Evidence of microbial activity in siderite and calcite deposits on gastropod shells in Pliocene sand and clay beds from Lipovljani, Croatia

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ABSTRACT

Freshwater Pliocene sand and clays found near Lipovljani in western Slavonia, Croatia, contain gastropods preserved by diagenetic mineral incrustations of alternating calcite and siderite. The geochemical possibility of siderite formation is evaluated, and evidence for microbial mediation of siderite deposition around fossil carbonate shells is presented.

Keywords: concretions, fresh water diagenesis, iron bacteria, calcite, siderite, Pliocene, Slavonia, Croatia

INTRODUCTION

Many ancient early diagenetic siderite concretions are thought to have been precipitated by microbially-mediated reactions, and their trace element chemistry has been used to infer palaeoenvironments of formation (e.g. marine versus freshwater). The strongly varying chemical compositions of siderite concretions are governed both by pore-water origin and by microbial influence, (COLEMAN & RAISWELL, 1993; DUAN et al., 1996). MOZLEY (1989, 1989a), showed that early diagenetic siderites from marine environments are »impure«, containing considerable amounts of Mg and Ca, and never approaching end-member siderite compositions, while siderites from fresh-water environments often attain end-member composition. This »impure« chemical composition of the studied micro-concretions may be linked to crystallization from marine waters rather than from fluvial ones. Formation of sideritic concretions – around or within calcareous macrofossil skeletons, or in close association with these – is frequently interpreted as a diagenetic process early in the host sediments burial history, mediated by bacterially generated carbon dioxide and interaction of sediment and pore-water cations (MOORE et al., 1992).

It is well known that microbes play an important role in the formation of various early diagenetic nodular structures (CASANOVA et al., 1999; CASTAINER et al., 1999; DAHANAYAKE and KRUMBEIN, 1986; PREAT et al.,1999, 2000). Some bacteria deposit ferric iron oxides and hydroxides on their cell surface, either directly as a product of the respiration process or indirectly by influencing the pH and Eh of their enviroment (GADD, 2004; NEALSON, 1983).

There are numerous occurrences of carbonate shells in concretions suggesting that calcareous hard parts are sites of nucleation, but there are also findings of unfossiliferous concretions and concretions containing noncarbonate fossils (BAIRD, 1986; ALLISON & PYE, 1994; MARTIN, 1999). Such unfossiliferous concretions indicate that shell carbonate alone cannot be responsible for concretion formation and that microbial mediation is a significant factor in the formation of early diagenetic concretions.

### Siderite as an indicator of the depositional environment

Siderite, the simplest Fe^{2+} bearing carbonate, occurs as an authigenic mineral in sedimentary rocks (*e.g.* MOZLEY & CAROTHERS, 1992). It usually forms concretions, which precipitated within the pore-spaces of sediments after deposition (CURTIS et al., 1986). The ideal solid-solution between Mg- and Fe-carbonate was proven by CHAI & NAVROTSKY (1994). These authors showed that the positions of X-Ray reflections, and the unit-cell parameters, gradually migrate along with the change of chemical composition. The angular positions of these discrete reflections are, however, not characteristic of end-member carbonate compositions, but they can be assigned to general compositional zoning. They could also be attributed to intermediate compositions within the non-ideal mixing series of Ca-Fe carbonates. In this compositional series, the occurrence of broad bands instead of discrete, well-defined reflections, might result from the mixture of sub-micritic Ca- and Fe-carbonate crystals which are smaller than the domains of coherent scattering of X-Rays. The occasional input of brackish waters into the estuary was proven by the occurrence of brackish microfauna in the sediments. It is very likely that the sandy layers directly underlying the layer bearing the discussed micro-concretions of siderite, may well be the pathway of infiltration of fresh water carrying the dissolved iron, which subsequently forms the siderite micro-concretions growing in pore-spaces of the sediment.

