Bacterially-mediated authigenesis of clays in phosphate stromatolites

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Authigenic clays in close textural relation to carbonate fluorapatite within finely laminated phosphate stromatolites of Upper Jurassic age have been studied using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and analytical electron microscopy (AEM). Stromatolite laminae consist of hexagonal prisms of francolite (sizes ranging between 0·1 and 1·0 μm) that are surrounded by poorly crystalline smectite and amorphous Fe·Si·Al oxyhydroxides. Microanalyses show that smectite is Fe rich, with highly variable composition, particularly regarding Fe and Si contents. Smectite has significant beidellitic, montmorillonitic and non-tronitic substitutions. Although the lack of fringe contrast in some areas adjacent to the smectite packets with 1·0–1·3 nm spacing is due to differences in orientation of layers, textural and analytical data clearly indicate the presence of Fe·Si·Al amorphous phases intimately intergrown with smectite. The occurrence of poorly crystalline smectite and associated amorphous phases within microbially precipitated stromatolite laminae, both as envelopes around, and as pore-fillings between extremely small calcium phosphate crystals, demonstrates authigenic smectite growth from a precursor Fe·Si·Al amorphous material. This material is formed in close association with a phosphate-rich precursor. The textural and structural relations, the preservation of chemical precursors of glauconite such as nontronitic montmorillonite, and the presence of Fe·Si·Al amorphous mineral phases, imply crystallization of the observed crystalline phases from synsedimentary (bacterially precipitated) amorphous precursors during early diagenesis in postoxic environments. Carbonate fluorapatite was the first phase to crystallize from the primary gel; smectite and associated amorphous Fe·Si·Al oxyhydroxides were the residual material of the crystallization process. The slow rate of transformation (at low temperatures) from Fe·Si·Al-rich gels to smectite, explains the
textural relations between the poorly crystalline phases and the phosphate crystals, as well as the preservation of amorphous substances in relation to clays. Authigenic smectite represents the first step in glauconitization.

**INTRODUCTION**

An authigenic origin of clays associated with phosphorites has been inferred by analytical and X-ray diffraction (XRD) studies. The relatively high iron content (7 wt % Fe₂O₃) of montmorillonite intercalated between primary phosphate laminae, and the relative sharpness of (0 0 1) XRD peaks were considered by Nathan and Soudry (1982) and Soudry (1992) as evidence of an authigenic origin. The substitution of Fe³⁺ and K⁺ in smectite is particularly important because of its implications for the genesis of several minerals, in particular for that of the glauconitic mineral family (glaucony), the end-members of which are glauconitic smectite and glauconitic mica according to the nomenclature of Odin and Matter (1981). Nontronite occurs as a widespread authigenic mineral in recent marine sediments. It has been studied in more detail than any other smectite (Güven, 1988) and it is also a precursor of glauconite (Giresse & Odin, 1973; Velde, 1976; Odom, 1976, 1984; Buatier et al., 1989). According to O’Brien et al. (1990), glaucony currently forming today, together with apatite, on the East Australian continental margin is an immature, low-potassium, iron-rich smectite. Glauconite/smectite mixed-layer material has been considered to have a complete range of smectite and glauconite layers, and to precede glauconite formation (Velde & Odin, 1975) analogous to the way in which illite/smectite mixed-layered material evolves to illite (Thompson & Hower, 1975; Buatier et al., 1989).

The texture and structure of glaucony pellets have been described by Amouric and Parron (1985) using transmission electron microscopy (TEM). They established that crystallization of glauconite occurs via a smectite-like phase with d_{(0 0 1)} = 12·5 Å (1·25 nm) which was probably derived from a precursor gel. Using TEM and analytical electron microscopy (AEM), Eggleton (1987) studied the texture, structure and chemistry of Fe-Si-Al-oxyhydroxide gels in soils, in order to establish their precise role in the weathering of silicate minerals and in the neoformation of clays. These non-crystalline Fe-Si-Al oxyhydroxides form hollow-packed spheres with walls showing an incipient layer structure, which evolve to clay minerals (smectite or kaolinite, according to the gel composition).

