of 1.0 liter) in laboratory Denver scrubbing unit. Mixing speed was 1500 rpm for 30 min.
2. Degritting the slurry through sieve (200 mesh U.S standards).
3. Addition of a dispersing agent (Tetrasodium Pyrophosphate) which amounts to 8% by weight of clay, with mixing at 1200 rpm for 10 minutes.
4. The suspension was allowed to rest and hence separated by gravity sedimentation into a suspended clay layer and settled non-clay impurities layer.
5. The clay suspension was decanted and subjected to centrifugation at speed of 2000 rpm for 15 min, to separate the purified clay and was referred to as bulk sample (1/14-T). This was the final step reached by Al-Ajeel *et al.*, 2008.

Visual observation indicated that the separated bulk clay is comprised of two distinct colored layers; pale gray at the bottom and brown at the top. To identify the mineralogy and chemical composition of these layers individually, the separated bulk clay is re-slurred by two stages of centrifugation. At a speed of 500 rpm for 10 min, the gray color material was separated (sample number 1/14-G). Subsequently the brown material was separated at a centrifugal speed of 2000 rpm for 15 min (sample number 1/14-B).

The separated materials (bulk clay and brown layer) were mineralogically (XRD) analyzed; the results are shown in Fig. (8) and (Table 2). The brown color sample (1/14-B) represents the purified palygorskite. The separation between palygorskite (brown layer) and associated minerals (grey layer) may be attributed to the variation in specific gravity; the specific gravity of palygorskite is about 2.3, while those of the montmorillonite, dolomite and kaolinite are 2.53, 2.74 – 2.9 and 2.63 respectively (Christie, 2007).

Subsequently, other 7 samples (richer in palygorskite) were treated similarly and the results were passed to obtain a high purity palygorskite. Some of those samples do not show any mineral peak, except palygorskite, as sample 1/14-B (Fig.8B). This encouraged the detailed mineralogical study of the Gercus Formations palygorskite.

Table 2: Estimation of mineral constituents of the tested samples

Sample No.	Palygorskite %	Montmorillonite %	Kaolinite %	Feldspar %	Quartz %	Dolomite %
1/14	29	14	20	5	12	20
1/14-T	59	10	9	4	4	14
1/14-G	20	21	16	6	7	30
1/14-B	100	—	—	—	—	—

