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UNIVERSITÀ DEGLI STUDI DI TORINO

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

25 The seven Messinian microbial carbonate-rich layers cropping out in the Pollenzo section (Tertiary 26 Piedmont Basin, NW Italy) are interbedded with a precession-related cyclic succession composed 27 of euxinic shale/marl couplets and straddle the onset of the Messinian salinity crisis (MSC). A sharp 28 change of sedimentological, compositional and geochemical characteristics was observed from the 29 onset of the MSC onward, suggesting strong differences in the mechanisms responsible for 30 carbonate precipitation. Pre-MSC beds are mainly composed of dolomite and are interpreted as the 31 product of early diagenesis, formed by bacterial sulphate reduction in the shallow subsurface along 32 the sulphate-methane interface. Dolomite precipitation was temporarily enhanced by an upward flux 33 of methane-rich fluids, possibly sourced by gas hydrate destabilisation. Conversely, from the onset 34 of the MSC onward, carbonate beds are thinly laminated and show abundant filaments interpreted 35 as *Beggiatoa*-like bacteria, while calcite (and aragonite) are the dominant authigenic phases. These 36 beds are interpreted as microbialites, resulting from the lithification of chemotrophic bacterial mats 37 dominated by sulphide-oxidizing bacteria. The carbonate necessary for their preservation was 38 provided by bacterial sulphate reduction. These microbialites, that appear as the deeper water 39 counterpart of bottom-grown selenite layers deposited in the marginal part of the basin, formed on 40 an anoxic sea bottom under a density stratified water column. The high sulphate concentration in 41 the pore waters, related to the presence of concentrated brines and to the regeneration of sulphate by 42 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 δ^{18} O values of 43 carbonates, observed from the onset of the MSC onward, was probably related to fractionation 44 45 processes operated by sulphate-reducing bacterial communities in the pore waters. This suggests 46 that care must be taken, when dealing with microbial carbonates, in the interpretation of the oxygen 47 isotope values in term of fluctuating salinity condition of the water mass. In conclusion, this study 48 suggests that the onset of the MSC had a strong impact on microbial populations governing

49 carbonate precipitation, in a sector of the basin dominated by depositional conditions not suitable50 for gypsum precipitation.

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

54

55 **1. Introduction**

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Studies of modern environments and culture experiments have shown that microbially-57 58 induced carbonate precipitation is a common process active in various types of marine sediments 59 (e.g. Irwin et al., 1977; Vasconcelos et al., 1995; Wright and Oren, 2005). In particular, sulphate-60 reducing bacteria are considered to play a fundamental role in triggering the precipitation of 61 different carbonate minerals (calcite, aragonite, dolomite) in a wide range of organic-rich sediments 62 from peritidal microbial mats (e.g. Baumgartner et al., 2006, Dupraz et al., 2009) to anoxic deep sea 63 sediments (e.g. Meister et al. 2008). A prolonged and intense activity of the degradation of organic 64 matter by sulphate-reducing bacteria can lead to the formation of lithified layers and masses, 65 commonly referred to as microbialites. However, other prokaryotes are also thought to be related to 66 carbonate precipitation and sediment lithification, including methanogenic archaea, anaerobic 67 methane oxidizing communities, and cyanobacteria (see Wright and Oren 2005 and references 68 therein). The correct identification of the prokaryotes involved in the formation of diagenetic 69 carbonate bodies can provide fundamental information on the environmental conditions governing 70 carbonate precipitation both at the sea bottom and in the shallow subsurface. 71 Microbial carbonate rocks are a common component of the Messinian salinity crisis (MSC) 72 stratigraphic record. They have been mainly reported from: 1) the Terminal Carbonate Complex

73 (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

75 thrombolite and stromatolite domes (Feldmann and Mc Kenzie, 1997; Arenas and Pomar, 2010); 2) 76 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 77 78 summarised by Manzi et al. (2011), the Calcare di Base was interpreted as a chemical precipitate 79 from concentrated brines immediately prior to evaporite deposition (Schreiber and Friedman, 1976; 80 Decima et al., 1988) and/or as a microbial product formed in a restricted basin (Bellanca et al., 81 2001; Blanc-Valleron et. al., 2002). In particular, beds of carbonate "stromatolites" were reported 82 (Oliveri et al., 2010) and interpreted as the record of progressively shallower, more restricted and 83 hypersaline conditions, favouring the development of microbial communities at the sea floor 84 immediately prior to the onset of gypsum deposition (e.g. Rouchy and Caruso, 2006). Wide salinity 85 fluctuations and sharp dilution events of the brines have also been highlighted (Guido et al., 2007). 86 A complex diagenetic evolution, including microbial sulphate reduction coupled to the oxidation of 87 biogenic methane, was also proposed (Ziegenbalg et al., 2010, 2012). Similar beds were described 88 below the gypsum from other Mediterranean localities such as the Vena del Gesso basin (Vai and 89 Ricci Lucchi, 1977; Manzi et al., 2011) and Cyprus, where these features have been referred to as 90 stromatolites and considered to record basin shallowing and restriction (Rouchy and Monty, 1981; 91 Krijgsman et al., 2002; Orszag-Sperber et al., 2009).

92 A recent revisitation of the Calcare di Base in Sicily, Calabria and northern Apennines 93 (Manzi et al., 2011) showed that this unit actually consists of several types of carbonates formed in 94 different setting and during different stages of the Messinian salinity crisis. In particular, the unit 95 includes three types of carbonates: a) thin dolostone beds interbedded to tripolaceous facies, 96 representing the deep water equivalent of primary gypsum deposited in marginal basins during the 97 first MSC step (type 2); b) clastic bodies deposited during the second MSC stage (type 3); c) late 98 diagenetic products after original resedimented gypsum layers (type 1). 99 Thin carbonate beds are also known from the Piedmont succession, just below the gypsum

100 (Sturani, 1973). In previous studies (Sturani, 1976) these beds, that abruptly overlie lower

101 Messinian deep water marls, were interpreted as the record of a dramatic sea level fall (of the order 102 of 200-500 m) at the onset of the MSC. This interpretation was based on the presence of a variety of 103 features thought to indicate deposition in very shallow waters and subaerial exposure (stromatolitic 104 lamination, desiccation and expansion cracks, calcite pseudomorphs after gypsum crystals). 105 However, a recent revisitation of the MSC record of the southern margin of the Piedmont Basin 106 (Dela Pierre et al., 2011) suggested that these carbonate beds actually straddle the onset of the MSC 107 and that part of them are the lateral deep-water counterpart of the lowermost gypsum layers 108 deposited in the shallow marginal part of the basin, hence corresponding to the type 2 Calcare di 109 Base (sensu Manzi et al., 2011, see above) of the Sicilian succession. 110 In this paper we present the results of an integrated sedimentological, petrographical and 111 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.

