MICROBIALITES AS PRIMARY BUILDERS OF THE LADINIAN – CARNIAN PLATFORMS IN THE DOLOMITES: BIOGEOCHEMICAL CHARACTERIZATION

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With 4 Figures

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Introduction

The importance of automicrites or microbialites is well known in carbonate platform and reefal environments throughout Earth history (Reitner, 1993; Camoin et al., 1999). During the Proterozoic and early Palaeozoic, microbial carbonate mounds and reef-like structures were the world's first large-scale biotic constructions (Riding, 1991; Flügel et al., 1993; Riding & Awramik, 2000). From the late Palaeozoic onward, skeletal framebuilders, always associated with microbialites and microbially induced cements, played a leading role in constructing carbonate platforms. The ratio of microbialites to skeletal metazoans during geological time is characterized by phases in which microbialites greatly prevail, as in stressed environments or in the immediate aftermath of biological crises, and phases of equal coexistence of the two components (Webb, 1996; Russo et al., 1997, 1998; 2000; Kiessling et al., 2002; Riding, 2002; Russo, 2005).

An important example is constituted by the carbonate successions belonging to the Wengen and S. Cassiano formations, located in the Eastern Dolomites, Punta Grohmann, Sassolungo (Bz) (Fig. 1).

The Punta Grohmann section is one of the most classical Late Ladinian – Early Carnian basin successions of the Dolomites, described in several important papers (Ogilvie-Gordon, 1927; Leonardi, 1967; ScudelerBaccelle, 1971; Russo et al., 1997; Gianolla et al., 1998; Gianolla & Neri, 2007).

Many levels, occurring within this succession, contain gravity-displaced carbonate olistoliths, the so-called *"Cipit boulders*" of Richthofen (1860). They are fed to the basin by coeval prograding Cassian carbonate platforms (Assereto et al., 1977; Bosellini, 1984) or, in some cases, by pre-existing buildups undergoing erosion. While these platforms are completely dolomitized, generally the changes did not affect the Cipit boulders, because they are embedded in a marly matrix impermeable to diagenetic fluids (Biddle,1981; Russo et al., 1991). Therefore, the olistoliths and, in general, the gravity-resedimented carbonates occurring within the basin deposits, represent the unique evidence of the original fabric and texture of the ancient carbonate platform margin/ upper slope (Fürsich & Wendt, 1977; Fois & Gaetani, 1981; Biddle,1981; Brandner et al., 1991).

To corroborate the microbialitic model proposed by Russo et al. (1997) for the Late Ladinian – Carnian platform buildups, together with classical micro- and nanomorphological studies and EDS microanalyses we carried out detailed biogeochemical analyses on organic matter extracted from selected samples of carbonate boulders in order to confirm the role of microbialites as "primary builders" in the sense that they are syndepositionally cemented and dominate volumetrically the bioconstruction.



Fig. 1: Location map of Punta Grohmann (Sassolungo, BZ).

Sample Location

A stratigraphic scheme of the Punta Grohmann section is represented in Figure 2. The studied boulders are indicated with labels from U1 to U5 and have been sampled from two different sedimentary settings: unit c (olistolith fed by dismantling of a previous platform), unit d (swarm of Cipit boulders inserted randomly in the S. Cassiano succession). The third unit, labeled "e" in figure 2 is characterized by two coarsening upward cycles at the toe-of-slope, recording the progradation of an active platform, yielded samples not well preserved and unsuitable to be studied for the organic matter content.

Methods

The micro and nanomorphological analyses were performed using optical, UV fluorescence and scanning electron microscope (SEM) observations. Geochemical characterization was carried out with energydispersive X-ray spectrometer (EDS).

Organic matter characterization was made up in selected samples. They were grounded to a fine pow-

der and organic compounds extracted using a mixture of solvents by ultrasonication. Total lipid extracts were fractionated by column chromatography into polar and apolar compounds. These hydrocarbon fractions were analyzed by Fourier Transform–Infrared Spectroscopy (FT-IR), in order to obtain a first global characterization of organic functional groups, and then by Gas Chromatography coupled to Mass Spectrometer (GC– MS), to detect and recognize specific macromolecules (biomarkers).

