A Messinian Gypsum Deposit in the Ionian Forearc Basin (Benestare, Calabria, Southern Italy): Origin and Paleoenvironmental Indications

Mara Cipriani †, Rocco Dominici †,*, Alessandra Costanzo ‡, Massimo D’Antonio § and Adriano Guido †

1 Department of Biology, Ecology and Earth Science, University of Calabria, Arcavacata di Rende, 87036 Rende, Italy; mara.cipriani@unical.it (M.C.); adriano.guido@unical.it (A.G.)
2 Earth and Ocean Sciences, School of Natural Sciences, National University of Ireland, IF91 TK33 Galway, Ireland; alessandra.costanzo@nuigalway.ie
3 Department of Earth, Environment and Resources, University of Naples Federico II, 80126 Napoli, Italy; massimo.dantonio@unina.it
* Correspondence: rocco.dominici@unical.it

Abstract: This study reports the first accurate record of the Messinian Resedimented Gypsum in the forearc and back-arc basins connected to the Calabrian-Peloritan orogen. A multidisciplinary approach has been used to investigate a gypsum deposit located in the Benestare’s area (Calabria, Southern Italy). Such deposit is made of bedded gypsrudites displaying clastic selenite with chaotic textures. On the top, the gypsrudites are interspersed with gypsum lenses belonging to the branching-like facies. Despite these two facies seem different macroscopically, they show petrographic features, fluid inclusions, organic matter and Strontium isotopic values very similar to each other. On the other hand, both facies show fractured and folded crystals. Crystals are only locally corroded and preserve primary structure relict as well as allochthonous (organic debris) and autochthonous putative microbial remains. All crystals are rich in fluid inclusions but these are visibly affected by stretching and leaking (re-equilibration processes) suggesting a moderate plastic deformation during re-sedimentation and subsequent burial. Minimal transport of the deposit is testified by subangular shapes of the gypsum crystals. The gypsrudite and branching-like facies reveal an $^{87}\text{Sr}/^{86}\text{Sr}$ average value of 0.709045 and 0.709082, respectively. These values suggest a strong connection with the global Ocean and reduced freshwater input. The Benestare’s deposit originated from the partial to complete dismantling of selenite crystals related to the first stage (5.97–5.60 Ma) of the Messinian Salinity Crisis through gravitational collapse due to local controlling factors.

Keywords: Messinian Salinity Crisis; selenite; resedimented facies; fluid inclusions; organic matter; strontium isotopes

1. Introduction

The Messinian Salinity Crisis (MSC), which occurred approximately 6 Ma ago, is a complex geological event which transformed the Mediterranean Sea into a giant saline basin, causing a catastrophic hydrological and biological crisis [1]. This event is one of the most important and controversial topics being debated in the scientific community. The MSC triggered the formation of extensive evaporite deposits known as Lower Evaporites, Halite and Upper Evaporites which, in less than 640 ka, accumulated on the bottom of the Mediterranean basin [2–5]. During the CIESM workshop (Almeria, 7–10 November 2007), it was proposed a new MSC scenario involving three phases [2]. Stage 1 (5.97–5.60 Ma) is the first evaporitic stage associated with the deposition of Primary Lower Gypsum (PLG). Stage 2 (5.60–5.55 Ma) is the MSC acme where the Resedimented Lower Gypsum (RLG) and Salt Unit formed. RLG, consisting of large blocks of the Primary Lower Gypsum unit emplaced by gravity flows and it is considered as the best candidate for a possible equivalent of the deep Mediterranean Basin’s Lower Evaporites unit. Stage 3 (5.55–5.33 Ma)
is represented by the Upper evaporites and Lago Mare event(s) and defines the end of MSC. The environmental conditions controlling the deposition of Messinian gypsum are still debated, especially due to the lack of modern analogues [6].

Each of the three Messinian units show a characteristic $^{87}\text{Sr}/^{86}\text{Sr}$ signature, which records changes in the hydrological balance of the Mediterranean. Indeed, $\text{Sr}$ isotope ratio is a function of the balance between ocean and riverine input, which are characterized by strong variations in $\text{Sr}$ concentration and $^{87}\text{Sr}/^{86}\text{Sr}$ signature, thus providing a valuable proxy of its hydrological structure and may thus have a good chronostratigraphic value [2,4,7]. An extensive $^{87}\text{Sr}/^{86}\text{Sr}$ database has been established for the Messinian onshore and offshore evaporitic deposits [7–11]. The compiled data show that the Mediterranean $^{87}\text{Sr}/^{86}\text{Sr}$ values progressively diverged from the global ocean at the dawn of the MSC [11–14]. This change has been related to the progressive isolation of the Mediterranean Sea and the consequent gradual decrease of the oceanic input into the basin and/or to the increase of freshwater input from rivers [15,16] and/or the Paratethys [11–20]. These factors allowed the development of a distinct $\text{Sr}$ isotopic signature for the Mediterranean basin during the MSC, which significantly differs from the coeval global ocean signal. According to the revised version of the $\text{Sr}$ isotope curve proposed by Roveri et al. [11], the three phases of the crisis are characterized by well-defined non-overlapping $^{87}\text{Sr}/^{86}\text{Sr}$ ranges:

- **Lower Gypsum** showing values between 0.709024 and 0.708890 that are in the range or slightly detached from the global ocean.
- **Resedimented Lower Gypsum and Halite** displaying values between 0.708960 and 0.708820, and between 0.709034 and 0.708801, respectively. These values suggest the presence of an even more diluted water mass with respect to the previous one, but still connected with the global ocean.
- **Upper Gypsum** showing the lowest and most depleted values compared with the coeval global ocean, mainly below 0.708800 (as low as 0.708600).

Moreover, an important role in the study of evaporites and facies analyses is played by the fluid inclusions and the ancient microbial remains hosted in the crystals. Fluid inclusions represent multicomponent brines trapped during crystal growth. They are a common feature in evaporitic minerals and provide important information on the composition of ancient seawater. They are a key component for the reconstruction of environmental changes [11,21–27]. However, they provide microthermometric data that can be used to infer trapping conditions only if the inclusion satisfies several criteria referred to as “Roedder’s Rules” [28,29]: (a) the inclusion must trap a single, homogeneous phase; (b) the inclusion must remain a constant volume system after trapping (excluding reversible elastic volume changes); (c) nothing has been added to, or removed from, the inclusion following trapping. If the inclusion volume changes, or if anything is added to or lost from the inclusion following trapping, the inclusion is said to have re-equilibrated.

