IBGM 2017 – 2018
IRAQI BULLETIN OF GEOLOGY AND MINING
Arcif: 0.0755
GIF: 0.936

Iraqi Bulletin of Geology and Mining *Special Issue, No.8, 2019,*
The Geology and Economic Potential of Mineral Deposits and Occurrences of Iraq *p 203 – 224*

PALYGORSKITE DEPOSITS AND OCCURRENCES IN IRAQ: AN OVERVIEW

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Received: 07/ 06/ 2018, Accepted: 14/ 02/ 2019
Key words: Palygorskite; Attapulgite; Clay minerals; Industrial applications; Iraq

ABSTRACT

Numerous palygorskite deposits and showings have been recorded and studied in Iraq. They range in age from Maastrichtian to Holocene, and are found in about 10 different formations. The Iraqi deposits are of sedimentary origin, deposited in marine, lagoonal, lacustrine, fluvial, and pedogenic environments as well as epigenetic fillings of fractures and veins. The majority was formed by the alteration of precursor minerals and to a lesser extent by direct precipitation from solution. The marine black shale deposits of the Upper Cretaceous Safra Beds of the Digma Formation and Lower Paleocene Traifawi Member of the Akashat Formation represent important palygorskite resources in the Western Desert of Iraq. Moreover, palygorskite is the dominant clay mineral in the lagoonal facies of the Tayarat Formation (Upper Cretaceous) in the Southern Desert. Other occurrences in the desert include thin palygorskite-rich claystone horizons in the lagoonal deposits of the Nfayil Formation, (Middle Miocene), and thin lenses of palygorskite-rich claystones in the fluvial deposits of the Zahra Formation (Pliocene – Pleistocene). In the Najaf – Karbala region, palygorskite is the dominant clay mineral in the fluvial and lacustrine mudstones of the Injana Formation (Upper Miocene), and in the sandy claystone lenses in the fluvial deposits of the Dibdibba Formation (Pliocene – Pleistocene). In the northern parts of Iraq, palygorskite veins and fracture-fill deposits are recorded in the sandstones of the Injana Formation, near Jabal Maqlub area, forming one of the most peculiar palygorskite showings in Iraq. In the Shikhan area, another interesting showing was recorded within the fluvial deposits of the Gercus Formation (Eocene). Furthermore, palygorskite forms the main clay mineral in the Holocene deposits of the Ahwar region of the Mesopotamia, as well as in the Recent soils of Iraq in general.

رواسب وشواهد معدن الـپاليغورسكايت في العراق: نظرة شاملة

خلدون صبحي البصام

المستخلص

توجد في العراق رواسب وشواهد عديده لمعدن الـپاليغورسكايت جرى توثيقها ودراستها في عشرة تكوينات جيولوجية جميعها رسوبية الأصل مترسبة في بيئات بحرية أو لاغونية أو بحيرية أو نهرية أو نواتج عمليات التجوية وهي من منشأين: **الاول،** وهو الاكثر انتشارا، تحول وتحوير معادن أخرى، **والثاني** ترسيب مباشر من المحاليل. تمثل الرواسب البحرية الموجودة في السجيل الأسود ضمن طبقات الصفرة/ تكوين الدگمة (الطباشيري الأعلى) وعضو الطريفاوي/ تكوين عكاشات (الباليوسين الأسفل) أهم رواسب الـپاليغورسكايت في الصحراء الغربية العراقية فضلا عن وجود شواهد للـپاليغورسكايت في السحنات اللاغونية لتكوين الطيارات (الطباشيري الأعلى) في آبار محفورة في الصحراء الجنوبية. توجد شواهد أخرى للـپاليغورسكايت في سحنات حوضية لتكوين النفايل (المايوسين الأوسط) وعدسات من الأطيان الغنية بالـپاليغورسكايت في رواسب المياه العذبة لتكويات انجانة (المايوسين الأعلى) والدبدبة والزهرة (البلايوسين –

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البلايستوسين) في المناطق القريبة من مدن السماوة والنجف وبحيرة الرزازة. وقد تم توثيق شواهد من الـپاليغورسكايت في شمال العراق قرب الشيخان في تكوين الجركس (الإيوسين) وقرب جبل مقلوب في الرواسب المالئة للشقوق في تكوين انجانة (المايوسين الأعلى). ولوحظ وجود شائع للـپاليغورسكايت في أطيان الرواسب الحديثة للسهل الرسوبي في مناطق الاهوار في جنوب العراق.

INTRODUCTION

Palygorskite and attapulgite are two names for one mineral; the former is the earlier and was used for a leather-like Mg-Al hydrosilicate from the Urals (Nemecz, 1981). The name attapulgite was introduced by Bradley (1940) for the same mineral from attapulgus, Georgia (USA). Other names for the same mineral include pilolite and lassallite, which are not in use now. Palygorskite is the name more commonly used in recent literature. It is a fibrous clay mineral with a structural formula of $Si_8\ Mg_5\ O_{20}\ (OH)_2\ (OH_2)_4\ 4\ H_2O$ (Carroll, 1970), where significant substitution of Mg^{2+} by Al^{3+} and Fe^{3+} occur in the octahedral position, and Ca^{2+}, Na^+ and K^+ occur as interlayer cations. The crystal structure of palygorskite was investigated in detail for the first time by Bradley (1940). The crystal form is monoclinic or orthorhombic.

Palygorskite may be found in a variety of sedimentary environments, as well as in hydrothermal deposits. It was mainly reported in brackish and lacustrine environments, but marine and fluvial deposits may also contain palygorskite, as well as weathering products of Mg-rich rocks and soils of arid and semi-arid regions (Singer and Galan, 1984). Palygorskite has proved to be one of the very important clay minerals in industry; it has been used as a "Fullers Earth" since the beginning of the 20th century. The main uses include: Drilling-mud in salt media, decolorizing oils, fats and waxes, isomerisation of essential oils and catalysts, polymerization of essential oils, catalytic cracking of petroleum oils, separation of hydrocarbons, adjustment of pH in sugar industry, cleaning material, pesticide carrier, conditioning agent of fertilizers, diluent for field strength insecticide dust, carrier for insecticide dust bases, carrier for pharmaceuticals and cosmetics, antiblocking agent in rubber and other products, gelling agent in plastisols, flatting agent in paints, reagent pigment in paints and inks, polishing agent, filler in rubber goods, dehydration of hydraulic oil and absorbent in general (Alvarez, 1984).

The first discovery of palygorskite as a mineral showing in Iraq was recorded by Al-Sayegh *et al.* (1976), as veins and fracture-fill deposits in the sandstones and mudstones of Injana Formation in Jabal Maqlub area, North Iraq. Since then several palygorskite showings and deposits were recorded by Iraqi Earth scientists in the Western and Southern Deserts, Mesopotamia and northern Iraq (Fig.1). The Iraqi palygorskites were deposited in a variety of sedimentary environments, including marine, lagoonal, fluvio – lacustrine, pedogenic and fracture filling. Some of the Iraqi palygorskite deposits were proved to be of industrial value in quality and quantity. They have been tested in laboratory and some in full industrial scale in drilling of oil wells, decolorizing paraffin wax, dehydration of hydraulic oil and in cosmetics (Al-Bassam *et al.*, 1992, 1994 and 2000a; and Al-Dulaimi *et al.*, 1994).

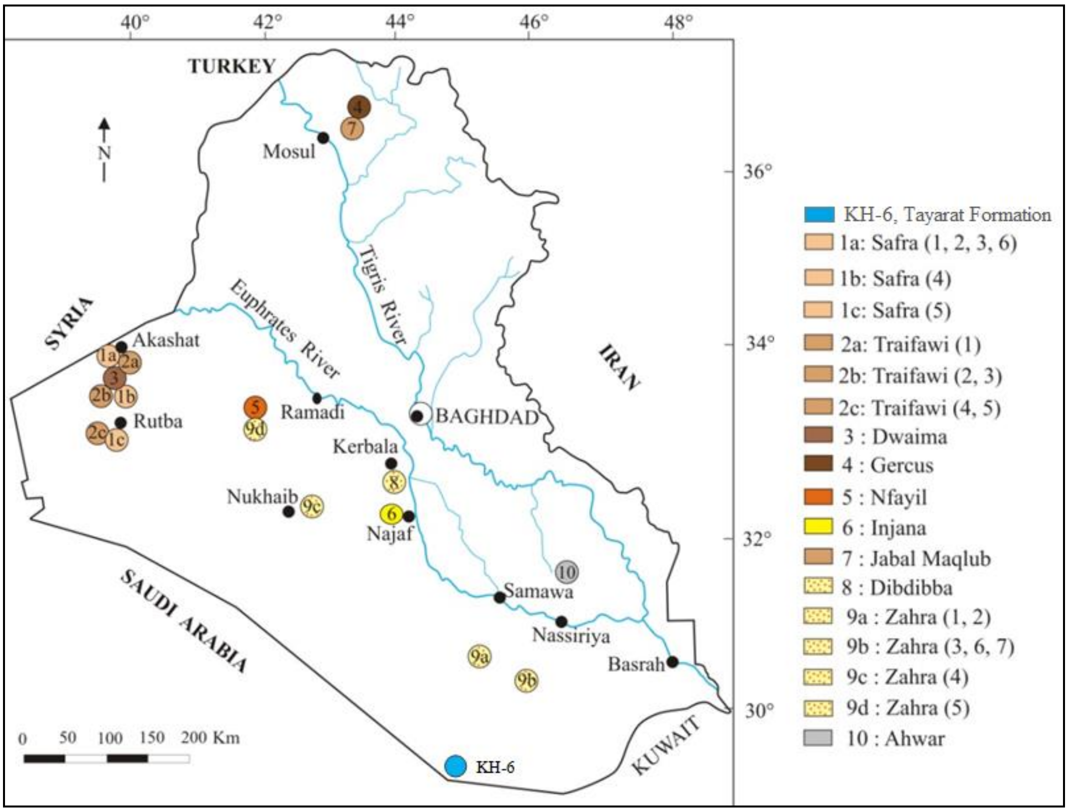

Fig.1: Distribution of palygorskite deposits and occurrences in Iraq
(Modified after Al-Bassam, 2000)

GEOLOGY

The palygorskite deposits and showings have been reported in sedimentary formations and sediments ranging in age from Upper Cretaceous to Holocene (Fig.2).

