

Mineralogical and Geochemical Study of the Subsurface Acidification Products Ninivite, Alunite and Jarosite, Northern Iraq

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ABSTRACT

Petrographic, mineralogical and chemical analyses of marl were investigated to verify the formation processes of many alteration products under low temperature-pressure conditions, where an ample source of sulphate exists. Marl (calcareous claystone) comprising about one third of the lithological constituents of the Middle Miocene Fat'ha Formation (previously named Lower Fars Formation) in northern Iraq in addition to evaporites and limestones. The extensive reduction of its sulphate members produces economically significant deposits of sulphur as well as sulphate and salt. Oxidation of H₂S produces sulphuric acid due to the effect of Thiobacillus bacteria. The interaction of H₂SO₄ with marl, leaching of K, Na, Al, Fe and Ca leaves behind a porous silica-rich (ninivite) center of the zoning pattern due to the alteration-precipitation processes, followed outwards by alunite, which is, in turn, surrounded by a narrow zone of jarosite and finally iron oxides in the rim. Secondary gypsum (selenite) is precipitated in shrinkage cracks as veins or as floating crystals in the ninivite.

KEYWORDS: Acid wetland, Alteration products, Redox, Alunite, Jarosite, Ninivite.

INTRODUCTION

Microbiologically induced formation of iron-silica minerals are widely distributed in various geochemical environments, such as in hot springs (Ferris et al., 1986), acid sulphate soils (Willett et al., 1992) and in iron ore sediments (Akai et al., 1999). Various iron-aluminosilicates associated with bacteria have been reported from river and lake sediments (Konhauser et al., 1993) and from weathering environments of volcanic ash deposits (Kawano and Tomita, 2001). Among these geochemical environments, the acid mine drainages are commonly produced by biotic and/or abiotic alteration of iron-sulphides such as pyrite leading to the formation of sulphuric acid and the release of Fe²⁺ into aquatic environments (Kittrick et al., 1982; Bigham and Nordstrom, 2000). Under such conditions, poorly ordered iron minerals such as schwertmannite and ferrihydrite are initially formed as a metastable phase resulting from bacterial oxidation of Fe²⁺, and jarosite and goethite are produced as thermodynamically stable phases by subsequent crystallization (Brady et al., 1986; Schwertmann et al., 1995; Bigham et al., 1990). Many field observations suggest that occurrences of these minerals are strongly dependent on solution chemistry, specifically the pH and SO₄²⁻ activity (Webster et al., 1996).

In the area of study, marl (calcareous claystone) dominates in the Middle Miocene Fat'ha Formation of northern Iraq and is exposed to subsurficial acid waters resulting in various alteration phases (Aswad et al., 1995). The general pattern of this alteration-precipitation embraces silica at the center, followed outwards by alunite, which is, in turn, surrounded by a relatively narrow zone of uneven distribution of jarosite and iron oxides. Secondary gypsum

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(selenite) may be associated with silica and alunite, or with jarosite and iron oxides as veinlets or as floating crystals in ninivite.

This marl-H₂S interaction, which was aided mostly by the action of bacteria was not reported in detail in the literature (Aswad et al., 1995). Extensive studies were done on such alteration from northern Iraq (Jassim and Al-Naqib, 1989; Aswad et al., 1995; Jajjo, 1999; Al-Naqib, 2006). The majority of these studies focus on overviews of mineral genesis, providing descriptions of the environmental variables responsible for these alterations under low temperature-pressure conditions.

In the present work, scanning electron microscopy is used to investigate the unaltered and altered marls of the Fat'ha Formation and various mineral products of the acidification process. The aim was to investigate the mineralogy and geochemistry of the marl and the alteration phases resulted from H₂S interaction in order to elucidate the acidification process and their associated mineral formation.

REGIONAL GEOLOGY

Iraq is divided into shelf and geosynclinal areas, with the former subdivided into stable and unstable, longitudinal units parallel to the Zagros Suture (Fig. 1) (Buday and Jassim, 1987). The Unstable Shelf contains three tectonic zones, which 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 High Folded Zone (Paleogene molasses and harmonic folded structures). 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). The basin of deposition of the Fat'ha Formation was dominated by quiet lagoonal environment at early Middle Miocene that led to the deposition of the lower member of the formation which characterized mostly by rhythmic alternations of carbonates, marls and evaporites. During Middle to late Miocene the reactivation of the basement blocks took place marked by the deposition of the clastic detritus (red sandstones and mudstones) in the upper member of Fat'ha Formation. The Middle Miocene age Fat'ha Formation (formerly Lower Fars Formation, Al-Rawi et al., 1993) is one of the most extensive and economically important formations in the entire Middle East region (Al-Juboury et al., 2001). The formation covers a large area (ca 1500 km x 300 km) and extends northwestward into Syria (there termed Lower Fars Formation) and southeastward into Iran (there termed the upper part of Gachsaran Formation) (Bellen et al., 1959). The extensive reduction of its sulphate members produces economically significant deposits of sulphur (Jassim et al., 1999) in certain areas where specific hydrogeological and bacteriological conditions should be available.