- 115
- 116 **2**. **The Messinian salinity crisis**
- 117

118 The MSC affected the Mediterranean basin between 5.96 and 5.33 Ma and resulted in the 119 deposition of huge volumes of evaporites that are presently preserved both at the basin margins and 120 in deep basinal areas, where they are buried below the abyssal plains of the Western and Eastern 121 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 122 123 remain the object of a lively scientific debate, mainly because a detailed correlation between the 124 marginal sub-basins, that provide most of the outcropping successions (e.g. Clauzon et al., 1996; 125 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, 126

127	is still lacking (Ryan, 1976; Bertoni and Cartwright, 2007; Lofi et al., 2011). Recently, a MSC
128	evolutionary model has been proposed (CIESM, 2008). This model derives from the two step
129	scenario of Clauzon et al. (1996) and envisages three MSC stages. During the first one (5.96-5.60
130	Ma) primary evaporites were deposited only in shallow, silled, peripheral basins (Primary Lower
131	Gypsum unit; Roveri et al., 2008). Carbonate microbialites are often reported below these deposits
132	(e.g. Rouchy and Monty, 1981; Rouchy and Caruso, 2006). Conversely, in deep basinal setting,
133	only euxinic shales and dolomite-rich beds (the type 2 Calcare di Base of Manzi et al., 2011) were
134	deposited during this stage. The absence of gypsum and the concomitant formation of dolomite
135	seem related to anoxic conditions, responsible for the decrease of the dissolved sulphate content via
136	organic matter degradation by bacterial sulphate reduction (De Lange and Krijgsman, 2010).
137	During the second MSC stage (5.60-5.55 Ma) the marginal basins underwent subaerial
138	exposure and erosion as evidenced by an erosional surface, referred to as the Messinian erosional
139	surface (Lofi et al., 2011). This surface can be traced basinward in a correlative conformity placed
140	at the base of thick accumulations of chaotic and resedimented evaporites, the Resedimented Lower
141	Gypsum unit (Roveri et al., 2008).
142	During the third stage (5.55-5.33 Ma) a rapid transition to environments characterised by
143	fluctuating salinity conditions is recorded by deposition of evaporites (Upper Evaporites) and clastic
144	sediments containing brackish to fresh water fossil assemblages. The reestablishment of fully
145	marine conditions at 5.33 Ma (Zanclean) marks the end of the salinity crisis.
146	
147	3. Geologic and stratigraphic setting
148	
149	The Tertiary Piedmont Basin (Figs. 1A, B) is filled with Upper Eocene to Messinian
150	sediments deposited unconformably on a wedge of Alpine, Ligurian and Adria basement units
151	juxtaposed in response to the collision between the Europe and Adria plates (e.g. Mosca et al.,

152 2009; Rossi et al., 2009). Messinian strata were deposited in a wide wedge top basin (Figs. 1B, 2A),

153 bounded to the north by the more external Apennine thrusts (Rossi et al., 2009; Dela Pierre et al., 154 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 155 156 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 157 158 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 159 160 precession-related cyclic stacking pattern, evidenced by the rhythmic repetition of euxinic 161 shale/marl couplets (Lozar et al., 2010), and is followed at basin margin by the Primary Lower 162 Gypsum unit (Fig. 2A). The latter shows the same precession-driven lithologic cyclicity, 163 represented by shale/gypsum couplets (Dela Pierre et al., 2011). No *in situ* primary evaporites are 164 documented in the depocentral zones, but seismic data show that their time equivalent sediments are 165 represented by shales (Irace et al., 2010).

166 The transition between the shallow marginal area and the buried depocentre is exposed on 167 the southern sector of the Piedmont Basin (Alba region) and was reconstructed in detail along a 168 SW-NE transect (Dela Pierre et al., 2011) (Fig. 2B). On the basin margins, six Primary Lower 169 Gypsum cycles were recognised, composed of bottom grown-selenite layers; the sixth bed 170 represents a distinct marker bed referred to as the Sturani key-bed (Dela Pierre et al., 2011). Moving 171 towards the NE (i.e. towards the depocentral zone), only two gypsum beds are present below this 172 marker bed. In the Pollenzo section they overlie a cyclic succession of euxinic shales, marls and 173 carbonate-rich beds (the object of this study), belonging from the lithostratigraphic point of view to 174 the Sant'Agata Fossili Marls (Fig. 2B). Due to their position with respect to the Sturani key-bed, the 175 uppermost three cycles must be considered as the deeper water equivalent of the lower cycles of the 176 Primary Lower Gypsum unit deposited in marginal setting (Dela Pierre et al., 2011). This 177 correlation is confirmed by bio-magnetostratigraphic data, indicating that the onset of the MSC

178	should be placed at Pollenzo three cycles below the first gypsum bed, in correspondence of the peak
179	abundance of the calcareous nannofossil Sphenolithus abies (Lozar et al., 2010).
180	The Primary Lower Gypsum unit is followed by resedimented and chaotic evaporites (Valle
181	Versa Chaotic Complex, Dela Pierre et al., 2007), that are considered to be equivalents of the
182	Resedimented Lower Gypsum unit (Fig. 2B) deposited during the second MSC stage (5.60-5.55
183	Ma). This latter unit is finally followed by fluvio-deltaic and lacustrine deposits (Cassano Spinola
184	Conglomerates) recording the third MSC stage (5.55-5.33 Ma), in turn overlain by Zanclean marine
185	clays (Argille Azzurre Formation).
186	
187	3.1 The Pollenzo section
188	
189	In this section, located along the Tanaro River, a complete Messinian succession,
190	comprising the Sant'Agata Fossili Marls, the Primary Lower Gypsum, the Resedimented Lower
191	Gypsum units and the Cassano Spinola Conglomerates, is exposed (Fig. 3). Only the Sant'Agata
192	Fossili Marls, in which the studied carbonate beds are hosted, will be described below. For the

193 chrono-biostratigraphic data of this unit and for the description of the overlying succession, the

194 reader is referred to Lozar et al. (2010) and Dela Pierre et al. (2011).