▪ Cretaceous palygorskites

The oldest occurrences of palygorskite, as a dominant clay mineral in the sedimentary formations of Iraq, are reported in the Upper Cretaceous units. The upper part of the Tayarat Formation (Upper Cretaceous) in Well KH-6 at Al-Ansab area in the Iraqi Southern Desert (Tamar Agha and Al-Janabi, 2000) was reported to consist of carbonates, marl and subordinate claystone and black bituminous claystone with evaporite. Several sedimentary facies have been recognized representing shelf margin, shelf lagoon, restricted platform and platform evaporite environments. Palygorskite was reported as the only clay mineral present in the fine fraction (– 2 µm) in the restricted platform facies. The Safra Beds of the Digma Formation (Maastrichtian) in the Iraqi Western Desert is of marine sedimentary origin, comprised of claystone, marl, dolostone, limestone and phosphorite. The claystone deposits are rich in palygorskite and montmorillonite, with accessory dolomite and calcite, and minor amounts of apatite and sepiolite. They represent one of the most extensive palygorskite deposits of Iraq. The claystones are found in several horizons ranging in thickness from (0.5 – 2.0) m and interbedded with dolomite, marl and thin horizons of phosphorite. The upper part of the Safra Beds is comprised of shelly limestone. The claystones are ocher to green in color, fissile and friable in outcrops (Al-Bassam *et al*., 1990; Mohamad, 1993 and Aswad *et al*., 2000a). Palygorskite showings were also reported in the Upper Cretaceous marls of the Shiranish Formation (Hadad, 1980).

- **Paleogene Palygorskites**

Several palygorskite occurrences have been reported in the Tertiary sequences in Iraq, including the in the Paleocene sandstones and shales of the Kolosh Formation and the red marls and carbonate beds of the Gercus Formation (Al-Rawi, 1980 and Kadhum, 2009). The Gercus Formation (Lower–Middle Eocene) in NE Iraq comprises clastic sequences of upwards fining cyclothems of fluvial and deltaic carbonate-rich sandstone, siltstones, marls, conglomerates and a few thin micritic carbonate beds (Al-Rawi, 1980 and 1983). The sandstones, siltstones and red marls are composed of various proportions of terrigenous dolomite fragments, serpentine (antigorite), palygorskite, montmorillonite, chlorite, quartz, chert and volcanic rock fragments. The clay fraction was reported to contain up to 85.5% of palygorskite (Dhannoun and Al-Dabbagh, 1988). Important occurrences of palygorskite have been reported, in association with smectite, in the Traifawi and Dwaima members of the Akashat Formation (Paleocene) (Mohamad, 1988; Al-Bassam *et al.*, 1990 and Mohamad, 1993).

- **Neogene Palygorskites**

Palygorskite has been reported as a dominant clay mineral in the Nfayil Formation (Middle Miocene) in the Iraqi Western Desert within a lagoonal sequence composed of clayey limestone, sandy limestone and claystone, stacked in a cyclic alternation. The Nfayil Formation sequence is composed of shelly limestone at the base followed by a cyclic alternation of marl, claystone and limestone. The claystone is green in the lower part, but reddish brown in the upper part. Variable amounts of palygorskite have been reported as the main clay mineral, the highest of which was reported in the green claystone, at the lower part of the sequence, compared to the overlying reddish brown claystone, which is highly calcareous (Al-Bassam *et al.*, 1995 and 2000b). Palygorskite is the dominant clay mineral in the claystone beds of the Injana Formation (Upper Miocene) exposed in the Najaf – Razzaza area. It is present in association with smectite, illite – smectite, kaolinite, chlorite, calcite, quartz, traces of illite with secondary gypsum and halite (Al-Bassam and Al-Baidari, 2000). The claystone is gray and bluish green in color, (0.5 – 1.0) m thick and found in lenticular bodies at the lower part of the sequence. Palygorskite has been also discovered in shear fractures in brownish claystone lenses of the Upper Miocene Injana Formation in outcrops near Mandan village, NE of Mosul. It is present as creamy white fibrous mineral filling fractures, locally reach (2 – 3) cm in thickness (Al-Sayegh *et al.*, 1976). Palygorskite is found in the lenses of clayey sandstone and/ or gypsiferous claystone within the sandstones of the Dibdibba Formation (Pliocene – Pleistocene) in the area between Karbala and Najaf (Al-Barri, 1996; and Taka *et al.*, 2000). The Dibdibba Formation is about 60 m thick in this area and is generally composed of friable sediments of gravel and sand with interbeds of claystone and marl. Palygorskite occurrences within the Zahra Formation (Pliocene – Pleistocene) are exposed in the Western and Southern Deserts of Iraq. The Zahra Formation is comprised of two units: the Clastics Unit in the lower part and the Limestone Unit in the upper part. The palygorskite is found in the Clastic Unit within thin lenses of red mudstone facies and also as the dominant clay mineral of the insoluble residue in the Limestone Unit (Tamar Agha *et al.*, 2000).

- **Quaternary Palygorskites**

Palygorskite has been reported within the Quaternary soils of the Mesopotamia (Al-Rawi *et al.*, 1969; and Eswaran and Barazanji, 1974) and has been widely reported as a clay phase in the recent sediments of the northern Arabian Gulf (e.g. Aqrawi and Sadooni, 1988). Palygorskite was reported and investigated in the clay fraction of recent surface sediments of the Ahwar region which are either fluvio – lacustrine or aeolian in origin with minor contribution from other sources of sediments including those formed by biological activity and chemical precipitation within the lakes and marshes (Aqrawi, 1993).

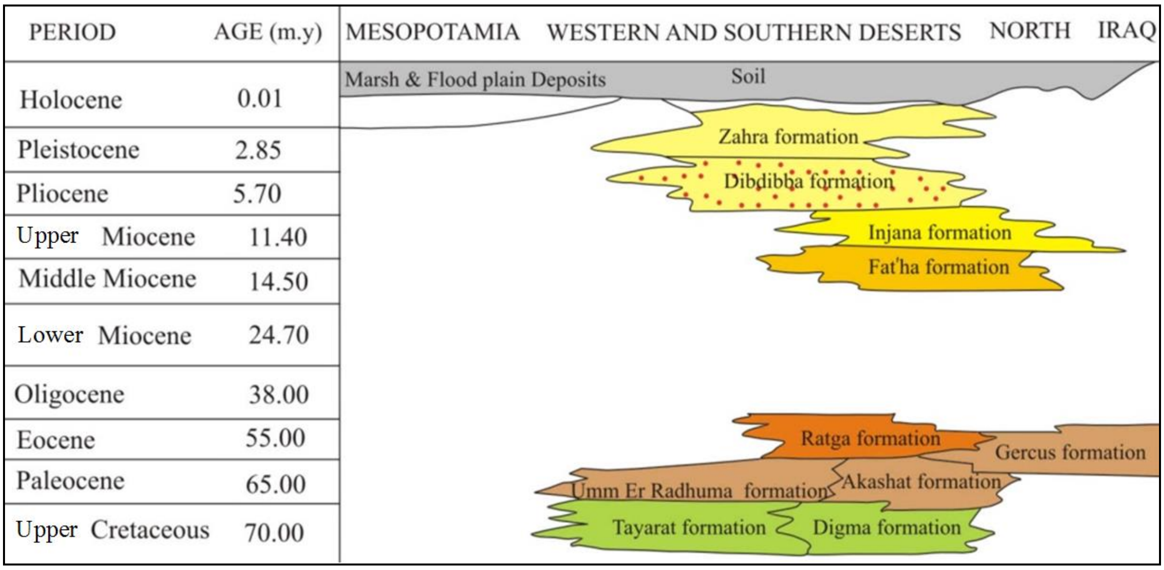

Fig.2: Distribution of the Iraqi palygorskites in space and time
(modified after Al-Bassam, 2000)

MINERALOGY OF THE PALYGORSKITE-BEARING ROCKS

Smectite and interstratified illite – smectite are the most common clay minerals associated with the Iraqi palygorskite deposits, except those found in Jabal Maqlub. A low-potassium smectite has been reported in the marine sedimentary rock units of Gercus, Safra, Traifawi and Dwaima. Whereas, the majority of the smectite in the fluvial deposits of the Nfayil, Injana and Zahra Formations as well as the Ahwar sediments, and to a lesser extent Dibdibba deposits show significant interstratifications with illite, reaching up to 50% illite layers as in the Nfayil and Injana deposits (Al-Bassam *et al*., 2000b). True illite is rare, except in the saline deposits of the Ahwar (Aqrawi, 1993). Sepiolite was detected in significant quantity only in one sample from the Gercus palygorskite deposits, derived from the alteration of near-by mafic rocks ((Dhannoun and Al-Dabbagh, 1988). Kaolinite is rare and was detected in the Nfayil, Dibdibba and Injana deposits only (refer to Table 1 for references).

