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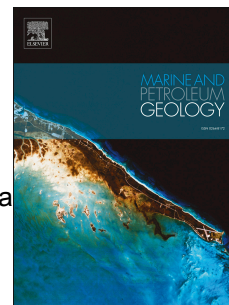
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Onset of the Messinian Salinity Crisis: Sedimentological, petrographical and geochemical characterization of the pre-salt sediments from a new core (Caltanissetta Basin, Sicily).

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ABSTRACT

The present study aims to reconstruct the environmental changes leading to the Messinian Salinity Crisis during the transition from the Tortonian-Messinian marine conditions to the Messinian evaporitic environments. The core 3AGN2S04, recently drilled in the Caltanissetta Basin (Sicily), was analyzed to reveal the petrographic, mineralogical and geochemical characteristics of the late Tortonian – early Messinian pre-salt sediments. In particular, the facies characterization of the carbonates and organic-rich shales of the Calcare di Base (CdB) member allowed to understand its significance in the paleoenvironmental evolution towards salt deposition and to the reconstruct the brecciation processes inside the CdB. The sedimentological and mineralogical analyzes revealed that core 3AGN2S04 consists of the inner shelf facies of the Tripoli Formation passing to the typical carbonate platform facies of the CdB. The local transition between the upper part of the Tripoli Formation and the CdB member indicates that stressful environmental conditions were constant in the central Mediterranean shelf zones during the late Messinian. The CdB carbonates indicate the occurrence of a carbonate platform characterized by peritidal environments rich in different microbial communities and evaporitic deposits, whereas the embedded organic-rich shales

suggest a confined, low energy, anoxic and stratified saline system with high productivity and good preservation of organic matter. A complex set of syndiagenetic brecciation processes, interpreted as in situ brecciation, have profoundly marked the CdB deposits.

1. INTRODUCTION

The Messinian Salinity Crisis (MSC) is one of the most complex and fascinating paleoceanographic events that affected the Mediterranean Basin in the late Miocene, generated by geodynamic and climate triggers. It was described as an ecological crisis leading to the sedimentation of thick layers of halite and other evaporite minerals in a short time interval of ~0.64 Ma (Krijgsman et al., 1999a,b; CIESM, 2008; Manzi et al., 2013). These deposits were initially studied onshore (Selli, 1960), where outcropping Messinian successions are easily accessible and have permitted extensive studies in the last 60 years. Several numbers of Messinian outcrops are located in the Italian peninsula, from north to south respectively, in Piedmont and in the Apennines (e.g. Vai, 1997; Lugli et al., 2007, 2010; Dela Pierre et al., 2011), in Calabria (e.g. Lugli et al., 2007; Roveri et al., 2008; Caruso et al., 2015; Perri et al., 2017; Gindre-Chanu et al., 2020; Borrelli et al., 2020) and in Sicily (e.g. Butler et al., 1995; Hilgen and Krijgsman, 1999; Bellanca et al., 2001; Rouchy and Caruso, 2006; Roveri et al., 2008; Caruso et al., 2015; Perri et al., 2017), which helped to expand knowledge on the MSC in the Central Mediterranean. The Messinian records are almost always incomplete due to the deposition in tectonically active areas during and/or after the MSC or due to erosional processes during sea level lowstands.

In the central Sicilian Caltanissetta Basin, the Messinian record displays the most complete sedimentary successions in uplifted basins (Bellanca et al., 2001). Local Messinian deposits have been commonly considered to have formed in shallow marginal basins (Clauzon et al., 2005). Different hypothesis upon the marginal (Butler et al., 1995; Rouchy and Caruso, 2006; Raad et al., 2020) vs. deep character (Krijgsman et al., 1999a) and lately the intermediate character (200 – 1000 m water depth; see Roveri et al., 2014 for more details) of the Sicilian basins led to the establishment of several chrono-stratigraphic models (e.g. Decima and Wezel 1971; Garcia Veigas et al., 1995; Butler et al., 1995; Rouchy and Caruso 2006; Roveri et al., 2008a; 2014).

The onset of the MSC has already been subject to various studies in the Caltanissetta Basin (Sicily), focusing on the pre-MSC Tripoli Formation commonly considered as the beginning of restricted paleo-environmental conditions. High-resolution cyclo-stratigraphic reconstructions of pre-MSC successions permitted to date the MSC onset at 5.96 ± 0.02 Ma (Krijgsman et al., 1999b) later re-evaluated at 5.97-5.98 Ma by Manzi et al. (2013). The establishment of restricted conditions was gradual and mainly documented by the increased deposition of

diatom-rich sediments (Tripoli's diatomites), the drop in diversity and near complete disappearance of calcareous plankton (Blanc-Valleron et al., 2002), the wide range of stable isotope variations and the precipitation of authigenic calcite, dolomite and/or aragonite (Roveri et al., 2014; Caruso et al., 2015). One peculiarity of the Sicilian succession is the presence of the 'Calcare di Base' (CdB or Basal Limestone) and of the 'Sulfur limestone' (SL) overlying the Tripoli Formation, also outcropping in Calabria. A few theories were proposed to give a paleo-environmental meaning to the origin of these carbonates in terms of genesis, environmental conditions and timing of deposition. According to Caruso et al. (2015), the CdB and the SL were formed diachronously between 6.08 and 5.75 Ma in restricted perched sub-basins during the first stage of the MSC and corresponded to autochthonous deposits of shallow-water carbonate/evaporitic platform domains, dominated by microbial communities (Perri et al., 2017; Gindre-Chanu et al., 2020). They are precession-related deposits (Hilgen and Krijgsman, 1999; Bellanca et al., 2001; Caruso et al., 2015) and mark a transitional period between the marine pre-evaporitic Tripoli deposits and the overlying evaporites in Southern Italy (Sicily and Calabria), reflecting the worsening of marine connections and progressive individualization of the basin(s) (Decima et al., 1988; Rouchy and Caruso, 2006; Caruso et al., 2015; Perri et al., 2017; Gindre-Chanu et al., 2020; Borrelli et al., 2020). Other authors (Roveri et al., 2008a; Manzi et al., 2011) state that not all CdB carbonates mark the MSC onset (stage 1), some formed during the peak of the MSC (stage 2) and that a hiatus of ~400 kyr occurs between the Tripoli Formation and the CdB carbonates.

The present study provides the petrographic, mineralogical and geochemical characteristics of the MSC sediments from the recently drilled core 3AGN2S04 in the Caltanissetta Basin, in order to reconstruct the environmental changes leading to the MSC during the transition from the Tortonian-Messinian marine conditions to the Messinian evaporitic environments.

1. GEOLOGICAL SETTING

1.1. Morpho-structural framework of the Caltanissetta Basin

The Late Oligocene-Early Miocene rifting of the Ligurian/Provençal and the Algerian basins was accompanied by translation and counterclockwise rotation of the Sardinian-Corsican margin (Malinverno and Ryan, 1986; Patacca et al., 1990; Faccenna et al., 2001). This event was coupled during the whole Neogene to the progressive southeastern rollback of the west-dipping Apennines-Calabrian subduction zone beneath Calabria and Sicily, leading to the Mid-Miocene opening of the southern Tyrrhenian Sea (Malinverno and Ryan, 1986; Kastens et al., 1988; Patacca and Scandone, 1989; Gvirtzman and Nur, 1999, 2001; Faccenna et al., 2001; Jolivet et al., 2006; Carminati et al., 2012; Critelli et al., 2017; Conti et al., 2017).

In the Sicilian region, as a consequence of these events and due to the Africa-Europe convergence (Dewey et al., 1989), thrusting and shortening of the Sicilian-Maghrebian chain occurred (Caputo et al., 1970; Malinverno and Ryan, 1986; Patacca et al., 1990; Doglioni, 1990; Facenna et al., 2001) through the formation of the south-migrating front of the Sicilian Fold and Thrust Belt (SFTB) (Pedley and Grasso, 1993).

From the late Miocene, the Caltanissetta Basin was a dynamic foredeep basin joining the Hyblean Foreland to the front of the SFTB, but between the early Pliocene and early Pleistocene, this front advanced about 50 km southwards and south-eastwards (Roure et al., 1990; Catalano et al., 2000; Di Grande and Giandinoto, 2002; Catalano et al., 2013). The Caltanissetta Basin corresponds to the main depozone of the Sicilian-Maghrebian foreland basin system and is currently located between the northern Sicilian Mountains (Sicani and Madonie Mts.) and the southern SFTB (Fig.1a). Its complex morpho-structural framework results from the progressive accretion of thrust sheets (Catalano et al. 2000) and duplex formation (Catalano et al. 1996) from paleogeographic domains of the oceanic realm of Neotethys (Şengör, 1979) and the Africa continental paleo-margin (Bello et al., 2000; Bianchi et al., 1987; Roure et al., 1990). During Neogene times, a series of wedge-top basins were formed characterized by several depocenters separated by intrabasinal highs and related to the Messinian active thrusting synclines (Butler et al., 1995; Catalano et al., 2013).

Fig.1.

1.2. Stratigraphic setting

The Caltanissetta Basin contains one of the best exposed and most complete records of the Messinian evaporites (Bellanca et al., 2001), the so-called “Gessoso-Solfifera Group”, deposited in the wedge-top basins (Butler et al., 1995). It is also the only place in the Mediterranean, together with Calabria, where halite is outcropping. Post-depositional uplift, faulting, folding and erosion have resulted in the removal of up to 0.5 km of the original cover (Decima et al., 1988). The stratigraphic model of the MSC evaporitic sequence has been refined over the years (first established by Decima and Wezel, 1971, 1973; and then Decima et al., 1988; Butler et al., 1995; Garcia-Veigas et al., 1995; Rouchy and Caruso, 2006; Manzi et al., 2013 Roveri et al., 2014) and recognizes two evaporitic units, the Lower Gypsum (LG) and the Upper Gypsum (UG), separated by an intra-Messinian tectonic unconformity (Decima and Wezel, 1971), commonly known as the Messinian Erosional Surface (MES) (Cita and Ryan, 1978). The MES is associated with an angular discordance recording a main phase of tectonic deformation followed by a sedimentary and hydrological change (e.g.

Rouchy and Caruso, 2006) linked to the main Mediterranean drawdown event (e.g. Hsü et al., 1973; Roveri et al., 2008b).

The oldest thrust-top sequence deposited in the wedge-top basins is the late Serravallian – early Tortonian Castellana Sicula Formation, located in the innermost areas of the Caltanissetta Basin (Ruggieri and Torre, 1982; Catalano et al., 2000; Accaino et al., 2011) (Fig.1c). Late Tortonian – early Messinian siliciclastic deposits of the Terravecchia Formation (Flores, 1959; Schmidt Di Friedberg, 1962) unconformably overlie the previous unit (Fig.1c), and their thickness progressively decrease from the inner to outer wedge-top depozones (Gugliotta, 2012). The Terravecchia Formation constitutes a deltaic framework sourced from the rising orogenic belt in the north (Catalano, 1979; Grasso and Pedley, 1988, 1989) and is composed of three major heteropic lithofacies (Catalano et al., 2010): a) the lower one is characterized by reddish polygenic conglomerate (TRVa) with clasts of sandstone, Mesozoic limestone and metamorphic rocks of continental-deltaic environment; b) the intermediate one is represented by grey-blue, weakly cemented, quartz-sands of deltaic-inner shelf environment (TRVb); and, 3) the upper one is constituted by marly and/or silty brown clays (TRVc) of inner-outer shelf environment (Fig.1b and 1c). TRVa and TRVb are deposited in the northernmost Caltanissetta Basin cut by an erosional surface, while TRVc is encountered southernmost towards the main foredeep (Fig.1c). During this time-interval and until the early Messinian, marine fossiliferous marls of the Licata Formation were deposited in the deeper part of the Caltanissetta Basin in more distal areas (Fig.1c). The Terravecchia and the Licata formations are overlain by the early Messinian Tripoli Formation (Fig.1b and 1c) characterized by 49 cycles made of marls, red laminites and diatomitic beds and deposited between 7 to ~6 Ma (Hilgen and Krijgsman, 1999). The diatomitic beds contain diatoms, inshore plant and fish remains (Gaudant et al., 1996). The Tripoli Formation is transitionally passing to the Calcare di Base (CdB) and to the Sulfur Limestones (SL), comprising a wide spectrum of carbonate and evaporitic facies (see 1.3). The CdB and SL are coeval to the Lower Gypsum (or ‘Gessi di Cattolica’; Decima and Wezel, 1971; Rouchy, 1982; Butler et al., 1995; García-Veigas et al., 1995; Rouchy and Caruso, 2006) and according to Caruso et al. (2015), they are laterally equivalent of the Primary Lower Gypsum (PLG). Further, for Butler et al. (1995), Rouchy and Caruso (2006) and Caruso et al. (2015), the CdB passes laterally into halite and K- and Mg-rich potash salts (Fig.1c). On the contrary, other authors (Roveri et al., 2008a,b; Lugli et al., 2010; Manzi et al., 2011) recognized three different types of CdB that are not correlatable as a whole with the PLG (see 1.3 for more details). Southwards an erosional surface cut the topmost part of the CdB and the PLG, respectively.

The UG or ‘Gessi di Pasquasia’ comprises a cyclic succession of thick gypsum and fine clastic deposits (Manzi et al., 2009) in which marine and brackish biota of Paratethyan origin characterizes the silty-marly interbeds (Andreetto et al., 2021). The siliciclastic Arenazzolo

unit overlies the UG. Finally, the whole succession is sealed by the Zanclean marine Trubi Formation, which marks the re-establishment of normal marine conditions, as the result of flooding from the Atlantic Ocean (Cita, 1975; Di Stefano et al., 1999; Rouchy et al., 2001; Pierre et al., 2006; Garcia-Castellanos et al., 2009; Caruso et al., 2020).

1.3. “Calcare di Base” review

The CdB was initially called ‘Siliceous limestone (Calcare siliceo)’ by Mottura (1871) because of its enriched base in silica, in proximity to the diatomites of the uppermost part of Tripoli Formation. Its name has been later reconsidered and the term ‘Calcare di Base’ has since then been used, due to the position of the limestone at the base of the evaporitic succession (Ogniben, 1957, 1963; Decima and Wezel, 1971). The description of the CdB lithologies and the characterization of their depositional environments were made for the first time by Ogniben (1957, 1963). The facies comprises faecal pellets and clotted micrite, identified as a *zone grumeleuse* by Cayeux (1935). Mineralogical and stable isotopes studies revealed the occurrence of aragonite and suggested an evaporitic origin for much of the limestone (Decima et al., 1988). The presence of halite and gypsum molds, laminar algal limestones and syn-sedimentary dissolution breccias confirm the latter interpretation of deposition in hypersaline conditions as suggested by Decima et al. (1988). Decima and Wezel (1971) had already proposed that the evaporitic limestones would represent shallow-water lagoonal sediments. Barthurst (1976) brought to light the diagenetic alteration of the aragonite limestones to calcite and the consequent precipitation of celestine (SrSO_4) and strontianite (SrCO_3), while a combination of meteoric and evaporated waters often associated to bacterial activity (sulfate reduction or methanogenesis) was put forward by McKenzie (1985). Tamajo (1961) reported organic life forms for all or part of this carbonate and assigned these forms rich in organic sources to ‘algal concretions’. Stromatolitic structures showing layered features made up of filamentous bacteria were later described by Oliveri et al. (2010) in the dolomitic beds of the lower CdB member. They were associated to *Beggiatoa*-like sulfur bacteria communities established in shallow hypersaline marine conditions and involved in the precipitation of the CdB limestones (Oliveri et al., 2010). In fact, the CdB has been lately interpreted as ‘peritidal microbial carbonates’ (Perri et al., 2017). The SL, also called ‘sulfurous CdB’ (Decima et al., 1988), was first investigated to aid in determining the origin of the valuable sulfur deposits in Sicily (Dessau et al., 1959, 1962). It is sporadically found overlying the CdB, embedded in the CdB or rests directly on the Tripoli Formation when the CdB is missing. The presence of native sulfur is considered to be bacterial in origin (Dessau et al., 1962). Ziegenbalg et al. (2010) added that the native sulfur and carbonate deposits observed in the Sicilian basins were formed as a consequence of microbial metabolism,

during early diagenesis prior to compaction (syngenetic formation) or during late diagenesis subsequent to compaction (epigenetic formation).

