

THE MINERALOGY, GEOCHEMISTRY AND SEDIMENTATION OF THE SHARK TOOTH SHALE MEMBER, BAHRAIN

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ABSTRACT

The Shark Tooth Shale (STS) is of Middle Lutetian age and consists of ocher or green fissile shale, marl, carbonate mudstone and subordinate phosphate, stacked in a multi cyclic rhythm. Each cycle consists, from bottom to top of phosphates-shale-marl-carbonate mudstone. The top of each cycle is usually a bioturbated hardground. The mineralogy consists of carbonate fluorapatite, palygorskite, dolomite, calcite and quartz, with less amount of glauconite, halite and gypsum. The phosphates are granular, composed of phosphoclasts mainly bioclasts including fish bones, shark teeth and coprolites. The chemical composition is dominated by SiO₂, CaO and MgO with variable amounts of P₂O₅ (1.0 – 13.5%). The purified concentrates of phosphate coprolites and bones show 34 – 35% P₂O₅, about 52.5% CaO, 3.7% F and 6.6 – 7.2% L.O.I (CO₂ and H₂O⁺). The STS was deposited on a shelf controlled locally by the Bahrain Anticline or Dome. The sedimentation took place in several sharp transgressive episodes; each was concluded by temporary shallowing and emergences. The phosphate are mainly related to the early stages of transgression; the shale-rich sediments were laid down at the maximum transgression under subtidal anoxic conditions and the carbonate mud were deposited and simultaneously dolomitized in the tidal mud flats at shallowing stage and were later emerged and bioturbated. The phosphate showings of the STS are correlatable, as a phosphogenic event, and geological setting with other Tythian deposits (of the same age i.e. Lutetian) in Saudi Arabia, Qatar, Jordon, Iraq, and probably other same age deposits in North Africa.

معدنية وجيوكيميائية ورسوبية عضو طفل أسنان القرش، البحرين

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المستخلص

يتألف عضو طفل أسنان القرش العائد الى عمر اللوتيشي الأوسط من طبقات بلون كاكي أو أخضر من الطين الصفحي، والمارل، الطفل الكربوناتي والفوسفات المترسبة دورياً بصورة متعاقبة. وتتألف كل دورة من الأسفل للأعلى من فوسفات، طين صفحي، مارل، طفل كربوناتي. وينتهي الجزء العلوي من كل دورة بسطح صلب متحفر. تألفت المعدنية من كربونات فلور أبتايت، باليغورسكايت، الدولوميت، الكالسيت والكوارتز، مع كمية أقل من الغلوكونايت الهاليت والجبس. الفوسفات حبيبي، حبيباته عضوية في الغالب مؤلفة من عظام أسماك، أسنان سمك القرش والكوبرولايت (فضلات الأسماك). التركيب الكيميائي مؤلف أساساً من SiO₂ و CaO و MgO مع كميات متباينة من P₂O₅ تتراوح بين 1.0 و 13.5%. فيما تراوحت نسبة P₂O₅ في العينات المركزة لحبيبات الكبرولايت والعظام الفوسفاتية بين 34 – 35%، ونحو 52.5% من CaO و 3.7% من F و 6.6 – 7.2% من L.O.I (CO₂ و H₂O⁺). ترسب عضو الطفل STS في منطقة الرف الذي سيطرت عليه محلياً قبة أو طية البحرين المحدبة. حصل الترسيب بصورة دورات تقدمية حادة؛ كل منها تنتهي بتضلل وقتي وانكشاف. الترسيبات الفوسفاتية تموضعت في المراحل

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المبكرة للتقدم البحري فيما تموضعت الرواسب الغنية بالطين الصفحي في أقصى تقدم بحري في ظروف لاهوائية تحت المد، فيما ترسبت الكربونات والطفل في مناطق المسطحات المدية وتعرضت لعمليات دلمتة آنية في مرحلة التضحل ومن ثم تكشف وتعرضت للحفر. فوسفات STS تضاهي كفترة أو حدث فوسفاتي ووضع جيولوجي مع ترسبات التيثس الأخرى التي تعود لعمر اللوتيشي في كل من المملكة العربية السعودية، وقطر، والأردن، والعراق، وربما الرواسب الأخرى من نفس العمر في شمال أفريقيا.

INTRODUCTION

▪ Location

The Kingdom of Bahrain is located between 25° 32 and 26° 20 North and between 50° 20 and 50° 50 East. It is an archipelago consisting of thirty six low-laying islands, shoals, islet sand patches of coral reef over an area of 8,269 km² in a relatively shallow bay of the Arabian Gulf between Saudi Arabia and Qatar Peninsula (Fig.1). The main Island, Bahrain (765 Km²), about 48 Km long and 16 Km wide, accounts for about 85% of the total kingdom area. The maximum altitude is about 134 m at Jebel Ad Dukhan, near the center of Bahrain Island.

▪ Geological Setting

Bahrain Islands are covered by Tertiary rocks and Quaternary superficial sediments. The oldest rocks exposed are the Rus Formation (Early Eocene), exposed only in the core of the Bahrain Anticline or Dome, which is a N – S trending structure believed to be an expression of a deep-seated salt intrusion (Powers *et al.*, 1966; Tleel, 1973).

The Rus Formation is composed of chalk and chert-bearing dolomitic limestone with subsidiary shale, anhydrite intercalations and quartz geodes. The Rus Formation is conformably overlain by the Dammam Formation of Early to Middle Eocene age. The Dammam Formation is divided in Bahrain into four members (Fig.2); from older to younger: 1) Shark Tooth Shale Member, 2) Khobar Member, 3) Orange Marl Member and 4) Alat Member. The name “Shark Tooth Shale (STS)” was derived from the lowest clay-shale beds of the Dammam Formation where fossil shark teeth are abundant (Willis, 1967). The STS member generally ranges in thickness from 8 to 15 m in Bahrain, but the thickness decreases to 2 m only northwards at Fasht Al Jarim area. It is conformably overlying the chalky beds of the Rus Formation.

