

# EVIDENCE OF AN AUTHIGENIC ORIGIN FOR THE PLYGORSKITE IN A MIDDLE EOCENE CARBONATE SEQUENCE FROM NORTH QATAR

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## النشأة المكانية لمعدن الباليجوسكيت بتتابع صخور الكربونات للعصر الايوسيني الأوسط - شمال قطر

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يتكون عضو السيمسما بمنطقة رأس لفان بشمال قطر أساساً من صخور الدولوميت التي تكونت في بيئة بحرية ضحلة، ومعادن الطين المتواجدة مع الدولوميت بنسبة تصل الى 4% وتكون أساساً من معدن الباليجوسكيت والمتواجد في شكل تجمعات ليفية كثيفة على هيئة أفلام رقيقة تغطي حبيبات الدولوميت الدقيقة. كما أن التجمعات الليفية الطويلة لهذا المعدن.

تصل بين حبيبات الدولوميت الخشنة وقملأ الفراغات الموجودة بينها، وهذا يدل على أن معدن الباليجوسكيت لم يتعرض لعملية نقل وأنه ذو نشأة مكانية نتيجة ترسيب مباشر من محاليل غنية بعناصر الألومنيوم، السليكون والماغنسيوم.

وقد دلت التحاليل الكيميائية على أن تركيب معدن الباليجوسكيت بمنطقة الدراسة مشابه لتركيب معدن الباليجوسكيت بمناطق أخرى غير أن التركيز العالي لعنصري الكالسيوم والماغنسيوم يدل على تواجد بعض الشوائب من معادن الكربونات.

وأكدت دراسة نظائر قيم الأكسجين ( $\delta^{18}\text{O}$ ) أن معدن الباليجوسكيت قد تكون من محاليل عالية الملوحة. وأن معدن الدولوميت ومعدن الكالسيت الخشن قد تكون من محاليل ذات تركيب كيميائي مختلف عن المحاليل التي كونت معدن الباليجوسكيت.

**Key Words:** authigenic origin, palygorskite, Middle Eocene, North Qatar, Stable isotope

### ABSTRACT

The "Simisma Member" from the Ras Laffan area in North Qatar is mainly composed of dolomites of shallow marine origin. Clay minerals contained in the dolomite (average 4%) are mainly palygorskites. There is no indication of the presence of any transitional forms between palygorskite and other clay minerals. Delicate dense aggregates of the palygorskite fibres form matted films covered fine-grained dolomites. The long palygorskite fibres are also bridged and fill pore spaces between the coarse dolomite crystals. The presence of well preserved long fibres indicates that the palygorskite could not have been transported; they are authigenic and must have been formed directly by precipitation from solutions rich in Al, Si and Mg. The elemental compositions of the studied palygorskite are similar to previously published data. However, the high concentrations of Ca and Mg indicate that the palygorskite samples are mixed with carbonate minerals. The relatively high  $^{18}\text{O}$  values (average + 18.7) of the palygorskites support the hypothesis that the palygorskite has been formed from solutions of high salinity. Meanwhile, the  $^{18}\text{O}$  contents of dolomites (range from + 0.3 to +2.7‰ PDB) and late sparry calcite crystals (range from -5.7 to -11.8‰ PDB) argue against the formation of dolomite, calcite and palygorskite from the identical fluid.

## INTRODUCTION

Most clay minerals in carbonate sediments are assumed to be detrital [1-3], but authigenic clay minerals also occur in many carbonate sediments and calcretes [4-7]. These minerals are readily recognized under the scanning electron microscope by their delicate crystal habits. They occur as coatings on carbonate grains and interparticle pore-lining and pore-bridging and as pore-fillings. Authigenic palygorskite occurs as fibres associated in bundles and forming a mesh around carbonate grains. These delicate coatings cannot be the result of transport and deposition processes. Authigenic palygorskite also has high microporosity, often associated with large irreducible water-saturations. A detrital origin of palygorskite is also possible.

Authigenic palygorskite is commonly associated with dolomitic carbonates and is also formed under subarid conditions in calcareous pedogenic crusts [8-10] and several mechanisms for palygorskite formation have been proposed. A high pH (from 9 to 11), and high Si, Mg and low Al activities in precipitated fluids appear to be the optimum conditions for palygorskite formation [11]. In the Arabian Gulf various occurrences of authigenic palygorskite in carbonates and calcretes have been reported [12-14]. These occurrences have prompted a closer study of the conditions for palygorskite formation in the area. The purpose of this study is to present new mineralogical and geochemical data for palygorskites in the middle Eocene carbonate succession from North Qatar and to elucidate a possible origin of the palygorskite in this succession.

## GEOLOGIC SETTING

Qatar is a peninsular state about 200 km long that projects northwards from the Arabian peninsula into the Arabian Gulf, and is centered at about 25°N, 51°E. Waters around the country are shallow which providing major constraints on reef development. Topographically, Qatar has a low relief landscape with a maximum elevation of about 80 meters near Dukhan. Structurally, the Qatar peninsula appears as an elliptical anticlinal arch, with a N-S main axis, defined by outcrops of Eocene carbonate rocks (Fig. 1A). This relatively symmetrical anticlinal arch is

complicated by secondary anticlinal structures, with a NW-SE main axis (the Simsima Dome). The Qatar peninsula is an area of Tertiary outcrops primarily composed of Eocene carbonate rocks (about 80% of the total surface), is overlain unconformably by Miocene marls, carbonate rocks and gravels in the south and southwest (Fig. 1B). The overall geological succession is thus composed of Tertiary carbonates with interbedded clays, marls and shales covered in places by a series of Quaternary superficial deposits [15]. The Eocene stratigraphy of Qatar was outlined by Cavelier [15] and Abu Zeid & Boukhary [16]. Palygorskite samples were collected from the dolomites of the middle Eocene (Simsima Member) in the Ras Laffan area (Fig. 1B).

