Microbial pathways and palaeoenvironmental conditions involved in the formation of phosphorite grains, Safaga District, Egypt

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Phosphorite grains of the shallow marine phosphorite deposits of Egypt are classified as either phosphatic bioclasts preserving biological structure (e.g. skeletal fragments such as fish bones and teeth) or phosphatic peloids and intraclasts. This study describes the destructive and constructive microbial pathways represented by bioerosion of bones by endolithic cyanobacteria and accretion of phosphoritic peloids by bacteria. The palaeoenvironmental conditions and post-depositional/diagenetic history of these grains have also been considered. Scanning and transmission electron microscopy showed that the phosphatic peloids under transmitted light microscopy are composed mainly of microspheres (0.5 to 2.5 μm) similar in shape and size to coccolid-like bacteria. Chemical mapping showed that these microspheres are composed of carbonate-fluorapatite (CFA) and surrounded by degraded carbonaceous matrix. These grains are suggested to be reworked from pre-existing microbial mats during transgressive-regressive cycles affecting the southern Tethyan Campanian–Maastrichtian shallow continental shelf. The bioerosion of phosphatic bones is characterized by a network of meandering microborings that penetrated inward from the bone surface by endolithic cyanobacteria. The bioerosion of bones resulted in a gradual centripetal digestion and conversion of bones into micritic phosphate peloids. The bioerosion mechanism is probably started in the acidic sheath surrounding cyanobacteria followed by supersaturation of PO₄ and reprecipitation of crystalline CFA as electron dense remineralized rims. Electron microprobe microanalyses showed that the remineralized microbored areas are higher in CaO, P₂O₅, and F and depleted in Cl, relative to unaltered bones. A gradual demineralization of remineralized rims followed by dissolution of cyanobacterial cells is probably occurred during diagenesis and meteoric water alteration leaving behind empty microborings. Bone exposed to meteoric water alteration is lower in CaO and P₂O₅ and higher in F and Cl than the unaltered bones. Understanding bone bioerosion has significant implications for palaeoenvironmental and taphonomic reconstruction, archaeological applications and a regional correlation of the late Cretaceous to Palaeogene phosphogenic province extending from Middle East to North Africa.
Neoproterozoic microfossils of the Ediacaran Doushantuo phosphate formation in southern China (Xiao et al., 1998). These purported fossilized microorganisms were interpreted as animal embryos (Chen et al., 2000), sulphur bacteria (Bailey et al., 2007), encysting protists (Huldtgren et al., 2011) and cyanobacteria (She et al., 2013). Fossilized microstructural microstructures in ancient phosphorites have been interpreted based on comparison of their morphological features with modern, microscopical (cocci), rod-shaped (bacilli), or filamentous microbes (e.g. O'Brien et al., 1981; Bréhéret, 1991; Soudry, 1992, 2000; Lamboy, 1994; Alvaro and Claussen, 2010; Cosmidis et al., 2013). In the modern environments, bacteria are intimately involved in the biogeochemical cycling of phosphorus (e.g. Schulz and Schulz, 2005; Goldhammer et al., 2010). In all of these studies it has been assumed that microbes are involved in the precipitation of phosphate minerals and accretion of phosphatic grains. Although a biogenic origin of the microbial structures in many phosphorite grains has been documented, a debate around their origin has been recently raised (Baturin and Titov, 2006). The latter authors have suggested the abiotic origin of globular and elongated grains phosphorites from the Namibian shelf. Moreover, hollow apatite microspheres have been produced in the lab with no microbial involvement (e.g. Perez et al., 2011; Li et al., 2014). The produced apatite microspheres are composed of porous, flower-like structures. These microstructures consist of elongated apatite crystallites that grew from the centre toward the external surface of the microspheres.

In addition to the constructive role of microbes in the precipitation of phosphate minerals and accretion of phosphatic coprolites (e.g. Cosmidis et al., 2013), bioerosion is another important microbial pathway for degradation of phosphatic bones and bioclasts. Bone microboring organisms include fungi (Soudry, 2000), bacteria (e.g. Pesquero et al., 2010), and in marine environments, endolithic cyanobacteria (e.g. Davis, 1997). Bioerosion is a significant microbial alteration pathway that destroys archaeological (Trueman et al., 2003) and palaeontological bones (Pesquero et al., 2010). Understanding bioerosion of bones and identification of the microbore have significant implications for taphonomic and palaeoenvironmental reconstruction (e.g. Trueman et al., 2003; Pesquero et al., 2010) and archaeological applications (Ascaso et al., 2002).

In this work, we examined the micro- and nano-structures and mineral chemistry of phosphatic pebbles and bones collected from a suite of Upper Cretaceous (Campanian) granular phosphorites, the Quseir–Safea area, Red Sea region, Egypt. Application of field emission scanning and transmission electron microscopy (SEM and TEM), scanning transmission X-ray microscopy (STXM) and electron probe micro-analyses (EPMA) provides high resolution images and complementary information on the nanostructures, and mineralogical and chemical compositions of the phosphatic grains. Our data shed light on the depositional/post-depositional (microbial) and diagenetic processes involved in the accretion and biochemical dissolution of phosphatic grains. The current work also focuses on the crucial role of endolithic cyanobacteria in bioerosion of phosphatic bones and coccoid-like bacteriomorphs in the formation of phosphatic pebbles. This, in turn, led to propose mechanisms for biochemical dissolution of bones during bioerosion and accretion of phosphatic pebbles during deposition and diageneese. These mechanisms might be applicable to other marine phosphorites and can be used in regional correlation of the late Cretaceous to Palaeogene phosphogenic province extending from Middle East to North Africa.

2. Geologic setting

The Upper Cretaceous–Lower Tertiary sedimentary succession represents the main sedimentary sequence in the Quseir–Safea area, Red Sea region. This succession was generally deposited in a faulted basin before the Red Sea rifting (e.g. Akkad and Dardir, 1966; Khalil and McClay, 2002). The succession was studied and sampled in the Wassief area, 25 km southwest of Safaga Harbor, Red Sea area, between latitudes 26°25' and 26°32'N, and longitudes 33°48' and 33°56'E (Fig. 1). The pre-rift succession shows a general deepening trend in the NE direction as a result of Campanian to Maastrichtian transgressions in North Africa (Baioumy and Tada, 2005). The initial stage of these Late Cretaceous marine transgressions is represented by the deposition of the Duwi Formation which hosts the main economic phosphate deposits in Egypt. These deposits attain up to 75 m thick and extending as a belt from Red Sea to the Western Desert in the middle latitudes of Egypt. This phosphatic belt is a part of a giant Late Cretaceous–Early Tertiary phosphate belt spreading in the Middle East and North Africa (Said, 1990). It has been extensively investigated due to the economic importance of phosphorites as fertilizers (El-Kammar and Basta, 1983; Glenn and Arthur, 1990). Phosphorus is the crucial constituent which characterizes the grade of the ore. The P₂O₅ content ranges from 14 to 32% for the Egyptian phosphorites. The mean P₂O₅ contents of the Red Sea, Abu Tartur and Nile Valley regions are estimated to be 23.03%, 24.96% and 23.42%, respectively (Germann et al., 1984). The economic importance of the Duwi Formation is not only represented by the occurrence of phosphate beds, but also by the occurrence of black shale, as they are excellent source rock for oil (El-Kammar, 1993).

