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Messinian carbonate-rich beds of the Tertiary Piedmont Basin (NW Italy): microbially-mediated products straddling the onset of the salinity crisis

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ABSTRACT

The seven Messinian microbial carbonate-rich layers cropping out in the Pollenzo section (Tertiary Piedmont Basin, NW Italy) are interbedded with a precession-related cyclic succession composed of euxinic shale/marl couplets and straddle the onset of the Messinian salinity crisis (MSC). A sharp change of sedimentological, compositional and geochemical characteristics was observed from the onset of the MSC onward, suggesting strong differences in the mechanisms responsible for carbonate precipitation. Pre-MSC beds are mainly composed of dolomite and are interpreted as the product of early diagenesis, formed by bacterial sulphate reduction in the shallow subsurface along the sulphate-methane interface. Dolomite precipitation was temporarily enhanced by an upward flux of methane-rich fluids, possibly sourced by gas hydrate destabilisation. Conversely, from the onset of the MSC onward, carbonate beds are thinly laminated and show abundant filaments interpreted as Beggiatoa-like bacteria, while calcite (and aragonite) are the dominant authigenic phases. These beds are interpreted as microbialites, resulting from the lithification of chemotrophic bacterial mats dominated by sulphide-oxidizing bacteria. The carbonate necessary for their preservation was provided by bacterial sulphate reduction. These microbialites, that appear as the deeper water counterpart of bottom-grown selenite layers deposited in the marginal part of the basin, formed on an anoxic sea bottom under a density stratified water column. The high sulphate concentration in the pore waters, related to the presence of concentrated brines and to the regeneration of sulphate by sulphide-oxidizing bacteria, is considered as the driving factor controlling the mineralogical change from dolomite to calcite and aragonite. Finally, the sharp shift toward negative δ¹⁸O values of carbonates, observed from the onset of the MSC onward, was probably related to fractionation processes operated by sulphate-reducing bacterial communities in the pore waters. This suggests that care must be taken, when dealing with microbial carbonates, in the interpretation of the oxygen isotope values in term of fluctuating salinity condition of the water mass. In conclusion, this study suggests that the onset of the MSC had a strong impact on microbial populations governing
carbonate precipitation, in a sector of the basin dominated by depositional conditions not suitable for gypsum precipitation.

Key words: bacterial sulphate reduction, bacterial sulphide oxidation, Messinian salinity crisis, microbial mats, Tertiary Piedmont Basin.

1. Introduction

Studies of modern environments and culture experiments have shown that microbially-induced carbonate precipitation is a common process active in various types of marine sediments (e.g. Irwin et al., 1977; Vasconcelos et al., 1995; Wright and Oren, 2005). In particular, sulphate-reducing bacteria are considered to play a fundamental role in triggering the precipitation of different carbonate minerals (calcite, aragonite, dolomite) in a wide range of organic-rich sediments from peritidal microbial mats (e.g. Baumgartner et al., 2006, Dupraz et al., 2009) to anoxic deep sea sediments (e.g. Meister et al. 2008). A prolonged and intense activity of the degradation of organic matter by sulphate-reducing bacteria can lead to the formation of lithified layers and masses, commonly referred to as microbialites. However, other prokaryotes are also thought to be related to carbonate precipitation and sediment lithification, including methanogenic archaea, anaerobic methane oxidizing communities, and cyanobacteria (see Wright and Oren 2005 and references therein). The correct identification of the prokaryotes involved in the formation of diagenetic carbonate bodies can provide fundamental information on the environmental conditions governing carbonate precipitation both at the sea bottom and in the shallow subsurface.

Microbial carbonate rocks are a common component of the Messinian salinity crisis (MSC) stratigraphic record. They have been mainly reported from: 1) the Terminal Carbonate Complex (Esteban, 1979), a syn- to post-evaporitic unit found in the western Mediterranean basins (e.g. Riding et al., 1998; Braga et al., 2006; Roveri et al., 2009) that is mostly composed of large
thrombolite and stromatolite domes (Feldmann and Mc Kenzie, 1997; Arenas and Pomar, 2010); 2) the Calcare di Base, a composite unit found in Sicily and Calabria below the gypsum or passing laterally into it (Decima et al., 1988; Garcia-Veigas et al., 1995; Oliveri et al., 2010). As summarised by Manzi et al. (2011), the Calcare di Base was interpreted as a chemical precipitate from concentrated brines immediately prior to evaporite deposition (Schreiber and Friedman, 1976; Decima et al., 1988) and/or as a microbial product formed in a restricted basin (Bellanca et al., 2001; Blanc-Valleron et. al., 2002). In particular, beds of carbonate “stromatolites” were reported (Oliveri et al., 2010) and interpreted as the record of progressively shallower, more restricted and hypersaline conditions, favouring the development of microbial communities at the sea floor immediately prior to the onset of gypsum deposition (e.g. Rouchy and Caruso, 2006). Wide salinity fluctuations and sharp dilution events of the brines have also been highlighted (Guido et al., 2007). A complex diagenetic evolution, including microbial sulphate reduction coupled to the oxidation of biogenic methane, was also proposed (Ziegenbalg et al., 2010, 2012). Similar beds were described below the gypsum from other Mediterranean localities such as the Vena del Gesso basin (Vai and Ricci Lucchi, 1977; Manzi et al., 2011) and Cyprus, where these features have been referred to as stromatolites and considered to record basin shallowing and restriction (Rouchy and Monty, 1981; Krijgsman et al., 2002; Orszag-Sperber et al., 2009).

A recent revisitation of the Calcare di Base in Sicily, Calabria and northern Apennines (Manzi et al., 2011) showed that this unit actually consists of several types of carbonates formed in different setting and during different stages of the Messinian salinity crisis. In particular, the unit includes three types of carbonates: a) thin dolostone beds interbedded to tripolaceous facies, representing the deep water equivalent of primary gypsum deposited in marginal basins during the first MSC step (type 2); b) clastic bodies deposited during the second MSC stage (type 3); c) late diagenetic products after original reedimented gypsum layers (type 1).

Thin carbonate beds are also known from the Piedmont succession, just below the gypsum (Sturani, 1973). In previous studies (Sturani, 1976) these beds, that abruptly overlie lower
Messinian deep water marls, were interpreted as the record of a dramatic sea level fall (of the order of 200-500 m) at the onset of the MSC. This interpretation was based on the presence of a variety of features thought to indicate deposition in very shallow waters and subaerial exposure (stromatolitic lamination, desiccation and expansion cracks, calcite pseudomorphs after gypsum crystals).

However, a recent revisitation of the MSC record of the southern margin of the Piedmont Basin (Dela Pierre et al., 2011) suggested that these carbonate beds actually straddle the onset of the MSC and that part of them are the lateral deep-water counterpart of the lowermost gypsum layers deposited in the shallow marginal part of the basin, hence corresponding to the type 2 Calcare di Base (*sensu* Manzi et al., 2011, see above) of the Sicilian succession.

In this paper we present the results of an integrated sedimentological, petrographical and geochemical study of Messinian carbonate beds, from the Pollenzo section. The results offer the opportunity to discuss the impact that the environmental changes related to the onset of the MSC had on microbial populations governing carbonate precipitation, in a sector of the basin dominated by depositional conditions not suitable for gypsum precipitation.