A close textural association between Fe-rich smectite-like or glauconite-smectite phases and Fe-Si-Al amorphous phases and francolite crystals has been found by Martín-Algarra and Sánchez-Navas (1995) within open marine phosphate stromatolites. In this paper, we present a detailed textural, structural and compositional study of these clays and associated amorphous phases, using scanning electron microscopy (SEM), TEM and AEM.

**MATERIAL AND METHODS**

Table 1. Chemical analysis obtained by AEM and expressed as smectite formulae*.

Table 2. Pearson correlation matrix of selected compositional variables.

Table 3. Principal component analysis of selected compositional variables.

Fig. 1. Optical image...
The clays described in this study occur in close textural relation to carbonate fluorapatite (francolite) within phosphate stromatolites (centimetric oncoids and crusts) sampled in the Almola Sierra (Serranía de Ronda, SW Spain; Martín-Algarra, 1987; Martín-Algarra & Sánchez-Navas, 1995). These stromatolites occur in Upper Jurassic (latest Oxfordian Kimmeridgian) condensed fossiliferous limestones, which were deposited on a pelagic swell. A preliminary textural and mineralogical study of phosphate stromatolites was carried out by optical microscopy, SEM and XRD.

Samples selected for TEM study correspond to primary (microbially controlled) stromatolitic phosphate laminae (see Martín-Algarra & Sánchez-Navas, 1995; for details). They were detached from thin sections, ion-milled and carbon coated. Lattice fringe images, qualitative analyses in TEM nannoprobe mode (19-nm electron probe diameter) and quantitative chemical analyses in scanning tunnelling electron microscope (STEM) mode of the various zones observed in the microtexture were obtained with a Philips CM20 instrument operated at 200 kV. An objective aperture of 40 μm was used as a compromise between optimum amplitude and phase contrast for images. Reflections with d-values >0.4 nm were therefore used to obtain lattice fringes. Quantitative microanalyses were carried out using a 5-nm beam diameter and a scanning area of 100 × 20 nm. Muscovite, albite, biotite, spessartine, olivine and titanite were used to obtain k-factors to correct energy dispersion X-ray (EDX) data by the thin-film method of Lorimer and Cliff (1976). Errors for analysed elements (two standard deviations), expressed in percentage of the atomic proportions, are 6 (Na), 3 (Mg), 2 (Al), 4 (K), 4 (Ca), 5 (Ti), 3 (Mn) and 3 (Fe). Instrumental conditions for spectra acquisition were 200 s of live time for all elements except for K, for which a time of 30 s was used because of volatilization problems.

RESULTS

TEM and SEM images

Stromatolite lamination is well defined macro- and microscopically by alternation of pristine, brownish to yellowish phosphatic laminae, and darker laminae containing trapped clastic particles of calcite, quartz, Fe-oxyhydroxides, terrigenous clays and feldspars (Fig. 1). Phyllosilicates occur within non-phosphate laminae as detrital mica (Fig. 2A,B), but also inside phosphate laminae, closely associated with francolite crystals. Carbon-rich particles (organic matter) are also common (see Fig. 11D in Martín-Algarra & Sánchez-Navas, 1995).