The study of the CdB facies' led to different sedimentary models. Roveri et al. (2008a) and Manzi et al. (2011) proposed three types of CdB (including the SL) mentioned above, with different timing of deposition/diagenesis. Concisely, CdB type 1 consists of sulfur-rich deposits involving bacterial sulfate reduction processes, likely formed in post-Messinian time. CdB type 2 corresponds to laminated dolomitic limestones interbedded with diatomites, sapropels and marls and is considered to be formed in situ during the first stage of the MSC. This CdB type represents the deep-water equivalent of the shallow-water (<200 m) PLG (Roveri et al., 2014). Finally, CdB type 3 is the most common facies and consists of brecciated limestones resulting from gravity flow deposits under evaporative conditions of previously sedimented shallow-marine evaporitic carbonates. This CdB type could correspond to the brecciated limestones previously described by Mezzadri (1962), that he associated to olistostrome-type deposits. Hence, CdB type 3 corresponds to the Resedimented Lower Gypsum (RLG), formed after the PLG. For these authors, together with CdB Type 1 (or SL), CdB type 3 is stratigraphically located upon the MES (post 5.60 to 5.55Ma) (Manzi et al., 2011). This scenario is not in accordance with the sedimentary model proposed by Caruso et al. (2015) and Perri et al. (2017), which attributed three facies of carbonates to different paleoenvironment settings. According to the latter authors, the first facies is a 'microbial boundstone' consisting of stromatolitic laminated limestones with filamentous micrite, peloids and pseudomorphs after evaporite crystals, formed in hypersaline shallow-marine conditions. The second CdB facies is a 'marlstone' intercalated with microbial boundstones reflecting more humid climate and finally, the third facies represents 'evaporites' characterized by microbial boundstones typified by gypsum and formed during marine hypersaline and evaporitic conditions. According to this model, the MES is located upon the CdB marking an important environmental change. Recently, Borelli et al. (2020) described ten facies associations (FAs). Some of the FAs were assimilated to those described by the previous authors, in particular the 'microbial boundstones' (FA-1), the 'marlstones' (FA-2) and the 'monogenic breccias' (FA-3). However, Borelli et al. (2020) also described 'carbonate megabreccia' (FA-8) consisting of angular to sub-angular blocks and boulders, made up of FA-1 fabrics mixed with reworked pebbles and cobbles, re-sedimented in the outer slope of the carbonate platform by gravity flows, coeval to the PLG and before the MES (5.9 – 5.6 Ma). Finally, Gindre-Chanu et al. (2020) established the Calcareous Evaporitic unit (CE) in which the CdB 1 Fm is described as a microbialitic limestone associated with shallow-water evaporites sometimes interlayered with autobreccias in shallow-water platform setting or with a mud lime matrix microbial carbonate clasts and finer debrites and turbidites in slope environment.

2. MATERIALS AND METHODS

2.1. Description of core 3AGN2S04

The core 3AGN2S04 is located in the northern part of the Caltanissetta Basin, 3 km south of the town of Marianopoli (Fig. 1b), along the SP42 road coming from the town of San Cataldo (37°35'12.6"N 13°55'31.4"E). The core is 270 m long. Depths are shown in meters from the ground surface. In this study, we focus on the core depths ranging from 110 to 270 m, in which have been recognized from bottom to top, the Terravecchia Formation (270 to 220 m), the Tripoli Formation (220 to 185 m) and the Calcare di Base (CdB) member (185 to 110 m) (Fig.2). The Terravecchia Formation records silty and sandy claystones, while the Tripoli Formation is composed by diatomitic marlstones. Thin beds of carbonate (T1, T2, T3 and T4) appear in the upper part of the Tripoli Formation and become thicker upwards. A ten meters-thick bed of marlstones rich in organic matter alternating with thin (mm- to cm-thick) carbonates marks the end of the Tripoli Formation. On top, 9 massive carbonate beds (C1 to C9) often rich in organic matter define the 'CdB' member. Their thickness varies between 2 and 17 m. The massive CdB beds are separated by intercalations ranging between 50 cm to 5 m-thick of organic matter rich shales. The CdB member is capped by a dark-coloured layer.

2.2. Petrography

A macroscopic description was performed in terms of lithology, textures, colour, fluid conduits and fossil content whereas the microfacies characterization was realized from 19 thin-sections of the CdB member investigated using conventional petrographic methods. Thin sections were prepared by the LABSTONE laboratory (Palermo). Moreover, 3 samples of CdB were also analyzed using a scanning electron microscope (SEM PHENOM PROX) at the ATEN (Advanced Technologies Network) Center of the University of Palermo.

2.3. Mineralogy and carbonate content

A semi-quantitative mineral phase analysis of 50 powdered samples selected along the core was conducted at the ATEN Center of the University of Palermo, by means of X-ray diffraction (XRD) methods using Bruker D8 advance diffractometer. The Diffrac.Eva V3 acquisition program permitted to identify the peaks of each mineral. The carbonate content of each sample was also measured on 100 mg of powdered sediment using a manocalcimeter Mélières (MCM) apparatus, derived from the « carbonate bomb » technique first described by Müller and Gastner (1971). The total carbonate content (in weight %) was calculated from CO₂ volume evolved from the reaction of 100 mg of finely crushed sediment with 8 N HCl. Semi-quantitative calcite, aragonite and dolomite percentages are given, based on the

surface of the main peak of each mineral corrected by arbitrary factors (I/I_{cor} values given in the ICCD database) and on the MCM value for absolute wt%.

2.4. Oxygen and carbon stable isotopic compositions

The oxygen ($\delta^{18}\text{O}$) and carbon ($\delta^{13}\text{C}$) stable isotopic composition of the calcite/aragonite and dolomite were determined on 50 powdered samples at the DiSTeM of the University of Palermo. Due to the often micro-brecciated texture of the carbonate samples, sampled powder corresponds to a melange of matrix and carbonate fragments. However, areas of high carbonate cementation and veins were avoided. The CO_2 was obtained by the classical $\text{H}_3\text{PO}_4 - \text{CaCO}_3$ reaction method by an automated Carbonate Preparation Device (Thermo Scientific GasBench II). Considering the different reaction rates of calcite/aragonite and dolomite, analyzes were performed following the methods proposed by Al-Aasm et al. (1990). Isotope composition of calcite/aragonite was estimated on CO_2 collected after 3 hours of reaction at 25°C ; immediately upon the measure, the released CO_2 was discarded. Temperature was afterwards increased to 50°C and CO_2 produced by the reaction after 24 hours was used to determine the isotopic composition of the dolomite. The carbonate isotopic compositions ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) were measured by Thermo Scientific Delta V Advantage continuous flow isotope ratio mass spectrometer. Results are reported with typical delta (δ) notation relative to the Vienna Pee Dee Belemnite (V-PDB) standard. Every 10 samples, an internal laboratory standard (Carrara Marble with $\delta^{18}\text{O}_{\text{V-PDB}} = -2.43\text{‰}$ and $\delta^{13}\text{C}_{\text{V-PDB}} = 2.43\text{‰}$) was run, the NBS19 international standard ($\delta^{18}\text{O}_{\text{V-PDB}} = -2.20\text{‰}$ and $\delta^{13}\text{C}_{\text{V-PDB}} = 1.95\text{‰}$) was also measured every 20 samples. The relative precision for duplicate analyzes improved to 0.1‰ for carbon and oxygen.

2.5. Rock-Eval measurements

A quantitative and qualitative study of the organic matter content from 50 powdered samples was conducted using a Rock-Eval 6 Turbo apparatus (Vinci Technologies) at the Institut des Sciences de la Terre de Paris (UMR7193/Sorbonne Université). The Total Organic Carbon (TOC) was obtained by means of Rock-Eval thermal analysis, on around 65 mg (30mg when rich in organic matter) of powdered samples, following the method described by Lafargue et al. (1998) and Behar et al. (2001). TOC content is expressed as weight percentage (wt%), with precision of $\pm 0.1\%$. The type of kerogen was estimated using the Hydrogen Index (HI, in mg HC/g of TOC) and Oxygen Index (OI in mg CO_2 /g of TOC) standard parameters, whereas the thermal maturation of the organic matter was assessed using the T_{max} parameter expressed in $^\circ\text{C}$.

2.6. Biostratigraphy

A detailed biostratigraphic analysis of the planktonic foraminifera was carried out in order to pinpoint accurately the position of bio-events, following the biostratigraphic scheme proposed by Lirer et al. (2019). They have been analyzed in a qualitative way to check the position of events. Fifty grams of dried sediment were washed through a 63 μm sieve and the residual fraction was oven-dried at 50 °C. The identification of the foraminiferal bio-events has been based on a semi-quantitative study of the fraction greater than 63 μm following the biostratigraphic scheme proposed by Lirer et al. (2019). For the present study, 97 samples have been analysed, respectively from bottom to top, 35 in the Terravecchia Formation, 34 in the Tripoli Formation and 28 in the Calcare di Base member. The micro- and macro-paleontological description will be mentioned together with the lithological and facies description for the Terravecchia and Tripoli formations, while samples of the CdB member were sterile and description will be solely focused on facies.

3. RESULTS

3.1. Mineralogy and stable isotopes geochemistry

The lithological variations of core 3AGN2S04 are evidenced by wide mineralogical and $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ fluctuations (Fig.3).

Fig.3.

Terravecchia Formation (270 to 220 m)

The Terravecchia grey/brownish clay-siltstones are primarily composed of quartz (30 to 55%) (Fig.3). Clay minerals including illite and kaolinite, feldspar minerals (mainly albite) and micas (mostly muscovite) are also abundant (Fig.3 and suppl. table). The carbonate content is low (11 to 17%), calcite being the main carbonate mineral (mean value of 10%), followed by dolomite (mean value of 3%) (Fig.3). Pyrite was identified in low amount (< 1%) (suppl. table). Calcite in limestones-claystones is characterized by $\delta^{18}\text{O}$ values ranging from -3.90 to -1.25‰ and $\delta^{13}\text{C}$ values between -3.17 and -1.65‰ (Fig.3).

Tripoli Formation (220 to 185 m)

The Tripoli Formation starts with a strong change both in the mineralogical and stable isotopes compositions. Quartz progressively decreases, while carbonate contents increase

(Fig.3). Among the carbonate mineral, aragonite (> 88%) and dolomite (> 84%) are the most abundant, whilst calcite reaches peaks of 50%. At 210 m appear the carbonate beds T1, T2, T3 and T4 in the marls. The first thin carbonate bed T1 is composed of 29% of aragonite, 24% of dolomite and 15% of calcite. The carbonate beds T2 and T3 are thicker and show higher contents of aragonite, respectively 88% and 83% (Fig.3). The thin carbonate bed T4 is a dolostone, with a peak of dolomite reaching 83% (Fig.3). The carbonate beds have low detrital components (<10%), and celestine was identified (Fig.3 and suppl. table). Stable isotope composition of calcite and aragonite in beds T1, T2, T3 and T4 shows a range of values between +4.18 and +6.59‰ for $\delta^{18}\text{O}$ and between -1.98 and 1.85‰ for $\delta^{13}\text{C}$. The isotopic composition of dolomite in these four beds is characterized by $\delta^{18}\text{O}$ values ranging from +7.26 to +8.39‰ and $\delta^{13}\text{C}$ values between -0.13 and +2.70‰.

In the grey marls of the Tripoli Formation, calcite is the main carbonate fraction (up to 55%), while quartz ranges between 5 to 30%. The isotopic composition of calcite and aragonite is characterized by values between -0.33 and +5.43‰ for $\delta^{18}\text{O}$ and between -3.06 and 1.96‰ for $\delta^{13}\text{C}$. Stable isotope composition of dolomite shows a range of $\delta^{18}\text{O}$ values ranging from +1.30 to +6.38‰ and $\delta^{13}\text{C}$ values between -6.83 and +1.89‰.

Calcare di Base (185 to 110 m)

In the Calcare di Base member, two units were distinguished.

Unit 1 (185 - 160 m). The carbonate beds C1 and C2 show high values of aragonite, respectively 67.4% and 51.8% (Fig.3). Celestine (around 10%) and small quantities of gypsum (< 5%) are also present in the carbonate beds C1 and C2 (Fig.3 and suppl. table). Stable isotope composition of calcite and aragonite in beds C1 and C2 fluctuates between +3.48 and +3.89‰ for $\delta^{18}\text{O}$ and between -3.09 and -0.85‰ for $\delta^{13}\text{C}$. The isotopic composition of dolomite in bed C2 is characterized by $\delta^{18}\text{O}$ values, ranging from +3.66 to +6.44‰ and $\delta^{13}\text{C}$ values between -2.15 and +0.19‰.

The shales surrounding beds C1 and C2 show high contents of dolomite (up to 85%) (Fig.3). In these intervals, quartz fluctuates but is present in great amounts (from 12 up to 59%). Pyrite and celestine are more significant than in the Tripoli Formation, while gypsum is absent or < 0.5% (Fig.3 and suppl. table). Stable isotope composition of calcite and aragonite between beds C1/C2 and C2/C3 fluctuates between +3.32 and +7.69‰ for $\delta^{18}\text{O}$ and between -8.86 and -1.72‰ for $\delta^{13}\text{C}$. The isotopic composition of dolomite is characterized by $\delta^{18}\text{O}$ values, ranging from +4.04 to +7.65‰ and $\delta^{13}\text{C}$ values between -7.21 and -0.34‰.

Unit 2 (160 - 110 m). Sharp changes occur in the mineral content at the bottom of bed C3. The carbonate fractions show a change of trend. The massive carbonate beds contain high

to very high amounts of calcite and magnesian calcite: an average of 87% in C3, 86% in C6, 67% in C7, 51% in C8 and 79% in C9. The dolomite and aragonite fractions remain stable in the carbonate beds, both with an average of 10%. Beds C4 and C5 show high contents of aragonite ranging between 30 and 47%, while calcite ranges between 15 and 19%. Quartz, feldspar and clay minerals are scarce to absent in the carbonate beds. The massive carbonate beds may comprise high amounts of celestine, reaching a value of up to 45% in bed C4 (Fig.3 and suppl. table). Pyrite is also present, while low amounts of gypsum (<5%) are sparsely present in the carbonate beds (Fig.3 and suppl. table). Stable isotope composition in the carbonate beds C3, C6, C7, C8 and C9 rich in calcite shows $\delta^{18}\text{O}$ values between -2.02 and +0.90‰ for and $\delta^{13}\text{C}$ values between -2.51 and +1.97‰. The carbonate beds C4 and C5, rich in aragonite, are characterized by values of $\delta^{18}\text{O}$, ranging from +2.72 to +3.26‰ and $\delta^{13}\text{C}$ values between -2.68 to -2.29‰.

The shale intercalations show high contents of aragonite, reaching 70% and 85% (Fig.3 and suppl. table). The dolomite fraction remains stable in shales, with an average of 10%, except in the shales located at 123 m in which dolomite (35%) is the predominant carbonate fraction. Shale intervals show low quartz contents reaching a maximum of 5% and low content of clay and feldspar minerals. Pyrite and celestine are present in shale beds and show both lower values than in Unit 1 (suppl. table). Stable isotope composition of calcite and aragonite in the shale beds shows a range of values between +2.04 and +3.64‰ for $\delta^{18}\text{O}$ and between -4.55 and -2.29‰ for $\delta^{13}\text{C}$. The isotopic composition of dolomite in the shale beds is characterized by $\delta^{18}\text{O}$ values, ranging from +2.76 to +5.18‰ and $\delta^{13}\text{C}$ values between -4.34 to -0.60‰.

The upper part of bed C9 becomes finely brecciated and is predominantly aragonitic (mean value of 57%), associated with dolomite and calcite (mean value of <10% for both) for which the composition of calcite and aragonite is of -1.69‰ for $\delta^{18}\text{O}$ and -5.50‰ for $\delta^{13}\text{C}$. The isotopic signature of dolomite is of +2.95‰ for $\delta^{18}\text{O}$ and -1.25‰ for $\delta^{13}\text{C}$.

3.2. Organic carbon characterization

3.2.1. Organic carbon contents and thermal maturity

The Total Organic Carbon (TOC) contents also follow the lithological variations. In the Terravecchia Formation, the TOC contents are low (<1%; Fig.3), with a mean value of 0.74%. From the Tripoli Formation, the TOC contents sharply increase. In the carbonate beds T1, T2, T3 and T4, TOC contents are low (mean value of 0.55%), while marls show high TOC values (> 1%), with values up to 2.84% between carbonate beds T2 and T3. In the CdB member, TOC contents show similar trends as for the Tripoli Formation with low TOC contents in the carbonate beds (<1%) and high TOC contents (mean values of 2.86%) in

shales, ranging from 1.17 to 5.06%. The upper part of bed C9 becomes finely brecciated and a significant amount of organic matter (TOC contents passing from 0.54% to 1.83%) characterizes an important lithological change.