Quartz and calcite are the most common non-clay minerals in the studied Iraqi palygorskite deposits. Quartz is especially common in the fluvial and lacustrine deposits, and is the only mineral impurity detected in the Jabal Maqlub palygorskite deposits. Dolomite occurs occasionally in some samples only, like in the Traifwi and Ahwar deposits, being significantly less frequent than calcite. Apatite (carbonate-fluorapatite) is only present in the Safra Beds, which are part of the Tethyan phosphorite-bearing sequence of Iraq. Halite and gypsum are minor minerals in most deposits; the former is especially common in the Nfayil lagoonal deposits, whereas the latter is present in higher amounts with the saline lake palygorskites of the Ahwar deposits (refer to Table 1 for references).

Table 1: Description of the Iraqi palygorskites and references of previous work

Location code, formation and age	Description of the deposits	Mineral association
KH-6 Tayarat Formation (Upper Cretaceous) Al-Ansab, S. Iraq	Carbonates, marl, subordinate claystone and black bituminous claystone with evaporites of shelf margin, shelf lagoon, restricted platform and platform evaporite environments.	Dolomite, smectite, mixed layer smectite-illite, kaolinite, chlorite, gypsum
la, lb and lc Safra Beds, Digma Formation, (Maastrichtian)	Olive green (black in subsurface) claystone, 0.5 m to several meters thick, laminated, forms part of a cyclic alternation of siliceous dolomitic lime mudstone (with chert nodules), shale and phosphorite. Pass laterally (towards open sea) to smectite-rich claystone	Smectite, calcite, apatite, halite and gypsum
2a, 2b and 2c Traifawi Member – Akashat Formation, (Danian)	Olive green, ocher, purple or red (black in subsurface) claystone (0.5 – 1.0) m thick, thinly laminated and chert-bearing lime mudstone or porcelanite. The palygorskite-rich facies pass to a smectite-rich claystone towards open sea	Smectite, calcite, quartz, apatite, dolomite halite, gypsum
3 Dwaima Member – Akashat Formation, (Thanetian)	Olive green, ocher, purple or red (black in subsurface) claystone, (0.5 – 1.0) m thick, thinly laminated and chert-bearing lime mudstone or porcelanite. The palygorskite-rich facies pass to a smectite-rich claystone towards open sea	Smectite, calcite, quartz
4 Gercus Formation (Lower – Middle Eocene)	Light green palygorskite distributed sporadically within red marl, and sometimes as cementing material in conglomerates. The deposit is part of a fining upward clastic sequence comprised of conglomerates, sandstone, siltstone and marl	Smectite, quartz, calcite, sepiolite
5 Nfayil Formation Middle Miocene	Green, ocher and red claystone beds (0.2 – 0.5) m thick, forming part of a cyclic alternation of lime mudstone and marl sequence	Illite – smectite, calcite, dolomite, quartz, halite, gypsum, kaolinite
6 Injana Formation Upper Miocene	Bluish green and gray claystone, 0.5 m thick, with plant remains associated with red marl, calcareous siltstone and lithic arenite in a fining upward sequence	Illite – smectite, quartz, calcite, kaolinite
7 Injana Formation Upper Miocene	White, almost pure palygorskite vein-, fissure-, and fracture-fill deposits in lithic arenites rich in quartz, feldspar and mica. The palygorskite fillings are several centimeters thick and several meters deep, thinning downward	Generally pure, but traces of quartz and calcite may be present
8 Dibdibba Formation Pliocene – Pleistocene	Gray, clayey sandstone and sandy claystone lenses, 0.5 m thick, embedded in quartz arenites	Smectite, Illite – smectite, calcite, quartz, kaolinite
9 Zahra Formation Pliocene – Pleistocene	Reddish brown claystone lenses, (0.2 – 0.5) m thick, associated fluvial sandstone, marl and freshwater limestone	Illite – smectite, calcite, quartz, halite
10 Ahwar deposits Holocene	Clay lenses associated with sand and silt alternation in a fining upward sequences	Illite – smectite, quartz, illite, dolomite, halite

Continue Table 1

Depositional environment	Source rocks	Palygorskite origin	References
Shelf lagoon and restricted platform environments	Older sedimentary rocks of the Arabian Platform	Early diagenetic Transformation of precursor terrigenous clays	Tamar-Agha and Al-Janabi (2000)
Semi-restricted marine inner shelf facies, deposited in a warm, anoxic and alkaline subtidal environment and semi-arid climate	Older sedimentary rocks of the Arabian Platform	Transformation of detrital smectite	Al-Bassam and Al-Sa'adi (1985), Hirmiz (1988), Al-Bassam *et al.* (1990), Mohamad (1993), Aswad *et al.* (2000a)
Semi-restricted marine inner shelf facies, deposited in a cool, anoxic and alkaline subtidal environment and semi-arid climate	Older sedimentary rocks of the Arabian Platform	Transformation of detrital smectite	Aba Hussain (1987), Al-Bassam *et al.* (1990) Mohamad (1993)
Restricted and semi -restricted marine inner shelf facies, deposited in a warm and alkaline subtidal environment and arid climate	Older sedimentary rocks of the Arabian Platform	Transformation of smectite	Aba Hussain (1987), Al-Khafaji (1989), Al-Bassam *et al.* (1990)
Flood plain deposits; cementing material in wadi-fill deposits, under warm and arid to semi-arid climate	Serpentinites of basic and ultrabasic rock complexes of the Zagros Zone	Pedogenic alteration of mafic minerals (samples 1, 2, 3) and transformation of smectite of the same origin (samples 4, 5)	Al-Rawi (1980), Dhannoun *et al.* (1988), Dhannoun and Al-Dabbagh (1988), Dhannoun (1989)
Semi-restricted lagoonal facies deposited in an alkaline, brackish and subtidal environment under arid to semi-arid climate	Basic igneous, metamorphic and older sedimentary rocks of the Zagros Zone	Transformation of illite – smectite	Al-Bassam *et al.* (1995) Al-Bassam *et al.* (2000b)
Flood plain marsh and lake deposits, alkaline and reducing conditions, warm and arid to semi-arid climate	Basic igneous, metamorphic and sedimentary rocks of the Zagros Zone	Transformation of illite – smectite with minor diagenetic outgrowth of palygorskite	Al-Dulaimi *et al.* (1994), Al-Baidari (1997), Al-Bassam and Al-Baidari (2000)
Epigenetic direct precipitation from Mg-and Si-rich solution in veins, fractures and fissures at atmospheric pressure and temperature and arid and warm climate	Basic igneous, metamorphic and sedimentary rocks of the Zagros Zone	Direct precipitation from solution	Al-Sayegh *et al.* (1976), Al-Banna (1977)
Lacustrine deposits at the distal end of a gentle and wide fan or delta lobe, arid to semi- arid and warm climate	Older rocks of the Arabian Shield	Transformation of smectite and illite – smectite with some diagenetic outgrowth	Sadik (1977) Ghalib (1988) Al-Barri (1996) Taka *et al.* (2000)
Ephemeral fresh-water lakes (playa) deposits under arid and warm climate and alkaline oxidizing conditions	Older sedimentary rocks of the Arabian Platform	Transformation of illite – smectite with minor diaenetic outgrowth	Al-Haza'a (1996) Tamar-Agha *et al.* (2000)
On-delta; marsh, lake and playa deposits. Lacustrine and alkaline environment, and hot arid climate	Basic igneous, metamorphic and older sedimentary rocks of Zagros Zone	Detrital of mixed origins (samples 1, 2, 4) and diagenetic outgrowth (sample 3)	Aqrawi (1993) Aqrawi and Sadooni(1988), Aqrawi and Evans (1990)

PETROGRAPHY OF THE IRAQI PALYGORSKITES

In view of the microcrystalline nature of the palygorskite, the petrographic characteristics of the mineral are usually studied using very high magnifications of the scanning electron microscope (SEM) and these observations are commonly used to predict origin of the palygorskite. The tree texture and mesh-work texture are considered indications of direct precipitation from solution (authigenic), whereas, broken and rod-like fibers are probably indicators of a detrital origin.