195 The Sant'Agata Fossili Marls consist of muddy marine sediments characterised by a 196 distinctive precession-driven cyclicity, given by the alternation of euxinic shale/marl couplets, 197 forming up to 3 m-thick cycles (Dela Pierre et al., 2011). A 80 m-thick slumped interval divides the 198 section into two portions (Fig. 3). The lower portion, below the slump, consists of seven cycles; in 199 the upper portion, above the slump, the lithologic cyclicity is enhanced by the regular repetition of 200 carbonate-rich beds easily distinguishable for their whitish colour (Fig. 4). Seven cycles (Pm1-Pm7) 201 with an average thickness of 3 metres were recognised, each one including a distinct carbonate bed. 202 The integration of physical-stratigraphic (position with respect to the Sturani key-bed) and 203 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.
205 2011). Hence four pre-MSC cycles (Pm1-Pm4) are present, followed by three MSC cycles (Pm5Pm7) 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 208 209 followed by a calcareous marly bed that hosts a dm-thick carbonate-rich bed. The strong 210 impoverishment of foraminiferal assemblages, that include only rare stress tolerant planktic 211 (*Turborotalita quinqueloba* and *T. multiloba*) and benthic taxa (*Bolivina dentellata* and *Bulimina* 212 echinata), suggests the establishment of restricted conditions, a severe stratification of the water 213 column and the impoverishment in dissolved oxygen of bottom waters (Lozar et al., 2010). The 214 MSC cycles show analogous lithologic characteristics, but no marls were observed in cycle Pm6; 215 moreover the carbonate beds here show a laminated structure, not observed in the underlying ones 216 (see below). An hemi-ellipsoidal convex-upward indurated body has been observed 50 cm above 217 layer e, within cycle Pm6 (Fig.3). This feature was not reported in Dela Pierre et al. (2011) because 218 completely submerged at that time by the Tanaro River. Foraminifers and calcareous nannofossils 219 are extremely rare and disappear at the top of cycle Pm6, confirming the final disruption of the 220 water column and the definitive establishment of anoxic bottom conditions. The upper carbonate 221 bed (g, Figs. 3, 4) is overlain by the first gypsum-bearing cycle (Pg1, Fig. 3), that is composed of 222 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). 223

224

225 **4.** Methods

226

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

230 petrographic and geochemical analyses. Twelve standard thin sections of the most representative 231 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 232 233 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 234 235 Cambridge Instruments Stereoscan 360 equipped with an energy-dispersive EDS Oxford 236 Instruments Link System microprobe (Department of Earth Sciences, Torino University). 237 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-238 239 rich beds and the host sediments) at the Inductively Coupled Plasma-Optical Emission 240 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 241 242 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 243 244 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 Ca²⁺ was then subtracted 245 from to the whole Ca²⁺ pool (obtained in the further step) in order to avoid an overestimation of the 246 247 carbonates. As a second step, 200 mg of sample powder were processed in 10 ml of hot acetic acid 248 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 249 abundance of calcite and dolomite in the samples was calculated (after subtraction of the amount of 250 Ca^{2+} derived from gypsum, as mentioned above) assigning the total amount of Mg²⁺, with the 251 corresponding amount of Ca^{2+} , to stoichiometric dolomite; the remaining Ca^{2+} was assumed to 252 253 derive from calcite and was used to calculate the abundance of stoichiometric calcite. EDS analyses 254 performed on some samples confirmed the near stoichiometric composition of calcite (less than 1%

255	of Mg ²⁺), and dolomite (51- 53 CaCO ₃ mole%). The results of Inductively Coupled Plasma (ICP)
256	analyses (Table 1) are expressed as mass percent on the whole sediment.
257	Bulk rock C and O stable isotope analyses were performed on 22 samples from both
258	carbonate-rich beds and unlithified sediments at the ISO4 laboratory (Torino, Italy) and in the
259	MARUM Stable Isotope Laboratory (Bremen, Germany). The carbonate fraction was analysed
260	following the classical method (McCrea, 1950). The ${}^{13}C/{}^{12}C$ and ${}^{18}O/{}^{16}O$ ratios of the CO ₂ were
261	obtained using Finnigan MAT 251 and 252 mass spectrometers. For the carbonate-rich beds, both
262	calcite and dolomite were measured, whereas in the unconsolidated sediments only calcite was
263	analysed. The isotopic ratios are expressed as $\delta^{13}C$ and $\delta^{18}O$ per mil versus the PDB standard (Fig.
264	3, Table 3); the analytical error is $\pm 0.5\%$ and $\pm 0.1\%$ for $\delta^{13}C$ and $\delta^{18}O$, respectively.
265	
266	5. Results
267	5.1. Lithology
268	
269	5.1.1 Unconsolidated sediments
270	In the host sediments, the carbonate content ranges from 10 to 41% and consists of both
271	calcite and dolomite that are mixed in variable proportions (Table 1). The total carbonate ranges
272	from 23 to 41% in the homogeneous marl and reaches the lowest values (<23%) in the laminated
273	shale. As a general rule, pre-MSC sediments contain a higher calcite fraction, probably related to
274	the higher content of skeletal grains (foraminifers and calcareous nannofossils), that are generally
275	very rare or even absent in MSC sediments.
276	
277	5.1.2 Pre-MSC carbonate-rich beds
278	Pre-MSC beds (a, b, c, d) are dm- thick and are interbedded within the marly part of the
279	lithologic cycles (Pm1 to Pm4, Fig. 3). The lower and upper contacts are transitional, except for bed

280 *a* in which they are sharp (Fig. 5A). These beds are the product of local cementation of host

281 sediments and contain variable amounts of a silt-sized terrigenous fraction, mainly consisting of 282 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. 283 284 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 285 286 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 287 288 (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%, 289 290 respectively) (Fig. 3, Table 2). Pyrite framboids, up to 10 mµ across, are very common in all beds 291 (Fig. 5E).

292

293 5.1.3 MSC carbonate-rich beds

294 Beds deposited during the salinity crisis are about 20 cm-thick and show transitional 295 contacts with the host sediments (Fig. 6A). Bed *e* is located at the top of the marly interval and 296 contains mm-sized intraclasts, floating in a clotted micrite matrix containing rare foraminifers. A 297 remarkable feature is the presence of contractional cracks developed around the clasts 298 (circumgranular cracks) (Fig. 6B). Beds f and g show different features, because they are not 299 bioturbated and display a well-developed lamination. Bed f lies in strongly laminated shales (no 300 marl was observed in cycle Pm6) and shows a lamination marked by the alternation of mm-thick 301 whitish and grey wrinkled laminae (Fig. 6C). The formers are composed of clotted micrite, contain 302 abundant pyrite framboids and are crossed by a network of mm-wide contractional cracks, running 303 perpendicular to the lamina surfaces, that are empty or filled with late diagenetic gypsum (Fig. 6D). 304 These laminae contain abundant fish vertebrae and scales. The grey laminae are richer in 305 terrigenous material, mostly represented by clay particles and mica flakes (Fig. 6D). At the 306 boundary between the two types of laminae, cracks were commonly observed. Micrite laminae

307 exhibit a stronger epifluorescence than the terrigenous ones, suggesting a higher content in organic 308 matter (Fig. 6E). Moreover, epifluorescence microscopy permits the recognition of filaments, up to 309 100 µm across and more than 300 µm long, showing different fluorescence shades (Fig. 6E). Bed g 310 is similar to bed f, except it is made up of more wrinkled and thinner laminae (less than 1 mm). 311 Pyrite framboids are abundant and are frequently grouped together to mimic filaments about 100 312 μm across and up to 800 μm long (Figs. 7A, C). Epifluorescence observations reveal that filaments 313 show a stronger fluorescence than the enclosing matrix (Fig. 7D). The same features, despite less 314 abundant, were observed in bed f.