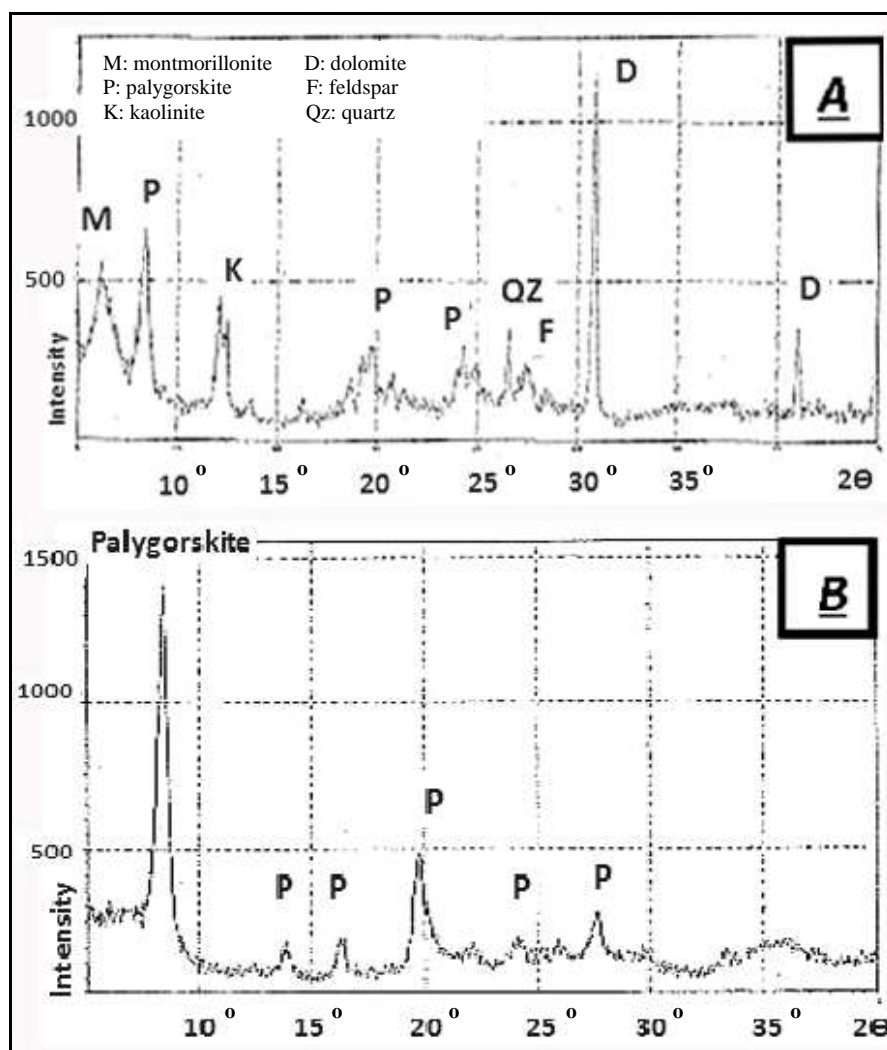


Fig.8: X-ray diffractograms of **A)** Bulk sample (1/14), **B)** Beneficiated sample (1/14-B)

#### ▪ XRD Results of the Separated Palygorskite

The 8 samples of the separated palygorskite were scanned by XRD. The results show that palygorskite is the only mineral or only major mineral with average of 93.9% and ranges between 90 and 100%. Minor or trace amounts of montmorillonite, kaolinite, quartz and feldspar may be present (Table 3). All these minerals were identified by their characteristic peaks (in bulk and clay fraction).

Table 3: Estimation of mineral composition of the separated palygorskite samples (%)

Sample No.	Palygorskite	Montmorillonite	Kaolinite	Feldspar	Quartz
28/5B	94	3	3		
1/9B	95			2	3
4/15B	90	5	2		3
19/6B	91	6			3
5/10B	94			4	2
1/14B	100				
1/12B	97				3
2/10B	90	4	6		

#### ▪ Thermogravimetric Analysis (TGA)

Palygorskite contains several types of water in addition to the hydroxyl (Grim, 1968). Hydroscopic water is usually loosely attached to the outer surface. Zeolitic water filling the internal channels and coordinate or bound water, where four molecules are found per unit cell; each two are bound with  $Mg^{2+}$ , in the edge of the octahedral layer. Two hydroxyl groups are present per unit cell and are located in the middle of the octahedral layer (Grim, 1968).

The thermogravimetric behavior of the separated palygorskite sample of the Gercus Formation (sample 1/14B) is shown in (Table 4 and Fig.9). By comparing this curve with TGA and DTA results of the palygorskite in the world and Iraq, the (TGA) curve in the present study can be interpreted as follows; the loss of weight (water) under 200 °C is about 6.56% and can be related to the hydroscopic and zeolitic water, the loss in water between 200 and 225 °C and about 500 °C is about 5.8% and is due to the partial loss of the coordinated water which represents the weakly bound part of the water. Its loss marks the beginning of folding and deformation of the lattice due to the rotation of the unit cell along the axis, passing through the Si-O-Si bond, which links the fibers with each other (Serna *et al.*, 1977). At this stage the mineral can be rehydrated and is known as “palygorskite anhydride” (Grim, 1968). The loss of water over 500 °C up to 800 °C is about 3.0% and can be attributed to the loss of the remaining part of the coordinated water (strongly bond), which means the loss of 3 molecules of  $H_2O$ . No further structural deformation takes place at this stage, but the heated palygorskite cannot be rehydrated and the deformation is permanent (Singer, 1989). The relaxation in the curve between 500 and 600 °C can be attributed to the high resistance of the strongly bond water before it starts to breakdown. The remnant small amount (0.3%) of the lost water under 900 °C represents the loss of the last hydroxyl and structure collapse (Ayoubi and Ottner, 2005). Therefore, heating above 900 °C up to 1000 °C does not record any change in the weight, due to the absence of the water in the tested sample.