The Fat'ha Formation was deposited in a cyclic fashion of mud rocks, limestone and gypsum (Bellen et al., 1959). The mud rocks found in the region are exclusively carbonate rich, and include marls, silty marls and sandy marls. These mud rocks vary in thickness from 0.5 to 7 m. in the upper member of the Fat'ha Formation. Thickness fluctuations are related to variations in sediment supply to the basin, the duration of deposition and the relatively active erosion of the source area (Al-Naqib and Aghwan, 1993).

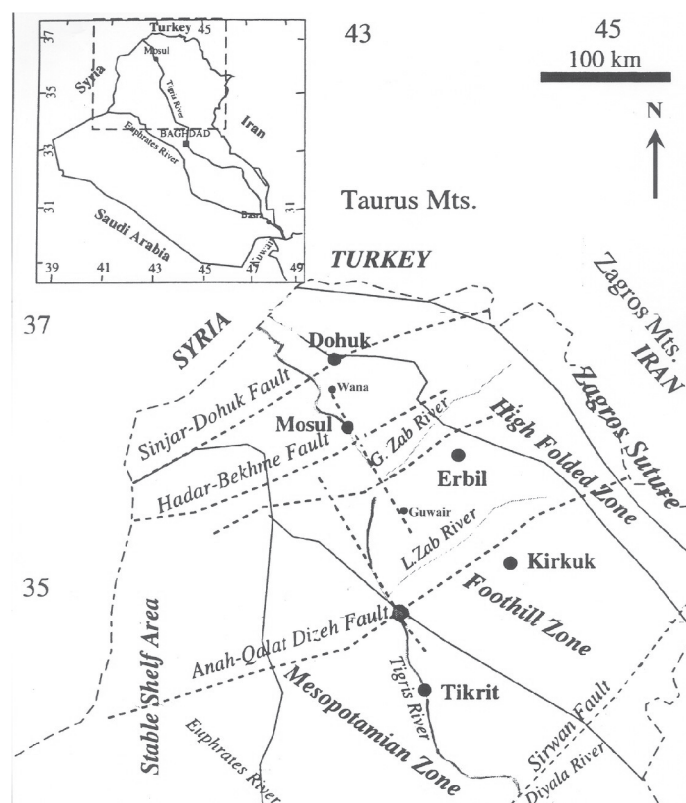


Figure 1. Tectonic zones and faulting of northern Iraq (after Buday and Jassim, 1987).
 Illustrating the occurrence of ninivite along alignment extending from Guwair to Babnet

Methods and materials

Fifteen samples were collected from the studied locality of ninivite located about 25 kilometers south of Mosul City. Ten samples were taken from the center of the alteration model outwards and five samples from the original (unaltered) marl.

Detailed petrographic observations using scanning electron microscopy of the altered and unaltered marl samples were done. A Camscan MV 2300 SEM equipped with a calibrated energy dispersive X-ray analysis system. Mineralogical analysis includes the XRD analysis of unaltered green and yellow marl as well as of the alteration phases, ninivite, jarosite and alunite which was performed using D8 Advance (Bruker axs), with Cu- α radiation. Chemical analysis of the bulk unaltered varicolored marl was made using a Siemens SRS 303 X-ray fluorescence spectrophotometer, whereas, the chemical composition of ninivite, alunite and jarosite was performed using atomic absorption spectrophotometer.

RESULTS

1. Mineralogy and geochemistry of unaltered marl

Marl comprises about one third of the lithological components of the Fat'ha Formation (Middle Miocene) of northwest Iraq. The Fat'ha marl shows various mineralogical and chemical phases, CaCO₃ forms about 45% of the marl composition, the rest belong to silica of both amorphous and crystalline phases as well as the clay minerals.

The studied marl displays variable colors of grey, green and yellow. The yellowish grey marl is, in some cases, referred to as the basal marl, since it is found at the base of a complete

rhythmic unit within the Fat'ha Formation (Mustafa, 1980). The contact between this basal marl and overlying gypsum beds is usually irregular and erosional, whereas with limestone beds the contact is gradational.

The marls contain large amounts of fossils (gastropods, pelecypods and oysters). Fossil populations and sizes decrease gradually upwards, accompanied by an increase in the frequency and size of gypsum nodules. The oysters are brackish-water fauna and the host sediments are interpreted as having been deposited in subtidal lagoonal setting (Ma'ala et al., 1988).

Scanning electron images show that the quartz is embedded within calcite cement (Fig. 2A). The clay mineral assemblage is dominated by palygorskite illite and kaolinite (Fig. 2B-D). The dominance of palygorskite in the claystones of the Fat'ha Formation may reflect the gradual conversion of this mineral from smectite in restricted, evaporitic lagoonal conditions (the major environment in the Fat'ha Formation).

