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Biomineralization of primary carbonate cements: a new biosignature in the fossil record from the Anisian of Southern Italy

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Biomineralization is a generic term used to indicate biological-mediated mineral formation. In carbonate mineralization, nucleation of crystals can be: (1) controlled directly by the organisms, like in the skeletal formation of most metazoans; (2) induced by microbial communities, by indirect precipitation mediated by their metabolic activities; or (3) influenced by organic matter decay, with mineral precipitation on specific non-living organic cell surfaces. Recognition of these products is a direct marker of biological activity in time and space and is a key element in the study of the biological evolution and of its interactions with the geological processes. In this paper, primary carbonate cements from the Anisian microbial build-up of the 'Monte Facito' Formation (Basilicata region, Southern Italy) have been studied from a geobiological point of view. Optical microscopy, UV-epifluorescence and micro-Raman spectroscopy have been applied to investigate the organic mediation on their precipitation. The cements formed in microcavities or on grain substrates, and often show a microstromatolite-like pattern of growth. They are composed of alternations of cloudy organic and whitish inorganic bands that point to a double phase of mineralization. In the first phase, a biologically induced/influenced biomineralization is confirmed by the presence of organic matter strictly connected with the cloudy bands. This phase is followed by a pure abiotic mineralization that leads to the formation of whitish bands. This process repeated cyclically, ending at the complete filling of the microcavities or because of changes in the chemical conditions of the microsystem, for example, due to burial processes. This model of mineralization is similar to that proposed for primary cements forming in recent beach rocks. The Monte Facito Formation cements could be considered as the product of unconventional biomineralization, and the understanding of their growth process could provide an innovative tool in the research of biological signatures in the fossil record. The term unconventional is here utilized to discriminate this type of biomineralizations from those related to well-known biotic mineralization processes, like those involved in skeletons and microbialites growth, which can be considered as conventional biomineralizations. ☐ *Anisian, biomineralization, fossil record, Monte Facito Formation, organic matter, primary cements.*

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Biological mineralization, also known as biomineralization, is a term that indicates mineralization processes associated with biotic activity. Biomineralization is a broad field of study that involves very different organisms, processes and products (Riding 2000, 2011). It includes the formation of metazoan skeletons, with a marked control of the organisms over the crystallization processes; mineral precipitation by different types of microbes, as by-products of their metabolic activities; and mineral precipitation mediated by concentrations of organic matter on cell surfaces (Lowenstam & Weiner 1989; Benzerara *et al*. 2011; Phillips *et al*. 2013; Anbu *et al*. 2016; Riding & Virgone 2020). In all these cases, the formation of biominerals also depends on the chemical, physical and climatic conditions of the environment (Riding & Liang 2005; Riding 2011). These products can be thus considered as a remarkable archive, documenting the presence and characters of biotic associations as well as their relations with the

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environmental conditions. This is particularly true when the occurrence of skeletal remains is scarce or even absent. In several cases, such as during large part of the Precambrian, after major extinction events, or in correspondence of extreme environments, microbialites may provide the only source of information on biotic presence in the geological record (Riding 2011).

One of the most crucial issues on the dynamics that control carbonate cements formations, concerns their biogenic *versus* abiogenic precipitation that still remains a matter of debate (Schneidermann & Harris 1985; Russo *et al.* 2000, 2006; Schlager 2005). The relevance of this topic relies in the cardinal role of cement mineralization in the carbonate factory. One of the most remarkable examples of this importance is the Dolomites depositional system (eastern Alps, north Italy). There, from Anisian to Carnian times, low-relief terrigenous-carbonate ramps, rich in loose micritic mud, evolved into isolated high-relief carbonate pinnacles, in which syndepositional cements, together with autochthonous micrite, played a key role in the carbonate production and in the stabilization of the depositional geometries (Bechstädt & Brandner 1970; Biddle 1981; Brandner & Resch 1981; Gaetani *et al.* 1981; Bosellini 1984; Brandner *et al.* 1991, 2007, 2012; Harris 1993, 1994; Blendinger 1994, 1996; Keim & Schlager 1999, 2001; Emmerich *et al.* 2005; Russo 2005; Seeling *et al.* 2005; Stefani *et al.* 2010; Brandner & Keim 2011; Marangon *et al.* 2011; Sánchez-Beristain & Reitner 2012, 2016, 2018a, 2018b, 2019; Guido *et al.* 2016, 2018, 2019a). Russo *et al.* (2000) recognized the role and the abundance of primary cements in the carbonate facies of the Dolomites, where they represent the major constituent of the Triassic Marmolada platform, forming more than 50% of the rock volume. Much earlier, similar cements were also recognized by Stoppani (1858) in the Middle Triassic build-ups of the Western Southern Alps. This author underlined the litho-genetic importance of these cements, but interpreted them as encrusting sponges and created the new genus *Evinospongia*. Evinosponges, also known as 'Großoolith' in the Austroalpine Triassic (Schmidegg 1928), were later re-interpreted as early diagenetic precipitates, modified by fresh water diagenesis (Brandner & Resch 1981; Henrich & Zankl 1986).

The importance of primary cements has been also recently emphasized in the Anisian build-up of the 'La Cerchiara' succession, located in the area of Sasso di Castalda (Basilicata, Southern Italy) (Guido *et al.* 2021). Here, a rare exposure of well-preserved Triassic carbonates bodies represents a unique site where microfacies and biogeochemical study can be performed in detail. Primary cements, together with microencrusters and autochthonous micrite represent the main components of the upper slope/margin deposits of this build-up. The present research focuses on these Anisian cements, with the characterization of their micromorphology, microstructure, mineralogy, geochemistry and diagenetic features. The main aim is to investigate their mineralization dynamics and to test their dependence from biotic processes. This can potentially provide a new perspective on carbonate cements studies, increasing the understanding of their depositional processes. Their recognition as biominerals could actually represent an innovative tool in the study of the relations between biotic associations and sedimentary record.

Biomineralization processes

The term biomineralization indicates a general relationship between biotic activities and mineralization. More specific definitions, like 'organic matrix mediated' and 'biologically induced', were introduced by Lowenstam (1981) to distinguish the differing degrees of influence exerted by organisms over biomineralization. Trichet & Défarge (1995) introduced the term organomineralization for precipitation mediated by non-living microbial organic substrates in soils and sediments *via* acidic macromolecules randomly distributed throughout the EPS-matrix. Rearrangement of these acidic sites through diagenetic processes provides an organized nucleation template for complete biofilm organomineralization (Reitner 1993; Reitner *et al.* 1995; Trichet & Défarge 1995). Successively, Dupraz *et al.* (2009) utilized the term 'organomineralization *sensu lato*' for all the processes that mediate mineral precipitation on an organic matrix not genetically controlled, including in the definition either the active (biologically induced) or passive (biologically influenced) processes. In biologically influenced mineralization, external, environmental parameters, rather than microbial activities, are responsible for creating the conditions (e.g. increased alkalinity) for mineral precipitation, and the presence of living organisms is not required (Dupraz *et al.* 2009). An organic matrix is, however, involved in biologically influenced precipitation, affecting the morphology and composition of the crystals through interactions between the growing mineral and the organic matter (serving as template for precipitation) (Dupraz *et al.* 2009). Cuif *et al.* (2011) highlighted the difficulties in defining clear criteria (morphological, structural, crystallographic and chemical) for the distinction of biomineralization pathways.

Summarizing, three different mechanisms can be recognized in the production of carbonate biominerals: 'biologically controlled', 'biologically influenced' and 'biologically induced'. However, these processes are not always well-defined and recognizable, and a uniform terminology is still a matter of debate (Perry *et al*. 2007; Altermann *et al*. 2009; Dupraz *et al*. 2009; Anbu *et al*. 2016; Riding & Virgone 2020).

Biologically controlled mineralization involves regulation of solubility, supersaturation, nucleation and crystal growth by cellular activities (Lowenstam & Weiner 1989; Mann *et al*. 1993; Mann 2001; Weiner & Dove 2003; Benzerara *et al*. 2011; Phillips *et al*. 2013; Anbu *et al*. 2016; Riding & Virgone 2020). In this process, minerals are directly synthesized at a specific location within or on the cellules of the organisms that control nucleation and growth of minerals.

Biologically influenced mineralization is the process in which the precipitation of minerals is triggered by the presence of cell surface organic matter, such as extracellular polymeric substances associated with biofilms (Benzerara *et al*. 2011; Phillips *et al*. 2013; Anbu *et al*. 2016).

Biologically induced mineralization involves the precipitation of minerals as a consequence of localized response to the production of metabolic by-products (e.g. OH^{-}, HCO^{3-}). This is the case of the metabolic activity of microbial communities that contributes to the chemical modification of the micro-environment, resulting in supersaturation and in the precipitation of minerals (Lowenstam & Weiner 1989; Stocks-Fischer *et al*. 1999; Frankel & Bazylinski 2003; De Muynck *et al*. 2010; Phillips *et al*. 2013; Riding & Virgone 2020).

When mineralization occurs without connections to any biological or organic control, it is regarded as abiotic precipitation. In this case, the type of mineralization is related to the carbonate saturation state, influenced by the physicochemical properties of the environment and by climatic factors (Stumm & Morgan 1996; Zeebe 2012; Riding & Virgone 2020).