The STS member consists of gray to yellow shale and marl with thin beds of argillaceous dolomite and dolomitic limestone that are often pyretic. The STS Member is overlain by the Khobar Member that is about 30 m thick massive hard very porous dolomite overlying porous light colored, finely crystalline dolomitized limestone with bands of nodular chert and Nummulites in the basal part. The STS is assumed to equate with the Midra Shale Member at the base of the type Dammam Formation, the Midra and Saila Shale in Dammam Dom, KSA (Tleel, 1973; Alsharhan and Nairn, 1995) and Qatar (Sugden and Standring, 1975; Doornkamp *et al.*, 1980; Boukhary and Alsharhan, 1998).

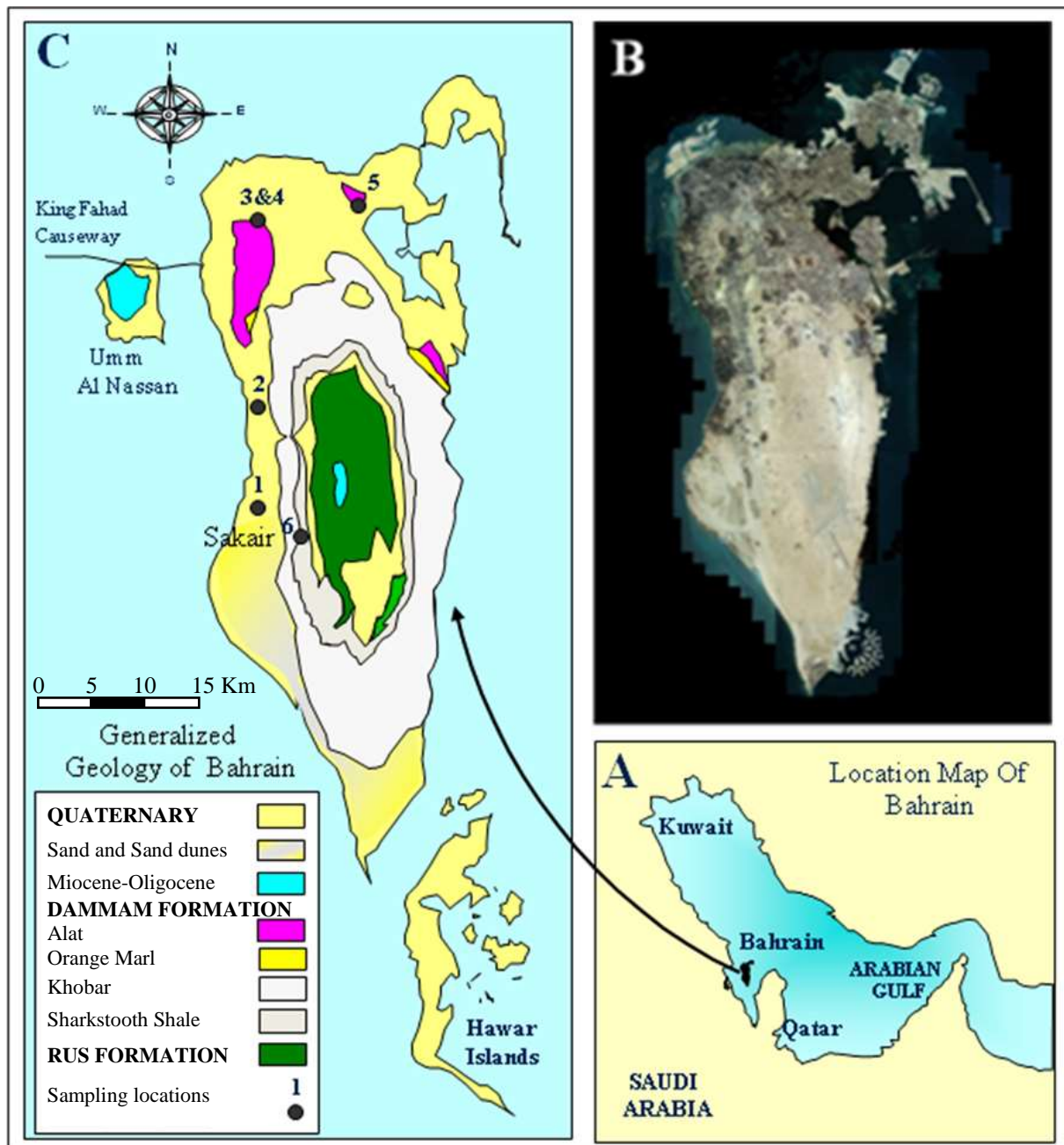


Fig.1: A) Location map of Bahrain; B) Satellite Image of Bahrain Island; C) Generalized geology of Bahrain, (after Doornkamp *et al.*, 1980) showing sampling locations.

1 – 5 boreholes, 1: BS 11 U; 2: BP O3 R; 3: BP O5 K; 4: BT O4 U; and 5: BS O9 U.,
6: Sakair Outcrop section