Siderite has often been used as an indicator of the depositional environment of a sediment, as it can only form under restricted geochemical conditions. This usually neglects the possibility that siderite was formed later, diagenetically, due to interaction with groundwater. Although carbonates enriched with ferrous iron (siderite, ankerite, ferroan dolomite) are rarely found in sediments derived from well-aerated ancient deposits including soils and paleosols, they are not uncommon in marine and freshwater sedimentary rocks of various geologic ages. Precipitation of siderite requires the following conditions: very low partial pressure of oxygen (generally below 10^{-6} atm), very high partial pressure of carbon dioxide (ca. $10^{-1.5}$ atm), and a neutral to slightly acidic depositional environment, usually between pH 5.5 and 7.5 and high total concentration of Fe^{2+}. Subsurface waters such as the lower columns of euxinic water bodies or sediment pore fluids, can acquire the conditions requisite for siderite formation through a series of microbial and abiotic reactions involving iron-bearing minerals and organic matter of various origin (LANGMUIR, 1969, 1997). Siderites of different geologic ages have widely different Fe/Ca ratios and $\delta^{13}C$ values. Many modern siderites, however, possess very positive and variable $\delta^{13}C$ and $\delta^{18}O$ values, suggesting that the CO_2 required for their formation was generated from the decomposition of organic matter by methanogens (ADAMS et al., 2006; MORTIMER & COLEMAN, 1997; MOZLEY & WERSIN, 1992). Processes that can cause a decrease in the $\delta^{18}O$ value of pore-fluid, (and hence $\delta^{18}O$ value of the siderite), are mineral-water interactions in partially closed chemical microsystems (MOORE et al., 1992), and bacterial organic degradation under reducing environments (SASS et al., 1991).

In marine settings, pyrite is commonly more prevalent than siderite due to the high sulfate concentrations in seawater. However, even in marine or brackish environments, siderite may precipitate during early diagenesis if the waters contain low levels of bioavailable organic matter. Even in such cases, under conditions of restricted availability of organic matter, Fe(III)-reducing bacteria can outcompete sulfate-reducing bacteria for the organic substrate, resulting in a preferential precipitation of siderite at the expense of pyrite (ADAMS et al., 2006). Hence, pyrite and siderite are usually mutually exclusive within a single sample.

Dissolved iron is present in both marine and fresh waters and is derived from the reduction of fine-grained detrital iron oxide minerals by organic material in the sediment. Oxygen is rapidly depleted upon deposition in sediments rich in organic carbon, due to exhaustive aerobic decay. Even if the overlying water is oxygenated, aerobic decay within the upper few millimetres of organic-rich sediment will maintain anoxic reducing conditions.

Given anoxic conditions and reduced iron, the primary factor that determines whether pyrite or siderite will form is the presence of sulfide (H_2S and HS^-). Pyrite is the end product of a series of reactions that first combine reduced iron and sulfide to form metastable monosulfide iron minerals, which then subsequently react with aqueous sulfur species to form the disulfide. The overall reaction is given by BERNER (1981):

$$3H_2S + S_0 + Fe_2O_3 = 2FeS_2 + 3H_20$$
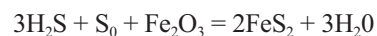
Sulfides are produced from sulfate (SO_4^{2-}) during bacterial decomposition of organic matter. Marine waters are enriched in sulfate relative to fresh waters by a factor of 100 so that marine sediments rich in organics produce abundant sulfide, while freshwater sediments are sulfide poor. Organic decay also provides some sulfate to the sedimentary environment, but this source is negligible relative to the quantity of sulfate available from interstitial marine water, and from the diffusion into the sediment of sulfate from the essentially infinite source in the overlying water column. Marine sedimentary environments« are thus termed »sulfidic environments« in Berner's classification, with pyrite being the characteristic early diagenetic mineral.

Siderite forms through the combined effects of iron reduction and bacterial methanogenesis of organic carbon compounds by the following overall reaction (CURTIS et al., 1986):

$$7CH_2O + 2Fe_2O_3 = 3CH_4 + 4FeCO_3 + H_2O$$

As with pyrite, the source of iron is the reduction of detrital iron oxides in a strongly reducing, organic-rich sedimentary environment. Siderite is rarely precipitated in marine environments because Ca^{2+} reacts preferentially with bicarbonate at normal marine concentrations. The Fe^{2+}/Ca^{2+} ratio in normal marine waters is two orders of magnitude too small to permit siderite precipitation (MATSUMOTO & IIJIMA, 1981). In a reducing marine sedimentary environment, Fe^{2+} is prevented from building up to a concentration that would permit siderite formation by its reaction with sulfides to form pyrite. There-

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fore, only in a »nonsulfidic environment« can Fe^{2+} be precipitated as siderite (BERNER, 1981).