Table 4: Water content lost by heating of the separated sample (1/14B)

Temperature °C	Loss in weight (%)	Accumulated (%)	Accumulated without moisture water (%)
200	1.84	6.56	1.84
300	1.72	8.28	3.56
400	2.22	10.5	5.78
500	1.83	12.33	7.61
600	0.6	12.93	8.21
700	1.3	14.23	9.51
800	1.13	15.36	10.64
900	0.3	15.66	10.94
1000	0.0	15.66	10.94

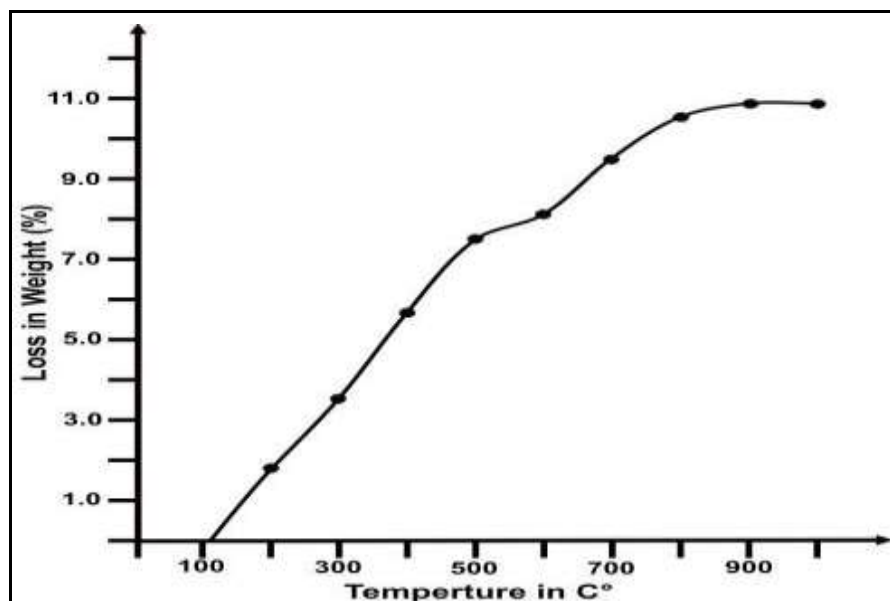


Fig.9: Thermogravimetric Analysis (TGA) curve of sample (1/14B)

#### ▪ Fourier Transform Infrared Spectrophotometry (FTIR)

Fourier Transform Infrared Spectrophotometry is employed as a supporting technique in the identification of clay minerals and studying the effect of chemical change at the structural lattice texture of clay minerals. The FTIR is also employed to study the bonds between the ions, which reflect the internal lattice and the chemical composition of the mineral, in addition to identify the kind of water in the clay minerals and the effect of water on the internal lattice of the minerals at different thermal conditions (Farmer, 1974). The palygorskite of the Gercus Formation (separated palygorskite samples) was investigated by FTIR for wave numbers ranging between (250 – 4000)  $\text{Cm}^{-1}$  (Fig. 10).

The results showed four broad absorption bands that occurred at (3700 – 3000)  $\text{Cm}^{-1}$ , (1700 – 1600)  $\text{Cm}^{-1}$ , (1200 – 900)  $\text{Cm}^{-1}$  and (700 – 400)  $\text{Cm}^{-1}$  (Fig.10). In order to interpret the FTIR results, several published studies in this field were reviewed (Farmer, 1974; Gionis *et al.*, 2006 and Myriam *et al.*, 1998). Accordingly the absorption bands at (3548 and 1650)  $\text{Cm}^{-1}$  are indicative of the zeolitic water. The shoulder at 1695  $\text{Cm}^{-1}$  in the Gercus palygorskite indicates hygroscopic water.

