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Syndepositional cements associated with nannofossils in the Marmolada Massif: Evidences of microbially mediated primary marine cements? (Middle Triassic, Dolomites, Italy)

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Abstract

The Marmolada platform is characterized by striking globose masses (“evinosponges”), arranged in concentric bands, of fibrous calcite cements ranging in size from centimeters to several decimeters. The lithogenetic importance of these peculiar cements has been recognized in many Middle Triassic buildups of the Western Tethys. EDS microanalyses revealed that these fibrous cements contain 1–3 mol% of Mg and detectable amounts of Sr, over 1000 ppm, sometimes exceeding 10,000 ppm. The strontium geochemical signature in neomorphic calcite could reflect the replacement of an aragonitic carbonate precursor. The boundaries between the fibrous calcite bands are marked by alignments of microcrystalline aggregates of fluorapatite and/or dolomite. The presence of fluorapatite may indicate a depositional microenvironment eutrophic or rich in microbial communities. Epifluorescence analyses showed bright bands alternated to dark ones, confirming that organic matter remains occur within the studied cements and could have played a significant role in supporting the widespread syndepositional cementation.

High magnification SEM observations on bright epifluorescent bands showed the presence of widespread, more or less spherical bodies ranging in size 100–300 nm. These bodies could represent the relicts of nannobacterial cells.

Keywords: Marine cements; Aragonite–calcite; Biomineralization; Epifluorescence; Nannofossils; Triassic
1. Introduction

A general description of carbonate facies of the Marmolada Platform has been already provided by Russo et al. (2000). The authors recognized the main role and the abundance of striking concentric cements which characterize the outer margin and slope facies. These represent the major constituent of the platform, forming more than 50% of the rock volume. These peculiar cements were already recognized by Stoppani (1858) in the Triassic buildups of the Western Southern Alps. The author interpreted these structures as encrusting sponges and created the new genus *Evinospongia*. He also underlined their lithogenetic importance in the Middle Triassic. Evinosponges, also known as “Großoolith” in the Austroalpine Triassic (Schmidegg, 1928), were interpreted as early diagenetic precipitates, modified by fresh-water diagenesis (Brandner and Resch, 1981 and Henrich and Zankl, 1986). Frisia Bruni et al. (1989), in a comprehensive study on evinosponges of the Western Southern Alps, recognized a low-Mg calcite composition, but drew no final conclusion with regard to the origin and primary mineralogy (Mg calcite vs. aragonite) of these cements.

Thus “evinosponges” appear to be a phenomenon relatively narrow in geological time and in paleogeographic distribution but they dominated the platforms in which they were present.

Our research is focused on describing the microstructure, mineralogy, geochemistry, and diagenesis of these peculiar cements cropping out in the Marmolada Platform, with the aim to understand the cause of their mineralization. We chose this buildup because it is little affected by dolomitization and shows good outcrops, reasonably easy to sample.

Fig. 1. Location map of the study area, on the northern slope of the Marmolada, Western Dolomites, Italy. The black spot indicates the sampled zone.
2. Location

We collected ten samples of evinosponges on a transect stretched from margin to upper slope setting, on the north-eastern side of the Marmolada Platform, at the Glacier front (Pian dei Fiacconi, between Q 2650 and 2750); here the retreat of the glacier has recently exposed this excellent outcrop (Fig. 1). The ammonoid content indicates an uppermost Anisian age (Secedensis Zone, Brack and Rieber, 1993 and Brack and Rieber, 1996) for these sedimentary rocks.

3. Marine cements (Evinosponges)

Outer margin and upper slope of the Marmolada Platform are dominated by a network of globose masses, decimeter in size, which are coated and linked to each other by large amounts of fibrous cements, arranged in concentric bands. These cements form more or less isolated or laterally linked bodies: the evinosponges (Fig. 2a, b). The syndepositional origin of these elements is clearly demonstrated by the fact that they are frequently reworked as clasts in mid to low slope deposits.

