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Nodules and chert layers in the Ichtyolitic Limestones Formation of Civita of Pietraroja (Southern Apennines, Italy). A genetical model

Sergio Bravi *, Piergiulio Cappelletti , Concetta Rispoli , Manuel Lorusso

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***Correspondence:**
sergio.bravi@unina.it
https://orcid.org/0000-0003-0403-9386

Affiliation:
Department of Earth Sciences, Environment and Resources (Di.S.T.A.R.). University of Naples Federico II, Naples, Italy

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Abstract

The present paper concerns the study of the silicization processes occurring in the "Ichthyolitic Limestone" outcropping at the Civita of Pietraroja (Benevento), in the Matese Mountains. (Southern Apennines, Italy). Previous Authors provided descriptions of these deposits, without proposing a specific genetic model. Different types of cherts were observed, sampled, and studied in optical microsocopy, characterizing their sedimentological features, the contained microfauna, and their state of conservation. Observations confirm that silicization is penecontemporary to the sedimentation of the fine-grained lagoonal limestones. Specifically, to explain silicization processes in limestones, the following paleo-environmental context of the Pietraroja lagoon, and the surrounding areas, must be taken into account: a first source of primary silica may have been located in the emerged areas overlooking the lagoon, where carbonate weathering processes, leading to the formation of bauxites, had probably begun. This leaded to the accumulation of residual materials (including siliceous ones). The "Orbitolina Level of the Campania" too, derived at least in part from the accumulation of pyroclastic materials, slightly older than the "Ichthyolitic Limestones" and cropping out in the area in the uppermost Aptian-lower Albian, could be regarded as an additional source of primary silica. The richness in silica of this neritic-lagoon environment could consistently have supported the development of siliceous sponge colonies, whose spicules, originally consisting of Opal A, are often very abundant in lagoonal sediments. According to the described conditions, a mixing zone between fresh meteoric and continental waters and lagoonal marine waters, was very likely present in the sediments bordering the lagoon and within it. In accordance with a previously proposed model, the dissolution of sponge spicules (Opal A, biogenic silica), and the reprecipitation of silica phases as colloidal gels within the carbonatic sediments could give rise to silicizations in the form of nodules and layers.

Keywords: lower Cretaceous, chert, lagoonal environment, stratigraphy, sedimentology, Southern Apennines.

Riassunto

Il lavoro prende in considerazione le silicizzazioni presenti nei "Calcari ad Ittioliti" affioranti alla Civita di Pietraroja (Benevento), nel Matese orientale (Appennino Meridionale, Italia). Precedenti Autori ne hanno fornito descrizioni, senza però proporre uno specifico modello genetico. Le diverse tipologie di selce osservate sono state campionate e studiate in sezione sottile, caratterizzandone le litologie sedimentarie, le microfaune e le loro condizioni di conservazione. Le osservazioni confermano che la silicizzazione è penecontemporanea alla sedimentazione lagunare. Riguardo la genesi delle silicizzazioni nei calcari, considerando il quadro paleoambientale della laguna di Pietraroja e delle aree a contorno, vengono individuate come fonti primarie di silice le aree emerse prospicienti dove, con ogni probabilità, erano iniziati i processi di "*weathering*" dei carbonati che condurranno alla formazione di bauxiti, con accumulo di materiali residuali, tra cui quelli silicei. Il "Livello a Orbitoline della Campania", in parte a matrice piroclastica, poco più antico dei Calcari ad Ittioliti, ed evidentemente affiorante o subaffiorante nell'area nell'Aptiano terminale - Albiano basale, poteva costituire una ulteriore fonte di silice primaria nei terreni a contorno della laguna. La ricchezza in silice di tale ambiente neritico-lagunare poteva pertanto favorire lo sviluppo di colonie di spugne silicee, le cui spicole, originariamente costituite da opale A, sono abbondantissime nei sedimenti lagunari dei Calcari ad Ittioliti di Pietraroia.
Nelle condizioni descritte, una zona di mixing tra acque dolci meteoriche e continentali e acque marine lagunari, era certamente presente nei sedimenti a contorno della laguna e nella laguna stessa. In essa potevano avvenire i processi di soluzione della silice biogenica (opale-A) derivata dalle spicole di spugne e la riprecipitazione di essa in forma di gel colloidali nei sedimenti carbonatici, formando noduli e letti di selce sui fondali lagunari.

Parole chiave: lower Cretaceous, selce, laguna, stratigrafia, sedimentologia, Appennino Meridionale.

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Introduction

The Civita of Pietraroja (Fig. 1) is a monocline structure which is part of the Matese Mountain group. It is located at the eastern edge of this fold and thrust belt.

The Lower Cretaceous stratigraphic succession consists of about 320 meters of dolomitic limestone and limestone, finely detrital, sometimes pseudoolitic, in layers and banks. In the upper part of the sequence the "Orbitolina level", Upper Aptian in age, is present (Cherchi *et al.*, 1978). The Ichthyolitic Limestone Formation *(Plattenkalk*) is a lower Albian, thin layered level, in the uppermost part of this succession, heteropic with limestone in massive layers, in neritic facies of more open carbonate platform (D'Argenio, 1963; Freels, 1975; Bravi & Garassino, 1998). It is constituted by brown and grey, thin and fine-grained layers showing conchoidal fracture, interbedded with chert layers and nodules and thinly laminated marls (D'Argenio, 1963; Catenacci & Manfredini, 1963; Freels, 1975; Bravi, 1997). D'Argenio (1963), Freels (1975), Bravi & Garassino (1998), in contrast to Catenacci & Manfredini (1963) and Carannante *et al*.