In SEM images (Fig. 3), stromatolitic phosphate laminae appear as closely packed, ovoid to ellipsoidal objects, sometimes grouped in complex aggregates or sausage-like strings. TEM images (Fig. 4) show that most phosphate grains are hexagonal prisms (sizes ranging between 0.1 and 1 μm) surrounded by a poorly crystalline material that confers the rounded morphology to the phosphate grains observed under SEM. TEM data show that this poorly crystalline material is formed by clay minerals associated with non-crystalline substances (Fig. 5). Compositional (see below), textural and structural features (selected area electron diffraction: SAED) of these phyllosilicates correspond to those of smectite. These include subparallel

[Full Size]
arrangement of packets 20–50 nm in thickness, abundant layer terminations, and wavy layers (the common fringe spacing is 1 nm: Figs 5 and 6). Although orientations within and between packets of smectite layers are variable, they tend to form stacks consisting of a subparallel array of packets (Fig. 5). Some areas which lack fringe contrast and which are adjacent to smectite packets with 1–1.3 nm spacing, have been confirmed to correspond (as noted by Peacor, 1992), to smectite packets with different orientations than those with fringe contrast (central areas of Figs 6 and 7).

The existence of Fe–Si–Al-rich non-crystalline substances has been established based on the following data: (1) lack of a diffraction pattern (SAED photographs were quickly taken before exposure to the beam for other purposes in order to minimize damage); (2) absence of lattice fringes and of Moiré pattern; (3) no change of amplitude contrast of images when sample is tilted; (4) mottled appearance when a marked dark contrast is observed; (5) variable chemical compositions producing anomalous stoichiometries on smectite analyses or compositions that do not correspond to any observed crystalline phase (see below). Non-crystalline areas with a mottled appearance and associated with smectite (Figs 6 and 7) sometimes form aggregates of rounded structures (arrows in Fig. 9) similar to the spherical structures shown by ferrihydrite gels in Eggleton (1987; Fig. 2). Non-crystalline phases appear both within (intrapackets: Fig. 5) and between (interpackets: Fig. 8) smectite packets. The observed textures demonstrate that smectite and amorphous substances are intergrown at diverse scales, an observation that points to a common origin.

Chemical composition of smectite and associated amorphous phases

Smectite formulae, obtained from chemical analyses of clays by AEM, are listed in Table 1. Because of the large dimensions of the areas of analysis (100–20 nm) relative to the small crystal sizes of smectite packets (5–20 nm normal to the layer), and to the intimate intergrowth of smectites and non-crystalline phases, quantitative analysis of pure smectite or only of the associated non-crystalline phase, without contamination by another phase, proved difficult. Two quantitative analyses (squares in Fig. 10A) correspond to an Fe-rich amorphous substance, one of which is probably a ferrihydrite (compare with Fig. 1 of Eggleton, 1987), as confirmed by textural observation in TEM images (see above: Fig. 9A,B). Those corresponding to smectite have been confirmed according to crystal chemical constraints. Taking into account Güven's (1988) data and the precision of our AEM results, analyses corresponding to smectite have been selected according to the following criteria: where E(VI) and E(XII) represent, respectively, the sum of octahedral and interlayer cations.

Some of the selected analyses show particularly high interlayer charge, which results from the summation of interlayer cations multiplied by their respective charges (K + Na + 2Ca in this case), the overall range being 0.23

**Fig. 6.** Smectite packets (SM) curved in the area adjacent to a phosphat crystal (PH). In the lower right hand side, Fe-rich material is observed.