Geological setting

The 'La Cerchiara' outcrop, located in the area of Sasso di Castalda (Basilicata) (Figs 1, 2), contains one of the most representative successions of the Monte Facito Formation (Early-Middle Triassic) (Scandone 1967; Wood 1981; Ciarapica *et al*. 1990a, b,c; Palladino 2015; Palladino *et al*. 2019; Guido *et al*. 2021). The succession starts with tens of metersthick units of shallow-water carbonates, which regularly alternate with finely laminated deep-water yellow and red shales. The age of the carbonates has been doubtfully attributed to Late Anisian–Early Ladinian (Scandone 1967; Panzanelli Fratoni *et al*. 1987; Miconnet 1988; Rettori *et al*. 1988; Martini *et al*. 1989; Ciarapica 1990; Ciarapica *et al*. 1990a,b,c; Panzanelli-Fratoni 1991; Marsella *et al*. 1993; Ciarapica & Passeri 2000), however Guido *et al*. (2021), considering the strong similarity of the microfacies with those of the typical Anisian carbonate sequences of Southern Alps (Gaetani *et al*. 1981; Gaetani & Gorza 1989) suggest a similar age also for the 'La Cerchiara' carbonate units. Along the section, the carbonate interval is followed by brown shales, alternating with turbiditic sandstones and conglomerates dated to the Late Ladinian (Ciarapica & Passeri 2000). This succession records the change from shallow to deep-water environments during the Middle Triassic evolution of the Lagonegro Basin. The remaining portion of the succession mainly consists of shales and radiolarites, alternating with gravity-induced deposits, such as olistoliths, breccias and slide deposits (Late Ladinian). The final part of the section consists of alternating pelagic limestones and shales that characterize the transition towards the overlying 'Calcari con Selce' Formation.

This research is focused on the carbonates of the lower part of the 'La Cerchiara' outcrop, represented by the superimposition of four intervals: Unit IIIa (110 m thick), Unit IIIb (64 m), Unit II (6 m) and Unit I (42 m), interposed by 10–20 m thick shale deposits (Figs 2, 3).

Even though these carbonate units suffered tectonic deformation, they have been interpreted as parts of a single build-up, characterized by the absence of a primary skeletal framework and by the great abundance of microencrusters, microbialites and synsedimentary cements (Guido *et al*. 2021). The build-up records the evolution from the distal slope facies, located on the western part of the succession (Units IIIa and Unit II) to syndepositionally cemented and bioconstructed upper slope/margin deposits on the eastern part (Unit IIIb and Unit I). The bioconstructed facies are characterized by a large amount of primary cements that represent the focus of this research.

Microfacies distribution in the build-up

Quantitative analyses of the microfacies of the 'La Cerchiara' carbonates allowed Guido *et al*. (2021) to reconstruct the depositional geometry and the palaeoenvironmental setting and to recognize a microbial-mound style of growth of the build-up. In this study, allochthonous facies were recognized in the lower part of the succession (distal slope) that evolved in autochthonous facies toward the upper slope/margin.

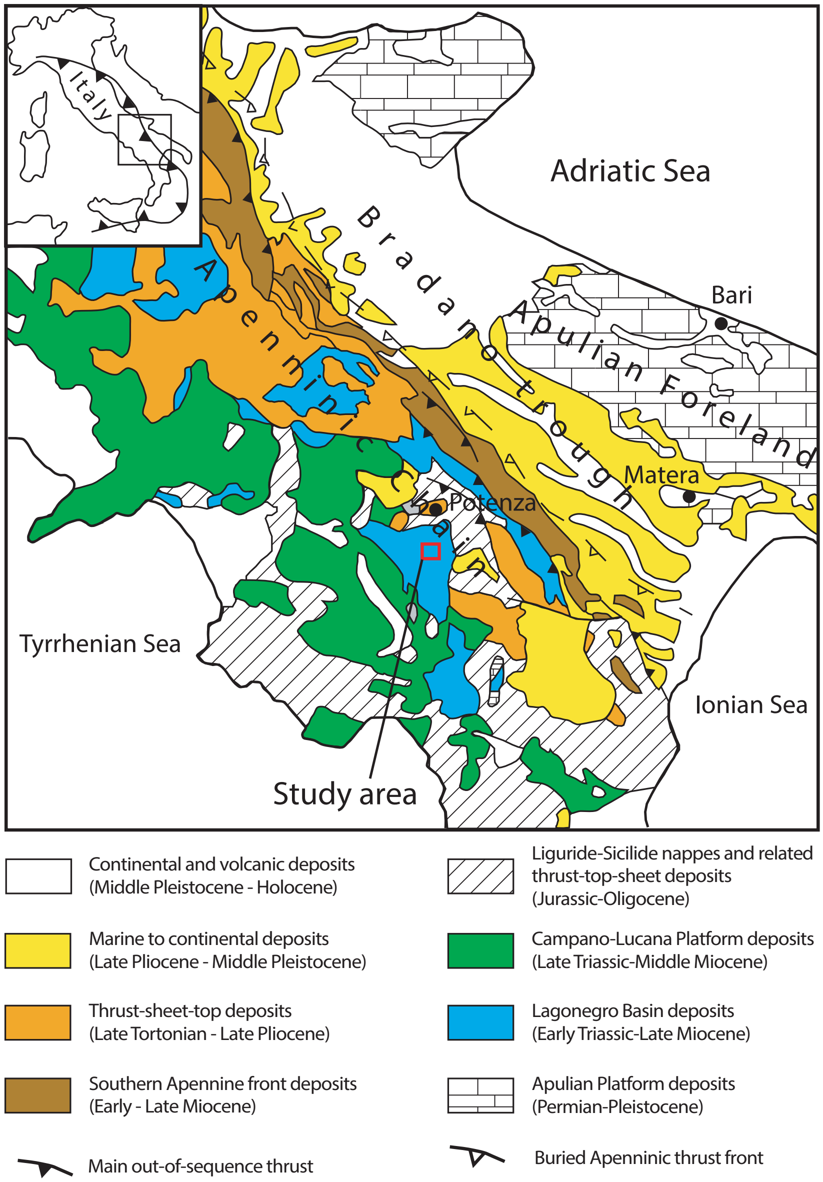

Fig. 1. Simplified geological map of the Southern Apennines thrust-belt in the Campano-Lucano sector, showing the location of the study area. Modified from Patacca *et al.* (1992).

Allochthonous microfacies of the distal slope. – Unit IIIa and Unit II represent the distal slope portion of the build-up (Guido *et al.* 2021). Textures vary from wackestone to packstone, with densely packed allochthonous micrite (Fig. 4). Carbonate grains are mainly detrital in origin, represented by intraclasts derived from the bioconstructed facies of the upper margin. They are boundstone fragments, mainly composed of microproblematica (*Tubiphytes* sp., *Baccanella floriformis*), cyanobacterial crusts (*Girvanella* sp.) and autochthonous micrite. Skeletal grains are also present: green algae, thin-shelled bivalves and occasional fragments of calcisponges, gastropods and polychaeta. Few microbialite crusts occur as well, cementing and stabilizing the medium-fine allochthonous components.

Bioconstructed upper slope/margin microfacies. – Unit IIIb and Unit I represent the upper slope/margin facies of the build-up (Guido *et al.* 2021). The main texture is a boundstone (Fig. 5), forming a three-dimensional framework supported mainly by autochthonous micrite (microbialite) and microencrusters (microproblematica and cyanobacteria) (Figs 5, 6). The organic origin and syndepositional cementation of the micrite is testified by fine-grained, light and dark wavy-wrinkled laminations forming crusts with antigravitative fabric.

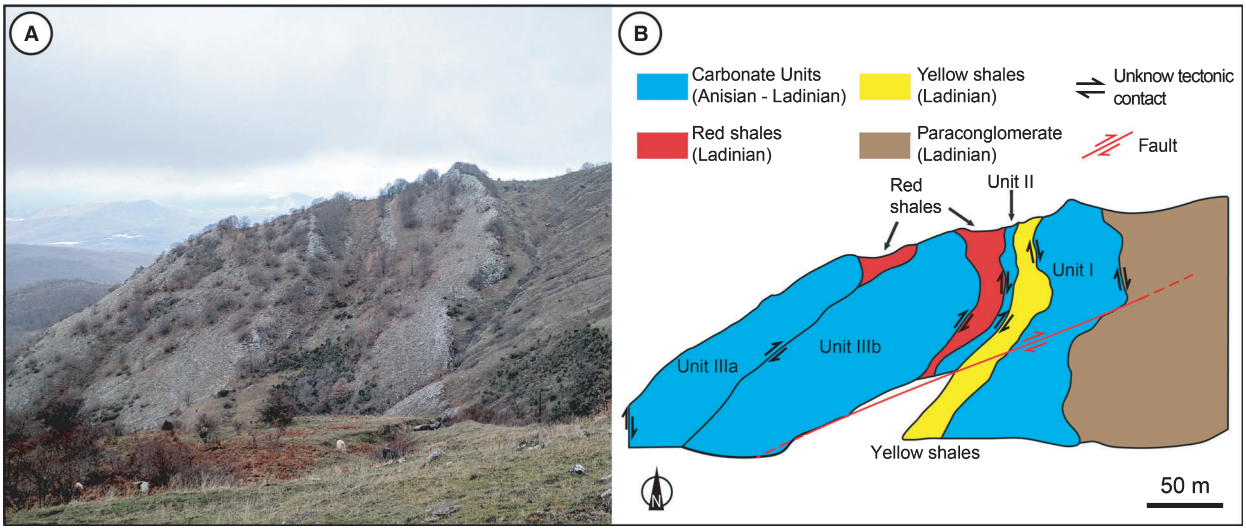

Fig. 2. A, panoramic view of the 'La Cerchiara' section. B, simplified line drawing showing the distribution of the main lithologies. Modified from Guido *et al.* (2021).