This area is located in northern Qatar, which during the Eocene formed part of the northern Eocene carbonate basin (Fig. 1A). Several drill holes with excellent full recovery permit a detailed facies study in this area, which has unique lithologic characteristics when compared to most of the Simsima dolomite and limestone sequences in Qatar (Fig. 1A). Dolomites occur in all facies. Limestones are found locally in the upper part of the studied sequence. Brown chert intercalations are recognized, as well as palygorskite red clay patches (Fig. 1B). It is hard to infer the original thickness of the dolomites because the top of the dolomite sequence is intensively karstified in the study area. Locally, karst cavities may extend to about 5 metres. The dolomitization obliterated most of the sedimentary structures, but it can be inferred, from non-dolomitized limestone intercalations and cherts within the dolomites that the depositional environment was a shallow subtidal marine with periodic emergence and local evaporite development. Within the sequence a gradual shallowing upward trend is clear.

## METHODS

Twenty palygorskite samples (Fig. 1B) were separated from subsurface core samples of the Middle Eocene (Upper Dammam Subformation) carbonate rocks using standard sedimentation methods [17]. Crystal habit and petrofabric relationships were studied using scanning electron microscope (SEM) on gold-coated chips of palygorskite and dolomite. For observation by TEM, the separated clays

were diluted in water and treated in an ultrasonic device; a drop of this suspension was deposited on a carbon-coated microscope grid and examined using a Phillips 30XL equipped with an energy dispersive system (EDAX).

The samples were sieved through a 63  $\mu\text{m}$  mesh, and treated with diluted HCl, pH=5 to remove carbonates. Mineralogic compositions were determined from the X-ray diffraction (XRD) analysis of oriented aggregates. Diffraction patterns were obtained before and after ethylene glycol treatment and after heating at 550°C for 2 hours. Fused-glass discs and pressed-powder pellets were prepared for major-element and trace-element analysis, respectively, by X-ray fluorescence.

The oxygen isotopes for palygorskite samples were run by the normal  $\text{BF}_3$  digestion against the SMOW standard [18]. Microsamples of dolomite and sparry calcite, for carbon and oxygen isotopic analysis, were heated under vacuum at 380°C for one hour to remove volatile contaminants, and reacted at 73°C with anhydrous phosphoric acid in individual reaction vessels of an on-line, automated Kiel device coupled to a Finnigan-MAT 251 mass spectrometer. Oxygen isotope ratios were corrected for  $^{17}\text{O}$  contribution [19] and reported as per mil (‰) relative to the PDB standard. Precision was better than 0.1‰ for both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values.

### MORPHOLOGY AND MINERALOGY

The carbonate sequence studied consists of parallel stratified, mottled and massive homogeneous rocks. The estimated volume of dolomite in the studied sequence varies from 60% to over 95% in all samples (Fig. 2). There is no evidence of evaporite minerals or their former presence. Dolomite crystal size generally ranged from about 10 to 130  $\mu\text{m}$  and crystal shape varied from planar to nonplanar (20). Dolomite rhombs exhibited a range in physical and chemical characteristics. Some are inclusion-free euhedral rhombs, while other dolomite rhombs were cloudy and contain up to three petrographically distinct zones defined by the presence of iron oxide inclusions. The cloudy dolomite cores are stained by iron oxide, and it is difficult to determine if the inclusions are mainly of calcite or if they include significant proportions of clay minerals and/or organic accumulations.

No recognizable fossils were found in any dolomites. Substantial early-calcite cements are absent, whereas original intercrystal porosity is commonly filled by palygorskite (Figs. 2B, 2C & 2D).

Palygorskite was first observed in Middle Eocene Simsima dolomites of Qatar in the present study; it is the predominant clay mineral in the studied carbonate sequence (Fig. 3). Palygorskite in dolomites and limestones of Tertiary age have been widely reported [2, 10]. The studied palygorskite occurs disseminated in lenses and pockets and fills irregular cavities (Fig. 1B).

In the analyzed samples, the palygorskite ranges from 2% to 9% (averaging 4%). No evidence of illite or smectite was observed in the XRD patterns, which showed peaks at 10.46, 6.35, 5.40 and 4.49 °A (Fig. 3), almost identical to those given by the Joint Committee on Powder Diffraction Standards for palygorskite. Heating palygorskite at 200°C and 300°C did not affect the XRD patterns, but heating at 400°C caused the disappearance of the 4.46 and 4.09 °A reflections. In general, palygorskite was determined by its 10.5°A peak which was unaffected by glycolation.

The fibrous character of the palygorskite was readily recognized from SEM observations (Figs. 2B & 2C). The delicate, dense aggregates of fibrous palygorskite form matted films usually covering fine-grained dolomites (Fig. 2A). The palygorskite fibres are 6 to 14  $\mu\text{m}$  long and sometimes form bundles (Fig. 2B). Elsewhere, the palygorskite fibres fill and bridge the pore spaces between the coarse dolomite crystals (Figs. 2C & 2D). No unusual morphology or configuration of the palygorskite fibres was observed. The identification of palygorskite was further confirmed by X-ray qualitative analysis (Fig. 4). Transmission electron micrographs indicate that the palygorskite fibres are relatively uniform in length and width (Fig. 5A). Electron diffraction pattern (Fig. 5B), shows considerable variation in the number of observed diffractions of palygorskite, as well as intensities and line profiles. We cannot suggest explanations for these diffraction features. All the above mentioned observations indicate that the studied palygorskite is highly crystalline and composed of well defined fibres.

The fibrous morphology of the palygorskite indicates

that crystal growth occurred after dolomitization and cementation of the associated Middle Eocene sediments. Insoluble residue analyses of the samples gives no evidence to suggest a volcanic origin for palygorskite. Quartz, zircon, feldspar, garnet and other minerals found in fresh and altered ash are completely lacking. Furthermore, there is no transitional form between the palygorskite and other clay minerals. All observations suggest that the studied palygorskite is authigenic and that it did not grow from a clay but precipitated directly from solution.