Regarding the thermal maturity of the organic matter, all $T_{\max}$ values are below 435°C, indicating that the samples are immature with respect to the petroleum generation.

3.2.2. Origin and preservation of the organic matter

The Hydrogen Index (HI) shows values ranging from 74 to 942 mg HC/g TOC. In the Terravecchia Formation, HI is very low (mean value of 95 mg HC/g TOC). In the Tripoli Formation, HI increases (mean value of 303 mg HC/g TOC), while in the CdB member, HI values are high (mean value of 676 mg HC/g TOC) and decrease in the upper CdB beds (mean value of 381 mg HC/g TOC). Plotting HI vs. OI (Oxygen Index), samples cover all the areas of the pseudo van Krevelen diagram (after Espitalié et al., 1985-6) and three types of kerogen were identified (Filho and Gonçalves, 2017). The Terravecchia Formation samples are located in the Type III area (Fig.4) usually related to higher plant biomass. The Tripoli Formation samples are located in various areas of the diagram, located between the Type III area and the Type II area, usually associated to marine phytoplankton organic matter. The CdB member samples are located between the Type II area and the Type I, the latter related to algal organic matter reworked by bacteria.

Fig.5

3.3. Facies

Eight facies (FA-1 to 8) have been defined in core 3AGN2S04 (Fig.2). The key elements used to distinguish these facies are (1) lithology, including the main types of sediment and their colour; (2) sedimentary structures, including their shape, texture, lamination/stratification; (3) paleontological composition, including micro- and macrofossils; (4) mineralogical composition and petrographic features, including terrigenous particles and authigenic crystals, microbial structures, brecciation features.

Claystones (FA-1 and FA-2) of the Terravecchia Fm

FA-1 corresponds to grey clays or siltstones, with occasional mm- to cm-thick sand layers embedded in the claystones and evolving to a grey-brownish clayey sandy siltstone that

characterizes FA-2 (Fig.2). Terrigenous minerals (mica, feldspar and quartz) are abundant in FA-1 and FA-2 (suppl. Table). Rare shells of Cardid molluscs have been found. Planktic assemblages are characterized by common individuals of *Globigerinoides obliquus*, *G. quadrilobatus*, *Globigerina bulloides* and *Neogloboquadrina acostaensis*. In this lithology, keeled globorotalids and *Globorotalia suterae* were not found, with the exception of two influxes of conical globorotalids belonging to *Globorotalia miotumida* group recognized at 243.8 m and 237.8 m. Benthic foraminifera of well oxygenated conditions, typical of shelf domain are present, as well as abundant species of deltaic environment (i.e. *Ammonia*, *Elphidium*, *Nonion*, *Brizalina*, *Cassidulina*).

Diatomaceous marlstones (FA-3) of the Tripoli Fm

In FA-3, grey and silty marls are locally associated to laminated marly limestones and sparse mm to cm-thick marly layers rich in organic matter (Fig.2). Millimetric-thick, diatomitic layers also occur in the diatomaceous marlstones, in which pennate diatoms (*Thalassionema nitzschoides* and *Thalassiotrix* spp.) have been identified. The foraminiferal assemblage is characterized by few planktonic species as *Turborotalita quinqueloba*, *Turborotalita multiloba*, *Neogloboquadrina acostaensis* and *Globigerina bulloides*, while Globorotalids are not present in this interval. More precisely, four influxes of *T. multiloba* occur at 213.38 m, 212.24 m, 208.32m and 203.22 m, respectively. In some particular layers, benthic foraminifera of hypoxic conditions (*Bulimina echinata* and *Bulimina aculeata*) are present. An oligotypic assemblage of pteropods (dominated by the genus *Creseis*) rarely occurs between 206.70 and 206.80m (Fig.5a). When marls are rich in organic matter, the latter microfauna disappear. In thin section, this facies consists of marls with dispersed detrital minerals (quartz, muscovite, glauconite) and authigenic pyrite (Fig.5b, 5c and 5d).

Fig.5

FA-4. The 'fenestral microbial boundstone' is a boundstone characterized by mm-thick planar or low-angled laminations (Fig.2). In thin section, these boundstones are characterized by fenestrae filled with sparry calcite (Fig.6a). The matrix mostly consists of clotted to aphanitic micrite with peloids and bacterial filaments, and with sparsely framboids of pyrite (Fig.6b). Fish remains were also observed (Fig.6c and 6d).

Fig.6

Shales (FA-5) and deformed shales (FA-6) of the Calcare di Base

FA-5 corresponds to 'shales' (Fig.2). They have also been described by Borelli et al. (2020) as 'marlstones' (FA-2). They comprise silt-sized clays, commonly laminated with planar or low-angle bounding surfaces. Organic matter is commonly abundant and clays are dark grey to black coloured with a strong hydrogen sulphide (H₂S) gas smell. In thin section, shale interbeds have a silty-clay matrix and are characterized by thin-bedded reddish to grey and/or black argillaceous laminites rich in pyrite (FA-5; Fig.7a). Lamination is planar and is also evidenced by kerogen veins (Fig.7b). Terrigenous detrital minerals are present and correspond mainly to grains of silt-sized quartz and mica, feldspar and clay (suppl. table). Shales are barren of fossils.

Some of the shale interbeds are deformed (FA-6; Fig.2). The nature and the texture of the rock is the same with FA-5, but instead of a thin-bedded structure, brecciated morphologies are observed. In thin section, the lamination is absent or deformed (Fig.7c) and beds are characterized by a chaotic facies (Fig.7d), in which reworked foraminifera occur (noted F in Fig.7e). Kerogen veins are also present (Fig.7d and 7e). Laminae are bending upwards and contractional cracks are observed with a width of 10 to 20 µm thick and micro-fractures (Fig. 7c). Irregular micro- to centrimetric peloidal carbonate fragments corresponding to facies FA-7 (see below) are dispersed within this facies (Fig.7e and 7f). The latter have already been described by Perri et al. (2017) as nodules and micro-nodules of carbonates surrounded by authigenic clay.

Fig.7

Carbonates (FA-7 to 8) of the Calcare di Base member

Two main facies illustrate the variety and complexity of the CdB beds, regarding their lithology and sedimentary structures.

FA-7. The 'microbial boundstone' (C1; Fig.2) is a whitish fine-grained carbonate rock with preserved biogenic textures. In thin section, the facies is commonly dominated by a multitude of micritic rounded, rod-shaped or filamentous morphologies, sometimes taking a yellowish color, and by aphanitic to clotted peloidal micrite (respectively noted B and P, in Fig.8a), which interspace is filled by a microsparitic calcite and celestine cement (Fig.8b). SEM observation confirms that this lithofacies is mainly composed of rhombic crystals of calcite and, in smaller quantities, of celestine (Fig. 8c). The peloidal and filamental micritic features are sometimes localized with the shape of a wide range of patterns, including angular morphologies (Fig.8a). They correspond to pseudomorphs after evaporite crystals, mainly reminiscent of cubic to prismatic crystals of halite. The pseudomorphs are only observed in thin section.

Fig.8

FA-8. This facies includes all the brecciated boundstones, however due to the different petrographic and geochemical features they have been subdivided in four subfacies indicated as 8a, 8b, 8c and 8d.

FA-8a. The 'vuggy brecciated boundstone' (C3 and C6; Fig.2) is commonly known as 'vuggy limestone' (Decima et al., 1988). All the components are the same as in the 'microbial boundstone' (FA-7). However, this boundstone is characterized by cm-thick vugs, which are irregular in shape and may be open to partially open. Native sulfur occurs as disseminated mm-thick nodules. In thin section, filamentous and peloidal morphologies dominate the facies. Filaments are occasionally folded and can reach a length of 2 mm (Fig.9a). Stromatolitic features are also present, characterized by lenticular to wavy laminae in which filaments are observed (Fig.9b). The latter biolamination often surrounds pseudomorphs (Fig.9b and 9c). Cubic, prismatic or twinned arrow-head pseudomorphs are filled by secondary mineral mostly celestine and calcite (Fig.9c and 9d). These pseudomorphs were originally halite or gypsum crystals, hence their respective outlines, and are known as 'evaporite pseudomorphs'.

Fig.9

FA-8b. The 'shale-filled brecciated boundstone' consists of mm to cm-thick carbonate fragments dispersed in a fine and dark-colored mud matrix. Clasts are poorly sorted and they are mainly composed of FA-7, generally having an angular shape. Breccia unit mostly occur with a thickness of 1 meter, intercalated in the massive carbonate beds (C1, C3 and C9; Fig.2). In thin section, this facies is differentiated from FA-8a by the presence of branching cavities that are randomly distributed and filled by dark-colored and chaotic microbial fragments in a sparitic calcite cement (Fig.10a and 10b).

FA-8c. The 'brecciated boundstone' (C2, C4, C5, C7 and C8; Fig.2) is composed of massive beds of white or pale tan to grey-colored breccias. They are mostly characterized by cm-thick angular fragments that are dispersed in a silty dark-coloured matrix with a strong smell of H₂S. In thin section, fitted boundstone fragments and a silty matrix consisting of FA-5 are both peculiarities of this facies (Fig.11a). The fitted fragments consist of a lumpy limestone facies filled by peloidal, rod-shaped and filamentous micrite (Fig.11b and 11c) and occasionally, by millimetric halite voids and/or halite pseudomorphs (Fig.11c). Pyrite is

dispersed in the matrix and locally in the lumpy fragments, but is also concentrated along stylolites probably with residual clays (Fig.11d).

Fig.11

FA-8d. The 'recrystallized brecciated boundstone' (C9; Fig.2) is represented by the same macroscopic and microscopic characteristics with FA-8c, mainly consisting of microbial peloids. In thin section, what differentiates these two sub-facies is the highly recrystallized facies of FA-8d. This high recrystallization makes difficult to distinguish the boundstone fragments from the matrix, the latter characterized by less sparitic calcite and a high quantity of pyrite (Fig.11e and 11f).

5. DISCUSSION

5.1. Stratigraphy

The lithological and petrographical descriptions permitted to identify part of the classical evaporitic succession of the 'Gessoso-Solfifera' Group. From bottom to top, core 3AGN2S04 consists of the upper Tortonian-lower Messinian Terravecchia Formation, followed by the Messinian Tripoli Formation that precedes the Messinian Salinity Crisis (MSC), and of the Calcare di Base (CdB) member representing the MSC onset *sensu* Rouchy and Caruso (2006). The observation of fossils allowed to validate the lithostratigraphic units of the core and to define biostratigraphic units. A few reliable biostratigraphic events were recognized and confirmed the dated Mediterranean planktonic foraminiferal biostratigraphic zonation of the late Tortonian - Messinian MSC onset (Hilgen and Krijgsman, 1999; Hüsing et al., 2009; Krijgsman et al., 1999; Sierro et al., 2001; Blanc-Valleron et al., 2002). In the Terravecchia Formation, planktonic assemblages belong to MMi12 biozone, while the two influxes of *Globorotalia miotumida* group belong to the top of biozone MMi12a (Lirer et al., 2019) both late Tortonian in age. In the Tripoli Formation, four *T. multiloba* influxes belong to the MMi13d biozone *sensu* Lirer et al. (2019) and correspond to the Tripoli cycles 40 to 46 (Hilgen and Krijgsman, 1999; Blanc-Valleron et al., 2002). The observation of foraminiferal assemblages together with diatom assemblages permitted to verify the boundary between the Terravecchia and the Tripoli formations. A stratigraphic gap seems to separate the two formations, confirmed by the absence of large part of MMi13 biozone. In fact, only part of MMi13b biozone is present. Finally, the CdB corresponds to the Non Distinctive zone (Lirer et al., 2019).

5.2. Evolution of the depositional conditions

5.2.1. From Terravecchia to Tripoli

The mineralogical composition of FA-1 and FA-2 of the lowermost section of core 3AGN2S04 is strictly terrigenous and corresponds to the Tortonian Terravecchia Formation. More specifically, the facies correspond to the members TRVb and TRVc. The terrigenous provenance of the Terravecchia Formation is supported by the organic carbon origin related to higher plant biomass (type III kerogen; Fig.5). The Terravecchia Formation corresponds to "postorogenic" deposits and is interpreted as the product of the dismantling of the northern Maghrebian-Sicilian mountain belt molasse into the 'deltas' (Catalano, 1979; Gugliotta and Gasparo-Morticelli, 2012; Henriquet et al., 2020) and deposited in the perched wedge-top basins of the Caltanissetta Basin during a period of marine transgression (Butler, 1995). The location of the studied core south of the Maghrebian chain in the northern Caltanissetta Basin (Fig.1b) allow to suggest that the terrigenous deposits here observed are the result of the erosion of emerged parts of the orogenic prism, most likely transported from these mountains in a setting corresponding to a river-dominated deltaic environment.

Fig.12

The lithology, mineralogy, stable isotope and organic carbon composition mark a change around 220 m that corresponds to the passage between Terravecchia and Tripoli formations. At this depth, the lithology changes to diatomaceous marlstones (FA-3) corresponding to the Tripoli Formation characterized by cyclic repetition of marls, marls rich in organic matter and the scarce presence of thin layers of white diatomites. Cyclicity is not as clear as in the Tripoli Formation of Falconara/Giblicemi or Serra Pirciata sections located in the southern area of the Caltanissetta Basin, but similar lithologies characterized by diatomitic marls poor in diatoms were described in Marianopoli and Torrente Vaccarizzo sections located in the northern Caltanissetta Basin (Bellanca et al., 2001), respectively located at 1 km north and 12 km east from core 3AGN2S04. Organic carbon characterization permitted to identify abundant detrital inputs (Type III kerogen) corresponding to FA-1 in the diatomaceous marlstones (FA-3) of the studied core, and may derive from the still ongoing dismantling of the northern Maghrebian-Sicilian mountain belt. The latter inshore plant input (Type III kerogen) defines the majority of FA-3 organic material, but other main sources of organic matter in the Tripoli Formation are supplied by fish remains and diatom assemblages, the latter dominated by the planktonic species *Thalassionema nitzschoides* and *Thalassiotrix* spp. typified by a high productive marine environment (Type II kerogen). The rarity of diatoms and the type of organic matter between Types II and III kerogen suggest that there is also a contribution of terrestrial organic matter linked to runoff in these levels. That organic

matter may have entered the basin during its shoaling or during periodic phases of enhanced riverine runoff carrying terrestrial plants and nutrients stimulating the productivity of the waters. The increase of organic material buried in sediments implies eutrophication and, sensitive to oxygen availability or to changes in the chemical composition of waters (high alkalinity that occurs during intense photosynthesis), faunal diversity is strongly reduced at 215 m of core 3AGN2S04. Marine diatom species with a predominance of the *T. nitzschoides* have already been described in the Tripoli Formation of Falconara/Giblisce mi section, but also in the western Lorca Basin (Spain) and the eastern Pissouri section (Cyprus) (Saint Martin et al., 2001; Pestrea et al., 2002). These planktonic species have persisted in the upper part of the Tripoli preceding the major evaporitic episode (gypsum or CdB deposits), while marine microfauna have entirely disappeared, revealing the ability of diatoms to mark brief marine influences in a restricted environment (Pestrea et al., 2002). The worsening of the environmental conditions is testified by the progressive impoverishment of the microflora and microfaunal assemblages and by the presence of pyrite associated to dolomite which indicates the beginning of the reduction of sulfates. Progressively, conditions became even more saline and precipitation of aragonite began. However, conditions remain fluctuating in this interval.

5.2.2. Pre-MSC beds – towards evaporitic conditions

The first signs of evaporitic conditions occur in the upper part of the Tripoli Formation, where the carbonate beds T1, T2, T3 and T4 (FA-4) appear within the organic-rich diatomaceous marlstones (FA-3). The carbonate beds mainly consist of thin beds of aragonite (T1, T2 and T3) and dolomite (T4). The high $\delta^{18}\text{O}$ values of the aragonite and dolomite beds ($+4.18\text{‰}$ $<\delta^{18}\text{O}_{\text{ar}}< +6.59\text{‰}$ and $+6.18\text{‰}$ $<\delta^{18}\text{O}_{\text{dol}}< +8.4\text{‰}$; Fig.12) document evaporative conditions. The grey marls surrounding the thin carbonate beds are characterized by the association of calcite and dolomite, both showing positive but lower $\delta^{18}\text{O}$ values ($+0.19\text{‰}$ $<\delta^{18}\text{O}_{\text{cal}}< +3.16\text{‰}$ and $+2.90\text{‰}$ $<\delta^{18}\text{O}_{\text{dol}}< +6.38\text{‰}$) probably related to dilution from normal marine influxes. A similar pattern has been described in several sections of the Caltanissetta Basin at Falconara, Giblisce mi, Marianopoli, Serra Pirciata and Torrente Vaccarizzo (Bellanca et al., 2001; Blanc-Valleron et al., 2002; Caruso et al., 2015) exhibiting heavier oxygen isotopic values in the carbonate beds at the top of the Tripoli Formation.