**Fig. 7.** Spindle-like smectite (SM) lacking complete fringe contrast as a result of slight misorientation.

**Fig. 8.** Association between Fe–Si–Al-rich non-crystalline substance and smectite. Amorphous substance...

**Fig. 9.** (A) Non-crystalline Fe-rich material (AM) with minor amounts of smectite surrounding francolite...

**Fig. 10.** (A) Triangular Fe–Si–Al

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and 0.87. The larger interlayer charge values are normally associated with illite, but a significant proportion of the high charges is due to the inclusion of unknown quantities of amorphous domains in the analyses (because very small areas of such material were undetectable, despite care taken in analytical procedures see below). In addition, AEM analyses include very small volumes of material, and the large range of charge may simply because of local heterogeneities which are typical of a range of low- to high-charge smectite, in comparison with averaged bulk analyses. Such heterogeneity in smectite has been implied by AEM analyses of several authors (Buatier et al., 1992; Freed & Peacor, 1992; Nieto et al., 1994, 1996). Other analyses could be considered as intermediate in octahedral occupancy to ideal di- or trioctahedral smectites, but these have not been accepted because such smectite has rarely been reported previously, and such 'ideal' compositions are always derived from bulk chemical analyses. Moreover, experimental syntheses of smectite with intermediate compositions have produced only a physical mixture of dioctahedral and trioctahedral smectites (Grauby et al., 1993; Yamada et al., 1991). Analyses not reproduced in Table 1 were considered to correspond to mixtures of clay minerals and associated amorphous phases. In several analyses (e.g. Analysis 1, Table 1) an excess of Ca was detected that cannot be incorporated in the smectite structure, and that necessarily must correspond to the adjacent non-crystalline material.

Qualitative nanoprobe analyses of the amorphous areas indicate that they are Fe-rich (Fig. 11A,C,D), with minor amounts of Si, Al, Ca, K, Mg, P, S, Cl, and Na, in decreasing order of abundance. This is in agreement with the dark contrast, which implies relatively high atomic number elements in these Fe-rich areas. Although most of the analyses from areas corresponding to a mixture of smectite and amorphous phases project onto smectite fields (montmorillonite nontronite) in the Si-Al-Fe triangular composition diagram, two clusters are observed, one close to the Si apex and another close to the Fe apex (Fig. 10A). The presence of Si-rich amorphous phases was also detected by qualitative nanoprobe analyses (Fig. 11A and B) inside zones where analyses of mixtures between smectite and non-crystalline phases were obtained (triangles nearest to the Si apex in Fig. 10A), although their presence was difficult to detect in TEM images.

Microanalyses show that smectite has a highly variable composition, particularly regarding Si, Mg and Fe contents (Table 1). Most of the analyses may be plotted on the Al2 − AlFe − AlMg ternary diagram (Fig. 10B), and may be designated as Fe-rich montmorillonite according to Güven (1988). They have both important beidellitic (Si AlIV) and montmorillonitic (AlVI Mg) components that produce a particularly high interlayer charge, because both substitutions are compensated by an increase of the total positive charge of the interlayer (K + Na + 2Ca) (Fig. 12, Table 2). In the case of both substitution mechanisms, our data vary nearly all of the previously described range of compositions (Güven, 1988): AlIV from 0.1-0.5 atoms per formula unit (hereafter atoms
p.f.u.); Mg from 0.2-0.6 atoms p.f.u. In addition, the nontronitic component is also very important (Fig. 12, Table 2), with Fe ranging from 0.16-0.65 atoms p.f.u. (Table 1). Principal component analysis has been performed to quantify these substitutions (Labotka, 1983), using the covariance matrix of Si, Al\text{VI}, Fe, Mg, K + Na + 2Ca, and \( \Sigma \) (VI). This analysis considers the cations and vacancies as coordinate axes in \( n \)-dimensional space, and each smectite composition is considered to be a point in this \( n \)-space. Principal component analysis represents a transformation to a new set of coordinates that are linear combinations of the original cation coordinates. This new set of coordinates is chosen so that the new matrix, formed from the covariances of smectite compositions expressed in terms of the new coordinates, is diagonal. The diagonal elements of the new matrix are the eigenvalues of the original covariance matrix. The new coordinate axes are the eigenvectors of this matrix, called principal components, and represent the variation in the chemical composition of the smectite (Table 3). The sum of the eigenvalues is identical to the total variance, and the relative contribution of each eigenvector to the total variance of the data set is given by the associated eigenvalue. The first principal component has the largest associated eigenvalue, the second principal component has the second largest eigenvalue, and so on. The first principal component (eigenvector I in Table 3) explains \( \Sigma = 81\% \) of the total variance: 0.731 Si + 2.040 Al\text{VI} + 0.069 \( \Sigma \) (VI) = 0.731 Al\text{IV} + 1.299 Fe\text{III} + 0.673 Mg + 1.582 (K + Na + 2Ca). This first component is, in turn, decomposed as follows:

**Bacterially mediated authigenesis of smectite via precursor Fe-Si-Al gels**

The studied clays and amorphous phases occur within stromatolites, laminated sedimentary structures accreted at the sediment-water interface by bacterially mediated precipitation of minerals, mainly phosphates (Martín-Algarra & Sánchez-Navas, 1995). Both clays and amorphous phases form the rind of the oval to ellipsoidal objects that constitute the phosphate-rich stromatolitic laminae (Figs 3, 4). The size and the shape of these objects, which have cores composed of francolite crystals, resemble internal moulds of coccoidal and rod-shaped bacteria, which have been interpreted as fossil remnants of the stromatolite-building bacterial community (compare with Lamboy, 1990, 1993; Krajewsky et al., 1994; see also Martín-Algarra & Sánchez-Navas, 1995; and references therein). Such intimate textural and structural relations between the francolite crystals, smectite and the associated amorphous substances demonstrate their close genetic relations. This implies that the chemical components of all these phases must have been concentrated and precipitated within microbial mats, forming a common precursor for them (Fig. 13). This primary precursor was probably an extracellular, mucilaginous, bacterial gel, rich in
polysaccharides, where \( \text{PO}_4^{3-}, \text{Ca}^{2+}, \text{CO}_3^{2-}, \text{Fe}, \text{Al}, \text{Si}, \) and other elements were bound and concentrated from seawater, degrading organic matter and/or particulate sediments trapped within the stromatolite structure.

Degradation and dehydration of a polysaccharide-rich primary bacterial gel, would have produced non-crystalline inorganic precursor gels of the observed mineral phases (francolite, smectite and Fe-Si-Al-rich amorphous phases). The location of smectite and Fe-Si-Al-rich amorphous phases at grain boundaries and filling pores between francolite crystals, demonstrate that francolite crystallized from the precursory precipitate first, an Fe-Si-Al-rich precursor gel being a residue of this first crystallization process (Fig. 13). Taking into account the poor crystallinity of the smectite, the common presence of amorphous phases intimately associated with smectite, and the rather similar chemical composition of much smectite and Fe-Si-Al amorphous substances, we infer that both phases come from a primary Fe-Si-Al-rich precursor gel. The smectites should have formed authigenically by an incomplete process of crystallization of this primary non-crystalline precursor. The observed amorphous phases can be considered either as residues of smectite crystallization, or as partially dehydrated relics of the primary gel having original compositions that made the formation of smectite impossible. In this sense, although smectites have a wide range of compositions, they are not exactly scavengers, and cannot incorporate any element present within the bacterially precipitated precursor.

The ability of bacteria to bind, concentrate and cause crystallization of many different minerals (including sulphides, phosphates, oxyhydroxides and carbonates) is well established (Lowenstam, 1981; Krumbein, 1983; Ehrlich, 1990). Cation exchange in cell walls and sorption of different metals, even from dilute solutions and sometimes selectively, has also been demonstrated (Marquis et al., 1976; Mayers & Beveridge, 1989; Ferris et al., 1988). Bacterial surfaces are reactive sites that allow either direct nucleation of crystals or interaction between metals and biofilms by complexation of metastable organo-mineral phases (Morel et al., 1973; Deggens & Ittekkot, 1982; Jannasch, 1984; Ferris et al., 1986, 1987). Bacteria also play an important role in the weathering of silicate minerals (Ferris et al., 1989a, b) and in nucleation of Fe-Si amorphous compounds in geothermal environments (Ferris et al., 1986; Konhauser & Ferris, 1996; Jones & Renaut, 1997). Moreover, the extracellular formation of fine-grained, compositionally heterogeneous, non-crystalline and poorly crystalline Fe-Si-Al, phosphate and metal precipitates around bacterial cells has been demonstrated recently in the laboratory (Urrutia & Beveridge, 1993, 1994). These precipitates slowly evolve to crystalline phases, among which short range-ordered aluminosilicates have been identified (Urrutia & Beveridge, 1995). In conclusion, the inferred participation of bacteria in the
extracellular concentration and precipitation of phosphate-rich and Fe-Si-Al-rich substances fully agrees with geomicrobiological studies undertaken both in the laboratory and in present-day natural environments.

