

Palygorskite in Miocene rocks of northern Iraq: environmental and geochemical indicators

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ABSTRACT:

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The mineralogical characteristics of palygorskite from the Lower Miocene Euphrates Formation and the Middle Miocene Fat'ha (Lower Fars) succession in north and northwestern Iraq were studied by X-ray diffraction (XRD), Infrared spectroscopy (IR) and scanning electron microscopy (SEM) with EDAX analysis. Palygorskite is the common clay mineral in the rocks studied, together with small amounts of illite, chlorite, and kaolinite, in addition to various amounts of quartz, feldspar, dolomite and calcite. It is believed that most of the clay minerals are detrital in origin, except palygorskite, which is formed by authigenesis in evaporitic environments. Marl beds of the Euphrates Formation were deposited in a lagoonal, relatively saline environment, suitable for the neoformation of palygorskite. The Fat'ha Formation is composed mainly of an evaporitic sequence. It consists of numerous shallowing-upward cycles of alternating mudrock, limestone, gypsum and/or anhydrite and halite in the basin centre. This depositional environment favours the authigenic formation of palygorskite and partly its diagenetic formation by transformation of precursor clays, mainly smectite and mixed-layer illite-smectite, as revealed by scanning electron microphotographs.

Key words: Palygorskite; Authigenesis; Miocene; Iraq.

INTRODUCTION

Palygorskite is a member of the palygorskite-sepiolite group, often called fibrous clays or pseudo-layered clays. These minerals have a fibrous texture and a chain structure; both are magnesium-rich clay minerals, differing from each other in the width of the inverted ribbons (broader for sepiolite) and in specific chemical characters. Palygorskite is less enriched in magnesium and presents more structural diversity than sepiolite (Chamley 1989).

These fibrous minerals are formed either by chemical sedimentation as authigenically formed minerals in lagoons and evaporitic basins (Grim 1953; Millot 1970) or by transformation from former clays during early diagenesis in epicontinental and inland seas and lakes, by direct crystallization in calcareous soils, or by

hydrothermal alteration of basaltic glass or volcanic sediments or clays in the open oceans in association with fore-arc basins (Callen 1984).

Palygorskite commonly forms under superficial conditions in soils or sediments. It is associated mostly with pedogenic calcareous crusts or other superficial carbonates of semi-arid regions. Arid climatic conditions favour the formation of palygorskite in soils. Al-Rawi *et al* (1969) have described the palygorskite in arid regions of Iraq, El-Gabaly (1962) in the desert soils of Egypt, Van Der Heuvel (1966) in the calcareous desert soils of New Mexico, Perez-Rodriguez *et al* (1990) in arid calcareous soils of Spain, Khademi and Mermut (1999) in arid soils of Iran, Stahr *et al* (2000) in duricrusts of southern Portugal, Bolle *et al* (2000a,b) and Bolle and Adatte (2001) in the northeastern and southeastern margins of the Tethys and in many other

arid regions around the world. Lacustrine and lagoonal environments are favourable for the neof ormation and/or conversion of palygorskite from smectite, as indicated by Chamley and Müller (1991). Conditions for authigenic formation of palygorskite require an alkaline and saline environment with high activity of silica and magnesia (Weaver and Beck 1977). SiO₂ ions for clay building, arid conditions, strong evaporation and low clastic detrital supply may all be realized in both lacustrine and peri-marine environments (Chamley 1989).

Palygorskite is known as a useful palaeoclimatic indicator, typical of arid and semi-arid soils (Singer 1980; Singer and Galan 1984). Callen (1984) concluded that fibrous clays originate in soils, lakes and shallow seas with a semi-arid and warm climate, occurring globally in certain time intervals, the Early Miocene to early Middle Miocene being one such interval.

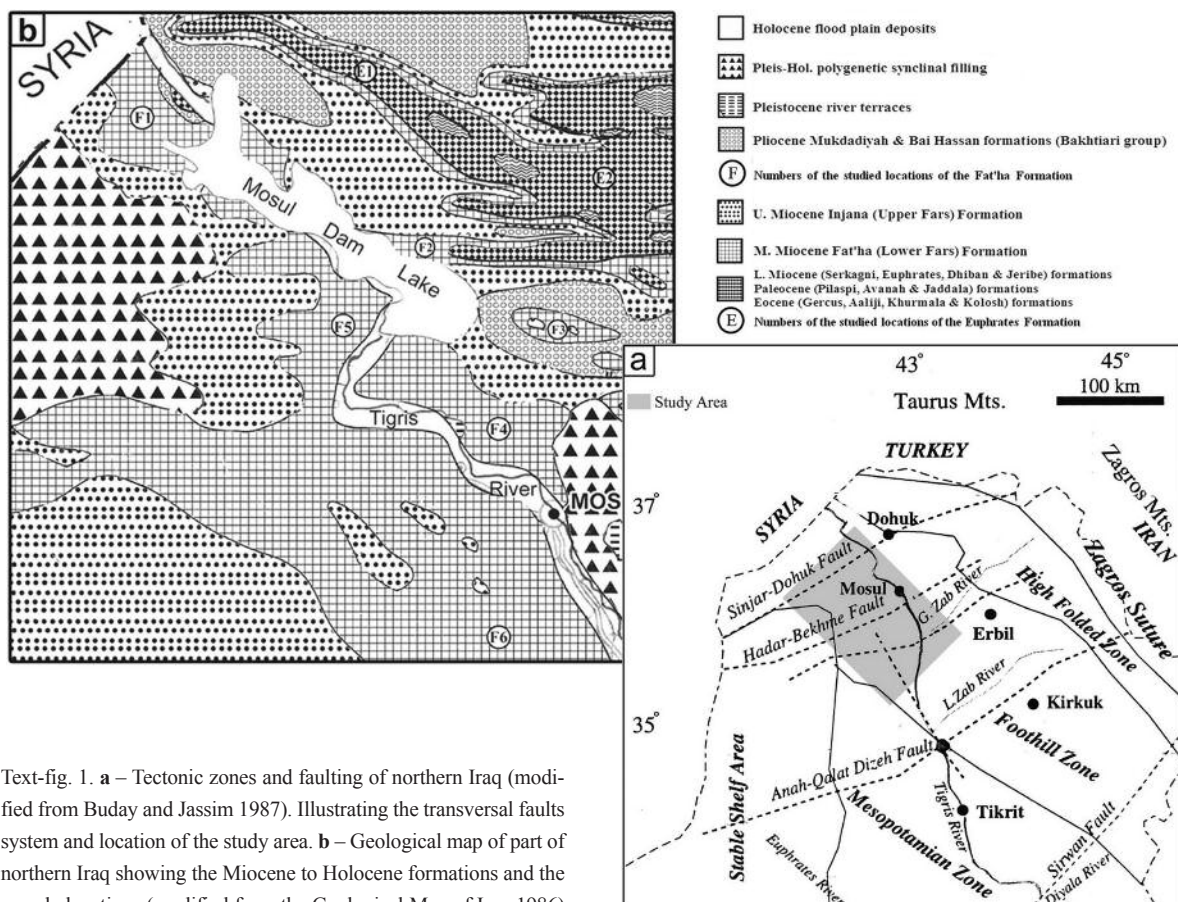
The present work discusses the mineralogy and chemistry of the palygorskite-bearing rocks from the Miocene sediments of northern Iraq, with special emphasis on the depositional environment and origin.