Another important aspect of the evaporitic minerals is the entrapped organic matter as sourced by putative microbial organisms. The presence of traces of ancient microbial life in different salt-saturated environments (shallow and deep) may provide information about salinity, depth of the basins, light penetration, oxygen and nutrient availability. Recent studies described a diversified and well-preserved body and molecular fossil assemblage within Messinian selenites, confirming that gypsum evaporites represent an excellent archive of microbial life [6,30,31].

Over the years, numerous scientific studies have been carried out on several deposits of the Mediterranean basin (e.g., Spain, Central-Northern Italy, Sicily, Turkey, Cyprus) contributing to a better understanding of their formation mechanisms. These studies agree with the new MSC scenario proposed during the CIESM workshop [1], however the environmental interpretations of the depositional systems during the three steps remain unresolved.

Among the overall basins studied, evaporite basins of the Calabria region (Southern Italy) are the least investigated. Indeed, they were the subject of only preliminary stratigraphic and petrographic studies [32–37].
The research is aimed at settling the origin of the gypsum deposit in order to add a new element on the MSC scenario and implement the paleo-environmental data of the Calabrian forearc.

2. Geological Setting

The Cattolica Formation represents the southernmost Messinian evaporitic stratigraphic unit of the Ionian forearc basin [38]. The Ionian forearc basin represents a sedimentary succession that covers unconformably the plutonic and metamorphic tectonostratigraphic unit of the Calabria-Peloritani Orogen (CPO). The Calabria-Peloritani Orogen is made up of two different fragments of continental plates separated by the fault systems of the Catanzaro Trough [39–41]. The northern sector of the CPO has been subjected to a continental collision since the Oligocene, while in the southern sector, the subduction of the Tethyan ionian oceanic crust is active since the Cretaceous [42–44]. In the study area (Figure 1), located south of Catanzaro Trough, in the central part of the Ionian forearc, the sedimentary succession is >2000 m thick. The basement is the result of stacking of three tectonostratigraphic units involving Palaeozoic crustal rocks: the Africo-Madonna di Polsi Unit (phyllites, marbles, schists), the Aspromonte Unit (gneiss, granitoids) and the Stilo Unit (phyllites, marbles, schists, granitoids), [37,45,46]. On top lies a Palaeozoic metasedimentary succession of Cambrian-to-Carboniferous age, constituted of phyllites, metarenites, metalimestones and metasiliceous rocks intruded by a late Variscan large plutonic body [46–51]. This Unit is largely covered by Late Triassic-earliest Jurassic continental to marine deposits [52]. The Oligocene to Middle Miocene succession is represented by the Stilo-Capo d'Orlando Formation [53–59]. This Formation has been interpreted as continental depositional and slope deposits [54,55,57–59] and as submarine-canyon deposits passing upward and laterally to overbank and slope deposits [53,58]. The Variegated Clays rest on the Stilo-Capo d’Orlando Formation and are characterized by a predominant mélange type internal structure [37,39,60]. The Serravallian to Messinian sequences rest unconformably on the oldest units and start with Serravallian-to-Tortonian marine strata (conglomerates, sandstones and pelites) and continue with the Messinian Gessoso-Solfifera Group (MGSG) of the Cattolica Formation. Critelli et al. [37] and Tripodi et al. [61,62] describe the MGSG in the Benestare area as made up of limestone (Calcare di Base Formation—GTL1), massive or laminated, vacuolar, brecciated, microcrystalline limestone passing upward to selenite crystals and gyspurdite (GTL2) and interbedded olistoliths of Variegated Clays Formation (ob).

The Pliocene (Zanclean to Piacenzian) Trubi Formation (marls and marly-limestones), unconformably overlies Messinian deposits and older sedimentary units [37,63–67].

From the Piacenzian-Calabrian sequence, the sandstone strata (the Monte Narbone Formation) abruptly interrupt the typical pelagic sedimentation [68,69]. Pleistocene, composed of continental to marine deposits is located on top of the stratigraphic succession [62,70–72].
3. Materials and Methods

The sampling was preceded by a stratigraphic analysis of the selenite outcrop (38°11′17.65″ N, 16°8′15.93″ E) and a macroscopic facies analysis to describe the principal elements of the gypsum deposit. Fifteen samples from the gypsrudites facies and branching-like facies were sampled at the bottom and top of the quarry, respectively. The sampling has been carried out following the criteria to prevent external contaminations see [74]. All samples were cleaned and studied to determine the best orientation for the cutting. Samples were cut parallel to the crystal growth direction to preserve the trapped fluid inclusions. Ten gypsum samples were sent to the ALS Petrophysics Laboratory (Normandy) to obtain fluid inclusion wafers (~200 µm in thickness).

3.1. Petrography and Mineralogy

Petrographic and fluid inclusions study was carried out in the Geofluids Research Laboratory at the National University of Ireland in Galway. Petrographic investigations have been carried out using transmitted light microscopy on a Nikon Eclipse E200 polarizing microscope, at various magnifications (4×, 10×, 40×, 60×) to determine the presence and types of fluid inclusions and their suitability for microthermometric analyses. Macroscopically, crystals from the gypsrudite and branching-like facies are not well developed and show chaotical distribution. Petrographic investigations were performed on five wafers cut longitudinally to the crystal growth direction.
Further analysis was carried out through the Laser Raman Spectroscopy (Horiba Scientific LabRam, Lille, France) to investigate the mineralogy of the samples. The technical specifications consist of confocal system, 600 slit grating (~1 cm^{-1} spectral resolution), spectral range (100–400 cm^{-1}, laser excitation (~785 nm NIR) and spatial resolution of ~2 mm.