**Kinetics of the crystallization process**

The formation of metastable Fe-Si-Al-rich and P-rich precursor gels instead of direct crystallization of mineral phases is favoured by: (a) high degrees of supersaturation which create strong interactions among involved ions, leading to irregular coordination complexes large enough in size to precipitate; (b) the presence of organic compounds that favour stabilization of metastable inorganic amorphous precipitates (see Termine et al., 1970; for amorphous calcium phosphate -ACP- stabilization); (c) the lower surface and strain energy of bubbly or foamy structures, typical of non-crystalline materials (see Eggleton, 1987; for Fe-Si-Al non-crystalline oxyhydroxides). Bacterial surface microenvironments are able to create rapid supersaturation conditions by ionic complexation, that account for the development of a gel-like matrix formed of hydrous (Fe, Al)-silicate precursors (Ferris et al., 1987; Urrutia & Beveridge, 1993, 1994, 1995).

Laboratory experiments demonstrate a rapid transformation of amorphous to crystalline phosphate phases (Posner et al., 1984; Van Capellen & Berner, 1991; Krajewski et al., 1994) that occurs through a solution-mediated, solid-solid conversion (Boskey & Posner, 1973). Although the transformation of Fe-Si-Al-rich precursor gels into smectites could be interpreted to occur by a similar mechanism, smectite crystallization from a precursor Fe-Al-Si-rich gel could also have occurred via a bubble-wall mechanism, such as that proposed by Eggleton (1987) for clay mineral formation in weathering profiles.

As demonstrated by the textural relations (outer position of Fe-Si-Al precipitates relative to francolite crystals, and common preservation of Fe-Si-Al amorphous phases in close association with the smectites), the crystallization rate of the smectite from its Fe-Si-Al-rich precursor was slower than that of the francolite from its P-rich precursor (possibly ACP according to Martín-Algarra & Sánchez-Navas, 1995). This is consistent with experimental evidence of high reaction rates for the transformation of ACP to hydroxyapatite (Posner et al., 1984), and with slow reaction rates at low temperatures, that favour the persistence of metastable phases (Berner, 1984).

**Physicochemical conditions**

The marked variability in composition from site to site of the amorphous phases and smectites located among francolite crystals is interpreted as a
consequence of the heterogeneity of the precursor bacterial gel. Growth of an array of francolite crystals subsequently produced isolated domains of gel with varied local Fe-Si-Al-rich compositions. The variable compositions were retained because of the slow mobility of ions at low temperatures, and lack of connectivity of gel domains. Where the original compositions were appropriate, crystallization of smectite took place, its final composition being a consequence of the local chemical environment. In this sense, Tardy et al. (1987) have shown that the stability field of smectites at low temperatures depends on the chemical activities of the various elements. Equilibrium may be reached only locally in a large variety of aqueous microsystems, which, therefore, produce an extreme diversity of clay particle compositions within a given population, as in the studied smectites. In particular, a change from the stability field of nontronite to that of beidellite and to amorphous silica is a consequence of increasing $H_4SiO_4$ activity (Tardy et al., 1987; Fig. 2). Moreover, experimental studies have demonstrated that complete solid solution does not occur between different smectite types; when the composition of the starting material did not correspond to an 'allowed' formula of smectite, a mixture of various types of smectites, ± silica, was synthesized (Yamada et al., 1991). Regarding the physicochemical conditions of the sedimentary environment, Tardy et al. (1987) also pointed out that montmorillonite forms in solutions of higher pH (7-4), characterized by higher concentrations of cations and silica, than kaolinite (pH = 6-8). These conditions could easily be reached inside, or immediately below, the microbial mat when crystallization of francolite and of authigenic clays occurred (compare with pH data in Ferris et al., 1989a; and Urrutia & Beveridge, 1994). In spite of the great variety of compositions of smectites obtained, no trioctahedral smectite has been found; such smectite requires a high activity of Mg, and consequently its presence is usually related to volcanic influences, which are completely absent in the studied materials.