### ELEMENTAL COMPOSITION

The elemental analyses of twenty palygorskite samples (Table 1) show that the values of  $Al_2O_3$  and  $SiO_2$  are similar to those of perviously published analyses of palygorskites (Fig. 6). However, Ca, Mg and Fe contents are high, and this is contrary to most reported compositions of palygorskite deposits (Table 2). The relatively high concentrations of CaO and MgO might indicate that the samples contain carbonate phases. The iron contents are close to those of palygorskites from Saudi Arabia, Iraq and Morocco and but less than the Jordan Valley palygorskite (Table 2). These authors have pointed out that palygorskite developed in calcretes and soil are generally richer in iron than those found in carbonate sequence. The distribution of trace elements within the studied palygorskite samples show a narrow range. This implies that the palygorskite has formed in the same environment with similar formation fluids. The relatively high concentrations of Sr and Rb are most probably relate to the high contents of Ca and K in the palygorskite samples.

### STABLE ISOTOPE DATA

The isotopic compositions of the Middle Eocene dolomite can aid in environmental interpretations. Isotopic analyses were obtained for the present study in order to investigate the relative degree of evaporative concentration of waters during Middle Eocene formation of dolomite and palygorskite. The  $\delta^{18}O$  values of dolomite ranged from +0.3 to +2.7‰ PDB [21]. The variation of about 2.4‰ in  $\delta^{18}O$  values of the dolomites can be attributed to either precipitation from slightly evaporated water, which would result in higher  $\delta^{18}O$  values, and/or to exchange of the

Middle Eocene dolomites with younger waters which had lower  $\delta^{18}O$  values than the original marine values (Fig.7). The calculated isotopic composition of water that formed the Middle Eocene dolomite at about 20°C (ranging from +1.1 to +4.7‰ SMOW) supports the formation of dolomite from slightly evaporated water. The isotopic compositions of these waters are enriched relative to Gulf water and groundwater (Fig. 7). However, the likelihood of isotopic exchange with younger waters (groundwater and precipitation) is supported by the presence of late sparry calcite cements. Their oxygen isotopic signatures (ranging from -5.7 to -11.8‰ PDB; [21] indicate a meteoric origin for these cements. Moreover, petrographic evidence for dissolution and reprecipitation in the Middle Eocene dolomite is clear.

The wide negative range in the  $\delta^{13}C$  values for dolomites (ranging from -1.0 to -8.9‰ PDB) suggests that organic reaction rather than evaporative concentration were dominant in determining the  $^{13}C/^{12}C$  ratio of dolomite in a marine environment. The negative  $\delta^{13}C$  signatures of the late sparry calcite (ranging from -4.1 to -8.2‰ PDB) are in agreement with a meteoric cementation scenario suggested by very negative  $\delta^{18}O$  values and by petrographic data.

The  $\delta^{18}O$  values of the studied palygorskite vary within rather wide limits (Table 1), averaging +18.7‰ SMOW (n=20). The relatively high  $\delta^{18}O$  values of the palygorskite support the scenario that palygorskite formed in waters of higher salinity and evaporated than those of the late sparry calcite. However, it is likely that the palygorskites and dolomites of the Middle Eocene carbonate formed from formation fluids of different isotopic compositions.

### ORIGIN

The genesis of palygorskite has been the subject of much discussion [1, 2, 22, 23]. There are four possible origins for the studied palygorskite from the Middle Eocene dolomite: 1) it is a detrital constituent of the parent sand and has the same origin as detrital quartz inherited from the weathering of pre-Eocene sediments before and after deposition; 2) it was formed as a result of the post depositional alteration of volcanic ash; 3) it was formed by diagenetic alteration of smectite; or 4) it was formed as a

result of chemical precipitation from solution after dolomite formation in Middle Eocene time.

Based on the field evidences and petrographic observations, the fourth assumption seems a more plausible for the origin of the studied palygorskite. Basin conditions during the Middle Eocene were probably ideal for direct precipitation in a shallow marine environment with relatively elevated salinity and arid climate [21]. Chamley [2] summarized the conditions for palygorskite formation as being "alkaline conditions in restricted basins subject to marine transgressions, limited water exchange, warm and humid contrasted climate, and strong evaporation". These conditions similar to those anticipated for the formation of the dolomite and palygorskite. In this study, SEM investigation showed that palygorskite fibres cover dolomite crystals (Fig. 2). This implies that the palygorskite must have formed after dolomite, when the basin fluids were slightly impoverished in Mg, Si and Al. The SEM observations also reveal that the long palygorskite fibres fill and bridge the pore spaces between the dolomite crystals (Figs. 2C & 2D). Long palygorskite fibres could have been broken or destroyed by transportation, implying that fibrous clays may therefore be either authigenic or detrital in a given sedimentary environment. However, the absence of short or broken palygorskite fibres in this study argue against a detrital origin and suggests that the palygorskite fibres grow in situ.

Chemically, the genesis of palygorskite is favored by formation waters enriched in Si, and having a high pH and a  $Al^{3+} : Mg^{2+}$  ratio of ~1 [11, 22, 24]. Therefore, it is necessary to evaluate whether the formation waters could have provided the essential elements for the formation of the palygorskite. The following points support the contention that the Middle Eocene environment was favorable to palygorskite neoformation:

- 1) The Mg could have been supplied from the surrounding Middle Eocene dolomites and/or from the transformation of high-Mg calcite to low-Mg calcite. The environment must have been slightly alkaline, where Si and Mg supplied slowly by dissolution of diatoms and dolomites;
- 2) The study area was subjected to an arid climate during Eocene time [21]. Such a climate leads to a concentration of basic elements in solution and consequently an increase in pH and salinity. These conditions were favorable for the formation of dolomite and palygorskite [25]. In this study, the palygorskite fibres are seen to cover the dolomite crystals. This indicates that the palygorskite fibres formed after the formation of dolomite;
- 3) The precipitation of palygorskite requires a medium in which Al has a very low solubility and in which Si and Mg are soluble [25]. Si and Al may have been provided by degradation of phyllosilicate clays which are unstable in the hyperalkaline conditions and therefore dissolved, releasing Al and Si [26].  $Al_2O_3$  may have also entered the basin as an organic complex.