3.2. Microthermometry

Fluid inclusion microthermometric studies were performed on doubly polished wafers using a Linkam THM&-600 heating-freezing stage mounted on a Nikon Labophot transmitted light microscope equipped with a range of objective lenses including a 100× lens. The phase behaviour of fluid inclusions was analysed over the temperature interval −80° to +50 °C in gypsum samples. The estimated accuracy of measurements is ±0.2 °C during freezing runs and ±1.0 °C during heating runs. The rate of heating and freezing experiments varied as a function of the velocity of phase transitions in the inclusions and ranged from 0.1 to 10 °C/min. The error in estimating salinity using the depression of freezing point methods of NaCl equivalent is ± 0.05 wt% at all temperatures [75].

3.3. Organic Matter

A Zeiss Axioplan optical microscope, outfitted with a Hg vapor lamp and high-performance wide band pass filters (BP 436/10 nm/LP 470 nm for green light; BP 450–490 nm/LP 520 nm for yellow light) was utilized to observe mineral epifluorescence, in order to reveal the distribution of organic matter [76,77].

The wafers were examined under ultraviolet (UV) light using a Nikon Eclipse E200 microscope with an epi-fluorescence attachment. This technique was used to record the fluorescence emitted by the organic material trapped in the gypsum-hosted fluid inclusions.

3.4. 87Sr/86Sr Analyses

The procedure to determine 87Sr/86Sr has been carried out in an ISO 6 class clean room and the mass spectrometry laboratory at Department of Earth, Environment and Resources Sciences of the University of Naples Federico II. Four samples from gypsrudite facies and four samples from the branching-like facies have been powdered; ca. 20 mg of powder were weighted in a clean PFA Savillex™ (Savillex vials: Eden Prairie, MN, USA) vial. Each sample dissolution was achieved through (i) addition of 4 mL of 18.2 MΩ resistivity Milli-Q® deionized water, leaving the vial closed on hot plate at 120 °C for 1 h; (ii) ultrasonication for 8 min; (iii) transfer of the solution into a clean centrifuge tube and centrifugation at 4500 rpm for 10 min; (iv) picking up of 3.5 mL of the supernatant solution and transfer to a clean PFA vial, left open under a laminar flow hood equipped with HEPA filters on hot plate at 90 °C until complete dryness; (v) re-dissolution in 1 mL 2.5 N Suprapur® HCl (Merck KGaA, Darmstadt, Germany) and ultrasonication for 8 min; (vi) transfer of the then clear solution to a clean centrifuge tube and centrifuged at 4500 rpm for 10 min. Chromatographic separation of strontium from the matrix was achieved through AG® 50W X-8 (200–400 mesh BioRad™—BioRad resins: Bio-Rad Laboratories Inc., Hercules, CA, USA) ion-exchange resin packed in quartz columns, using 2.5 M Suprapur® HCl as liquid phase, collecting the Sr-bearing solution in a clean PFA vial and allowing complete evaporation on a hot plate at 120 °C, under a laminar flow hood.

Sr samples were loaded on previously degassed 99.98% pure rhenium filaments and introduced in the source of a Thermo Scientific™ Triton Plus® (Thermo Fisher Scientific Inc., Waltham, MA, USA) solid-source nine-collector mass spectrometer for Sr-isotope ratio determination. Possible mass interference on 87Sr by 87Rb was checked and corrected throughout all measurements. 87Sr/86Sr was normalized for within-run isotopic fractionation to 88Sr/86Sr = 8.37520 using an exponential low for correction. The final 87Sr/86Sr value is reported as the mean of 150 single runs (15 blocks of 10 cycles each; integration time 16.777 s) at 2σ confidence level according to Goldstein et al. [78]. Replicate measurements of the NIST SRM 987 international standard in the period of samples anal-
ysis provided an average value of $^{87}\text{Sr}/^{86}\text{Sr} = 0.710243 \pm 0.000006$ (2σ, N = 29; external reproducibility according to Goldstein et al. [78]). Therefore, a correction of + 0.000005 has been applied to the measured $^{87}\text{Sr}/^{86}\text{Sr}$ values to normalize them to the recommended value (0.710248 ± 0.000012; [78]). The Sr blank has been on the order of 100 pg during the period of chemical processing of the samples, thus negligible.

4. Results
4.1. Field Observations and Sampling

In the Benestare’s quarry, located north of the homonym village, outcrops the most important gypsum deposit of the Cattolica Formation passing upward to Upper Messinian conglomerates and sandstones (NTO) and pliocenic marls of Trubi Formation (TRB) (Figure 2). At field observation scale, the gypsum deposit is massive with thickness of 15 metres. At mesoscale, the strata are characterized by two facies: (i) clastic (gypsrudites) and (ii) branching-like selenite deposits.

The gypsrudite strata, from 1 to 10 cm thick, are interbedded by thin argillaceous/calcareous laminae (from 0.5 and 3 cm thick), (Figure 2a,b). The boundary on the laminae shows dissolution or mechanical reworking.

The branching-like facies is arranged in lenses made of clastic gypsum recognizable within thin argillaceous/calcareous laminae (Figure 2c). They are located at the top of the gypsrudites and show “nodular” features composed of millimetre-sized crystals.

Figure 2. Panoramic view of the Benestare’s quarry and sampling sites (a–c); (a) branching-like facies made of elongated gypsum nodules (black dashed lines) within the laminated matrix (grey colour); (b,c) gypsrudites intervals (vertically repeated) showing variable thickness, and interbedded by thin argillaceous/calcareous laminae (in brown colour). Scale bar is 2 cm.
4.2. Petrographic Observations

The observation on the wafers reveals that crystals belonging to the gypsrudites facies have two types of morphologies: (1) fractured and folded crystals (>1 cm in size) showing elongated shape ([120] and [111] faces) and chaotic orientation (Figure 3a–d), and (2) hexagonal and tabular crystals (<1 cm in size) immersed in a clear brown-orange matrix occurring either in groups or as isolated crystals (Figure 3e–h). In most of the crystals, relics twin planes are recognised.

Wafers from the branching-like facies display gypsum crystals of few millimetres in size (Figure 3i–k). Wafers confirm the irregular shape and chaotical orientation of the crystals observed during the observation at mesoscale.

![Figure 3.](image-url)
Raman spectroscopy was carried out on all crystals to investigate the mineralogy of the samples and to exclude the presence of anhydrite. All crystals show peaks distinctive of gypsum. The main vibration bands (cm$^{-1}$) are 492–494, 1006–1008 and 3405 [79].