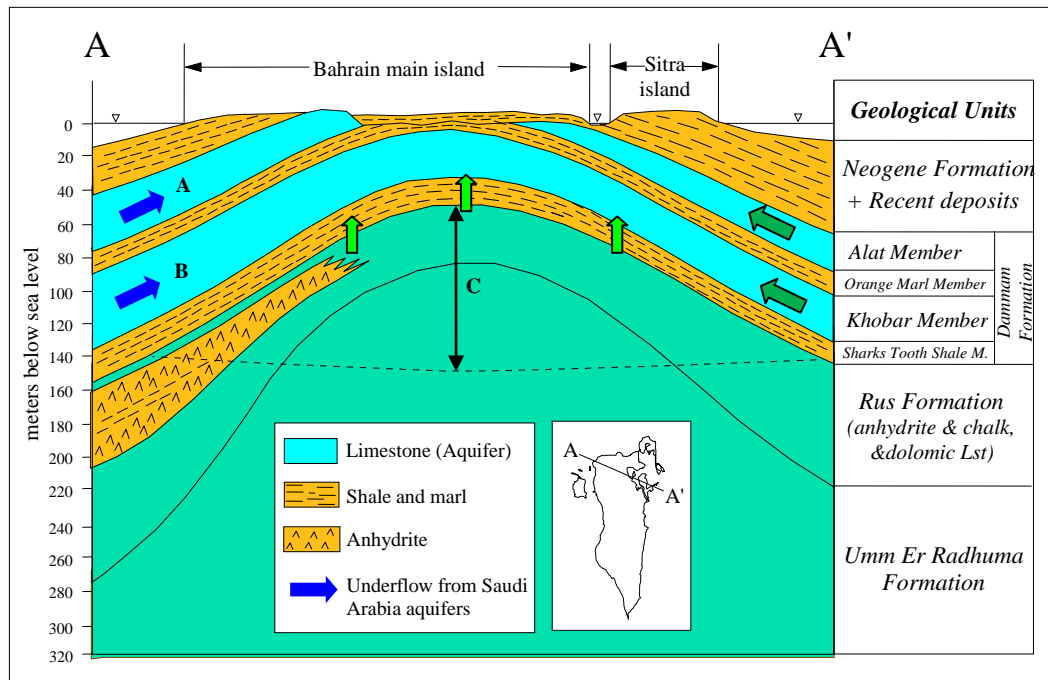


Fig.2: A sketch section of Bahrain Dome, showing the main geological units (after Zubari, 2005)

METHODOLOGY

Rock samples were collected from the Groundwater Development Consultant (GDC, 1979) through cores of 5 boreholes previously drilled for hydrogeological purposes. The sampling was carried out to include the STS member as well as the overlying and underlying units (Fig.3). Additional samples were collected from outcrops in Sakair area at Jebel Ad Dukhan near Well No.1 (Fig.3). The total number of samples was about one hundred. The samples were studied in thin sections for petrographic characterization and some of them for paleontologic purposes. The mineralogy of the samples was further investigated by X-ray diffractometry with special emphasis on the phosphates and clay minerals. Selected samples were chemically analyzed for major and trace elements using X-ray fluorescence spectrometry and wet chemical methods. Moreover, two types of phosphate grains were concentrated by hand picking and purified, using Silverman *et al.* (1952) method for chemical analysis.

LITHOLOGY OF THE STS

The STS succession appears in outcrops as alternations of relatively thick and friable ocher, green and yellow phosphatic fissile “shale”, and relatively thin and tough lime mudstone, usually bioturbated (borings) at top. The phosphate constituents are usually more concentrated at the base of the “shale” beds. This pattern (phosphorite-shale-marl-hardground) forms a cycle which is repeated several times in the STS (Fig.4). The core samples of STS are composed of marl and fissile shale layers. It is generally unfossiliferous, but considered to be of Middle Lutetian age on the basis of its stratigraphic position, being between two zones of Middle Lutetian age.