## CONCLUSIONS

Several analytical techniques (XRD, SEM, TEM, major and trace elements and stable oxygen and carbon isotopes) reveal that palygorskite associated with Middle Eocene dolomite in North Qatar. The dolomites are of replacement origin and the associated palygorskite was formed after the dolomitization of the original Middle Eocene carbonate. The absence of tectonic activity during that time, prevented the influx of clastic materials into the carbonate depositional basin. Because of this lack of clastic materials interbedded with the Middle Eocene dolomites, the palygorskite can only owe its origin to the accumulation of Al, Si and Mg from dissolution of the dolomite and the amorphous silica, and the influx of meteoric water.

Chemically the conditions in the depositional basin during Middle Eocene (high salinity, high pH, release of Al, Si and Mg) were favourable for the formation of palygorskite. The variation of 2.4‰ in  $^{18}O$  values of the dolomites can be attributed to formation from slightly evaporated water ( $^{18}O$ -enriched) and/or to exchange of the dolomite with younger water ( $^{18}O$ -depleted). The relatively high  $^{18}O$  values of the palygorskite support the scenario that the palygorskite formed from solution of high salinity. However, the isotopic data suggest that the dolomites and

palygorskites were not precipitated from the same water types.

A volcanic origin for the palygorskite is unlikely due to the lack of any significant amount of ash in Middle Eocene dolomites of Qatar. Palygorskite formation by the transformation of smectite is also unlikely, since no transitional textures or minerals were observed by XRD or electron microscopy. Therefore, such is frequently the case where palygorskites are formed by direct precipitation from solution.

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**Table (1): Ranges of chemical and isotopic compositions of North Qatar palygorskite (20 samples).**

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	MnO						
50.25-57.65	7.80-12.45	1.69-5.60	12.21-7.95	2.43-0.98	0.92-0.48	1.21-0.56	0.86-0.34						
Rb	Sr	Nb	Zr	Y	Cu	Ni	Cr	V	B	La			
45-14	320-110	12-6	210-115	6-3	24-18	48-18	16-10	16-9	149-98	19-7			
$\delta^{18}\text{O}$ (SMOW)													
16.2-23.4													

**Table (2): Average chemical composition of the studied palygorskite compared with palygorskite from other localities.**

Sample No.	1	2	3	4	5	6	7	8	9	10	11	12	13
<b>Major Oxides (Wt%)</b>													
SiO <sub>2</sub>	53.85	52.68	52.35	52.70	52.60	52.00	51.50	70.47	53.75	55.86	51.00	58.18	55.64
Al <sub>2</sub> O <sub>3</sub>	10.20	11.90	7.01	8.40	12.60	17.50	10.03	6.84	10.23	10.54	12.89	11.81	8.76
Fe <sub>2</sub> O <sub>3</sub>	3.54	4.59	4.59	7.00	4.60	1.60	2.88	5.65	2.09	3.23	2.77	0.94	3.36
MgO	9.14	10.59	11.96	13.40	8.40	7.00	12.08	15.90	9.39	9.20	7.54	6.36	9.05
CaO	1.39	1.88	1.35	0.30	2.20	1.40	1.81	0.22	2.29	1.56	1.02	0.97	2.02
Na <sub>2</sub> O	0.78	1.65	0.32	0.10	-	-	0.12	-	-	0.68	0.27	0.65	-
K <sub>2</sub> O	0.82	0.70	1.09	1.00	-	-	0.13	0.01	0.02	0.05	0.44	0.81	0.75
MnO	0.65	1.02	-	-	-	-	-	0.07	-	-	0.08	0.30	-

1. This study, 2. Saudi Arabia [12], 3. Iraq [22], 4. Jordan Valley [28], 5. Morocco [29], 6. Algeria [30], 7. Spain [31], 8. Australia [32], 9. Japan [33], 10. Georgia, USA [1], 11. Scotland [34], 12. New Zealand [35], 13. France [36].