Microbialite laminations display microcolumnar structures, resembling microstromatolites. Other microbialite fabrics are represented by peloidal to clotted peloidal micrite, often associated with cyanobacteria, microproblematica, sponges, agglutinated polychaeta and aphanitic micrite, combined with microencrusters. Subordinate skeletal fragments can be found in association with microbialites, such as dasycladacean algae and agglutinated polychaeta. Gravitative fillings of detrital micrite derived from the erosion of the boundstone are also present. The microbialite framework is reinforced by abundant crusts of isopachous polyphasic cements, millimetric in thickness (Fig. 6), which represents the main focus of the current research. Secondary druse cements, filling residual microcavities, are also present.

Material and methods

Selected samples were cut into small blocks (5 × 3 × 1 cm), and from each, an uncovered thin section (48 × 28 mm) and a polished slab have been obtained. Both thin sections and polished slabs have been observed by a Zeiss Axioplan 2 Imaging optical microscope, up to 40× magnification, and subsequently analysed for UV-epifluorescence. Polished slabs were further analysed by micro-Raman spectroscopy.

UV-Epifluorescence

A Zeiss Axioplan optical microscope, outfitted with a Hg vapour lamp and a high-performance wide band pass filters (BP 436/10 nm/LP 470 nm for green light; BP 450–490 nm/LP 520 nm for yellow light) was utilized to observe carbonate epifluorescence, to reveal the distribution of the organic matter (Neuweiler & Reitner 1995; Russo *et al.* 1997). Residual organic matter as well as Mn^{2+} appear to be the most abundant and important activators of fluorescence in calcite and dolomite. Organically activated luminescence is interpreted to be caused mainly by aromatic and certain conjugated organic molecules. In the present study, the absence of inorganic activators and the presence of organic bands in Raman spectra confirm the attribution of the epifluorescence to biomolecules strictly related to the crystals of the primary cements.

Micro-Raman spectroscopy

Raman spectroscopy allows the identification of the mineral matrix in samples through the detection of characteristic wavelengths with specific intensities (Greco *et al.* 2018). Raman spectroscopy is a non-destructive technique that allows to perform rapid *in situ* analyses prior to the eventual application of more expensive and destructive tests (Sauerer *et al.* 2017; Schmidt *et al.* 2017; Henry *et al.* 2018, 2019; Khatibi *et al.* 2018b; Schito & Corrado 2018; Wilkins *et al.* 2018). Mineral identification is accomplished through the comparison of the acquired spectra with those stored in databases (Giarola *et al.* 2012; Bloise *et al.* 2018; Miriello *et al.* 2018). In addition, confocal micro-Raman spectroscopy can be applied to characterize solid, liquid, or gaseous inclusions within samples (Frezzotti *et al.* 2012); for example, this

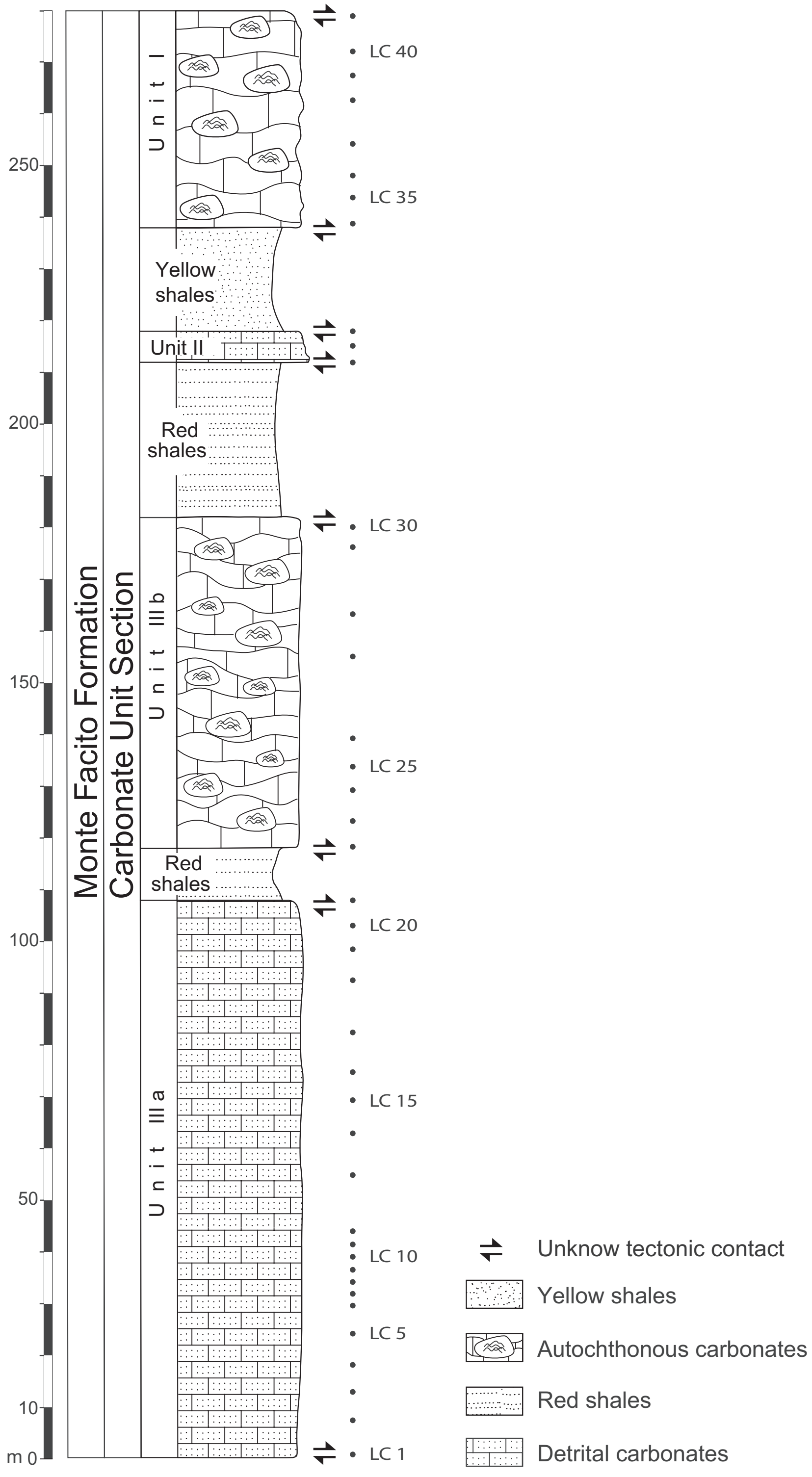

Fig. 3. Stratigraphical column with the positions of the studied carbonate samples. Detrital carbonates characterize the lower part of the succession (Unit IIIa and Unit II), whereas autochthonous carbonates predominate in the upper part (Unit IIIb and Unit I). Modified from Guido *et al.* (2021).

technique has been utilized to characterize amorphous materials and non-crystalline molecules within rocks, allowing the discrimination between different types of carbonaceous materials and other non-crystalline organic or inorganic compounds within rocks (Greco *et al.* 2018).

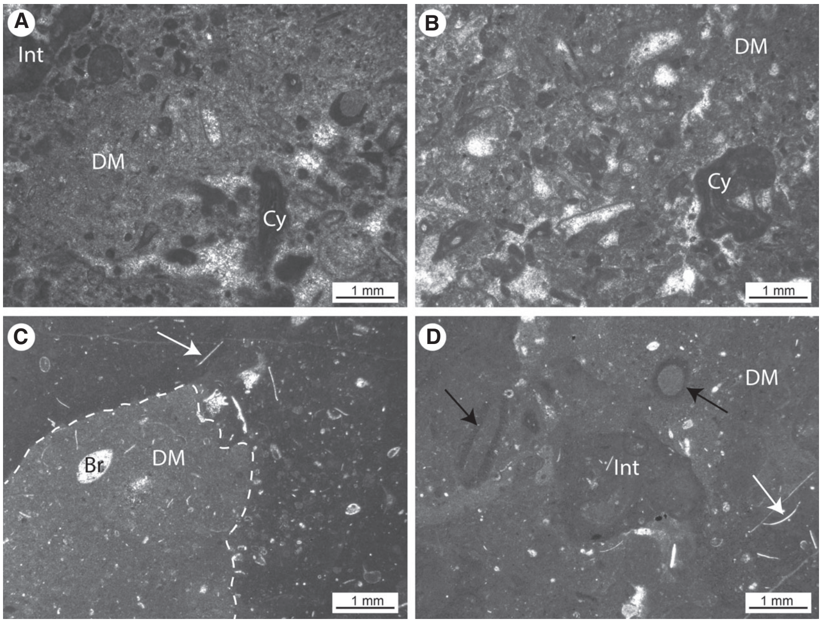

Fig. 4. A–D, detrital facies of Unit IIIa and Unit II dominated by allochthonous micrite (DM) and with the presence of intraclasts (Int), brachiopods (Br), terebellids (black arrows), fragments of thin-shelled bivalves (white arrows) and cyanobacterial crusts (Cy). The allochthonous micrite shows traces of bioturbation (dashed line).