In bed T1, the presence of pteropods belonging to *Creseis*, euryhaline marine gastropods (Almogi-Labin and Hembelen, 1991), may explain the high amount of aragonite in form of biogenic shells. Nevertheless, mostly in the overlying marls and in T2 and T3 levels, aragonite precipitation related to organic matter degradation and bacterial activity can be invoked as suggested by the presence of microbial peloids and pyrite in form of scattered crystals and framboids. Many authors have already investigated the aragonite precipitation in

microbial mats associating it to the degradation of extracellular and cellular organic matter by microbial communities, as sulfur-reducing bacteria (SRB; Reid et al., 2000; Schneider et al., 2013; Pace et al., 2016; Dunham et al., 2020). Among them, Pace et al. (2016) studied microbial mats from the Great Salt Lake (Utah, United States) and found that aragonite precipitation took place in photosynthetic microbial mats, due to localized increase in alkalinity. Dunham et al. (2020) improved this model documenting that the increase in alkalinity was mainly induced by photosynthetic CO₂ consumption rather than the activity of SRBs. Where (or when) the activities of fermentative bacteria created a slightly acidic microenvironment, aragonite precipitation was becoming thermodynamically unfavorable. In these conditions, the activity of SRBs promotes the authigenic precipitation of pyrite and, of a very high Mg-Calcite and protodolomite. Actually, a commonly proposed model for dolomite formation in brines rich in MgSO₄ involves depletion of SO₄²⁻ by SRB making Mg²⁺ available for incorporation into carbonate lattice (Baker and Kastner, 1981; Vasconcelos and Mckenzie, 1997; Castanier et al., 1999; Warthmann et al., 2000; Bontognali et al., 2010).

Besides aragonite, in core 3AGN2S04 beds T1, T2 and T3 are characterized by a fenestral microbial boundstone (FA-4). They also show lower TOC (0.3% <TOC< 0.6%) and higher δ¹³C values (in both aragonite and dolomite), with respect to most of the surrounding marls (FA-3) (Figs.3 and 12). These data draw a scenario in which the preservation of fenestral fabrics accounts for an early lithification that well-fit with an early aragonite precipitation in a shallow-water photosynthetic microbial mats and that tends to become evaporitic, as testified by oxygen isotope ratios. Lower organic carbon content is compatible with decomposition of organic matter in early lithified sediment which is, in turn, responsible for the fenestrae textures. The ¹²C-enriched fluids related to this decomposition migrate upwards in the overlying marls (FA-3) leaving a positive isotope signal in the fenestral carbonate. During a subsequent diagenetic phase, fenestral pores of FA-4 were filled by sparry calcite (Fig.6b). On the other side, FA-3 may have formed during rising sea-level periods responsible of fine-grained sedimentation and dilution events marked by the lightening of oxygen isotope composition and preservation of marine organic matter (Fig.5). According to Dunham et al. (2020), the high organic carbon content (mean value of 2.68%), the abundant pyrite and the precipitation of dolomite testify the organic matter degradation by SRBs activity and subsequently, concentration of the lighter ¹²C in carbonate. The latter SRBs consume sulfate and produce sulfide (H₂S) in order to degrade organic matter, which favor FeS₂ precipitation (Berner, 1980; Herbert et al., 1998; Dupraz et al., 2004). This interpretation is compatible with the paleogeography of the northern area of the Caltanissetta Basin located nearby of the thrust belt that may have been influenced by tectonic uplift, implying more shallow waters (regarding to southern areas of the Caltanissetta Basin) periodically subject to sea-level

variations controlled by astronomical forcings (Sierro et al., 2001; Blanc-Valleron et al., 2002).

5.2.3. MSC beds – onset of the MSC

Shales of the CdB member

A seven meters thick organic-rich interval characterized by laminated and deformed shales (respectively, FA-5 and FA-6) confirms the end of the Tripoli Formation at 178 m, with the total disappearance of foraminifera assemblages together with diatoms. The transition from the Tripoli Formation to the CdB member is well marked by the $\delta^{18}\text{O}$ values that evolve from significant fluctuations to more constant values, the latter characterized by heavier values and implying the establishment of a steadier and more restricted environment. In particular, in the lower organic-rich interval of shales are encountered the highest $\delta^{18}\text{O}$ values ($\delta^{18}\text{O}_{\text{cal}}$: +7.69‰ and $\delta^{18}\text{O}_{\text{dol}}$: +7.65‰) which may indicate hypersalinity and probably the peak of evaporative conditions. The organic carbon contents become high (TOC around 3%) and the nature of the organic material passes from marine (Type II kerogen) to algal organic matter reworked by bacteria (Type I kerogen) (Fig.5). Very low $\delta^{13}\text{C}$ values ($\delta^{13}\text{C}_{\text{cal}}$: -8.86‰ and $\delta^{13}\text{C}_{\text{dol}}$: -7.21‰) confirm periods of increased stagnation that favors the consumption of the available dissolved oxygen and organic matter degradation processes. Hence, this interval may correspond to the onset of the MSC marked by the peak of evaporative conditions and the stabilization of a eutrophic environment. From the lower to the upper CdB member, shales composition transcribes a progressive evolution towards less restricted conditions. Detrital minerals are abundant in shales and it is mainly the case of shales that surround C1 and C2 (quartz values up to 60%) located in the lower part of the CdB member. The carbonate composition of shales varies between the two facies, FA-6 being mainly composed of aragonite while FA-5 of dolomite, both minerals of primary precipitation most likely for same mechanisms invoked for FA-3 and FA-4. The isotopic data of shales evolve throughout the CdB member. The oxygen isotopic composition of shales reflect evolution from saline-hypersaline conditions ($+2\text{‰} < \delta^{18}\text{O}_{\text{arag+dol}} < +8\text{‰}$) to saline conditions towards the upper part of the core. Shales also transcribe intervals of eutrophic conditions ($-9\text{‰} < \delta^{13}\text{C}_{\text{arag}} < -4\text{‰}$ and $-7.21\text{‰} < \delta^{13}\text{C}_{\text{dol}} < -0.34\text{‰}$) that evolve to less stagnant conditions towards the upper part of the CdB member.

FA-5 and FA-6 are cyclically embedded between the carbonate beds in the CdB member (Fig. 13). In every cycle, FA-6 is capped by FA-5. On top of every brecciated CdB beds (FA-8), deformation of shales is significant becoming sometimes chaotic (FA-6), in which reworked foraminifera and carbonate fragments are embedded (Fig.7d, e). The carbonate fragments contain peloidal features and filaments similar to FA-7 or FA-8 and may

correspond to fragments from the CdB bed respectively located below (Fig.7f). Deformation becomes progressively less significant towards the top of the cycle (Fig.13). The presence of contractional cracks and of upwardly deformed laminites were observed within FA-6 (Fig.7c). The lack of vertical- or subvertical-oriented dikelets that generally result from the intrastratal dewatering and subsequent injection of liquidized material from swelling clays or flocculating particles in a subaqueous setting, either because of salinity changes, gravitational compaction or seismic shaking (Burst, 1965; Plummer and Gostin, 1981; Pratt, 1998; McMahon et al., 2017) discards the possibility of syneresis cracks. These intrastratal features may correspond to subaerial desiccation cracks that, together with the resulting convoluted bedding, may originate as shrinkage cracks into the shales caused by the slow drying-out of muddy sediments exposed to subaerial actions such as the sun and the wind. Desiccation structures may give evidences of a shallow water deposition, commonly observed in playas and tidal mudflats. This could be consistent also with the presence of dolomite, which can be formed within the sabkha environment through microbial mediation (Vasconcelos et al., 1995, 2005; Vasconcelos and McKenzie, 1997; Warthmann et al., 2000; van Lith et al., 2003a, b; Wright and Wacey, 2005; Strohmenger et al., 2010). The microbial boundstone fragments and organic-rich laminae with abundant framboids of pyrite observed in thin sections may provide evidence for sulfate reduction and decay of organic matter at shallow waters within the sediment (Gehling, 1999; Harazim et al., 2013; Shen et al., 2016). Microbial mats development has commonly been observed with intrastratal shrinkage cracks and are a prerequisite for such features, as it is the case in the microbial mat of the Beach Formation in Bell Island (Harazim et al., 2013).

FA-6 is capped by laminated silty claystones rich in framboids of pyrite and inclusions of terrigenous clasts (FA-5). Similar beds of clayey laminites have been already observed in Torrente Vaccarizzo section in the Caltanissetta Basin and in San Donato section in Calabria (Perri et al., 2017). The fine laminae in shale (FA-5) indicate sedimentation in calm bottom-water anoxic environment ($-9\text{‰} < \delta^{13}\text{C} < -4\text{‰}$), during which organic material had time to be oxidized and microbial activities to consume all the available dissolved oxygen.

Organic-petrographical observations indicate a reddish-orange-colored kerogen maceral composition (Fig.7b) which may suggest intensive sulfurization of organic matter (Kolonis et al., 2002) in the organic-rich FA-5 intervals. This hypothesis may be confirmed by sharp decrease in T_{max} (suppl. table) in the shales of CdB, which may be indicative of less thermally stable organic matter due to the incorporation of sulfur into the kerogen during early diagenesis. SRB grow under anaerobic conditions in sediment pore waters or in the water column and in the presence of organic matter and they promote the reduction of sulfate to sulfide (e.g. Madigan et al., 2000). Major sinks for sulfide (H_2S or HS^-) are the formation of iron-sulfides such as pyrite (Berner, 1986) abundantly present in FA-5 and FA-6. Abundant

sulfurization of kerogen may result from the excess of sulfide and organic matter combined with a limited availability of iron during early diagenesis (Kolonic et al., 2002). Early sulfurization of organic matter has already been mentioned in the Cenomanian-Turonian black shales of the Tarfaya Basin, characterized by an euxinic and iron-limited environment (Kolonic et al., 2002). The different abundances of kerogen observed in shales, may imply variable sulfurization intensities of the organic matter, probably related to changes in palaeo-environmental boundary conditions and sea-level driven fluctuations during sedimentation (Kolonic et al., 2002). FA-5 and FA-6 may transcribe a tidal flat-lagoon setting through the deposition of laminated dark shales in a suboxic environment. Located in the transition between marine and continental region, the detrital minerals in FA-5 may be related to runoff increases events in a more humid environment. FA-6 underwent brecciation, that will be discussed in detail below.

Carbonate beds of the CdB member

At 170 m, the deposition of the first thick carbonate bed (C1) shows the settlement of an environment in which conditions were favorable to the formation of a carbonate platform mainly mediated by microbial mats. CdB carbonates are characterized by a microbial boundstone facies particularly rich in filaments, peloids and pseudomorphs of evaporite crystals. The clotted and peloidal microfabrics are typical of microbial carbonates (Riding, 2000). Foraminifera and microalgae have not been observed, whilst microbial features are sometimes very abundant. As already mentioned by Perri et al. (2017), this gives a hint on the microbial formation of the carbonate beds. In thin section, these filaments are observed among abundant micritic peloids surrounded by (micro)-spar typical of the CdB facies. The latter reminds the carbonate environments of the Timan-northern Ural region, in which Antoshkina et al. (2014) observed the association of pelitomorphic and microbial components and suggested that peloids are the product of the bacterial reworking of the muddy substrate. The clotted-micropeloidal texture in FA-7 and FA-8 possibly results from filamentous and/or coccoid-type bacteria, that degrade organic material within microbial mats (Oliveri et al., 2010) and progressively precipitate spheres of Mg-calcite forming a discontinuous micritic micropeloidal microstructure, as observed in the Salt Pan hypersaline lake in Eleuthera Island (Bahamas) by Dupraz et al. (2004). According to the latter authors, the micropeloidal cement corresponds to the complete calcification of the extracellular polymeric substance (EPS) biofilm that surrounds the bacteria. Other authors associated the micritic peloids to faecal pellets corresponding to the remains of copepods (Guido et al., 2007) or the crustacean *Artemia* (Caruso et al., 2015), both developing highly specialized physiological adaptations for tolerating hypersaline environments and hypoxic to anoxic conditions.

831
832 Bed C1 is the only microbial boundstone (FA-7) bed that does not have a brecciated aspect
833 and is rich in filaments, peloids and pseudomorphs after evaporite crystals in which
834 (microbial) peloids are now filled in (Fig.8a). Apart from the 'non-brecciated' aspect of C1, the
835 particularity of FA-7 is its high amount of celestine (Fig.3 and 8b, c). Celestine is commonly
836 associated with coastal marine carbonate and evaporite sediments and could be formed as a
837 diagenetic mineral by a) syngenetic precipitation from evaporative water associated to
838 hypersaline conditions during which concentrated brines lead to the removal of most Sr-
839 content from sea-water as dispersed sulfate phases (Hanor, 2004); b) epigenetic
840 replacement of carbonates and calcium sulfates involving Sr-rich formation waters, by
841 changing the Sr-bearing aragonite or biogenic calcite to low Sr-calcite or dolomite (Hanor,
842 2004; Pourkaseb et al., 2017). In C1, the early celestine mineralization may be the result of
843 Sr-bearing aragonite to Sr-calcite transformation (calcite composition up to 22%, while
844 dolomite up to 2%). The high amount of fossil bacteria observed in thin section (Fig. 8a) may
845 also suggest the microbial-mediated celestine precipitation (Sanz-Montero et al., 2009). The
846 $\delta^{13}\text{C}$ is slightly negative (-0.85‰) and organic carbon content low (0.15%) indicating a
847 moderate contribution of organic matter degradation. However, the microbial activity may
848 have been important as suggested by the high amount of fossil filaments, the presence of
849 pyrite and the nature of organic matter (Type I kerogen characterized by algal organic matter
850 reworked by bacteria; Filho and Gonçalves, 2017). All these evidences indicate anoxic
851 conditions and eutrophication that may have promoted bacterial growth. The characterization
852 of the microbial features permitted to suggest the presence of both sulfate reducing bacteria
853 (SRB) and sulfide oxidizing bacteria (SOB). The yellowish-colored fossil bacteria observed in
854 thin section (Fig.8a) have been described by Dela Pierre et al. (2015) in Messinian gypsum,
855 as 'remains of colorless' sulfide-oxidizing bacteria and were associated to the giant sulfur
856 bacteria *Beggiatoa*, *Thioploca* and *Thiotrix*. These living bacteria oxidize reduced sulfide
857 (H_2S or HS^-) produced by SRB to sulfate (SO_4^{2-}), via elemental sulfur that they host within
858 their cytoplasm as granules (Jørgensen et al., 1983; Bailey et al., 2009). The latter may
859 explain the yellowish-color observed in thin section. Nevertheless, the marine
860 chemolithoautotrophic *Beggiatoa* strain sp. 35Flor investigated by Schwedt et al. (2012),
861 develops a 'survival strategy' under anoxic and sulfidic conditions alternating between both
862 sulfide oxidation and sulfur reduction in spatially separated environments (oxygen/nitrate
863 section vs. anoxic sulfide section of the oxygen–sulfide interface), controlling the amount of
864 stored sulfur (Dupraz et al., 2004; Schwedt et al., 2012). Hence, in the CdB, sulfate reduction
865 processes by SRB may have been particularly active in the biogeochemical cycle promoting
866 carbonate precipitation, with respect to sulfide oxidation processes by SOB that lead to
867 dissolution (Dupraz et al., 2004). The CdB carbonate platform may have been formed in a

hypersaline environment by different microbial communities and a migrating oxygen-sulfide interface, also observed in the modern hypersaline ponds of Salins-de-Giraud (Camargue, France; Fourçans et al., 2004), the coastal lagoons of Araruama and Itaipu (Rio de Janeiro, Brazil; de Albuquerque et al., 2009) or other soda lakes and hypersaline habitats (e.g. Sorokin et al., 2012).