2. **The Messinian salinity crisis**

The MSC affected the Mediterranean basin between 5.96 and 5.33 Ma and resulted in the deposition of huge volumes of evaporites that are presently preserved both at the basin margins and in deep basinal areas, where they are buried below the abyssal plains of the Western and Eastern Mediterranean sea (*e.g.* Rouchy and Caruso, 2006). After the formulation of the desiccated deep basin model (Hsü et al., 1973; Cita et al., 1978), the nature and timing of the MSC events still remain the object of a lively scientific debate, mainly because a detailed correlation between the marginal sub-basins, that provide most of the outcropping successions (*e.g.* Clauzon et al., 1996; Krijgsman et al., 1999; Rouchy and Caruso, 2006; Manzi et al., 2007; Roveri et al., 2008; Lugli et al., 2010) and the deep basins, whose buried sedimentary record was analysed by seismic profiles,
is still lacking (Ryan, 1976; Bertoni and Cartwright, 2007; Lofi et al., 2011). Recently, a MSC evolutionary model has been proposed (CIESM, 2008). This model derives from the two step scenario of Clauzon et al. (1996) and envisages three MSC stages. During the first one (5.96-5.60 Ma) primary evaporites were deposited only in shallow, silled, peripheral basins (Primary Lower Gypsum unit; Roveri et al., 2008). Carbonate microbialites are often reported below these deposits (e.g. Rouchy and Monty, 1981; Rouchy and Caruso, 2006). Conversely, in deep basinal setting, only euxinic shales and dolomite-rich beds (the type 2 Calcare di Base of Manzi et al., 2011) were deposited during this stage. The absence of gypsum and the concomitant formation of dolomite seem related to anoxic conditions, responsible for the decrease of the dissolved sulphate content via organic matter degradation by bacterial sulphate reduction (De Lange and Krijgsman, 2010).

During the second MSC stage (5.60-5.55 Ma) the marginal basins underwent subaerial exposure and erosion as evidenced by an erosional surface, referred to as the Messinian erosional surface (Lofi et al., 2011). This surface can be traced basinward in a correlative conformity placed at the base of thick accumulations of chaotic and resedimented evaporites, the Resedimented Lower Gypsum unit (Roveri et al., 2008).

During the third stage (5.55-5.33 Ma) a rapid transition to environments characterised by fluctuating salinity conditions is recorded by deposition of evaporites (Upper Evaporites) and clastic sediments containing brackish to fresh water fossil assemblages. The reestablishment of fully marine conditions at 5.33 Ma (Zanclean) marks the end of the salinity crisis.

3. Geologic and stratigraphic setting

The Tertiary Piedmont Basin (Figs. 1A, B) is filled with Upper Eocene to Messinian sediments deposited unconformably on a wedge of Alpine, Ligurian and Adria basement units juxtaposed in response to the collision between the Europe and Adria plates (e.g. Mosca et al., 2009; Rossi et al., 2009). Messinian strata were deposited in a wide wedge top basin (Figs. 1B, 2A),
bounded to the north by the more external Apennine thrusts (Rossi et al., 2009; Dela Pierre et al., 2011). The shallow marginal zones are presently exposed in the northern (Torino Hill and Monferrato) and southern (Langhe) sectors of the Piedmont Basin, whereas the depocentral zones are buried below Pliocene and Quaternary sediments (Savigliano and Alessandria basins) (Fig.1A).

The succession begins with outer shelf to slope muddy sediments referred to as the Sant’Agata Fossili Marls (Tortonian-lower Messinian) that record progressively more restricted conditions heralding the onset of the MSC (Sturani and Sampò, 1973). This unit displays a precession-related cyclic stacking pattern, evidenced by the rhythmic repetition of euxinic shale/marl couplets (Lozar et al., 2010), and is followed at basin margin by the Primary Lower Gypsum unit (Fig. 2A). The latter shows the same precession-driven lithologic cyclicity, represented by shale/gypsum couplets (Dela Pierre et al., 2011). No in situ primary evaporites are documented in the depocentral zones, but seismic data show that their time equivalent sediments are represented by shales (Irace et al., 2010).

The transition between the shallow marginal area and the buried depocentre is exposed on the southern sector of the Piedmont Basin (Alba region) and was reconstructed in detail along a SW-NE transect (Dela Pierre et al., 2011) (Fig. 2B). On the basin margins, six Primary Lower Gypsum cycles were recognised, composed of bottom grown-selenite layers; the sixth bed represents a distinct marker bed referred to as the Sturani key-bed (Dela Pierre et al., 2011). Moving towards the NE (i.e. towards the depocentral zone), only two gypsum beds are present below this marker bed. In the Pollenzo section they overlie a cyclic succession of euxinic shales, marls and carbonate-rich beds (the object of this study), belonging from the lithostratigraphic point of view to the Sant’Agata Fossili Marls (Fig. 2B). Due to their position with respect to the Sturani key-bed, the uppermost three cycles must be considered as the deeper water equivalent of the lower cycles of the Primary Lower Gypsum unit deposited in marginal setting (Dela Pierre et al., 2011). This correlation is confirmed by bio-magnetostratigraphic data, indicating that the onset of the MSC
should be placed at Pollenzo three cycles below the first gypsum bed, in correspondence of the peak abundance of the calcareous nannofossil *Sphenolithus abies* (Lozar et al., 2010).

The Primary Lower Gypsum unit is followed by resedimented and chaotic evaporites (Valle Versa Chaotic Complex, Dela Pierre et al., 2007), that are considered to be equivalents of the Resedimented Lower Gypsum unit (Fig. 2B) deposited during the second MSC stage (5.60-5.55 Ma). This latter unit is finally followed by fluvio-deltaic and lacustrine deposits (Cassano Spinola Conglomerates) recording the third MSC stage (5.55-5.33 Ma), in turn overlain by Zanclean marine clays (Argille Azzurre Formation).

3.1 The Pollenzo section

In this section, located along the Tanaro River, a complete Messinian succession, comprising the Sant’Agata Fossili Marls, the Primary Lower Gypsum, the Resedimented Lower Gypsum units and the Cassano Spinola Conglomerates, is exposed (Fig. 3). Only the Sant’Agata Fossili Marls, in which the studied carbonate beds are hosted, will be described below. For the chrono-biostratigraphic data of this unit and for the description of the overlying succession, the reader is referred to Lozar et al. (2010) and Dela Pierre et al. (2011).

The Sant’Agata Fossili Marls consist of muddy marine sediments characterised by a distinctive precession-driven cyclicity, given by the alternation of euxinic shale/marl couplets, forming up to 3 m-thick cycles (Dela Pierre et al., 2011). A 80 m-thick slumped interval divides the section into two portions (Fig. 3). The lower portion, below the slump, consists of seven cycles; in the upper portion, above the slump, the lithologic cyclicity is enhanced by the regular repetition of carbonate-rich beds easily distinguishable for their whitish colour (Fig. 4). Seven cycles (Pm1-Pm7) with an average thickness of 3 metres were recognised, each one including a distinct carbonate bed. The integration of physical-stratigraphic (position with respect to the Sturani key-bed) and biostratigraphic data (peak abundance of the calcareous nannofossil *S. abies*), demonstrated that the
onset of the MSC must be placed at the base of cycle Pm5 (Lozar et al., 2010; Dela Pierre et al. 2011). Hence four pre-MSC cycles (Pm1-Pm4) are present, followed by three MSC cycles (Pm5-Pm7) that correspond to the lowermost Primary Lower Gypsum cycles recognised in the marginal part of the basin (Fig. 3).