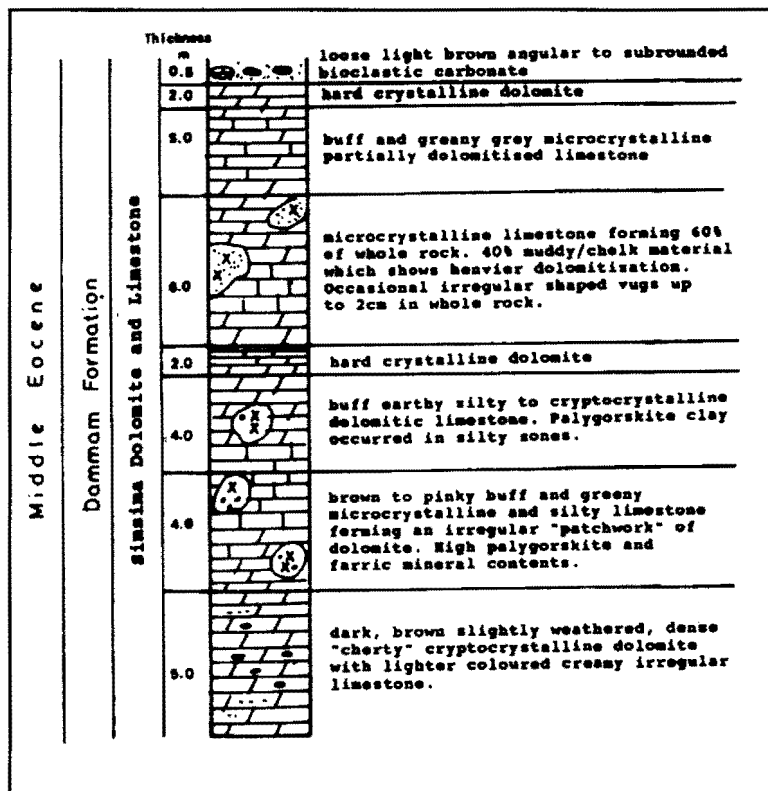
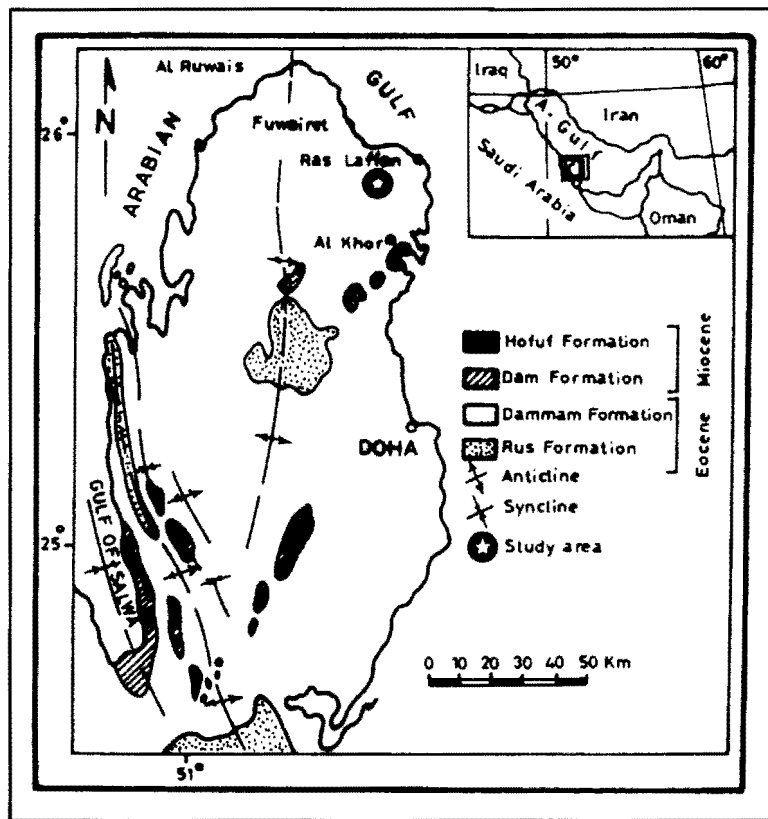


Figure 1. A- Geologic map of Qatar showing location of study area. B- Stratigraphic section of the Middle Eocene carbonate rocks in North Qatar.

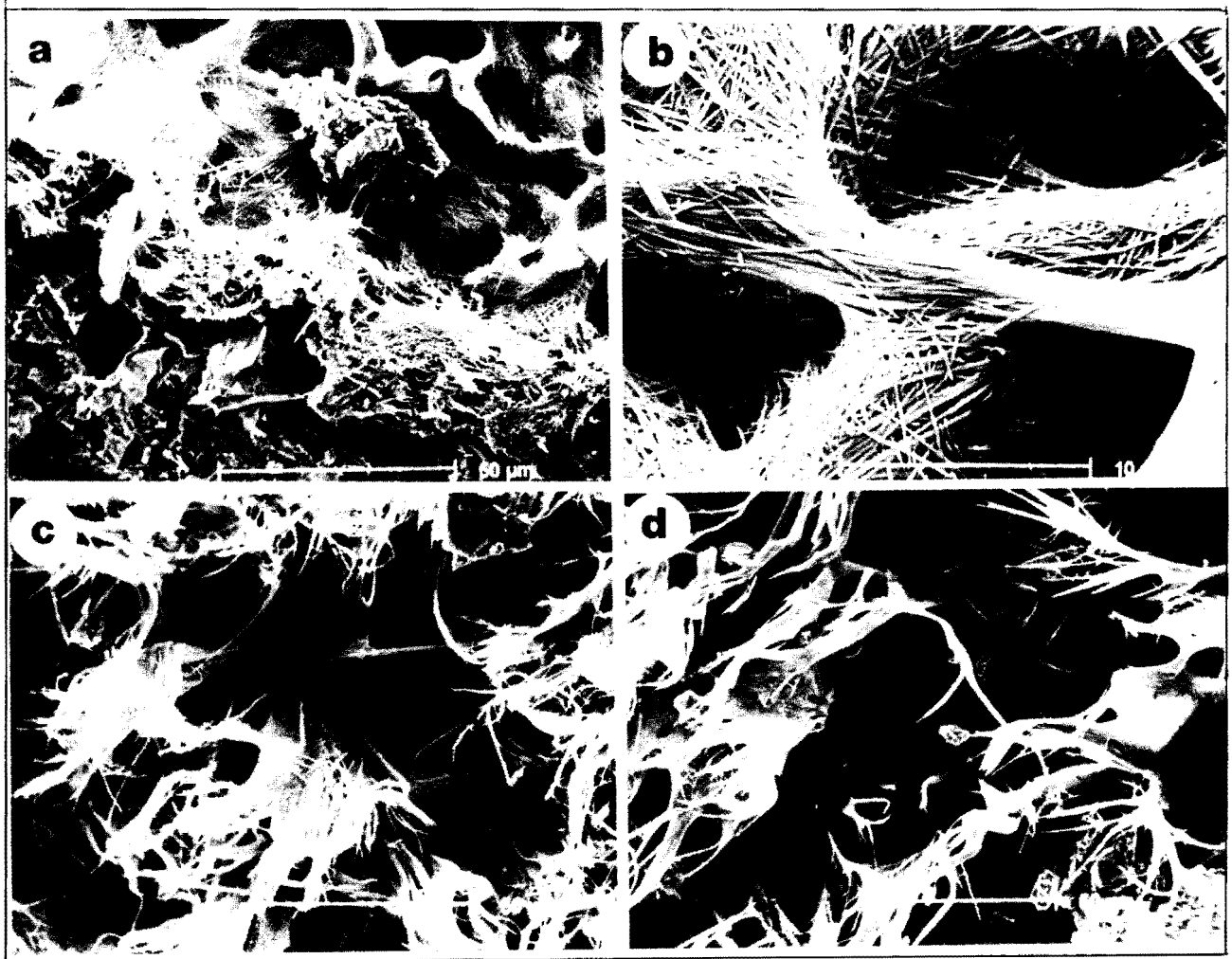


Figure 2. A- Scanning electron photomicrographs of palygorskite showing fibrous morphology (note that the palygorskite covers the fine-grained dolomite). B- Scanning electron micrograph of long and unbroken palygorskite fibres. C- Scanning electron micrograph of the palygorskite filling the pore spaces between dolomite crystals. D- Scanning electron micrograph of dense aggregates of the palygorskite fibres bridging between dolomite crystals.