Raman spectroscopy has been also proved useful for the characterization of mineralizations induced or influenced by biotic activities, for example, in the study of stromatolites and microbial mats (Allwood *et al.* 2006; Ferretti *et al.* 2012). Greco *et al.* (2018) applied this method to recognize and characterize ancient microbial remains within Archean meta-sedimentary rocks. Recently, Guido *et al.* (2018), by this technique, were able to ascertain the role of microbialites in dolomitization processes in Carnian carbonates from the Dolomites. Raman spectroscopy was successfully utilized also to investigate and compare microbial metabolic mediation involved in microbialite deposition in modern submarine caves and in Triassic patch reefs (Guido *et al.* 2019a). In these studies, Raman methodology was applied to characterize and prove the biogenicity of micromorphologies in which the contribution of bacteria was already implied by specific fabric, notably thin wrinkled laminations, peloidal and clotted peloidal micrite with gravity-defying fabric and aphanitic micrite. Differently from these studies, here we apply micro-Raman spectroscopy to detect the influence of biological activity, or of decaying organic matter in mineralization products that do not show any specific microbial-related morphologies and that are not generally attributed to biomineralization processes (i.e. primary cements). In geomicrobiological studies that utilize destructive methodologies like XRD or GC-MS analyses, the lack of knowledge of the exact original position of the organic molecules makes difficult to associate mineral precipitates to the presence of particular microbes and specific biogeochemical pathways. On the contrary, Raman spectroscopy allows *in situ* measurements on polished slabs and thin sections and enables areal detection of organic matter preserved within the complex mineral matrix at microscopic level without extraction. This technique has proved to be a unique tool to distinguish biominerals from precipitates not directly mediated by microorganisms or organic matter (Leefmann *et al.* 2014). For this reason, we applied Raman spectroscopy for *in situ* investigation of organic compounds involved in cements mineralization following the approach described by Leefmann *et al.* (2014), Greco *et al.* (2018) and Guido *et al.* (2018, 2019a).

Micro-Raman analyses were performed using a Thermo Fisher DXR Raman microscope (Waltham, MA, USA), equipped with OMNICxi Raman Imaging software 1.0, an objective of 50x, a grating of 900 ln/mm (full-width at half-maximum, FWHM), and an electron multiplying charge-coupled device (EMCCD). The 532 nm line (solid-state laser) was used at an incident power output ranging from 1.8 to 7 mW. The spatial resolution of the laser beam was about 3–5 µm. The acquisition time of the spectra varied from 5 to 40 s. Data were collected in the 50–3360 cm^{-1} range to capture the first-order and second-order Raman bands. The measurements were collected on randomly oriented grains with a fixed orientation of the polarized laser beam.

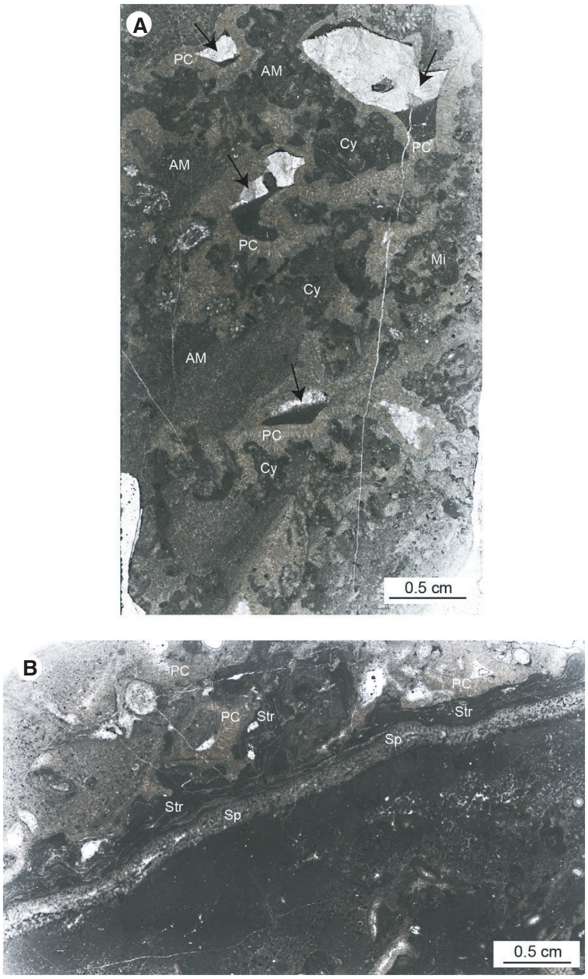

Fig. 5. Boundstone microfacies of the Units IIIb and I. A, microbial/microencrusters boundstone showing a framework rich in autochthonous micrite (AM), cyanobacterial crusts (Cy) and microproblematica (Mi). The microstructure is reinforced by primary cements (PC). Cavities, outlined by primary cements show geopetal fillings (black arrows). B, microbial/skeletal boundstone showing a framework formed by microbialite with stromatolitic texture (fine wrinkled laminations, Str), Calcisponge (Sp) and primary cements (PC).

Even though the occurrence of high intensity fluorescence complicates the identification of individual Raman-active vibrational modes, making the corresponding Raman bands more difficult to detect, we were able to identify the main organic matter peaks within the microbialite and cement mineral phases.

Results

Micromorphology and epifluorescence analysis of the primary cements

Polished samples show fibrous calcite cements arranged in bands of different thickness (ranging in size from millimetre to centimetre) and colours (cloudy and whitish; Fig. 7). In UV-excitation this component reveals high epifluorescence (Fig. 8). Isopachous cements occlude the primary porosity of the build-up structure and formed on various substrates. Often, they mineralize in the microcavities of the microbialite/microencrusters framework (Fig. 6), representing a secondary supporting component of the boundstone, or deposited on the surface of the grains, playing in this case a primary role in the boundstone formation. The early mineralization of the isopachous cements is testified by their geopetal structure (Fig. 5A). Microcavities within the microbialite/microencrusters framework were lined by subsequent generations of isopachous rims (Fig. 9). The crystals of the isopachous fibres range in length from tens to hundreds of microns (Figs 8, 9). In the residual cavities, detrital micrite is deposited, following a gravitative filling and showing gradated laminations (Fig. 9A, B). The cavities were subsequently filled by late sparry calcite showing drusa micromorphologies (Figs 6A, 9A).

The boundary between the cloudy and whitish bands is not always well-defined due to aggrading recrystallization processes (Fig. 9G–I). The alternance of cloudy and whitish bands sometimes displays wrinkled laminations, mimicking a microstromatolitic fabric (Fig. 7). These microstructures, here named microstromatolitic isopachous cements, show whitish bands ranging in size from 50 to 300 μm and cloudy bands from 15 to 50 μm (Figs 7, 8). Under UV-excitation, this alternance exhibits a variable distribution of the epifluorescence. The cloudy bands are characterized by bright fluorescence in comparison to the whitish, which show no evidence of epifluorescence (Figs 8, 9). This feature is linked to biomolecules strictly associated with the crystals forming the areas with cloudy aspect.

Biochemical characterization of the primary cements with micro-Raman spectroscopy

Raman spectra of the isopachous cements were compared with those of the autochthonous micrite Raman spectra were collected also from detrital micrite and secondary cements (Fig. 10).