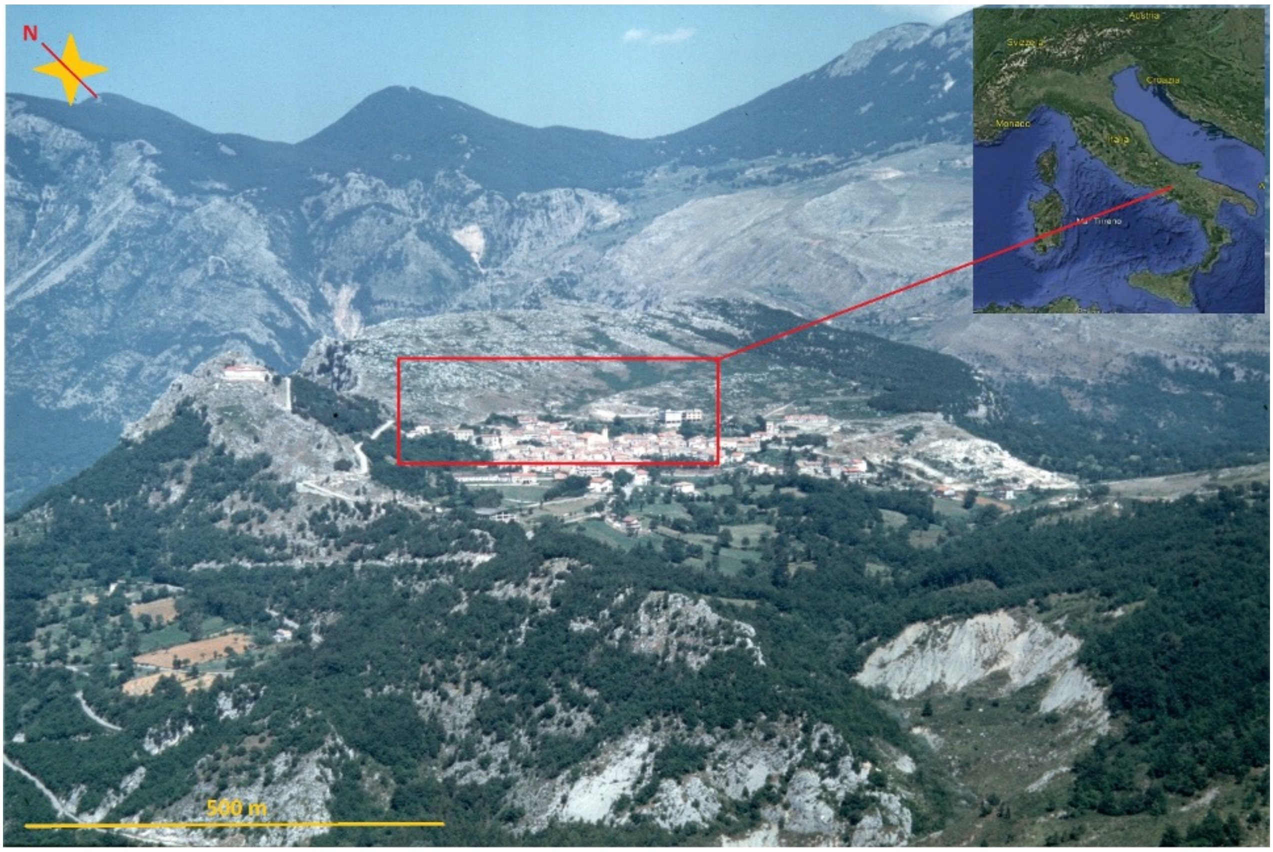

Figure 1: Location of the study area, Civita of Pietraroja (Matese Mts., Southern Apennines, Italy).

(2006), considered the Ichthyolitic Limestone of Pietraroja as deposited into a shallow lagoon environment. The chert in the Ichthyolitic calcareous formation, is represented by nodules, angular clasts, and layers. Considering that chert layers are mostly found in deep marine sediments, these thin chert layers in the Ichthyolitic Limestone of Pietraroja, sometimes very widespread (Figs. 2A-D), represent a peculiarity. The above-mentioned Authors provided descriptions of these cherts but, up to now, without hypothesizing a specific genetical model. The purpose of this paper is to explain their genesis, in a paleoenvironmental and sedimentary context such as that of the lagoon basin, where the Ichthyolitic Limestones of Pietraroja were deposited.

The Uppermost Aptian – Lower Albian local paleoenvironment

During lower Albian, a marked low-stand phase of the sea level determined extensive emergences of land and the formation of lagoons bordering the emerged areas, such as the lagoon of Pietraroja, within the carbonate platform area, today represented by the Eastern Matese Mts. (Bravi, 1995). In this lagoon, animals as the dinosaur *Scipionyx samniticus* (Dal Sasso & Signore, 1998; Dal Sasso & Maganuco, 2011) and other reptiles, together with land plants as *Frenelopsis* sp. and *Brachyphyllum* sp., (Bartiromo *et al.*, 2006; Bartiromo *et al.*, 2012; Bartiromo, 2013) were occasionally transported and fossilized, along with the lagoonal fauna (fish and crustacean). On these lands, most likely freshwater reservoirs (marshy areas, small streams) transported in the lagoon: 1) faunal and floristic elements as fish of brackish or freshwater environment (e.g., *Pleuropholis* and *Lepidotes*) and 2) remains of land plants, oogons of Carophytes (Bravi, 1988; Bartiromo *et al.*, 2006, 2012).

This paleoenvironmental framework implies the existence of a mixing zone between continental fresh waters and salty (probably temporarily oversalted) waters of the lagoon. On this basis, we propose an in-depth study and a justification for the chert nodules and layers presence in the Ichthyolitic Limestones of Pietraroja.

Knauth (1979) proposed a model of chert genesis in marine shallow water limestones. This paper stands with this hypothesis, due to the paleoenvironmental characteristics of the Pietraroja Ichthyolitic Limestone depositional basin that, in accordance with D'Argenio (1963), Freels (1975), Bravi & Garassino (1998), can be considered as effective.

Knauth (1979) theorizes a geological situation in which meteoric water can mix with sea water into the mixing zone, in coastal marine environment, in sediments enriched of silica (Opal A) due to the siliceous organisms remains (Fig. 3A). The mixing of fresh and salt water can produce silica supersaturated waters, due to high solubility of biogenic Opal A, but undersaturated in calcite and aragonite (Fig. 3B).

Materials and methods

This work involved a first phase of field study and sampling, where main formations present in the "Civita of Pietraroja" area and their relationships were studied. Based on pre-existing investigations and geological maps (Freels 1975), we proceeded to add further data and to identify and describe the