Each pre-MSC cycles is composed of a basal layer of laminated euxinic shale, transitionally followed by a calcareous marly bed that hosts a dm-thick carbonate-rich bed. The strong impoverishment of foraminiferal assemblages, that include only rare stress tolerant planktic (Turborotalita quinqueloba and T. multiloba) and benthic taxa (Bolivina dentellata and Bulimina echinata), suggests the establishment of restricted conditions, a severe stratification of the water column and the impoverishment in dissolved oxygen of bottom waters (Lozar et al., 2010). The MSC cycles show analogous lithologic characteristics, but no marls were observed in cycle Pm6; moreover the carbonate beds here show a laminated structure, not observed in the underlying ones (see below). An hemi-ellipsoidal convex-upward indurated body has been observed 50 cm above layer e, within cycle Pm6 (Fig.3). This feature was not reported in Dela Pierre et al. (2011) because completely submerged at that time by the Tanaro River. Foraminifers and calcareous nannofossils are extremely rare and disappear at the top of cycle Pm6, confirming the final disruption of the water column and the definitive establishment of anoxic bottom conditions. The upper carbonate bed (g, Figs. 3, 4) is overlain by the first gypsum-bearing cycle (Pg1, Fig. 3), that is composed of laminated muddy siltstones followed by a 1-m thick massive selenite bed; this cycle corresponds to the 4th cycle of the Primary Lower Gypsum unit (Dela Pierre et al., 2011).

4. Methods

Field studies of the lithology and geometry of the carbonate beds, including the relationships with the host sediments, were carried out on the upper portion of the Sant’Agata Fossili Marls, above the slump. Both the carbonate beds and the unconsolidated host sediments were sampled for
petrographic and geochemical analyses. Twelve standard thin sections of the most representative
samples were studied under the optical microscope and were further analysed for their fluorescence,
using a Nikon microscope equipped with a B-2a filter block (illumination source with an excitation
wave length of 450-490 nm) (Department of Plant Biology, Torino University). Scanning Electron
Microscopy (SEM) analyses were performed on 30 slightly etched polished surfaces using a SEM
Cambridge Instruments Stereoscan 360 equipped with an energy-dispersive EDS Oxford
Instruments Link System microprobe (Department of Earth Sciences, Torino University).
Semiquantitative analyses on the amount of the carbonate fraction and on its mineralogical
composition (calcite and dolomite) were carried out on 40 samples (including both the carbonate-
rich beds and the host sediments) at the Inductively Coupled Plasma-Optical Emission
Spectroscopy (ICP-OES) laboratory (Department of Earth Sciences, Torino University), using an
IRIS II Advantage/1000 (Thermo-Jarrel Ash Corp.). As a first step, 2000 mg of sample powder
were stirred for 48 h in 200 ml of distilled water, in order to dissolve the (diagenetic) gypsum
possibly present in the sediments. The filtered solution was analysed and the amount of sulphur was
measured. Assuming that all the sulphur derived from dissolution of gypsum (pyrite or silicates are
not dissolved in distilled water), a corresponding stoichiometric amount of Ca$^{2+}$ was then subtracted
from to the whole Ca$^{2+}$ pool (obtained in the further step) in order to avoid an overestimation of the
carbonates. As a second step, 200 mg of sample powder were processed in 10 ml of hot acetic acid
for 12 h, in order to dissolve the carbonates but at the same time preserving the silicates. The
filtered solution was analysed and the amount of Ca$^{2+}$ and Mg$^{2+}$ was measured. The relative
abundance of calcite and dolomite in the samples was calculated (after subtraction of the amount of
Ca$^{2+}$ derived from gypsum, as mentioned above) assigning the total amount of Mg$^{2+}$, with the
corresponding amount of Ca$^{2+}$, to stoichiometric dolomite; the remaining Ca$^{2+}$ was assumed to
derive from calcite and was used to calculate the abundance of stoichiometric calcite. EDS analyses
performed on some samples confirmed the near stoichiometric composition of calcite (less than 1%
of Mg$^{2+}$, and dolomite (51- 53 CaCO$_3$ mole%). The results of Inductively Coupled Plasma (ICP) analyses (Table 1) are expressed as mass percent on the whole sediment.

Bulk rock C and O stable isotope analyses were performed on 22 samples from both carbonate-rich beds and unlithified sediments at the ISO4 laboratory (Torino, Italy) and in the MARUM Stable Isotope Laboratory (Bremen, Germany). The carbonate fraction was analysed following the classical method (McCrea, 1950). The $^{13}$C/$^{12}$C and $^{18}$O/$^{16}$O ratios of the CO$_2$ were obtained using Finnigan MAT 251 and 252 mass spectrometers. For the carbonate-rich beds, both calcite and dolomite were measured, whereas in the unconsolidated sediments only calcite was analysed. The isotopic ratios are expressed as $\delta^{13}$C and $\delta^{18}$O per mil versus the PDB standard (Fig. 3, Table 3); the analytical error is ±0.5‰ and ±0.1‰ for $\delta^{13}$C and $\delta^{18}$O, respectively.

5. Results

5.1. Lithology

5.1.1 Unconsolidated sediments

In the host sediments, the carbonate content ranges from 10 to 41% and consists of both calcite and dolomite that are mixed in variable proportions (Table 1). The total carbonate ranges from 23 to 41% in the homogeneous marl and reaches the lowest values (<23%) in the laminated shale. As a general rule, pre-MSC sediments contain a higher calcite fraction, probably related to the higher content of skeletal grains (foraminifers and calcareous nanofossils), that are generally very rare or even absent in MSC sediments.

5.1.2 Pre-MSC carbonate-rich beds

Pre-MSC beds ($a, b, c, d$) are dm- thick and are interbedded within the marly part of the lithologic cycles (Pm1 to Pm4, Fig. 3). The lower and upper contacts are transitional, except for bed $a$ in which they are sharp (Fig. 5A). These beds are the product of local cementation of host
sediments and contain variable amounts of a silt-sized terrigenous fraction, mainly consisting of mica flakes. All beds are strongly bioturbated (Figs. 5B, C), suggesting deposition on an oxygenated sea bottom, and contain planktic and benthic foraminifers, and calcareous nannofossils.

The intergranular cement mostly consists of idiomorphic rhombohedral crystals of dolomite, ranging in size from 2 to 10 μm (Fig. 5D). Calcite is also present, both of biogenic and diagenetic origin. The mixture is confirmed by data from ICP analyses (Tables 1 and 2); they show that in beds a, b and d dolomite represents 91.9, 68.0 and 83.3% of the total carbonate content (76.1, 63.1 and 45.1% respectively over the bulk composition). Conversely in bed c the total carbonate fraction (48.2%) consists of similar proportions of calcite and dolomite (51.7 and 48.3%, respectively) (Fig. 3, Table 2). Pyrite framboinds, up to 10 μm across, are very common in all beds (Fig. 5E).