The band positions of the spectra match the values of calcite reference bands. The detected peaks are located in the range between 50 and 3360 cm^{-1}. The main calcite peaks correspond to the symmetric stretching (ν1) of the CO_3 group at ~1100 cm^{-1}, asymmetric stretching (ν3) at ~1450 cm^{-1} and symmetric deformation (ν4) at ~710 cm^{-1}. The lower wave numbers of calcite (~280 cm^{-1}) arise from the external

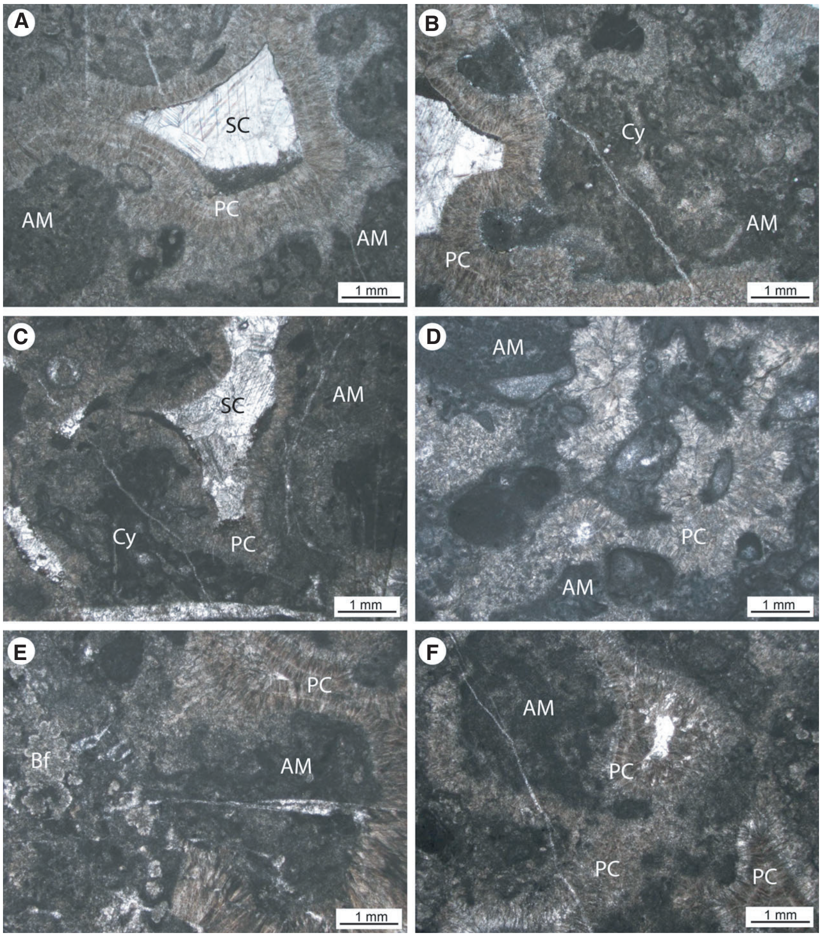

Fig. 6. A–F, microbialite-microencrusters boundstone textures of the upper slope/margin facies. Note the abundance of primary cements (PC) contributing to the stabilization of the bioconstruction together with autochthonous micrite (AM), cyanobacterial crusts (Cy) and microproblematica (Bf: *Baccanella floriformis*). Late sparry calcite (SC) fill the residual cavities.

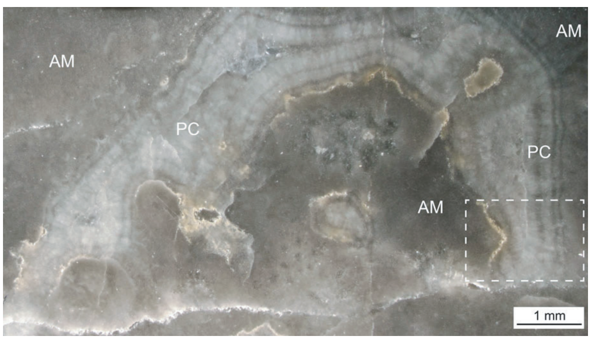

Fig. 7. Photo of a polished plane slab showing a microcavities inside the autochthonous micrite (AM) filled by primary cements (PC). Primary cement is formed of wrinkled cloudy and whitish bands mimicking microstramatolitic fabric. Dashed rectangle represents the area analysed by Raman spectroscopy in Figure 11.

vibration of the CO_3 group that involve translatory oscillations of the group. The four prominent absorption bands were recorded in the analysed samples around 150, 280, 710 and 1085 cm^{-1} (Fig. 10). Minor shifts in the positions of the calcite bands between the analysed samples and the spectra published in literature may be due to the effects of natural impurities present in the sample (Buzgar & Apopei 2009; Guido *et al*. 2018, 2019a; Miriello *et al*. 2018).

The autochthonous micrite and cloudy laminae of isopachous cements show a distinctive peak around 1600 cm^{-1} related to the presence of G-bands, and minor peaks at 1340 cm^{-1} related to the D-band (Fig. 10). These peaks are characteristics of the amorphous carbon (AM) and record the presence of residual organic matter in the autochthonous micrite and in the cloudy isopachous cements. The micro-Raman data confirm that the bright fluorescence of these components is related to the presence of organic matter strictly connected with the carbonate crystals. These bands were not recorded in the spectra of the detrital micrite, sparry drusa calcite and whitish band of the isopachous cements (Figs 10, 11).

In particular, within the microstromatolitic isopachous cements the distribution of organic bands

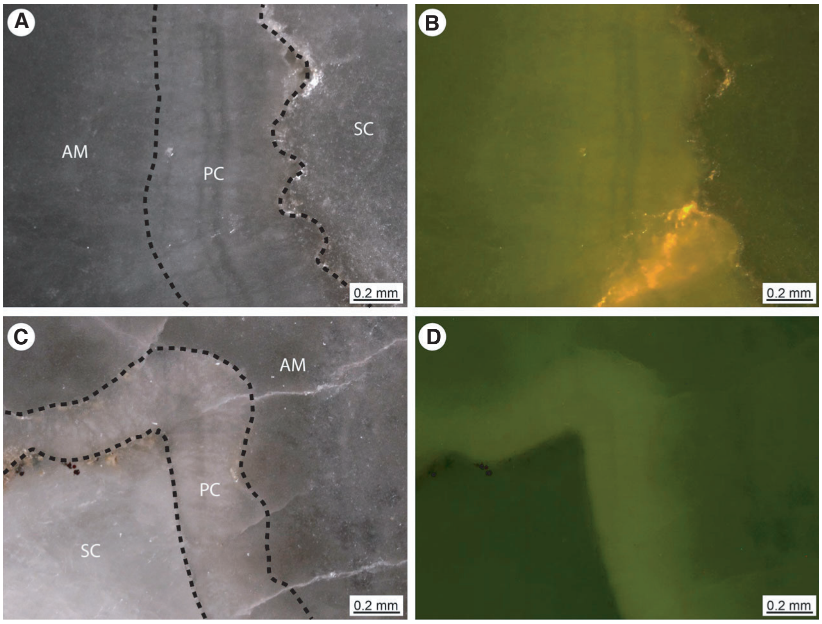

Fig. 8. Photos in reflected (A, C) and ultraviolet light (B, D) attained on polished plane slabs. Autochthonous micrite (AM), primary cements (PC) and late cements (sparry calcite, SC) denote different behaviour under UV-excitation. The organic rich primary cements and autochthonous micrite show bright epifluorescence, whereas inorganic sparry calcite appears dark.

follows the alternance of the microlaminae (Fig. 11). G- and D-bands were recorded only in the cloudy laminae, whereas the whitish laminae do not show any organic bands (Fig. 11). The spectra of these components are characterized also by small bumps in the region between 450 and 850 cm^{-1} and in the region between 1250 and 1650 cm^{-1} (Fig. 11). It is worth to note that these bumps are only present in concomitance with G- and D-bands and they are absent in the spectra of detrital micrite, sparry drusa cements and whitish laminae of the isopachous cements.

Interpretation and discussion

Microbial activity and autochthonous micrite production

One of the main hydrogeochemical parameters regulating the carbonate precipitation is pH. Actually, a rise in pH may contribute to the increase of bicarbonate, enhancing the precipitation of $CaCO_3$ (Reimer & Arp 2011). Precipitation is a function of both carbonate alkalinity and availability of free calcium, which are combined in the saturation index (Dupraz *et al.* 2009). Various processes can increase carbonate alkalinity promoting carbonate precipitation. Alkalinity may be influenced by extrinsic factors like the physicochemical parameters of the macroenvironment, or by intrinsic factors like microbial communities altering their immediate microenvironment through their metabolism (Arp *et al.* 2001, 2003; Dupraz *et al.* 2009). Different metabolic pathways can lead to the formation of organominerals, in which environmental conditions have a direct influence, particularly by controlling the potential impact of microbial metabolism on mineral products. For example, photosynthesis promotes precipitation but only under specific environmental conditions (e.g., low content of dissolved inorganic carbon and high amount of calcium) (Merz-Preiß & Riding 1999; Arp *et al.* 2001; Dupraz *et al.* 2009).

The ‘La Cerchiara’ carbonates are a classic example where microbial activity represents the main process involved in autochthonous micrite production and build-up growth. Microbialites and microencrusters are the main framework constituents in the build-up (Figs 5, 6) together with primary cements that contribute to stabilize the bioconstruction (Figs 5–9). The close coexistence within this system of autochthonous micrite and primary cements allows us to compare the processes leading to their deposition.

Production and accumulation of autochthonous micrite suggest the presence of high amount of organic matter. This biomass promoted the activity of heterotrophic bacteria whose metabolism induced the precipitation of autochthonous micrite. Autochthonous micrite has commonly been associated with anaerobic bacteria thriving in cryptic cavities characterized by suboxic to anoxic conditions.