The most likely way to achieve a nonsulfidic environment is to exhaustively react all available sulfide in the sediment pore waters. This is most easily accomplished in sulfate-poor, non-marine sedimentary environments. Organic-rich, non-marine sedimentary environments harbour optimal conditions for siderite formation. The scarcity of sulfate (and therefore sulfide) in non-marine water limits sulfate reduction of organic matter and pyrite formation. Reduced iron accumulates in solution as methanogenesis produces abundant bicarbonate ions that combine with Fe^{2+} to produce siderite. Attainment of this »methanic environment« during the early stages of diagenesis suggests that the initial depositional environment was sulfate-poor and, therefore, non-marine (EMERSON, 1976; BERNER, 1981; MCMILLAN & SCHWERTMANN, 1998).

Our aim in this paper is to demonstrate that carbonate shells with their organic matrix provide a substrate for microbial growth, and microorganisms are responsible for processes favouring concretion growth.
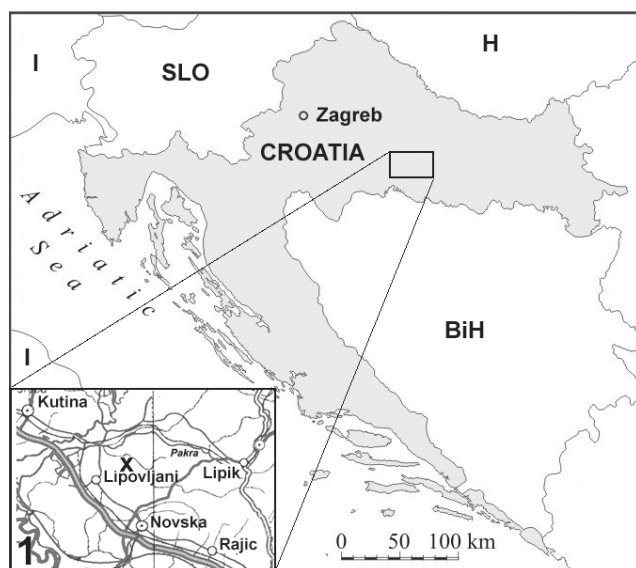

Figure 1: Location map, **X**-sampling site.

MATERIALS AND METHODS

Sampling location

Gastropod shell samples and concretions were collected in Pliocene sand and clay beds of Lipovljani, western Slavonia, Croatia (Fig.1).

These sediments are known as the Paludina beds after an old name Paludina (NEUMAYR & PAUL, 1875), which was used for gastropods today known as Viviparidae. The Lipovljani Pliocene sands and clays with viviparid gastropods are freshwater lake sediments with a significant fluvial input of detrital siliciclastic and carbonate material (TAKŠIĆ, 1951).

These sediments represent the final sedimentation stages in lakes that were the last remnant of the Parathethys basin.

EXPERIMENTAL

Morphologic observations of samples were carried out using an optical polarization microscope and a Tescan TS 5136 scanning electron microscope (SEM). The same SEM microscope equipped with the Oxford energy dispersive spectrometer (EDS), coupled with INCA system, was used for elemental distribution analysis in the samples.

Mineral phase determinations of the studied concretion and host sediment samples were done by Philips X'pert powder diffractometer, running at 45 kV and 40 mA. Samples for morphologic SEM observation were prepared from fractured gastropod shells and concretions. In the first case, small parts of the shell or concretions were simply mounted on the SEM stubs and sputtered with gold or carbon. The other concretions were broken in half to expose the central section of the gastropod shell – such fractured concretions were carbon coated. These samples were examined by SEM operating in secondary electron (SE), or back scattered (BSE) mode at an accelerating voltage of 1–30 kV. EDS qualitative analysis was performed on carbon coated samples at an accelerating voltage of 20 kV. Polished thin sections of the concretions were used for elemental mapping and quantitative EDS analysis. Some of the fractured concretions were selectively etched with 1% HCl solution to remove carbonate cement between microbial filaments. The gastropod shell in the centre was protected from etching by the following procedure: thin aluminum foil was cut in the shape of the concretion section with an opening above the location of the gastropod shell. This »shield« was fixed over the concretion. Shielded concretions were carbon coated, and after the foil shield was removed only the central part was covered by carbon, while the rest of the shell was in its natural state. The carbon film thus protected the shell from dissolution during the etching process. The etching of selectively coated concretions was monitored and controlled under a stereomicroscope. Samples for optical microscopy were resin embedded prior to cutting. Some of the slides for optical
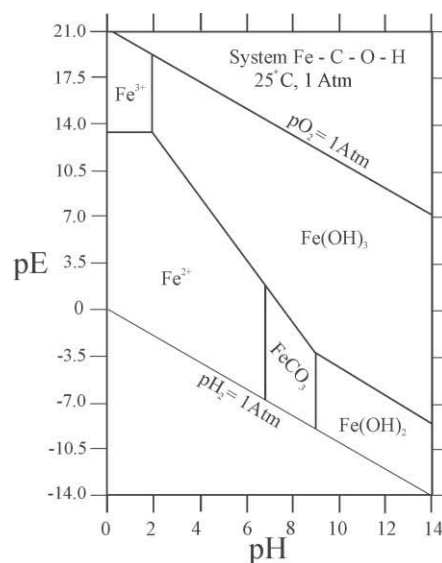