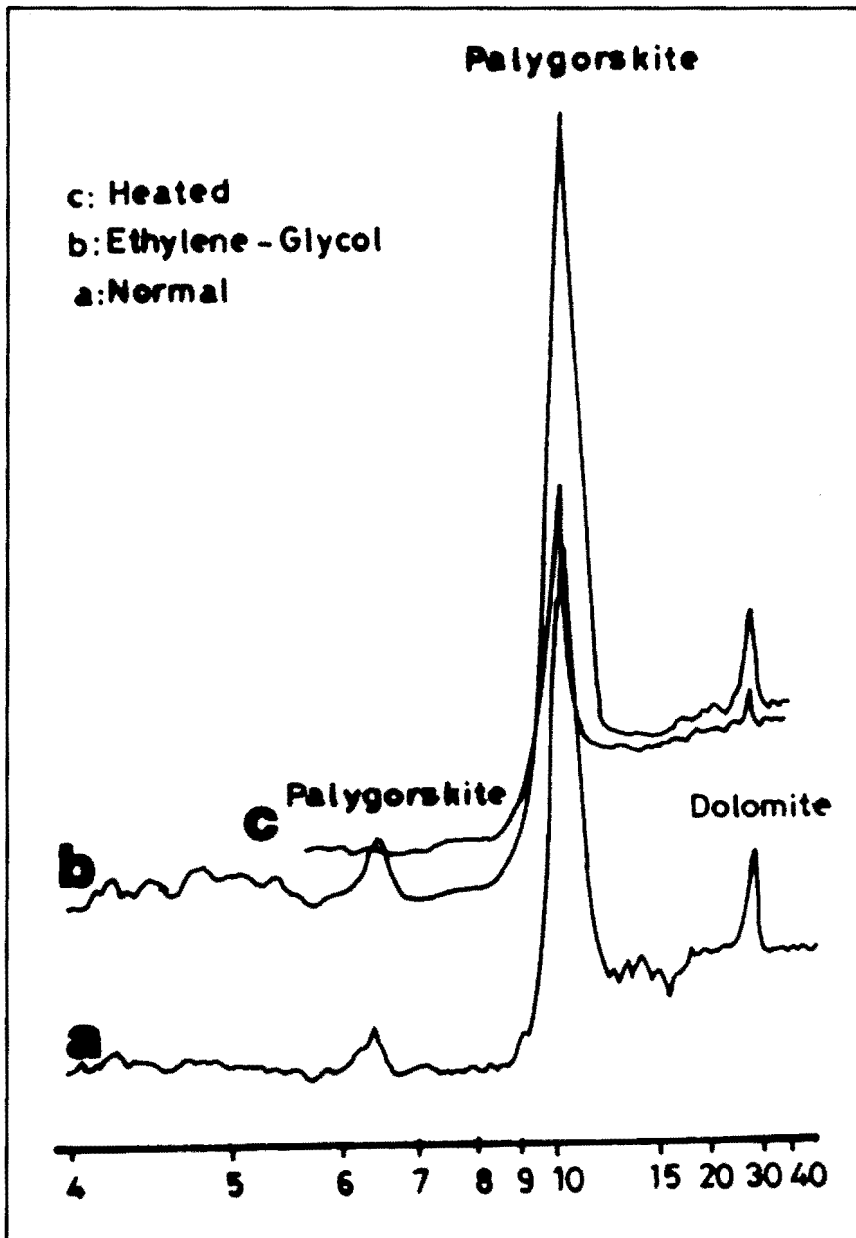


Figure 3. X-ray diffraction patterns of palygorskite samples.