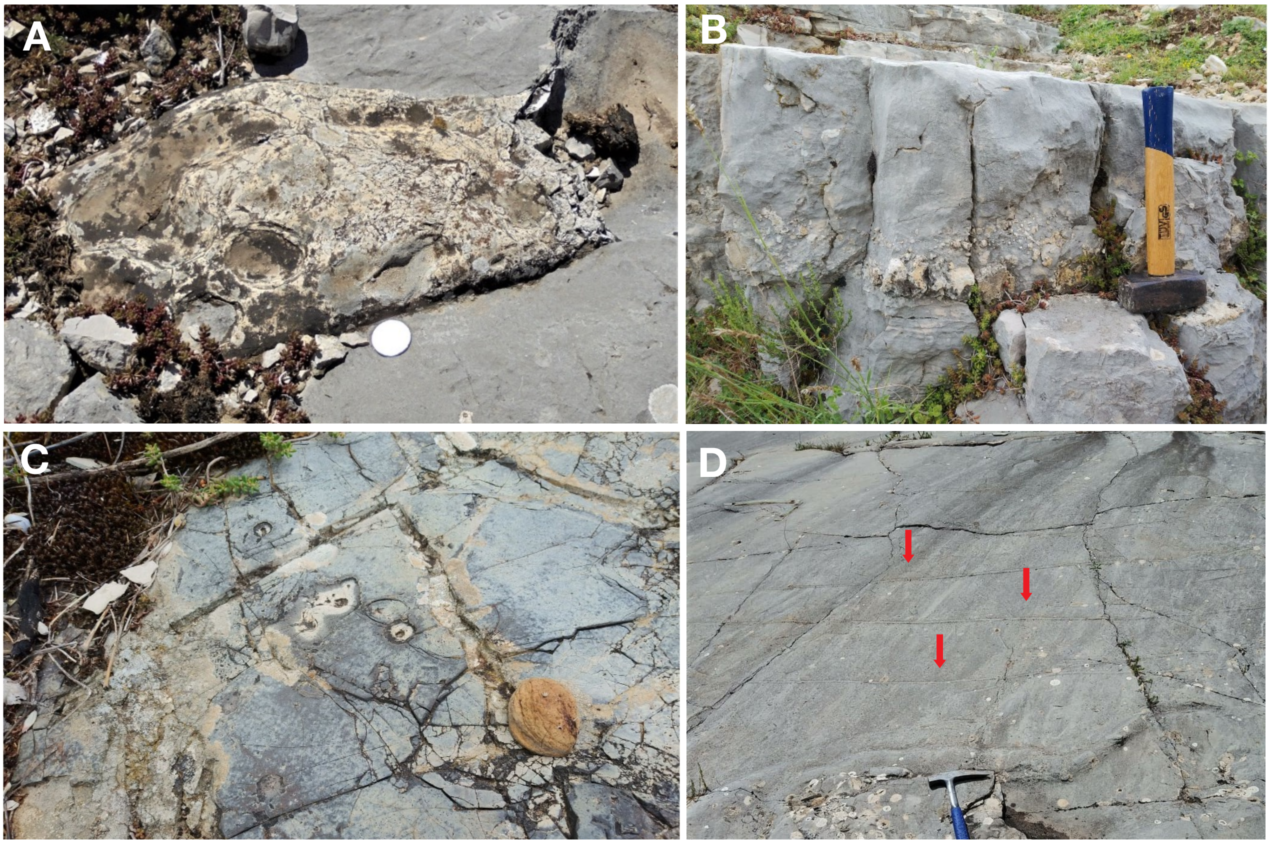

Figure 2: A) Siliceous nodule of lobed shape. "Collapse" structures can be observed on its surface, due to the leakage of gas (H2S) from the inside of the nodule, and the consequent collapse of the roof of the cavity that contained it. Dimensional reference at the bottom, under the nodule: 1euro coin. **B)** Layers of Ichthyolitic Limestones (upper part of the sequence), with chert scattered as angular clasts, at the base of the layer. **C)** Centimeter "gas-pits" on the surface of a chert bed, fractured into polygons for syneresis. Basal layer of the Ichthyolitic Limestones, locality: "Le Cavere". The walnut shell in the lower right is a dimensional reference. **D)** Long lineations on a metric scale (indicated by arrows), with inverted V section, present on the basal calcareous layer of the Ichthyolitic Limestones. They were produced by the "sinking" of the overlying siliceous layer, broken into large blocks in the early stages of the syneresis process. Locality: "Le Cavere".

main chert formations (nodules, beds, polygons, and clasts immersed in the limestone layers), specifying their characteristics in terms of position and sampling them. Samples from the whole stratigraphic succession of the Ichthyolitic Limestone formation (about 8 meters; see Fig. 4) cropping out at "Le Cavere" locality and its surroundings, were observed in optical microscopy to describe their fossil content and their sedimentological microfacies (Tab. 1).

Some samples (Spic1, Spic2, PS 12A, P5, among the others; see Tab. 1) were prepared for chemical and petrographic analyses. In these samples, sponge spicules were still clearly evident and often, very abundant. The purpose of these analysis was to verify the composition of the spicules, since these could potentially be of calcareous origin (Calcisponges), instead of siliceous (Silicosponges).

Mineralogical analyses were performed by X-ray powder diffraction (XRPD) using a Malvern Panalytical X'Pert Pro diffractometer

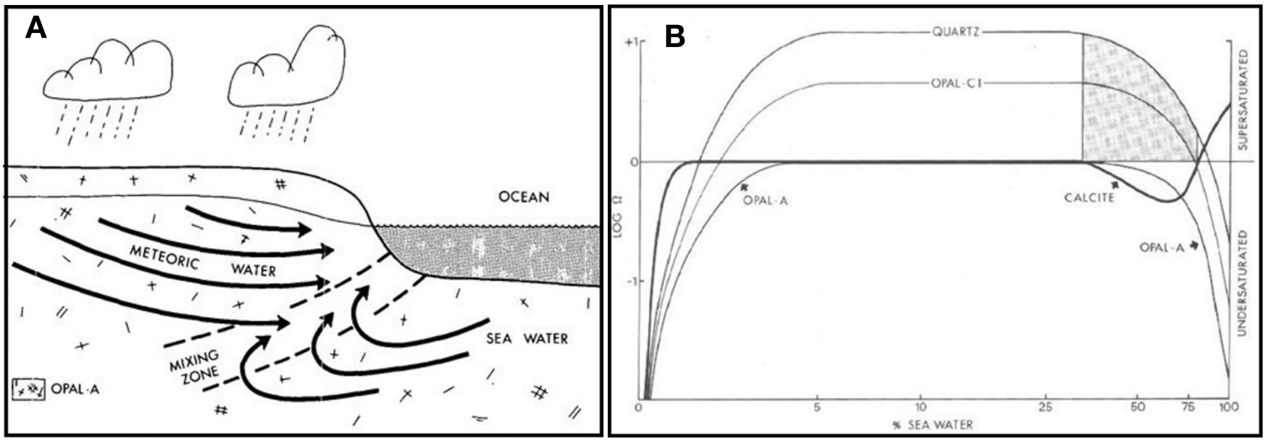

Figure 3: A) Schematic model of the mixing zone in which the silicization processes of the sediments take place. (From Knauth, 1979). **B)** Solubility relationships of calcite and silica in mixed meteoric-marine ground waters closed with respect to CO_2. The saturation state is expressed in terms of log Ω, where Ω = ratio of the ion activity product to the mineral equilibrium constant. A solution is saturated with respect to the mineral phases when log Ω = 0. Positive values of log Ω indicate supersaturation, and negative values indicate undersaturation. In the hypothetical case depicted, mixing of meteoric and marine waters has produced ground water simultaneously undersaturated with respect to calcite and supersaturated with respect to crystalline silica. The shaded zone defines conditions in which it is thermodynamically possible for silica to replace carbonate. The spacing of abscissa increments is arbitrary. (Drawing and caption from Knauth, 1979).