The stratigraphy of the Upper Cretaceous–Lower Tertiary sedimentary succession in Wassief area consists, from the base, of the Campanian Quseir Formation, Campanian–Maastrichtian Duwi Formation, Early to Middle Palaeocene Dakhla Formation, Late Palaeocene Esna Formation, and Early Eocene Thebes Formation (Fig. 2). At the northern and southern parts of Wassief area, this stratigraphic succession is overlain by the non-fossiliferous Nubia Sandstones, which is the oldest sedimentary rock unit that unconformably overlies the Precambrian basement rocks. The thickness of this unit varies from 61 m to 99 m at the northern and southern part of Wassief area, respectively.

The Quseir Formation consists of fluvial shales of variable colours with and sandstone intercalations. It conformably overlies the Nubia Sandstone Formation with gradational contact and underlies the Duwi Formation (e.g. Said, 1990). This formation is non-fossiliferous, with the exception of the presence of few plant remains, fossil wood, bone fragments, and fish teeth. In the present study, the upper part of Quseir Formation is dominated by mudstones of different shades, while the lower part is dominated by multicoloured shales with disseminated pyrite crystals, hematite, and glauconite pellets.

The Duwi Formation conformably overlies the Quseir Formation and underlies the Dakhla Formation (e.g. Akkad and Dardir, 1966; Said, 1990). Although, Baioumy and Tada (2005) reported that the Duwi Formation unconformably overlies the Quseir Formation and conformally underlies the Dakhla Formation. In general, the Duwi Formation consists of three phosphate beds which are intercalated with shale, clay, chert, and limestone (e.g. Said, 1990).

The Duwi Formation is composed of coarse-grained phosphorites and phosphatic sandstone that alternate with shale, siliciclastic sandstone, siltstone, chert, porcelanite, marl and calcarenite (Baioumy and Tada, 2005). Baioumy and Tada (2005) subdivided the Duwi Formation into four lithostratigraphic members based on lithology and the occurrence of ravinement and subaerial erosional surfaces. The phosphate beds occur in the lower member in the Abu-Tartur area, Western Desert and in the uppermost member in the Nile Valley and Red Sea areas.

In the current study, the Dakhla Formation is composed of two horizons of black to dark grey, fossiliferous, calcareous shale with disseminated pyrite crystals. These two shale horizons are separated by black fossiliferous (little forams) marls. The contact between the Esna and Dakhla formations is unconformable and abrupt due to the absence of the Late Palaeocene Tarawan (Chalk) Formation. The Esna Formation comprises, from the base, dark grey to black, highly fossiliferous calcareous shale with scattered pyrite crystals and pyrite micro-veins as well as few glauconitic and phosphatic grains. This changes upward into greenish grey, bioturbated, fossiliferous marls and calcareous shale (with Pecten sp.) with occasional dissemination of pyrite. The Thebes Formation consists of fossiliferous limestone with some brown chert
bands and nodules. This limestone is changing downward into successive intercalations of greenish grey, fossiliferous, calcareous shale and argillaceous limestone.

3. Sampling and methods

The present study is based on samples collected from 230 m core drilled in the Wassief area, near Safaga, by the Egyptian Mineral Resources Authority (EMRA) and sponsored by DanaGas© Egypt in 2009. Two hundred and twenty samples covering the entire Upper Cretaceous–Lower Tertiary sedimentary succession were collected from the core. The outcropping sedimentary succession in the study area was also investigated (Morsy, 2013). This drill hole is cutting alluvial deposits downward through Thebes, Esna, Dakhla, Duwi, until Quseir formations, respectively.

Freshly broken surfaces and 25 polished thin sections were studied from the black phosphatic beds and phosphatic limestones of the Duwi Formation. Samples consisting of apatitic skeletal fragments and phosphatic peloids were coated with carbon and analyzed using a Zeiss Ultra Plus scanning electron microscope (SEM) with a field emission gun. The Zeiss SEM is coupled with a Brucker X-Flash EDX detector for elemental analysis. Backscattered SEM images were acquired with the microscope operating at an accelerating voltage of 20 kV, a beam current of 3 nA and a working distance of 6.5 mm. SEM observations were made in secondary electron mode for morphological investigations and in back-scattered electron mode for elemental maps. The SEM analyses were performed at CSIRO, Perth, Western Australia.

In addition to the detailed SEM studies, the site specific features were mapped and further investigated using the transmission electron microscope (TEM). The TEM specimens were prepared with a FEI xT Nova Nanolab 200 Dual beam Focused Ion Beam (FIB) and scanning electron microscope (SEM) at the Electron Microscope Unit, University of New South Wales, Australia. The mounted and polished samples were baked in an oven overnight at 60 °C to remove the moisture, and then sputter coated with 30 nm Au surface layer to eliminate charging effects. The region of interest for retrieving a thin-foil specimen was covered by a strip of 1 μm thick Pt deposition with the gas injection system in the FIB. This top layer is mainly used to prevent the beam damage during the ion beam milling. The beam damage on the side walls of the membranes during the fast rough cut in the initial stage were carefully managed by stepping down the ion beam current from 5 nA to 100 pA in the later processes. The completed specimens less than 100 nm thick were placed on a standard Cu grid with a strong carbon supporting film using an ex-situ lift-out method for further study in the TEM.

High Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM) imaging and element mapping were carried out using a FEI Titan G2 80–200 TEM/STEM with ChemiSTEM Technology operating at 200 kV. The elemental maps were obtained by energy dispersive X-ray spectroscopy using the Super-X detector on the Titan with a probe size ~1 nm and a probe current of ~0.9 nA. The TEM imaging and elemental maps were carried out at the Center for Microscopy, Characterization and Analysis (CMCA), University of Western Australia.

Carbon-coated polished thin sections were analyzed with a JEOL 8530F Electron microprobe at the Center for Microscopy, Characterization and Analysis (University of Western Australia). Operating conditions were 20 kV accelerating voltage and 10 nA emission current. Standardization was completed using specific reference minerals, including pyrite for S, jadeite for Na, orthoclase for K, corundum for Al, spessartite for Si and Mn, periclase for Mg, Cr₂O₃ for Cr, ZnO for Zn, vanadium metal for V, nickel metal for Ni, cobalt metal for Co, magnetite for Fe, sodalite for Cl, rutile for Ti, barite for Ba, and Durango apatite for Ca, P and F.