Figure 2: The Eh – pH diagram for the system Fe-C-O-H at 25 C, showing the calculated stability field of siderite.
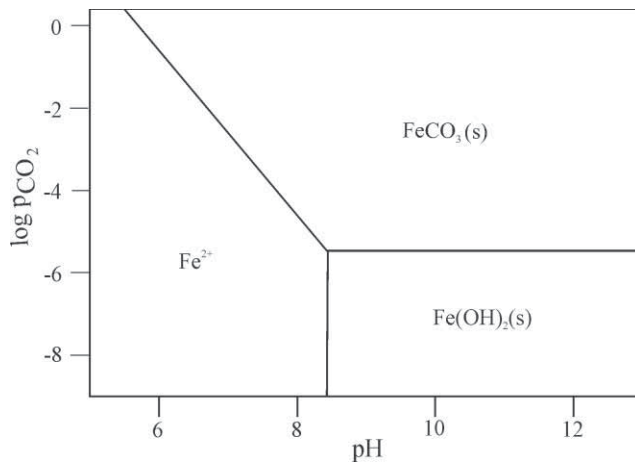
Figure 3: Predominance diagram of the stable phases in the mineral-solution system Fe^{2+} – $Fe(OH)_{2(s)}$ – $FeCO_{3(s)}$, at $\Sigma Fe = 10^{-4}$ mol L^{-1}.

Figure 4: SEM backscatter image of the fractured concretion with gastropod shell in the centre.

microscopy were stained with potassium ferricyanide. XRD analysis was performed on untreated material, but also repeated on the same material after treatment with 1% HCl solution to remove calcite.

Two batches of the sediment with the gastropod shells were used for the determination of pH when mixed with an aqueous phase. About 20 g of sediment was equilibrated with (a) deionized – MilliQ water, and (b) with normal tap water – and left to equilibrate for 7 days. After equilibration the pH of the aqueous phases were (a) = 8.78 and (b) = 7.38.

This equilibrium pH value and the enthalpy of siderite formation (LANGMUIR, 1969) was used to calculate the Eh-pH diagram shown in Fig. 2. The Eh-pH stability fields of the above minerals (and/or their precursors) indicate anoxic conditions for the original depositional environment. A pCO2 vs. pH predominance diagram was constructed, showing the stable phases and solubilities in a mineral-solution system. The assumed $\Sigma Fe = 10^{-4}$ mol L^{-1} (Fig. 3).

RESULTS AND DISCUSSION

Normally, the outer surface of the concretions is irregular and composed of submillimetric mounds. Examination of the fractured concretions containing gastropod shells, using stereo and SEM microscopy indicated an excellent state of shell surface preservation without any signs of dissolution (Fig 4).

The aragonitic shell in the concretion centre has an envelope of radially emanating filaments extending from the shell in the centre to the outer edge of the concretion. Evidence of shell mineral replacement was not found in the concretions. The filaments are embedded in the transparent matrix with microlaminated structure (Figs. 5–7).

EDS analysis of microbial filaments shows Fe, Mn, O with minor traces of Cu, As, Zn. The matrix between filaments contains Fe, Ca, Mn, C, O (Fig. 8).