equipped with a RTMS X'Celerator and a X'Pert High Score Plus 3.0c software.
Operating conditions were: CuK radiation, 40 kV, 40 mA, 2ϴ range from 4 to 70°, equivalent step size 0.0172°, equivalent counting time 120 s per step. Powders with grain size <10 μm were obtained using a McCrone micronizing mill (agate cylinders and wet grinding time of 15 min). An Al_2O_3 internal standard (1 μm, Buehler Micropolish) was added to each sample (20 wt.%). Micro-textural observations and quantitative micro-chemical analyses were carried out by Scanning Electron Microscopy, equipped with an Energy Dispersive detector (SEM/EDS; Zeiss Merlin VP Compact and JEOL JSM-5310, respectively coupled with Oxford Instruments Microanalysis Units X-Max and INCA X-act detectors. Measurements were performed with using a stream pulse processor (15-kV primary beam voltage, 50–100 A filament current, variable spot size, from 30,000 to 200,000x magnification, 20 mm WD and 50 s net acquisition real time). INCA Energy software was employed using XPP matrix correction scheme and pulse pile up correction. Quant optimization was carried out using cobalt (FWHM–full width at half maximum peak height- of the strobed zero = 60–65 eV). Smithsonian Institute and MAC (Micro-Analysis Consultants Ltd., Saint Ives. UK) standards were used for calibration using these phases: diopside (Ca), fayalite (Fe), San Carlos olivine (Mg), anorthoclase (Na, Al, Si), rutile (Ti), serandite (Mn), microcline (K), apatite (P), fluorite (F), pyrite (S) and sodium chloride (Cl). Precision and accuracy of EDS analyses are reported in Rispoli *et al.*, 2019.

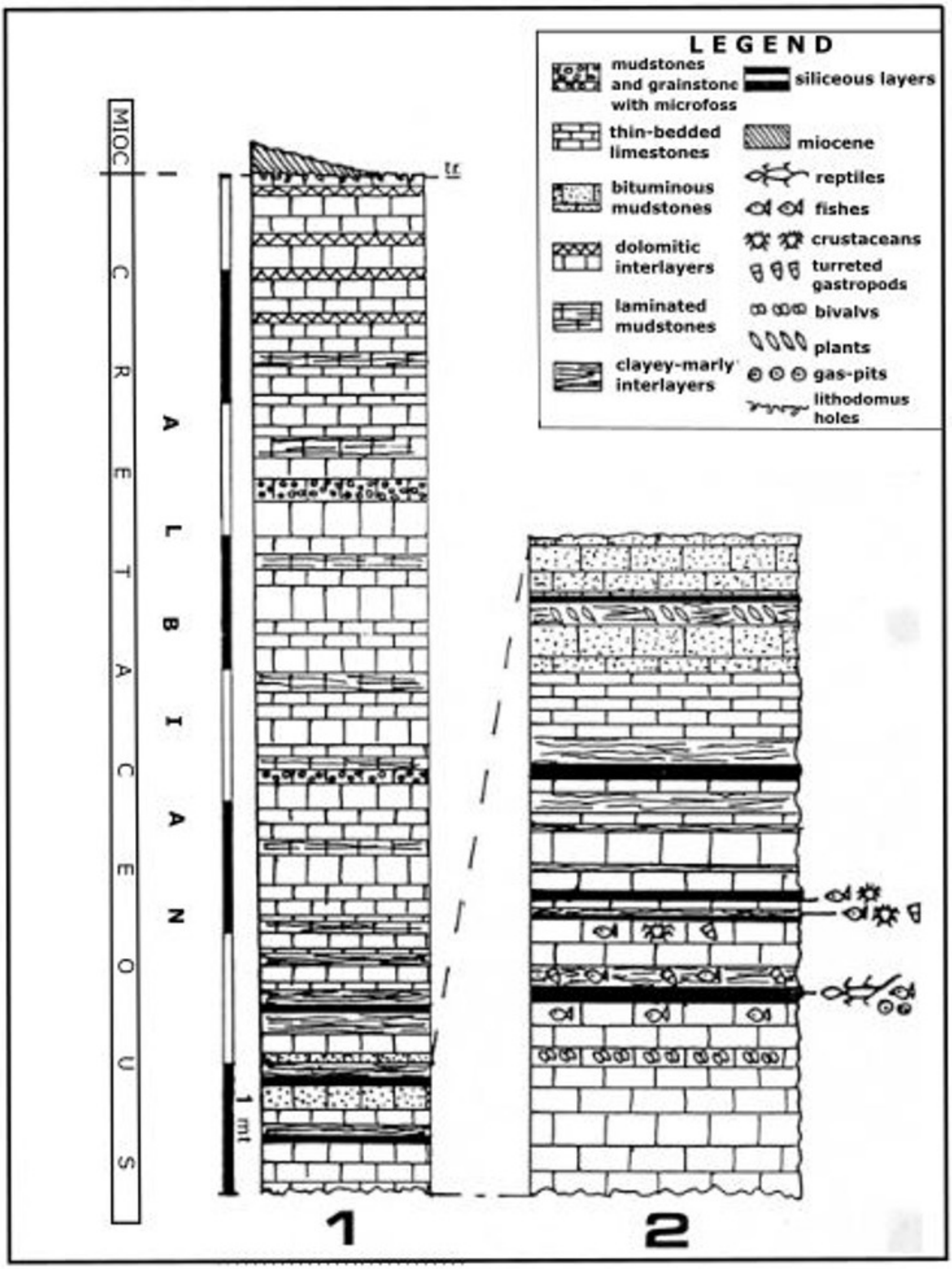

Figure 4: Detailed stratigraphic succession of Ichthyolitic Limestones in "Le Cavere", Civita of Pietraroja **(1)**. The detail of the stratigraphic column **(2)** displays the alternation of calcareous, siliceous, and calcareous-marly-clayey laminated layers, as well as their most characteristic fossiliferous content. From: Bravi, 1997.

Table 1: Main characteristics of the selected samples.