4. Results

4.1. Lithostratigraphy and textures of phosphatic grains

The Duwi Formation in the Wassief area consists, from the base, of black to light grey massive mudstone with few calcareous and siliceous micro-veins as well as disseminated pyrite. The mudstone is overlain by
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<th>Epoch</th>
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<th>Formation</th>
<th>Depth (m)</th>
<th>Rock Type</th>
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<tr>
<td>Early Eocene</td>
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<td>Thebes Fm</td>
<td>20</td>
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<td></td>
<td>Late</td>
<td>Esna Fm</td>
<td>40</td>
<td>Successive intercalations of light greenish gray fossiliferous weathered calcareous shale with whitish fossiliferous weathered argillaceous limestone</td>
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<td></td>
<td>60</td>
<td>Intermediate dark greenish gray fossiliferous marlstone</td>
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<td>80</td>
<td>Very dark gray to black highly fossiliferous slightly calcareous shale</td>
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<td>Dakha Fm</td>
<td>120</td>
<td>Black to dark gray fossiliferous slightly calcareous shale</td>
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<td></td>
<td>Early</td>
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<td>Danian</td>
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<td>Black fossiliferous phosphorite</td>
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<td>180</td>
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<td>Black to light gray massive mudstone</td>
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<td>Black fossiliferous phosphorite</td>
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<td>Multicolored silty mudstone</td>
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<td></td>
<td></td>
<td>Quseir Fm</td>
<td>220</td>
<td>Laminated brownish and greenish black hematitic and glauconitic silty to sandy shale</td>
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Fig. 2. Summary of the lithological description of the sedimentary succession of Wassief area, Safaga, Red Sea region (after Morsy, 2013).
grey, fossiliferous, pelletic phosphate rich in pyrite and organic matter. The pelletic phosphate bands change upward into black fossiliferous (forams and pyritized Pecten sp.) marls with few phosphatic grains, and disseminated pyrite crystals. The upper part of the Duwi Formation comprises of black, fossiliferous phosphatic limestone with pale blue spots, siliceous mottles and micro-veins, as well as disseminated pyrite crystals. The lower and upper boundaries of the Duwi Formation are marked by black fossiliferous phosphorites beds (Fig. 2). The total thickness of the Duwi Formation is approximately 60 m.

The three black phosphate beds of the Duwi Formation in the Wassief area are principally composed of phosphatic and non-phosphatic grains that are supported by laminated clay matrix and/or cement. Phosphate grains constitute approximately 60 to 90% of the rock by volume. These grains comprise fine- to medium-grained, sand-sized phosphatic peloids, gravel-sized intraclasts, fish bones and bioclasts, and are densely packed, moderately to poorly sorted and grain-supported, and embedded in microcrystalline to well-crystalline calcareous (calcite and dolomite) cement (Fig. 3). These grains might also form laminated granular phosphate facies. There are no coated grains or grains with internal concentric structures observed in the Wassief phosphorites. Phosphatic peloids are also common in the phosphatic limestones of the upper part of the Duwi Formation.

Mineralogically, the P in the Wassief phosphate deposits simply occurs as francolite (carbonate-fluorapatite; CFA) as analyzed by Raman spectroscopy (Ciobotă et al., 2014). In the upper sequence of the Wassief phosphorites, where phosphorites occur with dolomitic and phosphatic limestones and dolostones, dolomitization, followed by pyritization, of phosphatic peloids is observed. Non-phosphatic grains are mainly represented by detrital quartz grains, calcareous forams and glauconite peloids. Framboidal pyrite occurs as a cavity filling phase in the phosphate grains and calcareous forams. The phosphatic and non-phosphatic grains are cemented by calcite, dolomite, chaledony, iron oxy-hydroxides and pyrite.

4.2. Phosphatic peloids

The shape of phosphatic peloids ranges from angular to sub-rounded and low sphericity (Figs. 3, 4A, B). When viewed under transmitted plane polarized light, they are predominantly homogeneous and structureless; their diameter ranges from 400 μm to 1.2 cm, and varying in colour from white to brown (Fig. 3B). When viewed between crossed nicols, they appear isotropic (Fig. 3A, C). The proportion of the bone fragments relative to the gross phosphatic components ranges from 40 to 50%. The shark teeth are triangular in shape, ranging in size from 200 to 1000 μm. They are less common than the fish bone fragments.

Petrographic observations under high magnification clearly show that many phosphatic bones are microbiobially infested by microborings. The infested areas of bones lose their anisotropy and gradually become faint brown and isotropic (Fig. 3C, D). The extensive microbial infestation of the phosphatic bones results in destruction of the physiological microstructure and a gradual centripetal digestion of the bone materials and their conversion into phosphomicritized peloids (Figs. 3C, D, 7).

Under SEM, the microbrovers exhibit markedly different sizes, shapes and orientations. They range in size from 2 to 20 μm in width and few tens of micrometres in length depending on their orientation with respect to the surface (Fig. 7A, B). These microbrovers vary from highly irregular, densely-crowded, amoeboid-like to slightly curved, unbranched and elongated in shape (Fig. 6B). Some microbaviours are smooth and rounded in cross-section with almost equal dimensions. They are mostly perpendicular to the outer surfaces of the bones and may or may not extend toward the centre of the bones (Fig. 7B, C). These microborings do not usually follow any particular structure within the bone itself. In few cases, microborings are linear and developed within osteonal systems parallel to the osteonal canal of the bones. The complete conversion of the bone materials into micritic phosphate peloids obliterates the original histological structures, abrading and rounding bone grains (Fig. 7C, D). In few microbored grains euhedral to subhedral, single or clustered pyrite grains rarely occur as discontinuous laminae close to the surface, but commonly fill interstitial spaces (Fig. 7C). Microborders consist of sub-spherical to oval or polygonal cells of 2–10 μm in diameter (Fig. 8A, B). They are surrounded by their own, distinct remineralized rims (0.5–1 μm in width) of microcrystalline CFA (Fig. 8A, B). They do not exhibit dichotomous cell division and are grouped together by an external common remineralized rim (Fig. 8A, B). These remineralized rims are much brighter than the non-bored parts of the bone tissues which are invariably much darker in BSE images (Fig. 8A, B). TEM images show that there are also variations in grain size and texture of the CFA between the cells of microborders and their surrounding remineralized rims, which might explain the contrast variations (Fig. 8C). The remineralized rim consists of successive colloform layers of radially-oriented and elongated prismatic crystals of CFA (up to 600 nm). The cells of microborders consist of porous, nanocrystalline CFA (10–40 nm) that are separated from the external rims by a line of empty nanopores. These nanopores are also developed between each colloform layers (Fig. 8C, D).