REGIONAL GEOLOGY

Location and tectonic framework

The Arabian Plate formed part of the long and wide northern passive margin of Gondwana bordering the Paleo-Tethys Ocean (Beydoun 1991; Loosveld *et al* 1996). Iraq forms the northeastern part of the Arabian Plate, which lay in the southern hemisphere in high latitudes. The stratigraphy of Iraq is strongly affected by the structural position of the country within the main geos t ructural units of the Middle East region, as well as by the structure within Iraq. Iraq lies in the border area between the major Phanerozoic units of the Middle East, i.e., between the Arabian part of the African Platform (Nubian-Arabian) and the Asian branches of the Alpine tectonic belt.

The platform part of Iraq is divided into two basic units, i.e., a stable and an unstable shelf. The stable shelf is characterized by a relatively thin sedimentary cover and the lack of significant folding. The unstable shelf has a thick and folded sedimentary cover, with the intensity of the folding increasing toward the northeast (Buday 1980).



Text-fig. 1. **a** – Tectonic zones and faulting of northern Iraq (modified from Buday and Jassim 1987). Illustrating the transversal faults system and location of the study area. **b** – Geological map of part of northern Iraq showing the Miocene to Holocene formations and the sample locations (modified from the Geological Map of Iraq 1986)

The study area lies within the unstable shelf, which contains three tectonic zones. These are, from west to east: the Mesopotamian Zone (Quaternary molasses and buried structures), the Foothill Zone (Neogene molasses and long anticlinal structures separated by broad synclines), and the High Folded Zone (Paleogene molasses and harmonic folded structures) (Text-fig. 1a). These longitudinal tectonic zones are segmented into blocks bounded by ENE-WSW (shifting to NE-SW) transverse faults with both vertical and horizontal displacement (Jassim *et al* 1999). The transverse blocks have been active at least since the Late Cretaceous and greatly affected the sedimentary facies of the Cretaceous and Tertiary sequences (Numan 1997). These basement blocks played an important role in the location and configuration of small basins that received thicker sedimentation and later on were the sites of anticlinal structures (Numan 1984). By the Middle Miocene, continuing uplift of these structures caused the shelf sea to be further broken up into sub-basins in which the poor circulation allowed intense evaporite production (Beydoun *et al* 1992).

The morphology of the area reflects the structure faithfully (Jassim *et al* 1997). Anticlinal structures form the hilly terrains whereas the synclines, which are usually wide, form relatively flatter expanses. The study area of study lies at the intersection of the Zagros NW-SE trend and the Taurus E-W trend and is traversed by major lineaments. In the stable shelf of Iraq, the lineament directions are parallel to the lineament directions and major geotectonic trends in the surrounding mobile belts of the Alpine orogeny, namely the Taurides, Zagrosides and Palmyrides in Turkey, Iraq, Iran and Syria. These lineaments seem to have been initiated by the opening and closure of the Neo-Tethys Ocean between Late Triassic and Pliocene times (Numan and Bakose 1997), and has great importance to hydrogeology, and mineral formation, oil and gas exploration.

Stratigraphy

The palaeogeographic evolution of the stable shelf of Iraq during the Early and Middle Miocene was marked by the development of a broad but relatively shallow marine basin (Buday 1980). Shallow epicontinental seas and lagoons prevailed in the Early Miocene and deposited the Serikagni/ Euphrates Formation, the Dhiban Anhydrite Formation and the Jeribe Formation in the marginal basins. However, marine conditions became progressively less open, with the development of a series of lagoons that were occasionally replenished with sea water and gave rise to the cyclic deposition of the evaporites of the Fat'ha Formation in Middle Miocene times (Numan 1997). This elongated series of lagoonal basins was

periodically isolated from the Indian Ocean by a barrier across the Hormuz Strait, resulting in an alternation of normal and hypersaline conditions (Buday 1980). The Fat'ha evaporites would appear to mark the closure of the fragmented Tethyan Ocean.

The Miocene sedimentation of northern Iraq is marine, and started with the deposition of Early Miocene carbonates and evaporates of Serikagni, Euphrates, Dhiban and Jeribe formations, with shallow epicontinental seas characterized by lagoonal condition in proximal areas (Text-fig. 1b). Marine conditions became progressively more restricted, with many small seas and lagoons replenished sporadically with normal marine water. These gave rise to the shallowing-upward cyclic deposition of evaporites in the Middle Miocene Fat'ha Formation. Progressive post-Palaeocene regression in the Zagros Basin favoured the deposition of these evaporitic and detrital sediments (Bahroudi and Koyi 2004).

The basin of deposition of the Fat'ha Formation was dominated by a quiet lagoonal environment in the early Middle Miocene that led to the deposition of the lower member of the formation, which is characterized mostly by rhythmic alternations of carbonates, marls and evaporites. During the Middle to Late Miocene, reactivation of the basement blocks took place, marked by the deposition of the clastic detritus (red sandstones and mudstones) of the upper member of the Fat'ha Formation.

The Fat'ha Formation is composed mainly of an evaporitic sequence. It consists of numerous shallowing-upward cycles of alternating mudrock, limestone, gypsum and/or anhydrite and halite in the basin centre (Dunnington 1958; Bellen *et al* 1959). The mud rocks found in the region are exclusively carbonate-rich, and include marls, silty marls and sandy marls. In the marginal parts of Fat'ha basin the clastics dominate and are represented by fine sandstones and silty claystones occupying the upper two-thirds of the upper unit of the formation. These clastics were interpreted to be deposited in a fluvial-dominated deltaic system (Al-Naqib and Aghwan 1993; Al-Juboury *et al* 2001).