SAMP	LITHOLOGY (DUNHAM)	FOSSILIFEROUS CONTENT	NOTES / OTHERS	LOCATION
PLS1A	G (coarse)	Unrecognizable silicized foraminifers	High degree of silicization. Fractured chert.	Plattenkalk base, "Le Cavere"; chert bed.
PLS1B	P	Miliolids	High degree of silicization. Brownish organic matter remains.	Plattenkalk base, "Le Cavere"; chert bed.
PLS1C	P	Miliolids	High degree of silicization. Brownish organic matter remains.	Plattenkalk base, "Le Cavere"; chert bed.
SPIC1	P (fine)	Sponge spicules. *Thaumatoporella* sp.; *Glomospira* sp.; dwarf foraminifers fauna.	Simulated dwarfism of faunas due to the selection of granules. Brownish organic matter remains.	"Le Cavere" Plattenkalk outcrop.
SPIC2	P - W	Sponge spicules. Dwarf foraminifers (miliolids), *Glomospira* sp., textulariids; valulinids; *Thaumatoporella* sp.	Normal graded. Lamination.	"Le Cavere" Plattenkalk outcrop.
SPIC3	W – p (fine)	Sponge spicules; fragments of molluscs; dwarf foraminifers, *Thaumatoporella* sp.	Normal graded. Simulated dwarfism of faunas due to the selection of granules.	"Le Cavere" Plattenkalk outcrop.
PS2	P - G	Foraminifer (miliolids); ostracods	High degree of silicization.	"Le Cavere" Plattenkalk outcrop.
PS4	P (fine)	Dwarf valvulinids and miliolids; shell fragments.	Normal graded. Lamination.	"Le Cavere" Plattenkalk outcrop.
PS4.2	P	Fragments of fossil fish.	High degree of silicization.	"Le Cavere" Plattenkalk outcrop.
PS7	W (dark laminae); P/G (clear laminae)	W: Miliolids; *Thaumatoporella* sp.; textulariids; *Cuneolina pavonia*; *Pseudonummoloculina* sp.; sponge spicules. P-G: fragments of molluscs; *Thaumatoporella* sp.	Normal graded. Lamination.	"Le Cavere" Plattenkalk outcrop.
PS7.2	P (coarse at the (base). W (top)	*Thaumatoporella* sp.; ostracods, fragments of molluscs.	Lamination.	"Le Cavere" Plattenkalk outcrop.
PS8	G - P	*Cuneolina* sp.; textulariids; *Pseudonummoloculina* sp.; *Cuneolina pavonia*, *Sabaudia minuta*; little orbitolinids (*Paracoskinolina tunesiana*); fragments of molluscs.		"Le Cavere" Plattenkalk outcrop.
PS9	P - W (fine)	Oriented sponge spicules; dwarf textulariids; miliolids; *Glomospira* sp., dwarf valvulinids.	Simulated dwarfism of faunas due to the selection of granules.	"Le Cavere" Plattenkalk outcrop.
PS10	W - M (dark laminae);P-G (clear laminae).	*Cuneolina* sp	High degree of silicization.	"Le Cavere" Plattenkalk outcrop.
PS11	P	*Cuneolina pavonia*; *Thaumatoporella* sp.; miliolids; textulariids; *Glomospira* sp; *Debarina hahounerensis*, *Pseudonummoloculina* sp., Sponge spicules.		"Le Cavere" Plattenkalk outcrop.
PS12	M?		Nodules in limestone beds. Microcrystalline, high degree of silicization. Unrecognizable primary structure. Brownish organic matter remains.	Stratigraphically higher in "Le Cavere" stratigraphic sequence.
PS12A	W?	Sponge spicules. Unrecognizable, silicized foraminifers.	High degree of silicization. Unrecognizable primary structure.	Plattenkalk base, "Le Cavere"; chert bed.
PS12B	M?		High degree of silicization. Unrecognizable primary structure.	Nodules along the road. Out from "Le Cavere" outcrop.
PS12T	W – P (fine)	Sponge spicules. *Pseudonummoloculina* sp., miliolids; orbiltolinids in chert; *Paracoskinolina tunesiana*, valvulinids; *Thaumatoporella* sp., textulariids; *Cuneolina pavonia*; *Nezzazzatinella picardi*.		"Le Cavere" Plattenkalk outcrop.
P5	M	Sponge spicules.		"Le Cavere" Plattenkalk outcrop. Upper part.

Results

Chert in the Ichthyolitic Limestones formation is represented by layers, nodules, and angular fragments dislocated within the limestone beds. Layers are compact, thin bedded and parallel to the limestone layers. Nodular structures are ellipsoidal or lobed in shape, sunk in the underlying limestone layer, due to their greater specific weight. Their central part is more silicified, while edges are richer in carbonate component. Sometimes chert is fragmented in angular or polygonal clasts, giving rise to breccia-like facies. According to D'Argenio (1963), fragmentation predates incorporation in limestones. More nodules are observed in the marginal areas of the basin outcropping at "Le Cavere". Conversely, thin and continuous chert layers are present in parts corresponding to a more distal and deeper area, characterized by a flat bottom (Bravi, 1997). Moreover, the higher specific weight of silica could have favoured gravitational accumulation of siliceous gels (e.g., "sliding" from the steeper and marginal areas of the basin towards the deeper areas), producing even more silica saturation within the sediments and in waters present at the "basinal" flat bottom zone. Metric-scale slumping are present near marginal areas of the Ichthyolitic Limestone basin. These likely caused sediment to be transported towards its depocenter, and influencing the transport of chert, thus originating mild turbidity currents (laminations; according to Freels, 1975; Bravi & Garassino, 1998).

Cherts sampled at "Le Cavere" outcrop show macro-sedimentary structures such as gas-pits (shallow water-depth indicators), syneresis polygons and often well-preserved microstructures, such as laminations (Figs 2C, 2D. Shrock, 1948; Twenhofel, 1950; D'Argenio, 1963; Freels, 1975; Bravi, 1997; Bravi & Garassino, 1998). Nodules sampled in the marginal areas and in the upper part of the Ichthyolitic Limestones sequence, often show collapse structures on surfaces (Fig. 2A). The samples have been subdivided into three main groups, using their distinct microfacies: 1) fine-grained, microlaminated facies; 2) non-laminated facies, with generally homogeneous microcrystalline structure; 3) non-laminated, coarse-grained facies (Fig. 5).

Microlaminated samples (Figs. 5C, 5D) show micro-turbidity and millimetric lamination with normal gradation (packstone-grainstone at the lamina base, wackestone-mudstone up to the lamina top). Within the coarse-grained part, a microfauna and microflora (miliolids, valvulinids, textulariids, G*lomospira* sp., *Thaumatoporella* sp., fragments of molluscs, sponge spicules) is present. Silicization affected limestone laminae after their deposition, due to the precipitation of siliceous gel in the pores of the sediment.

Non-laminated facies group is mostly found within chert nodules. Strongly silicified facies (Fig. 5E) and partially silicified facies (Fig. 5F) are present in this group. In the first case, an unrecognizable microfauna and brownish organic matter are also present. In the second case, foraminifer shapes can be clearly recognized, but whenever silicization process is more intense, they are completely replaced by silica and therefore transparent (e.g., miliolids).

In the last group (coarser-grained facies as grainstone and grainstone-packstone), foraminifers are abundant (Figs 5A, 5B). Strong silicization is present, as coarser particle size influenced permeability of the sediment, permitting a good circulation of silicizing fluids.

EDS chemical composition of investigated materials (Fig. 6) confirmed the observations from optical microscopy and the results basically show SiO_2 as the solely constituent of the rock portions attributable to the spicules (Tab. 2; Fig. 6); the surrounding matrix, on the contrary, appears to be totally composed by calcite (Tab. 2), as also evidenced by XRPD analysis (Fig. 7), with a very weak magnesian component that appears to be enriched in the sample P5 (MgO = 0.92 wt %), compared to the one surrounding the spicules (MgO = 0.41-0.59 wt %). As above reported, XRPD analyses evidenced the presence of calcite along with a major component constituted by quartz.