Unlike the pre-MSC beds, the carbonate fraction of the salinity crisis layers is dominated by 315 316 calcite whereas dolomite is subordinate; frequently micron-sized calcite crystals show a globular 317 shape with a central hollow, suggesting a possible microbial origin (Cavagna et al., 1999). This type 318 of crystals (Fig. 7B) was observed also within the filaments, together with abundant pyrite 319 framboids. Remarkably, no terrigenous grains, abundant in the enclosing matrix, were observed 320 within the filaments. The predominance of calcite over dolomite is confirmed by ICP analyses; in 321 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%, 322 respectively) (Fig.3, Table 2).

323

324 *5.1.4 The hemi-ellipsoidal body*

325 The hemi-ellipsoidal cemented body observed within cycle Pm6 is 1.70 metres by 1 metre in 326 size and shows transitional lateral contacts with the host laminated shale (Fig. 8A). Its most 327 remarkable feature is the wrinkled lamination (Fig. 8B), given by the alternation of submillimetric 328 whitish and grey lamine, that strongly resembles the structure described as the "stromatolites" of the 329 Sicilian Calcare di Base (Oliveri et al., 2010). The whitish laminae are composed of filaments, 150 330 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, 331 332 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).

- 339
- 340 5.2. Stable isotope data
- 341

342 5.2.1 Unconsolidated sediments

In both pre-MSC and MSC cycles, the δ^{13} C values are around zero (Fig. 3, Table 3), 343 suggesting carbonate precipitation from a fluid in isotopic equilibrium with sea water. The weak ¹³C 344 depletion observed in some samples from cycles Pm1 ($\delta^{13}C = -6.5\%$), Pm6 ($\delta^{13}C = -5\%$) and Pm7 345 $(\delta^{13}C = -4.7\%)$ points to the contribution of diagenetic carbon from decaying organic matter. All 346 samples are characterised by low δ^{18} O values, with a general trend towards more negative values in 347 the MSC sediments (cycle Pm5-Pm7). The interpretation of these negative δ^{18} O values is not 348 349 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 350 351 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., 352 353 2002), may reflect complex microbial fractionation processes on the oxygen pool (see paragraph 6.2.2). 354

355

356 5.2.2 Pre-MSC carbonate-rich beds

A significant ¹³C depletion was observed for both dolomite and calcite in beds a and b357 $(\delta^{13}C_{dol} = -19.8 \text{ and } -21\%; \delta^{13}C_{cal} = -16.7 \text{ and } -14.5\%, \text{ respectively})$. In the upper two pre-MSC 358 beds (c and d) less negative values were instead measured for both minerals (-4.4 and -5.2% for 359 dolomite; -9.2 and -5.7‰ for calcite, respectively). Positive $\delta^{18}O_{dol}$ values were observed in all 360 pre-MSC beds (Fig. 3, Table 3): the stronger ¹⁸O enrichment was measured in beds a ($\delta^{18}O_{dol} =$ 361 +7‰) and b ($\delta^{18}O_{dol} = +6.9\%$), whereas in beds c and d lower values were found ($\delta^{18}O_{dol} = +1.3$ 362 and +3.6%, respectively). More negative values were observed for calcite. In beds a and b the 363 $\delta^{18}O_{cal}$ is +5.7 and -1.0‰, respectively, whereas in beds c and d it is -3.9 and -1.5‰ (Fig. 3, 364 365 Table 3).

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367 5.2.3 MSC carbonate-rich beds

In the salinity crisis beds, the δ^{13} C values of both dolomite and calcite are moderately 368 negative (from -5 to -3.9% for dolomite and from -7.9 to -6.7% for calcite). A stronger ¹³C 369 depletion was measured for the calcite of the hemi-ellipsoidal body (cycle Pm6), with values around 370 -8.5%. For what concerns the δ^{18} O, a remarkable shift towards negative values was observed. The 371 $\delta^{18}O_{dol}$ values range from -6.1 to -4.9‰ whereas the $\delta^{18}O_{cal}$ are more negative (from -6.5 to -372 8.8‰). The hemiellipsoidal body yelded $\delta^{18}O_{cal}$ values as low as -7.7‰. 373 374 375 Discussion 376 6. 377 6.1. Pre-MSC beds: early diagenetic products from the shallow subsurface 378 379 380 In pre-MSC beds, the authigenic carbonate fraction is dominated by dolomite, mixed with

381 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.

387 Studies of modern environments and culture experiments have shown that dolomite 388 precipitation in the subsurface is induced by the metabolic activity of sulphate-reducing bacteria 389 that, by degrading organic matter, consume sulphate ions and increase overall alkalinity thus 390 overcoming the kinetic inhibition to dolomite precipitation (e.g. Baker and Kastner, 1981; Compton 391 et al., 1988; Vasconcelos et al., 1995; Wright and Oren, 2005; Baumgartner et al., 2006; Meister et 392 al., 2007; Wacey et al., 2008). In modern deep sea organic-carbon-rich hemipelagic sediments, 393 bacterial sulphate reduction is controlled by the downward diffusion of sulphate from sea water 394 (Compton, 1988; Wright and Oren, 2005). In these conditions, dolomite can precipitate from anoxic 395 sulphate-free pore waters, at the lower boundary of the sulphate-reducing zone. In present-day open 396 marine environments the depth of this surface, that corresponds to the sulphate-methane interface, 397 ranges from few metres up to few tens of metres, depending on the porosity and on the content and 398 type of organic matter (e.g. Borowski et al., 1999; Fossing et al., 2000; D'Hondt et al., 2002; Treude 399 et al., 2005; Jørgensen and Kasten, 2006). Apart from carbonate, sulphate reduction provides 400 hydrogen sulphide that subsequently can react with iron to form sulphide minerals (e.g. pyrite). 401 Carbonate precipitation at the sulphate-methane interface is however quantitatively limited and 402 commonly goes unnoticed in most sedimentary sequences (e.g. Raiswell and Fisher, 2004). In two 403 cases it becomes significant and may give origin to well recognizable carbonate-cemented layers: 1) 404 if large amounts of upward rising methane-rich fluids reach this geochemical interface; in this case 405 abundant carbonate (calcite, aragonite and dolomite) can precipitate resulting in extensive 406 cementation of the flushed sediments (e.g. Irwin et al., 1977; Raiswell, 1987; Raiswell and Fischer, 407 2000; Campbell, 2006; Ussler and Paull, 2008). Carbonate precipitation is induced by a consortium

408 of sulphate-reducing bacteria and methanotrophic archaea (Boetius et al., 2000), responsible for the 409 anaerobic oxidation of methane; 2) if the sulphate-methane interface remains stationary within the 410 sedimentary column for a prolonged time interval, resulting in focused dolomite precipitation; in 411 this case, a distinct dolomite-rich bed can form even though the supply of methane-rich fluids from 412 below is negligible (Meister et al., 2007, 2008).