The depositional environment of the Fat'ha Formation includes shallow-marine, supra-tidal and continental environments (Shawkat and Tucker 1978). The cyclicity was investigated by Tucker (1999), who suggested that the main controlling factors were tectonics, glacioeustatic sea-level changes and autocyclic processes of sabkha/tidal-flat progradation.

The deposition of the fluvial Injana (Upper Fars) Formation in the foreland basin of Iraq in the Late Miocene marked the end of marine conditions in northern Iraq. This formation is a clastic sequence of medium to coarse sandstones, siltstones and claystones

deposited in a fluvial–tidal environment (Al-Juboury 1994).

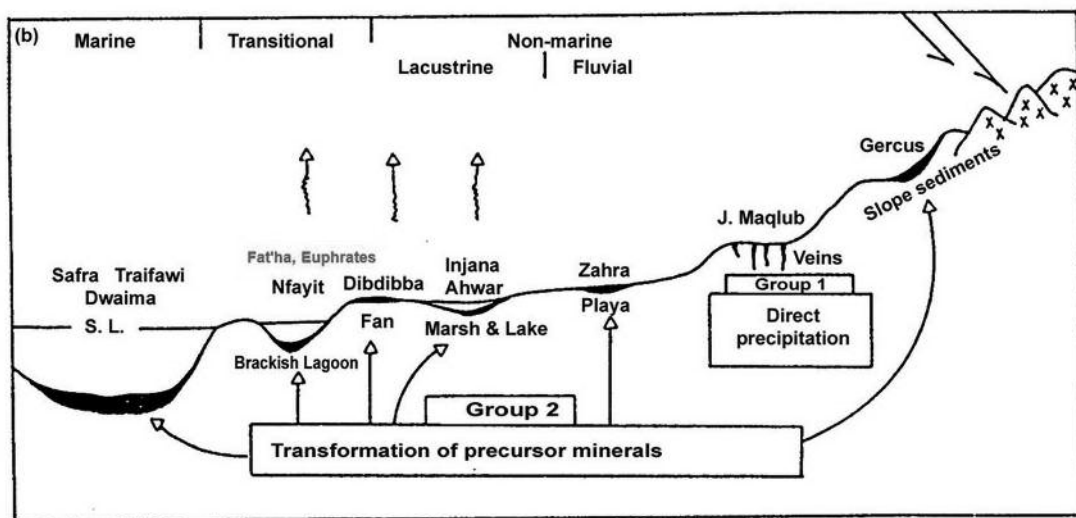
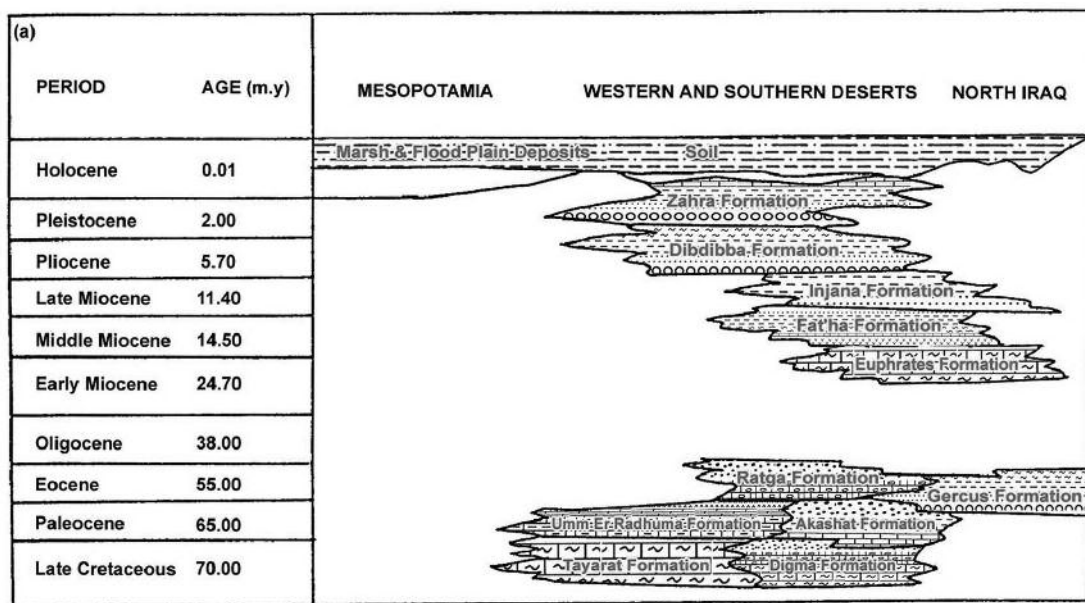
The major part of the study area is part of the Tigris River drainage system. The drainage within the anticlinal area is dendritic where softer strata of the sequence are exposed, and trellised where such a sequence is steeply inclined as a result of alternation between hard and soft beds (Jassim *et al* 1997). The Fat'ha Formation is karstified and most of the groundwater is in cavities, caves, channels, and joints within limestone and in sandstones and fractured marls (Al-Sawaf 1977). Incision of the Tigris River into the area and the structures changed the hydraulic gradient considerably (Jassim *et al* 1997); a deeper and faster rate

of incision was enhanced by active uplift and higher precipitation during the climatic fluctuation of the Holocene. These climatic/hydrological conditions of northern Iraq could affect the authigenic formation of palygorskite in the exposed rocks, which range in age from Miocene to Holocene.

PALYGORSKITE IN IRAQ

Occurrences

Palygorskite deposits and occurrences have been recorded in several lithological successions in Iraq



Text-fig. 2. a – Spatial and temporal distribution of Iraqi palygorskite; b – Geological environments and genesis of Iraqi palygorskite, modified from Al-Bassam (2000)

ranging in age from Maastrichtian to Holocene, and located in the western desert, southern desert, northern Iraq and the Mesopotamian Plain (Al-Bassam 2000), (Text-fig. 2). Most of the Iraqi palygorskite deposits are of sedimentary origin, including marine, lagoonal, lacustrine, fluvial, pedogenic, and epigenetic fillings of fracture and veins.