Discussion

The paleoenvironmental model of the Ichthyolitic Limestones of Pietraroja poposed in this paper, is the one of a typical shallow lagoon, with little exchange with the open sea, surrounded by emerged areas, subjected to carbonate weathering, soil formation and residual accumulation of iron and aluminium hydroxides, along with silica oxides (initial bauxitization processes). The "Orbitolina level", with its amount of volcanic components as an additional source of silica, was also an element of the uppermost Aptian – lower Albian terrains cropping out in the nearby environment. With this setup, a mixing zone between fresh and sea waters is very probable. In a warm-humid subtropical climate, rainfalls are also frequent, thus contributing with more, meteoric, fresh waters. Emerged lands were also very extensive, considering that they hosted flora of the *Phlebopteris* type (Bartiromo *et al.*, 2006), *Frenelopsis*, and freshwater plant *Montesechia vidali* (Bartiromo *et al.*, 2012), as well as reptiles such as the dinosaur *Scipionyx samnitucus* (Dal Sasso & Signore, 1998; Dal Sasso & Maganuco, 2011) at the apex of the food chain. There are also brackish or freshwater fossil fish such as *Lepidotes*, *Pleuropholis decastroi* (Bravi, 1988), beholding the contribute of fresh water to the lagoon.

In this context, we propose that one of the primary sources of silica was the weathering of silicatic material occurring above carbonates, as testified by the occurrence of bauxites in the "Regie Piane" locality (no further than 2 km from Civita of Pietraroja). Their presence indicates that there was an emerged area (carbonates) nearby, subject to weathering under a sub-tropical climate and intense rainfalls (Bardossy & Aleva, 1990). The formation of bauxite, very common during the Aptian-Coniacian, in the Apennine shelf areas (D'Argenio & Mindszenty, 1995), has been able to precipitate crystal phases such as gibbsite, diaspore, hematite and goethite. Bauxites were formed in part by pyroclastic materials (carried by the wind) which, covering the carbonate platform, were subjected to laterization and remobilization (D'Argenio & Mindszenty, 1995; Boni *et al.*, 2012). Karst areas, with excellent drainage, allowed "desilicification" of the bauxites, protecting them from erosion, and provided further source of silica (according to Mondillo *et al.*, 2011). Another source of silica can be considered the volcanic, detrital minerals of pyroclastic origin, occurring in the "Orbitolina level", (mineralogical associations with feldspar, muscovite, olivine, titanite, possible serpentine talc phase) (Mondillo *et al.*, 2011).

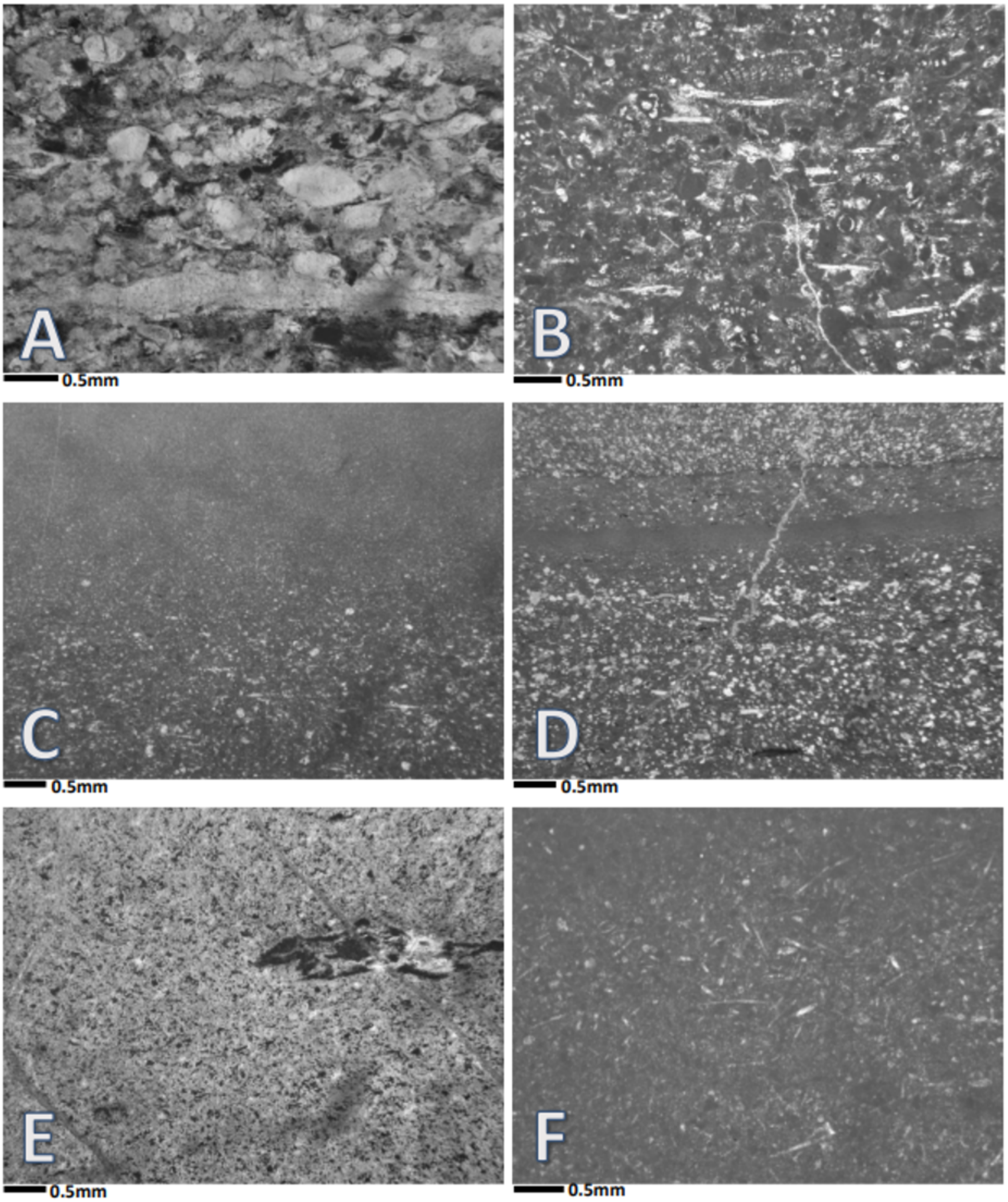

Figure 5: A) Grainstone-packstone, coarse-grained and non-laminated with silicified foraminifers, ostracods, miliolids (sample: PS2). **B)** Slightly silicized packstone with foraminifers and isooriented sponge spicules, textulariids, *Pseudonummoloculina* sp., valvulinids, *Cuneolina pavonia*, *Akaya minuta*, fragments of molluscs (sample: PS8). **C)** Micro-laminated packstone-wackestone with sponge spicules, textulariids, valvulinids, *Glomospira* sp., *Thaumatoporella* sp., (sample: SPIC2). **D)** Micro-laminated, fine grained packstone, with sponge spicules and foraminifers as valvulinids, miliolids; mollusc fragments (sample: PS4). **E)** Not laminated and highly silicized grainstone. Unrecognizable microfauna (sample: PS12). **F)** Not laminated and silicized wackestone with abundant sponge spicules (sample: PS12a).