The scanning electron microscope (SEM) study shows that palygorskites differ greatly in shape and fibre size from deposit to another, and within single deposits according to their origin. Palygorskites formed by direct precipitation form solution (Jabal Maqlub deposits) show elongated fibres, isolated or in bundles (Fig.3) The length of the fibres may reach up to 50 μm, and the width ranges from (0.5 – 1) μm. Shorter and thinner fibres were observed in the palygorskites formed by transformation of smectites and illite – smectite (Fig.4). They are generally less than l0 μm in length and (0.1 – 0.25) μm in width; those of smectite origin (marine facies) tend to be thinner. Various stages of transformation can be observed in these palygorskites, usually found associated with the parent material. In the early transformation stages, the planar character of the parent smectite or illite – smectite is maintained and the palygorskite fibres are stacked within the boundaries of the precursor grain (Fig.5). The following stage shows growth of short fibers to the outside of the grain, with their roots embedded in the transformed grain (Fig.6). In the later stages of transformation the palygorskite fibers merge and become a mosaic weave texture (Fig.7). Diagenetic outgrowth of palygorskite in its advanced stages resembles in texture the directly precipitated palygorskites in many respects (Fig.8). They occur as elongated fibres, isolated or in bundles, and sometimes associated with other minerals, but usually developed in cavities.

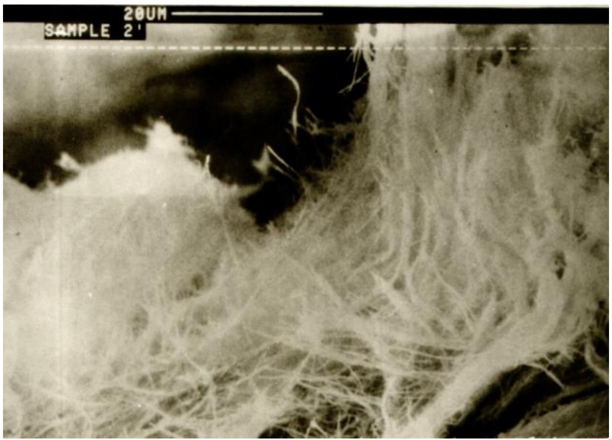

Fig.3: SEM image showing well developed fibres of palygorskite in Jabal Maqlub fracture-fill deposits
(after Al-Bassam *et al*., 2000b)

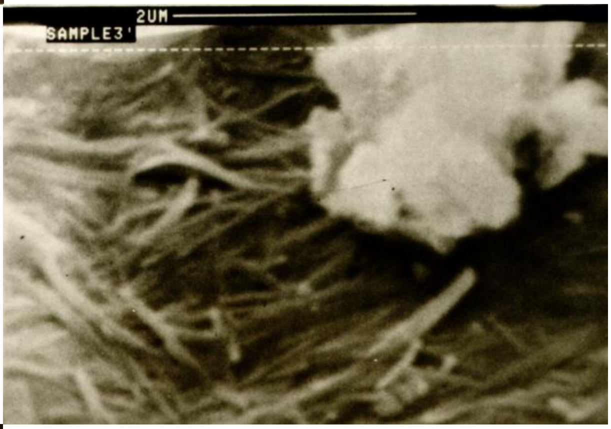

Fig.4: SEM image showing palygorskite fibres in the Safra Beds
(after Al-Bassam *et al*., 2000b)

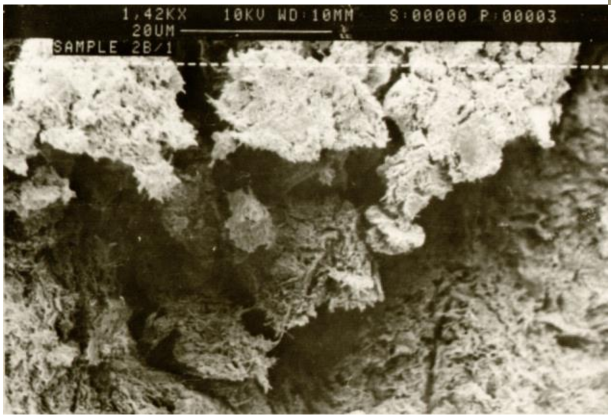

Fig.5: SEM image showing short palygorskite fibres stacked in a precursor smectite flakes, Injana Formation
(after Al-Bassam and Al-Baidari, 2000)

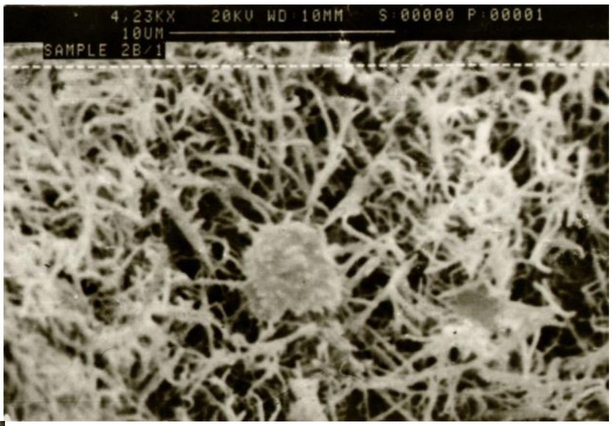

Fig.6: SEM image showing elongated palygorskite fibres merging out of a precursor smectite, Injana Formation (after Al-Bassam and Al-Baidari, 2000)

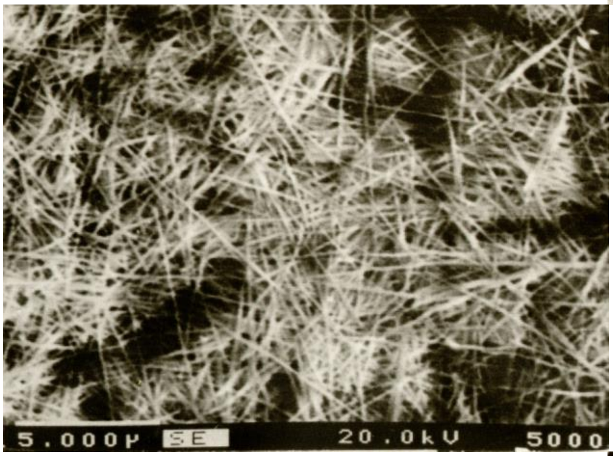

Fig.7: SEM image showing palygorskite fibres forming a mosaic weave, Dibdibba Formation (after Taka *et al*., 2000)

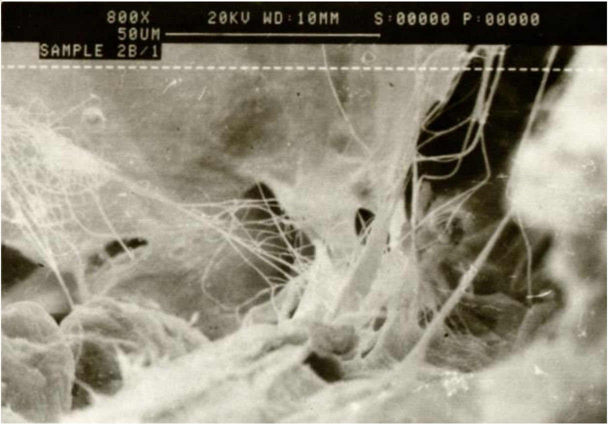

Fig.8: SEM image showing palygorskite fibres and bundles developed in cavities possibly extending from precursor clay minerals, Injana Formation (after Al-Bassam and Al-Baidari, 2000)

X-RAY DIFFRACTION ANALYSIS

X-ray diffraction analysis (XRD) shows well crystallized palygorskite with the major reflection at 10.57Å (Fig.9). The behavior of palygorskite upon heating was studied by some detail by XRD technique by various authors (e.g. Aswad *et al*., 2000a). At 210 °C the intensity of the reflections 3.23 Å, 4.47 Å and 10.57 Å is decreased and the intensity of the 3.71 Å reflection is increased, which could be attributed to the loss of zeolitic water. At 350 °C the intensity of the 10.57 Å reflection was highly reduced together with that of the 3.23 Å reflection, whereas the intensities of the 4.74 Å and 9.25 Å reflections were enhanced, which is attributed to the formation of "palygorskite anhydride" (Grim, 1962). At this temperature structural folding due to dehydration may occur in the palygorskite, which intern results in the intensity changes of the major reflections, as well as in the appearance of new peaks in the (8.6 – 9.2) Å region. At 600 °C the major reflection at 10.57 Å disappeared and the intensity of the new reflection at 9.25 Å decreased, whereas the intensities of the 4.47 Å and 6.38 Å reflections were reduced. At 800 °C the palygorskite structure collapsed and an amorphous phase was developed. Further heating to 1100 °C resulted in the crystallization of enstatite, hematite, cristobalite and tridymite (Fig.10).