In some cases, the structure of the remineralized rims is diagnostically altered and gradually dissolved (Fig. 8E, F) leaving phosphatic cyanobacterial cells in the microborders (Fig. 9A, B). These cells are...
cemented together by cavity filling calcite (Fig. 9C) or completely dissolved leaving a dense network of demineralized perforations that fitted together in a pattern resembling spongiform porosity (Fig. 9D). These empty microborings may or may not be filled by secondary CFA, calcite and/or framoidal pyrite (Fig. 9E, F).

In addition to the microbored phosphatic bones, the tissues of some bone debris have undergone a prior dissolution/reprecipitation event(s) visible as a change in texture of the bone (Fig. 10A–C). These chemical processes resulted in the formation of globular and colloform CFA which appears darker in tone under SEM than the microbored and unaltered areas in the bones (Fig. 10A–C). It may result in dissolution of the microbored areas (Fig. 10C).

4.4. Chemical composition of the phosphatic grains

Elemental mapping, using SEM/EDX, showed heterogeneous chemical variations between the unaltered bones and the microbially infested areas (Fig. 10D–F). The microbially infested areas in bones are richer in Ca and P and poorer in CI than the unaltered bones. Conversely, the colloform CFA of dissolved bones showed a slight increase in Cl relative to the unaltered and microbored bones (Fig. 10B). Detailed mapping performed by TEM/EDX across the boundary between the microborer cells and the surrounding remineralized rim did not reveal any chemical changes in P, Ca, C, O, F and CI associated with the variations in electron density (Fig. 11).

Chemical mapping performed by SEM/EDX showed homogeneous distributions of Ca, P, F and Cl in the phosphatic peloids and unaltered bones. Iron and S showed heterogeneous distributions and are concentrated in the cavity-filling pyrite inside these grains (Figs. 5B, 7C, 8B). However, detailed mapping performed by TEM/EDX revealed obvious chemical variations between the CFA that forms the bright microspheres and the surrounding dark, carbonaceous matrix (Fig. 12). The microspheres are rich in P, Ca and F; whereas the carbonaceous materials surrounding cell walls and matrix are rich in C and Cl (Fig. 12).

Average chemical compositions of CaO, P2O5, Cl, F, SO3, Na2O and MgO wt.% obtained by EPMA of the unaltered, microbored and dissolved bones as well as phosphatic peloids are presented in Fig. 13. The average chemical compositions of CaO and P2O5 in the microbored bones are ~49 wt.% and 32.5 wt.%, respectively. These values decrease in the dissolved bones (~46.5 wt.% and 28.5 wt.%, respectively) and the unaltered bones (~43.5 wt.% and 30.5 wt.%, respectively). The average compositions of CaO and P2O5 in phosphatic peloids are ~47.5 wt.% and 31 wt.%, respectively (Fig. 13).

Average chemical compositions of Cl and F vary strongly in the microbored and dissolved bones relative to the unaltered bones and phosphatic peloids (Fig. 13). On one hand, Cl is highly depleted in the microbored bones and enriched in the dissolved bones (~0.26 wt.% relative to the unaltered bones and phosphatic peloids (Fig. 12). On the other hand, F is enriched in the microbored and dissolved bones (>3.7 wt.% relative to the unaltered bones (~3 wt.%) and phosphatic peloids (~3.3 wt.%) (Fig. 13).

5. Discussion

5.1. Insights on the phosphorite origin

There are numerous models proposed for the origin of the granular phosphorites and their internal structures. These models are generally restricted to biogenic and abiogenic origins of the phosphorite grains,
particularly coprolites and peloids. These models include: (1) reworking of pristine (authigenic) phosphorite deposits that were originally precipitated as small peloids, concretions, crusts, and laminae just below the seafloor (e.g. Garrison and Kastner, 1990; Föllmi, 1996; Soudry et al., 2013); (2) in situ biogenic formation within fungal, algal and bacterial mats (e.g. Soudry and Champetier, 1983; Williams and Reimers, 1983; Dahanayake and Krumbein, 1985; Bréhéret, 1991; Nathan et al., 1993; Soudry, 2000); (3) abiogenic accretion of apatite on the surface of a nucleus forming ooidal structures (Swett and Crowder, 1982); (4) formation of phosphatic peloid through conversion of bone fragments (e.g. Soudry, 2000); (5) microbially-mediated accretionary growth (She et al., 2013).

The phosphatic grains of the Duwi Formation were suggested to be derived from pre-existing authigenic phosphorites that were formed under an upwelling area on the North African margin in southern Tethys during an Early Campanian highstand (e.g. Baioumy and Tada, 2005). These authigenic francolite grains were subsequently reworked, probably by storm, to a continental margin environment during transgressive–regressive cycles and deposited as lag deposits in a bioturbated, wave-dominated, near-shore environment creating the phosphorites (Baioumy and Tada, 2005). These phosphorite grains are probably formed during periods of stratigraphic condensation under multiple episodes of phosphogenesis similar to those described by Pufahl and Grimm (2003). Textural relationships, internal fabrics and the type of microbial activity involved in the formation of phosphatic peloids and bioclasts significantly provide information about the deposition of the authigenic phosphorites and their post-depositional reworking, mixing and diagenetic modification (Fig. 14). In the Wassief phosphorites, the subrounded to angular shapes, moderately to poorly sorted texture, grain-supported fabric, chaotic orientation and sometimes grains are aligned with their long axes parallel to laminations, the presence of bone fragments in phosphatic peloids and the absence of apatite cement all strongly supporting reworking of the phosphorite grains from a different depositional environment.

5.2. Microbial activity

The biological activity of microorganisms in the formation of the Wassief Phosphorites can be destructive in the bioerosion of bones and constructive in the accretion of phosphatic peloids.