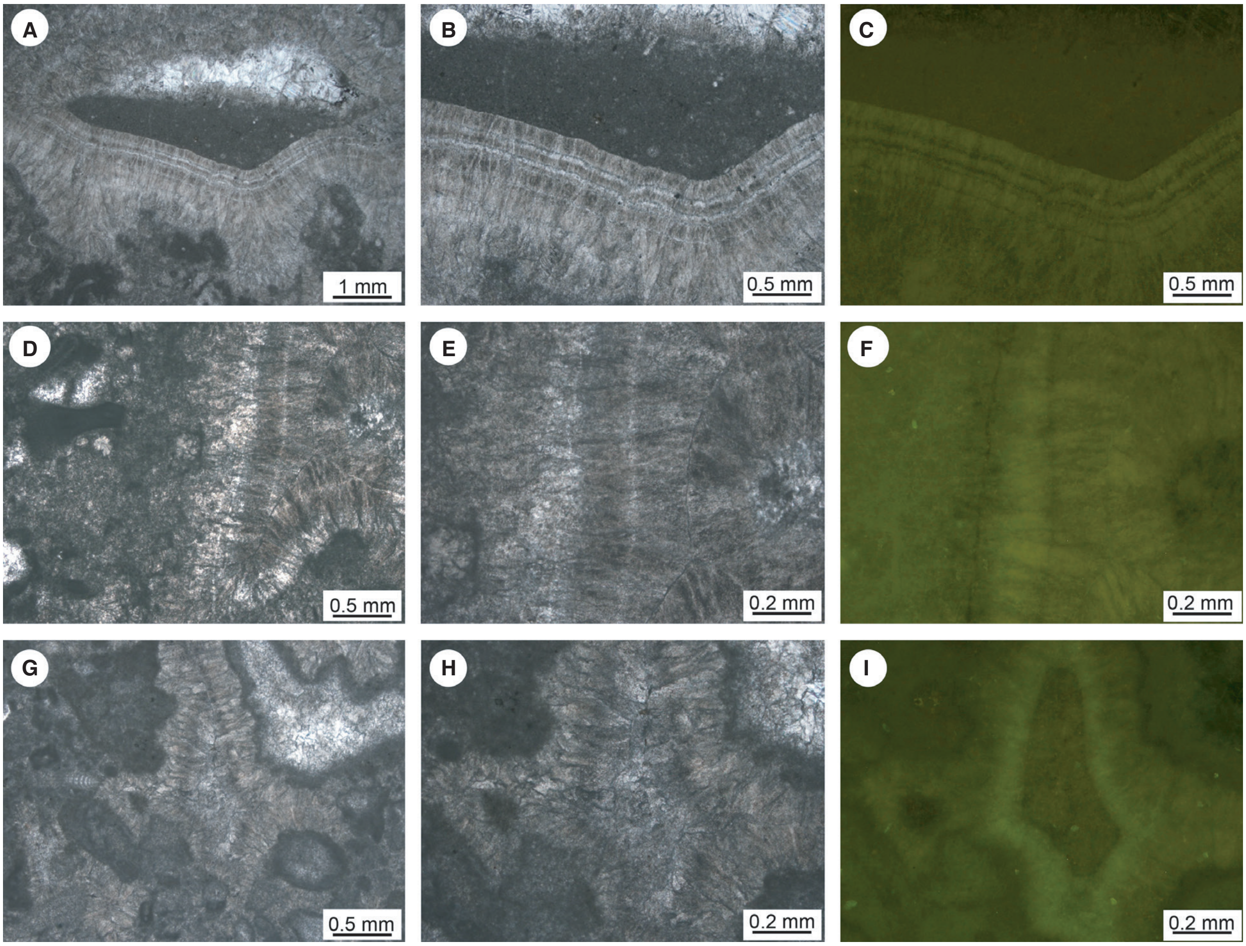

Fig. 9. Primary cements (A, D) and relative details (B, E) observed in transmitted light, and UV-Epifluorescence (C, F). The cements are characterized by alternation of cloudy (epifluorescent) and whitish (not-fluorescent) bands. The boundary between the cloudy and whitish bands is not always well defined, due to aggrading recrystallization processes that, sometime, seems to have displaced the organic remains from the original position (G–I).

Organic matter enrichment contributes to the feeding of sulphate-reducing bacteria in oxygen-poor cavities. Microbial sulphate reduction raises pH and increases alkalinity, while the negatively charged bacterial cell surface can serve as a nucleation surface for carbonate mineral growth. Production of exopolymeric substances (EPS) around the bacterial cells also aids the nucleation and the subsequent precipitation of calcium carbonate (Monty 1976; Chafetz 1986; Buczynski & Chafetz 1991; Reitner 1993; Kazmierczak *et al.* 1996; Folk & Chafetz 2000; Arp *et al.* 2001, 2003; Riding 2002; Riding & Tomás 2006).

Suboxic conditions indicated by the organic-rich autochthonous micrite in the 'La Cerchiara' section suggest the development of local stressed micro-environments within the cavities of the build-up framework. Seawater conditions were normal, as indicated by the presence of algae and cyanobacteria, but locally developed confined microcavities, characterized by restricted water circulation and low oxygen content (Guido *et al.* 2021). Similar redox conditions have been described by Sánchez-Beristain & López-Esquivel Kranksith (2011) for the microbialite deposition of the St. Cassian Formation, and by Tosti *et al.* (2014) for the microenvironments inside the skeletal framework of the Carnian patch reefs of Alpe di Specie, in the Italian Dolomites. Comparable microbialites in the Pleistocene–Holocene reef at Tahiti contain lipid biomarkers indicating a bacterial community dominated by sulphate-reducing bacteria (SRB) that degraded organic matter (Heindel *et al.* 2010, 2012). Similarly, the involvement of SRB in autochthonous micrite precipitation was recognized in cryptic bioconstructions of recent (Guido *et al.* 2012, 2013, 2016, 2017a) and Pleistocene (Guido *et al.* 2017b) submarine caves.

Kershaw *et al.* (2012) identified several microbialitic facies developed after the Permian extinction

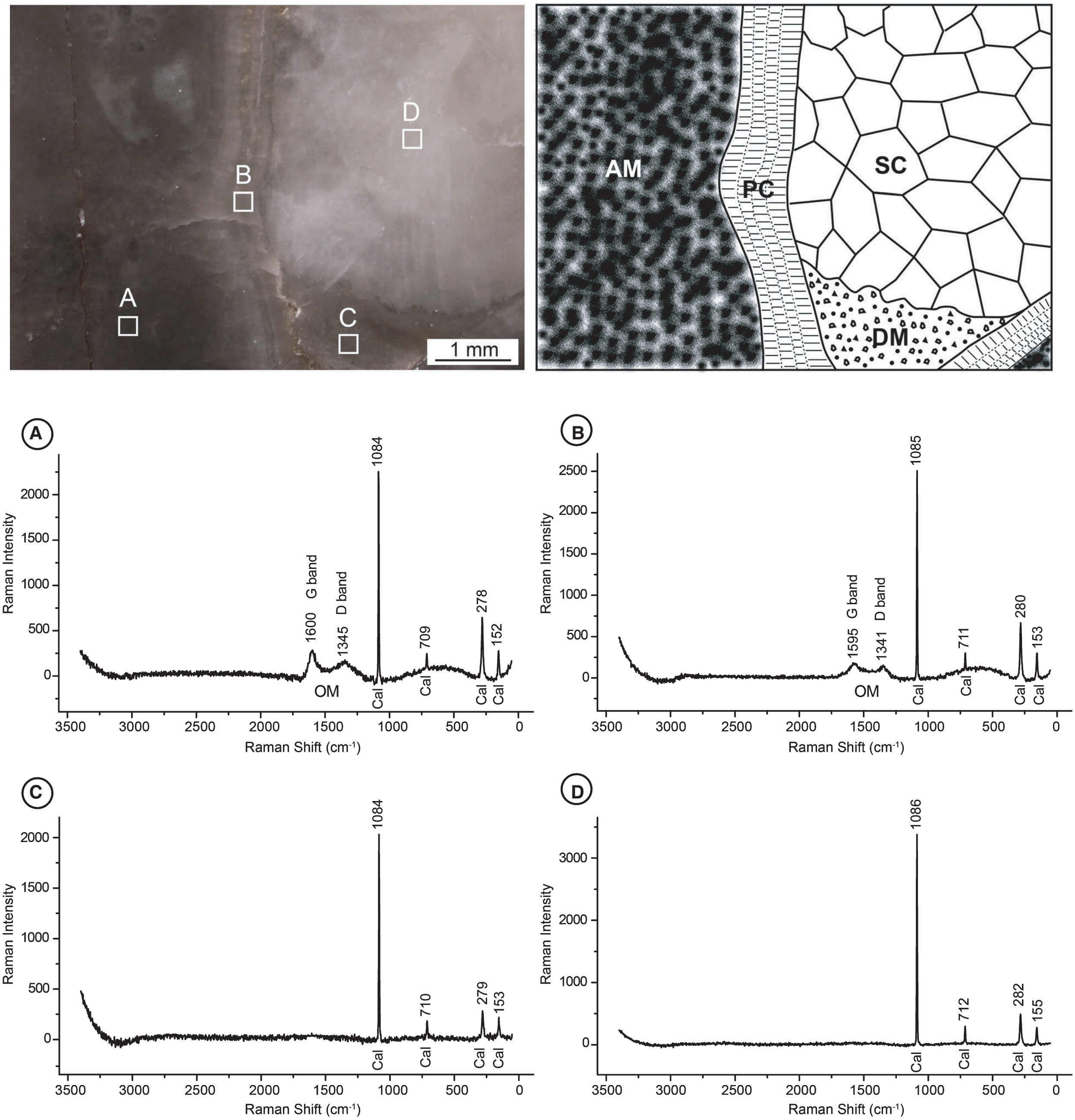

Fig. 10. Polished slab and relative simplified sketch, showing autochthonous micrite (AM), detrital micrite (DM), primary cements (PC) and secondary cements (SC). The squares indicate the areas analysed by micro-Raman spectroscopy. The Raman spectra obtained on the autochthonous micrite (A) and primary cements (B) show the G- and D-bands of the organic matter (OM) and the typical calcite picks (Cal). On the contrary, the Raman spectra obtained on the detrital micrite (C) and secondary cements (D) show only the peaks of calcite minerals (Cal).