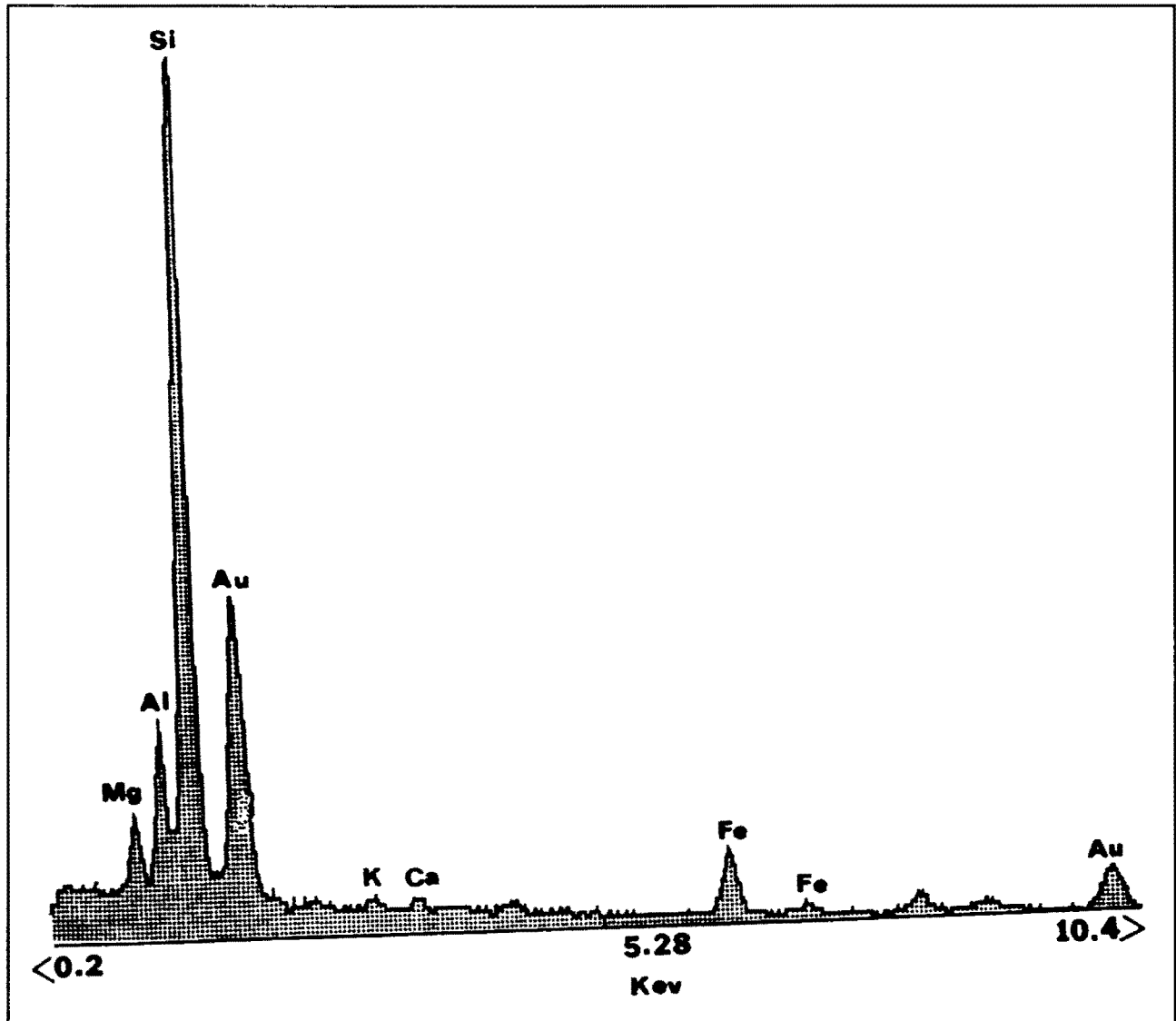


Figure 4. EDX spectrum of typical clay material shows the presence of Si, Al, Mg and Fe, a combination of elements typical of palygorskite.

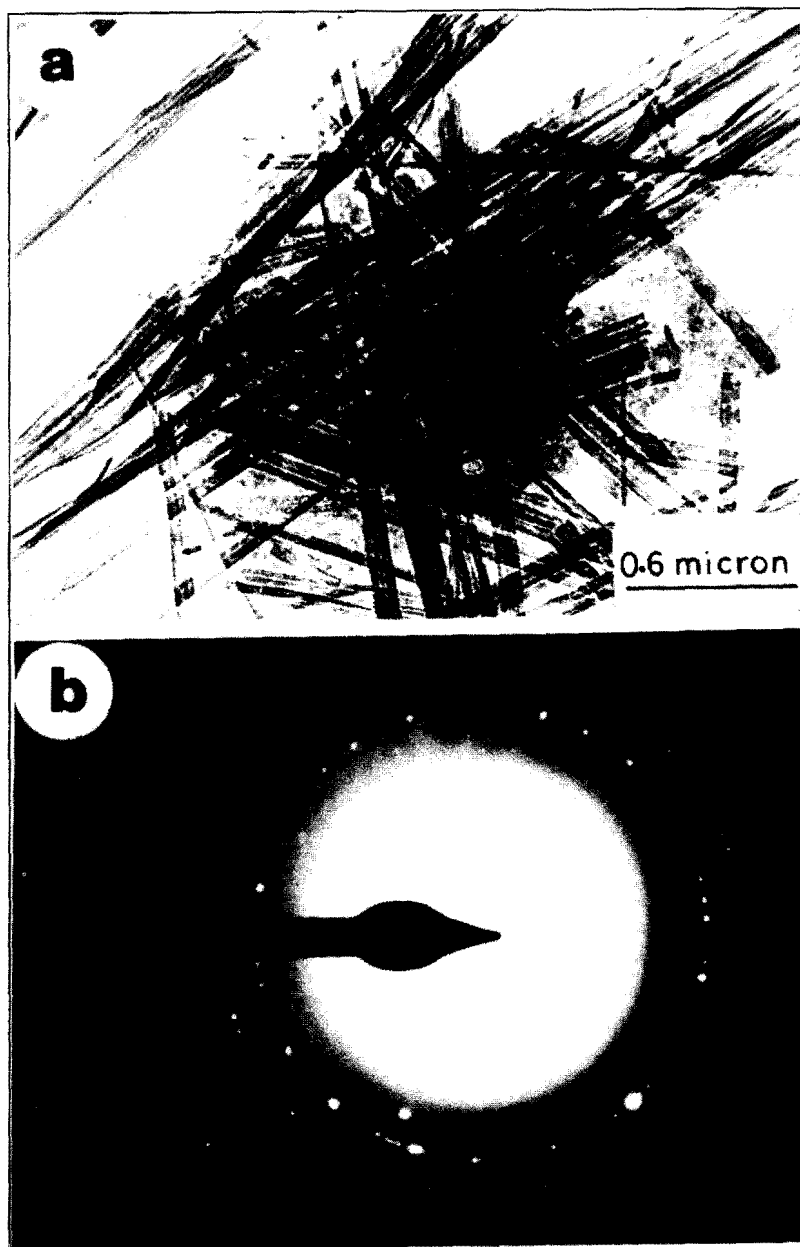


Figure 5. A- Transmission electron photomicrographs of the palygorskite fibres.  
B- Electron diffraction pattern of palygorskite.