4.3. Fluid Inclusions Study

All crystals from the analysed facies contain primary and secondary fluid inclusions (FIs). Primary FIs are two-phase liquid rich (L+V) and occur in trails along the crystal growth direction (Type 2 FIs). Secondary FIs are monophase liquid (L) or monophase vapour (V) and they are distributed in trails along annealed microfractures that display networks of crosscutting trails to the crystals (Type 1 FIs).

Type 1 and Type 2 inclusions show tabular to irregular shape (from 5 to 20 μm in size, rare 50 μm), (Figure 4a). At room temperature, the FIs within a fluid inclusions assemblage (FIA) do not show the same phases, volume proportions and shape. These petrographic differences suggest that the FIs are re-equilibrated (change of pressure and temperature post-entrapment).

In the studied samples, the type of re-equilibration process is not easily recognizable; however, no fluid inclusions affected by decrepitation have been observed.

Probably, these inclusions have likely undergone post-entrapment processes, such as stretching and leaking, associated with gradual plastic and low deformation [80–82]. Moreover, some FIs are affected by necking down phenomena. These inclusions are distributed alongside trails of Type 1 and Type 2 FIs (Figure 4b,c).

Rare larger inclusions show microtubules or microfractures, which radiate from the walls inferring an irregular appearance (Figure 4d).

Figure 4. Type 1 and Type 2 fluid inclusions observed in crystals from gypsrudites facies (a,b) with evidence of necking down process (b); crystal from the branching-like facies (c,d) displaying trail of FIs, necking down (c) and a large (~50 μm in size) irregular inclusion (d).
Microthermometric analysis has been conducted on Type 1 and Type 2 FIs hosted in crystals belonging to the gysprudite and branching-like facies to obtain paleoenvironmental information (salinity, temperature of trapping, chemical composition). Unfortunately, during microthermometric analyses, Type 1 inclusions did not nucleate the bubble during cooling step, while in Type 2 inclusions the bubble did not show any volume change and did not disappear during heating. The lack of any change during the analyses demonstrates that all fluid inclusions are re-equilibrated and not suitable for microthermometric studies.

4.4. Preliminary Organic Matter Data

Organic material can be subdivided in allochthonous and autochthonous remains. Allochthonous organic matter is present as fine debris filling the inter-crystalline spaces and crystal fractures. This debris shows variable sizes and morphologies (Figure 5a–d). Autochthonous organic matter is present as amorphous materials strictly related to the crystal lattice (Figure 5e–h).

Under plane polarized observations, the organic material shows four different colours: (a) transparent, (b) red, (c) brown and (c) black. All materials are fluorescent when exposed to UV light suggesting their organic nature.

Transparent materials are widespread among the crystals. They display tubular morphologies (<60 µm) and emit blue fluorescence under UV light (Figure 5a,b). Most of these organic debris show internal segmentation.

Red materials display irregular shape (<10 µm) and emit red fluorescence under UV excitation (Figure 5c,d). They do not show internal segmentation or specific morphologies.

Brown autochthonous materials are very abundant. They are located mainly in the core of the crystals belonging to the gysprudite facies. In some crystals, this material follows the crystallographic planes of the hosting crystals. The morphologies are similar to those observed by Lugli et al. [3] and called “dark core”. Under UV-excitation this material exhibits a variable distribution of green epifluorescence. The core of the crystals, showing brown material, is characterized by bright fluorescence, while the limpid rim of the crystal is not fluorescent (Figure 5c,f).

Black material is arranged in aggregates and observed in the fractures, between the crystals or in the matrix and under UV light show a bright fluorescence (Figure 5g,h).

Transparent (abundant) and red (rare) materials are observed only in the branching-like facies, on the contrary, brown and black materials (abundant) are recognised in all samples.

![Figure 5](image_url)

**Figure 5.** Allochthonous and autochthonous materials. (a) segmented debris (60 µm in size) composed of five cells and emitting blue fluorescence (b); (c) irregular red material (<10 µm in size) displaying red fluorescence (d); (e) hexagonal and fragmented crystal showing epifluorescent brown materials that follow the crystal’s morphology (f); (g) contact between crystals and matrix which shows a bright fluorescence (h).
4.5. $^{87}\text{Sr}/^{86}\text{Sr}$ Isotopic Study

A reliable hydrologic indicator to study the salinity crisis appears to be the strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) isotope ratio because it is not influenced by salinity change and evaporation conditions [4,6,12].

The gypsrudite facies displays $^{87}\text{Sr}/^{86}\text{Sr}$ average value of 0.709045 ± 0.000002, while branching-like facies show $^{87}\text{Sr}/^{86}\text{Sr}$ average value of 0.709082 ± 0.000001. Plotting these values on the global ocean field [1], it appears that both facies formed between 5.9 and 5.6 Ma, during the deposition of the Lower Gypsum Unit. These data strengthen the petrographic observations which attribute the gypsum origin of the Benestare’s deposit to primary selenite.

Moreover, these values fall in the range of the global ocean field and suggest an evaporite basin with limited freshwater input and strongly influenced by seawater ingressions.

Figure 6 shows the isotopic values of the samples from the gypsrudite and branching-like facies collected from the Benestare’s quarry; horizontal red line defines theoretically the max and min age that the Benestare’s sample could have in relationship with isotopic values of the samples reported by Roveri et al. [11].