The band at 3616  $\text{Cm}^{-1}$  is indicative of the structure bound water. The bands at (987, 1196 – 1190 and 1018)  $\text{Cm}^{-1}$  are due to (Si-O) stretching vibrations. The band (1196 – 1190)  $\text{Cm}^{-1}$  has not been reported in any other clay mineral. It appears to be characteristic for the palygorskite (Mendelovici, 1973). The band at 910  $\text{Cm}^{-1}$  is due to (Al-OH-Al) vibrations, which distinguishes the mineral from the related mineral sepiolite. The bands (510, 478, 462 and 447)  $\text{Cm}^{-1}$  are due to (Si-O) bending vibration. The intensity of palygorskite crystallization can be derived from the sharpness of the (3616 and 3550)  $\text{Cm}^{-1}$  (Kubler, 1964 in Mohammed, 1993). Comparing the FTIR results in the present study with FTIR results of the world and Iraqi palygorskite showed that the Gercus palygorskite is highly crystalline. Consequently, the palygorskite in this study includes various kinds of water (zeolitic and bound water) together with the hydroxyl group.



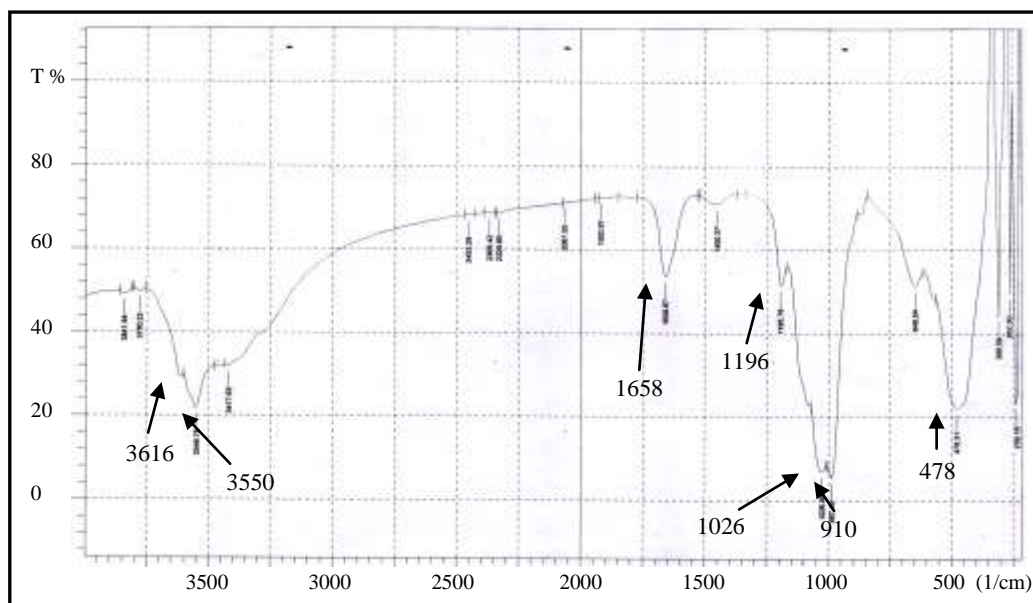


Fig.10: Infrared measurement of Gercus separated Palygorskite

### DISCUSSION: GENESIS AND ORIGIN OF THE STUDIED PALYGORSKITE

The authigenic formation of the palygorskite is suggested by TEM-analysis. The abundance of the palygorskite in the studied samples and its authigenic transformation from montmorillonite may reflect warm conditions and high pH value beside the enrichment of Mg in the sedimentary basin (Velde, 1995 and Calvo *et al.*, 1999). The crystallization degree of palygorskite may become an environmental indicator; palygorskites formed in continental and shallow marine environments have high degree of crystallization, in comparison with that formed in the other marine environments (Kubler, 1964 in Mohammed, 1993). In the studied separated palygorskite samples, the sharpness of the peaks in the X-ray diffractograms and infrared spectrum may promote the shallow marine (restricted) environment and the authigenic formation of this mineral in the study area. It may be pointed out here that Al-Rawi (1980 and 1983) and Hasso and Al-Naqib (1995) mentioned that these sediments were deposited mainly in fluvial, deltaic and partly marine (lagoon) environments.

### CONCLUSIONS

- The studied Gercus Formation palygorskite is authigenic in origin and rich in iron, it was transformed from montmorillonite in a shallow marine (restricted) environment with warm temperature and high pH as well as enrichment in Mg in the sedimentary basin.
- The origin of montmorillonite is detrital, transported to the depositional basin from the weathering of continental detritus.
- It is possible to separate palygorskite from other associated minerals by introducing new steps to the previous procedures applied in Iraq.

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