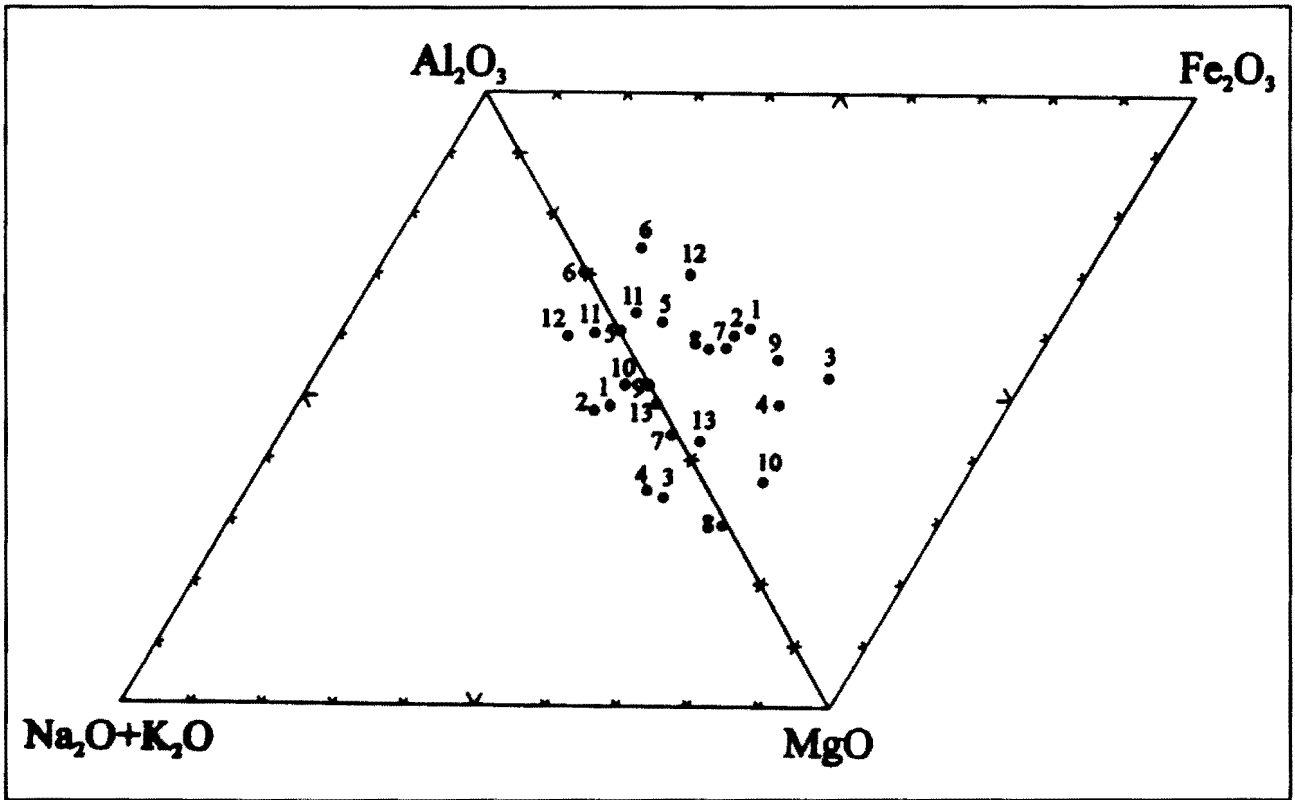


Figure 6.  $\text{Al}_2\text{O}_3$ - $\text{MgO}$ - $\text{Na}_2\text{O}+\text{K}_2\text{O}$  and  $\text{Al}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$ - $\text{MgO}$  ternary diagrams showing elemental compositions of palygorskite compared with those of palygorskite samples from other localities (numbers refer to the name of the localities as in Table 2).

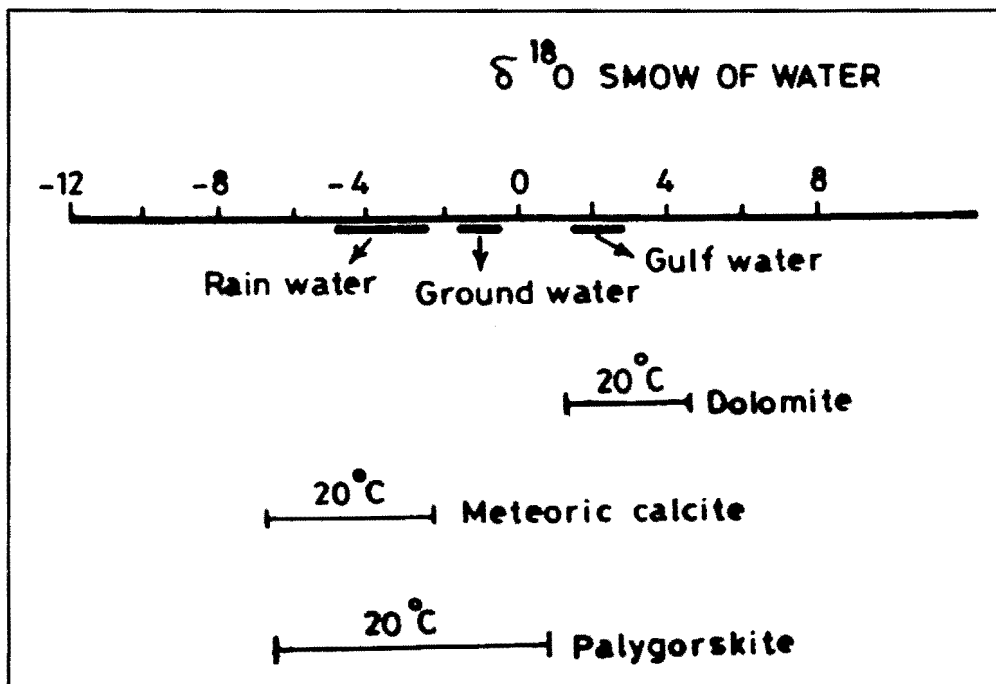


Figure 7. Values of  $\delta^{18}\text{O}$  (SMOW) compositions of water which had formed dolomite, meteoric calcite and palygorskite at  $20^\circ\text{C}$ . Note the isotopic compositions of Gulf water, groundwater and rain water.