![Sr isotope curve in the Mediterranean Sea and Global Ocean during the Messinian age. The distribution documents the progressive change in the isotopic composition of Mediterranean waters during the Messinian salinity crisis. The $^{87}\text{Sr}/^{86}\text{Sr}$ value obtained in samples from the gypsrudite (yellow circles) and branching-like facies (green circles) fall in the field of the Primary Lower Gypsum and they are comparable with samples collected in outcrop by Roveri et al. [11]; PLG: Primary Lower Gypsum; H: Halite; RLG: Resedimented Lower Gypsum; UG: Upper Gypsum; LM: Lago Mare. Figure modified from Roveri et al. [11].](image-url)

5. Discussions

5.1. Gypsrudites Facies

The selenite clasts of gypsrudite are slightly corroded. Microscopic analyses revealed the presence of fractured crystals with chaotic distribution and variable sizes. No crystals show the typical structure made of a single selenite crystal (swallow-tail) with the twin plane perpendicular to bedding and the re-entrant angle pointing upwards [3,36]. Only a few scattered relict crystals show twin plane [120] and [111] faces. Field and petrographic observations suggest a local massive erosion and a rapid deposition of primary selenite.
During sediment deposition and reworking abundant autochthonous and allochthonous organic materials were trapped. No information on crystal chemistry (salinity, brine type, temperature) was obtained from fluid inclusions study due to re-equilibration phenomena. However, the absence of anhydrite, suggest that the Benestare gypsum deposit, upon sedimentation, was not subjected to significant changes in pressure and temperature (low deformation and burial). Moreover, the presence of relict twin plane, crystals not rounded in shape and remains of autochthonous organic materials could testify limited transport.

5.2. Branching-Like Facies

Samples from the branching-like facies display fractured crystals with chaotic arrangement. The millimetres gypsum grains are separated by thin fine-grained carbonate or gypsum laminae. Abundant autochthonous and allochthonous organic materials have been observed within, between and on the top of the crystals, in the fractures and in the matrix. The branching-like facies have been described as “nodular and lenticular selenite” commonly displaying flaser bedding [83], “wavy, needle-like selenite layers” [84,85], or “hemi-radial to radial textures” [86]. They consist of clear selenite crystals, a few centimetres in diameter, with their long axis inclined or oriented horizontally. They are grouped into decimetre-large irregular nodules and lenses separated by thin fine-grained carbonate or gypsum laminae. This facies was originally interpreted as deriving from previous anhydrite nodules formed in a sabkha-like environment [85]. However recently, Lugli et al. [3] and Natalicchio et al. [87] have re-interpreted this gypsum facies as primary formed through two different mechanisms: crystals formed by an initial nucleation zone (into a matrix) and subsequently growing laterally, with crystals grouped in branches projecting outward and crystals grew in the subsurface at the expenses of pelagic gypsum crystals.

From a petrographic point of view, the branching-like facies from the Benestare’s quarry is something between the branching facies described by Lugli et al. [3], Natalicchio et al. [87] and, Vai and Lucchi [83]. According to Vai and Lucchi [83], we consider this facies as re-sedimented and not primary due to the fact that: (1) the crystals observed are fractured and show a chaotical orientation, they do not grow laterally and they are not grouped in branches projecting outward from an initial nucleation zone, and (2) the crystals do not show relict twin plane of primary crystallographic textures. However, the studied facies show differences from those observed by Vai and Lucchi [83], mainly: (1) absence of recrystallized gypsum or re-hydrated secondary anhydrite, and (2) presence of autochthonous organic materials in the crystals core.

5.3. Putative Source of Organic Matter

The crystal core of the gypsrudites show brown organic materials under optical microscopy. The morphologies of this material are similar to the “dark core” observed in the crystals from the Vena del Gesso basin (Northern Apennines) [3]. Our hypothesis is that the presence of brown matter is strictly related to the crystal growth because it follows the crystallographic morphologies of the hosting crystals. The nature of this autochthonous organic matter was not identified but it is believed it may have derived from putative benthic microbial assemblage or organic-rich peloids, like those described by Natalicchio et al. [87]. The relation between microbial communities and primary gypsum has been recently evidenced by Dela Pierre et al. [30] and Natalicchio et al. [6] which detected interwoven filaments in the Messinian gypsum and interpreted them as remains of colourless sulphide-oxidizing bacteria. Microbial mats dominated by these large prokaryotes are found also in coastal upwelling areas [88,89], in stratified basins [90], as well as in sulphide-rich marine sediments associated with methane seepage [91,92].

The allochthonous organic materials, visible as organic debris, is located in fractures between the crystals and in the inter-crystalline matrix. In our opinion, this material is not related to the crystal growth but that was trapped among the crystals after their formation, probably during the processes of erosion and re-sedimentation.
Similar organic matter has also been detected in the lenses of the branching-like facies. A biotic attribution of allochthonous remains is hampered by the absence of specific morphologies. They could represent plant-derived debris or rests of cyanobacteria, diatoms or other prokaryotes [74,83,93,94]. Green-blue microalgae have been suggested to live in shallow lakes, influenced by solar irradiation and affected by continuous mixing of the water column [95]. Other components of the allochthonous materials show irregular shape, red colour under optical microscopy and emits red fluorescence (UV light). A putative attribution of this material to red algae remains could be suggested. These organisms contain a variety of pigments but the most important is the phycocerythrin, which provides these algae with their red pigmentation by reflecting red light and absorbing blue light [96,97]. Red algae are found all over the world, from polar waters to the tropics, and are commonly found in tide pools and in coral reefs [96,97].

Autochthonous organic material of the branching-like facies is similar to that found in the gypsrudites. It appears as amorphous and cloudy, and it is strictly linked with crystal lattice. When excited with UV irradiation, the crystals show bright fluorescence in the area occupied by amorphous materials. Even in this case, it is plausible to hypothesize the presence of organic matter in close genetic association with the crystals, but more specific analyses (i.e., characterization of the lipidic fraction through gas chromatography) are needed to assess their nature.

In general, the organic matter content suggests a double source of the biological material. The allochthonous material could represent extrabasinal-derived debris, whereas autochthonous material could represent intrabasinal planktic and benthic remains that were entrapped within the crystals during primary gypsum formation.

5.4. Inferences from Sr-Isotope Geochemistry

The gypsrudite and branching-like facies recognised in the Benestare’s quarry show very similar isotopic values (0.70904 and 0.70908) suggesting a deposition in an evaporite basin with limited freshwater input and strongly influenced by seawater ingressions. Recently, studies [3,7] carried out on Primary Lower Gypsum of the Vena del Gesso, documented the seawater ingression starting from the 6th (5.84 Ma) gypsum bed where the branching-like facies appear for the first time in the section. These data suggest a global change in hydrology at 5.84 Ma (100 ka eccentricity minimum), when the brine became current-dominated for all the Mediterranean marginal basins [3].