On the basis of crystal habit and element content, as well as on XRD data of extracted samples from mineralized microbial filaments and surrounding matrix, it can be concluded that the filaments were mineralized with goethite. The matrix between the filaments has been determined as calcite and siderite (Fig. 9).
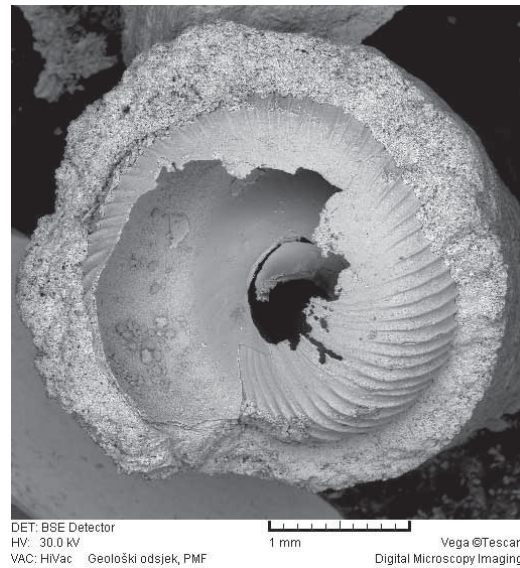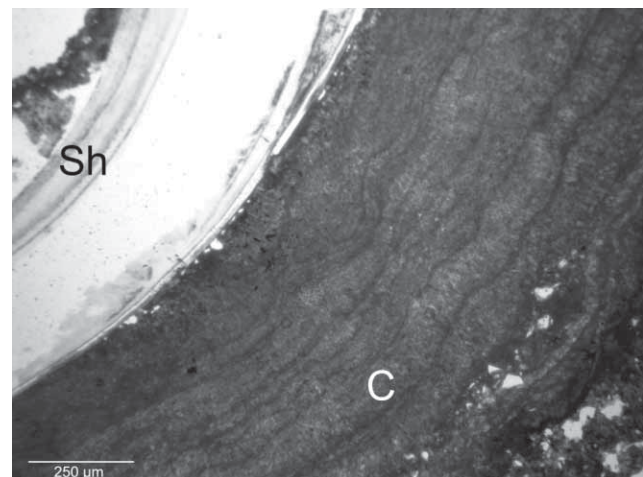

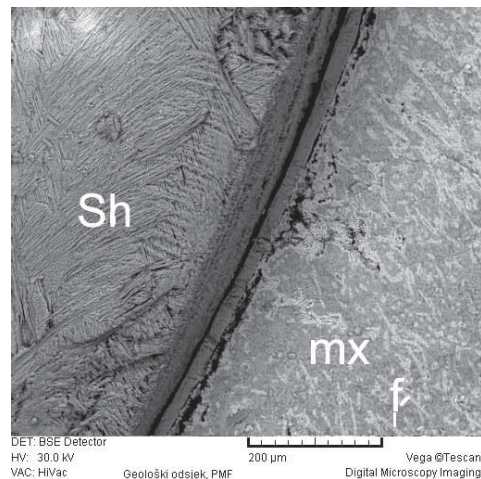**Figure 5:** Layered structure of the concretion, Sh – gastropod shell, C – concretion.

Figure 6: SEM backscatter image of the gastropod shell wall (Sh) and microbial filaments (f) embedded in carbonate matrix (mx).

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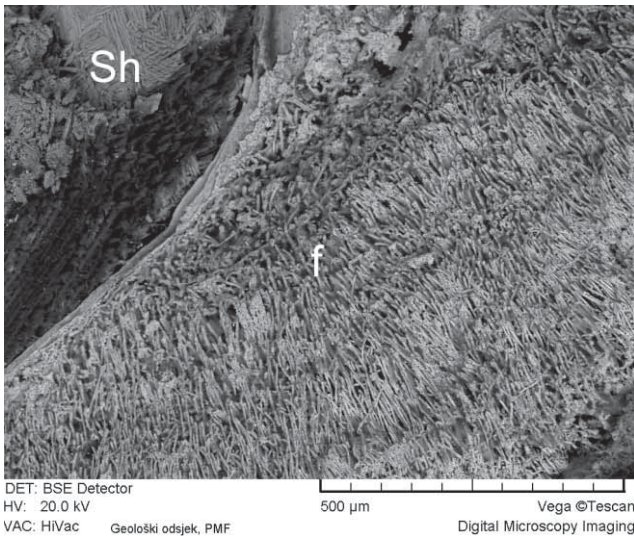