Fig.3a: The STS member outcrop in Sakair Area, Bahrain Island

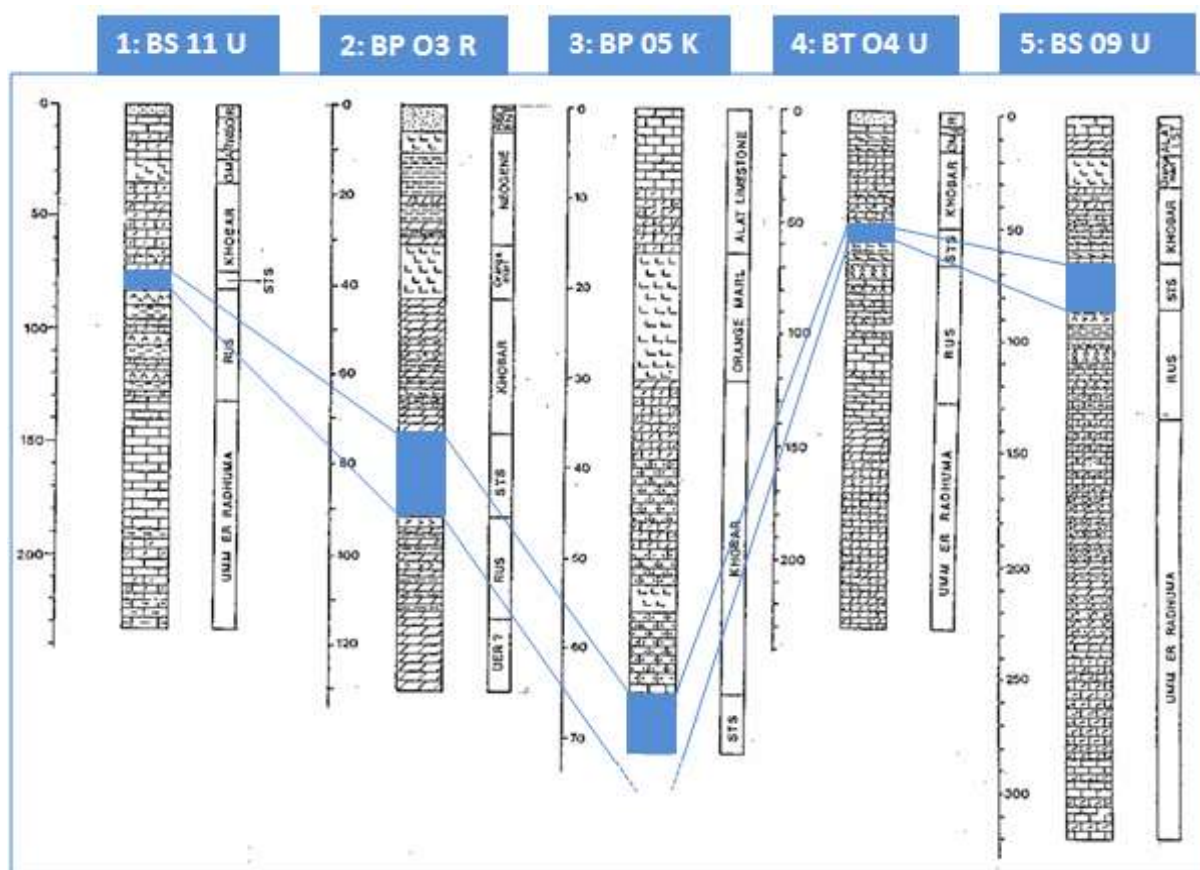


Fig.3b: The sampling boreholes for the STS Member in Bahrain

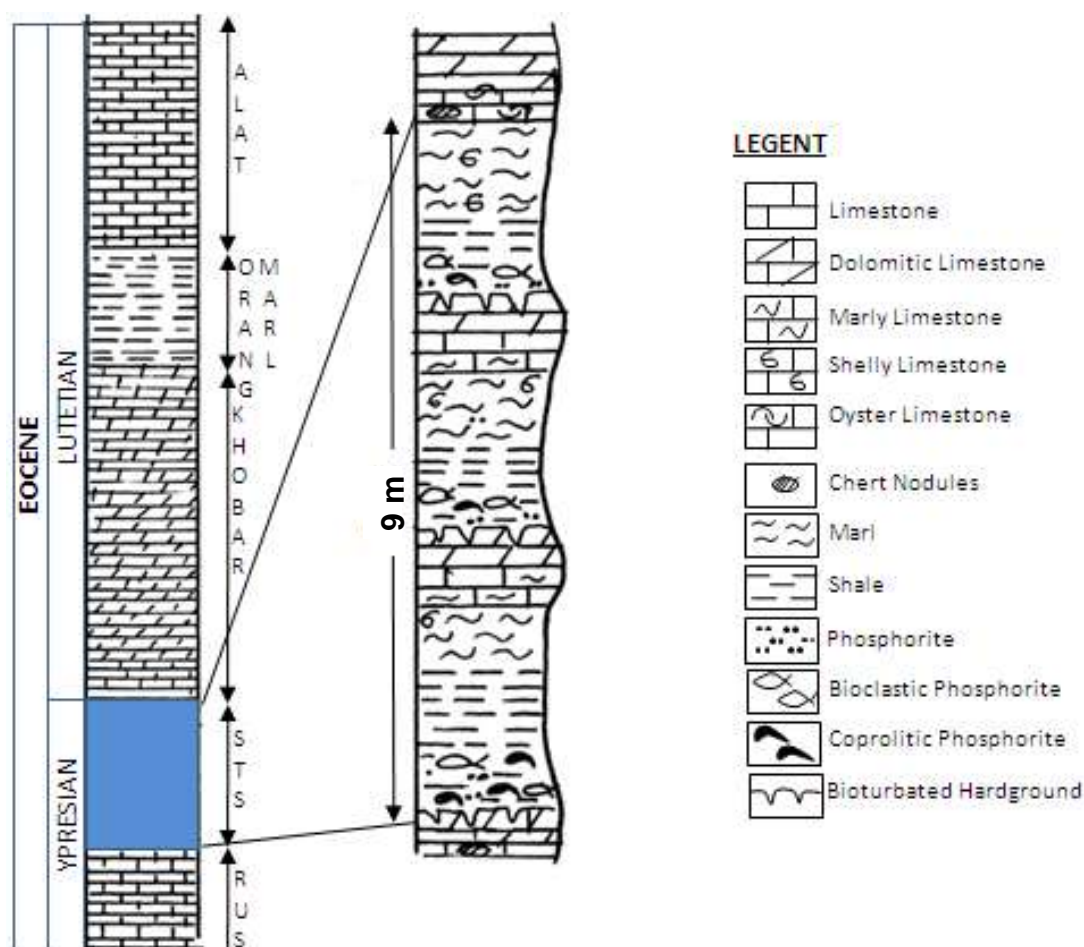


Fig.4: Lithostratigraphic Column of the Eocene succession in Bahrain, showing a composite section of STS Member

PETROGRAPHY AND MINERALOGY

Most of the carbonates in the STS-Bahrain are composed of fine crystalline dolomite (Fig.5). The original material is occasionally preserved as relics of micrite. Secondary sparry calcite is often found filling some vugs or cracks. The thinly laminated “shale” is highly dolomitic or calcareous. Silt-size quartz and phosphate grains, mainly bioclasts (bone scales, shark teeth and coprolites) with some peloids and intraclasts are common accessory components. The phosphatic bioclasts are composed of fragmented shark teeth and fish bones (Figs.5 and 6). The carbonate content may exceed 50% in some samples, where fine crystalline calcite (micrite) and dolomite (dolomicrite) are dominant. The clay minerals occur in the matrix as brown or green fine earthy material. Glauconite grains (green) are occasionally found in some samples of the “Shale” bed. The phosphate components appear isotropic in cross nicols, except bones. The fish bones are light brown to colourless and transparent under the microscope. Coprolites and phosphate peloids contain organic impurities and Fe-oxyhydroxide residues. Phosphatic grains are generally anisotropic except some bone fragments that show lamellar twinning and extinction parallel to the long axis.