6. Conclusions

A multidisciplinary approach allowed to improve the knowledge about the evaporitic deposits of the Benestare’s quarry in the Calabrian forearc basin (Calabria, Southern Italy). The gypsrudite and the detrital nature of the branching-like facies allow to suggest a clastic nature for the Benestare’s deposit. Considering the presence of relict structures (i.e., twin plane), the absence of recrystallization (anhydrite), angular crystals and remains of autochthonous organic materials in addition to the stretching and leaking re-equilibration of the fluid inclusions, it is plausible a limited transport and low to very low deformation grade and burial diagenesis of the primary gypsum.

The \(^{87}\text{Sr}/^{86}\text{Sr}\) values attribute the gypsum crystals to the first Messinian evaporitic phase, widening the poor dataset of the \(^{87}\text{Sr}/^{86}\text{Sr}\) curve for the period subsequent to the onset of the MSC in the Mediterranean basin. The Benestare’s deposit represents a unicum in the MSC sedimentary successions of the Calabrian arc. It is the first record of clastic selenite deposit in the Ionian forearc basin. Furthermore, this work confirms that gypsum evaporites have great potential to preserve the autochthonous and allochthonous organic materials, providing important information on the paleoecology of ancient evaporitic environments.

Author Contributions: M.C.: Conceptualization, Data curation, Investigation. Methodology, Resources, Validation, Visualization, Writing—original draft, Writing—review and Editing; R.D.: Conceptualization, Funding acquisition, Investigation, Methodology, Supervision, Validation, Visualization-
References

1. CIESM. The Messinian salinity crisis from mega-deposits to microbiology. A consensus reports. In 33ème CIESM Workshop Monographs; Briand, F., Ed.; CIESM Publisher: Monaco, France, 2008; Volume 33, pp. 91–96.
2. Roveri, M.; Lugli, S.; Manzi, V.; Schreiber, B.C. The Messinian Sicilian stratigraphy revisited: New insights for the Messinian salinity crisis. Terra Nova 2008, 20, 483–488. [CrossRef]
3. Lugli, S.; Manzi, V.; Roveri, M.; Schreiber, B.C. The Primary Lower Gypsum in the Mediterranean: A new facies interpretation for the first stage of the Messinian salinity crisis. Palaeogeogr. Palaeoclimatol. Palaeoecol. 2010, 297, 83–99.
4. Manzi, V.; Lugli, S.; Roveri, M.; Schreiber, B.C. A new facies model for the Upper Gypsum of Sicily (Italy): Chronological and palaeoenvironmental constraints for the Messinian salinity crisis in the Mediterranean. Sedimentology 2009, 56, 1937–1960. [CrossRef]
5. Manzi, V.; Gennari, R.; Lugli, S.; Roveri, M.; Scafetta, N.; Schreiber, B.C. High-frequency cyclicity in the Mediterranean messinian evaporites: Evidence for Solar-Lunar climate forcing. J. Sediment. Res. 2012, 82, 991–1005. [CrossRef]
6. Natalicchio, M.; Birgel, D.; Dela Pierre, F.; Ziegengalb, S.; Hoffmann-Sell, L.; Gier, S.; Peckmann, J. Messinian bottom-grown selenitic gypsum: An archive of microbial life. Geobiology 2021. [CrossRef] [PubMed]
7. Roveri, M.; Bertini, A.; Cosentino, D.; Di Stefano, A.; Gennari, R.; Gliozzi, E.; Grossi, F.; Iaccarino, S.M.; Lugli, S.; Manzi, V.; et al. A high-resolution stratigraphic framework for the latest Messinian events in the Mediterranean area. Stratigraphy 2008, 5, 323–342.
8. McCulloch, M.T.; De Deckker, P. Sr isotope constraints on the Mediterranean environment at the end of the Messinian salinity crisis. Nature 1989, 342, 62–65. [CrossRef]
9. Müller, D.W.; Mueller, P.A.; McKenzie, J.A. Strontium isotopic ratios as fluid tracers in Messinian evaporites of the Tyrrenian Sea (Western Mediterranean Sea). In Proceedings of the Ocean Drilling Program, Scientific Results, College Station, TX, USA, 17–20 September 1990; Volume 107, pp. 603–614.
10. Müller, D.W.; Mueller, P.A. Origin and age of the Mediterranean Messinian evaporites: Implications from Sr isotopes. Earth Planet. Sci. Lett. 1991, 107, 1–12. [CrossRef]
11. Roveri, M.; Lugli, S.; Manzi, V.; Gennari, R.; Schreiber, B.C. High-resolution strontium isotope stratigraphy of the Messinian deep Mediterranean basins: Implications for marginal to central basins correlation. Mar. Geol. 2014, 359, 113–125. [CrossRef]
12. Flecker, R.; de Villiers, S.; Ellam, R.M. Modelling the effect of evaporation on the salinity—$\frac{87}{86}$Sr/$\frac{86}{86}$Sr relationship in modern and ancient marginal-marine systems: The Mediterranean Messinian. Earth Planet Sci. Lett. 2002, 203, 221–233. [CrossRef]
13. Flecker, R.; Ellam, R.M. Distinguishing climatic and tectonic signals in the sedimentary succession of marginal basin using Sr isotope: An example from the Messinian salinity crisis, Eastern Mediterranean. J. Geol. Soc. Lond. 1999, 156, 847–854. [CrossRef]
14. Topper, R.P.M.; Flecker, R.; Meijer, P.T.; Wortel, M.J.R. A box model of the Late Miocene Mediterranean Sea: Implications from combined $\frac{87}{86}$Sr/$\frac{86}{86}$Sr and salinity data. Paleoceanography 2011, 26, 3223. [CrossRef]
15. McArthur, J.M.; Howarth, R.J.; Bailey, T.R. Strontium isotope stratigraphy: LOWESS version 3: Best fit to the marine Sr-isotope curve for 0–509 Ma and accompanying look-up table for deriving numerical age. J. Geol. 2001, 109, 155–170. [CrossRef]
16. Schildgen, T.F.; Cosentino, D.; Frijia, G.; Castorina, F.; Dudas, F.O.; Iadanza, A.; Sampalmieri, G.; Cipollari, P.; Caruso, A.; Bowring, S.A.; et al. Sea level and climate forcing of the Sr isotope composition of late Miocene Mediterranean marine basins. Geochim. Geophys. 2014, 15, 2964–2983. [CrossRef]
17. Gladstone, R.; Flecker, R.; Valdes, P.; Lunt, D.; Markwick, P. The Mediterranean hydrologic budget from a Late Miocene global climate simulation. Palaeogeogr. Palaeoclimatol. Palaeoecol. 2007, 251, 254–267. [CrossRef]
18. Topper, R.P.M.; Meijer, P.T. A modelling perspective on spatial and temporal variations in Messinian evaporite deposits. Mar. Geol. 2013, 336, 44–60. [CrossRef]
19. Roveri, M.; Manzi, V.; Bergamasco, A.; Falcieri, F.; Gennari, R.; Lugli, S. Dense shelf water cascading and Messinian canyons: A new scenario for the Mediterranean salinity crisis. Am. J. Sci. 2014, 314, 751–784. [CrossRef]
46. Pezzino, A.; Angi, G.; Fazio, E.; Fiannacca, P.; Lo Giudice, A.; Ortolano, G.; Punturo, R.; Cirrincione, R.; De Vuono, E. Alpine metamorphism in the Aspromonte Massif: Implications for a new framework for the southern sector of the Calabria—Peloritani Orogen (Italy). Int. Geol. Rev. 2008, 50, 423–441. [CrossRef]