Fig. 2. Fibrous cements, “evinosponges”, from the Marmolada Platform, Dolomites, Italy. (a) Field view of a network of globose masses, decimeters in size, which are coated and linked to each other by large amounts of fibrous cements, arranged in concentric bands. (b) Ice polished natural section of evinospongia, with alternating dark and light isopachous layers (Pian dei Fiacconi at about Q 2750 m). (c) Isopachous layers of fibrous calcite cement coating a boundstone nucleus, polished surface. Sample BB4. (d) Fibrous cements in thin section. Sample BB4.
Hand samples show isopachous bands of fibrous calcite of different thickness and colours: light and dark layers alternate with each other, millimeters to centimeters in size, and they exhibit a general tendency to increase in thickness from the nucleus toward the periphery (Fig. 2c, d).

Under the light microscope, the isopachous layers are less easily observable and generally separated by thin lenses which represent discontinuities. They are gaps, subsequently filled by sparry calcite, or by the alignment of small and dark crystalline aggregates (Fig. 3a, c). The calcite fibres show undulose extinction and curved cleavages (Fig. 3c).

Fig. 3. Isopachous layers of fibrous calcite cements in transmitted and epifluorescent light. (a) Thin section of fibrous cements showing isopachous layers separated by very thin alignment of dark microcrystalline aggregates (black arrows). (b) Epifluorescent image of field (a); note a characteristic alternation of strongly and feebly fluorescent bands. The bands are extremely variable in thickness and the boundaries between isopachous layers are always marked by bright epifluorescence (yellow fluorescence BP 450-490 nm/LP 515 nm). (c) Detail of the boundary between two isopachous layers; calcite fibres show curved cleavages. (d) Epifluorescent image of field (c); note the bright fluorescence of the dark microcrystalline aggregate alignment (green fluorescence BP 436/10 nm/LP 470 nm).
4. Methods

Micromorphologies and chemical compositions of cements were determined with a scanning electron microscope, Cambridge 360 linked to an EDAX energy-dispersive X-ray microprobe. The analysed samples were polished with 0.25 μm diamond-impregnated surface, then gently etched (0.05% HCl, 1 min) and carbon coated (ca. 250 Å); the data were corrected with the ZAF algorithm. The working conditions were: voltage 20 kV, tilt angle 0°, take-off angle 32.1°. Under these working conditions and with a spot size of 0.1 μm, the analysed CaCO3 volume measures a few cubic micrometers and the detectability limit for the measured elements (Mg, Al, Si, S, K, Ca, Mn, Fe, Sr, and Ba) is lower than 0.1 wt.%.

The sections were checked also for fluorescence to reveal the distribution of the organic matter (Dravies and Yurewicz, 1985, Machel et al., 1991, Neuweiler and Reitner, 1995 and Russo et al., 1997). To perform these observations, we used incident light emitted by Hg high-pressure vapour bulb attached to Axioplan Imaging II microscope (Zeiss), equipped with high performance wide bandpass filters (BP 436/10 nm/LP 470 nm, no. 488 006, for the green light; BP 450–490 nm/LP 515 nm, no. 488 009, for the yellow light).

5. Geochemistry

Minor elements microanalyses were carried out on ten samples. The fibrous calcite cements are characterized by a significant and surprisingly uniform Mg content (1–3 mol%). Detectable amounts of Sr, commonly over 1000 ppm, sometimes exceeding 10,000 ppm, have been measured (Fig. 4). The strontium geochemical signature in neomorphic calcite could reflect the replacement of an aragonitic carbonate precursor. (e.g. Scherer, 1977, Tucker, 1985 and Sandberg, 1985). The minor element contents and micromorphological fabrics indicate a simple diagenetic history: firstly, evinosponges suffered a neomorphic transformation which lead the metastable aragonite phase to be replaced by stable low-Mg calcite, secondarily, a general aggrading recrystallization.

The boundary between the fibrous calcite bands are marked by discontinuities, often constituted by alignments of microcrystalline aggregates of fluorapatite and/or dolomite (Fig. 3, Fig. 5 and Fig. 6). These boundaries possibly constituted the main ways for diagenetic fluids. The presence of fluorapatite can be considered as indicator of eutrophic water conditions and/or the presence of microbial communities (Rougerie et al., 1997 and Soudry, 2000).
Fig. 4. On the left, X-ray spectrum of a polished surface of fibrous calcite cement; on the right, ZAF quantitative data for the measurable elements. Note the 7800 ppm of Sr and the 1.8 mol% of Mg.