413 The bed-parallel geometry of the Pollenzo pre-MSC beds suggests that dolomite 414 precipitation occurred at a geochemical interface parallel to the sea bottom. In this regards the co-415 occurrence 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 416 measured in diagenetic dolomite of the lower two beds (a and b) (δ^{13} C around -20‰), points to the 417 418 contribution of anaerobic oxidation of methane in dolomite precipitation (Fig. 10A). The moderate ¹³C depletion (compared to typical methane-derived carbonates in which δ^{13} C values as low as – 419 420 60‰ are commonly measured; e.g. Peckmann and Thiel, 2004) may reflect the mixture of methane-421 derived carbon with other sources, such as heavier hydrocarbons (Roberts and Aharon, 1994), 422 marine dissolved inorganic carbon or skeletal material of marine organisms, that are actually 423 present in these beds (e.g. Peckmann and Thiel, 2004; Natalicchio et al., 2012). The same mechanism can explain the δ^{13} C signature of calcite. 424

425 Conversely, the less negative δ^{13} C values of beds *c* and *d* (δ^{13} C around -5‰) suggest that 426 dolomite precipitation was induced by organoclastic bacterial sulphate reduction alone, as the 427 upward methane flux ceased completely (Fig. 10B). These indurated layers likely developed along a 428 temporarily fixed sulphate-methane interface that favoured focused dolomite precipitation. Sulphate 429 reduction alone, however, was able to produce only a lesser amount of authigenic dolomite with 430 respect to anaerobic oxidation of methane, as indicated by geochemical data and by the minor 431 induration of these beds.

432 The oxygen isotope record of dolomite (the predominant carbonate mineral) reveals that 433 beds *a* and *b* are significantly enriched in the heavy ¹⁸O isotope (Fig. 3, Table 3). Three mechanisms 434 can explain such an enrichment:

a) evaporation of sea water (McKenzie et al., 1979). This mechanism, commonly invoked to
explain the ¹⁸O 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 δ^{18} O values with negative δ^{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 δ^{13} C ones, suggest that the input of ¹⁸Oenriched fluids, ceased together with the demise of methane-rich fluids.

450 As already mentioned, the more negative $\delta^{18}O_{cal}$ values probably reflect the mixing of 451 authigenic and sedimentary calcite. Positive values were only observed in bed *a*, in which the scarce 452 calcite content (8.1%) is likely diagenetic and cogenetic with dolomite.

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454 6.2. MSC beds
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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

458 separately below: a) the presence of wrinkled laminae containing filament remains, and of 459 contractional cracks; b) the sharp decrease of the dolomite content and the concomitant increase of 460 the calcite (and aragonite) content; c) the negative δ^{18} O values recorded both in calcite and 461 dolomite. The carbon isotope data are instead comparable to those of the underlying pre-MSC beds 462 and of the host sediments, testifying to the incorporation of light organic carbon in the authigenic 463 phase.

464

465 6.2.1. Wrinkled laminae, filaments and contractional cracks: vestiges of chemotrophic microbial466 mats?

467 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 468 469 features of carbonate microbialites, *i.e.* organo-sedimentary deposits formed by the activity of 470 benthic microbial communities (Dupraz and Visscher, 2005; Dupraz et al., 2009; Oliveri et al., 471 2010). Compelling evidence of the involvement of microbial mats in the formation of laminated 472 structure is given by the remains of microbial filaments, well recognizable in epifluorescence (Fig 473 6E) that in beds f and g are underlined by a concentration of pyrite framboids (Figs.7C, D). 474 Microbial filaments have been first observed in Messinian gypsum crystals (the so called spaghetti-475 like structures; Vai and Ricci Lucchi, 1977) and interpreted as remains of filamentous 476 photosynthetic cyanobacteria (e.g. Scytonema) on the basis of size and internal structure (Rouchy 477 and Monty, 1981; Panieri et al., 2010), thus providing evidence for shallow water (photic) 478 depositional conditions (but see also the discussion about the relevance of these features for water 479 depth determination in Lugli et al., 2010). Analogous features were then observed in carbonate 480 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 481 482 Monty, 1981; Orszag-Sperber et al., 2009). Hence, also these carbonates were classically

interpreted as shallow water deposits recording stressed environmental conditions heralding theonset of the MSC.

485 The absence of terrigenous grains within the Pollenzo filaments allows to rule out their 486 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 487 488 reach a diameter of 750 µm and a length of several cm, obtain the energy necessary for their life 489 from the oxidation of sulphide by using oxygen or nitrate as electron acceptors (Schulz and 490 Jørgensen, 2001) and do not necessitate light as the driving energy source. In modern settings, they 491 form dense microbial mats (known as chemotrophic-dominated mats) thriving at different water 492 depth (from peritidal to bathyal settings), especially at sites where high concentration of sulphide is 493 available at the sea bottom (e.g. Bailey et al., 2009) such as hydrothermal vents (e.g. Jannasch et al., 494 1989) and cold seeps (Larkin et al., 1994, Sahling et al., 2002; Teichert et al. 2005). However, 495 sulphide-oxidizing bacteria are also known to form extensive felt-like mats where organic-rich 496 sediments are exposed at the sea floor in contact with either oxic (Schulz et al., 1999) or oxygen-497 depleted waters, such as the continental shelf off Peru (Gallardo, 1977; Fossing et al., 1995) or the 498 Danish Limfjorden (Mussmann et al. 2003). In these cases the bacteria use nitrate (and not oxygen) 499 as electron acceptor for oxidizing sulphide to sulphate.