47. Amodio-Morelli, L.; Bonardi, G.; Colonna, V.; Dietrich, D.; Giunta, G.; Ippolito, F.; Liguori, V.; Lorenzoni, S.; Pagliionico, A.; Perrone, V.; et al. L’arco Calabro-Peloritano nell’orogene appenninico Maghrebid (The Calabrian-Peloritan Arc in the Apennine-Maghrebid orogen). Mem. Soc. Geol. Ital. 1976, 17, 1–60.

48. Colonna, V.; Lorenzoni, S.; Zanettin-Lorenzoni, E. Sull’esistenza lungo il bordo sudorientale del Massiccio Granitico delle Serre (Calabria). Boll. Della Soc. Geol. Ital. 1973, 92, 801–830.

49. Angi, G.; Cirrincione, R.; Fazio, E.; Ortolano, P.; Pezzino, A. Metamorphic evolution of preserved hercynian crustal section in the Serre massif (Calabria-Peloritani orogen, southern Italy). Lithos 2010, 115, 237–262. [CrossRef]

50. Bonardi, G.; Messina, A.; Perrone, V.; Russo, S.; Zuppetta, A. L’unità di Stilo nel settore meridionale dell’Arco Calabro—Peloritano. Boll. Soc. Geol. Ital. 1984, 103, 279–309.

51. Graesner, T.; Schenk, V. Low—pressure metamorphism of Palaeozoic pelites in the Aspromonte, southern Calabria: Constraints for the thermal evolution in the Calabrian crustal cross-section during the hercynian orogeny. J. Metamorph. Geol. 1999, 17, 157–172. [CrossRef]

52. Roda, C. Geologia della Tavoletta Belvedere di Spinello (Prov. Catanzaro, F. 237, I-SE). Boll. Soc. Geol. Ital. 1965, 84, 159–285.

53. Bonardi, G.; Giunta, G.; Perrone, V.; Russo, M.; Zuppetta, A.; Ciampo, G. Osservazione sull’evoluzione dell’Arco Calabro-Peloritano nel Miocene inferiore. Mem. Soc. Geol. Ital. 1980, 99, 365–393.

54. Zecchin, M.; Praeg, D.; Ceramicola, S.; Muto, F. Onshore to offshore correlation of regional unconformities in the Plio-Pleistocene sequence of the Aspromonte (southern Calabria, Italy). J. Petrol. Geol. 1996, 19, 279–309. [CrossRef]

55. Zecchin, M.; Civil, D.; Caffau, M.; Muto, F.; Di Stefano, A.; Maniscalco, R.; Critelli, S.; Maniscalco, R.; Di Stefano, A.; Muto, F.; et al. The Plio-Pleistocene succession of the Crotone Basin (southern Italy): A record of mixed-mod mode piggy-back basin evolution. J. Geol. Soc. Am. Bull. 1999, 110, 1297–1309. [CrossRef]

56. Weltje, G. Oligocene to early Miocene sedimentation and tectonics in the southern part of the Calabrian-Peloritan Arc (Aspromonte, southern Italy). J. Geol. Soc. Am. 1992, 4, 37–68. [CrossRef]

57. Dominici, R.; Sonnino, M. Interpretazione della successione basale della Formazione di stilo Capo d’Orlando nella zona di Aagna Calabra e canolo (Oligocene, Calabria jonica). G. Geol. Riv. di Geol. Sedimentaria Geol. Mar. 1992, 31, 17–34. [CrossRef]

58. Bouillin, J.P.; Majeste-Menjoulas, C.; Ollivier-Pierre, M.F.; Tambareau, Y.; Villatte, J. Transgression de l’Oligocene inferieur zone (southern Italy). Int. Geol. Rev. 1973, 50, 237–262. [CrossRef]

59. Tripodi, V.; Muto, F.; Brutto, F.; Perri, F.; Critelli, S.; Muto, F. Neogene-Quaternary evolution of the forearc and backarc regions between the Serre and Aspromonte Massifs, Calabria (southern Italy). Mar. Pet. Geol. 2005, 108, 459–473. [CrossRef]