Numerous authors have mentioned the presence of palygorskite in northern Iraq. It is found in many different formations deposited in different palaeoenvironments. Palygorskite occurs commonly associated with smectite, chlorite, illite and kaolinite in the deep marine Late Cretaceous marls of the Shiranish Formation (El-Anbaawy and Sadek 1979), in the Palaeocene sandstones and shales of the Kolosh Formation, in the red marls and carbonate beds of the Eocene Gercus Red Bed Formation (Al-Rawi 1980), in the marls of the Early Miocene Euphrates Formation (Al-Juboury and Kassim 1999), in the claystones, marls and limestones of the evaporite succession of the Middle Miocene Fat'ha (formerly Lower Fars) Formation (Al-Juboury *et al* 2001) and in the Late Miocene Injana Formation (Al-Banna 1977; Al-Juboury 1994). Most of these palygorskite occurrences were formed by transformation from precursor clay minerals, such as smectite and mixed-layer illite-smectite. Others formed by neof ormation under evaporitic conditions. Some of the Iraqi palygorskite deposits were found to have industrial applications (Al-Bassam 2000) and extensive rheological evaluation was carried out to find their suitability for various different applications. Additional studies revealed that there is a high potential to increase the Iraqi reserves of this clay mineral, both in quality and quantity, by more exploration and research.

Industrial uses and applications

Palygorskite exhibits sorption properties that are important for numerous industrial applications. Its specific sorptive, rheological and catalytic properties make palygorskite a valuable raw material for a wide range of industrial, agricultural, medical, and cosmetic applications. This mineral has many uses in different fields, including radioactive waste disposal, pharmaceuticals, cosmetics, in the production of paper and fertilizers, as floor absorbent, and as an additive to drilling mud (Grim 1962). Most commercially exploited palygorskite clay deposits formed less than 25 million years ago in terrestrial and lagoonal environments (Callen 1984; Pletsch 2003).

Palygorskite has an elongate chain-type structure: the elongate crystals are inert and non-swelling when

dispersed in water, and form a random lattice capable of trapping liquids and providing excellent thickening, suspending and gelling properties. They also do not flocculate with electrolytes and are stable at high temperatures, which make them uniquely applicable for many uses (Murray 2002).

In Iraq, extensive studies were carried out on palygorskite (attapulgitite) deposits of Miocene, Lower Eocene and Cretaceous clays in the laboratories of the State Company of Geological Survey and Mining and other Petroleum Research centres in order to find their significant industrial potential. Some of the specific industrial applications of this mineral are now available in oil-well drilling, decolorizing paraffin wax, decolorizing sunflower oil, dehydration of hydraulic oil of electrical power stations, as microporous absorbents, and in pottery (Anton *et al* 2000; Juma *et al* 2000; Al-Ajeel *et al* 2000; Al-Bassam *et al* 2000; Aswad *et al* 2000; Al-Baidari 2000).

MATERIALS AND METHODS

Clay mineral analyses were performed by X-ray diffraction of Miocene samples selected from marl and claystone lithologies at different localities in northern Iraq (Text-fig. 1b). A total of 30 samples (8 from Euphrates and 22 from Fat'ha formations) were collected from the above-mentioned localities and representative scans for X-ray diffractograms are included in Text figs 3 and 4. The marl and claystones comprise about one-third of the lithological components of the Fat'ha Formation, the remaining components consist of the limestone and evaporites (Text-fig. 3a). Marl beds of the Early Miocene Euphrates Formation are intercalated between marly limestone and well-bedded fossiliferous limestone (Text-fig. 3b). The bulk composition of green and yellow marl samples of the Fat'ha Formation was determined by XRD analysis (Text-fig. 4). This analysis was conducted at the Geological Institute of Bonn University, Germany using D8 Advance (Bruker axis), with Cu- α radiation. The bulk compositions were determined using the method of Moore and Reynolds (1989).

The clay fraction was concentrated before analysis by X-ray diffractometry techniques. Samples were dissociated in water and calcium carbonate was then removed by dissolving in 1/5 N hydrochloric acid. The fraction smaller than 2 μ m was decanted according to Stoke's law and oriented pastes were made on glass slides (Ostrom 1961). A Philips PW 1130 diffractometer (Ni-filter, Cu k α radiation) was used to make the X-ray diffraction scans at 2 θ °/min. on air-

dried, glycolated and heated samples. Identification of the clay minerals was carried out using the data given by Carroll (1970), Thorez (1979), Brindly and Brown (1980). The infra-red spectra were recorded on the 4000 to 1000 cm^{-1} ranges on a BRUKER EQUINOX 55 spectrometer. The samples were prepared using KBr pellet technique (Russell and Fraser 1994); these analyses were performed at Mosul University, Iraq. SEM analysis was performed using Cam Scan MV 2300 at the Palaeontological Institute, Bonn University, Germany.