5.1.3 MSC carbonate-rich beds

Beds deposited during the salinity crisis are about 20 cm-thick and show transitional contacts with the host sediments (Fig. 6A). Bed e is located at the top of the marly interval and contains mm-sized intraclasts, floating in a clotted micrite matrix containing rare foraminifers. A remarkable feature is the presence of contractional cracks developed around the clasts (circumgranular cracks) (Fig. 6B). Beds f and g show different features, because they are not bioturbated and display a well-developed lamination. Bed f lies in strongly laminated shales (no marl was observed in cycle Pm6) and shows a lamination marked by the alternation of mm-thick whitish and grey wrinkled laminae (Fig. 6C). The formers are composed of clotted micrite, contain abundant pyrite framboinds and are crossed by a network of mm-wide contractional cracks, running perpendicular to the lamina surfaces, that are empty or filled with late diagenetic gypsum (Fig. 6D). These laminae contain abundant fish vertebrae and scales. The grey laminae are richer in terrigenous material, mostly represented by clay particles and mica flakes (Fig. 6D). At the boundary between the two types of laminae, cracks were commonly observed. Micrite laminae
exhibit a stronger epifluorescence than the terrigenous ones, suggesting a higher content in organic matter (Fig. 6E). Moreover, epifluorescence microscopy permits the recognition of filaments, up to 100 µm across and more than 300 µm long, showing different fluorescence shades (Fig. 6E). Bed g is similar to bed f, except it is made up of more wrinkled and thinner laminae (less than 1 mm). Pyrite framboids are abundant and are frequently grouped together to mimic filaments about 100 µm across and up to 800 µm long (Figs. 7A, C). Epifluorescence observations reveal that filaments show a stronger fluorescence than the enclosing matrix (Fig. 7D). The same features, despite less abundant, were observed in bed f.

Unlike the pre-MSC beds, the carbonate fraction of the salinity crisis layers is dominated by calcite whereas dolomite is subordinate; frequently micron-sized calcite crystals show a globular shape with a central hollow, suggesting a possible microbial origin (Cavagna et al., 1999). This type of crystals (Fig. 7B) was observed also within the filaments, together with abundant pyrite framboids. Remarkably, no terrigenous grains, abundant in the enclosing matrix, were observed within the filaments. The predominance of calcite over dolomite is confirmed by ICP analyses; in beds e, f and g calcite is 80.2, 84.1 and 94.8% of the total carbonate content (84.6, 69.1 and 59.0%, respectively) (Fig.3, Table 2).

5.1.4 The hemi-ellipsoidal body

The hemi-ellipsoidal cemented body observed within cycle Pm6 is 1.70 metres by 1 metre in size and shows transitional lateral contacts with the host laminated shale (Fig. 8A). Its most remarkable feature is the wrinkled lamination (Fig. 8B), given by the alternation of submillimetric whitish and grey lamina, that strongly resembles the structure described as the “stromatolites” of the Sicilian Calcare di Base (Oliveri et al., 2010). The whitish laminae are composed of filaments, 150 µm across and up to few millimetres long (Fig. 8C), that are irregularly oriented or with their maximum dimension parallel to the lamina surface. The filaments are made of clotted micrite, composed of micron-sized strongly epifluorescent calcite crystals (Figs. 8D, F). They are
commonly curved and are surrounded by fringing aragonite (Figs. 8E, F). No terrigenous grains were observed in the filaments, as in beds f and g. Grey laminae are richer in terrigenous grains, are laterally discontinuous and seal the undulating microtopography formed by the former white laminar structures. Moreover, mm-sized fenestrae, likely resulting from dissolution of former gypsum crystals, are present. Pyrite framboids, up to 20 μm across, are very common in both types of laminae and frequently cap acicular aragonite crystals (Fig. 9).

5.2. Stable isotope data

5.2.1 Unconsolidated sediments

In both pre-MSC and MSC cycles, the $\delta^{13}$C values are around zero (Fig. 3, Table 3), suggesting carbonate precipitation from a fluid in isotopic equilibrium with sea water. The weak $^{13}$C depletion observed in some samples from cycles Pm1 ($\delta^{13}$C = −6.5‰), Pm6 ($\delta^{13}$C = −5‰) and Pm7 ($\delta^{13}$C = −4.7‰) points to the contribution of diagenetic carbon from decaying organic matter. All samples are characterised by low $\delta^{18}$O values, with a general trend towards more negative values in the MSC sediments (cycle Pm5-Pm7). The interpretation of these negative $\delta^{18}$O values is not straightforward, because the analysed carbonate fraction is sparse (<23%) and the resultant values can reflect the contribution of different carbonate pools (detrital, skeletal, diagenetic), mixed in unknown ratios. However, these low values, commonly interpreted as the result of an overall “freshening” of the water mass under the increased influx of fresh water (e.g. Blanc-Valleron et al., 2002), may reflect complex microbial fractionation processes on the oxygen pool (see paragraph 6.2.2).

5.2.2 Pre-MSC carbonate-rich beds
A significant $^{13}$C depletion was observed for both dolomite and calcite in beds $a$ and $b$ ($\delta^{13}$C$_{\text{dol}} = -19.8$ and $-21\%\text{o}$; $\delta^{13}$C$_{\text{cal}} = -16.7$ and $-14.5\%\text{o}$, respectively). In the upper two pre-MSC beds ($c$ and $d$) less negative values were instead measured for both minerals ($-4.4$ and $-5.2\%\text{o}$ for dolomite; $-9.2$ and $-5.7\%\text{o}$ for calcite, respectively). Positive $\delta^{18}$O$_{\text{dol}}$ values were observed in all pre-MSC beds (Fig. 3, Table 3): the stronger $^{18}$O enrichment was measured in beds $a$ ($\delta^{18}$O$_{\text{dol}} = +7\%\text{o}$) and $b$ ($\delta^{18}$O$_{\text{dol}} = +6.9\%\text{o}$), whereas in beds $c$ and $d$ lower values were found ($\delta^{18}$O$_{\text{dol}} = +1.3$ and $+3.6\%\text{o}$, respectively). More negative values were observed for calcite. In beds $a$ and $b$ the $\delta^{18}$O$_{\text{cal}}$ is $+5.7$ and $-1.0\%\text{o}$, respectively, whereas in beds $c$ and $d$ it is $-3.9$ and $-1.5\%\text{o}$ (Fig. 3, Table 3).

5.2.3 MSC carbonate-rich beds

In the salinity crisis beds, the $\delta^{13}$C values of both dolomite and calcite are moderately negative (from $-5$ to $-3.9\%\text{o}$ for dolomite and from $-7.9$ to $-6.7\%\text{o}$ for calcite). A stronger $^{13}$C depletion was measured for the calcite of the hemi-ellipsoidal body (cycle Pm6), with values around $-8.5\%\text{o}$. For what concerns the $\delta^{18}$O, a remarkable shift towards negative values was observed. The $\delta^{18}$O$_{\text{dol}}$ values range from $-6.1$ to $-4.9\%\text{o}$ whereas the $\delta^{18}$O$_{\text{cal}}$ are more negative (from $-6.5$ to $-8.8\%\text{o}$). The hemiellipsoidal body yielded $\delta^{18}$O$_{\text{cal}}$ values as low as $-7.7\%\text{o}$.

6. Discussion

6.1. Pre-MSC beds: early diagenetic products from the shallow subsurface

In pre-MSC beds, the authigenic carbonate fraction is dominated by dolomite, mixed with variable amounts of calcite whose specific origin (detrital, skeletal and/or diagenetic) could not be
determined. The beds formed in strongly bioturbated sediments, deposited on an oxygenated sea
bottom. The absence of traces of exposure of the indurated sediments at sea floor (e.g. firm ground
burrows, borings) suggests that carbonate precipitation occurred within the sedimentary column. On
the other hand the high authigenic carbonate content (45-76%) indicates that these beds formed in
the shallow subsurface, within still porous mud not yet affected by mechanical compaction.