in the low-latitude Tethys Ocean, with similar characteristics to those of 'La Cerchiara'. Permian-Triassic boundary microbialites (PTBMs; *sensu* Kershaw *et al*. 2012) represent the replacement by cyanobacteria-dominated communities of a complex trophic system that dominated the Late Permian reefs. Most microfacies observed in the 'La Cerchiara' build-up have similar features to the PTBMs described by Kershaw *et al*. (2012). In fact, the boundstones display a clotted appearance, with micrites and skeletal grains arranged in a very complex and irregular texture. These boundstones have been probably generated by the interplay of encrusting and microproblematic organisms with

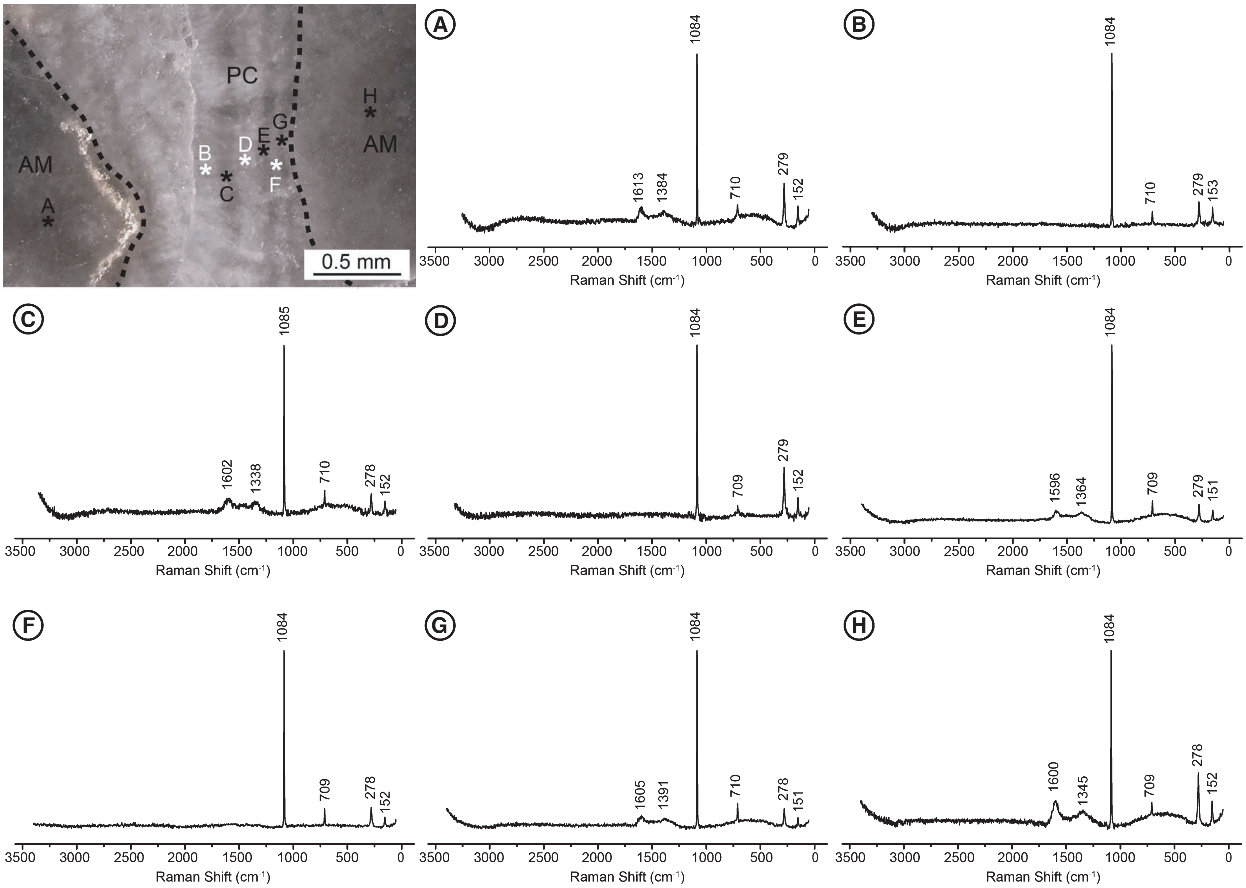

Fig. 11. Detail of the primary cement of Figure 7 (dashed rectangle) with location of microareas, in the autochthonous micrite (AM) and primary cement (PC), analysed by Raman spectroscopy. Cloudy laminae of the primary cement (c, e, g) show similar bands of autochthonous micrite (A, H); together with the calcite picks they shows the G- and D-bands of organic matter. Whereas the whitish laminae of the primary cements (B, D, F) show only the peaks of the calcite minerals, similarly to the spectra of secondary calcite and detrital micrite of the Figure 10.

microbialites that during the initial phases of colonization, stabilized the sediment, forming small millimetre cavities usually filled by micrites and primary cements (Fig. 6). The effects of the end-Permian mass extinction have been clearly recognized also in the microfacies association of Cipit boulders of the St Cassian Formation (NE Italy); also in this case, the microencrusters diversity and abundance played an important role for the development of Early and Middle Triassic reef systems (Sánchez-Beristain & Reitner 2018a, 2018b, 2019). The abundance of primary cements in the 'La Cerchiara' carbonate units (Figs 5–9), as well as the reduced amount of skeletal organisms represent the more significant difference in comparison to the Anisian facies of the Dolomites described by Fois & Gaetani (1984). The studied units show similarity also with Middle Anisian carbonates cropping-out in southeastern Romania (Popa *et al*. 2014) that consist of microbialitic boundstones, allochthonous micrite, and *Tubiphytes*, reinforced by large volumes of marine cements.

Organic matter characterization and comparison between microbialites and primary cements

Two distinct Raman bands of graphite were first published by Tunistra & Koenig (1970): the disordered (D) and graphite (G) bands. This pioneering paper was followed by numerous researches in which the specific bands of organic matter were identified in greater detail (see Henry *et al*. 2019 and reference therein). Organic matter is characterized by peaks in two region of the spectra: the first-order region (1000–1800 cm^{-1}) and the second-order region (2400–3500 cm^{-1}) (Wopenka & Pasteris 1993; Yui *et al*. 1996; Beyssac *et al*. 2002; Pasteris & Wopenka 2003; Hu *et al*. 2015; Henry *et al*. 2019). In the first-order region, two predominant peaks can be detected: the disordered (D) band (1340–1360 cm^{-1}) and the graphite (G) band (c. 1580 cm^{-1}) (Pasteris & Wopenka 1991; Wopenka & Pasteris 1993; Hu *et al*. 2015). The G-band is related to the in-plane vibration of carbon atoms in graphene sheets with E2g2 symmetry (Tunistra & Koenig 1970; Jehlička & Beny 1999; Henry *et al.* 2019). The D-band is related to disordered amorphous organic matter and is associated with structural defects and heteroatoms (Beny-Bassez & Rouzaud 1985; Henry *et al.* 2019). It has been described as the breathing motion of the sp2 atoms in an aromatic ring with a A1g symmetry mode vibration (Tunistra & Koenig 1970). The intensity of these bands is variable and depends by the organic matter maturity (Henry *et al.* 2019). In particular, the D-band should be deconvoluted in additional small bumps and asymmetric bands, the nomenclature and origin of which are conflicting (Beyssac *et al.* 2002; Li *et al.* 2006; Romero-Sarmiento *et al.* 2014; Ferralis *et al.* 2016; Schito *et al.* 2017; Henry *et al.* 2018, 2019). The second-order region is taken into account for samples that have undergone metamorphism. As for the first-order, even this region is characterized by different bands with different evolutionary paths from disordered to ordered organic matter (Pasteris & Wopenka 1991; Wopenka & Pasteris 1993; Cuesta *et al.* 1994; Spötl *et al.* 1998; Jehlička & Beny 1999; Beyssac *et al.* 2002; Jehlička *et al.* 2003; Rantitsch *et al.* 2004; Zeng & Wu 2007; Liu *et al.* 2013; Yuman *et al.* 2018; Henry *et al.* 2019).

The organic matter bands can be detected on different types of geological materials, as discussed by Henry *et al.* (2019): polished rock cut-surfaces and thin sections (Beyssac *et al.* 2003; Rahl *et al.* 2005; Allwood *et al.* 2006; Quirico *et al.* 2011; Mathew *et al.* 2013; Hinrichs *et al.* 2014; Wilkins *et al.* 2014; Henry *et al.* 2018), strew slides (Schmidt *et al.* 2017; Baludikay *et al.* 2018; Henry *et al.* 2018; Khatibi *et al.* 2018a) and rock chips (Muirhead *et al.* 2017; Sauerer *et al.* 2017; Henry *et al.* 2019).