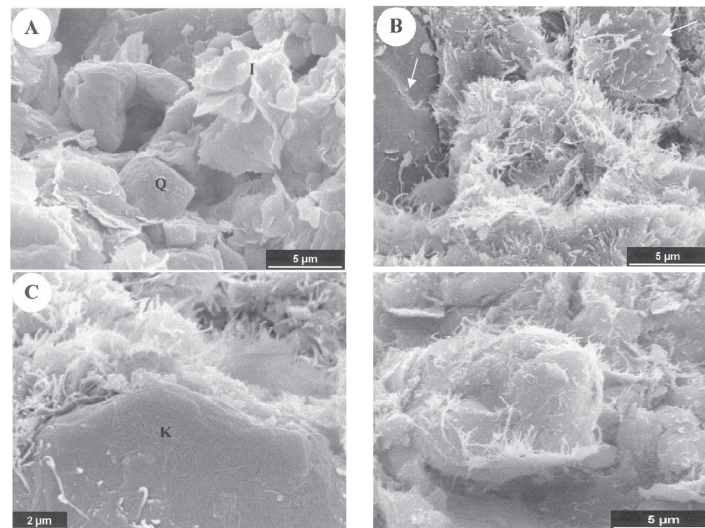


Figure 2. SEM images for the original unaltered yellow marl of the Fat'ha Formation,
A: quartz (Q) embedded in carbonates with platy illite (I) clay mineral
B: palygorskite in carbonate groundmass (arrows),
C: hexagonal plates of kaolinite (K) and fibrous palygorskite
D: palygorskite fibers and illite sheets.

The marl is composed of silt-sized quartz and feldspar grains embedded in clayey and carbonate matrix (Fig. 3). In thin sections, the color of marl is frequently red with dominate carbonate content as calcite and rare dolomite. The yellow marls have a high CaO and low SiO₂ content (Table 1). Other chemical features include the relatively high MgO content in both green and yellow marl, which may reflect the occurrence of palygorskite as one of the main clay minerals in the studied marl. Similarly, K₂O content marked also the presence of illite.

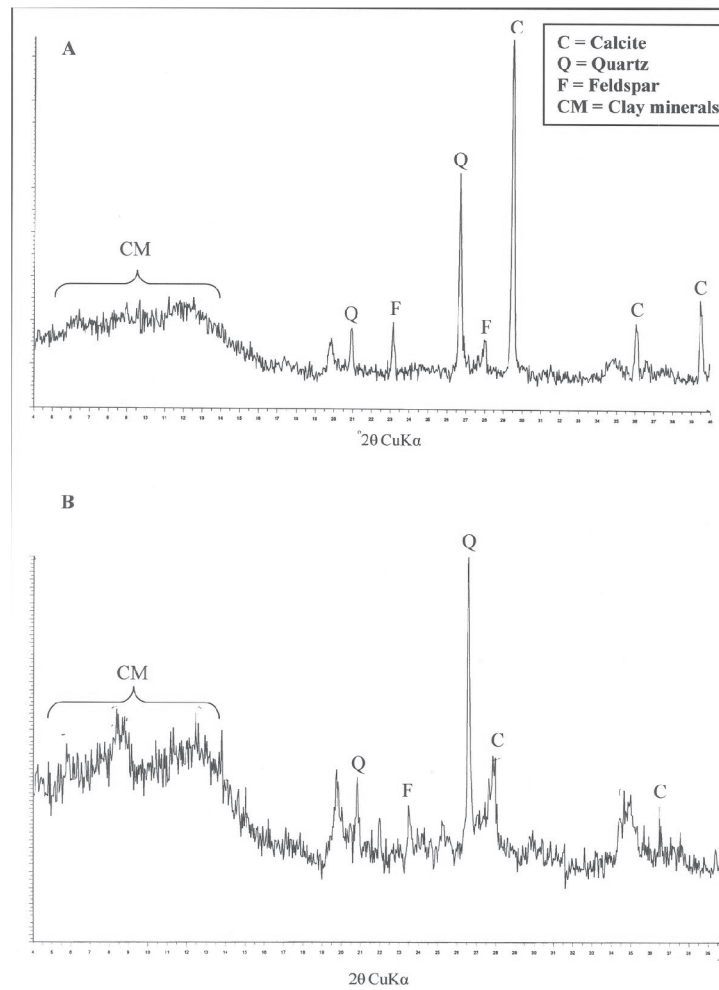


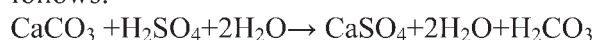
Figure 3. X-ray diffractograms for the bulk samples A- yellow marl; B -green marl showing different reflections of clay and non-clay minerals in the unaltered marl samples.

Table 1. Chemical composition of unaltered marl showing distribution of major oxides in the unaltered green and yellow marl of the Fat'ha Formation in the area of study.