Beds C1, C2, C4 and C5 are mainly composed of aragonite and may be related to the degradation of organic matter by a microbial community in which SRB may play an important role. The process of aragonite precipitation by microbial activity discussed above for the thin carbonate beds of the Tripoli Formation, seem to have been continued through time and progressively intensified in the CdB. These beds are grouped in FA-7 (C1) and FA-8c (C2, C4, C5). The latter facies consists of the fitted-microbial boundstone fragments and may be the result of autobrecciation *sensu* Rouchy and Caruso (2006) and instantaneous infilling by the matrix corresponding to FA-5 (Fig.12). Such a situation has been observed in the modern Great Salt Lake (Utah, USA) (e.g. Newell et al., 2017), a meromictic lake characterized by hypersaline lacustrine conditions rich in microbialites (Stephens and Gillespie, 1976; Wurtsbaugh and Berry, 1990). During wet periods, meteoric water inputs would stabilize the chemocline, due to a thermal and chemical stratification of the lake (e.g., Anderson et al., 2011; Garces et al., 1995; Horton et al., 2016), lowering the $\delta^{18}\text{O}$ of the mixolimnion. As a consequence, the sequestration of ^{12}C related to increased primary productivity would increase the $\delta^{13}\text{C}$ of DIC (dissolved inorganic carbon) and associated carbonates (Garces et al., 1995). During dry periods, the meteoric inputs lower (heavier $\delta^{18}\text{O}$), evaporative conditions occur and the chemocline is less stable allowing the mixing of the waters. $\delta^{13}\text{C}$ drops due to less primary production and more degradation of organic material. Isotope composition of the beds grouped in FA-8c ($+2\text{‰} < \delta^{18}\text{O} < +7\text{‰}$ and $-4\text{‰} < \delta^{13}\text{C} < +1\text{‰}$) may transcribe a dry period, during which low meteoric inputs and desiccation may have induced the in situ brecciation of FA-7, transforming the microbial boundstone into brecciated boundstone (FA-8c). Similar processes were described in Cropalati (Calabria) and Torrente Vaccarizzo sections (Sicily), where the CdB is mainly composed by aragonite carbonate beds and characterized by autobrecciation (Caruso et al., 2015).

Beds C3, C6, C7, C8 and C9 are almost exclusively composed of calcite and $\delta^{18}\text{O}$ values are moderately low ($-2.02\text{‰} < \delta^{18}\text{O} < +0.90\text{‰}$). These beds corresponding to facies FA-8a, FA-8b and FA-8d (Fig.12), all three of them characterized by abundant sparry calcite fillings or recrystallization. Respectively, the particularity of FA-8a beds is the presence of vugs empty or filled with sparry calcite (Fig.2; Fig.9c and 9d), FA-8b is characterized by shale-filled brecciation and branching forms in which sparry calcite was filled, and FA-8d corresponds to

fitted-fragments microbial boundstone that were recrystallized in sparry calcite. These features support the conclusion that low $\delta^{18}\text{O}$ values reflect the contribution of secondary diagenetic imprinting.

As a whole, mineralogical and oxygen isotope composition give evidence of an upward evolution from more evaporative and stagnant conditions, towards an environment characterized by freshwater dilution events likely responsible of carbonate recrystallization. Hence, the CdB carbonates may transcribe a tidal flat-shelf environment, probably affected by decreasing evaporated conditions. This change is further supported by the presence of halite and gypsum crystals preserved as molds and recrystallized. Similar pseudomorphs have already been described in the carbonates of the CdB member of several sections located in the Caltanissetta Basin of Sicily (Serra Pirciata, Torrente Vaccarizzo, Pietraperzia, Contrada Gaspa in Caruso et al., 2015; Perri et al., 2017) or in the Rossano and Crotone basins of Calabria (outcrops of Cropalati, S. Isidoro, S. Donato, Belvedere, Strongoli, Cunicelle, in Caruso et al., 2015; Perri et al., 2017; Borelli et al., 2020), but have also been recorded in modern environments, as at Mussafah Channel of Abu Dhabi (Strohmenger et al., 2010). Moreover, in these facies, pyrite is mainly absent or rare. More specifically in FA-8a, elemental sulfur has been observed together with abundant filaments (Fig.9a, b). The filamentous fabrics observed in thin section are elongated or recurved, sometimes segmented (chain of cells) and consist of dark micrite coated by microspar. They have a size of up to 300 μm long and up to 100 μm wide. The same characteristics were described by Perri et al. (2017) in the CdB of Sicily and Calabria, associated to the thick-sized bacterial forms of *Beggiatoa* sp., *Thioploca* and *Thiotrix*. Moreover, recurved cylindric solid-shaped filaments of up to 2 mm long were identified in FA-8a (Fig.9a). The latter have already been observed in Pollenzo section (Piedmont Basin, NW Italy; Dela Pierre et al., 2012) and in Sutera section (Caltanissetta Basin, Sicily; Oliveri et al., 2010) and were associated to the present-day *Beggiatoa* (Møller et al., 1985). The recurved morphology illustrates their chemotactic behavior by changing direction when seeking for optimal concentrations of oxygen or nitrate (e.g. Møller et al., 1985; Oliveri et al., 2010). Hence, the filaments observed in thin section, coupled to the varying abundance of framboids of pyrite, may also here correspond to the chemolithoautotroph *Beggiatoa* spp.

5.3.3. Syndiagenetic brecciation processes

In order to reconstruct the complex genesis of these evaporitic carbonates, it is necessary to consider the brecciation process, besides microbial mediated processes and authigenic precipitation of mineralogical phases described above. In this study, we propose that the origin of the brecciated carbonates (FA-8) is closely related to syndiagenetic processes, and consequently to a non-depositional brecciation.

These processes took place during desiccation phases, under progressive evaporation and gradual water depth fall. The lowering of the water depth led to subaerial exposure of wide areas that previously were domains of carbonate sedimentation. Desiccation caused in-situ brecciation of FA-7, generating breccia fragments characterized by angular fragments, common in the overlying CdB beds (FA-8) and surrounded by a matrix corresponding to FA-5 most of the time rich in organic matter. This brecciation is typified of the latter facies even if clear structures of desiccation such as teepees are not visible in core 3AGN2S04. Angular clasts have already been recorded in intertidal to supratidal areas in marine environments (Shinn, 1983) and in carbonate-rich saline lakes that underwent desiccation stages (Eugster and Hardie, 1978; Smooth, 1983), as it is the case of the Great Salt Lake (Arenas, 1993).

The brecciation varies from one bed to another. FA-8a may have been formed during dry periods in the sabkha-types environment where the infiltration of meteoric waters led to the dissolution of sulfate minerals and to the formation of new cavities, pseudomorphs and collapse breccias. This in-situ “breakage” of the carbonate fabric may also be caused by the early replacement of sulfate by SRB-mediated calcite and gypsum-to-anhydrite conversion causing a molar volume reduction (Ziegenbalg et al., 2010; Caruso et al., 2015). This process has already been discussed as ‘in situ dissolution’ of evaporitic minerals within the carbonate layers by unsaturated waters (e.g. Pedley and Grasso, 1993; Rouchy and Caruso, 2006; Caruso et al., 2015). The repeated freshwater infiltration (river floods, storms and phreatic freshwater) in the ‘new’ brecciated limestones induce the filling of the cavities by (micro-)sparitic calcite. The later mineral transformations intensify the already brecciated fabric.

FA-8b is characterized by angular fragments and a higher amount of matrix than FA-8a, FA-8c and FA-8d characterized by a very dark color. FA-8b is embedded into carbonate beds (C3 and C9) and may be interpreted as levels of condensed carbonate/shales cycles above described (section 5.3.3.; Fig. 13a).

FA-8c and FA-8d are characterized by escape burst-through structures that seem to be present through the beds. Sometimes fragments occur inside these structures (Fig.13b). This may imply that fluids are migrating towards the surface through the carbonate beds inducing their fragmentation or, if already brecciated, the intensification of brecciation and reworking of fragments. These fluids could represent the gas produced by the organic matter degradation from the shales intercalated between the carbonate beds and/or from the underlying early Messinian Tripoli Formation. The release of these gases, especially if pore-spaces were saturated (e.g. Spence and Tucker, 1997), could have been facilitated by the seismicity of the area, which was very active during this period and until the Pleistocene (Catalano et al.,

2013) and may have quickly trigger overpressure (e.g. Mutti et al., 1984; Mullins and Cook, 1986; Mullins et al., 1984; Talling et al., 2014).

The described processes may be responsible of autobrecciation but other events need to be taken into consideration such as progressive uplift, causing faulting, folding and lateral transfer (Caruso et al., 2015). It should be noted that core 3AGN2S04 is located in the innermost part of the SFTB, north of the Caltanissetta Basin. Accordingly, small shallow-water carbonate platforms that developed in the active structural highs could have undergone uplift and progressive dismantling due to subaerial exposure and erosion. In the margin of a sub-basin of the Caltanissetta Basin, small-scale gravitational processes could have intensified the brecciation of the carbonates. However, massive events such as debris-flows of previously deposited shallow-marine evaporitic carbonates under evaporative conditions and the resedimentation of these microbialitic or evaporitic limestones (CdB type 3; Roveri et al., 2006; Roveri et al., 2008a; Barone et al., 2008; Manzi et al., 2011, 2016) do not seem relevant. The brecciated limestones were probably formed much in the same place as we observe them now. Decima et al. (1988) have already reported that some beds of brecciated limestone might have been lithified, leached of halite and fragmented not long after their deposition because their upper surfaces are truncated and regular. Moreover, in the case of repeated debris flows, the clayey sediments deposited before such massive events would have swept away and the cyclic stratification observed in the CdB member (Fig.13) would have been impossible to occur. The repetition of i) fine-grained or laminated carbonates, ii) brecciated carbonates, iii) brecciated shales, iv) laminated shales would rather be the result of climate and sea-level variations. Cyclic humid climate episodes during the CdB formation have already been discussed by Caruso et al. (2015) and Perri et al. (2017). During these events, carbonate precipitation may have ceased and the deposition of shales may have taken the lead, marking the progressive environmental change. The carbonate fragments intercalated in the organic-rich and deformed laminites (FA-6) may derive from the carbonate beds and previously formed mats located below, that underwent brecciation during more evaporitic conditions. Carbonate-shale alternations reflect cyclic dilution/evaporation fluctuations probably linked to Milankovitch-scale climate variations.

5.4. Conclusive palaeo-environmental reconstruction

Fig.14

The studied core 3AGN2S04 allowed to go through a period that spans from late Tortonian to Messinian, recording the onset of the Messinian Salinity Crisis. Multi-proxy approach permitted to reconstruct the palaeo-environment of the northern part of the Caltanissetta Basin and to shed light on the passage from normal marine to hypersaline conditions. The Terravecchia Formation, characterized by terrigenous minerals records a river-dominated deltaic environment. During a period of high sea-level, continental inputs may have been transported from the Maghrebian Chain to the northern part of the Caltanissetta Basin. In the Tripoli Formation, detritic influxes were decreasing but still abundant due to the continuous dismantling of the Maghrebian chain.

Euxinic conditions occurred prior to the deposition of MSC evaporites. The upper Tripoli Formation is typified by marls extremely rich in organic matter, the disappearance of foraminifera assemblages, the presence of sparse diatomitic levels and the appearance of thin carbonate beds (T1 to T4), indicative of a progressive shallowing of the sea-level and the establishment of eutrophic conditions due to high primary productivity and probable tectonic uplift of the area. Carbonate sediments accumulated in relatively shallow-water and lagoonal settings occupied by tidal and shallow-water subtidal microbial mats (FA-4; Fig.14). In these lagoons, circulation was intermittently limited and the formation of anoxic conditions in bottom waters was stimulated by sulfate-reduction microbial activities and a progressive increase of water bodies salinity with periodic freshwater influxes (FA-3 and FA-4). The transition from Tripoli Formation to Calcare di Base (CdB) member illustrates gradual palaeo-environmental changes corresponding to the progressive deterioration of the marine conditions towards increasing salinity (McKenzie et al., 1979; Bellanca and Neri, 1986; Bellanca et al., 1986, 2001; Blanc-Valleron et al., 2002; Caruso, 1999; Caruso and Rouchy, in Roveri et al., 2008b; Rouchy and Caruso, 2006).

Extensive carbonate deposition took place (C1 to C9) in the CdB member, represented by microbialites and local precipitation of evaporitic minerals (FA-7 and FA-8) characterizing inner-platform environments (Fig.14). Halite and gypsum pseudomorph relics reveal hypersaline conditions. These evaporitic carbonates were more extensively deposited during evaporitic periods in stagnant bottom waters with frequent freshwater influxes. During that period, sea level variations and deflation processes may have induced the formation of salt flats in the inner platform displaying a tidal flat-shelf environment (Fig.14). In the southernmost regions of Italy (Calabria and Sicily), the CdB was associated to a platform comprising continental to shallow-water domains, dominated by widespread microbial carbonates and evaporitic deposits (Borrelli et al., 2020). The brecciated carbonate beds located in Rossano and Crotona basins (Calabria) were associated to autobrecciated carbonate facies of peritidal areas and to resedimented facies of slope environment by Borrelli et al. (2020). However, in the present study, several sedimentary features suggest

that the CdB member corresponds to carbonate beds that endured a complex set of syndiagenetic processes superimposed to the primary deposition of peloidal and microbial limestones in hypersaline settings. Diagenetic processes through the enhanced bacterial activity played a key role in the formation of large amounts of carbonates. The repetition of syndiagenetic processes through time led to mechanical and chemical compaction but also to brecciation. During periods of organic matter accumulation, the depositional environment was a confined, low energy, anoxic and stratified saline system with high productivity.

In the CdB member, the progressive passage from brecciated to laminated sediments indicates a changing environment, passing from desiccation to calm shallow-waters with frequent freshwater influxes. The repetitive alternation of laminated shales with microbial carbonates also crops out in the Cropalati, Cozzo S. Isidoro 1 and Cunicelle sections in Calabria (Borelli et al., 2020) and confirms the alternation of dry evaporitic periods with more humid phases (Perri et al., 2017). Caruso et al. (2015) suggested that humid periods seem to have affected the CdB platform with a cyclicity probably related to precessional orbital forcing, while Borelli et al. (2020) dated the humid-dry events during an early Messinian glacial event. Unfortunately, the absence of bio-events does not allow a precise temporal definition of the cyclicity.

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Figures and Captions

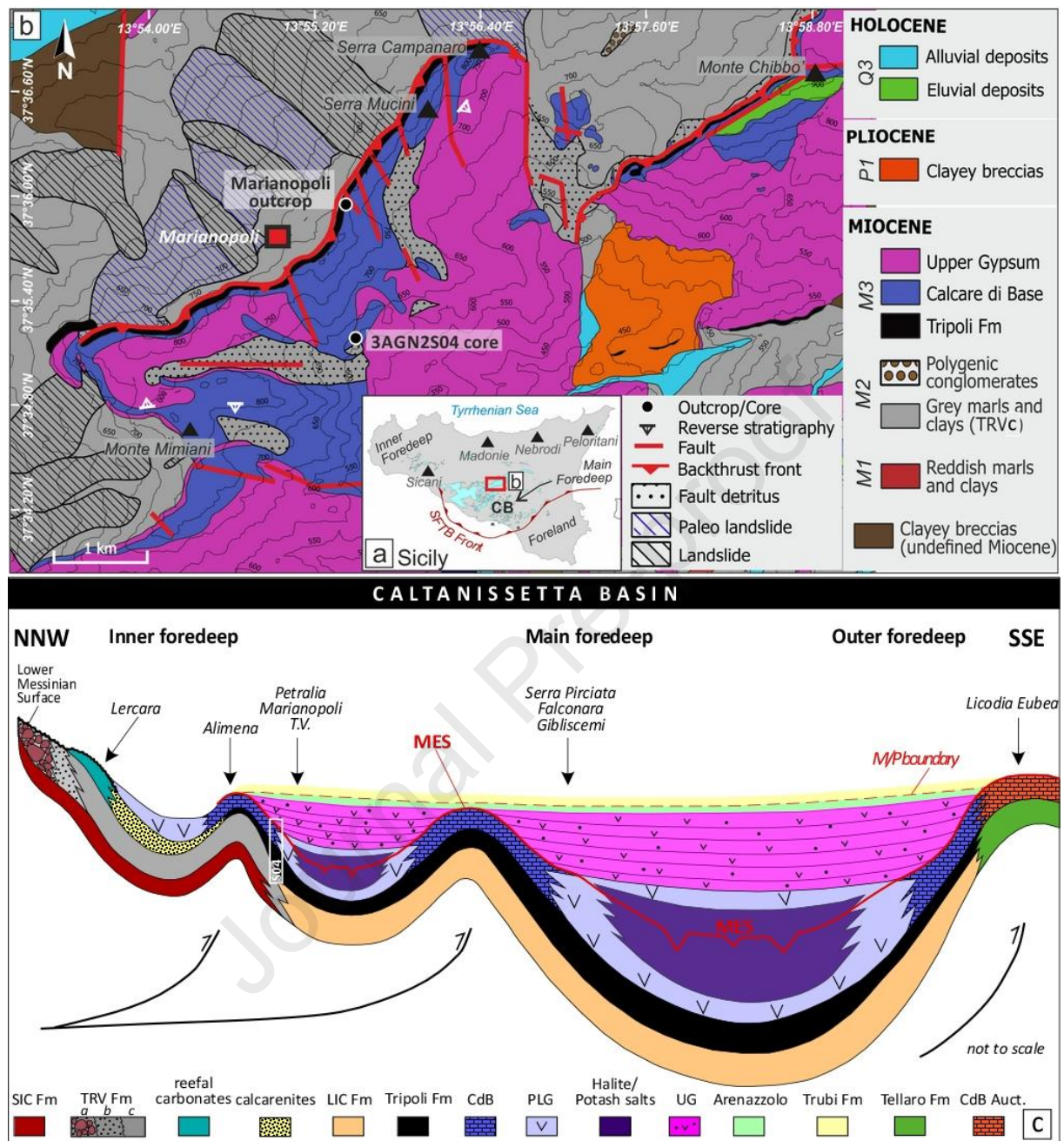


Fig.1. (a) Location of core 3AGN2S04 in the Caltanissetta Basin, Sicily. (b) Geological map of core 3AGN2S04 (modified after l'Ente Zolfi Italiani, Servizio Geologico Italiano). The isolines correspond to the present-day topography of the area and have been produced using the onshore digital elevation model produced using Copernicus data and information funded by the European Union EU-DEM layers (www.eea.europa.eu). (c) Schematic geologic cross section across the Caltanissetta Basin showing the Tortonian and Messinian deposits (modified after Roveri et al., 2006). SIC Fm: Castellana Sicula Formation; TRV Fm: Terravecchia Formation; LIC Fm: Licata Formation; CdB: Calcare di Base member; PLG: Primary Lower Gypsum; UG: Upper Gypsum; M/P boundary: Miocene/Pliocene boundary. The white rectangle corresponds to the stratigraphic position we assign to the study core 3AGN2S04.