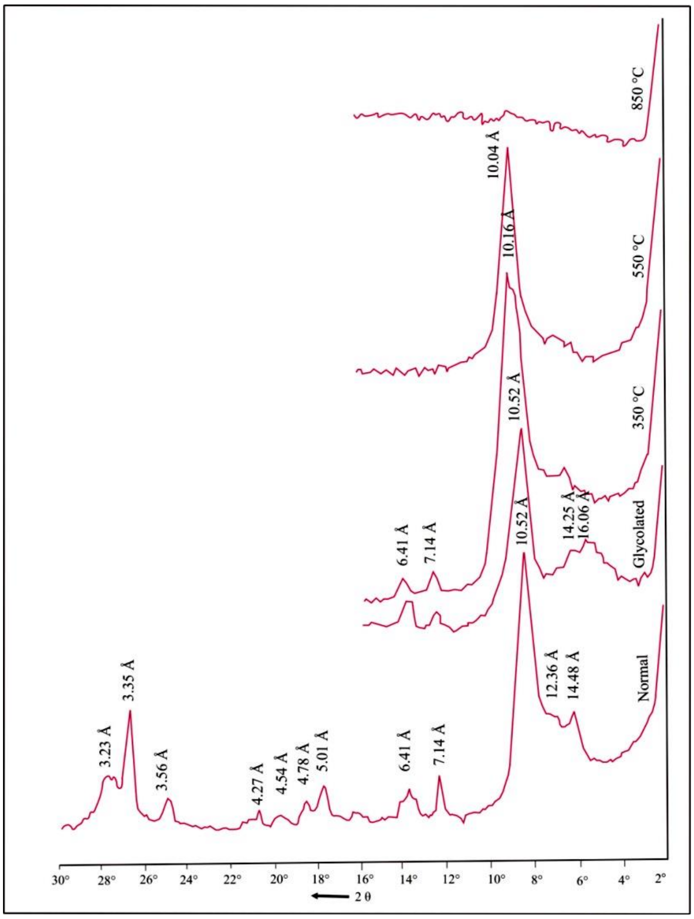

Fig.9: X-ray diffractograms of palygorskite in the – 2 μm fraction,
Nfayil Formation (Al-Bassam *et al*., 2000c)

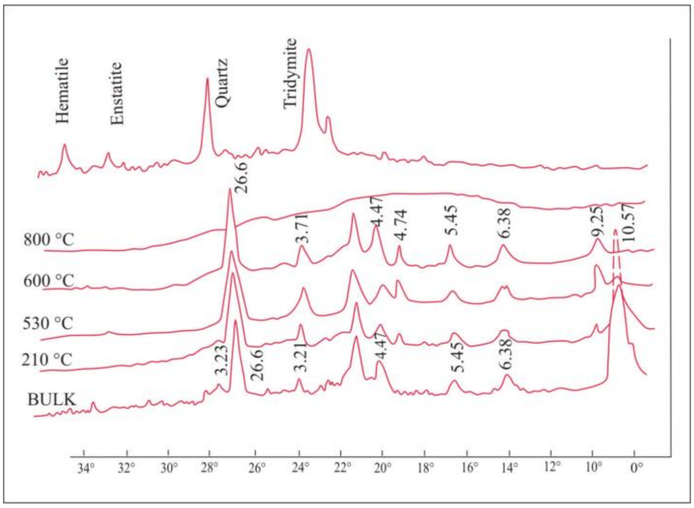

Fig.10: X-ray diffractograms of the Safra palygorskite after heating at
various temperatures (after Aswad *et al*., 2000a)

THERMAL ANALYSIS

Differential Thermal Analysis (DTA) and Thermal Gravimetric Analysis (TGA) are fundamental techniques to study thermal characteristics of palygorskite and other clay minerals. Palygorskite contain several types of water in addition to the hydroxyl. Hydroscopic water is usually loosely attached to the outer surface, zeolitic water fills the internal channels and coordinated or bound water, where four molecules are found per unit cell; each two are bound with Mg^{2+} at the edge of the octahedral layer (Mackenzie, 1957; and Russel, 1987). Two hydroxyl groups are present per unit cell and are located in the middle of the octahedral layer (Grim, 1968).

Four endothermic peaks and one exothermic peak are usually recognized in the DTA curve (Fig.11). The endothermic peaks appear at (80 – 210) °C, (220 – 340) °C, (350 – 570) °C and (670 – 760) °C. The exothermic peak appears at (950 – 990) °C. The TGA curve (Fig.12) shows four thermal gravity changes, which can be related to the endothermic peaks in the DTA curve and related to the loss of water from the various sites of the palygorskite. The first at 200 °C is due to 8.98 % water loss, the second at 300 °C is due to 8.0% water loss, the third at (400 – 500) °C with water loss of 5.5% and the forth at 800 °C with water loss of 1.9% (Aswad *et al*., 2000a).

The first thermal gravity change is related by Aswad *et al*. (2000a) to the loss of hydroscopic and zeolitic water. The second change is due to the partial loss of the coordinated water, which represents the weakly bounded 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". The third change is due to the loss of the remaining part of the coordinated (strongly bonded) water, which means the loss of 3 molecules of H_2O. No further structural deformation takes place at this stage, but the deformation is permanent. The fourth thermal gravity change represents the loss of the hydroxyl and structure collapse. The exothermic peak at 970 °C in the curve corresponds to the formation of new phases, such as enstatite and cristobalite.

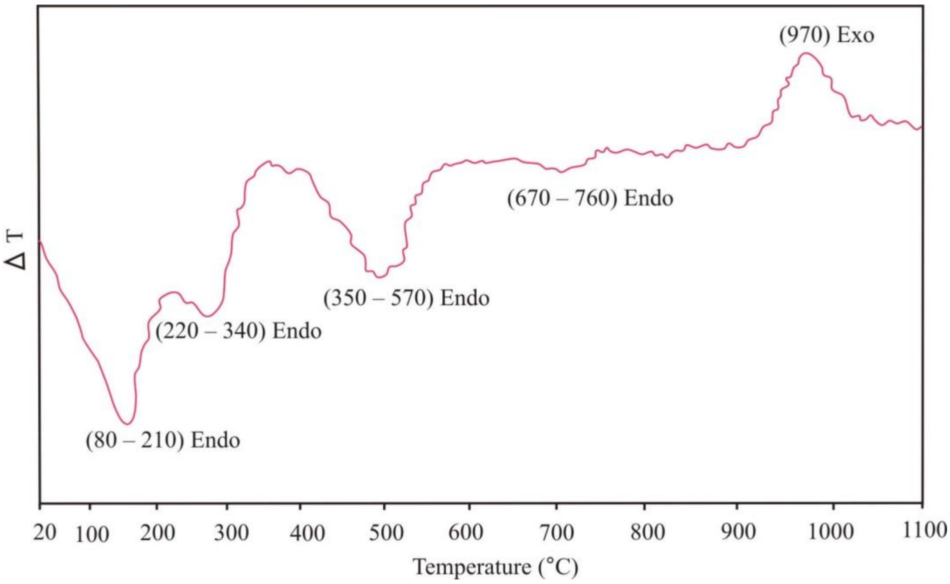

Fig.11: DTA curve of the Safra palygorskite (Aswad *et al*., 2000a)

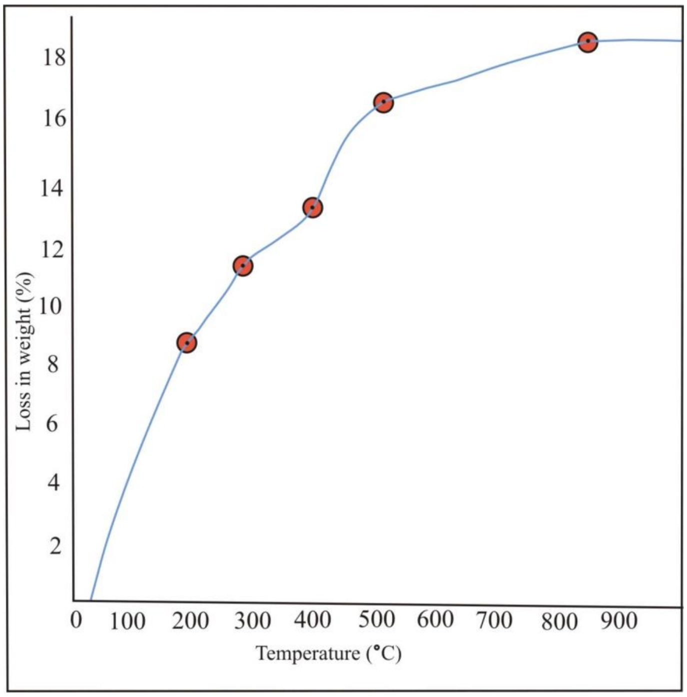

Fig.12: TGA curve of the Safra palygorskite (after Aswad *et al*., 2000a)

INFRARED SPECTROSCOPY

The – 2 µm fraction of a purified claystone sample from the Safra Beds (contains about 90% palygorskite) was analyzed by IR for the range (1400 – 5000) cm^{-1} (Fig.13) (Aswad *et al*., 2000a). The IR spectra showed the following absorption bands, which are analogous to those found by Hayashi *et al*. (1969): Sharp band at 3609 cm^{-1} with shoulders at 3640 cm^{-1} and 3683 cm^{-1}, sharp band at 3533 cm^{-1} with a shoulder at 3573 cm^{-1}, band at 1660 cm^{-1} with a shoulder at 1670 cm^{-1} and three broad bands at 3200, 3260 and 3340 cm^{-1}.