5.2.1. Origin of phosphatic peloids

Microspherical, rod-shaped and filamentous fossil forms of CFA have been described previously in various phosphorite deposits of different localities and ages (e.g. Bréhéret, 1991; Soudry, 1992; Cosmidis et al., 2013; She et al., 2013; Hiatt et al., 2015). These forms have been interpreted by these authors as fossilized microbial cells, based mainly on morphological parameters such as size and shape and similarities with coccoid bacteria and cyanobacteria (e.g. O’Brien et al., 1981; Bréhéret, 1991; Soudry, 1992, 2000; Lamboy, 1994; Alvaro and Clausen, 2010; Cosmidis et al., 2013). However, some authors have argued that these biomorphic spheres found in recent phosphorites refer to mineral rather than to biogenic formations (e.g. Krajewski et al., 1994; Baturin and Titov, 2006). Krajewski et al. (1994) suggested that the “bacteria-like” shapes of apatite particles described by many
authors could be the result of rapid nucleation events in the pore water medium. Baturin and Titov (2006) suggested that these biomorphic spheres showed a broad size distribution, while bacteria of the same species have similar sizes. They also mentioned that these biomorphic spheres often mutually grew into each other; formed regular growths and may feature truncated forms, which is characteristic of minerals rather than of bacteria. Therefore, they look different at the micrometre scale compared with the microspheres of the Wassief phosphorites, which show a uniform and small size distribution (0.5–2.5 μm), central hollows and outer envelopes and a random pattern of nanocrystalline apatite growth. In addition to the microspheres, curved filamentous forms (0.2 μm in width and up to 10 μm in length) have been observed in SEM photomicrographs (Fig. 6A). Some peloids display hollow microspheres of smaller size (<1 μm) that intimately associated with rod-shaped bodies (0.5–2 μm in length and 0.1–0.5 μm in thickness) (Fig. 6C, D). These variable morphological and textural characteristics of the Wassief microspheres, rod-shaped and filamentous morphotypes suggest their bacterial origin of diverse microbial communities. Moreover, the presence of fragments of stromatolite-like fabrics strongly recommends the former presence of microbial mats in the pristine phosphorite facies. Buick (1990), Westall (1999) and Schopf et al. (2007) have developed criteria to establish the biogenicity of purported fossilized microorganisms. These criteria include: 1) occurrence in groups and colonies; 2) visible cell wall structures; 3) preservation in carbonaceous materials; 4) microstructures must have the size and shape of modern bacteria; 5) numerous and diverse taxa; 6) variable modes of preservation, which range from well preserved and passing through degraded to biologically nondescript (Schopf et al., 2007); and 7) observation in thin sections. Here, there is a common agreement with all the above-mentioned criteria of biogenicity of the Wassief microspheres, rod-shaped and filamentous morphotypes. The textural pattern observed in the microspheres composing Wassief phosphatic peloids can be compared with the coccoid-like bacteria described from the Triassic Bravaisberget Formation of Spitsbergen, which are characterized by central hollows and outer apatitic precipitates (Krajewski et al., 1994). These spheres were filled by CFA and embedded in a partially degraded, carbonaceous matrix as indicated by TEM (Fig. 12). The total organic carbon (TOC) content in the Duwi phosphorites is very high (average TOC is 3.84% and maximum value exceeds 7.5%) (Morsy, 2013). In addition to the high TOC, the presence of thinly laminated, stromatolite-like structures of some phosphatic peloids may indicate that these grains were derived, by reworking, from a microbial (bacterial) mat. In this regard, phosphatic peloids and their source are probably equivalent to the Late Cretaceous pristine phosphorites of Mishash Formation in Negev, Israel (Soudry, 1992, 2000). Soudry (2000) suggested that the preservation of original bacterial structures non-deformed indicates a rapid mineralization process, produced through direct phosphatization of the organic framework. These phosphorites are characterized by thin, microbial laminations, lack of bioturbation, high organic carbon contents, low P and high carbonate concentrations (Soudry et al., 2013). The presence of pyritized microspheres in the phosphatic peloids of the Wassief phosphorites suggests that they were formed under reducing (sulphidic) conditions. Baioumy (2011) suggested that the Egyptian phosphorites formed under reducing conditions based on negative Ce and Eu anomalies. Moreover, sulphur isotopic composition of the Upper Cretaceous phosphorites of Egypt has revealed that the formation of pristine (authigenic) phosphorites was in the zone of sulphate reduction (Baioumy, 2011). Goldhammer et al. (2010) showed that under both anoxic and oxic conditions, large sulphide-oxidizing bacteria accumulate 33P in their cells, and catalyze the conversion of phosphate to apatite that was greatest under anoxic conditions and exceeds the rate of phosphorus release during organic matter.
Fig. 6. A) A SEM/BSE image showing bacterial filaments (arrows) associated with the microspheres. B) A SEM/BSE image showing angular peloids with pyritized microspheres. C) A SEM/BSE image showing microspheres and microrods (0.1–1 μm in diameter) cemented by francolite cement. D) A close-up view in C.

Fig. 7. A) A SEM/BSE image showing a phosphatic bone fragment altered along its rim by endolithic cyanobacteria. B) A SEM/BSE image showing perpendicular cyanobacterial microboring. C) A SEM/BSE image showing the advanced stage of microbial infestation by endolithic cyanobacteria. Note the gradual rounding of the edges of the phosphatic bone fragments. D) A SEM/BSE image showing the ultimate stage of microbial infestation and conversion of the phosphatic bone into peloidal structure. Note the growth of pyrite in cavities left behind diagenetic degradation of organic matter.
mineralization in the upper sediment layers. The fossilized microspheres of the Wassief phosphorites are also similar in morphology to the Gram-negative bacteria described from coprolites of the Palaeocene phosphorites of the Ouled Abdoun, Morocco (Cosmidis et al., 2013) and the Miocene to Quaternary phosphorites formed under an upwelling region at the Peru Margin (Lamboy, 1994).

In the present study, the selective phosphatization of the coccoid-like bacteria probably started inside the cells, while the outer envelopes and the surrounding carbonaceous matrix are still unmineralized (Fig. 5B). This observation is not consistent with the initial precipitation of Ca-phosphate precursor phase in the periplasm and around the outer membrane of the Gram-negative bacteria described by Cosmidis et al. (2013). The latter authors suggested that initial precipitation of a Ca-phosphate precursor phase was followed by precipitation of larger francolite crystals inside the cytoplasm of the bacteria. In this regard, Cosmidis et al. (2013) adopted the passive role of bacteria, where the cell is serving as a template for the nucleation of calcium phosphates. Bacteria could play an active role in the Ca-phosphate precipitation probably through release of phosphorus by degradation of organic matter. This mechanism of phosphogenesis has been suggested for the formation of recent phosphorites (O’Brien et al., 1981; Soudry and Lewy, 1988; Schulz and Schulz, 2005).

In many Phanerzoic phosphorites, chemosynthetic bacteria indirectly promote phosphogenesis at or just below the seafloor in organic matter-rich sediments by creating chemical gradients in sediment (e.g. Williams and Reimers, 1983; Schulz et al., 1999; Schulz and Schulz, 2005; Goldhammer et al., 2010; Bailey et al., 2013; Hiatt et al., 2015). Bacterial breakdown of organic matter is an effective process in the sulphate reduction zone (e.g. Arning et al., 2009) and this leads to release of organic P into porewater and precipitation of francolite (Van Cappellen and Berner, 1991). The presence of filamentous microstructures associated with the microspheres of Wassief phosphorites can be interpreted as symbiotic sulphate-reducing bacteria similar to those described by Bailey et al. (2007). Abundant pyrite in cavities of the calcareous microsils are also suggestive of reducing (sulphidic) conditions. Phosphorus released near or at the sediment–water interface can diffuse into the overlying water column (e.g. Ruttenberg and Berner, 1993) or effectively trapped by sulphur-oxidizing bacteria (e.g. Beggiatoa, Thioploca and Thiomargarita) and Fe-oxyhydroxides in the sediment (Hiatt et al., 2015). In modern organic-rich marine sediments, sulphur-oxidizing bacteria oxidize H₂S generated by bacterial sulphate reduction (e.g. Schulz and Schulz, 2005). Slow burial of this sulphur-oxidizing microbial community and Fe-oxyhydroxide led to degradation of phosphatic bacterial mats and dissolution of Fe-oxyhydroxides below the Fe-redox boundary (e.g. Coleman et al., 1993), which maintains the high concentrations of phosphate in porewater necessary for francolite precipitation (e.g. Pufahl and Grimm, 2003). Diagenetic modifications significantly affect the fossilized microspheres. When investigated under SEM and TEM, many microspheres are etched and pitted probably during early diagenetic, whereas others have central dissolution hollows and surrounded by carbonaceous matrix that are later replaced by nanocrystalline CFA precipitates.