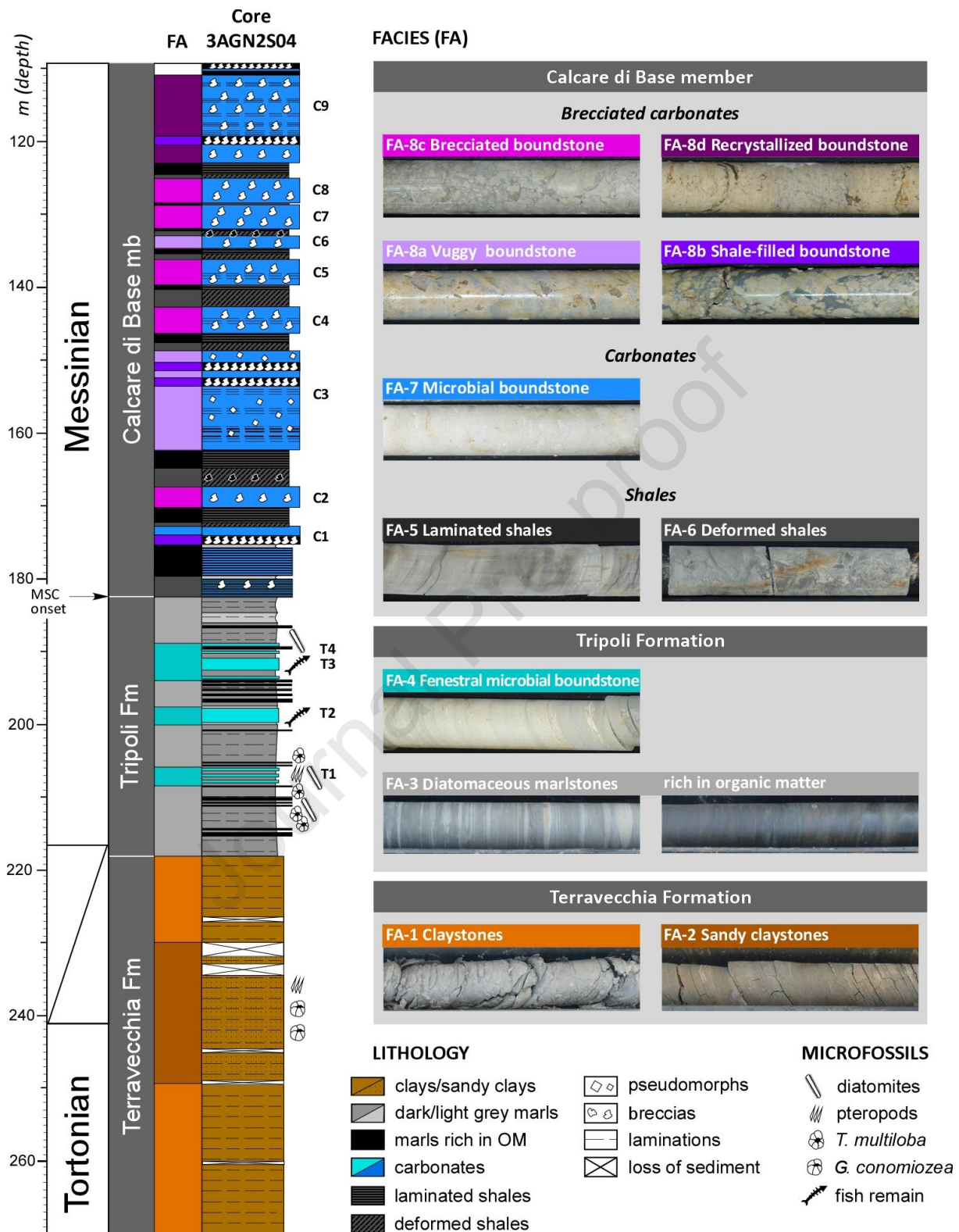


Fig.2 Detailed lithological, sedimentary and (bio)-stratigraphic log of core 3AGN2S04 and facies characterization.

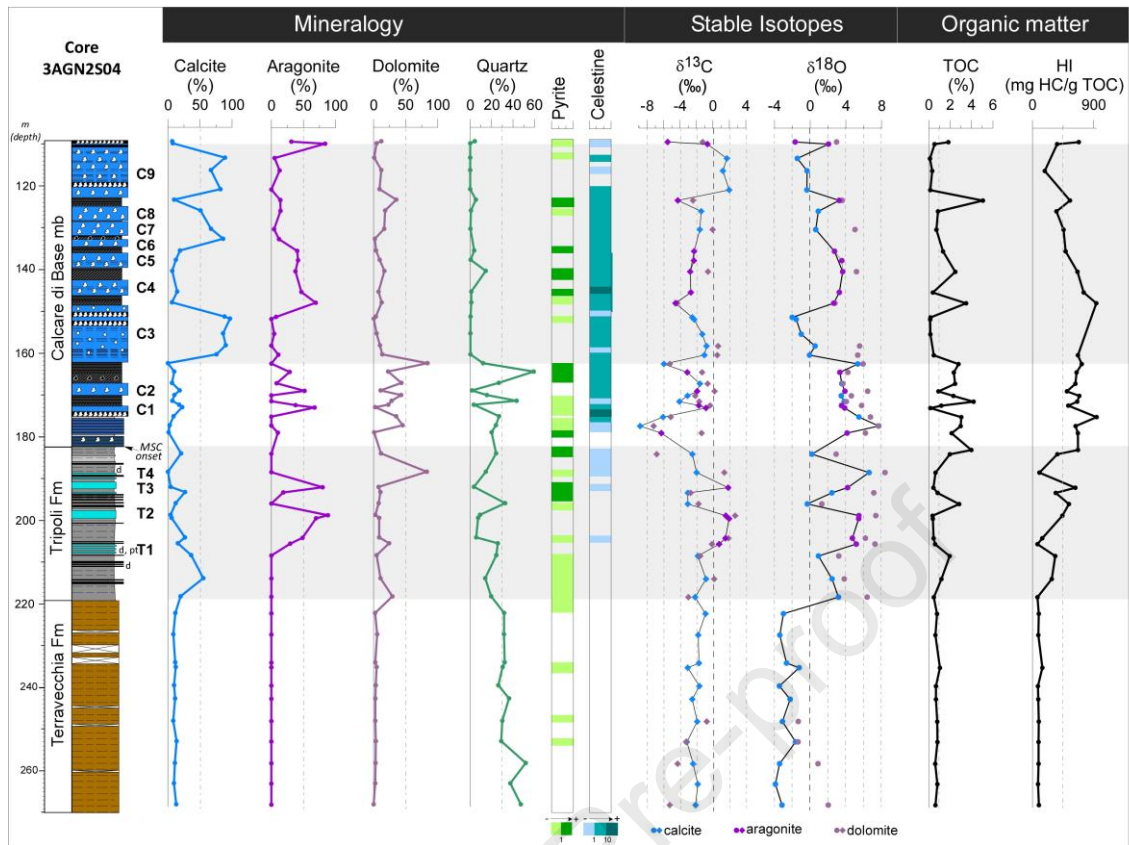
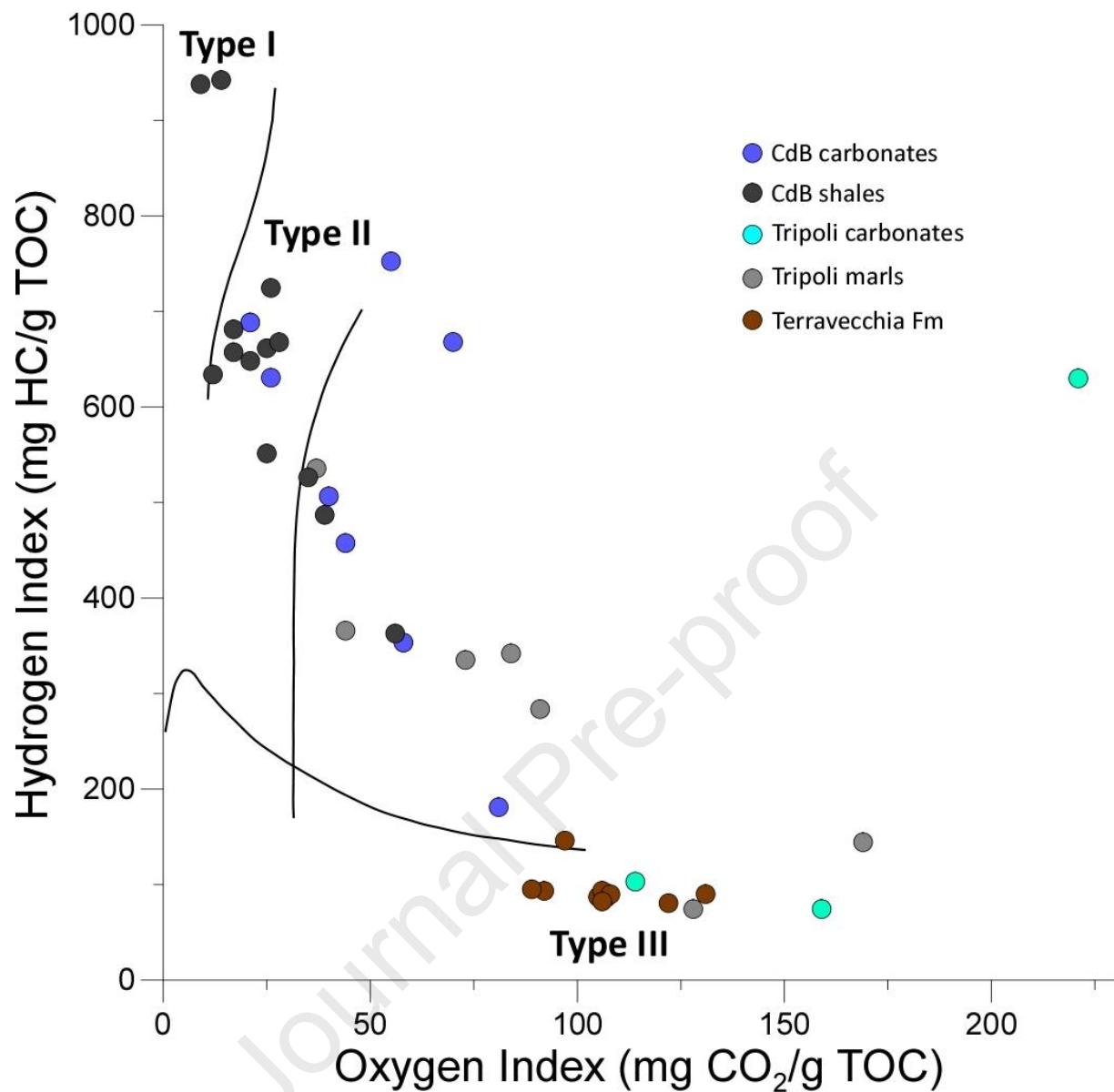


Fig.3. Depth-profiles of the mineralogy, stable isotopes and organic carbon geochemistry of the samples from core 3AGN2S04.



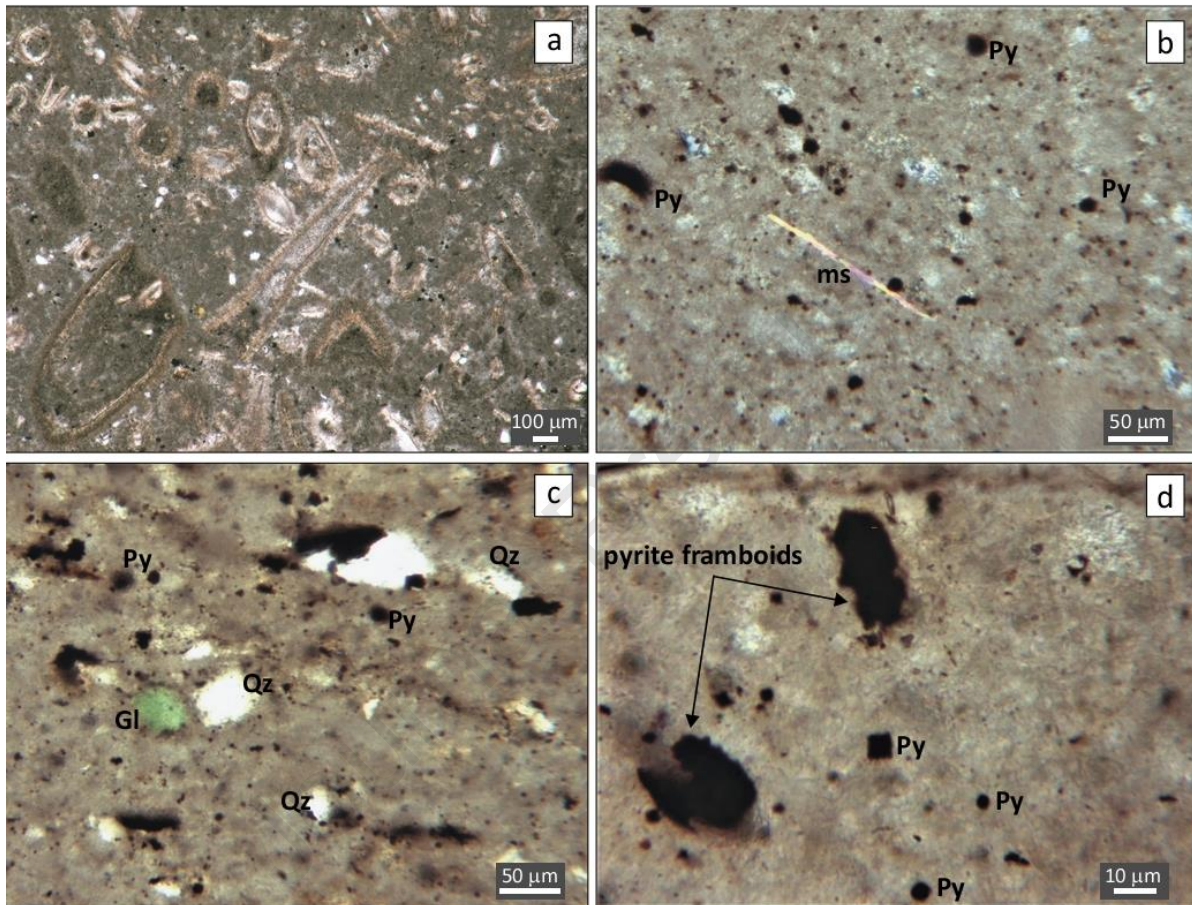


Fig.5. Photomicrographs of diatomaceous marlstones (FA-3) from the Tripoli Formation. (a) Pteropods embedded in marly matrix; (b) Muscovite and pyrite grains in marly matrix; (c) Detrital glauconite and quartz grains embedded in marly matrix; (d) Pyrite crystals and framboids. Py: pyrite; ms: muscovite; Gl: glauconite; Qz: quartz. (a,b) Crossed polarized light; (c,d) Plane polarized light.