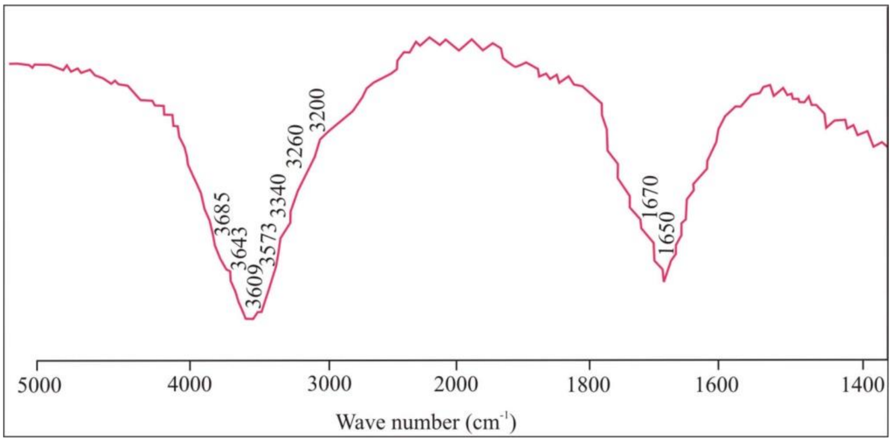

Fig.13: IR spectra of the Safra palygorskite (after Aswad *et al*., 2000a)

The absorption bands at (3260, 3200, 1660 and 3533) cm^{-1} were found by Aswad *et al*. (2000a) to correspond to zeolitic water of the palygorskite. The bands at (3573, 3643 and 3609) cm^{-1} correspond to the coordinated water. The band at 3683 cm^{-1} corresponds to the hydroxyl. When this band occurs at less than 3700 cm^{-1}, within a temperature range of

(610 – 730) °C the palygorskite structure is probably trioctahedral or there is significant substitution of Fe^{3+} for Mg^{2+} in the octahedral layer (Farmer, 1974).

CHEMISTRY

Geochemical criteria and textural observations are used to formulate a genetic classification for the Iraqi palygorskites based on data collected from various sources (see Table 1 for references). Two main genetic groups and several subgroups are suggested (Al-Bassam *et al*., 2000b):

Group 1: Direct chemical precipitation from solution (Jabal Maqlub deposits)

Group 2: Transformation and alteration of other minerals; classified as:

- **2.1:** Direct alteration of basic rocks (Gercus Formation deposits; samples 1, 2, 3)
- **2.2**: Transformation of smectite (Tayarat Formation deposits, Safra Beds deposits, and Gercus Formation deposits; samples 4, 5)
- **2.3:** Transformation of illite – smectite and illite (Nfayil, Injana, Dibdibba and Zahra Formations deposits; samples 1, 2, 3, 4)
- **2.4**: Diagenetic outgrowth (Zahra Formation deposits; samples 5, 6, 7 and Ahwar deposits.

▪ Major Elements

The chemical analysis presented in Table 2 show that $A1_2O_3$, MgO, Fe_2O_3 and K_2O contents vary significantly in the studied palygorskite deposits according to their origin. The highest alumina (12 – 15%) is found in subgroups 2.2 and 2.3 and the lowest alumina (7 – 9%) is found in subgroups 2.1 and 2.4, whereas Group 1 shows intermediate alumina content (11%). Magnesia shows an opposite trend. Iron (as Fe_2O_3) is high in Group 2 (generally above 5%), whereas it is remarkably low in Group 1 (less than 1%). Potassium is generally low in Group 1 and subgroups 2.1 and 2.2 (less than 1% K_2O), but it is remarkably high in subgroups 2.3 and 2.4 (generally above 1% and up to 3.6%).

Table 2: Chemical analyses of palygorskites (wt.%) (after Al-Bassam *et al*., 2000b)

Genetic Groups	Deposits	SiO_2	TiO_2	Fe_2O_3	Al_2O_3	MgO	CaO	Na_2O	K_2O	LOI
1	Jabal Maqlub	60.15	0.42	0.81	11.24	10.24	0.27	0.17	0.19	16.14
2.1	Gercus samples 1 – 3	56.80	0.72	7.46	7.41	12.57	0.58	1.16	0.35	12.61
2.2	Gercus samples 4, 5 Safra Traifawi Dwaima	53.62 57.85 56.02 57.11	0.61 0.59 0.46 0.72	8.39 6.15 7.33 7.39	11.98 12.56 12.25 14.05	7.71 8.60 7.83 7.26	0.41 1.78 1.75 1.24	0.09 1.35 1.76 1.58	0.62 0.59 0.64 0.52	16.57 10.53 11.96 10.13
2.3	Nfayil Injana Dibdibba Zahra; samples 1 – 4	54.98 53.93 51.08 55.57	1.01 0.65 n.a. 0.79	6.74 7.35 6.95 5.65	14.15 13.69 11.94 15.25	7.73 8.42 8.27 7.25	0.44 1.52 0.32 1.04	1.57 1.03 0.30 1.43	3.58 2.89 1.50 2.04	9.79 10.51 19.12* 10.99
2.4	Ahwar 3 Zahra; samples 5 – 7	52.35 56.55	0.96 0.65	4.95 5.97	7.01 9.20	11.96 10.29	1.35 2.79	0.32 2.32	1.09 1.09	20.00* 11.14

*Includes H_2O^- and H_2O^+, n.a.: not analysed

- **Trace Elements**

The trace elements analyses (Table 3) show that Group 1 (direct chemical precipitation) is highly depleted in trace elements relative to Group 2 (transformation and alteration of other minerals); all the elements analysed are less than average shale and are the lowest in most elements among the Iraqi palygorskites studied. However, Mn and Pb are enriched relative to other trace elements analysed in this group. Group 2 in general is rich in trace elements relative to Group 1. Most of the elements are enriched relative to average shale, except Mn, Sr and Cu. Subgroup 2.1 is characterized by anomalously high transitional trace elements (Cr, Ni and Co), and relatively low Mn. Higher Sr, Cr, Ni, U, Cu and Zr, and lower Mn, Co and Pb are noticed in subgroup 2.2. The Cr content is especially high in this subgroup, and the Mn content is extremely low. Subgroup 2.3 shows relatively high Cu, Mn, U, Co, Pb and low Cr, Zr and Sr relative to other members of Group 2. Relatively low Cr, Ni, Cu and Mn, and high Sr, Co and Pb are noticed in subgroup 2.4. Manganese, though low relative to the other groups, but it is high relative to some trace elements in this subgroup.

Table 3: Trace elements content of palygorskite genetic groups (ppm)
(after Al-Bassam *et al*., 2000b)

	Gl	**G2.1**	**G2.2**				**G2.3**				**G2.4**
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**	**K**
Sr	11	n.a.	n.a.	212	237	283	163	117	n.a.	101	182
Cr	26	3508	3628	306	510	305	167	306	167	89	64
Ni	9	397	636	120	226	170	220	314	140	86	88
Cu	4	n.a.	n.a.	20	24	24	37	47	n. a.	17	5
Mn	129	179	192	41	57	41	223	557	288	144	89
U	n.a.	n.a.	n.a.	11	8	6	16	n.a.	n.a.	15	5
Zr	7	n. a.	n.a.	249	146	300	150	111	n.a.	86	n.a.
Co	5	58	53	8	6	6	42	36	62	14	35
Pb	26	n.a.	n.a.	n.a.	13	n.a.	20	36	49	30	21

A: Jabal Maqlub, B: Gercus; samples1 – 3, C: Gercus; samples 4 – 5, D: Safra, E: Traifawi, F: Dwaima, G: Nfayil, H: Injana, I: Dibdibba, J: Zahra; samples 1 – 4, K: Zahra; samples 5 – 7, n.a.: not analysed

CRYSTAL CHEMISTRY

The major element chemistry is reflected in the structural composition of the palygorskites studied. The characteristic features of the various genetic groups are shown in the structural formulae calculated from the corrected mean analyses of each group (Table 4). Octahedral Mg^{2+} is high (more than 2 ions/ half unit cell) in Group 1 and subgroups 2.1 and 2.4. Octahedral Al^{3+} is low in subgroups 2.1 and 2.4 (less than 1 ions/ half-unit cell) and high in subgroups 2.2 and 2.3 (1.3 – 1.6). It is significantly high in Group 1 palygorskites (1.8 ions/ half unit cell). Tetrahedral Al^{3+} is the highest in subgroup 2.3 (0.6 – 0.9 ions), followed by subgroup 2.2 (0.5 – 0.6 ions) and subgroups 2.1 and 2.4 (0.4 – 0.5 ions). Group 1 palygorskites contains little or no tetrahedral Al^{3+}.