Figure 7: The same part of the concretion shown on Fig.5. etched with 1% HCl solution. Acid etching dissolved carbonate matrix and exposed insoluble iron-oxide coated microbial filaments. Sh – crossed lamellar structure of the gastropod shell wall, f – microbial filaments.
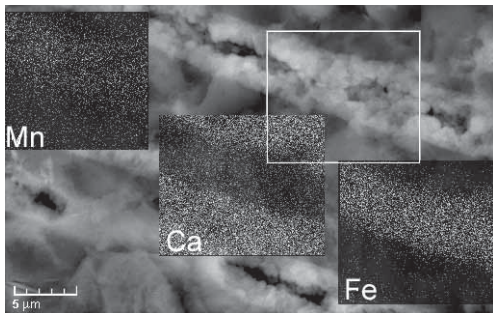

Figure 8: EDS element maps of Mn, Ca and Fe, recorded from decomposed and mineralized microbial filaments shown in the rectangle. BSE (Back scatter electron) image in background. Accelerating voltage of 20 kV.
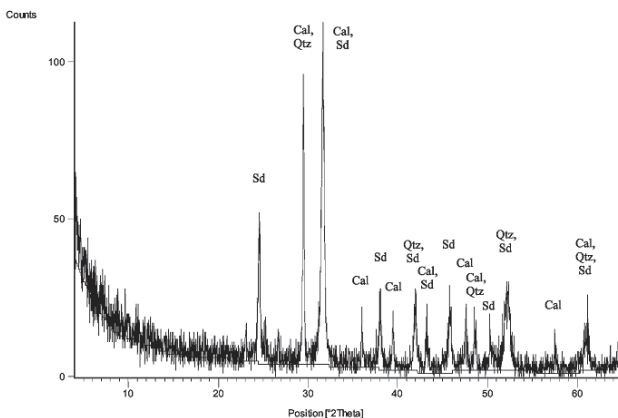

Figure 9: XRD spectra of the concretion material. Sd – siderite, Cal – calcite.

The very small size of the crystallites indicates that nucleation dominated over crystal growth, which implies very rapid precipitation from supersaturated solutions (KRAUSKOPF, 1994).

All host sediment material is laterally displaced by microbial growth and there is no detrital material embedded in the concretion. Each lamination sequence starts with transparent colourless laminae, which gradually become reddish in colour and transparent . The lamination sequence sometimes ends with completely opaque laminae (Figs. 10 and 11).
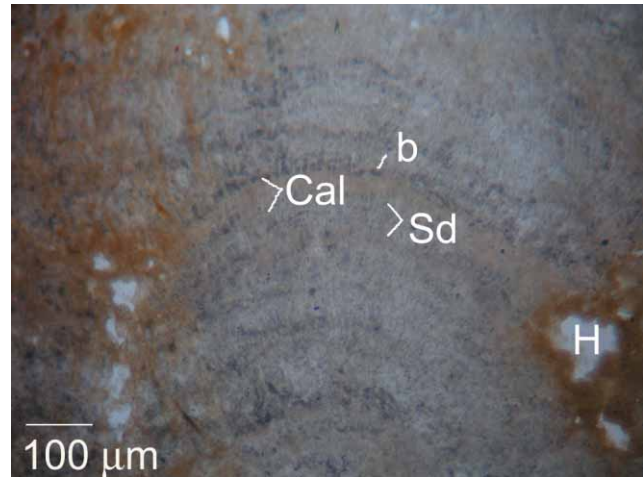

Figure 10: Thin section micrograph of the concretion showing lamination with different mineralizations. Sd – siderite, Cal – calcite, b – opaque lamina with increased carbon and sulphide content, H – corrosion pits with limonite rims.
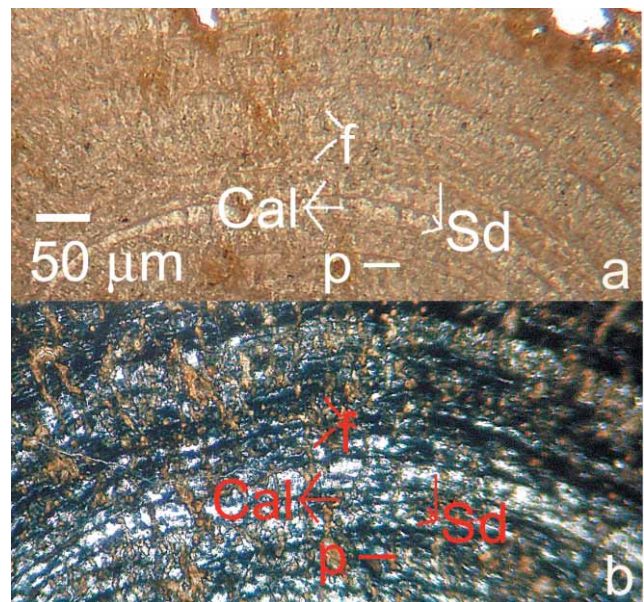