Oxides %	Green marl		Yellow marl	
	1	2	3	4
SiO ₂	52.07	40.31	25.83	35.21
TiO ₂	0.84	0.63	0.43	0.60
Al ₂ O ₃	12.31	9.67	6.37	9.95
Fe ₂ O ₃	6.39	7.22	3.21	6.80
CaO	1.26	13.15	17.85	22.63
MgO	7.56	8.47	12.66	3.12
Na ₂ O	0.49	0.55	0.23	0.30
K ₂ O	3.28	2.11	1.72	2.54
MnO	0.03	0.10	0.03	0.07
P ₂ O ₅	0.14	0.10	0.11	0.09

2. Mineralogy and geochemistry of the altered phases

Where H₂S-marl interaction took place, ninivite was formed as byproduct of this process in the center of the alteration body, which is located on the main fractured zone of the H₂S seepage and alunite and jarosite as aureoles and iron oxides precipitate in the rims. Disseminated carbonates dissolved preferentially and migrated in acid solution and eventually precipitating secondary gypsum (selenite) is deposited in shrinkage cracks as veins or as floating crystals in the ninivite (Fig. 4B) as a result of sulfuric acid-marl interaction as follows:



Field work reveals that ninivite occurs in semi-circular patches ranging from few meters to tens of meters in diameter, which are, in some cases; coalesce to elongated bodies up to one kilometer in length and 10 meters thick. Ninivite is closely associated with alunite and jarosite during sulphuric acid-marl interaction. Nodules or aggregates of white alunite, reddish-black iron oxides and ochreous yellow jarosite are common. Pure jarosite is seldom found on its own, goethite and limonite are weathering products of jarosite. Chemical composition of the altered phases ninivite, alunite and jarosite is given in Table (2). These data provide evidence of significant loss of aluminium, iron, calcium, concurrent with progressive enrichment of silica.

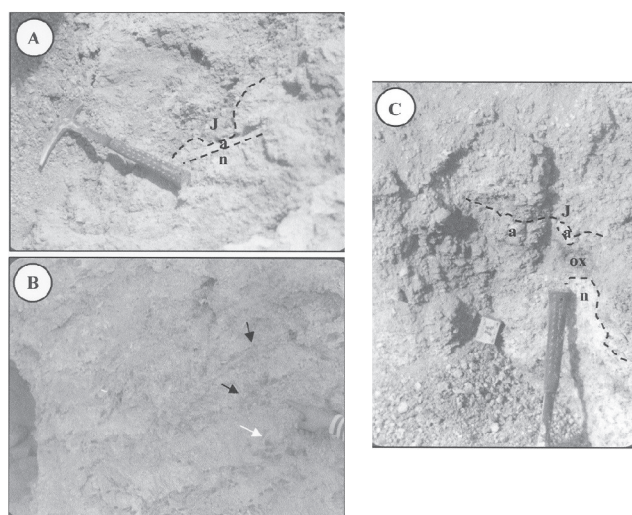


Figure 4. Field observations of the alteration products.

A: alteration of marl into ninivite (n), alunite (a) and jarosite (J).

B: Secondary gypsum (selenite) as veinlets (black arrows) and floated crystals (white arrow).

C: ninivite (n) in the center of alteration zone surrounded by violet iron oxides (ox) with alunite patches (a) and finally by yellow jarosite (J).

DISCUSSION

The structural setting, which includes longitudinal transversal fault trending in NW-SE direction and approximately extending along the Tigris River appear from Guwair anticline passing through Mosul and further towards NW until Babnet near Mosul Dam Lake (Fig. 1). In addition, there are hundreds of seepages along this lineament, which served as suitable geochemical environment to produce ninivite and related minerals as acidification products, alunite, jarosite, iron oxides and floated crystals of selenite (Fig. 4). Although the main geological formations embracing ninivite is the Fat'ha Formation, ninivite occurs as patches

in Injana Formation and even found within Tigris river terraces, which depends on paleoground water and stages of the Tigris River during succeeding periods of river development (Al-Naqib, 2006).

The studied calcareous claystones are highly affected by pulses of acid sulphate waters, which are characterized by low pH, high Al and Fe and sulphate concentration (Jajjo, 1999). H₂S gas seepage is probably derived from deep seated oil fields and/or as a byproduct of sulphur formation, where sulphur was oxidized by *Thiobacillus thiooxidans* bacteria (Al-Naqib and Mustafa, 1998) in the presence of water. The H₂S mingles with the suspended water in the vadose zone to produce H₂SO₄ wet soils aided mostly by action of bacteria (Jassim and Al-Naqib, 1989).

The evolved gas moved upwards through the extension of the longitudinal basement faults and the associating fractures, which are aligned in NW-SE direction along with the Tigris River lineament. This lineament extends from nearby Guwair passing to the NW through Mosul toward Wana village (near Babnet) SE of Mosul Dam Lake (Fig. 1) and produce acid solutions that led to the dissolution of calcium carbonates in the calcareous claystone leaving silica rich rock (ninivite), and hence leaching of Al⁺³ and Fe⁺³ to produce both alunite and jarosite, respectively (Al-Naqib, 2006).

By continuous exposure of marl that is rich in palygorskite, illite and kaolinite to acid sulphate water, which is common in the area, this marl is altered, resulting in various mineral phases. H₂SO₄ leaches most elements in the host marls and the released elements, which include K, Na, Al and Fe, from the clay minerals and iron oxides, are transported laterally (Aswad et al., 1995). The alteration products include ninivite, alunite and jarosite. This mineral association is formed in response to a continuous reaction of sulphuric acid (formed by H₂S oxidation above the water table) with clay minerals and carbonates. The alteration pattern displays zonation with siliceous central part (ninivite) rimmed by alunite and fringed by jarosite and iron oxides (Fig. 5) (Jassim and Al-Naqib, 1989).