5.2.2. Microborings

Microborings are responsible for the post-depositional alteration of bone microstructure and represent important taphonomic and environmental indicators of bones exposed in marine environment (Trueman and Martill, 2002; Bell and Elkerton, 2007). These organisms include bacteria, algae, cyanobacteria and fungi that can actively penetrate calcareous and phosphatic substrates, including bone, shells, skeletal carbonate, limestones and dolostones by means of chemical dissolution (Soudry and Nathan, 2000; Pesquero et al., 2010). Microborers are
widespread and environmentally significant in variable geographic regions, from the cold (e.g. Wisshak et al., 2005), through to the temperate (e.g. Kaehler, 1999), subtropical (e.g. Al-Thukair, 2002) and tropical (e.g. Perry, 1998). Although limestone and carbonate skeletons are the most studied marine substrates (e.g. Tribollet and Payri, 2001), microborings have been recorded in silicates (e.g. pillow lavas; Fisk et al., 2006); volcanic glass (Furnes et al., 2007); heavy minerals (Bischoff and Coenraads, 1994); quartz sand grains on sea floor (Tribollet and Payri, 2001; Radtke and Golubic, 2010) and phosphates (e.g. Soudry and Nathan, 2000; Königshof and Glaub, 2004; Zhang and Pratt, 2008).

Detailed morphology of the microborings yields information on the type of microbial endoliths and provides the basis for comparison with other fossil and recent microborings. In the Wassief phosphorites, fossilized microborings are described based mainly on their morphological features and internal cellular arrangements. The studied fossilized microborings are characterized by their undulated, unbranched, elongated shapes with approximately equal dimensions. Cells are spherical, oval, variable in size and enveloped by multilayered sheaths of uniform thickness. These morphological features are not produced by endolithic fungi, which produce fine microborings of uniform diameter and possibly with dichotomous branching (Golubic et al., 2005). These fine and uniform microborings are quite similar to those produced by the filamentous cyanobacteria (e.g. *Plectonema terebrans*). The fine, dichotomous branching and finely tapered openings are common in endolithic fungi, but not in endolithic cyanobacteria and algae (Golubic et al., 2005). Endolithic algae generally produce 1–4 μm in diameter straight or slightly curved borings and show evidence of reproductive cells (Golubic et al., 2005). The anellid genus *Osedax* lives and feeds exclusively on bones on the seafloor and its microborings are thin, cylindrical, elongate and branch into several lobe-like extensions (Kiela et al., 2010). This type of microboring starts as a circular hole in the surface of the bone and extends into a cavity in the interior of the bone (Kiela et al., 2010).

For these reasons, the studied microborings are possibly fossilized endolithic cyanobacteria that can be compared with those observed from the most diverse and abundant endolithic cyanobacteria *Hyella* genus and its ichnogenus *Fascichmus* (Glaub et al., 2001, 2001; Radtke and Golubic, 2011). In addition to the morphological features, cyanobacteria and eukaryotic algae (oxygenic phototrophs) were recently identified in the Duwi phosphorite belt by the presence of phytane and pristane biomarkers (El-Shafei et al., 2014). Cyanobacteria are the most pervasive destructive form of microbial bioerosion (Golubic et al., 2000). They colonize live and dead substrates, although more intensively in dead ones (e.g. Tribollet and Payri, 2001).

Microboring traces may contain palaeoenvironmental information about the depositional depth (Radtke and Golubic, 2011). Endolithic cyanobacteria and eukaryotic algae are oxygenic, light-dependent photosynthetic organisms, dominate in the shallow euphotic zone, and their significance decreases from deep euphotic zone to aphotic zone (e.g. Schneider and Le Campion-Alsumerd, 1999; Glaub et al., 2001; Wisshak, 2012). They are more dominant in the Phanerozoic Eon (Glaub et al., 2001), but are also noted in diverse Precambrian substrates (e.g. Zhang and Golubic, 1987; Xiao and Knoll, 1999; Banerjee et al., 2007).

In the Wassief phosphorites, the cyanobacteria microborings are typically oriented perpendicular to bone surfaces which are characteristic for the shallow euphotic zone that extends to depths of around 20–30 m in clear water tropical settings (Budd and Perkins, 1980; Glaub et al., 2001). Moreover, the absence of any indicative morphological features (present study) or biomarkers (El-Shafei et al., 2014) of fungi, which are more significant in aphotic settings (Glaub et al., 2001; Golubic et al., 2005; Wisshak, 2012), probably supports that fact...
that microboring occurred after reworking, winnowing and transportation of bioclasts in a near-shore, oxygenic environment.

5.2.3. Bone bioerosion

Bioerosion is an important example of demineralization (Ehrlich et al., 2008), which is a major process driving the degradation of phosphatic bones (e.g. Pesquero et al., 2010) and carbonate skeletal material and rocky limestone coasts in all marine and some freshwater environments (e.g. Wisshak, 2012). The exact mechanisms involved in bioerosion remain obscure although a number of plausible hypotheses have been proposed. The complexity of the bioerosion mechanism results from the fact that dissolution of Ca-phosphates occurs under low pH condition in marine environment, where the alkaline pH condition is expected. Most authors adopted the use of acidic substances secreted by the cells to dissolve the carbonate and phosphate substrates, which allow the cells to grow into the mineral (e.g. Golubic et al., 1984; Schneider and Le Campion-Alsumeard, 1999). Some authors have suggested specialized organelles that would sustain this function (Alexandersson, 1975), but current research does not support this idea. Others suggested that ocean acidification as the result of an increase in partial pressures of CO2 favours dissolution of calcium carbonate by euendoliths (Tribollet et al., 2009). The main problem of this interpretation is that cyanobacteria are autotrophs and by nature will consume CO2 through photosynthesis, thereby increasing the pH of their environment (García-Pichel, 2006). This process leads to carbonate, and similarly phosphate, precipitation, and this is exactly the opposite effect to microboring by dissolution that is widely envisaged.