In the studied Anisian carbonates, autochthonous micrite and primary cements show specific organic matter bands (Fig. 10). These organic compounds associated with the crystals suggest their biological induced or influenced mineralization. The G- and D-bands were recorded only in the microbialite components (autochthonous micrite) and primary cements, whereas they are absent in the detrital micrite and secondary (drusy) cements, implying in this case a pure abiotic mineralization (Fig. 10). The difference among the spectra of the various boundstone components is consistent with the distribution of the UV-epifluorescence and confirm that the bright fluorescence of microbialite and cloudy bands of primary cements is generated by their organic nature. The presence of small bumps in the region 450and 850 cm^{-1} and in the region between 1250 and 1650 cm^{-1}, only in the spectra of microbialites and primary cements, agree with an organic nature of these components (Fig. 10). Actually, this peculiar behaviour of Raman spectra was recorded only for sample rich in disordered organic matter (Beyssac *et al.* 2002; Li *et al.* 2006; Romero-Sarmiento *et al.* 2014; Ferralis *et al.* 2016; Schito *et al.* 2017; Henry *et al.* 2018, 2019).

The high intensity of the G-bands in comparison to the D-bands (Fig. 10) is related to the thermal evolution of the organic compounds (Henry *et al.* 2019). The organic matter suffered graphitization processes but minor disordered amorphous organic matter is still present and further investigation with characterization of the biomarker in GC-MS could elucidate the specific biogeochemical pathways involved in the microbialite formation and primary cements mineralization.

Primary marine cements as new tool to detect biomineralization

The UV analyses show the alternation of bright-fluorescent and non-fluorescent bands of the primary cements. The fluorescence indicates the presence of organic matter strictly connected to the crystals (Fig. 9). These organic compounds are autochthonous biomolecules, trapped among or inside the crystals during biomineralization process induced by microbial activity or influenced by organic matter decay in confined microsystems. A similar genetic origin has been suggested for cements known as 'evinosponges' in the Upper Anisian–Ladinian Marmolada Platform of Dolomites (Russo *et al.* 2006), although the cements in the 'La Cerchiara' section show a smaller size. The epifluorescence results and the occurrence of spherical bodies sub-micrometre in size (100–300 nm) suggest that they could have been formed via organic matter and/or microbial mediation (Russo *et al.* 2006).

Numerous organisms can induce carbonate precipitation (Chafetz 1986; Simkiss & Wilbur 1989; Addadi & Weiner 1992; Chafetz & Buczynski 1992; Neumeier 1998), either directly, by biochemical processes, or indirectly, through changes of the surrounding chemical microenvironments or by the trapping of dissolved Ca^{2+} onto organic templates (Lowenstam & Weiner 1989). Many experiments were carried out to unravel the mechanisms and metabolic pathways involved in biominerals formation (e.g., Castanier *et al.* 1997, 1999; Reid *et al.* 2000; Visscher *et al.* 2000; Reid *et al.* 2003; Dupraz *et al.* 2004, 2009). Autotrophic pathways induce carbonate precipitation by increasing pH through removal of CO_2 (Ehrlich 1996). Heterotrophic processes induce carbonate formation via ammonification of amino acid or nitrate/sulphate reduction leading to an increased pH (Chafetz & Buczynski 1992; Ehrlich 1996; Castanier *et al.* 1997, 1999; Neumeier 1998; Reid *et al.* 2000, 2003; Visscher *et al.* 2000; Dupraz *et al.* 2004, 2009). A biomineralization model based on the interaction of acidic organic macromolecules with inorganic compounds has been proposed studying the microbialites of reef cavities and modern atolls (Reitner 1993; Reitner & Neuweiler 1995; Reitner *et al.* 1996; Camoin *et al.* 1999; Sprachta *et al.* 2001; Gautret *et al.* 2004; Heindel *et al.* 2010, 2012). The role of decaying organic matter in biomineralization processes has been debated and a carbonate precipitation influenced by non-living organic substrates has been proposed (Leinfelder & Keupp 1995; Reitner & Neuweiler 1995; Reitner *et al.* 1995; Pickard 1996; Pratt 2000; Neuweiler *et al.* 2003; Reolid 2007, 2010; Guido *et al.* 2019b). Acidic amino acids, particularly humic and fulvic acids that may derive from degraded metazoan organic matter during early diagenesis may promote carbonate mineral nucleation, because Ca^{2+}-binding carboxyl groups, which are structurally similar to CO^{2-} anions in carbonates, may correspond to the lattice spacing of carbonate minerals. Hence, the binding of Ca^{2+} cations to these carboxyl groups may overcome barriers to nucleation, thereby inducing precipitation (Mitterer & Cunningham 1985; Neuweiler *et al.* 1999, 2007; Webb *et al.* 1999; Wood 2001; Shen & Neuweiler 2018). The processes reported in these studies clearly demonstrate the close relationship between carbonate biominerals and the occurrence of organic matter. This association is documented in our case through epifluorescence observations and the detection of specific organic bands of Raman spectra. Epifluorescence microscopy on polished thin sections reveals the distribution and concentration of potential chromophores, such as aromatic compounds, humic and fulvic acids (Vandenbroucke *et al.* 1985; Bertrand *et al.* 1986; Ramseyer *et al.* 1997). A range of chromophores exists with different fluorescences and there are also secondary absorbing effects controlled by other factors (Bertrand *et al.* 1986). However, by the detection of the organic G- and D-bands in Raman spectra, we are able to connect the source of primary cements epifluorescence to the presence of biomolecules. By this approach, it is not possible to ascertain if the biomineralization was induced by microbial metabolic activities or by processes related to organic matter decay. Nonetheless, an unequivocal control by biological processes over the precipitation of the primary cements has been clearly recognized.

Mineralization model of the primary cements

Epifluorescence and Raman spectra revealed the alternance of organic rich bands with non-organic bands in the primary cements. This alternance corresponds to the cloudy and whitish band observed on polished samples and thin sections. The microstromatolitic-like micromorphology of the isopachous cements seems to be related to phases of biologically induced/influenced growth (cloudy bands) and phases of abiotic precipitation (whitish bands; Fig. 7).

The possible sequence leading to the formation of this alternance could have started with the deposition of a biofilm on the substrate of the boundstone cavities or on the surface of the detrital grains, which induced the nucleation of crystals and the formation of the first cloudy band. After this phase of biological mineralization, the crystals seem to continue their growth without any organic matter input or biotic activity, forming in this way the whitish band. This alternance repeated cyclically until the complete filling of the cavity or because of a change in the chemical conditions of the microsystem, related for example to burial processes. A similar model of biological precipitation for marine cements has been proposed for the cryptic intertidal microbialites/cements in beachrock of Heron Island (Webb *et al.* 1999). There the isopachous fringes of cements start to grow on a layer of dark organic matter or organic-rich micrite. The crystals themselves are clear and the distal parts of fringes commonly do not contain abundant organic matter. Webb *et al.* (1999) suggested that aragonite fringe cements of Heron Islands nucleated on microbes on well-defined cohesive surfaces and then continued to grow without the presence of organic matter, presumably owing to a continued favourable saturation states in the ambient pore water. The contribution of cyanobacteria has been also discussed with regard to the formation of micritic cements in Mediterranean beachrocks (Bernier & Dalongeville 1988, 1996) and acicular marine cements have been associated with organic matter-rich nucleation zones also in other regions (e.g. Khalaf 1988; Bernier & Dalongeville 1996).

Conclusions

Research on mineral nucleation controlled, induced or influenced by organic molecules is continuously evolving and discoveries of new bioproducts are fundamental in geobiological studies. Here, we discuss the role of organic compounds in the deposition of primary cements in an Anisian build-up, suggesting to consider them as the product of unconventional biomineralization. The term 'unconventional' is used to discriminate these carbonate components from skeletons and microbialites, which are related to well-known biotic mineralization processes and thus considered as the product of conventional biomineralization.

In the studied build-up, microbialites and microencrusters represent the main building components of the carbonate boundstone, while diffuse primary cements deposited in the microcavities and among the grains contribute to strengthen the framework. These isopachous primary cements show the alternance of cloudy and whitish bands, often resembling microstromatolite textures. During their growth, organic matter remains were trapped only within the crystals forming the cloudy bands, as well as in the autochthonous micrite that form the microbialite texture. In particular, the studied Anisian primary cements show the alternance between phases of biologically induced/influenced growth (cloudy bands) and phases of abiotic growth (whitish bands) that are in line with the mineralization model proposed for primary cements forming in recent beachrocks.

The mutual approach by epifluorescence and Raman spectroscopy allows to prove the key role of biological processes in the deposition of the primary cements. Even if further investigation, with characterization of the biomarker in GC-MS, are necessary to elucidate the specific biogeochemical pathways involved of the mineralization, the present research supports the possible use of primary cements as a new tool to detect and investigate biological signature in the fossil record.

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