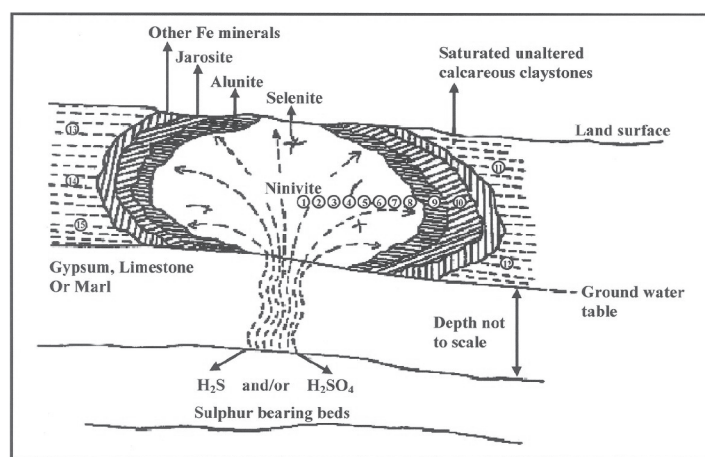


Figure 5. Model of formation of ninivite and associated minerals illustrating the alteration pattern displaying zonation with central silica rimmed by alunite and fringed by jarosite and iron oxides. (Numbered circles are sample locations) (Modified from Jassim and Al-Naqib, 1989).

Ninivite, which is a new form of porcelanite, is a porous silica rich rock, occurs mainly in isolated irregular shapes as white creamy bleached horizons which may coalesce forming relatively large bodies. SiO₂ content may range from 50% to 95% Table (2), and is primarily

related to the palaeo-ground water table that existed in the terraces of the Tigris River. Because of its mode of formation, this rock type may occur in any stratigraphic and structural position through the whole the Fat'ha Formation and the lower horizons of the overlying Injana Formation (Al-Naqib and Al-Dabbagh, 1994; Al-Naqib, 2006). Field relations show that ninivite is associated genetically with alunite $[KAl_3(SO_4)_2(OH)_6]$, jarosite $[KFe_3(SO_4)_2(OH)_6]$ and gypsum $[CaSO_4.2H_2O]$.

Table 2. Chemical composition of ninivite, alunite and jarosite, showing the variation in composition between semi-pure and pure ninivite, and the distribution of major oxides in the studied alunite and jarosite. Data (average of 10 samples) from Jassim & Al-Naqib, (1989) and Aswad et al., (1995), see Fig. 5 for the sample locations.

Oxides %	Ninivite		Alunite	Jarosite
	Semi	pure		
SiO ₂	85.86	95.70	3.09	22.90
TiO ₂	-----	0.59	0.01	-----
Al ₂ O ₃	0.30	0.22	36.25	1.40
Fe ₂ O ₃	0.12	0.08	0.29	26.90
CaO	4.20	0.98	0.08	1.70
MgO	-----	0.02	0.07	0.10
Na ₂ O	-----	-----	7.19	0.20
K ₂ O	-----	-----	4.69	9.60
P ₂ O ₅	-----	-----	-----	-----
SO ₃	3.40	0.07	34.68	23.50
Cl	-----	-----	1.00	0.10
L.O.I.	4.46	2.20	-----	-----

Scanning electron micrographs revealed the presence of ninivite as dense and large masses of amorphous silica, as white creamy bodies, mostly vuggy (Fig. 6 A & B). XRD diffraction pattern shows three modifications of these silica horizons, including opal, cristobalite and quartz (Aswad et al., 1995). In the present study, most peaks of silica belong to quartz. Amorphous silica is represented by hump (Fig. 6C), whereas, most peaks belong to quartz.

The investigated alunite is sodium alunite (Table, 2). Hamley et al., (1969) argued that solutions with very high Na⁺/K⁺ ratios (10-14:1) are required for alunite formation. The analysis of water from the springs in the area of study shows an approximate Na⁺/K⁺ of 10:1 (Aswad et al., 1995). SEM microphotographs showing tiny idiomorphic crystals of this mineral (Fig. 7, A-B) with an ellipsoidal to rod-shaped bacteria. XRD diffractogram of the studied alunite is shown in (Fig. 7C), which represents also the coexistence of alunite-jarosite in the altered marl.

Occurrence of early diagenetic Na-alunite was also described in the Middle Miocene evaporitic succession from the Sinai at Ras Sudar on the eastern coast of the Gulf of Suez (Rouchy and Pierre, 1987). There, Na-alunite was developed within cryptalgal sediments, which end a regressive sedimentary sequence represented by intertidal lithofacies grading to subtidal lithofacies. The formation of this sodium alunite was related to bacterial sulphate reduction, followed by the reoxidation of sulphide and production of sulphuric acid which reacted with clays (Goldberry, 1980) and can be regarded as an analogue to the alunite formation in the Middle Miocene marl of Iraq. The Na-alunite associated with evaporitic sediments constitutes an accurate indicator of multistep sulphur redox diagenetic reactions

involving bacterial sulphate reduction followed by organic or inorganic oxidation of sulphide to sulphur and sulphate (Rouchy and Pierre, 1987).