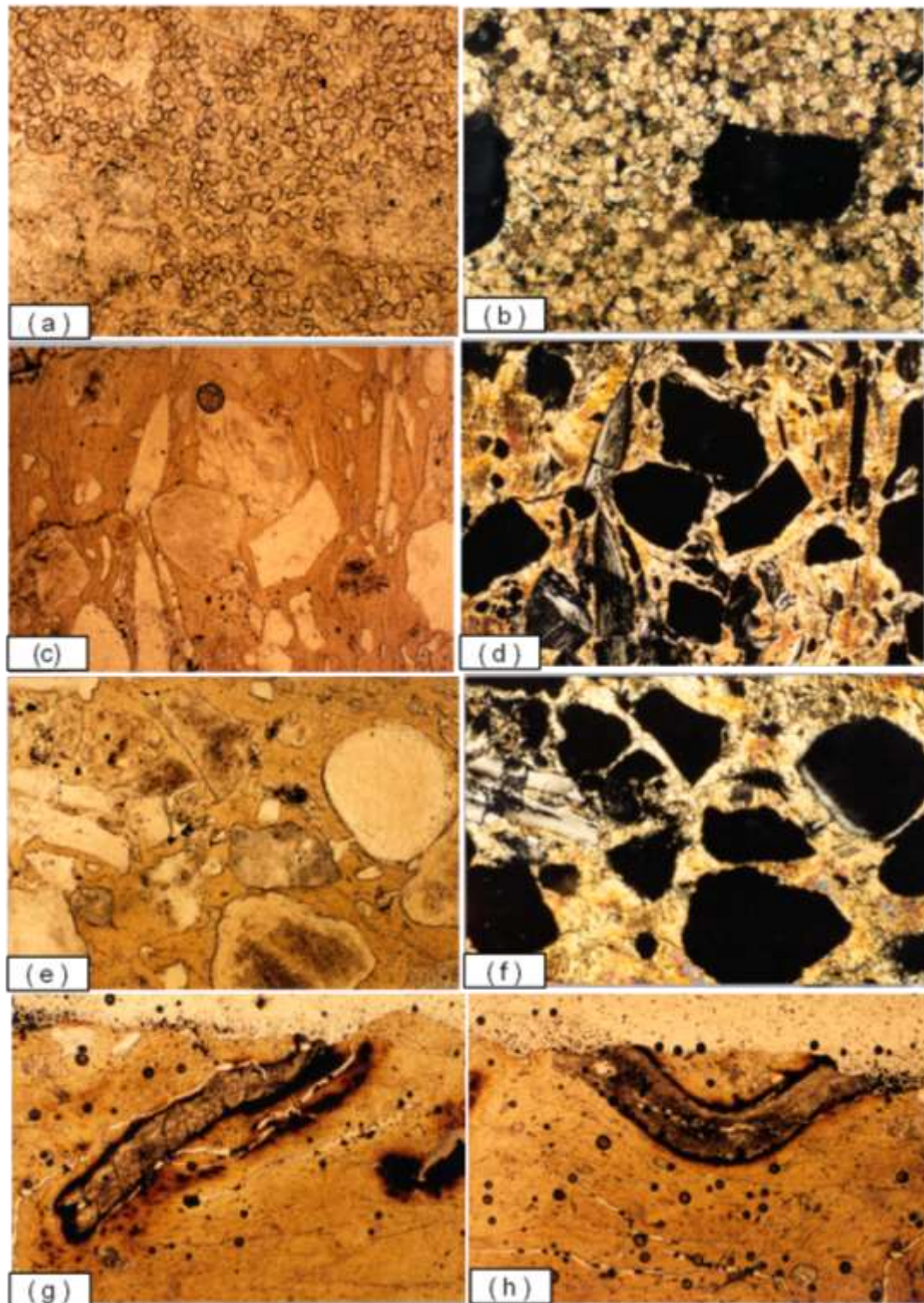


Fig.5: Set of thin sections from STS Member, left under polarized light and right under X nichols. **a** and **b**) Phosphatic Grains (peloids) in a dolomitic micrite 1 cm = 1 mm; **c** and **d**) Phosphate lithoclasts and bioclasts 1 cm = 0.5 mm; **e** and **f**) Coprolites showing high organic matter contents 1 cm = 0.5 mm; **g** and **h**) boring in shale with iron oxyhydroxides 1 cm = 1mm