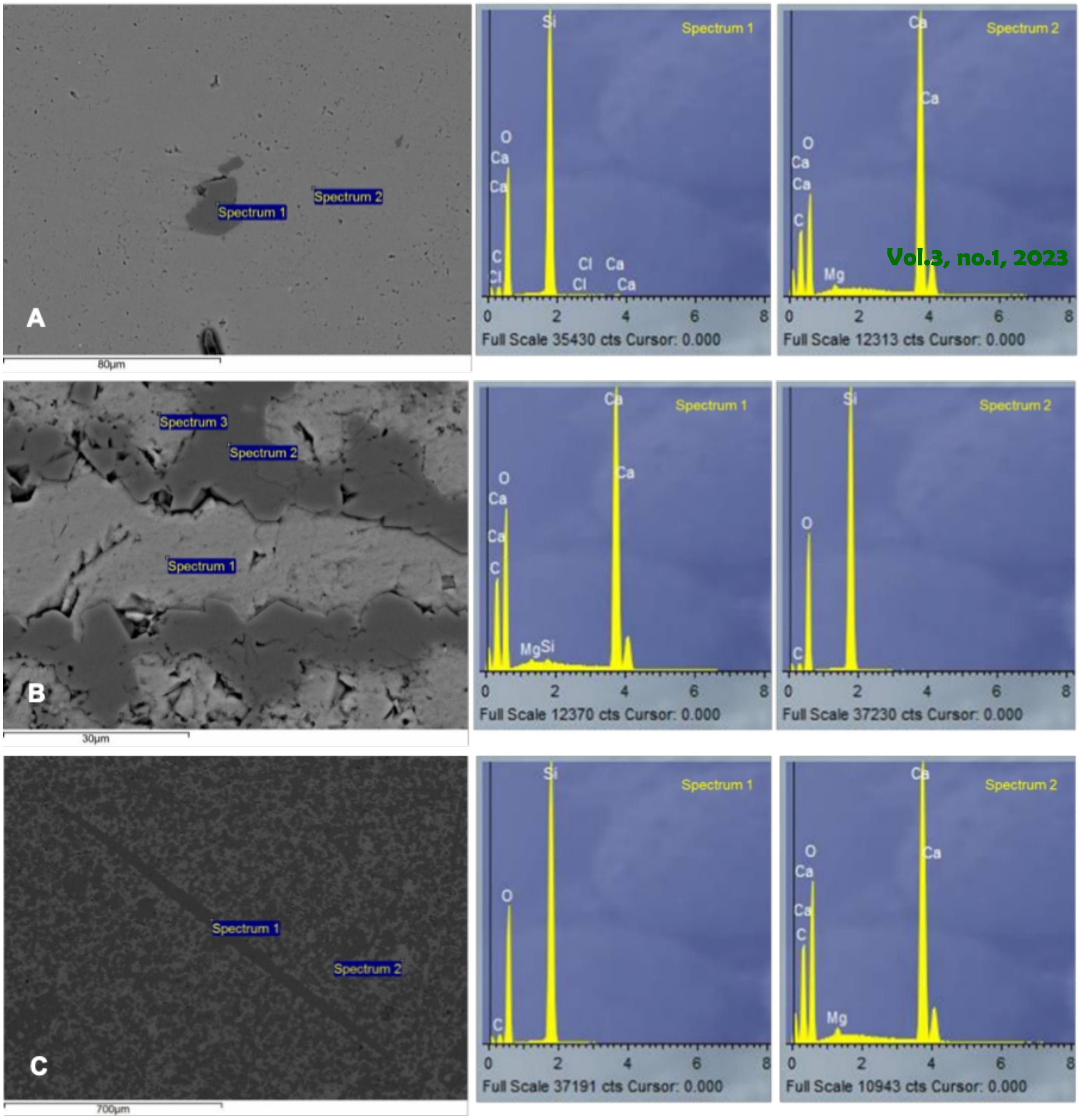

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Figure 6: Backscattered SEM images and relative chemical points analyses of matrix and sponge spicula. **A)** Sample Spic1. **B)** Sample Spic2. **C)** Sample P5.

Assuming the described conditions, abundant presence of spicules of siliceous sponges in the Ichthyolitic Limestones of Pietraroja, testifying the wide diffusion of porifera colonies in the area, living in shallow waters, probably on both incoherent and hardened substrates (early diagenesis, clasts) in areas overlooking the lagoon or in the lagoon itself, but where there was a better water circulation (sponge colonies are found on different substrates, both incoherent and hard, from the Cambrian up to the present. They can consolidate incoherent seabeds and are considered "ecosystem engineers". See for example: Aurell & Badenas, 2015; Tomas *et al*., 2019; Van Soest *et al*., 2012; Mercurio *et al*., 2006; Giraldes *et al*., 2020; Clarke, 1920; Renard *et al*., 2013). These organisms could greatly benefit from contributions of primary silica (carbonate weathering and "Orbitolina level"), obtaining material for the

Table 2: Values of major oxides (wt%, EDS, recalculated) of matrix and "spicule" in Spic1, Spic2 and P5 Samples. (1 and 2 are referred to point analysis in Fig.5).

Spic1	SiO_2	MgO	CaO	Tot.
1	99.55	-	0.45	100.00
2	-	0.59	55.41	56.00
Spic2	**SiO_2**	**MgO**	**CaO**	**Tot.**
1	-	0.41	55.59	56.00
2	99.74	-	0.26	100.00
P5	**SiO_2**	**MgO**	**CaO**	**Tot.**
1	100.00	-	-	100.00
2	-	0.92	55.08	56.00

construction of siliceous skeletons and proliferating. Sponge spicules, derived from the continuous process of death and renewal of the colonies, can then mix with the sediments of the lagoon and, being constituted by Opal A, they were easily solubilized in such specifical environmental conditions.

Based on the paleoenvironmental framework described above, formation of the different types of cherts in the Ichthyolitic Limestones of Pietraroja seems to be well explained by applying the genetic model proposed by Knauth (1979). This provides a mixing zone between fresh meteoric and salty sea water, which leads to supersaturated solutions in silica (dissolution of spicules) and subsequently, its reprecipitation in colloidal form, originating chert beds and nodules and replacing calcite in microfauna.