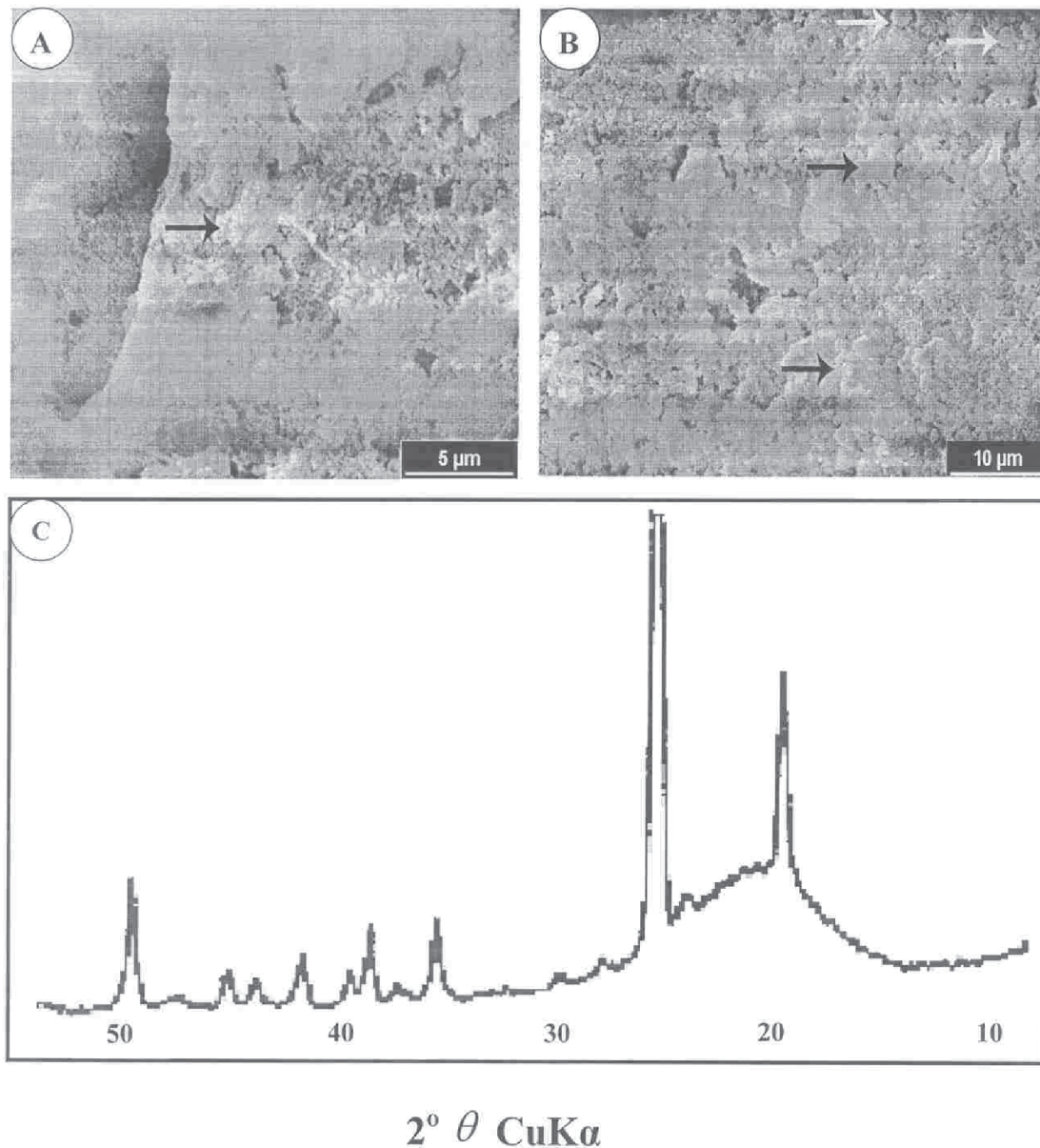


Figure 6. Scanning electron micrographs of the altered marl showing:
(A & B) large masses of amorphous porcelanite (ninvite) as white creamy bodies (black arrows) and tiny idiomorphic alunite crystals (white arrows).

(C) is the XRD graph of ninivite showing the hump for amorphous ninivite while most peaks belong to quartz.

Jarosite is formed under highly acidic conditions after all carbonate elimination when pH lowered to a value of 2-3 (Dauchafour, 1982), and is not stable in water, yielding iron hydroxides on hydrolysis. Therefore, jarosite occurs with the iron enriched part of the studied rocks. Jarosite occurs as weak and broad flakes (Fig. 8 A-B). XRD analysis for the jarosite-rich rock is shown in (Fig. 8, C).