500 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 501 502 the Pollenzo filaments are remains of sulphide-oxidizing bacteria on the basis of the following 503 elements: a) their diameter (>100 μ m), that is close to that of living forms. On the contrary, 504 cyanobacteria filaments rarely exceed 80 µm (e.g. Schulz and Jørgensen, 2001); b) the curved shape 505 of some filaments (Fig. 8E) consistent with the chemotactic behaviour of these prokaryotes that 506 often change their direction in the search of optimal concentrations of oxygen or nitrate (e.g. 507 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 508

509 cytoplasm, that can be further preserved as sulphur-containing minerals associated to the 510 filamentous body fossil (e.g. Bailey et al., 2009); d) the lack of any remain of shallow water 511 macrobiota that should accompany photosynthetic mats. The only features that could suggest a 512 shallow water origin for these laminated layers are the contractional cracks, either developed around 513 clasts and nodules (circumgranular cracks, Fig. 6B) or placed parallel and perpendicular to the 514 bedding (Fig. 6D). Similar features were previously interpreted as desiccation structures and hence 515 considered as a compelling evidence of the subaerial exposure of the Piedmont basin at the onset of 516 the MSC (Sturani, 1973). However, the geometry of crack, that are developed especially across the 517 carbonate-rich laminae and thin out both in the under- and overlying terrigenous laminae, contrasts 518 with an origin by subaerial exposure and desiccation. The microbial origin for the carbonates may 519 provide an alternative explanation for the genesis of these cracks, that can be interpreted as the 520 product of syneresis, related to the decay of bacterial extracellular polysaccharide substances (EPS) 521 binding clay particles (e.g. Dewhrust et al., 1999; Hendry et al., 2006) in a subaqueous 522 environment.

523 On this basis, beds f and g and the hemi-ellipsoidal body of cycle Pm6 are interpreted as the 524 product of the lithification of chemotrophic microbial mats dominated by sulphide-oxidizing 525 bacteria. Unlike their photosynthetic counterpart, chemotrophic mats are rarely preserved in the 526 fossil record, because the metabolism of sulphide-oxidizing bacteria increases acidity and 527 consequently induces carbonate dissolution rather than precipitation (e.g. Petrash et al. 2012). Their 528 preservation can however take place if other biogeochemical processes trigger the rapid 529 precipitation of authigenic carbonates necessary for the entombment of the delicate filaments before 530 their complete decay. This may explain why putative fossil remains of sulphide-oxidizing bacteria 531 are chiefly reported from ancient seep carbonate deposits, where anaerobic oxidation of vigorous 532 methane fluxes induced extensive syndepositional carbonate precipitation (Peckmann et al., 2004). 533 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 534

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 δ^{13} C values of the Pollenzo beds exclude a significant contribution of 538 539 anaerobic oxidation of methane and suggest that the main process responsible for carbonate 540 precipitation was degradation of organic matter via bacterial sulphate reduction. The characteristics 541 of the MSC beds allow to envisage the following scenario (Figs. 11, 12): changed environmental 542 conditions (anoxia of bottom waters, see below) favoured the shift of sulphate-reducing bacteria 543 communities toward the sea bottom and their establishment immediately below it, where they could 544 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 545 546 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 547 548 by these prokaryotes for oxidizing sulphides to sulphates (Fig.12A). Intervals of higher sediment 549 input and increase of continental runoff, recorded by the laminae richer in terrigenous grains, 550 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 551 552 dominated by sulphide oxidizers. The availability of abundant and "fresh" organic matter increased 553 the rate of sulphate reduction in the shallow subsurface, and resulted in the rapid precipitation of 554 large amounts of carbonates preserving the previously formed mat (Fig. 12C). The repetition of 555 these processes through time led to the formation of the laminated structure that characterizes these 556 rocks. According to the proposed scenario, sulphide oxidation, that promoted acidity and carbonate 557 dissolution, was hence spatially and temporally decoupled from the alkalinity generated by sulphate 558 reduction inducing carbonate precipitation. EPS degradation prior to complete lithification was 559 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. 560

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.

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569 6.2.2 The change from dolomite to Ca-carbonates and the oxygen isotope composition of MSC 570 beds

571 The other points to be discussed are: a) the mineralogical change recorded from the MSC 572 onset onward, evidenced by the sharp increase in the calcite content and by the appearance of 573 aragonite in the hemi-ellipsoidal body; b) the negative δ^{18} O values of the MSC carbonates.

574 Although still discussed (Sánchez-Román et al., 2009), the concentration of sulphate in the 575 pore waters is a critical factor controlling the composition of bacterially-induced carbonate 576 minerals. In particular, if the concentration of sulphate is high, dolomite is inhibited and other 577 carbonates (aragonite, calcite, Mg-calcite,) do form (e.g. Baker and Kastner, 1981; Kastner, 1984; 578 Wright and Oren, 2005). At Pollenzo, the main factor driving carbonate precipitation both in pre-579 MSC and in MSC layers was bacterial sulphate reduction. However in pre-MSC beds the sulphate 580 in pore waters was exclusively supplied by normal salinity sea water and carbonate precipitation 581 took place within the sedimentary column. Under these conditions, all sulphate was consumed by 582 bacterial sulphate reduction and dolomite precipitation took place from sulphate-free pore waters 583 along the sulphate-methane interface.

584 On the contrary, MSC beds and the hemi-ellipsoidal body formed at the sea bottom in 585 contact with sulphate-enriched bottom waters, being these layers the lateral equivalents of bottom-586 grown selenite beds formed in the shallower part of the basin, some tens of kilometres apart.

587 Moreover, the sulphate pool was continuously replenished by sulphide oxidation in the 588 chemotrophic microbial mats. As a consequence, sulphate could not be totally consumed, even in 589 the presence of an intense bacterial sulphate reduction, and precipitation of Ca-carbonates (calcite, 590 aragonite) was favoured. Minor amounts of dolomite, occupying the residual pore space formed 591 only after sediment burial, when all sulphate was consumed. This last mechanism was also 592 responsible for the minor amount of dolomite in the host sediments.

The shift towards more negative δ^{18} O values observed in MSC carbonates (-6.5 < δ^{18} O_{cal} < -593 8.8% PDB; $-4.9 < \delta^{18}O_{dol} < -6.1\%$ PDB) compared to the underlying pre-MSC ones remains a still 594 unresolved question. Such ¹⁸O depletion is reported from carbonates just below the first evaporitic 595 596 deposits in other Mediterranean basins (even if less severe than at Pollenzo) and is interpreted as the 597 result of sharp dilution events pointing to the isolation of the basin(s) prior to the onset of gypsum 598 deposition (e.g. Rouchy et al., 1998; Bellanca et al., 2001; Blanc-Valleron et al., 2002). This 599 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 600 as a possible source of ¹⁶O enrichment in the microenvironments of carbonate precipitation (Sass et 601 602 al., 1991). The effects of this process on oxygen isotopic ratios both of sulphate and water have 603 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 604 605 unresolved and, citing Turchyn et al. (2010) "more work is needed".