Figure 11: a) Thin section of the concretion with alternating calcitic and sideritic laminae. b) the same thin section stained with potassium ferricyanide. Cal – calcite lamina, Sd – siderite lamina, f – iron-oxide microbial filaments, p – marks of the same positions on stained and unstained sample.

EDS analysis of the opaque laminae indicates an increase in carbon and iron-sulfide content. Concretions sometimes feature corrosion pits on the surface but also within the concretion. Such corrosion structures are surrounded with reddish to yellow limonite rims (Fig. 10).

The radially emanating filaments, extending from the shell in the centre, are in centripetal symmetry, indicating non-phototropic growth of these non-photosynthetic organisms. Filaments are up to 5 μm in diameter and up to 1 mm in length. Although the filamentous microbes could not be identified taxonomically, on the basis of their non-phototropic growth, the size of the filaments and iron-hydroxide coating it can well be inferred that these filamentous structures are probably iron oxidizing bacteria such as *Leptothrix* (BERTHELIN et al., 2000).

The chronological sequence of processes resulting in mineral encrustation is as follows.

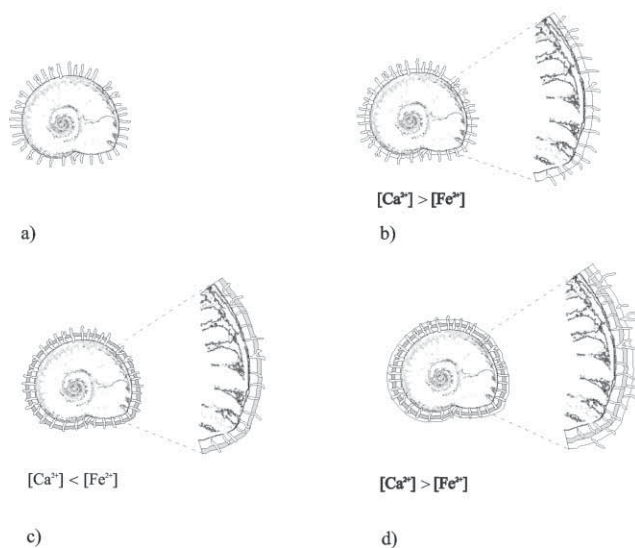**The processes can be sequenced in four stages** (Fig. 12)**:**

Figure 12: Chronological sequence of processes resulting in mineral incrustation (see text for details).

a) After the death of the gastropod, the initial decay and decomposition of the animals organic tissues was obviously rapid and without effect on the present mineral phase – carbonate shells with organic matrix were buried in muddy sediment containing substantial amounts of organic matter.
b) In the second stage, the shell was buried in the oxic or suboxic muddy sediment, while bacteria started to grow on the shell surface, surrounding the shell with a mantle of microbial filaments. Bacterial oxidation of ferrous iron and manganese resulted in the accumulation of iron and manganese in their microenvironment. Iron was adsorbed on the extracellular polysaccharide surface (EPS) of the filament, forming iron oxyhydroxides. The partial pressure of CO_2 must have been low, and during periods of oxic regimes (high Eh) and the oxidation of available iron to ferric iron, calcite was precipitated between microbial filaments.
c) During the third stage, the degradation of organic matter maintained a lower Eh and higher pCO_2 of the microenvironment. The bacterial rate of growth decrea-

sed, protected within the iron oxide coating. Under such conditions, the stability range of iron Fe^{2+} increased and there was a consequential increase in Fe^{2+} concentration. Increased CO_2 partial pressure, close to neutral pH, increased Fe^{2+} concentrations and low activity of S^{2-} favoured siderite precipitation (BERNER, 1971; PEARSON, 1979; SUESS, 1979; POSTMA, 1982; BROWNE & KINGSTON, 1993).
d) In the final stage the microenvironment again became oxic and pCO_2 low. Siderite laminae were partially oxidized to hematite resulting in a red coloration of the thin laminae. Some bacterial filaments survived the anoxic episode and continued their growth (Fig. 13). The next lamina would have been be formed according to the scenario described for the first stage.