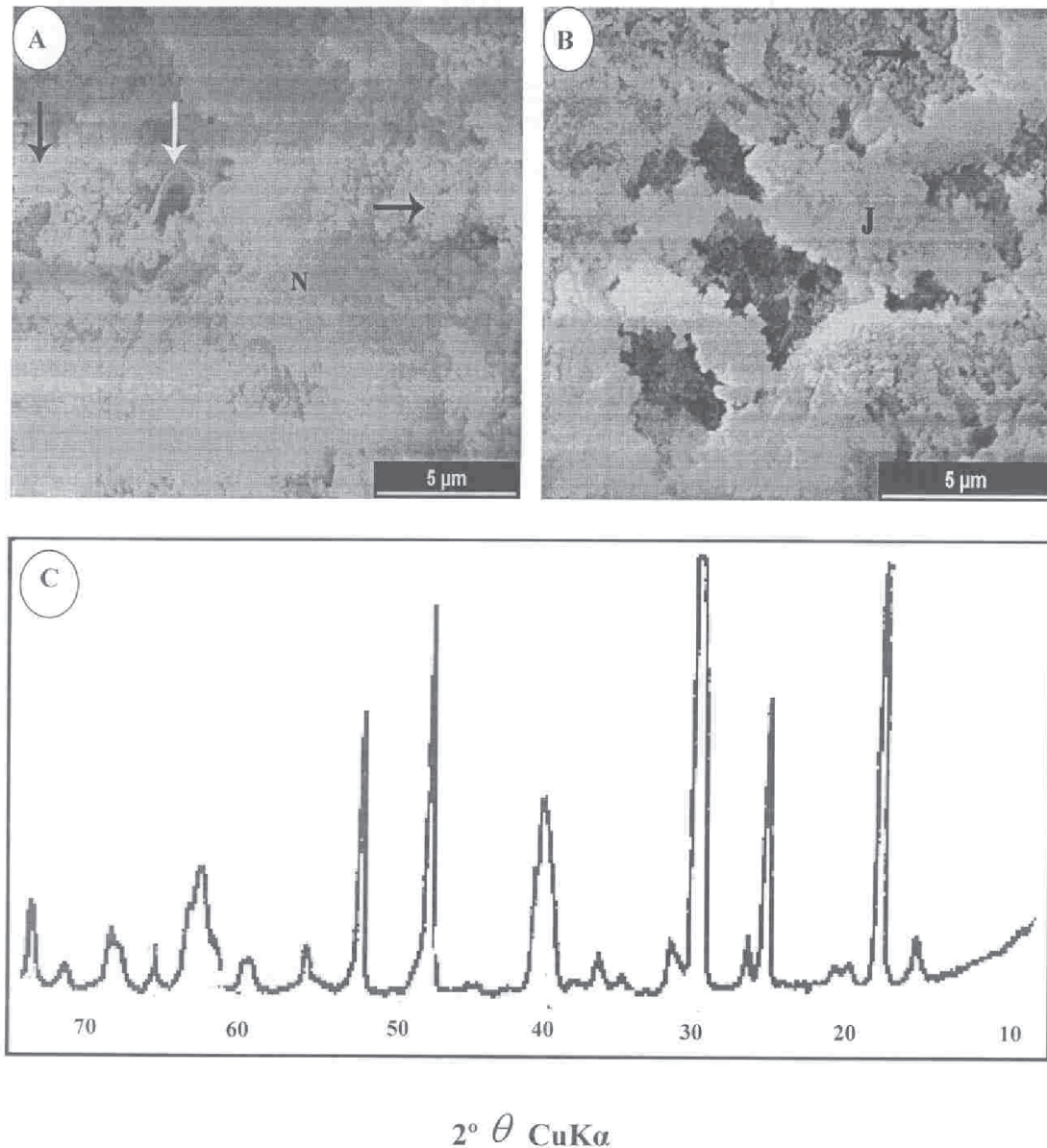


Figure 7. Scanning electron micrographs showing:
A: masses of white creamy ninivite (N) and tiny crystals of alunite (black arrows) with ellipsoidal shape of bacteria (white arrow),
B: alunite tiny idiomorphic crystals (arrow) with common jarosite flakes (J),
and C: representative XRD peaks for the studied alunite.