The increase in Al (tetrahedral Al^{3+}) is generally followed by an increase in the interlayer K^+; a general positive correlation exists between the two. The potassium ions are the highest in the palygorskites formed from the alteration of illite-smectite or illite of subgroup 2.3 (0.28 – 0.6 ions), followed by palygorskites formed as diagenetic outgrowths in subgroup 2.4 (0.18 – 0.2 ions); palygorskites from the alteration of smectite in subgroup 2.2 (0.09 – 0.11 ions); palygorskites formed by weathering of mafic minerals in subgroup

2.1 (0.6 ions) and the lowest K^+ ions are in palygorskites formed by direct precipitation in subgroup 2.1 (0.03 ions). Iron (as Fe^{3+}) shows high values and relatively narrow range in Group 2 (0.5 – 0.9 ions/ half unit cell), but it is as low as 0.08 ions in Group 1. Titanium (as Ti^{4+}) shows very little variation in the studied palygorskites; Group 1 is slightly lower in Ti^{4+}. Subgroups 2.2 and 2.3 exhibit lower R^2/R^3 in the octahedral site (less than 1.0), whereas subgroups 2.1 and 2.4 exhibit higher R^2/R^3 (more than 1.2). Group 1 shows a uniform and intermediate R^2/ R^3 ratio of about unity.

Table 4: Structural formulae calculated from corrected mean chemical analyses of main genetic groups of palygorskite (after Al-Bassam *et al*., 2000b)

Genetic Groups	Deposits	Tetrahedral		Octahedral				Interlayer		
		Si^{4+}	Al^{3+}	Al^{3+}	Fe^{3+}	Ti^{4+}	Mg^{2+}	Ca^{2+}	Na^+	K^+
1	Injana Formation at Jabal Maqlub (vein-fill deposits)	8.03	–	1.76	0.08	0.04	2.03	0.04	0.04	0.03
2.1	Gercus Formation; (samples 1 – 3)	7.60	0.40	0.77	0.71	0.07	2.51	0.08	0.30	0.06
2.2	Gercus Formation; (samples 4, 5)	7.45	0.55	1.41	0.88	0.06	1.60	0.06	0.03	`0.11
	Safra Beds	7.49	0.51	1.41	0.60	0.06	1.66	0.25	0.34	0.10
	Traifawi Member	7.43	0.57	1.35	0.73	0.05	1.55	0.25	0.45	0.11
	Dwaima Member	7.38	0.62	1.52	0.72	0.07	1.40	0.17	0.40	0.09
2.3	Nfayil Formation.	7.22	0.78	1.41	0.67	0.10	1.51	0.06	0.40	0.60
	Injana Formation	7.15	0.85	1.29	0.73	0.06	1.66	0.22	0.26	0.49
	Dibdibba Formation.	7.36	0.64	1.39	0.75	–	1.87	0.05	0.08	0.28
	Zahra Formation; (samples 1 – 4)	7.28	0.72	1.64	0.56	0.08	1.42	0.15	0.36	0.34
2.4	Ahwar; sample 3	7.61	0.39	0.81	0.54	0.10	2.59	0.21	0.09	0.20
	Zahra Formation; (samples 5 – 7)	7.50	0.50	0.94	0.60	0.06	2.03	0.40	0.60	0.18

GENESIS

Palygorskite in the deposits and showings of Iraq is believed to be polygenetic; two main genetic processes are suggested which are direct chemical precipitation and alteration or transformation of other minerals. The former is limited to the palygorskite deposits in fractures and veins of the Injana Formation at Jabal Maqlub, North Iraq, whereas the latter is found in all other palygorskites deposited in marine and fluvial systems as well as in continental weathering regimes (Fig.14). In the marine deposits, palygorskite is usually found in association with smectite in all environments between the shore and the shelf margin, but it dominates the clay mineral assemblages, as the only clay mineral, in the restricted platform deposits.

The majority of the palygorskites of the Tayarat Formation were most probably formed by transformation of precursor terrigenous clays (mostly smectites) in hypersaline inner shelf ponds and bays at the early diagenesis (Tamar-Agha and Al-Janabi, 2000). The palygorskite-rich claystones of the Safra Beds and the Traifawi and Dwaima members are believed to have formed in an alkaline, warm and anoxic subtidal environment of marine semi-restricted inner shelf, under semi-arid climate. The palygorskite was formed by transformation of low-potassium smectites (montmorillonite) (Hirmiz, 1989, Al-Bassam *et al*., 1990 and Mohamad, 1993). However, some indications pointing towards an illite-smectite and/or illite precursors have been suggested for the palygorskites in the Nfayil Formation (Al-Bassam *et al*., 2000b).

In fluvial systems (such as those of the Injana; Dibdibba and Zahra Formations) the palygorskite is mostly formed by the alteration of illite – smectite and illite (Al-Bassam and Al-Baidari, 2000; Taka *et al*., 2000; and Tamar-Agha *et al*., 2000). The palygorskite in recent deposits of the marshes in southern Iraq (Ahwar deposits) are exception to this; they are shown by SEM observation to develop from dolomite (Aqrawi, 1993). Continental weathering of basic and ultrabasic igneous rocks and alteration of mafic minerals has been reported as the origin of palygorskite in the Gercus Formation with some formed by alteration of smectite (Dhannoun and Al-Dabbagh, 1988). The clay mineral distribution and abundance are controlled by the environment; in continental deposits aridity is important for the formation of palygorskite. Montmorillonite and palygorskite are the dominant clay minerals in Iraq from Late Cretaceous onward, whereas kaolinite is more dominant in the Early Cretaceous and older units. This was attributed to climatic changes (Al-Bassam, 1996). In marine environment high pH and high salinity, with respect to Mg concentration, are controlling factors.

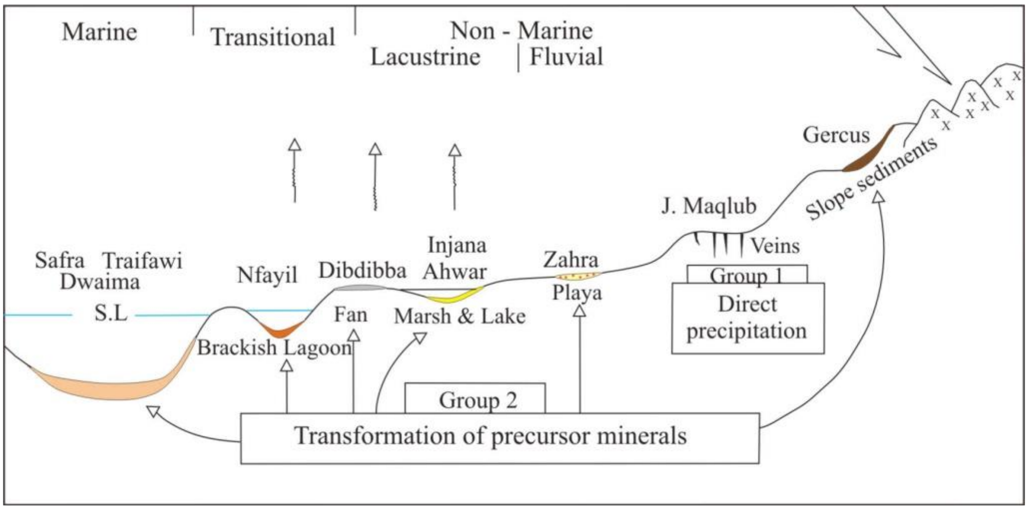

Fig.14: Geological environments and genesis of the Iraqi palygorskites (Al-Bassam, 2000)

RESOURCES

Palygorskite is associated with smectite in the Late Cretaceous deposits and becomes the dominant clay mineral in shallow, near-shore areas of the basin. Extensive deposits of palygorskite-rich claystones are exposed within the Safra Beds in the Akashat, Ga'ara and H3 areas (Al-Bassam *et al*., 1990). They are present as olive green (black in subsurface) claystone, 0.5 m to several meters thick, laminated, and form part of a cyclic alternation of diatomaceous dolomitic lime mudstone (with chert nodules), phosphorite and shale. They pass laterally (towards open sea) to smectite-rich claystones. The mineral association includes palygorskite, sepiolite, smectite, calcite, dolomite, quartz, apatite, gypsum and halite. The thickness of the palygorskite-rich claystone units of the Safra Beds ranges from (1 – 4 m). Thin palygorskite beds were also investigated in the fluvial claystones of the Injana Formation near Najaf City (Al-Bassam and Al-Baidari, 2000). The chemical composition of the palygorskites-rich claystones of these deposits is shown in Table (5).

Palygorskite deposits have been systematically assessed and their reserves were estimated in two localities. The first one is located near Akashat mines in the Western Desert, within the marine claystones of the Safra Beds (Digma Formation) (Al-Bassam, 1993; and Abdul Hassan *et al*., 1995) and the second is near Najaf city in central Iraq, within the Injana Formation (Abdul Hassan, 1999).