Crystallization of the studied smectites postdates that of francolite within empty bacterial cells. The crystallization of Fe-rich montmorillonite was probably favoured by a decrease in oxygen fugacity due to the decomposition of bacterial organic matter (evolution from oxic to postoxic environments; Fig. 13). This is consistent with independent experimental work on low-temperature synthesis of iron-rich smectite from silica and Fe-hydroxides, which is only possible under reducing conditions (Harder, 1978).

Some of the studied Fe-Si-Al-rich amorphous phases and Fe-rich smectite constitute chemical precursors of glauconite. The studied phases therefore may represent the first step in the glauconitization process or, in other words, the gradual passage between the Al-rich clay minerals and the Fe-rich glauconitic smectite, invoked by Odin and Matter (1981). Although the formation of glauconite sensu stricto did not take place in the studied samples, it is frequently associated with pelagic phosphate and Fe-Mn stromatolites of various ages (Martin-Algarra & Vera, 1994; Vera & Martin-Algarra, 1994; Föllmi, 1989; and references therein) and glauconitization is commonly associated with phosphatization (Bentor, 1980; Baturin, 1982; Jarvis, 1992; and many others). The existence of confined microenvironments is necessary for concentration of the chemical elements.
involved in the early stages of glauconite formation (Jiménez-Millán et al., 1998, and references therein). An intense reworking, which is commonly detected in glauconite-bearing sediments, and the repeated exhumation of the precursor authigenic clays, with resultant change from postoxic to oxic environments and exposure to bottom waters rich in K, would probably favour the maturation of Fe-rich smectites to glauconites. Although some evidence of reworking does exist in the studied phosphate stromatolites (see Martin-Algarra & Sánchez-Navas, 1995 for details), this was probably not intense or persistent enough to favour the Fe- and the K-enrichments necessary for the formation of glauconite s.s. from the studied Fe-rich smectite. Indeed, just as illite is the common prograde product of aluminium-rich smectite, glauconite is the product of iron-rich smectite (Buatier et al., 1989).

CONCLUSIONS

In the studied phosphate stromatolites the crystallization of Fe-rich smectite, which is a precursor to glauconite, occurred from Fe-Si-Al gels during early diagenesis. These precursor gels, together with associated P-rich gels, are of synsedimentary origin and were produced by stromatolite-forming bacteria. Authigenesis of the studied clays and the physicochemical evolution of the stromatolitic microenvironment during their formation can be summarized (Fig. 13) as follows:

1 formation of primary P-Si-Fe-Al-rich gels as extracellular mucilaginous bacterial precipitates under oxidizing conditions, because these substances were rich in ferric compounds and PO$_4^{3-}$ was enriched in the sediment surface by oxidative degradation of organic matter;

2 after death of the bacteria, carbonate fluorapatite crystallized first from the primary, organic-rich gel. The Fe-Si-Al-rich products changed slowly and partially (when allowed by the local gel composition) into poorly crystalline clays;

3 crystallization of Fe-rich montmorillonite occurred under reducing (postoxic) conditions, after oxygen consumption within the microbial mat as a consequence of the oxidation of bacterial organic matter during early diagenesis (possibly just below the living mat). Reactants were the Fe-Si-Al-rich gels remaining after apatite formation. The authigenic smectite is inferred to constitute the first step of an incomplete glauconitization process.

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