606

607 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

613 activity of chemotrophic prokaryotes are the lateral equivalent of bottom-grown selenite beds (Dela 614 Pierre et al., 2011, Fig. 2B). According to field and theoretical models, anoxic sea bottoms would be 615 unfavourable to gypsum formation and preservation, mainly because of low sulphate concentration 616 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 617 618 the development of dense chemotrophic microbial mats at the sea floor. Due to the low rate of 619 terrigenous supply, the latters could colonize the sea bottom for a prolonged time interval before 620 their final burial. This circumstance, along with an increased rate of bacterial-mediated carbonate 621 precipitation, allowed the preservation of discrete recognizable beds in the geological record.

622

623 7. Conclusions

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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 palaeocenographic 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.

637 Conversely, from the onset of the MSC onward, calcite (and aragonite) were the dominant
 638 authigenic phases. Microbial-orchestrated carbonate precipitation took place just below the sea

639 bottom, covered by chemotrophic microbial mats dominated by giant sulphide-oxidizing bacteria. 640 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 641 642 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-643 644 oxidizing bacteria (responsible for the continuous "regeneration" of sulphate) were the main factors 645 controlling the mineralogical change from dolomite to calcite. These microbialites do not provide 646 any evidence of sea level lowering at the onset of the MSC as frequently reported, because 647 sulphide-oxidizing bacteria are not light dependent and can live at any depth. Accordingly, the 648 contractional features observed in the sediments, that are commonly regarded as a proof of sea level 649 drop and subaerial exposure, may be ascribed to sediment syneresis due to bacterial EPS 650 degradation in a subaqueous environment.

651 The results of this study highlight how microbial activity can influence the type of 652 authigenic products and the resultant fabrics (dolomite beds versus microbialites); moreover, they 653 suggest that care must be taken in the interpretation of the isotope oxygen values in terms of 654 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 ¹⁸O enrichment of the pre-MSC (early 655 656 diagenetic) beds does not necessarily reflect the isotopic composition of sea water but rather the 657 contribution of diagenetic fluids in the shallow subsurface. In the same way, the sharp shift towards negative δ^{18} O values at the onset of MSC may reflect complex fractionation processes operated by 658 659 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

665	communities at the onset the MSC and on the role played by bacterial activity in modulating
666	evaporite and carbonate sedimentation during the MSC.
667	
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1071 **Figure captions**

1072 Fig. 1. A) Structural sketch of NW Italy (modified from Bigi et al., 1990). The asterisk shows the

1073 location of the Pollenzo section. TH: Torino Hill; MO: Monferrato: AM: Alto Monferrato; BG:

1074 Borbera-Grue; VVL: Villalevernia-Varzi Line; SVZ: Sestri-Voltaggio zone; IL: Insubric Line. B)

1075 Regional section in a N-S direction (redrawn after Bertotti and Mosca, 2009; Mosca et al., 2009).

- 1076 Location in Fig. 1A.
- 1077

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). Abbrevietions as in Fig. 2A. The trace of the cross section is shown in Fig. 1A.

1086 Fig. 3. The Pollenzo section (left) and detail of the upper part of the Sant'Agata Fossili Marls

1087 (right). ICP data (total carbonates, dolomite and calcite) and stable isotope data of pre-MSC and

1088 MSC cycles are shown. SKB: Sturani-key bed; RLG: Resedimented Lower Gypsum unit; AAF:

1089 Argille Azzurre Formation; hb: hemi-ellipsoidal body. Chrono-biostratigraphic data and distribution

1090 of foraminifers and calcareous nannofossils are from Lozar et al. (2010) and Dela Pierre et al.,

1091 (2011).

1092

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

- 1095 Fossili Marls; PLG: Primary Lower Gypsum unit.
- 1096

1097 Fig. 5. Pre-MSC beds. A) Outcrop view of bed a. Note the sharp lower and upper boundaries. B) 1098 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 1099 1100 etched broken chip of bed a. Rhombohedric dolomite crystals are clearly recognisable. E) SEM 1101 image of a slightly etched broken chip of bed d. Pyrite framboids and dolomite crystals are visible. 1102 1103 **Fig. 6**. MSC beds. A) Outcrop view of the uppermost part of the Sant'Agata Fossili Marls. Beds *e*, *f* 1104 and g and the hemi-ellipsoidal body (hb) can be recognised. B) Photomicrograph (plane light) of 1105 bed e, showing rounded clasts encircled by circumgranular cracks (arrows). C) Polished slab of bed 1106 f, showing whitish and grey laminae. Some cracks can be recognised within whitish laminae 1107 (arrows). D) Photomicrograph (plane light) of bed f, showing the alternation of carbonate and 1108 terrigenous-rich laminae. Note the contractional cracks in the carbonate laminae. E) 1109 Photomicrograph in epifluorescence of bed *f*. Note the stronger fluorescence of the carbonate 1110 lamina (lower part). Filaments (arrows) can be seen in the carbonate lamina. 1111 1112 Fig. 7. MSC beds. A) Photomicrograph (plane light) of bed g. Note the thin lamination and the 1113 black filaments (arrows) underlined by a concentration of pyrite framboids. B) SEM images of a 1114 broken chip of bed f showing globular calcite crystals with a central hollow. C) Photomicrograph 1115 (plane light) of bed g with a detail of a filament. D) Photomicrograph in epifluorescence of the same 1116 filament of Fig. 7C. Note its different epifluorescence with respect to the surrounding matrix and 1117 the abundant pyrite framboids preserved within it. 1118

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).

1126

1127 **Fig. 9.** The hemi-ellipsoidal body: pyrite framboids growing on aragonite fringes.

1128

1129 **Fig. 10.** Genesis of the pre-MSC carbonate-rich beds at the sulphate-methane interface (SMI).

1130 A) During formation of beds *a* and *b*, bacterial sulphate reduction was coupled to anaerobic

1131 oxidation of methane (AOM); methane derived (at least in part) from gas hydrate (GH)

1132 destabilization. B) Dolomite precipitation in beds c and d was induced by bacterial sulphate

1133 reduction alone, fuelled by organic matter oxidation. In these beds the dolomite content is lower

1134 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.

1136

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 sulphatemethane-interface (SMI). For further detail see text.

1142

1143 **Fig. 12.** Formation of laminated carbonate beds.