Studies of modern environments and culture experiments have shown that dolomite
precipitation in the subsurface is induced by the metabolic activity of sulphate-reducing bacteria
that, by degrading organic matter, consume sulphate ions and increase overall alkalinity thus
overcoming the kinetic inhibition to dolomite precipitation (e.g. Baker and Kastner, 1981; Compton
et al., 1988; Vasconcelos et al., 1995; Wright and Oren, 2005; Baumgartner et al., 2006; Meister et
al., 2007; Wacey et al., 2008). In modern deep sea organic-carbon-rich hemipelagic sediments,
the bacterial sulphate reduction is controlled by the downward diffusion of sulphate from sea water
(Compton, 1988; Wright and Oren, 2005). In these conditions, dolomite can precipitate from anoxic
sulphate-free pore waters, at the lower boundary of the sulphate-reducing zone. In present-day open
marine environments the depth of this surface, that corresponds to the sulphate-methane interface,
ranges from few metres up to few tens of metres, depending on the porosity and on the content and
type of organic matter (e.g. Borowski et al., 1999; Fossing et al., 2000; D’Hondt et al., 2002; Treude
et al., 2005; Jørgensen and Kasten, 2006). Apart from carbonate, sulphate reduction provides
hydrogen sulphide that subsequently can react with iron to form sulphide minerals (e.g. pyrite).
Carbonate precipitation at the sulphate-methane interface is however quantitatively limited and
commonly goes unnoticed in most sedimentary sequences (e.g. Raiswell and Fisher, 2004). In two
cases it becomes significant and may give origin to well recognizable carbonate-cemented layers: 1)
if large amounts of upward rising methane-rich fluids reach this geochemical interface; in this case
abundant carbonate (calcite, aragonite and dolomite) can precipitate resulting in extensive
cementation of the flushed sediments (e.g. Irwin et al., 1977; Raiswell, 1987; Raiswell and Fischer,
2000; Campbell, 2006; Ussler and Paull, 2008). Carbonate precipitation is induced by a consortium
of sulphate-reducing bacteria and methanotrophic archaea (Boetius et al., 2000), responsible for the
anaerobic oxidation of methane; 2) if the sulphate-methane interface remains stationary within the
sedimentary column for a prolonged time interval, resulting in focused dolomite precipitation; in
this case, a distinct dolomite-rich bed can form even though the supply of methane-rich fluids from
below is negligible (Meister et al., 2007, 2008).

The bed-parallel geometry of the Pollenzo pre-MSC beds suggests that dolomite precipitation occurred at a geochemical interface parallel to the sea bottom. In this regards the co-
ocurrence of authigenic carbonate and pyrite and isotopic data suggests that these beds may have formed at the sulphate-methane interface. In particular, the (moderately) negative $\delta^{13}C$ values measured in diagenetic dolomite of the lower two beds ($a$ and $b$) ($\delta^{13}C$ around $-20\%$), points to the contribution of anaerobic oxidation of methane in dolomite precipitation (Fig. 10A). The moderate $^{13}C$ depletion (compared to typical methane-derived carbonates in which $\delta^{13}C$ values as low as $-60\%$ are commonly measured; e.g. Peckmann and Thiel, 2004) may reflect the mixture of methane-derived carbon with other sources, such as heavier hydrocarbons (Roberts and Aharon, 1994), marine dissolved inorganic carbon or skeletal material of marine organisms, that are actually present in these beds (e.g. Peckmann and Thiel, 2004; Natalicchio et al., 2012). The same mechanism can explain the $\delta^{13}C$ signature of calcite.

Conversely, the less negative $\delta^{13}C$ values of beds $c$ and $d$ ($\delta^{13}C$ around $-5\%$) suggest that dolomite precipitation was induced by organoclastic bacterial sulphate reduction alone, as the upward methane flux ceased completely (Fig. 10B). These indurated layers likely developed along a temporarily fixed sulphate-methane interface that favoured focused dolomite precipitation. Sulphate reduction alone, however, was able to produce only a lesser amount of authigenic dolomite with respect to anaerobic oxidation of methane, as indicated by geochemical data and by the minor induration of these beds.
The oxygen isotope record of dolomite (the predominant carbonate mineral) reveals that beds \( a \) and \( b \) are significantly enriched in the heavy \( ^{18}O \) isotope (Fig. 3, Table 3). Three mechanisms can explain such an enrichment:

a) evaporation of sea water (McKenzie et al., 1979). This mechanism, commonly invoked to explain the \( ^{18}O \) enrichment of Messinian carbonates (e.g. Rouchy et al., 1998; Bellanca et al., 2001; Blanc-Valleron et al., 2002) should in our case be ruled out, because these beds formed before the onset of the MSC. Moreover, it strongly contrasts with the negative values of host sediments;

b) upward movement of deep fluids whose isotopic composition was modified by dehydration of smectite clay minerals (e.g. Dählmann and De Lange, 2003). The possible role played by this process can not be ruled out because of the lack of information on the source fluids and on clay mineralogy of underlying sediments;

c) flushing of sediments by methane-rich fluids sourced by gas hydrate destabilisation. This mechanism is consistent with the association of positive \( \delta^{18}O \) values with negative \( \delta^{13}C \) ones, as already suggested for lower Messinian dolomite layers and concretions found in the eastern part of the Piedmont Basin (Dela Pierre et al., 2010; Martire et al., 2010; Natalicchio et al., 2012), Spain and Northern Morocco (Pierre and Rouchy, 2004). Conversely, the lower oxygen values measured in beds \( c \) and \( d \), that are coupled with slightly negative \( \delta^{13}C \) ones, suggest that the input of \( ^{18}O \)-enriched fluids, ceased together with the demise of methane-rich fluids.

As already mentioned, the more negative \( \delta^{18}O_{\text{calc}} \) values probably reflect the mixing of authigenic and sedimentary calcite. Positive values were only observed in bed \( a \), in which the scarce calcite content (8.1\%) is likely diagenetic and cogenetic with dolomite.

6.2. MSC beds

A sharp change of sedimentological, compositional and geochemical characteristics is observed in the MSC beds. This change is shown by the following features that will be discussed
separately below: a) the presence of wrinkled laminae containing filament remains, and of contractional cracks; b) the sharp decrease of the dolomite content and the concomitant increase of the calcite (and aragonite) content; c) the negative $\delta^{18}$O values recorded both in calcite and dolomite. The carbon isotope data are instead comparable to those of the underlying pre-MSC beds and of the host sediments, testifying to the incorporation of light organic carbon in the authigenic phase.

6.2.1. Wrinkled laminae, filaments and contractional cracks: vestiges of chemotrophic microbial mats?

The submillimetric wrinkled lamination and the peloidal clotted microfabric of the micrite laminae, observed in beds $f$ and $g$ and in the hemi-ellipsoidal body of cycle Pm6, are typical features of carbonate microbialites, i.e. organo-sedimentary deposits formed by the activity of benthic microbial communities (Dupraz and Visscher, 2005; Dupraz et al., 2009; Oliveri et al., 2010). Compelling evidence of the involvement of microbial mats in the formation of laminated structure is given by the remains of microbial filaments, well recognizable in epifluorescence (Fig 6E) that in beds $f$ and $g$ are underlined by a concentration of pyrite framboïds (Figs.7C, D).