In the case study, due to the fine grain of the sediments, the mixing zone had a very limited thickness, also involving the lower part of the lagoon, and precipitating silica, thus forming extensive chert beds (Fig. 8).

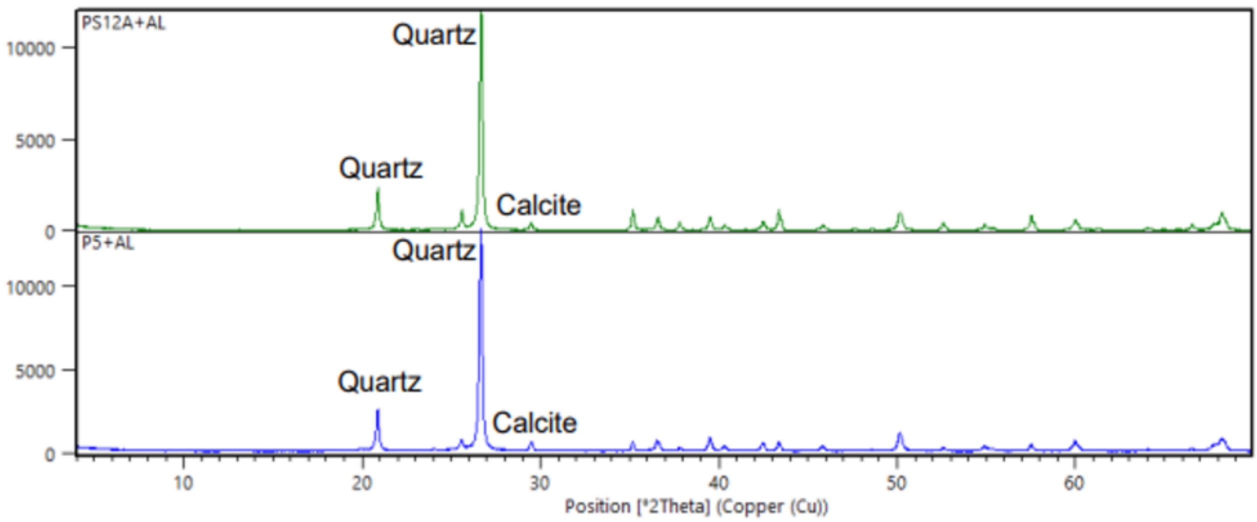

Figure 7: XRPD patterns of P12A and P5 samples.

In marginal, and more unstable areas of the lagoon, siliceous colloidal gel tended to form nodules, since the silica-supersaturated waters could not stratify here, conversely to what happens in the calm environment of the lower part of the lagoon. Nodules also prevail in the highest portion of Ichthyolitic Limestones formation, since the lagoon basin tends to be filled with coarser sediments, thus establishing itself in its "last stages of life".

In conclusion, chert in the Ichthyolitic Limestone formation of Pietraroja was formed due to:

- a shallow lagoon setting;
- presence of primary sources of silica, consisting of pyroclastic deposits affected by weathering on the emerged carbonate platform;
- transport of silica-rich fluids that favoured the development of silicosponge colonies in the lagoon or in its marine surrounding areas;
- sponge-derived biogenic silica present in the sediments (spicules). It was brought into solution by rain and freshwater and, in the mixing zone, at the edge of the lagoon, it was re-precipitated as colloidal siliceous gel, according to the model of Knauth (1979), forming chert nodules in the steeper, and unstable, marginal areas of the lagoon. In the distal areas, wide chert layers can stratify on the flat and calm basin bottom, with silica-saturated waters.

The proposed mechanism for the formation of chert in the Ichthyolitic Limestones of Pietraroja, is a further indication of their deposition into a shallow lagoon environment, close to emerged lands.

Author contributions

Conceptualisation: S. Bravi.
Field collecting: S. Bravi, M. Lo Russo.
Data Curation: S. Bravi, M. Lo Russo, C. Rispoli, P. Cappelletti.
Formal Analysis: S. Bravi, M. Lo Russo, C. Rispoli, P. Cappelletti.
Investigation: S. Bravi, M. Lo Russo, C. Rispoli, P. Cappelletti.
Methodology: S. Bravi
Project Administration: S. Bravi.
Resources: S. Bravi, M. Lo Russo, C. Rispoli, P. Cappelletti.

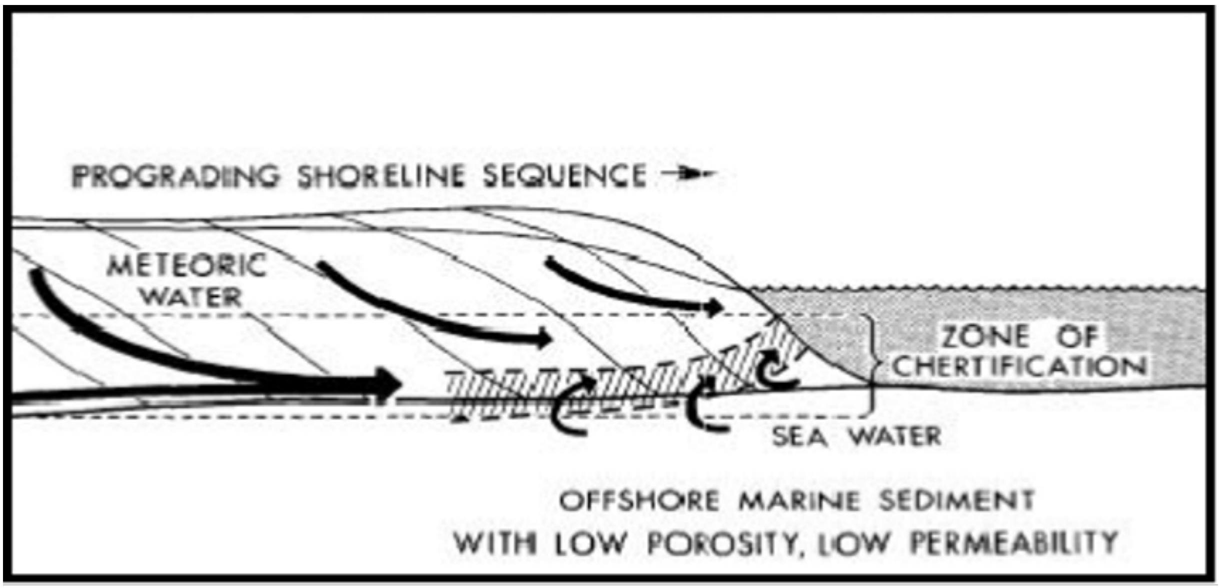

Figure 8: Scheme of the silicification model (from Knauth 1979).

Writing – Original and Final Draft Preparation: S. Bravi, M. Lo Russo, C. Rispoli, P. Cappelletti.

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