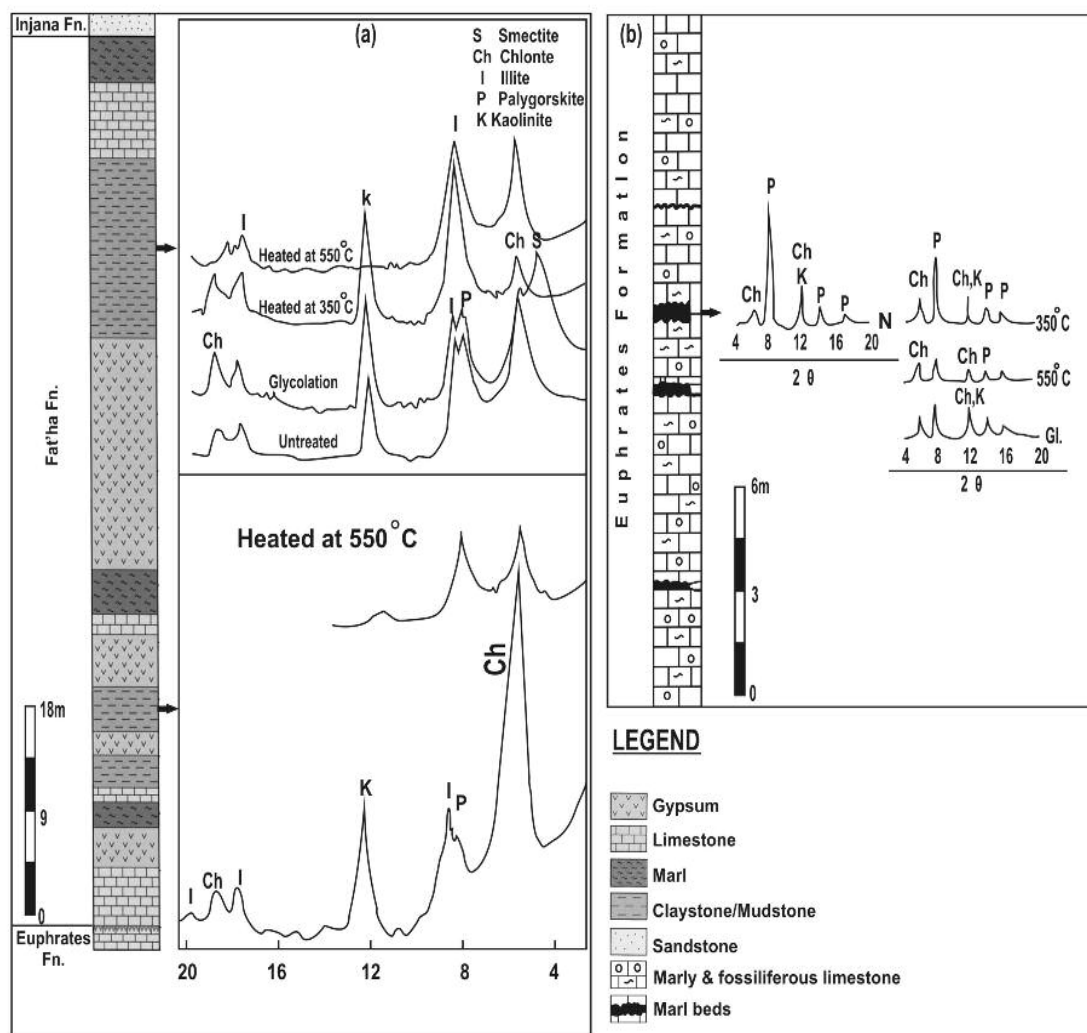
Chemical analysis of the bulk marl and claystones was made using a Siemens SRS 303 X-ray fluorescence spectrophotometer. Two samples of palygorskites were analyzed by energy dispersive X-ray analysis (EDAX).

RESULTS

Bulk rock mineralogy and geochemistry

Analysis of the whole-rock mineralogy of the marls of the Euphrates Formation has revealed that fine-grained quartz, calcite and clay minerals form the main constituents. These marls are commonly of a grey-green colour and are usually interlaminated with miliolid-rich limestones which indicate their deposition in a lagoonal, relatively saline environment.

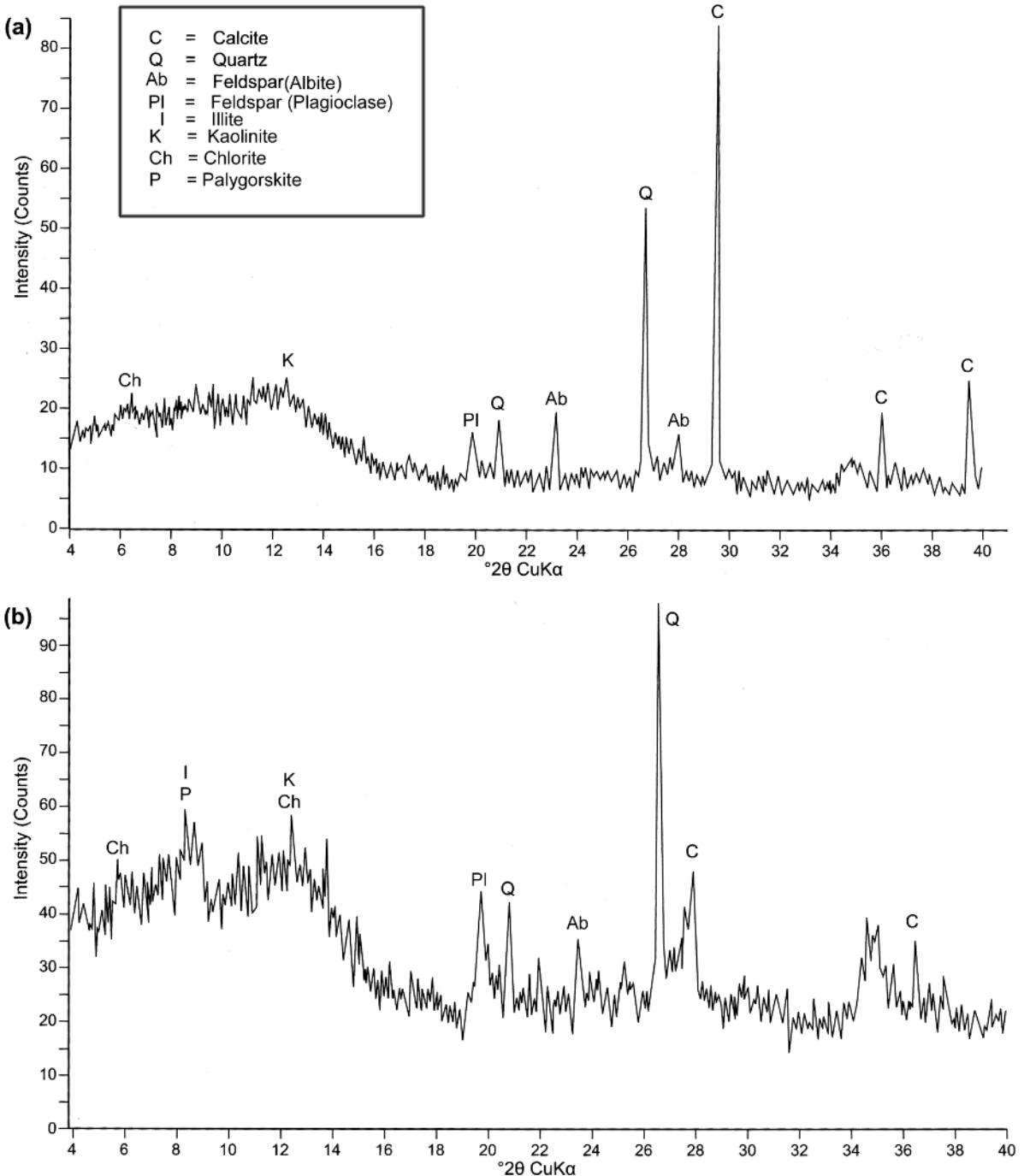
The claystones of the Fat'ha Formation are composed of quartz, calcite, feldspar and clay minerals (Text-fig. 4), whereas the marls are composed of silt-sized quartz and feldspar grains embedded in a clayey and carbonate matrix.