Microbial filaments have been first observed in Messinian gypsum crystals (the so called *spaghetti*-like structures; Vai and Ricci Lucchi, 1977) and interpreted as remains of filamentous photosynthetic cyanobacteria (*e.g.* Scytonema) on the basis of size and internal structure (Rouchy and Monty, 1981; Panieri et al., 2010), thus providing evidence for shallow water (photic) depositional conditions (but see also the discussion about the relevance of these features for water depth determination in Lugli et al., 2010). Analogous features were then observed in carbonate deposits below the gypsum and were considered either as faecal pellets (Guido et al., 2007) or as cyanobacteria remains on the basis of their similarities with the *spaghetti* structures (Rouchy and Monty, 1981; Orszag-Sperber et al., 2009). Hence, also these carbonates were classically
interpreted as shallow water deposits recording stressed environmental conditions heralding the onset of the MSC.

The absence of terrigenous grains within the Pollenzo filaments allows to rule out their faecal origin. An alternative hypothesis is that these filaments represent remains of colourless sulphide-oxidizing bacteria like *Beggiatoa*, *Thioplaca* and *Thiotrix*. These giant bacteria, that can reach a diameter of 750 μm and a length of several cm, obtain the energy necessary for their life from the oxidation of sulphide by using oxygen or nitrate as electron acceptors (Schulz and Jørgensen, 2001) and do not necessitate light as the driving energy source. In modern settings, they form dense microbial mats (known as chemotrophic-dominated mats) thriving at different water depth (from peritidal to bathyal settings), especially at sites where high concentration of sulphide is available at the sea bottom (e.g. Bailey et al., 2009) such as hydrothermal vents (e.g. Jannasch et al., 1989) and cold seeps (Larkin et al., 1994, Sahling et al., 2002; Teichert et al. 2005). However, sulphide-oxidizing bacteria are also known to form extensive felt-like mats where organic-rich sediments are exposed at the sea floor in contact with either oxic (Schulz et al., 1999) or oxygen-depleted waters, such as the continental shelf off Peru (Gallardo, 1977; Fossing et al., 1995) or the Danish Limfjorden (Mussmann et al. 2003). In these cases the bacteria use nitrate (and not oxygen) as electron acceptor for oxidizing sulphide to sulphate.

Though there are substantial similarities between the filamentous cyanobacteria and the sulphide-oxidizing bacteria and their distinction is difficult on morphology only, we propose that the Pollenzo filaments are remains of sulphide-oxidizing bacteria on the basis of the following elements: a) their diameter (>100 μm), that is close to that of living forms. On the contrary, cyanobacteria filaments rarely exceed 80 μm (e.g. Schulz and Jørgensen, 2001); b) the curved shape of some filaments (Fig. 8E) consistent with the chemotactic behaviour of these prokaryotes that often change their direction in the search of optimal concentrations of oxygen or nitrate (e.g. Møeller et al., 1985); c) the concentration of pyrite framboids outlining the filament shape (beds f and g, Figs. 7C, D). Living sulphide-oxidizing bacteria host elemental sulphur globules within the
cytoplasm, that can be further preserved as sulphur-containing minerals associated to the filamentous body fossil (e.g. Bailey et al., 2009); d) the lack of any remain of shallow water macrobiota that should accompany photosynthetic mats. The only features that could suggest a shallow water origin for these laminated layers are the contractional cracks, either developed around clasts and nodules (circumgranular cracks, Fig. 6B) or placed parallel and perpendicular to the bedding (Fig. 6D). Similar features were previously interpreted as desiccation structures and hence considered as a compelling evidence of the subaerial exposure of the Piedmont basin at the onset of the MSC (Sturani, 1973). However, the geometry of crack, that are developed especially across the carbonate-rich laminae and thin out both in the under- and overlying terrigenous laminae, contrasts with an origin by subaerial exposure and desiccation. The microbial origin for the carbonates may provide an alternative explanation for the genesis of these cracks, that can be interpreted as the product of syneresis, related to the decay of bacterial extracellular polysaccharide substances (EPS) binding clay particles (e.g. Dewhurst et al., 1999; Hendry et al., 2006) in a subaqueous environment.

On this basis, beds f and g and the hemi-ellipsoidal body of cycle Pm6 are interpreted as the product of the lithification of chemotrophic microbial mats dominated by sulphide-oxidizing bacteria. Unlike their photosynthetic counterpart, chemotrophic mats are rarely preserved in the fossil record, because the metabolism of sulphide-oxidizing bacteria increases acidity and consequently induces carbonate dissolution rather than precipitation (e.g. Petrasch et al. 2012). Their preservation can however take place if other biogeochemical processes trigger the rapid precipitation of authigenic carbonates necessary for the entombment of the delicate filaments before their complete decay. This may explain why putative fossil remains of sulphide-oxidizing bacteria are chiefly reported from ancient seep carbonate deposits, where anaerobic oxidation of vigorous methane fluxes induced extensive syndepositional carbonate precipitation (Peckmann et al., 2004). Described examples of filaments attributed to the genus *Beggiatoa* have been reported from cold seep deposits of the Miocene of Italy (Cavagna et al., 1999; Peckmann et al., 2004; Barbieri and
Cavalazzi, 2005) and the Oligocene of Poland (Bojanowski, 2007). Another example is the Messinian Calcare di Base of Sicily in which *Beggiatoa* filaments are entombed in a clotted peloidal dolomicrite resulting from bacterial sulphate reduction (Oliveri et al., 2010). The slightly depleted δ¹³C values of the Pollenzo beds exclude a significant contribution of anaerobic oxidation of methane and suggest that the main process responsible for carbonate precipitation was degradation of organic matter via bacterial sulphate reduction. The characteristics of the MSC beds allow to envisage the following scenario (Figs. 11, 12): changed environmental conditions (anoxia of bottom waters, see below) favoured the shift of sulphate-reducing bacteria communities toward the sea bottom and their establishment immediately below it, where they could rely on abundant “fresh” organic matter; bottom anoxia actually inhibited aerobic oxidation of the organic remains reaching the sea bottom (Fig. 11). Along with carbonate precipitation, bacterial sulphate reduction provided an upward flux of hydrogen sulphide that sustained sulphide-oxidizing bacterial communities at the sea floor. Due to bottom anoxia, nitrate was used as electron acceptor by these prokaryotes for oxidizing sulphides to sulphates (Fig.12A). Intervals of higher sediment input and increase of continental runoff, recorded by the laminae richer in terrigenous grains, resulted in the aggradation of the sea bottom (Fig.12B). In these renewed conditions, microbial communities were forced to migrate upward and the sea bottom was covered by a “new” mat dominated by sulphide oxidizers. The availability of abundant and “fresh” organic matter increased the rate of sulphate reduction in the shallow subsurface, and resulted in the rapid precipitation of large amounts of carbonates preserving the previously formed mat (Fig. 12C). The repetition of these processes through time led to the formation of the laminated structure that characterizes these rocks. According to the proposed scenario, sulphide oxidation, that promoted acidity and carbonate dissolution, was hence spatially and temporally decoupled from the alkalinity generated by sulphate reduction inducing carbonate precipitation. EPS degradation prior to complete lithification was responsible for the opening of contractional cracks. These features are also observed in bed e, confirming the active role played by microbial activity in its formation.
The hemi-ellipsoidal body within cycle Pm6 differs from under-and overlying beds for its geometry and for the more varied authigenic carbonate composition, including aragonite. This feature likely developed above a local source of decomposing organic matter, able to sustain an intense activity of the same bacterial consortia described above, as observed today around whale falls (e.g. Treude et al., 2009) or sunken woods (e.g. Palacios et al., 2009). Enhanced bacterial activity was responsible for the formation of large amount of calcite, that was followed by precipitation of the aragonite fringes rimming the bacterial filaments.