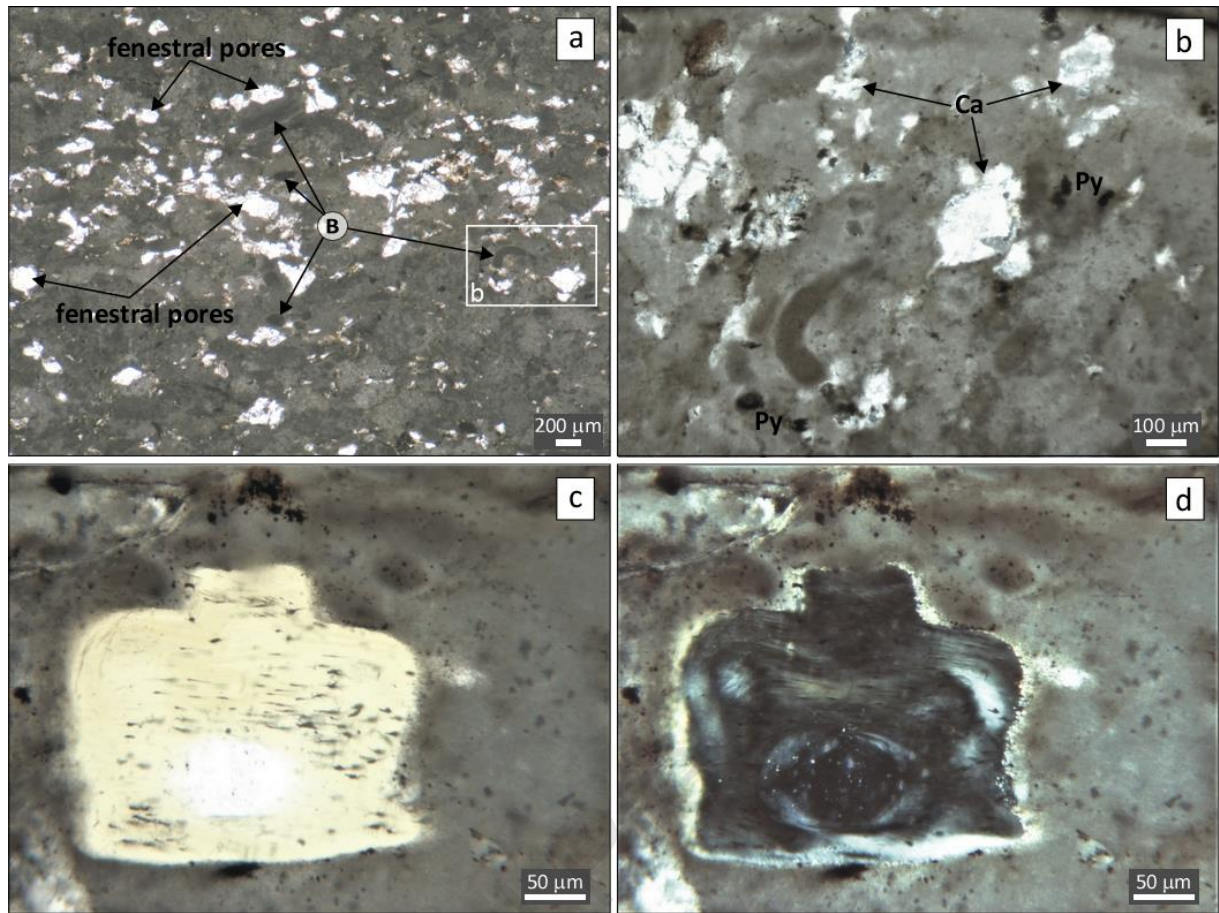


Fig.6. Photomicrographs of fenestral microbial boundstone (FA-4) from the Tripoli Formation. (a) Microbial boundstone with fenestral pores. (b) Boundstone with filaments, sparse crystals of pyrite and fenestral pores filled by sparry calcite. (c,d) Fish remains. (a,c) Plane polarized light; (b,d) Crossed polarized light.

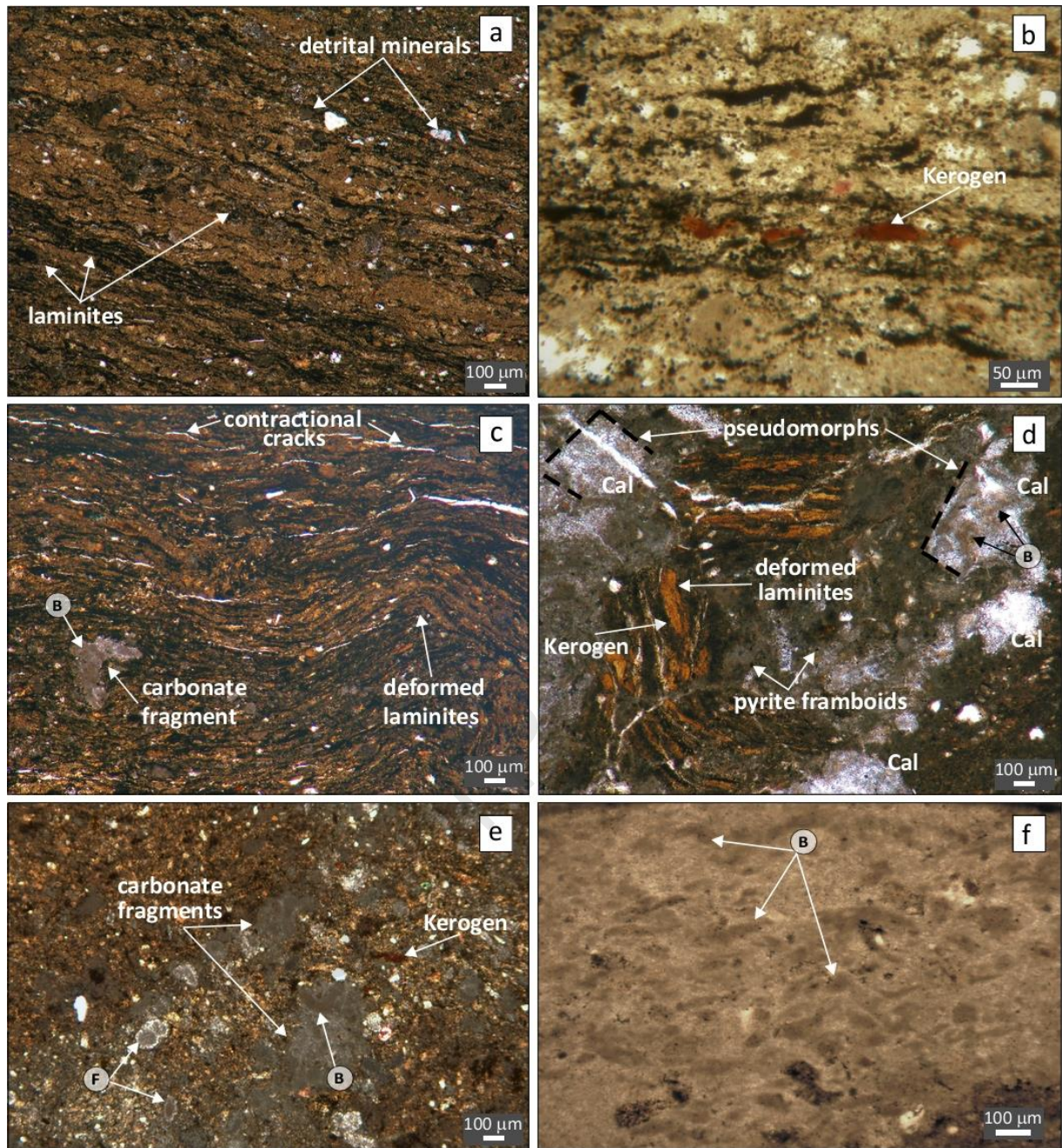


Fig.7. Photomicrographs of black shales (FA-5 and FA-6) from the Calcare di Base member. (a) Silty clayey laminites rich in detrital minerals, organic matter and carbonate fragments – FA-5. (b) Kerogen characterized by a reddish-orange-colored kerogen maceral; (c) Deformed laminites, contractional cracks and presence of carbonate fragments filled by filaments – FA-6; (d) Deformed laminites with sparse framboids of pyrite and pseudomorphs filled by filaments and a sparry calcite cement – FA-6; (e) Brecciated shales characterized by a chaotic facies in which carbonate fragments, kerogen and reworked foraminifera are embedded – FA-6; (f) Filaments filling a carbonate fragment of FA-6. B: filamentous, rod shaped bacteria; Cal: calcite. All photomicrographs are in plane polarized light.

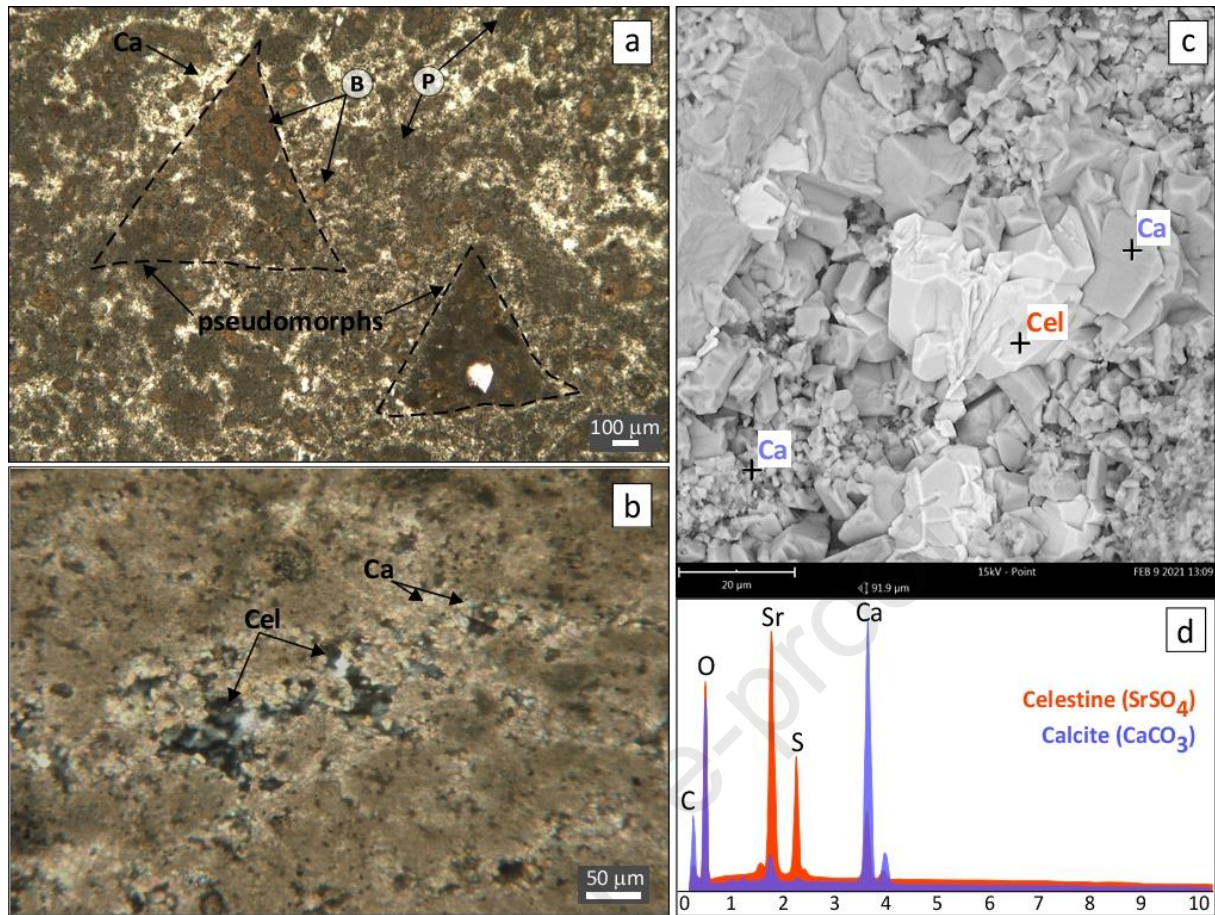


Fig.8. Photomicrographs of microbial boundstone (FA-7) from the Calcare di Base member. (a) Aphanitic to clotted peloidal micrite with pseudomorphs enclosing filaments and microsparitic cement. (b) Microsparitic calcite and celestine cement. (c) Scanning electron microscope (SEM) photomicrograph of microbial boundstone rich in calcite and celestine. (d) Elemental spectrum. Ca: calcite; Cel: Celestine; P: peloids; B: filamentous, rod shaped bacteria; black tick line: pseudomorphs after evaporite crystals. (a) Plane polarized light; (b) Crossed polarized light.

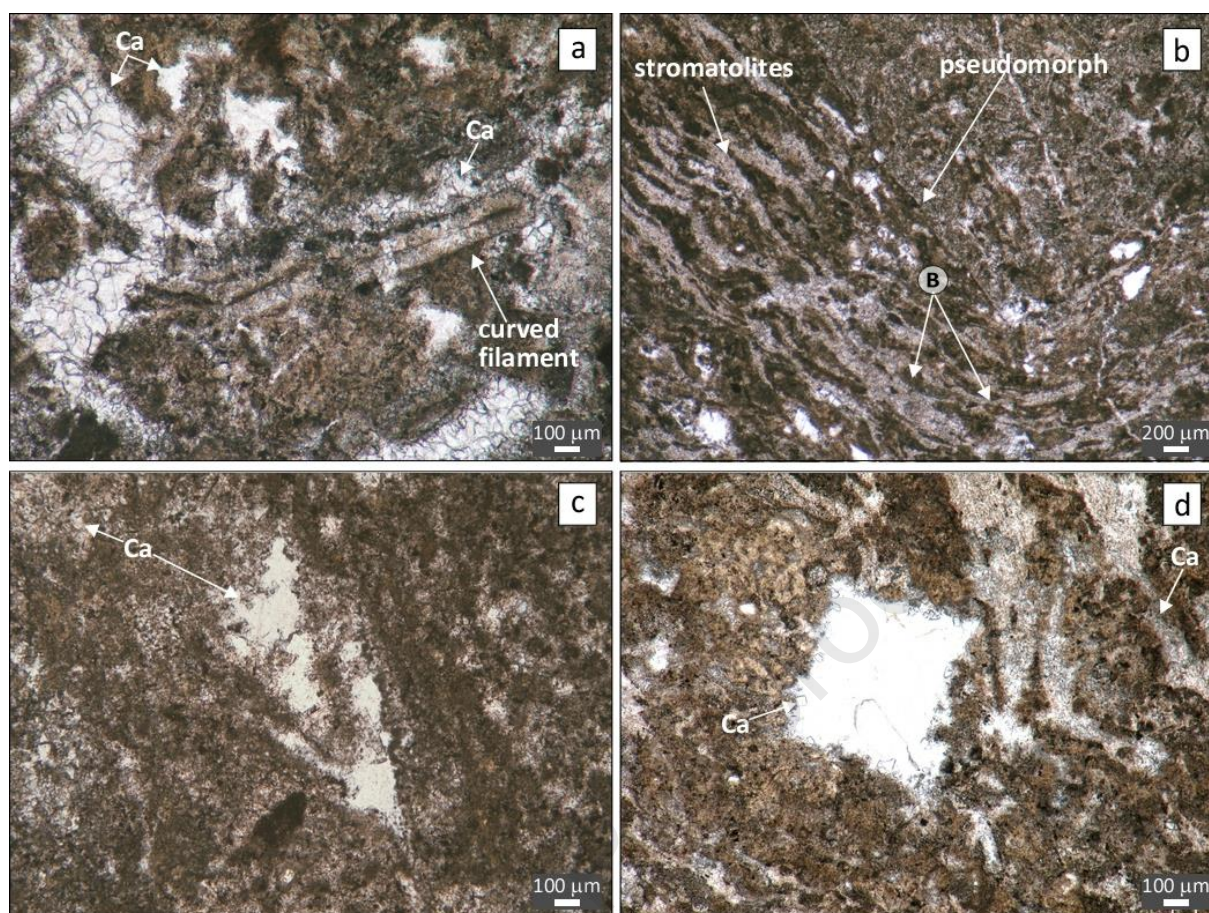


Fig.9. Photomicrographs of vuggy brecciated boundstone (FA-8a) from the Calcare di Base member. (a) Recurved filaments in a clotted peloidal micrite. (b) Stromatolitic structures surrounding a pseudomorph. (c) Swallow-tailed pseudomorph originally filled by gypsum. (d) Empty cubic pseudomorph delineated by sparry calcite in a stromatolitic facies. Ca: calcite; B: filamentous, rod shaped bacteria. All photomicrographs are in Plane polarized light.