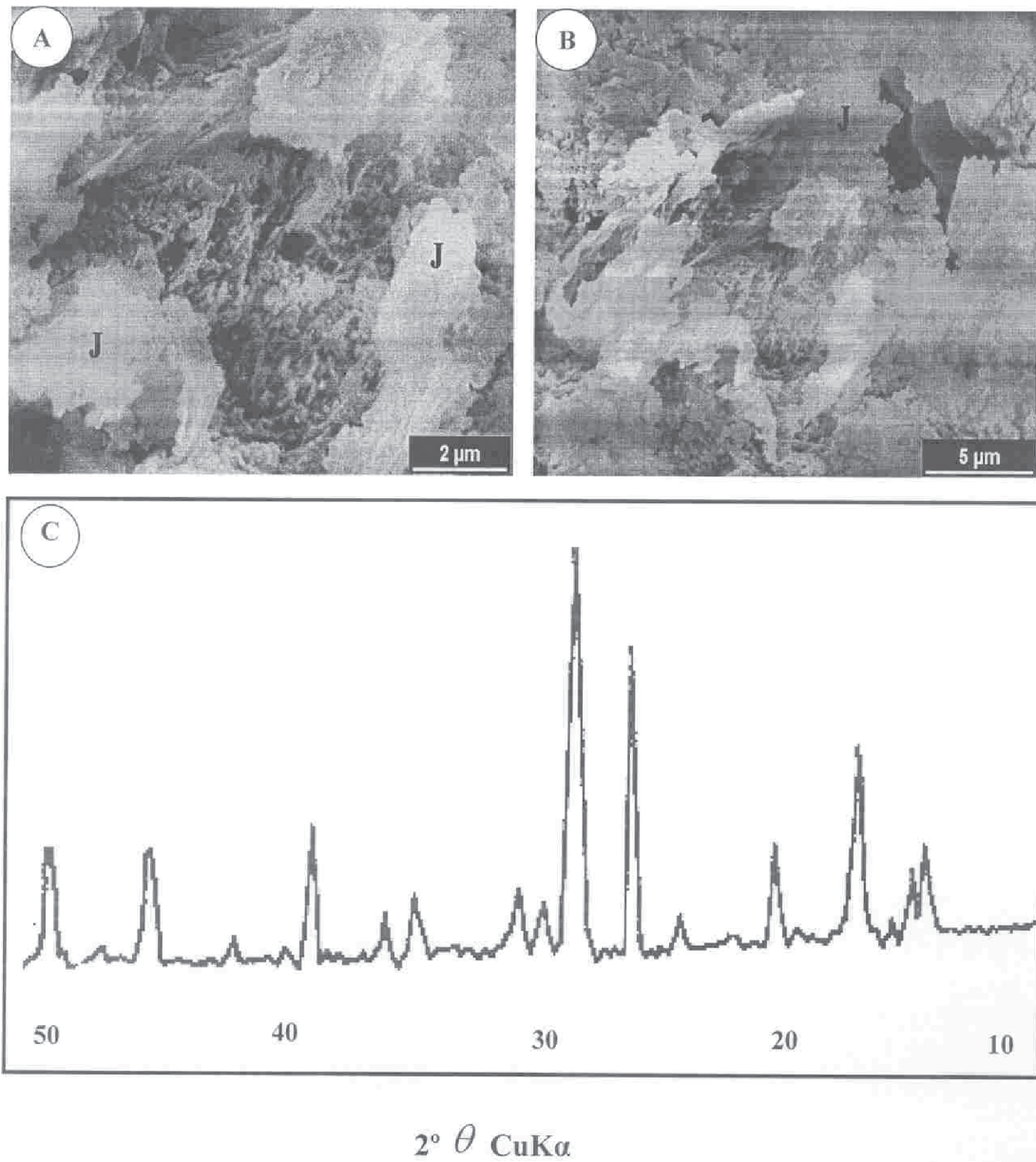


Figure 8. (A & B): Scanning electron micrographs showing jarosite masses (J), and C: XRD scan for jarosite- rich rock.

CONCLUSIONS

The acidification products resulted from marl-H₂S interaction in the Middle Miocene Fat'ha marl from northern Iraq constitutes important indicator of alterations under low temperature-pressure conditions. These products were formed in response to a continuous reaction of sulphuric acid (formed by H₂S oxidation above the water table) with the clay minerals and carbonates. Association of the alteration products alunite and jarosite with silica (ninivite, in the present study) and their occurrence in exclusively sedimentary sequence of marl, limestone and gypsum has not been reported elsewhere. The work could give an indication for both sulphur occurrence and primary prediction for the oil reservoir situation.

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دراسة معدنية وجيوكيميائية لنواتج التفاعلات الحمضية تحت السطحية نينيفايث والونايت وجاروسايت في شمال العراق

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الملخص

تم إجراء عدد من التحاليل البتروغرافية والمعدنية والكيميائية على صخور المارل لتوضيح عملية تكوين نواتج التحلل تحت تأثير الحرارة والضغط المنخفضين وبوجود مصدر تفاعل مستمر مع حامض الكبريتيك. تشكل صخور المارل (الحجر الطيني الكربوناتي) ما يقارب ثلث المكونات الصخرية ضمن تكوين الفتحة (المايوسين الأوسط) في شمال العراق بالإضافة إلى صخور المتبخرات والحجر الجيري. يسبب الاختزال الشامل والمؤثر على صخور المتبخرات بتكون كميات اقتصادية من الكبريت مع صخور الملح والكبريتات. كما تسبب أكسدة غاز كبريتيد الهيدروجين بتكون حامض الكبريتيك وذلك بتأثير وجود البكتريا من نوع (Thiobacillus). وعند تفاعل هذا الحامض مع صخور المارل والغني أصلاً ببعض المعادن الطينية مثل الاللايت والكاؤولينايت، يتم خلب الكثير من العناصر مثل (البوتاسيوم، الصوديوم، الألمنيوم، الحديد والكالسيوم) من صخور المارل وما يرافقها من أكاسيد حديد. يسبب هذا الخلب المستمر للعناصر بتكوين نمط شبه بيضوي من التغيرات في صخور المارل يتألف من صخور غنية بالسليكا في مركز نطاق التغير يتبعها نحو الخارج تكون معدن الالونايت ثم نطاق لمعدن الجاروسايت وأخيراً تكون أكاسيد الحديد في الحافة، كما يتكون الجبس الثانوي (السليينايت) ضمن العروق أو بشكل بلورات طافية داخل النينيفايث.