6.2.2 The change from dolomite to Ca-carbonates and the oxygen isotope composition of MSC beds

The other points to be discussed are: a) the mineralogical change recorded from the MSC onset onward, evidenced by the sharp increase in the calcite content and by the appearance of aragonite in the hemi-ellipsoidal body; b) the negative δ¹⁸O values of the MSC carbonates.

Although still discussed (Sánchez-Román et al., 2009), the concentration of sulphate in the pore waters is a critical factor controlling the composition of bacterially-induced carbonate minerals. In particular, if the concentration of sulphate is high, dolomite is inhibited and other carbonates (aragonite, calcite, Mg-calcite,) do form (e.g. Baker and Kastner, 1981; Kastner, 1984; Wright and Oren, 2005). At Pollenzo, the main factor driving carbonate precipitation both in pre-MSC and in MSC layers was bacterial sulphate reduction. However in pre-MSC beds the sulphate in pore waters was exclusively supplied by normal salinity sea water and carbonate precipitation took place within the sedimentary column. Under these conditions, all sulphate was consumed by bacterial sulphate reduction and dolomite precipitation took place from sulphate-free pore waters along the sulphate-methane interface.

On the contrary, MSC beds and the hemi-ellipsoidal body formed at the sea bottom in contact with sulphate-enriched bottom waters, being these layers the lateral equivalents of bottom-grown selenite beds formed in the shallower part of the basin, some tens of kilometres apart.
Moreover, the sulphate pool was continuously replenished by sulphide oxidation in the chemotrophic microbial mats. As a consequence, sulphate could not be totally consumed, even in the presence of an intense bacterial sulphate reduction, and precipitation of Ca-carbonates (calcite, aragonite) was favoured. Minor amounts of dolomite, occupying the residual pore space formed only after sediment burial, when all sulphate was consumed. This last mechanism was also responsible for the minor amount of dolomite in the host sediments.

The shift towards more negative $\delta^{18}O$ values observed in MSC carbonates ($-6.5 < \delta^{18}O_{\text{cal}} < -8.8\% \text{ PDB} ; -4.9 < \delta^{18}O_{\text{dol}} < -6.1\% \text{ PDB}$) compared to the underlying pre-MSC ones remains a still unresolved question. Such $^{18}O$ depletion is reported from carbonates just below the first evaporitic deposits in other Mediterranean basins (even if less severe than at Pollenzo) and is interpreted as the result of sharp dilution events pointing to the isolation of the basin(s) prior to the onset of gypsum deposition (e.g. Rouchy et al., 1998; Bellanca et al., 2001; Blanc-Valleron et al., 2002). This interpretation is hardly reconcilable with the Pollenzo beds, that are the lateral equivalents of gypsum. Alternative hypotheses have been proposed, that point to microbial sulphate consumption as a possible source of $^{16}O$ enrichment in the microenvironments of carbonate precipitation (Sass et al., 1991). The effects of this process on oxygen isotopic ratios both of sulphate and water have been studied, since the seminal work of Lloyd (1968), with theoretical and experimental approaches (e.g. Fritz et al., 1989; Brunner et al., 2005; Wortmann et al., 2007) but several aspect remain unresolved and, citing Turchyn et al. (2010) “more work is needed”.

6.2.3 The lateral equivalent of gypsum: microbialites reflecting chemotrophic activity

Recent MSC palaeohydrological models (Krijgsman and Mejers, 2008), predict that during deposition of the Lower Evaporites, the onset of gypsum deposition led to severe density stratification of the Mediterranean water column that resulted in turn in a well mixed, upper water mass underlain by an oxygen-depleted deep water mass. Similar conditions likely existed in the Piedmont Basin during the first MSC stage and may explain why microbialites reflecting the
activity of chemotrophic prokaryotes are the lateral equivalent of bottom-grown selenite beds (Dela Pierre et al., 2011, Fig. 2B). According to field and theoretical models, anoxic sea bottoms would be unfavourable to gypsum formation and preservation, mainly because of low sulphate concentration related in turn to intense bacterial sulphate reduction (e.g., Babel, 2007; De Lange and Krijgsman, 2010). On the other hand, this last process produced large amounts of hydrogen sulphide favouring the development of dense chemotrophic microbial mats at the sea floor. Due to the low rate of terrigenous supply, the latters could colonize the sea bottom for a prolonged time interval before their final burial. This circumstance, along with an increased rate of bacterial-mediated carbonate precipitation, allowed the preservation of discrete recognizable beds in the geological record.

7. Conclusions

The carbonate-rich layers of the Pollenzo section straddle the onset of the MSC and provide a detailed record of the environmental changes related to this palaeoecenographic event in a sector of the basin where depositional conditions were not suitable for gypsum formation. The integration of field and laboratory data permitted the recognition of the strong difference in the mechanisms responsible for carbonate precipitation before and after the salinity crisis onset. Dolomite rich-beds actually formed only prior to the onset of the MSC; this interpretation is partially at odds with previous theoretical models (De Lange and Krijgsman, 2010), according to which dolostone layers are the lateral equivalents of the Primay Lower Gypsum beds formed during the first stage of the MSC. The Pollenzo pre-MSC beds are early diagenetic products formed within the sedimentary column in the shallow subsurface within sediments deposited on an oxic sea bottom. Dolomite precipitation was temporarily enhanced by an upward flux of methane-rich fluids possibly sourced by gas-hydrate destabilization.

Conversely, from the onset of the MSC onward, calcite (and aragonite) were the dominant authigenic phases. Microbial-orchestrated carbonate precipitation took place just below the sea
bottom, covered by chemotrophic microbial mats dominated by giant sulphide-oxidizing bacteria. The development of these mats was triggered by the establishment of anoxic conditions at the sea bottom (hampering gypsum deposition), in turn related to density stratification of the water column and/or enhanced biological productivity in the water column. The high sulphate concentration in the pore water, related to the presence of concentrated brines and to the physiology of sulphide-oxidizing bacteria (responsible for the continuous “regeneration” of sulphate) were the main factors controlling the mineralogical change from dolomite to calcite. These microbialites do not provide any evidence of sea level lowering at the onset of the MSC as frequently reported, because sulphide-oxidizing bacteria are not light dependent and can live at any depth. Accordingly, the contractional features observed in the sediments, that are commonly regarded as a proof of sea level drop and subaerial exposure, may be ascribed to sediment syneresis due to bacterial EPS degradation in a subaqueous environment.

The results of this study highlight how microbial activity can influence the type of authigenic products and the resultant fabrics (dolomite beds versus microbialites); moreover, they suggest that care must be taken in the interpretation of the isotope oxygen values in terms of fluctuating salinity conditions of the water mass, with negative values reflecting dilution events and positive ones an increase of the rate of the evaporation. The $^{18}$O enrichment of the pre-MSC (early diagenetic) beds does not necessarily reflect the isotopic composition of sea water but rather the contribution of diagenetic fluids in the shallow subsurface. In the same way, the sharp shift towards negative $\delta^{18}$O values at the onset of MSC may reflect complex fractionation processes operated by sulphate-reducing bacterial communities.

Further studies are needed, especially devoted to the characterisation of the biomarker inventory preserved in the carbonates, that could provide more extensive information on the types of microbes involved in carbonate precipitation and on the mutual relationships (if any) with microbes preserved within the gypsum deposited in the shallower part of the Messinian basin(s).

This type of approach can contribute to provide information on the changes of microbial
communities at the onset the MSC and on the role played by bacterial activity in modulating evaporite and carbonate sedimentation during the MSC.