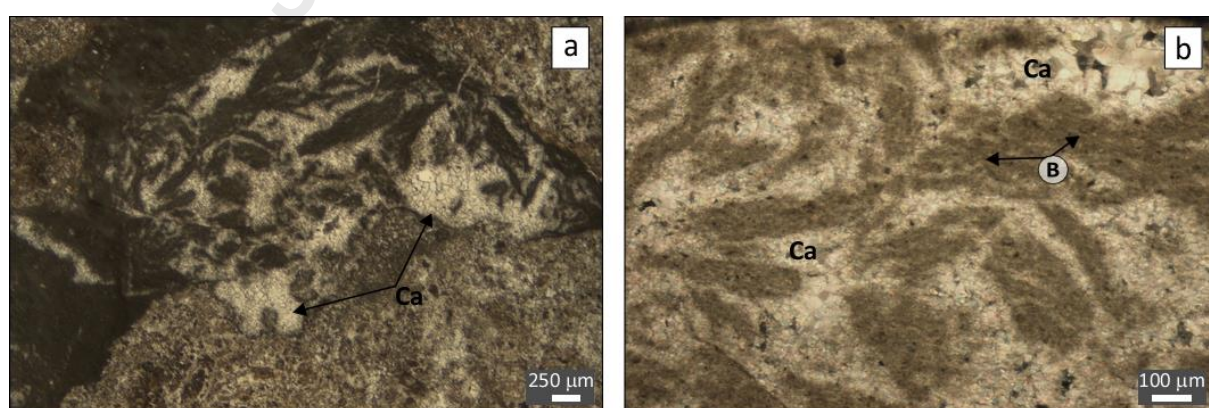


Fig.10. Photomicrographs of shale-filled boundstone (FA-8b) from the Calcare di Base member. (a) Dark-colored branching structures in an aphanitic to clotted peloidal micrite. (b) Branching structures filled by dark-colored and chaotic microbial fragments in a sparitic calcite cement. Ca: calcite; B: filamentous, rod shaped bacteria. (a) Plane polarized light; (b) Crossed polarized light.

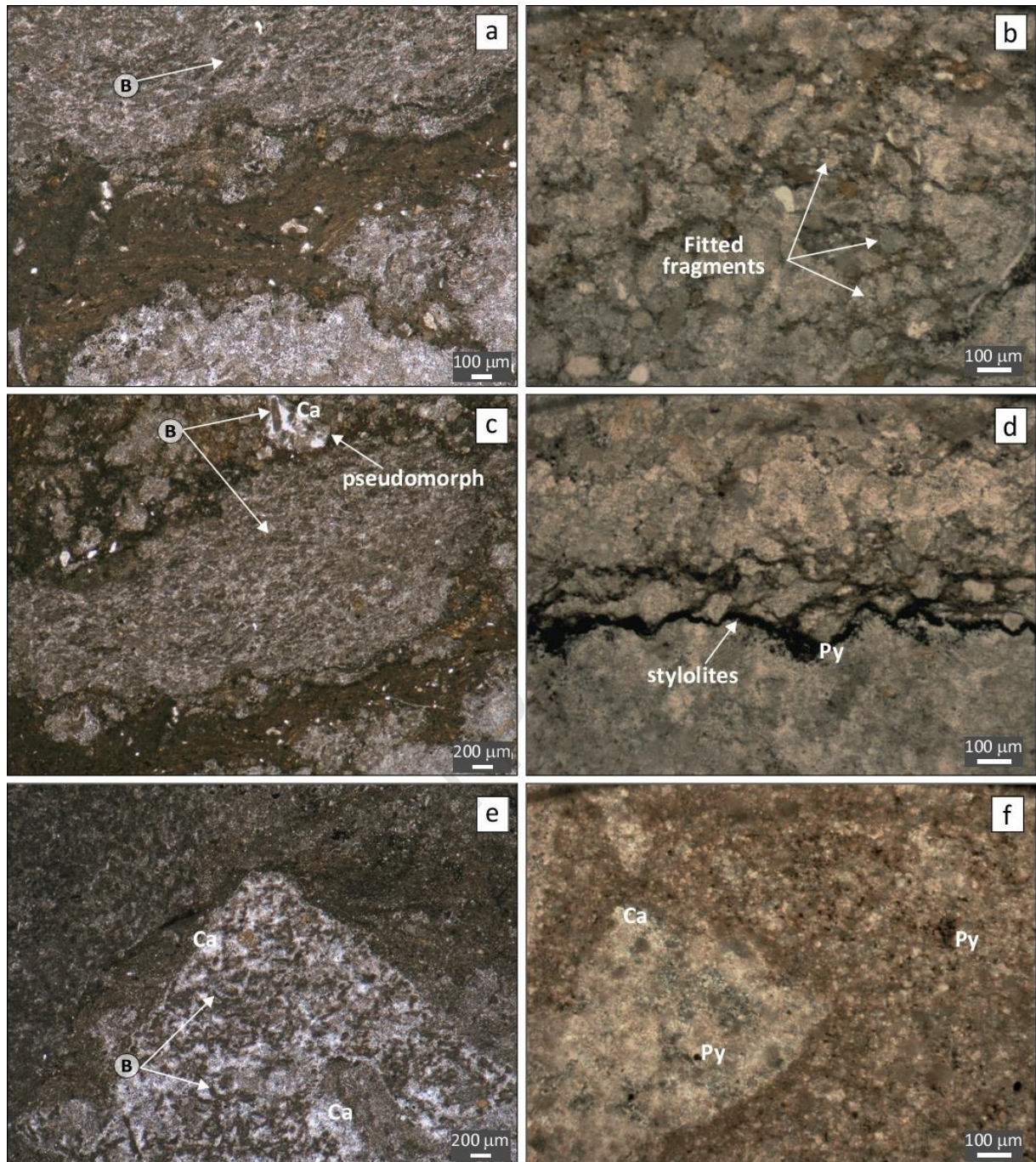


Fig.11. Photomicrographs of brecciated boundstone (FA-8c; a,b,c,d) and recrystallized brecciated boundstone (FA-8d; e,f) from the Calcare di Base member. (a) Boundstone fragments in a silty matrix consisting of FA-5. (b) Fitted - lumpy limestone facies filled by peloidal, clotted rod-shaped micrite and filamentous micrite. (c) Micrometric halite voids and/or halite pseudomorphs embedded in-between the boundstone fragments and a silty matrix. (d) Stylolites filled by pyrite. (e) Boundstone fragments and matrix in “recrystallized brecciated boundstone”. (f) Boundstone fragments totally recrystallized in sparitic calcite and abundance of pyrite in matrix. Py: pyrite; Ca: calcite; B: filamentous, rod shaped bacteria. (a,b,c,d,e) Plane polarized light; (f) Crossed polarized light.

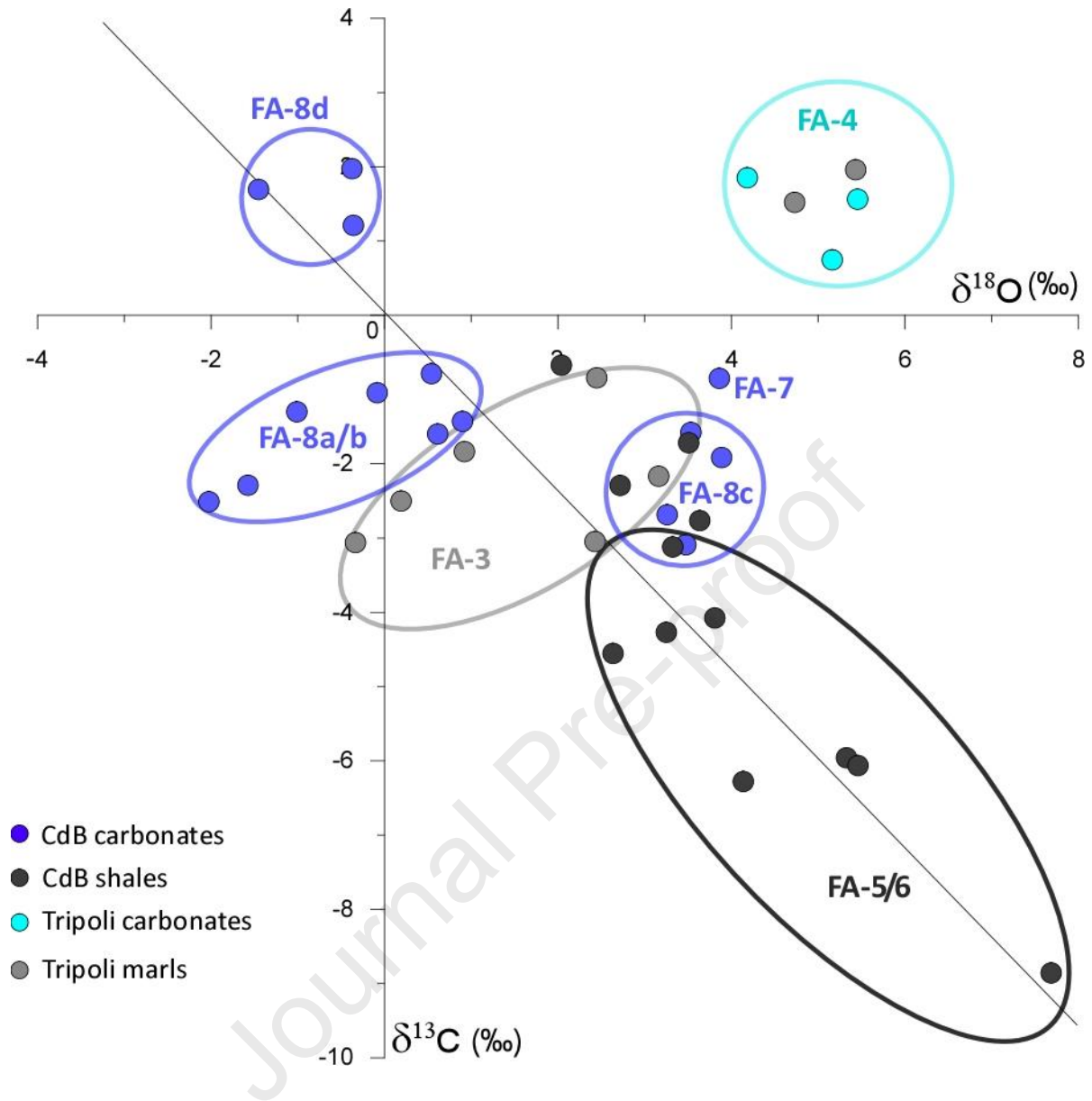


Fig. 12. Distribution of oxygen and carbon isotopic ratios of calcite and aragonite in the Tripoli and Calcare di Base samples from core 3AGN2S04. For the meaning of the groupings see text. FA: Facies.

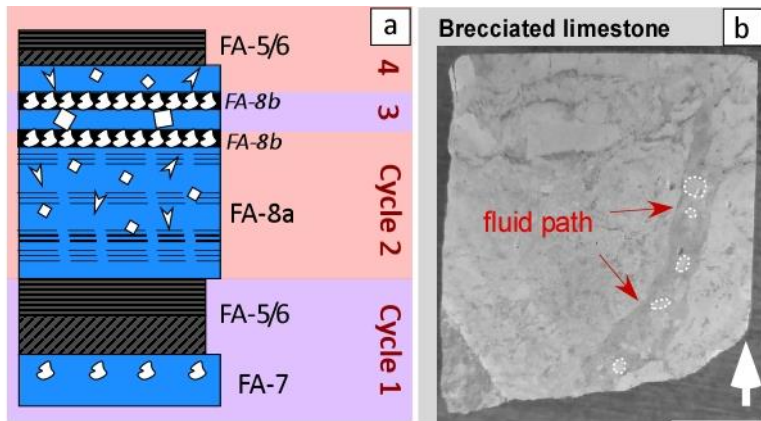


Fig.13. (a) Cyclical lithological variations within the Calcare di Base member (see text). (b) Fluid paths observed in the brecciated carbonate beds. White ticks: some of the fragments inside of conduit.

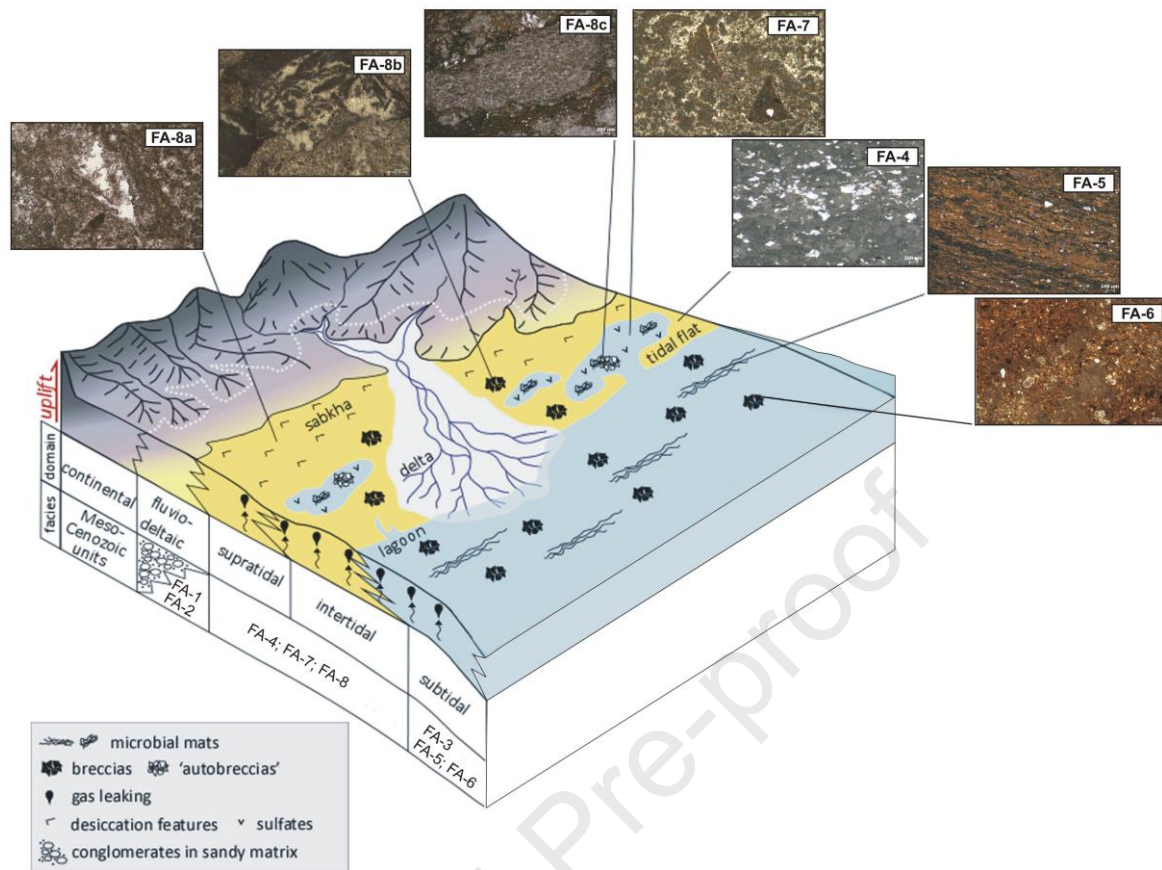


Fig. 14. Depositional environments of the pre-MSC and MSC evaporitic facies along the inner and middle ramp of a carbonate platform profile. See section 5.4.

Highlights:

- Pre-MSC and MSC sediments revealed by the recent drilled core 3AGN2S04 in the Caltanissetta Basin.
- Sedimentary and environmental changes during the transition between the Tortonian-Messinian marine conditions and the Messinian evaporitic events.
- The Calcare di Base (CdB) member corresponds to a carbonate platform characterized by wide sabkha to lagoonal environments, rich in microbialites probably *Beggiatoa* spp..
- CdB deposits profoundly marked by a set of syndiagenetic and “in situ” brecciation processes.
- Carbonate-shale alternations reflect cyclic dilution/evaporation environmental responses.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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