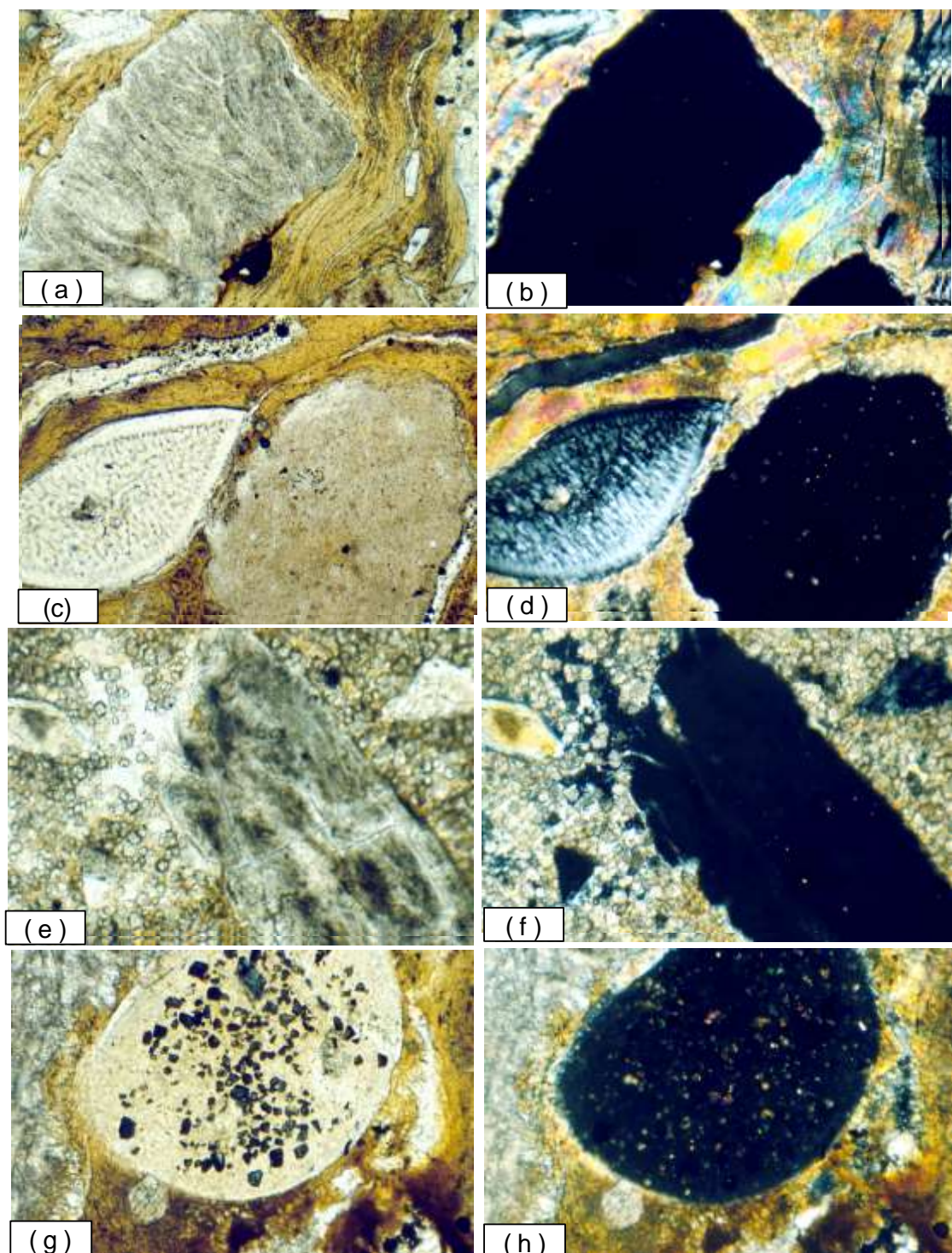


Fig.6: Set of thin sections from STS Member, left under polarized light and right under X Nichols. **a** and **b**) Coprolite, 1 cm = 0.5 mm; **c** and **d**) Bioclasts (fish bones) and coprolites 1 cm = 0.5 mm; **e** and **f**) Phosphate lithoclast 1 cm = 0.25 mm; **g** and **h**) Peloid with glauconite inclusions 1 cm = 0.25

The X-ray diffraction scans of bulk STS samples show calcite, dolomite, apatite, palygorskite, quartz and gypsum in varying proportions (Fig.7a). The separated phosphate grains (coprolites and bone fragments) show carbonate fluorapatite $[\text{Ca}_5(\text{PO}_4)_3\text{F}]$ only (Fig.7b). The separated clay fractions from STS samples show only palygorskite (Fig.7c).

An approximate estimation of the mineral proportions in the studied samples of STS was made on the basis of thin section study, XRD, and chemical analysis. It shows that the carbonates (calcite and dolomite) vary from 15% in the phosphate- rich samples to 78% in the carbonate- rich samples, the dolomite being dominant. The palygorskite content ranges from 5% to 45%; the clay rich samples ($> 40\%$ palygorskite) are deficient in phosphate ($< 3\%$ apatite). Quartz content is not related to the variation in the phosphate content and ranges from 4% to 23%. Less quartz is found in the carbonate-rich samples. The apatite content ranges from 3% to 43% being highest in the carbonate-poor samples.

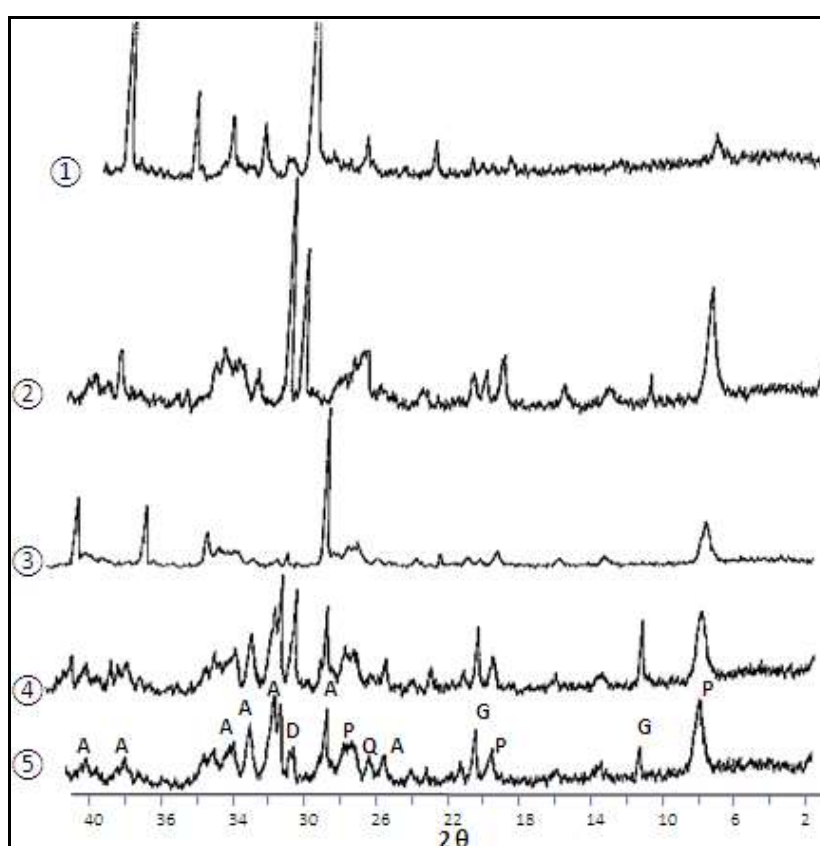


Fig.7a: X-ray diffractometric (XRD) diagrams of whole samples from STS Member;
A: Apatite; G: Gypsum; D: Dolomite; P: Palygorskite; Q: Quartz

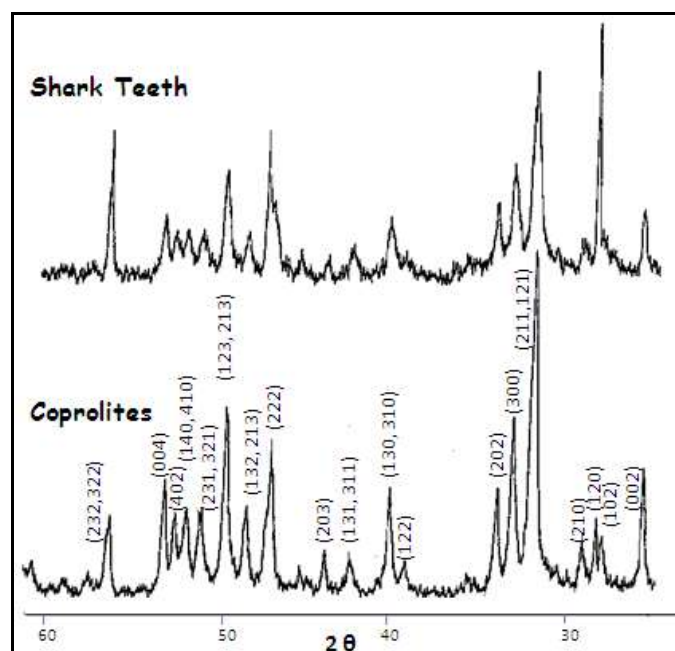


Fig.7b: X-ray diffractometric diagrams of concentrated phosphatic grains from STS Member