Results and Discussion

Microfacies are constituted on average by 15% of bioclasts, 10% of detrital micrite, 50% of microbialites, and 25% of cements. The bioclasts belong to metazoans, mainly stromatoporoids and inozoa, microproblematica (e.g. *Tubiphytes obscurus, Macrotubus babai, Plexoramea cerebriformis*), skeletal cyanobacteria (e.g. *Cladogirvanella cipitensis*), and rarely fragments of bivalves, gastropods and echino-



Fig. 3: Different types of micrites in the Punta Grohmann samples: a) thrombolitic micrite; b) stromatolitic micrite; c) detrital micrite; d) aphanitic micrite.

derms. The microbialites or automicrites, exhibit both dense microcrystalline (aphanitic) or peloidal microfabric, and sometimes are organized in stromatolitic laminae or thrombolitic fabric. Early cements are represented by botryoidal and fibrous infilling vugs and stromatactis-like cavities and late cements of ferroan blocky sparry calcite.

The distribution of organic matter remains was detected on the base of epifluorescence observations which revealed very bright fluorescence in the peloidal micrite.

Therefore, FT-IR and GC-MS analyses were carried out on total lipid extracts from this type of micrite. They revealed the presence of stretching C=C vibrations attributable to alkene and/or unsaturated carboxylic acids. GC-MS investigations indicated the presence of extended hopane series, short chain methyl-steranes (C_{22} , C_{23}), straight chain saturated (C_{14} , C_{16}), monounsaturated ($C_{17:1}$, $C_{18:1}$), and diunsaturated($C_{18:2}$) carboxylic fatty acids (Fig. 3).

The carboxylic acid pattern and pentacyclicterpanes series, recorded in the studied micrite, is similar to that found in microbial mats (Thiel et al., 1997; Ourisson et al., 1987; Brocks & Summons, 2004). Actually, straight chain saturated (C_{14} , C_{16}), monounsaturated ($C_{16:1}$, $C_{18:1}$) carboxylic acids and diunsaturated $C_{18:2}$ acids are also known as typical bacterial components (Kenyon et al., 1972; Cohen & Vonshak, 1991; Merrit et al., 1991; Thiel et al., 1997; Peters et al., 2005). Pentacyclicterpanes of the C_{27} to C_{31} extended hopane series are diagnostic of the bacteria domain. Biological precursors of extended hopanes, the bacteriohopanepolyols, likely have the physiological function of membrane rigidifiers in bacteria, a role in eukarya fulfilled by sterols (Ourisson et al., 1987; Brocks & Summons, 2004).

Although some authors suggested that thermal degradation of regular steranes ($C_{27}-C_{29}$) could be responsible for the formation of C_{21} and C_{22} short chain steranes (Huang *et al.*, 1994), 4-Methyl and 4,4-dimethyl steroids have been identified in cultures of methanotrophic bacteria (Bouvier et al., 1976; Schouten et al., 2000)

Conclusions

The Cipit boulders from the Punta Grohmann section contain automicrites analogous to those described in Reitner & Neuweiler (1995). These carbonate olistoliths are characterized by skeletal cyanobacteria and microproblematica, with a minor contribution by sponges, embedded in a large amount of stromatolitic and/or clotted peloidal micrite (Russo et al., 1997). Biomarker data confirmed the presence of bacteria/cyanobacteria communities during platform deposition, indicating that microbes have played a prominent role in the genesis of these carbonates. These communities created the chemical conditions that triggered the induced precipitation of great volumes of syndepositionally-cemented automicrites, which stabilized the carbonate bodies controlling their depositional geometries. Although following the Dunham classification (1962) these carbonates should be considered as "wackestone", the very early cementation of microbialites, confirmed by the presence of bacterial biomarkers and the steep depositional geometries suggest that Punta Grohmann carbonates must be classified as "boundstone" in which the bioconstructor role is played by microbialites.



Fig. 2: Stratigraphic log of the studied section (modified from Russo et al., 1997).



Fig. 4: FT-IR and GC-MS results of a selected sample showing functional groups and specific biomarkers of bacteria:

a)FT-IR spectrum on total lipid extracts;

b) Short chain steranes;

c) Hopanes;

d) Fatty acids distribution.