Text-fig. 3. Representative X-ray diffraction patterns of the studied samples ($<2\mu\text{m}$ fraction), a – Fat'ha Formation (locality F6); b – Euphrates Formation, locality E1 (see Text-fig. 1b for location). N – normal treated, GL – Ethylglycolated samples, 550° – heated to 550°C, black arrows indicate analyzed sample locations

The carbonates of the Fat'ha Formation include fine-grained dolomite as a dolomiticrite. This is generally porous; some of these dolomiticrites have recrystallized, either partly or completely, into sucrose dolomite.

The chemical composition of the samples analysed corresponds well with their mineralogy (Table 1). They are carbonate-rich, as indicated by the high content of CaO and MgO, which may be related to the presence of calcite and dolomite. The yellow marls of



Text-fig. 4. Representative X-ray diffractograms for the bulk marl samples, a – yellow marl; b – green marl (mudstone) of the Fat'ha Formation showing different peaks of clay and non-clay minerals

the Fat'ha Formation have a high CaO and low SiO₂ content. Silica is shared between clay minerals and quartz. Magnesium is shared between clay minerals (mainly palygorskite) and dolomite. Aluminium, sodium, potassium, iron and titanium are related almost totally to clay minerals and feldspars. Calcium is linked mainly to carbonates (calcite and/or dolomite).

The trace elements analyzed are distributed among the mineral constituents of the claystone and marl samples. Chromium, Ni, Cu, V, Zn, Co and Pb seem to be related to the clay minerals, either adsorbed or as minor substitutions in the structure (Mason 1966). Strontium, Rb and Ba are associated with the carbonate phases and gypsum in substitution of calcite. The clay minerals and feldspars have also contributed to the content of these trace elements. Zirconium is probably present as an independent phase as minute grains of zircon or as inclusions in quartz, and may be present in the structure of clay minerals in substitution for Al³⁺ (Hirst 1962).

Two samples of palygorskite were analyzed with an EDAX attached to a scanning electron microscope (Table

1). The palygorskite formula as proposed by Bradley (1940) is Si₈Mg₅O₂₀(OH)₂(OH₂)₄.4H₂O; Al incorporates in the structure and can fill any of the five vacant octahedral positions. The mineral can contain variable amounts of Ca as an exchange cation. Sometimes the presence of Ca, K and Ni may relate to the presence of calcite or illite impurities (Galán and Carretero 1999).

Clay mineralogy

Clay minerals separated from the marl beds of the Euphrates Formation and the claystones and marls of the Fat'ha Formation revealed that palygorskite is one of the common clay minerals, followed by illite, chlorite, kaolinite, and trace amounts of smectite (Text-fig. 3). On X-ray diffractograms of normal air-dried oriented samples palygorskite is characterized by reflections at 10.5 Å (110), 6.42 Å (200) and 5.43 Å (130) (Text-fig. 3). Palygorskite is not affected by glycolation but, on heating to 550°C for 2 hours, the major 10.5 Å peak shows slight broadening, with a drastic decrease in intensity, a slight shift of its position to 10.34

Oxides %	Green marl Fat'ha Formation		Yellow marl Fat'ha Formation		Marl Euphrates Formation		Palygorskite chemical analysis EDAX	
	1	2	1	2	1	2	This study	A
SiO ₂	52.07	40.31	25.83	35.21	27.76	31.34	82.78	81.34
TiO ₂	0.84	0.63	0.43	0.60	0.33	0.45	n.a	n.a
Al ₂ O ₃	12.31	9.67	6.37	9.95	5.43	6.75	6.95	9.52
Fe ₂ O ₃	6.39	7.22	3.21	6.80	4.31	2.73	0.004	0.007
CaO	1.26	13.15	18.35	22.63	28.04	22.65	1.48	1.32
MgO	7.56	8.47	12.66	3.12	6.14	3.34	8.78	7.81
Na ₂ O	0.49	0.55	0.23	0.30	0.66	0.76	n.a	n.a
K ₂ O	3.28	2.11	1.72	2.54	1.15	1.35	n.a	n.a
MnO	0.03	0.10	0.03	0.07	0.02	0.04	n.a	n.a
LOI	15.39	16.69	29.95	18.11	25.42	24.78		
Total	99.60	99.0	98.78	99.31	99.26	98.15	99.994	99.997
ppm								
Cr	148	203	65	203	176	132		
Co	14	26	4	17	14	11		
Ni	88	340	41	192	176	104		
Cu	60	74	46	72	75	64		
Pb	8	10	8	6	10	8		
Sr	1701	233	131	110	515	383		
Ba	348	204	115	283	104	292		
Rb	92	61	42	78	47	35		
V	507	569	479	636	695	653		
Zr	175	104	100	111	78	109		
Zn	81	83	41	78	64	61		

Table 1. Chemical composition of selected marl samples showing distribution of major oxides in the green and yellow marl of the Fat'ha Formation and marl of the Euphrates Formation and EDAX analysis of representative palygorskite sample. LOI: Loss of ignition at 1000 °C, na: not analyses. A: EDAX analysis of the Upper Cretaceous palygorskite (after Tamar Agha and Al-Janabi 2000)

Å and the appearance of a new reflection at 9.05 Å. These changes in the reflection pattern are attributed to dehydration and folding of the structure of palygorskite (Carroll 1970; Brindly and Brown 1980; Nemeč 1981).

Infra-red spectroscopy

The infra-red spectroscopy of the Middle Miocene palygorskite is shown in Text-fig. 5. The absorption bands found at 3615, 3550, 3400, 2860, 1645, 1380, 1192, 1025, 990, and 775 cm^{-1} closely resemble those given by Gadsden (1975) and are comparable with published spectra for typical palygorskite (Hayashi *et al* 1969; Farmer 1974; Serna *et al.* 1977; Soong 1992).