Fig. 5. On the left, X-ray spectrum on a dark microcrystalline aggregate typical of the boundaries between two isopachous calcite layers. On the right, ZAF quantitative data for the measurable oxides; the data fit well with the stoichiometric composition of fluorapatite (55.60% CaO, 42.22% P<sub>2</sub>O<sub>5</sub>).
6. Biomineralization, epifluorescence, organic matter, and nannofossils

Recent research suggests that bio-induced carbonate precipitation is often more important than the metazoan growth itself. In this study, the understanding of the primary precipitation mechanisms is limited by the recrystallization and by the lack of organic geochemical data.

Many organisms are known to induce carbonate precipitation (e.g. Chafetz, 1986, Simkiss and Wilbur, 1989, Riding, 1991, Addadi and Weiner, 1992, Chafetz and Buczynski, 1992 and Neumeier, 1998), either directly, by biochemical processes, or indirectly, through the changing of the surrounding chemical microenvironments or the trapping of dissolved Ca$^{2+}$ onto organic templates (Lowenstam and Weiner, 1989). Therefore it is possible to distinguish between “biologically induced” calcification, in which the induction take place in a solution, separated from mineral growth, and “organic matrix-mediated” calcification, which directly controls mineral crystallography. Autotrophic microorganisms can favour carbonate precipitation by increasing pH through removal of CO$_2$ (Ehrlich, 1996), whereas heterotrophic bacteria spur carbonate formation via ammonification of amino acid, or by nitrate or sulphate.


As a result of these processes, the carbonate phases are interlayered with an organic matrix. Such a strict interlayering of calcite and organic matter is documented in this study through epifluorescence observations. 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 and Ramseyer et al., 1997). However, the interpretation of the fluorescence of sedimentary organic matter cannot be based on a direct correlation between preserved aromatic compounds and intensity. In fact a range of chromophores exits with different fluorescences and there are also secondary absorbing effects controlled by other factors (Bertrand et al., 1986).

Residual organic matter as well as Mn$^{2+}$ appear to be the most abundant and important activators of luminescence in natural calcite and dolomite (Lumb, 1978, van Guzel, 1979, Dravies and Yurewicz, 1985 and Machel et al., 1991). Organically activated luminescence seems to be caused mainly by aromatic and certain conjugated organic molecules (Lumb, 1978).

Cuif et al. (1990), Müller-Wille and Reitner (1993), Reitner and Neuweiler (1995), and Russo et al., 1997 and Russo et al., 2000 used fluorescence microscopy to check the presence of residual organic matter.

Uncovered thin sections of evinosponge samples were checked for epifluorescence. The cements are characterized by an alternation of strongly and feebly fluorescent bands, both with yellow (Fig. 3b) or green light (Fig. 3d). The bands are extremely variable in thickness and the boundaries between isopachous layers are always marked by bright epifluorescence (Fig. 3b, d).

Epifluorescence data indicate a general and widespread presence of organic matter, preferably concentrated along parallel bands.

SEM observations at high-magnification on these strongly epifluorescent bands revealed the presence of more or less spherical bodies ranging in size 100–300 nm (Fig. 7a). These objects could represent the relicts of nannobacterial cells which may have played a significant role in supporting the widespread syndepositional cementation, with a possible mechanism analogous to that of microbialite deposition.
7. Nannofossils or artifacts?

Investigations of micromorphologies in various carbonates have shown nanometer-scale spherical bodies in the 25–300 nm range (Folk, 1993, Folk, 1999, Pedone and Folk, 1996, Vasconcelos and McKenzie, 1997, Camoin et al., 1999, Sprachta et al., 2001 and Gautret et al., 2004). The nature of such bodies, visible with scanning or transmission electron microscopes (SEM or TEM) at high magnification, is still debated and controversial.