References

- Assereto, R., Brusca, A., Gaetani, M., Jadoul, F. (1977): Le mineralizzazioni Pb-Zn nel Triassico delle Dolomiti: quadro geologico ed interpretazione genetica. – L'Industria Mineraria, 28: 367-402.
- Biddle, K.T. (1981): The basinal Cipit boulders: indicators of Middle to Upper Triassic buildup margins, Dolomite Alps, Italy. – Riv. Ital. Paleont. Strat., 86: 779-794.
- Bosellini, A., (1984): Progradation geometries of carbonate platform: example from the Triassic of the Dolomites, Northern Italy. – Sedimentology, 31: 1–24.
- Bouvier, P., Rohmer, M., Benveniste, P., Ourisson, G. (1976): △^{8 (14)} Steroids in the bacterium *Methylococcus capsulatus.* – Biochemistry, 159: 267–271.
- Brandner, R., Flügel, E., Koch, R., Yose, L.A. (1991): The Nothern Margin of the Schlern/Sciliar – Rosengarten/Catinaccio Platform. – Dolomieu Conference on Carbonate Platform and Dolomitization, Field Guide Book, Ortisei/St. Urlich, Italy, Guidebook Excursion A, 1-61.
- Brocks, J. J. & Summons, R. E. (2004): Sedimentary hydrocarbons, biomarkers for early life. – In: Schlesinger, W.H. (ed.): Treatise on Geochemistry. – Biogeochemistry, 63–115, Elsevier Pergamon, Oxford.
- Camoin, G. F., Gautret, P., Montaggioni, L. F., Cabioch, G. (1999): Nature and environmental significance of microbialites in Quaternary reefs: the Tahiti paradox. Sed. Geol., 126: 271–304.
- Cohen, Z. & Vonshak, A. (1991): Fatty acid composition of Spirulina and Spirulina-like cyanobacteria in relation to their chemotaxonomy. – Phytochem., 3130: 205–206.
- Dunham (1962): Classification of carbonate rocks according to depositional texture. - In: Ham, W. E. (ed.): Classification of carbonate rocks. - American Association of Petroleum Geologists Memoir, 108-121.
- Flügel, E., Hillmer, G., Scholz, J. (1993): Microbial carbonates and reefs: an introduction. - Facies, 29: 1–2.
- Fois, E. & Gaetani, M. (1981): The northern margin of the Civetta buildup. Evolution during the Ladinian and the Carnian. – Riv. It. Paleont. Strat., 86, 3: 469– 542.
- Fürsich, F.T. & Wendt, J. (1977): Biostratinomy and Palaeoecology of the Cassian Formation (Triassic) of the Southern Alps. - Palaeogeogr, Palaeoclimatol, Palaeoecol, 22: 257-323

- Gianolla, P., De Zanche, V., Mietto, P. (1998): Triassic Sequence Stratigraphy in the Southern Alps. Definition of sequences and basin evolution. In: De Gracianscky, P.C., Hardenbol, J., Jacquin, T., Vail, P.R., Ulmer-Scholle, D. (eds.): Mesozoic- Cenozoic Sequence Stratigraphy of European Basins. SEPM Special Publication, 60: 723–751.
- Gianolla., P. & Neri, C. (2007): Formazione di Wengen. In: Cita Sironi, M.B., Abbate, E., Balini, M. Conti, M.A., Falorni, P., Germani, D., Groppelli, G., Manetti, P., Petti, F.M. Carta Geologicad'Italia – 1:50.000, Catalogo delleFormazioni – Unitàtradizionali (2), QUADERNI serie III, 7/VIII, S.E.L.C.A., Firenze, 111-124.
- Huang, D.F., Zhang, D.J., Li, J., (1994): The origin of 4-methylsteranes and pregnanes from Tertiary strata in the Qaidam Basin, northwest China. – Geochemistry 22: 343–348.
- Kenyon, C. (1972): Fatty acid composition of unicellular strains of blue-green algae. – J. Bacteriol. 109: 827– 834.
- Kiessling, W., Flügel, E., Golonka, J. (2002): From patterns to processes: the future of reef research. – In: Kiessling, W., Flügel, E., Golonka, J. (eds.): Phanerozoic Reef Patterns. – SEPM Spec. Publ., 72: 735–743.
- Leonardi, P. (1967): Le Dolomiti. Geologia dei Monti tra Isarco e Piave. - 1019 pp., Manfrini Ed., Rovereto.
- Merrit, M. V., Rosenstein, S. P., Lojl, C., Chou, R. H., Allen, M.M. (1991): A comparison of the major lipid classes and fatty acid composition of marine unicellular cyanobacteria with freshwater species. – Arch. Microbiol. 155: 107–113.
- Ogilvie-Gordon, M.M. (1927): Das Grödner-, Fassa- und Enneberggebiet in den SüdtirolerDolomiten. – Abh. Geol. Bundesanst., 24 (2): 1–376.
- Ourisson, G., Rohmer, M., Poralla, K. (1987): Prokaryotic hopanoids and other polyterpenroid sterol surrogates. – Ann. Rev. Microbiol., 41: 301–334.
- Peters, K.E., Walters, C.C., Moldowan, J.M. (2005): The Biomarker Guide: Second Edition. – 1155 pp., Cambridge University Press, Cambridge.
- Reitner, J. (1993): Modern cryptic microbialite/metazoan facies from Lizard Island (Great Barrier Reef, Australia), formation and concepts. Facies, 29: 3–40.
- Reitner, J. & Neuweiler, F. (1995): Mud Mounds: a polygenetic spectrum of fine-grained carbonate buildups. - Facies, 32: 1–69.