60. Catalano, S.; De Guidi, G.; Monaco, C.; Tortorici, G.; Tortorici, L. Active faulting and seismicity along the Siculo-calabrian Rift zone (southern Italy). Tectonophysics 2008, 453, 177–192. [CrossRef]
72. Ferranti, L.; Monaco, C.; Morelli, D.; Antonioli, F.; Maschio, L. Holocene activity of the Scilla fault, southern Calabria: Insights from coastal morphological and structural investigations. Tectonophysics 2008, 453, 74–93. [CrossRef]
73. Servizio Geologico d’Italia. Carta Geologica d’Italia alla Scala 1:50,000, F. 603 Bovolino; ISPRA: Roma, Italy, 2016. Available online: https://www.isprambiente.gov.it/Media/carg/603_BOVALINO/Foglio.html (accessed on 10 November 2021).
74. Panieri, G.; Lugli, S.; Manzi, V.; Roveri, M.; Schreiber, B.C.; Palinska, K.A. Ribosomal RNA gene fragments from fossilized cyanobacteria identified in primary gypsum from the late Miocene, Italy. Geobiology 2010, 8, 101–111. [CrossRef] [PubMed]
75. Shepherd, T.; Rankin, A.H.; Alderton, D.H.M. A Practical Guide to Fluid Inclusions Studies; Blackie & Son Limited: Glasgow, UK, 1985; p. 239.
76. Neuweiler, F.; Reitner, J. Epifluorescence microscopy of selected automicrites from lower Carnian Cipit boulders of the Cassian formation (Seeland Alpe, Dolomites). Facies 1995, 32, 26–28.
77. Russo, F.; Neri, C.; Mastandrea, A.; Baracca, A. The mud mound nature of the Cassian Platform Margins of the Dolomites, a case history: The Cipit boulders from Punta Grohmann (Sasso Piatto Massif, northern Italy). Facies 1997, 36, 25–36. [CrossRef]
78. Goldstein, S.L.; Deines, P.; Oelkers, E.H.; Rudnick, R.L.; Walter, L.M. Standards for publication of isotopic ratio and chemical data in Chemical Geology. Chem. Geol. 2003, 202, 1–4.
79. Hurai, V.; Huraiová, M.; Slobodniuk, M.; Thomas, R. Geoﬂuids—Developments in Mirothermometry, Spectroscopy, Thermodynamics, and Stable Isotopes, 1st ed.; Elsevier: Amsterdam, The Netherlands, 2015; p. 426.
80. Bodnar, R.J. Re-equilibration of fluid inclusions. In Fluid Inclusions: Analysis and Interpretation; Samson, I., Anderson, A., Marshal, D., Eds.; Mineralogical Association of Canada: Quebec, QC, Canada, 2003; Volume 32, pp. 213–230.
81. Vityk, M.O.; Bodnar, R.J.; Doukhan, J.C. Synthetic ﬂuid inclusions. XV. TEM investigation of plastic ﬂow associated with re-equilibration of fluid inclusions in natural quartz. Contrib. Mineral. Petrol. 2000, 139, 285–297. [CrossRef]
82. Larson, L.T.; Miller, J.D.; Nadeau, J.E.; Roedder, E.L.; Rudnick, R.L.; Walter, L.M. Standards for publication of isotopic ratio and chemical data in Chemical Geology. Chem. Geol. 1995, 120, 247–275.
83. Vai, G.B.; Ricci Lucchi, F. Algal crusts, autochthonous and clastic gypsum in a cannibalistic evaporite basin; a case history from the Messinian of Northern Appennine. Sedimentology 1977, 24, 211–244. [CrossRef]
84. Schreiber, B.C.; Friedman, G.M.; Decima, A.; Schreiber, E. The depositional environments of the Upper Miocene (Messinian) evaporite deposits of the Sicilian Basin. Sedimentology 1976, 23, 729–760. [CrossRef]
85. Lo Cicero, G.; Catalano, R. Facies and petrography of some Messinian evaporites of the Ciminna Basin (Sicily). Facies 1976, 16, 63–81.
86. Lu, F.H. Lithofacies and water-body record of Messinian evaporites in Nijar Basin, SE Spain. Sediment. Geol. 2006, 188–189, 115–130. [CrossRef]
87. Natalichio, M.; Pellegrino, L.; Clari, P.; Pastero, L.; Dela Pierre, F. Gypsum lithofacies and stratigraphic architecture of a Messinian marginal basin (Piedmont Basin, NW Italy). Sediment. Geol. 2021, 425, 106099. [CrossRef]
88. Arning, E.T.; Birgel, D.; Schulz-Vogt, H.N.; Holmkvist, L.; Jørgensen, B.B.; Larson, A.; Peckmann, J. Lipid biomarker patterns of phosphogenic sediments from upwelling regions. Geomicrobiol. J. 2008, 25, 69–82. [CrossRef]
89. Bailey, J.V.; Orphan, V.J.; Joye, S.B.; Corsetti, F.A. Chemotrophic microbial mats and their potential for preservation in the rock record. Astrobiology 2009, 9, 843–859. [CrossRef]
90. Jessen, G.L.; Lichtschlag, A.; Struck, U.; Boetius, A. Distribution and composition of thiobacterial mats in the hypoxic zone of the Black Sea (150–170 m water depth, Crimea margin). Geomicrobiol. J. 2016, 1, 1011. [CrossRef]
91. Knittel, K.; Boetius, A.; Lemke, A.; Eilers, H.; Loche, K.; Pfannkuche, O.; Linke, P.; Amann, R. Activity, distribution, and diversity of sulfate reducers and other bacteria in sediments above gas hydrate (Cascadia margin, Oregon). Geomicrobiol. J. 2003, 20, 269–294. [CrossRef]
92. Zhang, C.L.; Huang, Z.; Cantu, J.; Pancost, R.D.; Brignol, R.L.; Lyons, T.W.; Sassen, R. Lipid biomarkers and carbon isotope signatures of a microbial (Beggiaota) mat associated with gas hydrates in the Gulf of Mexico. Appl. Environ. Microbiol. 2005, 71, 2106–2112. [CrossRef]
93. Rouchy, J.M.; Monty, C. Gypsum microbial sediments: Neogene and modern examples. In Microbial Sediments; Riding, R.E., Awramik, S.M., Eds.; Springer: Berlin/Heidelberg, Germany, 2000; p. 331.
94. Babel, M. Models for evaporite, selenite and gypsum microbialite deposition in ancient saline basin. Acta Geol. Pol. 2004, 54, 219–249.
95. Reynolds, C.S.; Huszar, V.; Kruk, C.; Naselli-Flores, L.; Melo, S. Towards a functional classification of the freshwater phytoplankton. J. Plankton Res. 2002, 24, 417–428. [CrossRef]
96. Guiry, M.D. The evolution of life history types in the Rhodophyta: An appraisal. Cryptogam. Algal. 1987, 8, 1–12.
97. Waggoner, B.M. Ediacaran Lichens: A Critique. Paleobiology 1995, 21, 393–397. [CrossRef]