Many authors assumed for these objects a biological origin and interpreted them as remains of nannobacteria/nannofossils (Folk, 1993, Folk, 1999 and McKay et al., 1996). In addition, similar spherical bodies have also been produced in laboratory experiments (Buczynski and Chafetz, 1991, Folk, 1993, Vasconcelos and McKenzie, 1997 and Chafetz and Buczynski, 1992). In contrast, Reitner et al. (1995) considers such precipitates as by-products of initial calcification of extracellular polymeric substances (EPS).

Recently remarkable papers have been developed on recent and Holocene microbialites, their environmental significance and biochemical controls (Camoin et al., 1999, Sprachta et al., 2001 and Gautret et al., 2004). The authors observed that the finest carbonate precipitates of the microbialites are constituted by rounded bodies 0.1- to 0.2-μm-sized, which represent the basic constructional elements of the automicrite. They maintained that both biomineralization and organomineralization (sensu Trichet and Défarge, 1995) were responsible for their formation and distribution and that their size and shape are reminiscent of calcified bacterial remains.

A similar relationship between organic matter decomposition, nannobacteria and carbonate precipitation has been reported by Pedone and Folk (1996) for the formation of micrometer-sized aragonite cements in modern stromatolites of the Great Salt Lake (Utah).

A totally different interpretation considers these small problematic carbonate objects as artifacts (Bradley et al., 1997 and Kirkland et al., 1999). Kirkland et al. (1999) performed numerous calcite precipitation experiments and demonstrated that nanometer-scale objects
can have inorganic origins. They also demonstrated the possibility that acid etching of calcite crystals could produce features similar to nannobacteria.

We paid particular attention to avoid the introduction of investigator product artifacts. First, we used carbon instead of gold for the conductive layer, which allowed more reliable quantitative EDS microanalyses. Second, nannofossils have been observed on strongly epifluorescent bands (Fig. 7a), while areas with feebly epifluorescence showed only crystal micromorphology and traces of the bent cleavages (Fig. 7b), suggesting that the detected small bodies have a biological origin.

In conclusion, we recognize in these marine cements (evinosponges) the presence of organic matter remains in alternated layers where the carbonate phase appears to be organized in nanometer-scale spherical bodies, very similar to those observed in the microbialites as basic constructional elements of the carbonate precipitates (Camoin et al., 1999, Sprachta et al., 2001 and Gautret et al., 2004). This fact suggests the possibility that evinosponges precipitated with a mechanism similar to that of microbialites.

**8. Conclusions**

The margin and upper slope of the Marmolada Platform (Upper Anisian–Ladinian) are dominated by peculiar carbonate cements known as “evinosponges”. They are decimeter-sized globular structures formed by isopachous fibrous layers enveloping a boundstone nucleus.

Evinosponges are constituted of low Mg-calcite (1–3 mol%). Morphological fabric and a discrete amount of Sr, sometimes exceeding 10,000 ppm, suggest a marine phreatic aragonitic precursor. The boundaries between adjacent isopachous layers are often marked by the alignment of microaggregates of dolomite and fluoroapatite crystals. The presence of fluoroapatite can be considered as indicator of eutrophic water conditions and/or the presence of microbial communities. These boundaries possibly constituted the main ways for diageneric fluids.

Geochemistry data indicate a simple diageneric history: evinosponges suffered a neomorphic transformation (aragonite–calcite) and, later, a general aggrading recrystallization.

Epifluorescence analyses revealed an irregular alternation of bright and dark bands of different thicknesses, which indicate the presence of organic matter remains in concentric bands. SEM observations at high magnifications on the bright epifluorescent bands, rich in organic matter remains, showed that the carbonate phase appear to be organized in spherical bodies, submicrometer-sized (100–300 nm). We interpreted these objects as nannofossils, suggesting that marine cements (evinosponges) like the microbialites could have been formed via organic matter and/or microbial mediation.

The presence of cyclic alignment of microcrystalline aggregates of fluorapatite, which corresponds to the bright fluorescent bands, indicates periods of high nutrient supply to the marine environment. These eutrophic water conditions could have facilitated the growth of these peculiar cements, which characterize the carbonate platforms in the Western Tethys during a short interval of geological time and space.
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