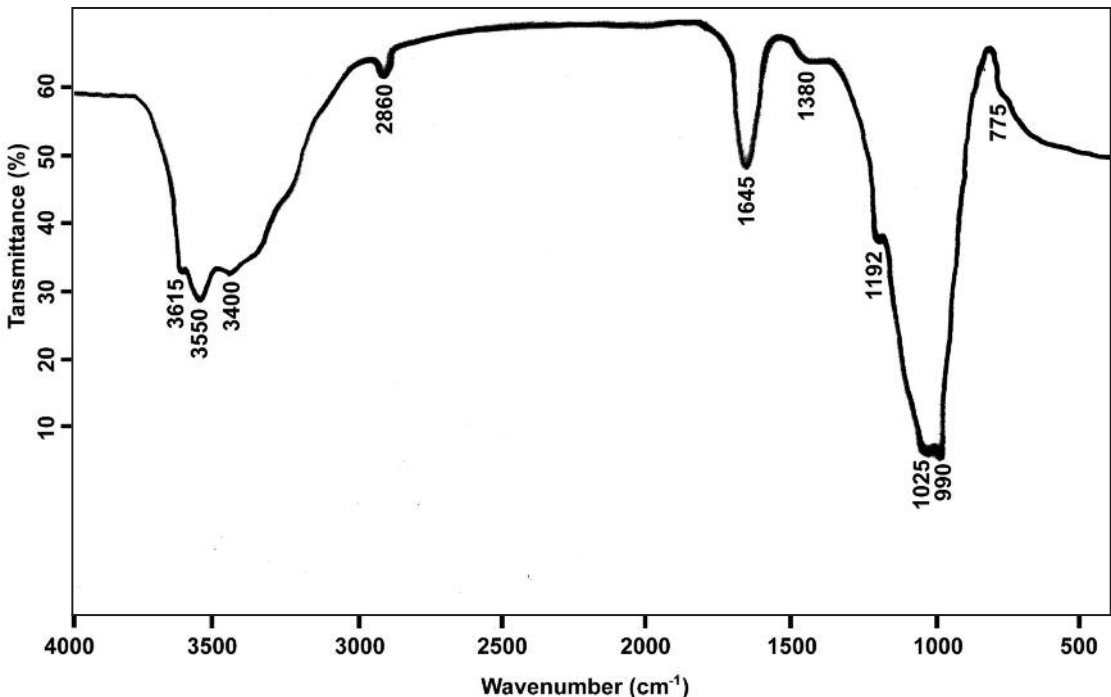
The absorption bands at 3615, 3550, 3400 and 1645 cm^{-1} are related to zeolitic water. In the SiO stretching region the absorption are represented at 1192, 1025 and 990 cm^{-1} . Other weak absorptions were noted at 2860 and 775 cm^{-1} , which could be attributed to quartz and some other impurities in the samples.

Scanning electron microscopy

Scanning electron images of the dolomites show fine clayey to coarse crystalline dolomite, with palygorskite and gypsum fibres in the pores between the dolomite rhombs (Pl. 1). This evidence is a good cri-

terion for evaporative dolomitization, a suitable environment for the authigenic formation of palygorskite. Dense delicate aggregates of fibrous palygorskite usually associated with, and covering the dolomite rhombs, are indicative of an authigenic origin (Pl. 1, Figs 1–3). Some of these palygorskite fibres occur as filling of cavities in dolomite with a honeycomb-like texture (Pl. 1, Fig. 4), other palygorskite fibres are associated with gypsum plates within dolomitic limestone (Pl. 1, Figs 5–6).

Different features typical of palygorskite are observed in the claystone and marl (Pl. 2). The palygorskite occurs mainly as long flexuous bundles of fibres (Pl. 2, Figs 1–2). Elongate and well developed fibres occur isolated or in bundles, but usually developed in cavities. Shorter and thinner fibres were observed in the palygorskites formed by transformation of smectite and mixed-layer illite-smectite (Pl. 2, Figs 3–4). These fibres are usually stacked within the boundaries of the smectite, forming a tree-like texture, or emerge from the precursor grain, forming a mosaic weave structure. Delicate filamentous outgrowths from a platy nucleus indicate a neoformed palygorskite (Pl. 2, Fig. 4); these features are similar to those portrayed by Chamley (1989) for the transformation of precursor clays. The tree-like texture and mesh-work texture (Pl. 2, Figs 1–3) are considered indicative of direct precipitation from solution (authigenic) of the Miocene palygorskite. Palygorskite fi-



Text-fig. 5. Infra-red absorption spectra of Middle Miocene Fat'ha palygorskite, (sample 3 of locality F5)

bres can also occur associated with kaolinite (Pl. 2, Fig. 5) or stacked with well developed kaolinite hexagonal plates (Pl. 2, Fig. 6).

DISCUSSION AND CONCLUSIONS

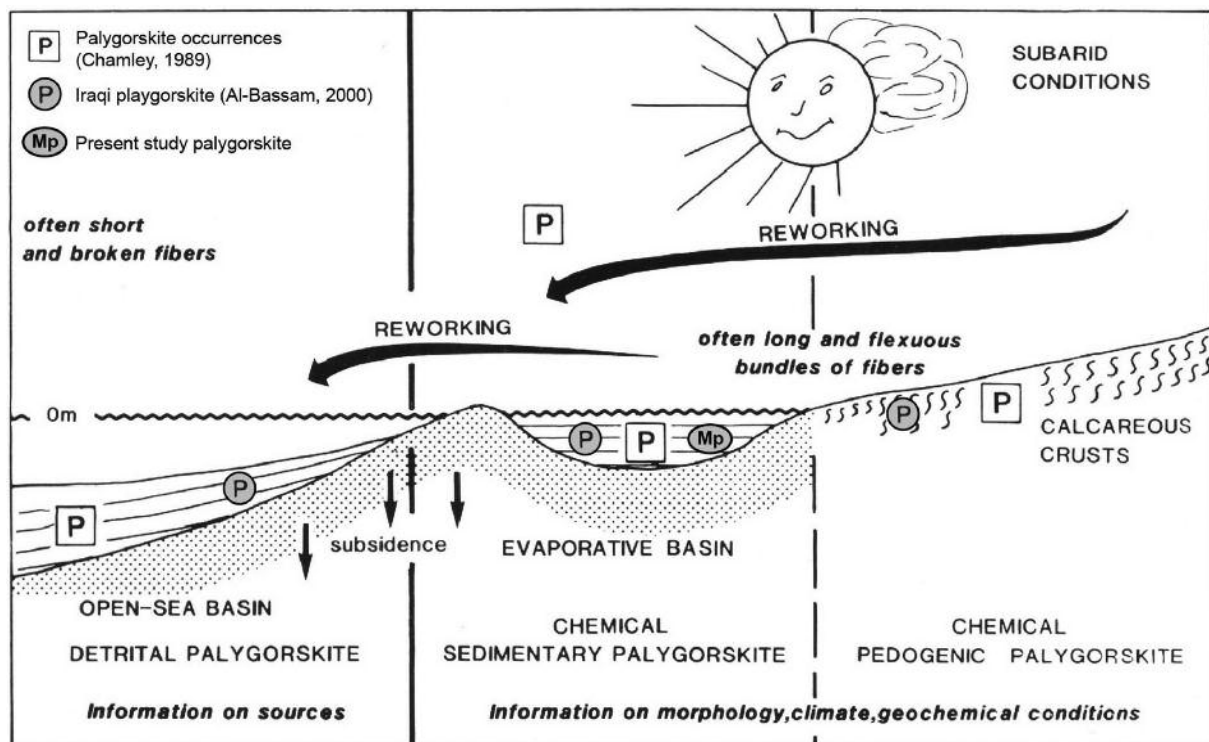
Palygorskite was identified in various formations in Iraq, ranging in age from Maastrichtian to Holocene, and deposited in different geological environments, including marine, lagoonal, lacustrine and fluvial.