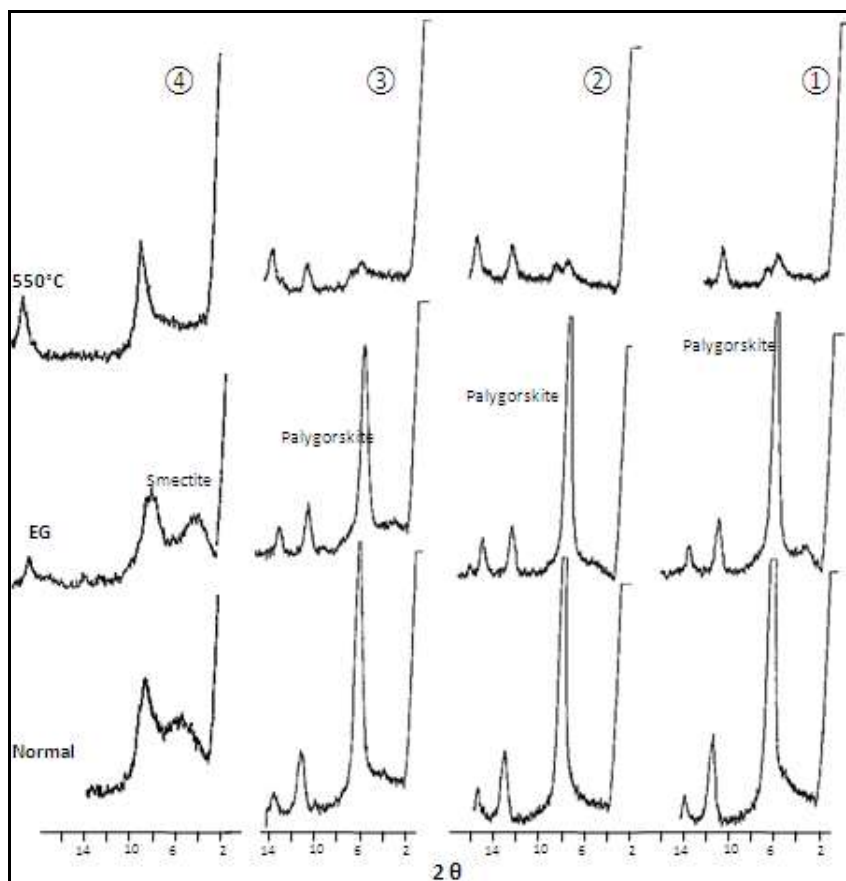


Fig.7c: X-ray diffractometric diagrams of clay minerals in the STS member;
 Normal: un-treated samples; EG: treated for 24 hrs with Ethylene Glycol;
 and heated up to 550 °C for two hrs

GEOCHEMISTRY

The impact of the variable mineral constituents of the STS is shown in the chemical composition of the bulk samples. All the analyzed samples are phosphatic in various degrees (P_2O_5 ranges from 1.0% to 13.5%) (Table 1). Alumina and part of magnesia are related to palygorskite. The remaining MgO is related to dolomite. Calcium is shared between apatite and the carbonate minerals (calcite and dolomite). Iron is related to palygorskite, Fe-oxyhydroxides and glauconite. Silica is shared between palygorskite and quartz. Sodium and chloride are present as halite, with some Na^+ in apatite and in palygorskite (as exchangeable cation). Potassium is mostly present in palygorskite. The sulfate is shared between apatite and gypsum. It forms coupled substitution with Na^+ in carbonate fluorapatite. The fluoride is assigned totally to apatite (McConnell, 1973; McArthur, 1985; Jarvis *et al.*, 1994; Abed, 2013).

The chemical analysis of concentrated phosphate coprolites and bones show 34 – 35.5% P_2O_5 , Na_2O and SO_3 contents about 1% each and F about 3.7% with loss on ignition (L.O.I) of about 7%, which accounts for CO_2 and H_2O^+ . Minor differences occur between the two types of apatite grains; the biological apatite has suffered slightly less substitutions of phosphate by sulfate and of calcium by sodium, and it contains higher fluoride (McConnell, 1973; Baturin, 1982; Soudry and Nathan, 2001).

The trace elements analysis show uranium increase as the P_2O_5 content increases, indicating the affinity of U for sedimentary marine apatite (Slansky, 1986; Al-Bassam *et al.*, 2010). The coprolitic apatite is richer in U than the biological apatite (bones). The former is also richer in Cr, probably related to the black organic residues in the coprolites which reflect burial conditions with intensive organic matter recycling (Kocsis *et al.*, 2014). Strontium, on the other hand, is relatively richer in the biological apatite; Sr is a common substitute of Ca in marine apatite (Altschuler, 1980; Prevot and Lucas, 1980; Kolodny, 1981, Jarvis, *et al.*, 1994).

Table 1: Chemical composition of some STS samples (majors in wt%, traces in ppm)