At the end of the concretion growth environmental conditions became inadequate for microbial life. Microbial filaments decomposed and decayed within their iron-oxide coating, and today every microbial filament is represented by an iron-oxide tube embedded in the siderite and calcite laminated concretion.

Because of the absence of dissolution and preserved aragonitic structure of the shell, we conclude that the pH of the environment was in near neutral range. Assuming that composition of early diagenetic siderite is strongly influenced by pore water chemistry and that fresh-water siderite should contain more Mn^{4+} and Fe^{2+} and less Mg^{2+} and Ca^{2+} than marine siderite (MOZLEY, 1989). It can be concluded that the siderite concretions described in this paper indicate a fresh-water environment during their formation. Concretion formation was rapid, and it is possible to find single microbial filaments extending from the surface of the shell in the centre, crossing the whole concretion and ending on the concretion's outer surface, indicating that the whole concretion formed in the life time of a single filament.

The predominance diagrams calculated from standard thermodynamic data using the equilibrium pH value of the sand-water mixture, indicate that conditions of Eh and pH favoured the formation of siderite in the depositional environment. The size of the $FeCO_3$ stability field and its range along the Eh and pH axes depend on the partial pressure (fugacity) of CO_2 used in the algorithm.

CONCLUSIONS

It can be concluded that these concretions were formed in a fresh-water environment with fluctuating oxygen levels, resulting in alternating periods of oxic, suboxic and anoxic conditions. The environment does not seem to have been impacted by strong hydrodynamic turbulence, indicating a lacustrine setting. Microbial filaments were mineralized during their life time, before their decomposition commenced.

An understanding of the precipitation of iron in low temperature systems at the Lipovljani sand beds, however, must account for the evidence of microbial activity. It is suggested here that the initially deposited ferric hydroxide would immobilize the ferrous iron into colloidal particles and thus provide a favorable ferrous substrate for the subsequent growth of iron
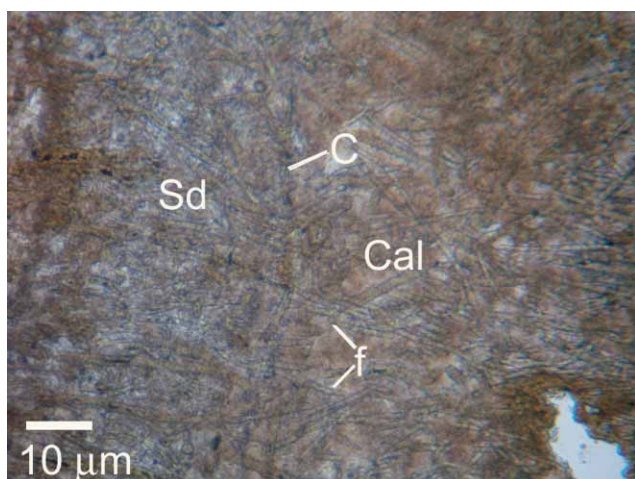
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Figure 13: Contact between sideritic and calcitic lamina with microbial filaments. Sd – siderite lamina, Cal – calcite lamina, C – contact between siderite and calcite lamina, f – microbial filaments extanding from sideritic (anoxic) into calcitic and hematitic (oxic) lamina.

oxidizing bacteria such as *Leptothrix*. Most of the filamentous textures observed in the oxyhydroxides probably formed in this fashion. Difficulties in the identification of filamentous textures arise due to their degradation, rather than due to additional iron deposition obscuring the morphology.

Further evidence on the microbial mediation of siderite formation in the depositional enviroment of the Lipovljani sand beds, including more information on the sulphate levels of the ambient waters, could be provided by $\delta^{13}C$ and $\delta^{18}O$ values of the carbonate phases. Oxygen isotopes can provide insight into the environmental conditions and mechanisms for biogenic iron mineral formation in natural systems and appropriate investigations are envisaged in the near future.

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