- Richthofen, F. & Freiherr von (1860): GeognostischeBeschreibung der Umgebung von Predazzo, Sanct Cassian und der Seisser Alpe. – 327 pp., J. PerthesVerlag, Gotha.
- Riding, R. (1991): Classification of microbial carbonates.
 In: Riding, R. (ed.): Calcareous Algae and Stromatolites, 21– 51, Springer-Verlag, Berlin.
- Riding, R. (2002): Structure and composition of organic reefs and carbonate mud mounds: concepts and categories. - Earth- Sci. Rev., 58: 163–231.
- Riding, R. & Awramik, S.M. (2000): Microbial Sediments. - Springer-Verlag, Heidelberg
- Russo, F. (2005): Biofacies evolution in the Triassic platforms of the Dolomites, Italy. – 33–44, Ann. Univ. Ferrara, volume speciale.
- Russo, F., Mastandrea, A., Neri, C. (1998): Le comunitàcostruttricidellepiattaformetriassichedelleDolomiti. – Mem. Soc. Geol. It., 53.
- Russo, F., Neri, C., Mastandrea, A., Laghi, F.G. (1991): Depositional and Diagenetic History of the Alpe di Specie (Seelandalpe) Fauna (Carnian, Northeastern Dolomites). – Facies, 25: 187–210,.
- Russo, F., Neri, C., Mastandrea, A., Baracca, A. (1997): The mud mound nature of the Cassian Platform Margins of the Dolomites A case history: the Cipit boulders from Punta Grohmann (SassoPiatto Massif, northern Italy). – Facies, 36: 25–36.

- Russo, F., Mastandrea, A., Stefani, M., Neri, C. (2000): Carbonate facies dominated by syndepositional cements: a key component of middle Triassic platforms. The Marmolada case history (Dolomites, Italy).- Facies, 42: 211–226.
- Schouten, S., Bowman,J.P., Rijpstra, W.I.C., Sinninghe-Damsté, J.S. (2000): Sterols in a psychrophilic methanotroph, Methylosphaerahansonii. – FEMS Microbiology Letters, 186: 193–195.
- ScudelerBaccelle, L. (1971): La serie ladino-carnicaalla base della Punta Grohmann (Gruppo del Sassolungo, DolomitiOccidentali). Strutturesedimentarie e petrologiadellafaciescarbonatica. – Mem. Geopaleont. Univ. Ferrara, 3 (1), Ferrara.
- Thiel, V., Merz-Preiß, M., Reitner, J., Michaelis, W. (1997): Biomarker studies on microbial carbonates: extractable lipids of a calcifying cyanobacterial mat (Everglades, USA). – Facies 36: 163–172.
- Webb, G.E. (1996): Was Phanerozoic reef history controlled by the distribution of non-enzymatically secreted reef carbonates (microbial carbonate and biologically induced cement?). – Sedimentology, 43: 947–971.

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