| Element | Shark Teeth Shale Samples | | | | | | | Concentrated phosphate grains | |
|---------------|---------------------------|--------------|--------------|--------------|--------------|--------------|--------------|-------------------------------|----------------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | Coprolites | Bones |
| P_2O_5 | 1 | 1.5 | 2.75 | 3.35 | 3.5 | 5 | 13.5 | 34 | 35 |
| Al_2O_3 | 5.29 | 1.94 | 1.3 | 0.623 | 2.55 | 3.02 | 2.17 | 0.377 | 0.377 |
| SiO_2 | 36.78 | 25.14 | 9.98 | 8.62 | 22.6 | 29.32 | 30.86 | 0 | 0 |
| CaO | 18.78 | 28 | 28.04 | 28.6 | 18.5 | 27.61 | 25.2 | 52.73 | 52.43 |
| MgO | 7.40 | 4.1 | 18.5 | 16.9 | 16.8 | 5.1 | 4.6 | 0.341 | 0.427 |
| Fe_2O_3 | 2.42 | 1.7 | 0.7 | 0.408 | 1.55 | 2 | 1.02 | 0.07 | 0.27 |
| Na_2O | 3.30 | 3.2 | 0.26 | 0.72 | 1 | 2.1 | 3 | 1 | 0.91 |
| K_2O | 0.60 | 0.53 | 0.07 | 0.1 | 0.28 | 0.29 | 0.52 | 0.08 | 0.05 |
| SO_3 | <0.35 | <0.35 | <0.35 | 0.4 | <0.35 | 0.65 | 1.25 | 1 | 0.75 |
| F | 0.148 | 1.44 | 0.48 | 0.52 | 1.44 | 0.64 | 1.68 | 3.68 | 3.75 |
| Cl | 2.94 | 3.37 | 0.187 | 0.97 | 3.37 | 1.665 | 2.34 | 0.068 | 0.083 |
| L.O.I. | 22.57 | 29.51 | 37.87 | 38.57 | 29.51 | 22.97 | 12.08 | 7.16 | 6.59 |
| | 101.2 | 100.4 | 100.1 | 99.78 | 101.1 | 100.4 | 98.22 | 100.506 | 100.637 |
| Cr | 64 | 32 | 24 | 24 | 32 | 18 | 140 | 36 | 11 |
| U | 1.45 | 2.3 | 6.45 | 5.72 | 2.3 | 8.55 | 50.63 | 153 | 74 |
| Sr | Not analyzed | | | | | | | 1599 | 1780 |

DISCUSSION

The Bahrain phosphate deposits are of marine sedimentary origin, of Early to Middle Eocene age and form part of the circum global E – W phosphate belt formed during the Late Cretaceous – Early Eocene along the southern edges of the Tethys Ocean and extents from Senegal in the West to Iraq and Turkey in the East (Sheldon, 1980; Al-Hashimi and Al-Bassam, 2006; Al-Bassam *et al.*, 2010; Abed, 2013).

The Bahrain area is located near the eastern edge of the Arabian Shelf. The major basin of deposition during Eocene time appears to have been N – NW of Bahrain; in the Burgan-Safanya area (Powers *et al.*, 1966; Willis, 1967). The sedimentation during Early Eocene was typical of a gentle shelf (ramp), where individual units extended for great distances laterally (Alsharhan and Nairn, 1995). The Rus Formation was deposited in a time of relative sea level fall within a semi-restricted (lagoonal) marine environment. Evaporates and carbonates were deposited in an intrashelf basin; the evaporates were deposited when the circulation with the main sea-body was cut off, whereas the carbonates indicate frequent contact with the sea. The Rus Formation represents a Low stand System Tract (LST) in sequence stratigraphy terminology (Brookfield *et al.*, 2009).

The Middle Eocene witnessed a regional transgression that was felt in other parts of Arabia (Alsharhan and Nairn, 1995; Al-Saad, 2005). Consequently, the lagoonal evaporitic character of the Early Eocene Rus Formation changed abruptly in the Middle Eocene to a more open-sea sedimentation with phosphates, shale and carbonates deposition forming the STS succession which represent the transgressive systems tract (TST) in sequence stratigraphy terminology whereas the phosphogenic episodes coincide with the beginning of each sequence and correspond to transgressive-regressive events, as the deposition of the STS was cyclic; started with a fast transgression when the phosphate-rich facies were laid down in an intertidal shallow marine environment, followed, as the transgressive phase continued, by a high sea-level stand, where the shale-rich facies were deposited under calm subtidal anoxic conditions. The presence of glauconite and phosphates in association with the shale may indicate a Highstand System Tract and a condensed section at this stage (Riggs, 1980; Udgata, 2007; Mete and Baki, 2009). As the transgressive phase diminished gradually, due to increased sedimentation rate over subsidence rate, limemudstone was deposited in a mud flat tidal environment, where penecontemporaneous dolomitization occurred. The shallowing of the sea continued to a stage when these carbonates were emerged, partly lithified and bioturbated forming hardgrounds (Tapanila *et al.*, 2004; Tarawneh and Moumani, 2006). The bioturbated – laminated cycles may had formed by slow sedimentation alternating with non-bioturbated, mainly laminated beds suggesting low rate of deposition (Damholt and Surlyk, 2004).

This cycle was repeated in a similar manner, several times in the STS, which may suggest local tectonic control on the sea-level fluctuations (Al-Saad, 2005). Locally, the submerged flanks of the Bahrain Anticline seem to have served as a structural platform for the deposition of the STS. The vertical stacking of the various facies and the cyclicity of the succession might have been the signature of tectonic uplift pulses related to this structural swell. The Bahrain Anticline and some other broad swells in the area began rising in the Late Jurassic or Early Cretaceous (Brown and Coleman, 1972; Perotti *et al.*, 2011).

However, the Lutetian transgression is of regional character and the phosphate showings of the STS are correlatable, as a phosphogenic event, with other deposits of Lutetian age in Saudi Arabia (Riddler *et al.*, 1989), Jordon (Tarawneh and Moumani, 2006), Iraq (Al-Bassam,

1992; Abahussain *et al.*, 2010) and probably some other deposits in North Africa (Al-Bassam *et al.*, 2010; Abed, 2013; Kocsis *et al.*, 2014). These deposits mark the last of the Tethyan phosphogenic sequence of events in the region, which lasted from Campanian to Lutetian.

CONCLUSIONS

The Middle Lutetian phosphorite occurrence in Shark Tooth Shale Member are mainly bioclastic in texture with dolomitic marly limestone. They were deposited in the early stages of a transgressive cycle, in an open shelf environment. The mineralogy and chemical composition show that carbonate fluorapatite is the only phosphate mineral in the STS Member. Uranium and Sr, are related to apatite. The Early Lutetian phosphorite of STS can be compared, as a well dated phosphogenic cycle, with other phosphorites of the same age in many East Mediterranean and North African countries. These phosphorites represent the concluding episode of the Tethyan phosphogenic event in Bahrain and the region.

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