Table 5: Chemical composition of the palygorskite-rich fraction in the main deposits

Wt.%	Palygorskite Deposits	
	Digma Fn.	Injana Fn.
SiO_2	57.9	53.50
Al_2O_3	12.6	13.30
Fe_2O_3	6.2	17.50
CaO	1.8	1.30
MgO	8.6	9.50
K_2O	0.6	3.50
Na_2O	1.1	0.5
L.O.I	9.5	8.3

- **The Akashat Deposit**

It is located about 3 km east of the Akashat phosphate mines in the Iraqi Western Desert. Two industrially suitable beds have been identified on the basis of rheological properties, mineralogy and chemical composition (Abdul Hassan *et al*., 1995). The upper bed is 0.4 m thick and the lower bed is 1.25 m thick, separated by 0.15 m thick shelly calcareous claystone bed. The reserves have been estimated on Category B by 87707 tons for the upper bed and 362757 tons for the lower bed. The chemical composition of the industrial beds shows a highly calcareous claystone with relatively low magnesia and high alumina (Table 6). The deposit has been mined and exploited as drilling mud (salt-clay) in oil fields of northern Iraq (Anton *et al*., 2000). It is estimated that about 20000 tons have been already mined from this deposit, but exploitation was terminated by 2003.

Table 6: Chemical composition of the investigated palygorskite reserves in Iraq (Abdul Hassan *et al*., 1995; and Abdul Hassan, 1999)

Oxides (wt.%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	L.O.I
Akashat deposit Upper Bed	44.17	11.89	4.74	10.58	4.74	0.47	0.91	10.58
Akashat deposit Lower Bed	39.73	9.99	3.77	17.05	4.10	0.84	0.81	17.05
Najaf deposit Area-1	50.87	12.78	6.40	4.75	7.47	n.a	n.a	12.13
Najaf deposit Area-2	49.00	12.60	6.18	6.20	6.04	n.a	n.a	11.71

n.a.: not analysed

- **The Najaf Deposit**

It is a small deposit located about 2 Km west of the Najaf city, at Tar Al-Najaf cliffs, in central Iraq. Two areas have been investigated and their reserves were estimated on Category B and Category C1 (Abdul Hassan, 1999). The former was 14750 tons and the latter 3250 tons. The industrial bed is 0.4 m thick in Area-1 and 0.3 m thick in Area-2 with overburden thickness of about 1.3 m. The mineral composition shows about 75% clay minerals, dominated by palygorskite, and about 20 % calcite. The chemical composition is shown in Table (6). This deposit has been exploited by local miners (mostly women) for several decades, using hand shovels and other digging tools. The clay produced is sold to old markets of central and southern Iraq as a hair-conditioner, used by Iraqis for long time ago and still in use, where most of the reserves of Area-2 have been already mined.

INDUSTRIAL APPLICATIONS

In the search for a local alternative for salt clays, used in oil-well drilling operations when penetrating salt formations, extensive field surveys were carried out to explore the potentiality of Iraqi palygorskite deposits for this purpose. Several rock units were shown, as a result of these surveys, to contain suitable clay deposits with high palygorskite content, including the Safra Beds (Digma Formation) in the Iraqi Western Desert, Injana Formation in the Najaf area and in Jabal Maqlub area. Extensive rheological evaluation was carried out on a laboratory scale at the Petroleum Research and Development Center (Ministry of Oil), from which it is concluded that all samples from these deposits are suitable for drilling in salt-saturated media, but the most suitable, as far as rheological specifications and clay behavior, are those of the Safra Beds in the Akashat area (Anton *et al*., 2000). Based on the successful laboratory tests, further work was conducted by the Iraq Geological Survey to ascertain suitable reserves of palygorskite-rich clays in this deposit. Field verification of the laboratory results was carried out by drilling an oil well in the northern oil fields using the palygorskite clay of the Safra Beds in the preparation of the drilling fluid. The results were successful and the clay behavior was up to the required specifications. The economic returns were estimated in the order of US $ 420 000/year, representing mainly input bill value for foreign materials. Capital and operating investment is expected to be very low due to the availability of the raw material and the little processing needed.

Palygorskite clays from the Safra Beds (Upper Cretaceous) of the Western Desert have been used in the industrial production of paraffin wax in the Daura Refinery (Juma *et al*., 2000). The clay was ground to -75 µm and thermally activated at 250 °C for 2 hrs. Laboratory tests were conducted at the beginning to optimize the decolorizing parameters of the wax, followed by full industrial production. About 0.5 ton of palygorskite was used to produce about 24 tons of wax. The color degree was well within the required specifications and was stable for a long time. The performances of the Iraqi palygorskite clays are compatible with the imported material and are economically more desirable.

A series of laboratory experiments were conducted on separated and purified samples of palygorskite from the Digma and Akashat formations for testing the clay as absorbent of lead from aqueous solutions (Awadh and Towfiq, 2013). Specific conditions have been controlled (metal concentration, solid to liquid ratio, equilibrium reaction time, pH and temperature). The sorption capacity is inversely correlated with metal concentration (99.5% for solution has Pb 10 ppm, and 22.2% for solution of Pb 250 ppm) under conditions of 1gm palygorskite added to 100 ml total volume for 1hour at 25 °C.

Laboratory and industrial application of palygorskite-rich claystones from the Akashat and Najaf areas have been tested in decolorizing sun-flower oil (Al-Ajeel *et al*., 2000). The results were compared with those obtained using imported bleaching earth of German and Spanish sources. The laboratory tests showed that using 3% of the Iraqi clays, activated at 400 °C for 2 hrs, have high efficiency in reaching the required color specification of the oil. According to the results obtained in the laboratory tests a successful industrial test was carried out using the Akashat claystone (Safra Beds of the Digma Formation, Maastrichtian). The test parameters were optimized and the results were well within the quality required for routine production of sun-flower oil.

Palygorskite-rich claystone samples were selected from two Iraqi deposits to be tested in the dehydration of hydraulic oil (Al-Bassam *et al*., 2000a). One sample is from the Safra Beds, Digma Formation (Akashat area) and the other from the Injana Formation (Najaf area). The clays were crushed to meet the grain size of the imported material, and were thermally activated at 300 °C for 2 hours. At the beginning the tests were performed on a laboratory scale; the results were satisfactory and the acidity of the oil was brought down from about 1.2 mg KOH/ gm oil to about 0.35 mg KOH/ gm oil or less. Following these successful trials, the Najaf palygorskite-rich claystone was selected for a pilot test using industrial-scale units. The results were well within the required standards.

Crystallochemical and thermal analyses showed that the palygorskite found in fractures and veins in the Injana Formation at Jabal Maqlub and surrounding areas is a good microporus absorbent with channel structure. The thermal desorption under partially evacuated condition has been experimentally investigated (Aswad *et al*., 2000b) aiming for its future application for solar energy utilization as thermochemical energy storage system and as a desiccant.

The palygorskite-rich claystones of the Injana Formation in the Najaf – Razzaza area have been tested in the production of pottery (Al-Baidari, 2000). The claystones were investigated by chemical analyses, mineralogical characteristics and physical properties including plasticity index, liquid limit, sticky limit and Rieke index. The claystones consist of palygorskite, montmorillonite, kaolinite, chlorite, calcite, quartz and feldspar. Special molds were made and were subjected to an experimental firing program in the temperature range from (150 – 1100) °C. Shrinkage, deformation, porosity, density and water absorption were determined in the produced material. This study has shown that the investigated mudstones are suitable for pottery, but mixing of various mudstone types is required to obtain the proper mineralogical ingredients and grain size.

CONCLUSIONS

Palygorskite is a common clay mineral in the claystones of the Upper Cretaceous – Upper Tertiary sedimentary formations of Iraq, as well as in the Quaternary sediments and recent soils. Palygorskite comes second after smectite in the clay mineral assemblage in these rock units and sediments replacing kaolinite which was the most common clay mineral in the older formations. The change in clay mineralogy probably reflects climatic changes towards more aridity in the region since Upper Cretaceous.

Two main processes of formation have been suggested for the Iraqi palygorskites: A direct precipitation from solution and transformation of other minerals. The former is restricted to fracture-fill deposits found in the Injana Formation at Jabal Maqlub, whereas the latter was suggested for all palygorskites found elsewhere and includes weathering products of mafic minerals, transformation of smectite, smectite-illite and illite. Dolomite was also suggested as a precursor for palygorskite.

The Iraqi palygorskites are well-crystalline and show sharp characteristic XRD peaks. Their behavior in heating, investigated by XRD, DTA and TGA analysis is typical of palygorskite reported in international literature. The chemical composition of major and trace elements vary according to the origin of the palygorskite and parent minerals. Those of direct chemical precipitation are close to theoretical composition, whereas those formed by transformation show the signature of parent minerals.

The palygorskite-rich claystone resources of Iraq are relatively small, but can be enlarged by further exploration, especially in the marine sedimentary claystones of the Safra Beds (Digma Formation) around the northern and western rims of the Ga'ara Depression and the eastern parts of the Akashat platform in the Western Desert. The Iraqi deposits are suitable for many industrial applications, especially in drilling mud (as salt clay), in the decolorization of vegetable oils and paraffin wax and in the dehydration of hydraulic oil.

ACKNOWLEDGEMENT

The information presented in this contribution was derived mainly from postgraduate work of the Iraqi universities, published papers and internal reports of Iraq Geological Survey. However most of the information was based on papers presented in the symposium held march 24 – 25, 1997 in the College of Science, University of Baghdad and were later included in the book: The Iraqi Palygorskites: Geology, Mineralogy, Geochemistry, Genesis and Industrial Uses, edited by Khaldoun S. Al-Bassam and its 1st edition was published in 2000 by Iraq Geological Survey.

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