1144 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

1146 calcite precipitation took place. B) A layer of organic-matter-poor terrigenous sediment buried the

1147 chemotrophic mat, slowing down the activity of sulphate-reducing bacteria. C) After the terrigenous

1148 influx ceased, the activity of sulphate-reducing bacteria resumed, focused in organic-rich layers (a

1149	buried chemotrophic mat in this example). The ensuing calcite (and pyrite) precipitation preserved
1150	the dead bacterial filaments, while a new chemotrophic mat developed on the aggraded sea floor.
1151	Calcite was followed by dolomite precipitation (see Fig. 11). For further detail, see text.
1152	
1153	Table 1. ICP data of pre-MSC (light grey shadow) and MSC (dark grey shadow) sediments; h.m.
1154	homogeneous marl; l.s.: laminated shale: T.C: total carbonate.
1155	
1156	Table 2 . Percentage of dolomite and calcite with respect to the total carbonate (T.C.) content in the
1157	pre-MSC (light grey shadow) and MSC (dark grey shadow) carbonate-rich beds.
1158	
1159	Table 3. Stable isotope data of pre-MSC (light grey shadow) and MSC (dark grey shadow)
1160	sediments. Carbonate-rich beds are in bold. Hem. body: hemi-ellipsoidal body.
1161	
1162	



Dela Pierre et al. Fig. 1



Dela Pierre et al. Fig. 2

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ш 5 m SAF PLG

Dela Pierre et al. Fig. 4

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Dela Pierre et al. Fig. 6





Dela Pierre et al. Fig. 7



Dela Pierre et al. Fig. 8

25 µm

Dela Pierre et al. Fig. 9

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Dela Pierre et al., Fig. 10





Dela Pierre et al., Fig. 11

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Sample		Cycle	T.C. [% on the	Dolomite [% on the	Calcite
			whole rock]	whole rock]	whole rock]
PL7.1	(h.m.)	Pm7	40.7	39.4	1.3
FF7	(bed g)	Pm7	59.0	3.1	55.9
PL6.5	(l.s.)	Pm7	17.2	9.1	8.0
PL6.4	(l.s.)	Pm7	16.7	5.8	10.9
PL6.3	(l.s.)	Pm7	16.7	6.1	10.6
PL6.2	(l.s.)	Pm7	16.4	4.3	12.2
PL6.1	(l.s.)	Pm7	13.2	5.8	7.4
FF6	(bed f)	Pm6	69.1	11.0	58.1
PL 5.4	(l.s.)	Pm6	13.6	12.8	0.7
PL 5.3	(l.s.)	Pm6	23.4	20.1	3.3
PL 5.2	(l.s.)	Pm6	24.9	14.1	10.8
PL 5.1	(l.s.)	Pm5	30.7	25.4	5.2
FF5	(bed e)	Pm5	84.6	16.7	67.9
PL 4.6	(h.m.)	Pm5	30.3	27.1	3.2
PL 4.5	(l.s.)	Pm5	22.4	19.4	3.0
PL 4.4	(l.s.)	Pm5	16.1	13.3	2.8
PL 4.3	(l.s.)	Pm5	17.0	15.5	1.5
PL 4.2	(h.m.)	Pm4	39.1	18.3	20.8
PL 4.1	(h.m.)	Pm4	33.9	29.7	4.2
FF4	(bed d)	Pm4	45.1	37.5	7.6
PL3.5	(h.m.)	Pm4	31.6	12.3	19.3
PL3.4	(l.s.)	Pm4	17.2	5.1	12.1
PL3.3	(l.s.)	Pm4	20.4	4.2	16.3
PL3.2	(h.m.)	Pm3	15.7	5.0	10.7
PL3.1	(bed c)	Pm3	48.2	24.9	23.3
DOL3	(bed c)	Pm3	36.1	20.3	15.9
PL2.5	(h.m.)	Pm3	18.2	7.0	11.2
PL2.4	(l.s.)	Pm3	17.5	4.8	12.8
PL2.3	(h.m.)	Pm2	22.4	8.3	14.1
PL2.1	(h.m.)	Pm2	17.9	12.2	5.7
FF2	(bed b)	Pm2	63.1	42.9	20.2
PL1.6	(h.m.)	Pm2	23.0	20.5	2.5
PL1.5	(l.s.)	Pm2	9.7	2.6	7.2
PL1.4	(h.m.)	Pm2	15.1	11.7	3.5
PL1.3	(h.m.)	Pm1	29.6	12.1	17.5
PL1.2	(h.m.)	Pm1	23.5	10.4	13.1
DOL1	(bed a)	Pm1	76.1	69.9	6.2

Dela Pierre et al. Tab. 1

Sample		Cycle	Dolomite [% vs T.C.]	Calcite [% vs T.C.]
FF7	(bed g)	Pm7	5.2	94.8
FF6	(bed f)	Pm6	15.9	84.1
FF5	(bed e)	Pm5	19.8	80.2
FF4	(bed d)	Pm4	83.3	16.7
PL3.1	(bed c)	Pm3	51.7	48.3
DOL3	(bed c)	Pm3	56.0	44.0
FF2	(bed b)	Pm2	68.0	32.0
DOL1	(bed a)	Pm1	91.9	8.1

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Sample	Cycle	$\delta^{l3}C_{cal}$	$\delta^{l8}O_{cal}$	$\delta^{l^3}C_{dol}$	$\delta^{l8}O_{dol}$
	-	[‰]	[%]	[‰]	[%]
STR 8 (hem. body)	Pm6	-9.2	-7.2		
STR 7 (hem. body)	Pm6	-8.7	-6.9		
STR 4 (hem. body)	Pm6	-8.2	-7.7		
FF 7 (bed g)	Pm7	-7.9	-8.8	-4.0	-5.8
PL 6.4	Pm7	+0.5	-5.4		
PL 6.2	Pm7	-4.7	-6.4		
FF 6 (bed f)	Pm6	-6.8	-7.9	-3.9	-6.1
STR 8 (hem. body)	Pm6	-9.2	-7.2		
STR 7 (hem. body)	Pm6	-8.7	-6.9		
STR 4 (hem. body)	Pm6	-8.2	-7.7		
PL 5.4	Pm6	-0.4	-5.2		
PL 5.2	Pm6	-5.0	-6.0		
FF 5 (bed e)	Pm5	-6.7	-6.5	-5.0	-4.9
PL 4.4	Pm5	+0.3	-3.4		
PL 4.3	Pm5	0.0	-4.1		
FF 4 (bed d)	Pm4	-5.7	-1.2	-5.2	+3.6
PL 3.4	Pm4	+0.5	-5.1		
PL 3.2	Pm3	0.0	-3.3		
FF 3 (bed c)	Pm3	-9.2	-3.9	-4.4	+1.3
PL 2.4	Pm3	-1.0	-3.2		
FF 2 (bed b)	Pm2	-14.5	-1.0	-21.0	+6.9
PL 1.5	Pm2	-0.6	-5.1		
PL 1 .2	Pm1	-6.5	-2.5		
FF 1 (bed a)	Pm1	-16.7	+5.7	-19.8	+7.0

Dela Pierre et al., Tab. 3