In the present work, the palygorskite of the Miocene successions in north and northwestern Iraq provided important palaeoenvironmental evidence. The clay minerals are composed mostly of palygorskite, illite, chlorite, kaolinite and smectite. It is believed that palygorskite was formed by authigenesis in evaporitic environments, whereas the other clay minerals are detrital in origin. The marl beds of the Euphrates Formation were deposited in a lagoonal, relatively saline environment (Al-Radwany *et al* 1993; Al-Juboury and Kassim 1999) suitable for the neoformation of palygorskite. The successions of the Fat'ha Formation were deposited in a restricted, evaporitic lagoonal setting (Tucker 1999; Al-Juboury *et al* 2001), which promoted the authigenic formation of palygorskite.

The coexistence of palygorskite fibres with dolomite rhombs is observed (Pl. 1, Figs 1–3). Some of the dolomite rhombs have subhedral-anhedral morphology due to partial dissolution. Secondary small palygorskite fibres were formed as an infiltration product on these subhedral dolomite rhombs. The honeycomb-like morphology of palygorskite that fills cavities in dolomite (Pl. 1, Fig. 4) is attributed to late-stage dissolution of dolomite that released Mg and led to palygorskite precipitation when excess silica from the transformation of clay minerals in the interbedded mudrock became available.

The association of gypsum with dolomitic limestone (Pl. 1, Figs 5–6) gives a good indication of the evaporative, warm and alkaline conditions suitable for the neoformation of palygorskite in the Middle Miocene successions of northern Iraq. A restricted back reef and lagoons environmental setting for the deposition of the marl beds of the Euphrates Formation may have provided similar conditions for the presence of abundant palygorskite in these deposits (Text-fig. 3b).

Palygorskite commonly derives from chemical precipitation in evaporative basins. However, this mineral may also form under sub-arid conditions in calcareous pedogenic crusts, and may be readily reworked by wind or water from sub-aerial, lacustrine or peri-marine environments. This fibrous clay mineral may



Text-fig. 6. Three possible origins of superficial palygorskites and sepiolites, including the occurrence of Iraqi palygorskite and the location of the palygorskite in the present study, modified from Chamley (1989)

therefore be either authigenic or detrital in a given sedimentary environment (Chamley 1989) (Text-fig. 6).

Detrital palygorskite occurs as aggregates of short and broken fibres and, commonly, of dissociated bundles, whereas long and flexuous bundles of fibres indicate authigenic palygorskite. The latter mode of palygorskite formation is well observed in the claystones and marls of the Fat'ha Formation. Long, well developed or flexuous fibres of palygorskite (Pl. 2, Fig. 2) and tree-like or mesh-work structures of this mineral (Pl. 2, Figs. 1–3) are good indications for authigenic formation. On the other hand, the presence of small, thin fibres of palygorskite indicates diagenetic formation of this mineral by transformation of precursor clays, mainly smectite and/or mixed-layer illite-smectite (Pl. 2, Fig. 4).

Cyclic deposition of gypsum, dolomitic limestone and mudrock of the Miocene Fat'ha series indicates a hypersaline evaporative palaeoenvironment, with rapid changes in lagoon or lake water chemistry related to cyclic changes in water depth and to the drastic global climatic changes during the Miocene. The formation is characterized by a low-diversity benthic foraminiferal assemblage, with a distinct lack of planktonic foraminifera, suggesting that the lagoon was semi-enclosed and predominantly hypersaline, but with periods of brackish to normal-marine conditions (Al-Juboury and Kassim 1999). Palygorskite formation in these evaporative, shallow-water settings is related to latitudinal positions during the Middle Miocene, which resembled that of the Pliocene to present day. This succession is represented generally by interbedded dolomite and gypsum that were deposited in lacustrine environments due to interplay between marine and non-marine environments (Chamley *et al* 1978).

The same chemical conditions for the authigenic formation of palygorskite were recorded from Holocene sediments from southern Iraq (Aqrabi 1993) and from several Cretaceous successions from the western and southern deserts of Iraq (Kas-Yonan 1989; Tamar Agha and Al-Janabi 2000). Analogous palygorskite formation is recorded as a result of chemical sedimentation in evaporitic facies of the Miocene Yeniçubuk Formation of Turkey (Türkmen and Bölücek 1998).

In conclusion, the palygorskite of the Middle Miocene Fat'ha Formation is most probably polygenetic. The lithofacies association of the palygorskite with dolomite and gypsum reflects lagoonal, brackish-hypersaline, alkaline waters and Mg-rich environments suitable for the authigenic formation of the mineral. Seasonably arid climatic conditions, with the absence of tectonic activity in the region, promoted elevated salin-

ity and intense evaporation which in turn supported the direct chemical precipitation of palygorskite. Transformation from precursor clay minerals such as mixed-layer illite-smectite is evident from SEM images.

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