Bone tunnelling is commonly considered to be produced by dissolution of the mineral and organic matrices of the bone by metabolic acids (Piepenbrink, 1989). Hydrated respiratory CO2 is an acid \( H_2CO_3 = HCO_3^- + H^+ \), and can assist dissolution of calcium carbonate (Ascaso...
et al., 1998; García-Pichel, 2006). García-Pichel (2006) suggested that this apparent paradox may be resolved by temporal and spatial separation of photosynthesis and respiration by euendolithic microorganisms during the daily cycle (dissolution due to the CO₂ produced during respiration at night). Support for spatial separation comes from the observation that some euendolithic cyanobacteria can bore on their lower...

Fig. 11. A) A TEM/BSE image showing a cyanobacterial cell and the surrounding remineralized rim. B–D) A TEM/BSE elemental mapping showing the homogenous distribution of O (B), P (C) and Ca (D) in the cyanobacterial cell and the surrounding remineralized rim.

Fig. 12. Elemental mapping of a TEM section of a coccoid-like microsphere showing the enrichment of P, Ca, O, F and S and depletion of C and Cl in the CFA microsphere relative to the surrounding carbonaceous matrix.
Fig. 13. A summary of EPMA showing the average chemical variations of CaO, P_2O_5, Cl, S O_3, Na_2O and MgO wt.% and standard deviations in the unaltered bone, microbored, dissolved areas and phosphatic peloids. The average content of P_2O_5 and CaO wt.% is enriched in the microbored and depleted in the dissolved areas relative to the unaltered bones and phosphatic peloids. The average content of Cl wt.% is enriched in the dissolved and depleted in the microbored areas relative to the unaltered bones and phosphatic peloids. The average content of F wt.% is enriched in the dissolved and microbored areas relative to the unaltered bones and phosphatic peloids. The average content of S O_3 wt.% is enriched in the microbored and unaltered bone areas relative to the dissolved areas and phosphatic peloids. The average content of Na_2O and MgO wt.% is enriched in the microbored areas relative to the dissolved and unaltered bone areas and phosphatic peloids.

Fig. 14. A model showing the depositional environment of the authigenic peloids that were formed as a part of microbial mat in the sulphate reduction zone. Reworking of the microbial mat and buried skeletal grains to a near-shore, oxygenic environment during transgression led to the exposure of phosphatic bones to bioerosion by endolithic cyanobacteria. Bioerosion process is responsible for the complete conversion of phosphatic bones to peloids (phosphomicritization).
surface while encrusting calcite around their exposed filaments above the substrate (Kobluk and Risk, 1977). The substrate dissolution, combined with active transport of Ca\(^{2+}\) from the boring front of euendolithic filaments to their distal ends would make dissolution thermodynamically favourable around the apical cell even while interstitial pH is high due to photosynthesis (Golubic et al., 1984; García-Pichel, 2006).

In the Wassief phosphorites, biochemical dissolution of bones appears to be started in the sheath of the endolithic cyanobacteria and then followed by reprecipitation of nanocrystalline CFA. These processes cause remineralization of bone without any chemical changes. The remineralized sheaths surrounding the microborings walls are much more electron dense than unaltered bone suggesting this bright, high density structure representing the redeposited mineral after its dissolution to expose the bone collagen. They contain higher contents of Ca and P and possibly lower organic matter (collagen) than the surrounding unaltered bone similar to that described by Soudry and Nathan (2000), Jackes et al. (2001) and Pesquero et al. (2010). Soudry and Nathan (2000) suggested that fluorine enrichment of phosphorite bones is strongly enhanced by microbial alteration.

In the localized, semi-closed environments created by the microboring network, demineralization of bones started by producing low pH conditions as a result of the activity of cyanobacteria which increases the concentration and supersaturation of PO\(_4\) in solution. It is assumed that the low-pH conditions maintained within the bone microborings vary from those outside of the bone (e.g. Trueman et al., 2003). The supersaturation of PO\(_4\) in solution is associated with buffering acidic pH conditions and probably inhibited further microbial dissolution of bone, and encouraged rapid precipitation of authigenic, colloform layers of well crystalline, acicular CFA as shown by TEM. This process is known as remineralization of bones, where the reprecipitated apatite preserves the bioeroded bones (Ebrlich et al., 2008).

Optical and scanning electron microscopy showed that precipitation of CFA started as micritic (nanocrystalline) in bone microborings and this affects the bone anisotropy. The loss of anisotropy can be attributed to the nanocrystalline nature and the random crystal arrangement of the micritic CFA replacing the bone tissues (Garland, 1989; Soudry and Nathan, 2000). This process resulted in a gradual centripetal (from rim to centre) conversion of the bone debris into micritic phosphate peloids (Fig. 14). This grain transformation observed in the studied phosphorites is equivalent to the phosphomicritization process described by Soudry and Nathan (2000) and to the well-known micritization process occurring in carbonates and affecting calcareous bioclasts (Tucker and Wright, 1990; Flügel, 2010). Partial phosphomicritization along the rim of bone fragments leads to the formation of phosphatic cortoids (cf. carbonate cortoids described by Flügel, 2010). Phosphomicritization is a fundamental process in obscuring the surface, destroying the original structures, abrading and rounding bone grains.

5.3. Palaeoenvironmental significance of phosphorite grains

The study of bone bioerosion has many significant implications for understanding the depositional/post-depositional and diagenetic processes involved in the formation of phosphorites. The distinction between microorganisms responsible for the bioerosion is usually problematic, as microborings can be produced by various microborers (Flügel, 2010). However, it is significant to identify the type of microboring to determine the palaeobathymetry of water and palaeoecological conditions during and after deposition (Glaub et al., 2001). Microboring activities in phosphatic bones of the shallow marine Negev Phosphorites have been attributed to fungi (Soudry, 2000) and to bacteria in fossil bones in continental carbonate palaeolake environment at the reference Spanish Miocene site of Cerro de la Garita (Pesquero et al., 2010). In the present study, the bioerosion of phosphatic bones by euendolithic cyanobacteria is equivalent in size, shape and distribution to the bacterial microboring of bones that occurs in terrestrial (Pesquero et al., 2010) and marine environments (Bell and Elkerton, 2007; Turner-Walker and Jans, 2008). Pesquero et al. (2010) described microspheres similar in shape and size to coccoid bacteria inside the microborings and suggested that they are responsible for removing collagen from the solubilized compactum and then reprecipitating bone mineral in a more dense form. Bell and Elkerton (2007) and Turner-Walker and Jans (2008) observed no distinct, highly electron dense rim at the edge of the microborings they examined. In transverse section, the remineralized rim at the edge of these examined microborings is highly electron dense, similar to the hypermineralized zones surrounding the microscopic focal destruction described in terrestrial environments (Pesquero et al., 2010). The latter authors suggested that bioerosion in continental environments is characterized by remineralized rims surrounding microborings walls, whereas in marine environments (Bell and Elkerton, 2007; Turner-Walker and Jans, 2008) microborings are not associated with such rims. Therefore, they adopted a new taphonomic bioerosion type. Bell and Elkerton (2007) suggested that this characteristic microboring was diagnostic of marine exposure and to be the product of endolithic microorganisms of unknown identity. Turner-Walker and Jans (2008) found similar microborings to those described by Bell and Elkerton (2007) in modern bone remains and attributed them to endolithic filamentous cyanobacteria. In the Wassief phosphorites, remineralized rims surrounding the euendolithic cyanobacterial microborings in bones were identified. Therefore, the presence or absence of the remineralized zones cannot be applied as solid evidence to differentiate between microborings in terrestrial and marine environments. Here, we propose that endolithic cyanobacteria were the responsible microborer of phosphatic bones and are still preserved in their microborings. Therefore, the complete history of the bioerosion process is preserved in the current record.