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References


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Figure captions

Fig. 1. A) Structural sketch of NW Italy (modified from Bigi et al., 1990). The asterisk shows the location of the Pollenzo section. TH: Torino Hill; MO: Monferrato; AM: Alto Monferrato; BG: Borbera-Grue; VVL: Villalevernia-Varzi Line; SVZ: Sestri-Voltaggio zone; IL: Insubric Line. B) Regional section in a N-S direction (redrawn after Bertotti and Mosca, 2009; Mosca et al., 2009). Location in Fig. 1A.

Fig. 2. A) Schematic cross section, flattened at the base of the Pliocene, showing the relationships among the Messinian units. PLG: Primary Lower Gypsum unit; RLG: Resedimented Lower Gypsum unit; MES: Messinian erosional surface; SKB: Sturani key-bed; CRB: carbonate-rich beds (from Dela Pierre et al, 2011). Not to scale. B) Stratigraphic model of the MSC record of Alba along a SW-NE cross section flattened at the base of the Pliocene. The location of the Pollenzo section is shown. The carbonate-rich beds discussed in the text are marked in yellow (from Dela Pierre et al., 2011). Abbreviations as in Fig. 2A. The trace of the cross section is shown in Fig. 1A.

Fig. 3. The Pollenzo section (left) and detail of the upper part of the Sant’Agata Fossili Marls (right). ICP data (total carbonates, dolomite and calcite) and stable isotope data of pre-MSC and MSC cycles are shown. SKB: Sturani-key bed; RLG: Resedimented Lower Gypsum unit; AAF: Argille Azzurre Formation; hb: hemi-ellipsoidal body. Chrono-biostratigraphic data and distribution of foraminifers and calcareous nannofossils are from Lozar et al. (2010) and Dela Pierre et al., (2011).

Fig. 4. The upper part of the Sant’Agata Fossili Marls at Pollenzo; the carbonate-rich beds discussed in the text are shown. From this perspective view bed a is not visible. SAF: Sant’Agata Fossili Marls; PLG: Primary Lower Gypsum unit.
Fig. 5. Pre-MSC beds. A) Outcrop view of bed a. Note the sharp lower and upper boundaries. B) Polished slab of bed a. Burrows (arrows) can be recognised. C) Photomicrograph (plane light) of bed c; silt-sized terrigenous grains and burrows can be recognised. D) SEM image of a slightly etched broken chip of bed a. Rhombohedric dolomite crystals are clearly recognisable. E) SEM image of a slightly etched broken chip of bed d. Pyrite frambooids and dolomite crystals are visible.

Fig. 6. MSC beds. A) Outcrop view of the uppermost part of the Sant’Agata Fossili Marls. Beds e, f and g and the hemi-ellipsoidal body (hb) can be recognised. B) Photomicrograph (plane light) of bed e, showing rounded clasts encircled by circumgranular cracks (arrows). C) Polished slab of bed f, showing whitish and grey laminae. Some cracks can be recognised within whitish laminae (arrows). D) Photomicrograph (plane light) of bed f, showing the alternation of carbonate and terrigenous-rich laminae. Note the contractional cracks in the carbonate laminae. E) Photomicrograph in epifluorescence of bed f. Note the stronger fluorescence of the carbonate lamina (lower part). Filaments (arrows) can be seen in the carbonate lamina.

Fig. 7. MSC beds. A) Photomicrograph (plane light) of bed g. Note the thin lamination and the black filaments (arrows) underlined by a concentration of pyrite frambooids. B) SEM images of a broken chip of bed f showing globular calcite crystals with a central hollow. C) Photomicrograph (plane light) of bed g with a detail of a filament. D) Photomicrograph in epifluorescence of the same filament of Fig. 7C. Note its different epifluorescence with respect to the surrounding matrix and the abundant pyrite frambooids preserved within it.

Fig. 8. The hemi-ellipsoidal body. A) Outcrop view. B) Polished slab of a sample collected in the upper part of the body; note the wrinkled lamination. C) and D) Photomicrographs in plane light and in epifluorescence of some filaments. Note in D) the stronger epifluorescence of the calcite infilling of a large filament. E) Photomicrograph (plane light) of curved filaments surrounded by
fringing aragonite (arrows). The central portion of the intergranular voids is filled with calcite (cc).  

F) SEM image of a slightly etched broken chip showing slightly curved calcite filaments, surrounded by aragonite fringes (ar).

Fig. 9. The hemi-ellipsoidal body: pyrite frambooids growing on aragonite fringes.

Fig. 10. Genesis of the pre-MSC carbonate-rich beds at the sulphate-methane interface (SMI).
A) During formation of beds a and b, bacterial sulphate reduction was coupled to anaerobic oxidation of methane (AOM); methane derived (at least in part) from gas hydrate (GH) destabilization. B) Dolomite precipitation in beds c and d was induced by bacterial sulphate reduction alone, fuelled by organic matter oxidation. In these beds the dolomite content is lower than in beds a and b. Depth of the SMI below the sea floor was probably of few metres and was shallower for beds a and b, due to the larger supply of methane from below.

Fig. 11. Genesis of the MSC carbonate-rich-beds. Carbonate precipitation was triggered by bacterial sulphate reduction in organic-matter-rich anoxic sediments immediately below the sea floor; the latter was covered by filamentous sulphide-oxidizing bacteria (F). Since sulphate was not completely consumed, calcite was favoured. Dolomite could precipitate only later at the sulphate-methane-interface (SMI). For further detail see text.

Fig. 12. Formation of laminated carbonate beds.
A) A mat of filamentous sulphide-oxidizing bacteria developed at the sea floor, sustained by a sulphide flux sourced by bacterial sulphate reduction working in the shallow subsurface; here active calcite precipitation took place. B) A layer of organic-matter-poor terrigenous sediment buried the chemotrophic mat, slowing down the activity of sulphate-reducing bacteria. C) After the terrigenous influx ceased, the activity of sulphate-reducing bacteria resumed, focused in organic-rich layers (a
buried chemotrophic mat in this example). The ensuing calcite (and pyrite) precipitation preserved the dead bacterial filaments, while a new chemotrophic mat developed on the aggraded sea floor. Calcite was followed by dolomite precipitation (see Fig. 11). For further detail, see text.

Table 1. ICP data of pre-MSC (light grey shadow) and MSC (dark grey shadow) sediments; h.m: homogeneous marl; l.s.: laminated shale; T.C: total carbonate.

Table 2. Percentage of dolomite and calcite with respect to the total carbonate (T.C.) content in the pre-MSC (light grey shadow) and MSC (dark grey shadow) carbonate-rich beds.

Table 3. Stable isotope data of pre-MSC (light grey shadow) and MSC (dark grey shadow) sediments. Carbonate-rich beds are in bold. Hem. body: hemi-ellipsoidal body.
Dela Pierre et al. Fig. 1
Figure

Dela Pierre et al., Fig. 3
Dela Pierre et al., Fig. 5
Dela Pierre et al. Fig. 9
Dela Pierre et al., Fig. 11

ANoxic BOTTOM WATER

Calcite precipitation

Anaerobic organic matter degradation via bacterial sulphate reduction

Dolomite precipitation

Organic matter fermentation

Sulphidic

SMI

Methanogenic

CH₄

CH₄

CH₄

Fig. 12
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<th>Sample</th>
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<th>Calcite [% on the whole rock]</th>
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Dela Pierre et al. Tab. 1
### Table

Dela Pierre et al., Tab. 2

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Dela Pierre et al., Tab. 3