The bioerosion process passed through four main post-depositional/diagenetic steps: (1) demineralization of bones: a local dissolution and supersaturation of PO\(_4\) in solution, (2) remineralization: reprecipitation of calcium phosphates along the sheath of cyanobacteria forming remineralized rim; (3) an initial stage of diagenetic alteration that led to removal of the remineralized rim leaving behind phosphatized cyanobacterial cells inside their microborings; and (4) an advanced stage of diagenetic alteration led to complete removal of the phosphatized cyanobacterial cells leaving behind empty microborings. Therefore, the absence of remineralized rim cannot be used as a taphonomic criterion to distinguish between the marine and terrestrial environment (Pesquero et al., 2010). The formation of phosphatic peloids at the expense of phosphatic bones (phosphomicritization of bones) by bioerosion should be differentiated from the authigenic phosphatic peloids formed as part of a microbial mat in the zone of sulphate reduction in terms of the places of formation and deposition. This assessment should be taken in consideration when skeletal and non-skeletal phosphatic components are used in facies, depositional and environmental analyses. The microboring activity is generally accelerated under warm and humid conditions of the tropical climate (Turner-Walker, 2012). The moderately to poorly sorted texture, grain-supported fabric of the phosphatic peloids and bioclasts, and their cementation by calcareous cement possibly indicate grains reworking and transportation from an offshore to a nearshore environment. This led to exposing of bones to microbial bioerosion that is accelerated when they are not covered by sediments (Davis, 1997; Tribollet, 2008). The dominance of endolithic microborings was considered as important taphonomic and environmental indicators of bones exposed in marine environment (e.g. Bell and Elkerton, 2007). Some of the microbored phosphatic bones show areas with a colloform-like texture, rich in chlorine and are darker in tone than the microbored and unaltered areas (Fig. 10A–C). These characteristics are interpreted as dissolution features, which probably related to post-depositional meteoric water alteration as a result of regression and subaerial weathering.
The meteoric water alteration is supported by the low δ18O values of structural CO2 of the CFA and variations in the Ce anomalies between the different localities hosting the Egyptian phosphorites (Baiony et al., 2007). This is also consistent with the palaeogeography of Egypt that was close to the equator (Said, 1990), which suggests warm wet, tropical to subtropical conditions with heavy rainfall and deep chemical weathering (Salama, 2014). The cyanobacteria microring of bones and their meteoric water alteration can be discriminated chemically based on the CaO, P2O5, F, Cl and CO2 content. Chemical dissolution and remineralization of bone by endolithic cyanobacteria increase CaO, P2O5, and F, while meteoric water alteration decrease CaO and P2O5 and increase Cl and F in the colloform CFA relative to unaltered bones. Chlorine is believed to be introduced to the bones by meteoric water alteration. Sulphur is mainly concentrated as microbial sulphate reduction which favours phosphogenesis during the formation of microbial mat at the depositional site. On the other hand, the porous-framing framboidal and euhedral pyrite and rarely as pyritized microspheres in the phosphatic peloids. On one hand, the pyritized microspheres in the phosphatic peloids could be related to microbial sulphate reduction which favours phosphogenesis during the formation of microbial mat at the depositional site. On the other hand, the porous-framing framboidal pyrite in the Wassief phosphorites postdates the formation, reworking and phosphatization of the bioclasts and peloids. This would occur when the palaeoenvironmental conditions in pore water were changed from oxic to anoxic during burial diagenesis to precipitate framboidal pyrite within vascular and other pore spaces. In addition, aryl isoprenoids biomarkers were identified by El-Shafei et al. (2014) close to the Duwi/Dakhla transition and in other facies of the Duwi Formation. These compounds indicate the former presence of green sulphur bacteria (Chlorobioceae) and are considered as indicators for water column anoxygen within the photic zone (e.g. Kuypers et al., 2004; Sepúlveda et al., 2009).

6. Conclusions

The shallow marine phosphorites of Egypt consist mainly of phosphatic peloids, intraclasts and bones. The phosphatic peloids almost exclusively consist of CFA microspheres (0.5–2 μm) and embedded in a carbonaceous matrix. These microspheres resemble coccolid-like bacteria that were once a part of bacterial mat formed close to the oxic–anoxic boundary in the sulphate reduction zone. The phosphatic peloids were reworked to a near-shore, oxic environment during intermittent transgressive–regressive depositional cycles. In this environment, the phosphatic bones underwent bioerosion by endolithic cyanobacteria that resulted in a gradual centripetal digestion and conversion of bones into phosphatic peloids.

Four main post-depositional/diagenetic steps are involved in the formation of the empty microborings: (1) demineralization of bones: local dissolution of phosphatic bones and supersaturation of PO4 in solution under low pH conditions created by the activity of the endolithic cyanobacteria; (2) remineralization: reprecipitation of calcium phosphates along the multilayered sheath of cyanobacteria forming remineralized rim due to buffering of the low pH conditions; (3) an initial stage of diagenetic alteration that led to removal of the remineralized rim leaving behind phosphatized cyanobacterial cells inside their microborings; and (4) an advanced stage of diagenetic alteration led to complete removal of the phosphatized cyanobacterial cells leaving behind empty microborings.

Microborred bones were probably subjected to dissolution when exposed to meteoric water alteration and this is confirmed by reprecipitation of Cl-rich, colloform CFA. Understanding the accretion mechanism of the phosphatic peloids and the bioerosion of the phosphatic bones in the Egyptian phosphorites is significant to understand the depositional/post-depositional and diagenetic history as well as the paleoenvironmental changes of the Late Cretaceous to Palaeogene phosphogenic province extending from the Middle East to North Africa.

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Buick, R., 1990. Microfossil recognition in Archean rocks: an appraisal of spheroids and carbonaceous matrix. These microspheres resemble coccoid-like bacteria that were once a part of bacterial mat formed close to the oxic–anoxic boundary in the sulphate reduction zone. The phosphatic peloids were reworked to a near-shore, oxic environment during intermittent transgressive–regressive depositional cycles. In this environment, the phosphatic bones underwent bioerosion by endolithic cyanobacteria that resulted in a gradual centripetal digestion and conversion of bones into phosphatic peloids.

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